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PETROLOGIC AND FLUID INCLUSION STUDY OF CALC–SILICATE ROCKS, PRINCE RUPERT, BRITISH COLUMBIA

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ABSTRACT. A coordinated petrologic and fluid inclusion study on calc–silicate samples, selected from an area of known metamorphic T and P, shows that the H_2O/CO_2 compositions of the fluid inclusions generally agree with those predicted from the observed mineral assemblages. In the calc–silicates fluid inclusions in matrix quartz grains are aqueous brines with high salinities and a high proportion of $CaCl_2$. Nearby carbonaceous semi-pelites contain dense CO_2 and CO_2–CH_4 inclusions in matrix quartz. The variations in fluid compositions in inclusions between samples supports the hypothesis that the fluid compositions are internally controlled. Density determinations, however, suggest the inclusions now observed were not formed at peak metamorphic T and P. The discrepancy between predicted and observed densities may permit deductions as to uplift history for the samples.

INTRODUCTION

Most analyses of metamorphic mineral assemblages include observations on the nature of the solid phases and evaluation of the composition of the fluid in the system during the establishment of the mineral assemblage. Interpretations and conclusions derived from experimental and theoretical studies on metamorphic mineral assemblages can be tested directly by comparing the predicted assemblages and compositions of minerals with those found in rocks. However, it has been generally assumed that the fluid phase present during metamorphism is not preserved and hence cannot be subjected to the same direct analysis. Typically, the nature and properties of the fluid phase are inferred from controlled experiments and from thermodynamic data which lead to predictions of the composition of the fluid in equilibrium with the solid phases. However, not all fluids leave the rock system after crystallization ceases and before the rock is exposed at the surface; a small proportion of fluid is trapped as inclusions in minerals, most commonly in quartz. It should be possible, therefore, by analysis of the composition and density of the fluids preserved in these inclusions, to determine if they correspond with the predicted fluids for the metamorphic conditions at which the mineral assemblages formed.

This study reports on the results of observation on fluid inclusions in calcareous rocks from an upper amphibolite facies terrane. The choice of rock type was governed by the large body of data that has accumulated on fluids in the C–O–H system (French, 1966; Holloway, 1977; Ohmoto and Kerrick, 1977) and on the equilibrium relations of these fluids and calc–silicate minerals (Kerrick, 1974; Skippen, 1975; Greenwood, 1975; Slaughter, Kerrick, and Wall, 1975). Predictions about the composition of CO_2–H_2O fluids coexisting with low variance mineral assemblages in

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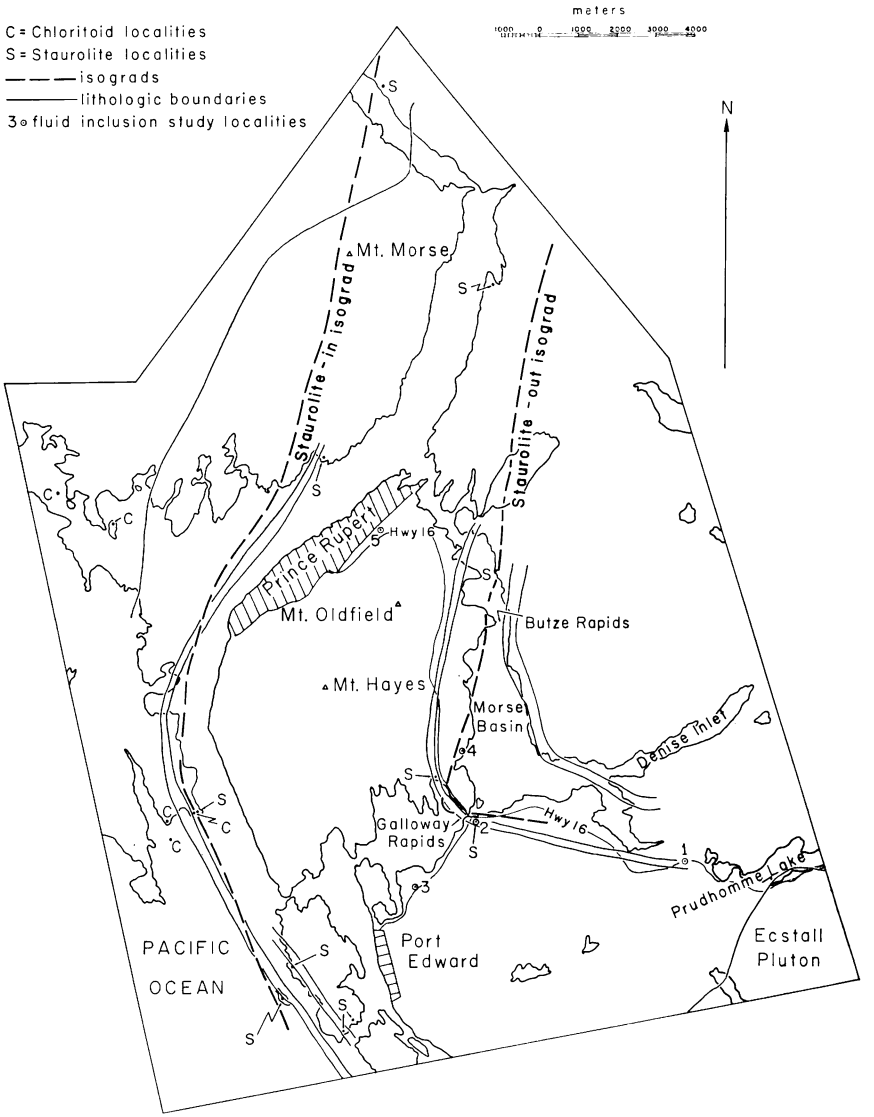


Fig. 1. Location map, Prince Rupert area, British Columbia. In addition to sample localities, the approximate trends of lithologic units and of isograds are indicated.

calc–silicate rocks are now routinely made from petrographic observation of the equilibrium mineral assemblages (Hewitt, 1973; Ferry, 1976a).

Recent studies of fluid inclusions in metamorphic rocks have permitted some investigators (Touret, 1974; Bilal and Touret, 1976; Hollister and Burruss, 1976; Burruss, ms; Kreulen, ms) to deduce that some fluid inclusions correspond to fluids present during peak metamorphic conditions, although most do not. These studies have been directed toward characterizing fluid inclusions in metamorphic rocks in general. The present study aims specifically at determining whether fluids predicted from mineral assemblages and mineral compositions crystallized at a known temperature and pressure are found as fluid inclusions in those minerals. If the predicted fluids are found as inclusions in these metamorphic rocks, then it can reasonably be assumed that, in general, metamorphic fluids are preserved as fluid inclusions. The converse, of course, would also be true.

PETROLOGY

The calc–silicate samples used in this study were collected between the city of Prince Rupert, British Columbia (fig. 1) and Prudhomme Lake. This area was chosen because a previous study (Hampson, ms; Hollister, Lappin, and Hampson, 1975) on the petrology of selected points along the metamorphic gradient defined by Hutchison (1967) showed that a relatively precise temperature and pressure of metamorphism could be estimated in the area. Hampson (ms) identified low variance calc–silicate assemblages, and he mapped two calc–silicate isograds that coincide approximately in trend with isograds in the pelitic rocks.

Semi-pelitic units found at Galloway Rapids (loc 2, fig. 1) contain assemblages that provide an estimate of the pressure and temperature of the metamorphic assemblages. The Galloway Rapids locality lies above the staurolite-in isograd (fig. 1). At slightly lower grades, staurolite is well developed in the pelites, and chloritoid occurs as inclusions within garnet. At Galloway Rapids, staurolite is not readily identifiable in hand specimen but is seen in thin section as small anhedral to subhedral grains in the matrix and as inclusions in garnet. No staurolite has been found in the matrix of rocks east of this point, although rocks of suitable composition for staurolite are found. Therefore, the Galloway Rapids locality is probably close to a staurolite-out isograd. Kyanite and muscovite occur together in the Galloway Rapids area. The first evidence of anatexis, reflected in abundant development of pegmatite and local migmatite, lies along the northeast shore of Morse Basin at Butze Rapids and in Denise Inlet (fig. 1). At Butze Rapids, staurolite was not observed as a groundmass phase but does occur as inclusions in garnet; orthoclase occurs there as a minor phase with kyanite, muscovite, garnet, biotite, and graphite.

At Galloway Rapids, an assemblage lacking quartz and plagioclase was found which closely constrains the temperature and pressure within the broader limits defined by the quartz-bearing pelitic assemblages. This assemblage is garnet–biotite–staurolite–margarite–zoisite–kyanite–chlorite –muscovite. Based on the experimental study of Storre and Nitsch (1974),

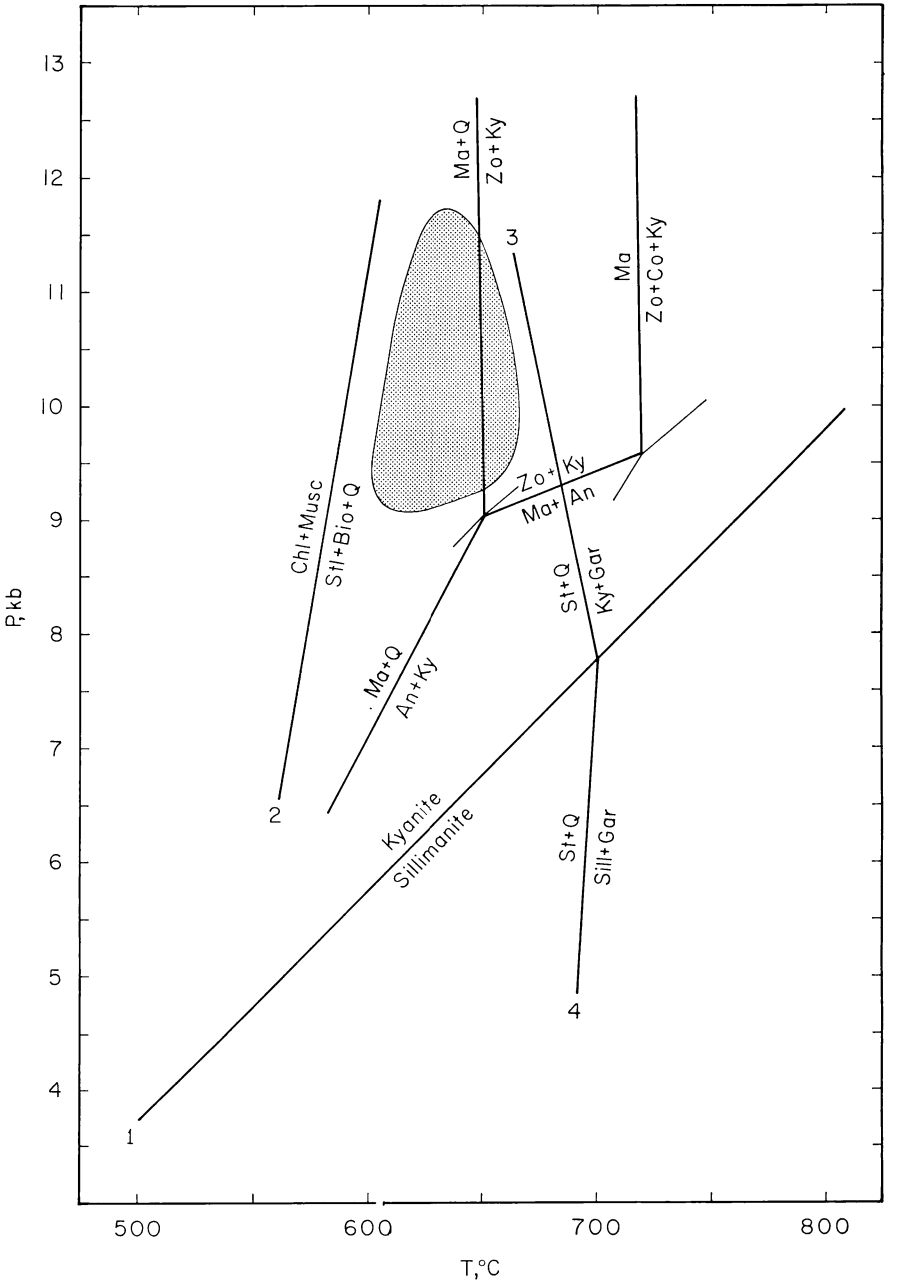
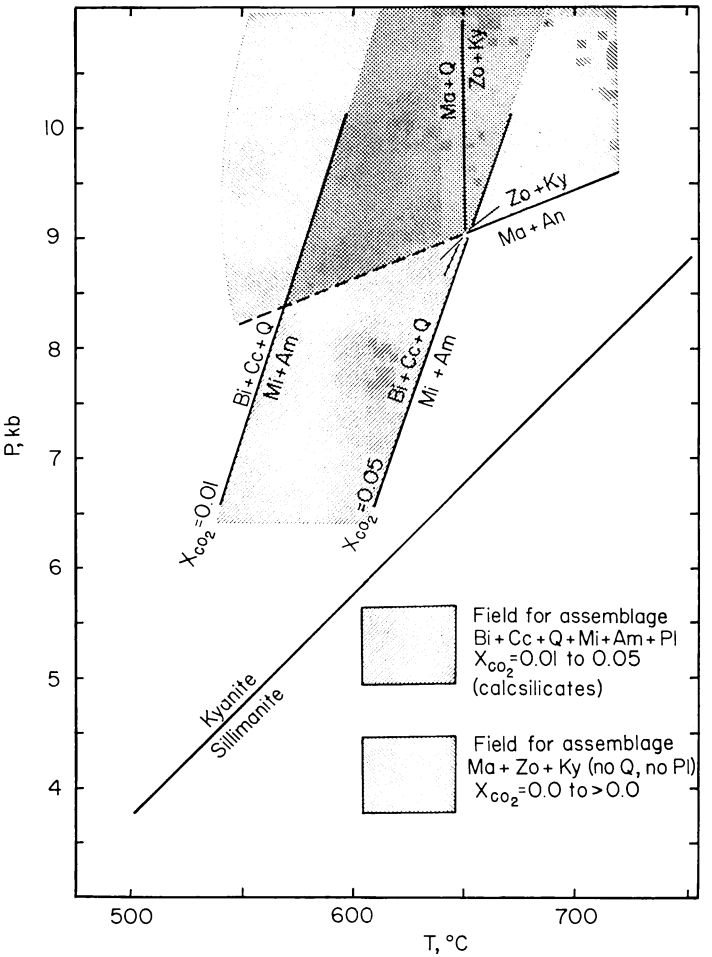


Fig. 2A. Experimentally determined phase boundaries used to estimate P-T conditions (shaded area) near Galloway Rapids (fig. 1, loc. 2). Curve 1 from Holdaway (1971); 2, Hoschek (1969); 3, Ganguly (1972); 4, Richardson (1968). Others from Storre and Nitsch (1974). All curves for $P_{H_2O} = P_{total}$.



B. The most probable P-T conditions for locality 2 (region of overlap of two buffered areas) based on the occurrence of margarite + zoisite + kyanite at $P_{H_2O} \leqslant P_{total}$ and the nearby occurrence of calcite + biotite + quartz + amphibole + microcline. The minimum pressure for the assemblage margarite + zoisite + kyanite for $P_{H_2O} \leqslant P_{total}$ is indicated by the dashed line. The temperature lies between the curves for calcite + biotite + quartz + microcline + amphibole at X_{CO_2} 0.01 and X_{CO_2} 0.05, based on arguments in the text summarized in figure 4.

TABLE 1
Analyses of Minerals

	Margarite			Zoisite			Kyanite			Biotite[9]		Amphibole[9]			Diopside[9]	
Ref. or Sample No.	S & N[8]	CKH[7]	DHZ[4]	S & N[8]	CKH[7]	DHZ[5]	S & N[8]	CKH[7]	DHZ[6]	10	7-17	10	11	7-17	10	11
SiO_2	30.34	31.04	31.98	42.3	39.82	39.2	39.9	37.08[3]	36.55	37.7	38.4	42.4	47.4	54.2	51.4	52.9
TiO_2	0.12	0.03	-	0.05	0.01	0.08		-	0.20	1.17	0.94	0.49	0.37	0.05	0.07	0.03
Al_2O_3	49.8	50.55	49.21	29.65	32.60	32.01	60.0	62.97[3]	62.72	17.3	17.4	14.1	9.81	3.34	0.90	0.51
Fe_2O_3	0.35			1.51		0.76			0.29							
FeO	0.51		0.79	0.48		0.54			0.36							
FeO[1]		0.36			0.44		0.5	0.17		17.0	9.4	16.1	12.6	5.6	14.4	8.6
CaO	11.43	11.39	10.64	23.46	23.66	25.68		-	0.30	-	0.10	11.7	12.1	12.8	23.4	24.1
MgO	0.59	0.43	0.76	0.10	0.03	0.20	0.3	0.3	tr	13.0	17.9	9.3	13.0	19.9	9.0	13.2
MnO	0.01	0.01	-	< 0.1	0.11	0.05		-	-	0.17	0.83	0.23	0.51	0.79	0.33	0.65
Na_2O	1.95	1.58	1.53	0.55	0.02	-	0.3	-	-	0.06	0.06	1.33	0.86	0.44	0.31	0.14
K_2O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	10.5	9.2	1.91	0.87	0.18	0.06	0.05
H_2O	4.65			1.45		2.03										
H_2O[2]		4.65	4.95		3.22					3.2	5.5	2.5	2.5	2.7		

Notes: S & N, Storre and Nitsch (1974); CKH, this paper; DHZ, Deer, Howie, and Zussman (1962); sample 10 from locality 1; samples 7-17 and 11 from locality 2.

[1] All Fe determined as FeO. [2] Deficiency from 100 percent assumed to be H_2O; may include excess O for Fe_2O_3, rare earth elements, and/or other elements (for example, K_2O) not determined (n.d.) with electron microprobe. [3] Stoichiometric proportions for pure Al_2SiO_5. [4] DHZ, v. 3, analysis 2, p. 97. [5] DHZ, v. 1, analysis 2, p. 188. [6] DHZ, v. 1, analysis 3, p. 139. [7] Analyst: L. Hollister, by electron microprobe. [8] Analyst: P. Mielke, by unspecified chemical techniques (note low Al_2O_3 and high SiO_2 for zoisite and kyanite relative to CKH and DHZ). [9] Analyst: M. L. Crawford, by electron microprobe.

using zoisite and margarite with compositions similar to those found in the natural assemblage (table 1) as starting materials, a minimum pressure of 9 kb at 650°C is defined (fig. 2A) for $P_{H_2O} = P_{total}$. The presence of staurolite and quartz in nearby rocks defines an upper limit of 685°C. We, therefore, assume that the *maximum temperature* for the rocks at Galloway Rapids was between 650 and 685°C, and the *minimum* pressure was near 9 kb. If P_{H_2O} was less than P_{total}, the actual temperatures of metamorphism estimated from the pelitic assemblages would be lower. On the other hand, the minimum pressure of 9 kb is not changed significantly within reasonable temperature limits (fig. 2B) by $P_{H_2O} < P_{total}$ because the reaction

$$\text{margarite} + \text{anorthite} = \text{zoisite} + \text{kyanite}$$

does not involve dehydration and has a relatively gentle positive slope, according to Storre and Nitsch (1974). Note also that no estimate of P_{H_2O} in the margarite-bearing specimen can be made, because it does not contain quartz (therefore no fluid inclusions) nor graphite or diagnostic oxide phases.

MINERAL-FLUID EQUILIBRIA

Given the pressure estimate from the pelitic rocks and the observed mineral assemblages in the calc–silicate rocks, the fluid composition in equilibrium with the calc–silicate mineral assemblages can be calculated at any temperature. The calc–silicate rocks contain the low variance assemblages:

A. muscovite–zoisite–plagioclase–calcite–microcline–quartz–fluid

B. diopside–amphibole–biotite–calcite–microcline–quartz–fluid

Assemblage (A) is univariant in the system Al_2O_3–CaO–SiO_2–K_2O–H_2O–CO_2 and assemblage (B) in the system $KAlO_2$–CaO–MgO–SiO_2–H_2O–CO_2. In the absence of other components, at a fixed pressure, the temperature and the composition of the fluid phase coexisting with each assemblage is fixed (points A and B on fig. 3A,B, respectively).

Three additional components, Na_2O, Fe_2O_3, and FeO, occur in significant amounts in some of the minerals: Na_2O in the plagioclase; Fe_2O_3 in clinozoisite; and FeO in amphibole, biotite, and diopside. For any given value of each of these additional components in each mineral an adjusted set of univariant equilibria (isobaric invariant points) can be calculated for use in determining temperature and fluid composition of a specific sample. Figure 3 shows the phase relations for the Al_2O_3–CaO–Na_2O–SiO_2–K_2O–H_2O–CO_2 and the $KAlO_2$–CaO–MgO–FeO–SiO_2–K_2O–H_2O–CO_2 systems for a pressure of 10 kb and a plagioclase composition of An_{40}. The area of each portion of figure 3 that corresponds to minerals observed in the samples studied are also shown. An_{40} was chosen for illustrative purposes as no plagioclase more calcic than this composition was observed.

The complete mineral assemblages in the rocks correspond to a superposition of the two simpler systems, as shown in figure 4. The assemblage

from locality 1 contains no muscovite, hence plots above the muscovite breakdown curves. Another observed low variance assemblage:

C. amphibole–biotite–muscovite–zoisite–plagioclase–calcite–microcline–quartz–fluid

is located at the intersection of two isobaric univariant curves radiating from isobaric invariant points A and B. The plagioclase composition observed in this assemblage is almost pure albite; more calcic plagioclase does not coexist with calcite and zoisite.

The calculations used to arrive at figure 4 include the fugacities of H_2O and CO_2 in H_2O–CO_2 mixtures determined by Holloway (1977) using a modified Redlich-Kwong equation. Calculations using the fugacity coefficients from Helgeson and Kirkham (1974) for H_2O and Melnick (1972) for CO_2 and an ideal mixing model predict significantly higher CO_2 contents in the fluid.

The mineral compositions used in the calculations are given in table 1, the other data used are listed in table 2. Activity coefficients for cation substitutions in amphibole, biotite, and diopside are not available; therefore, the assumption was made that the ion exchange in each of those phases is ideal and is not coupled with any other substitutions. This is

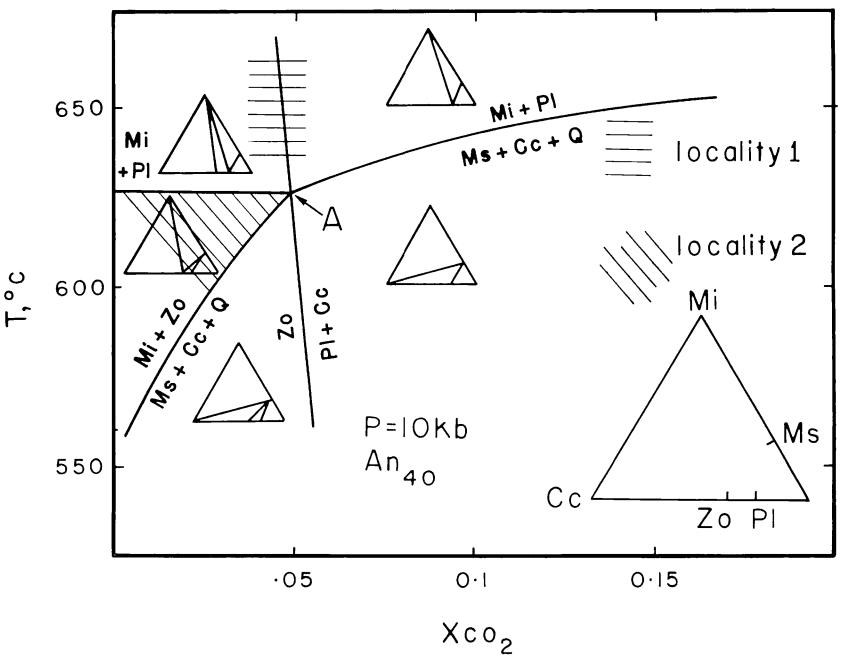
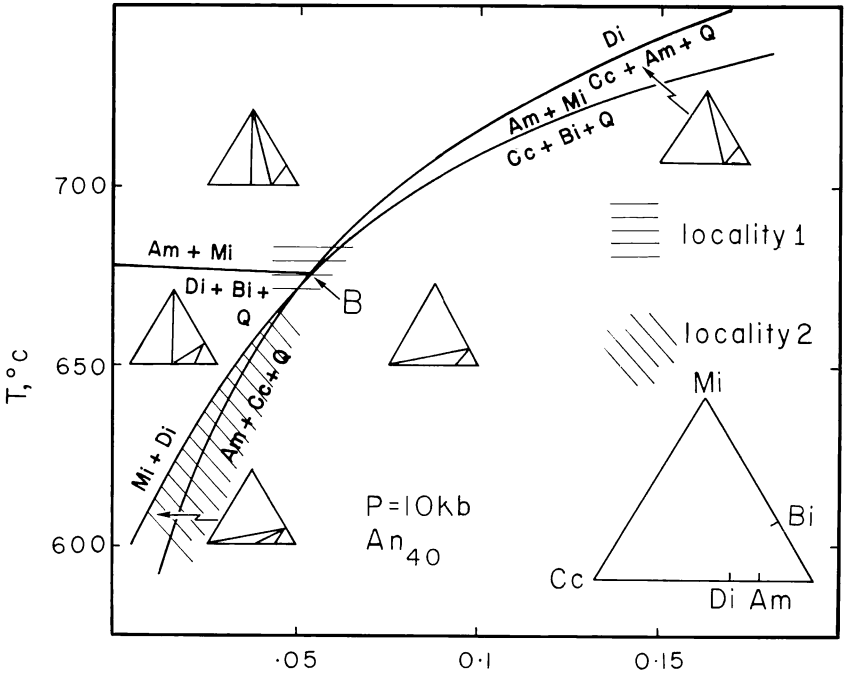


Fig. 3A. T-X_{CO_2} diagram for the system Al_2O_3–CaO–Na_2O–SiO_2–K_2O–H_2O–CO_2 calculated for 10 kb and plagioclase composition An_{40}. The univariant assemblage muscovite (Ms)–plagioclase (Pl, An_{40})–calcite (Cc)–microcline (Mi)–zoisite (Zo)–quartz–fluid (point A) occurs in samples at locality 2. The other assemblages at localities 1 and 2 used to define the shaded areas are given in table 2.

probably not correct for Fe–Mg substitution in amphibole, where Al/Si and Fe/Mg substitutions appear to be correlated (Crawford, 1971). As the amphiboles in these rocks vary considerably in Al content between samples, some error in the calculated equilibrium curves is unavoidable. An additional error is introduced by using $Ca_2Al_3Si_3O_{12}$ (OH) to represent the epidote group mineral. In some samples this mineral is clinozoisite containing 5 mol percent pistacite, in others it is virtually pure zoisite. The other phases, calcite, muscovite, and microcline, show little or no deviation from their ideal compositions.

The calculations of the position of the equilibrium curves in figure 4 also involve some judgements concerning choice of enthalpy and entropy values for specific reactions. Significant variations occur for the calculations of equilibria in the Al_2O_3–CaO–SiO_2–K_2O–H_2O–CO_2 system in which entropy and enthalpy data derived directly from experimental measurements on the system (Johannes and Orville, 1972) were used instead of data derived indirectly from the stability relations of zoisite, quartz, anorthite, grossular, and calcite (Hoy, 1976; Ferry, 1976b). The Johannes and Orville data predict the very low X_{CO_2} observed in the fluids more closely and also produce a phase diagram consistent with the ob-



B. T-X_{CO_2} diagram for the system $KAlO_2$–CaO–MgO–FeO–SiO_2–K_2O–H_2O–CO_2 calculated for 10 kb and diopside, amphibole, and biotite compositions reported for locality 2 (table 1). The univariant assemblage biotite (Bi)–amphibole (Am)–diopside (Di)–calcite (Cc)–microcline (Mi)–quartz–fluid (point B) occurs at locality 2. The other assemblages at localities 1 and 2 used to define the shaded areas are listed in table 2.

served metamorphic assemblages. As mentioned above, the position of equilibrium curves relating diopside, amphibole, and biotite are probably less accurately located than those for the Al_2O_3–CaO–Na_2O–SiO_2–K_2O–H_2O–CO_2 system.

The most probable temperature and fluid compositions that correspond to the observed mineral assemblages (table 2) can be obtained from figure 4, which incorporates all the observed calc–silicate assemblages and mineral composition data. This supports the conclusion reached from the study of the pelites that the rocks in the study area formed under a re-

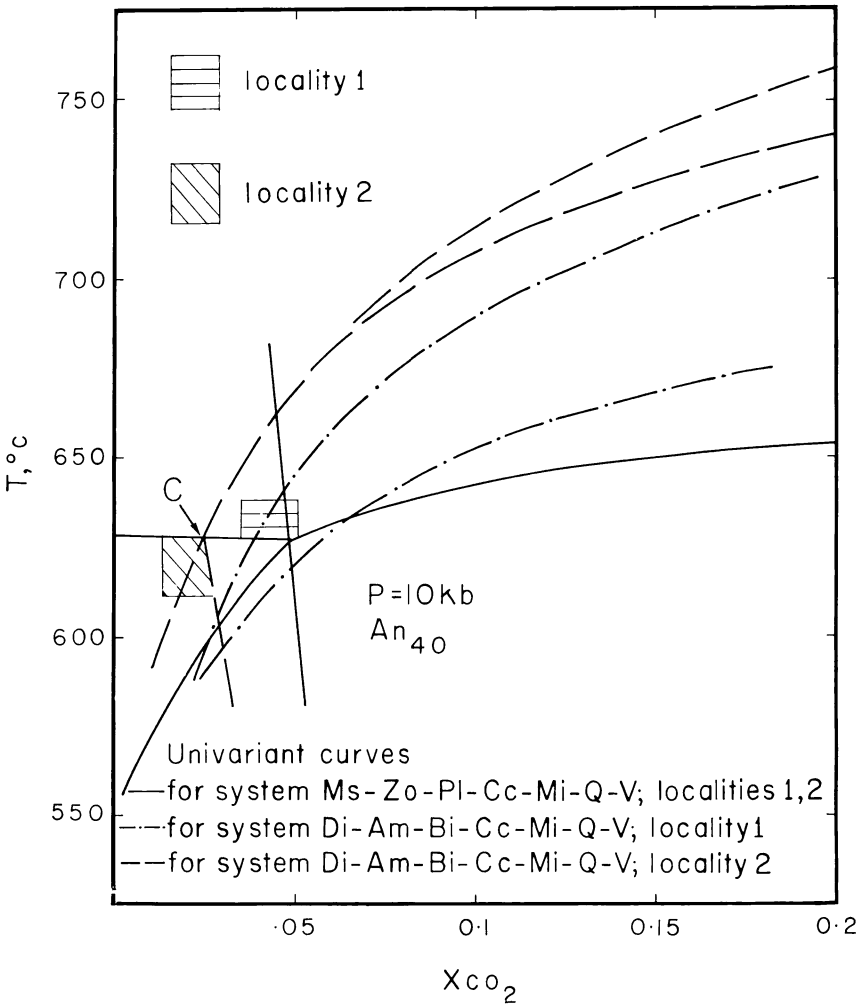


Fig. 4. Phase boundaries resulting from combining figure 3A and B for a pressure of 10 kb and mineral compositions from localities 1 and 2. Probable limits of T and X_{CO_2} for localities 1 and 2 deduced from the mineral assemblages are also indicated.

stricted set of physical conditions (fig. 2B). The metamorphic temperature calculated for the calc–silicate assemblages at 10 kb is approx 50°C lower than the *maximum* temperature predicted from the pelitic samples at locality 2.

FLUID INCLUSION STUDIES: TECHNIQUE AND ASSUMPTIONS

The technique for identifying fluid composition and densities in fluid inclusions is relatively routine if the appropriate equipment is available. The development of the microscope freezing and heating stage (Roedder, 1962; Poty, Leroy, and Jachimowicz, 1976) permits the identification of fluid composition from measurements of the freezing point(s) of the fluid phase(s) and an estimate of the density of the fluid through observations of fluid-vapor phase changes during heating from −160° to +600°C. The equipment we used has been described by Poty, Leroy, and Jachimowicz (1976), with modifications described in Burruss (ms). The

TABLE 2

Mineral assemblages, reactions and data used to construct T–X diagrams (figs. 3 and 4)

Mineral Assemblages

Locality 1: calcite–diopside–microcline–plagioclase–biotite–clinozoisite–amphibole–quartz
calcite–diopside–microcline–biotite–clinozoisite–amphibole–quartz–scapolite

Locality 2: calcite–muscovite–biotite–microcline–clinozoisite–quartz
calcite–muscovite–biotite–microcline–plagioclase–amphibole–quartz
calcite–muscovite–microcline–plagioclase–zoisite–amphibole–quartz
biotite–clinozoisite–amphibole–diopside–quartz

The calculations use the equation

$$\log f_{CO_2}{}^{a} f_{H_2O}{}^{b} = \frac{A}{T} + B + \frac{C(P-P_{ref})}{T} - \log K_s$$

a,b = stoichiometric coefficients for CO_2 and H_2O respectively

$$A = \frac{\Delta H}{2.303R} \quad B = \frac{\Delta S}{2.303R} \quad C = \frac{\Delta Vs}{2.303R}$$

P = 10 kb P_{ref} = pressure at which values of ΔH, ΔS were determined.

K_s = activity term for solid phases.

Reaction	A	B	C	P_{ref} (bars)	Source
$2zo+ms+2q = 4an+or+2H_2O$	−11080	22.4	−0.276	1	1
$2zo+CO_2 = 3an+cc+H_2O$	− 320	2.6	−0.346	1	1
$3ms+4cc=6q = 2zo+3or+4CO_2+2H_2O$	−31960	56.8	0.558	1	1
$ms+cc=2q = or+an+CO_2+H_2O$	−10760	19.8	0.0706	1	1
$tr+3cc+2q = 5di+3CO_2+H_2O$	−12486	27.96	0.515	2000	2
$6cc+5ph+24q = 5or+3tr+6CO_2+2H_2O$	−32000	65.28	0.808	2000	2

Activity coefficients for plagioclase from Orville (1972)

Activity coefficients for biotite, amphibole, and diopside calculated from $\{Mg_{/c}\}^{c}$

{Mg} = Mg cations/formula unit determined by microproble analysis.

c = number of Mg cations/formula unit in ideal Mg end member phlogopite, tremolite, and diopside.

Source of data

(1) Johannes and Orville (1972).

(2) Höy (1976).

cooling–heating stage is calibrated by observing melting temperature of compounds with known melting temperature.

One goal of this type of study is to identify fluids with a composition and density imposed at the peak of metamorphism. It is not presumed that all, or even a majority, of the inclusions will be representative of the metamorphic fluid. However, it is generally assumed

1. that the compositions of fluids trapped in mineral grains are the same as those of the bulk fluid at the time it was trapped; and
2. that the density and composition of fluid inclusions do not, in general, change significantly after entrapment.

In each study the validity of these assumptions must be examined before reaching definitive conclusions.

Inclusions may form throughout the history of the rock, during or following the crystallization of the host mineral. In this study the fluid inclusions in calc–silicate samples occur randomly in matrix quartz; a few lie on short healed fractures that do not cross the boundaries of the quartz grains. Vein quartz was avoided, as it is more likely to be associated with fluids that did not equilibrate with the matrix mineral assemblage. Isolated inclusions of the type observed in this study, which

TABLE 3

Melting and homogenization temperatures of aqueous inclusions

Sample (locality)	Tm_o	Tm_f	T_h
6-4F	-33	-15.6±0.2	210±1
(2)	-42	-12.3±0.2	204±1
	-26	-20.8±2.0	169±1
	n.d.	-15 ±2.0	152±1
	-37	-14.6±0.2	219±1
	-51	-17.8±1.0	178±3
	-51(?)	-24.6±0.2	167±2
	-43	-13.4±0.2	271±3
	-41	-26.8±1.0	n.d.
	-36	-26.8±0.2	212±4
6-4C	-40	-12.6±0.2	185±2
(2)	n.d.	n.d.	174±1
	-40	-12.4±0.2	207±1
	-31	-13.4±1.0	235±1
	-39	-20.1±0.2	283±3
	n.d.	n.d.	165±6
	n.d.	n.d.	173±6
	-36	- 6.8±0.2	n.d.
	-36	- 6.8±0.2	n.d.
	-41	- 6.4±0.2	n.d.
	-58	-35.0±0.2	150±2
MB10	-58	-44.2±0.2†	95±3
(1)	-60*	-19.6±1.0	n.d.
	-59*	-40.1†	n.d.

Notes: Tm_o, first observed melting on heating; Tm_f, final observed disappearance of solid on heating; T_h, homogenization of gas and liquid to liquid; n.d., not determined; * also observed disappearance of a solid phase between −51 and −52°C; † probable temperature of final melting of $NaCl \cdot 2H_2O$.

do not lie along fractures, are the most likely type to have been trapped during growth of the host phase. They are candidates, therefore, for fluids trapped during the peak of metamorphism.

An inclusion may have the composition of the fluid present in the rock when it was trapped but not the density. The density of an inclusion will be preserved only if the original inclusion cavity does not change in volume and if the walls of the cavity do not break during cooling and unloading of the rock. An inclusion may leak slightly so that the density is modified, but the inclusion is not substantially altered; an inclusion may rupture and the fluid may escape, possibly becoming retrapped along fractures, or the grain may recrystallize so the original inclusions disappear and new ones are formed. In each case the new inclusions will have a lower density than the original fluid. If leakage occurs, the composition of the fluids may also be modified. Intergranular fluids, differing in composition from those equilibrated with the matrix minerals, may be introduced and mix with the original fluids, or CO_2 and H_2O-rich phases may unmix from a homogeneous fluid and become trapped as separate phases. In each of these circumstances, the assumptions listed above will not hold.

FLUID DATA

Table 3 and figure 5 (left) summarize the data on melting points and homogenization temperatures for the fluid inclusions in calc–silicate samples from two localities (fig. 1). The inclusions in matrix quartz are 2 to

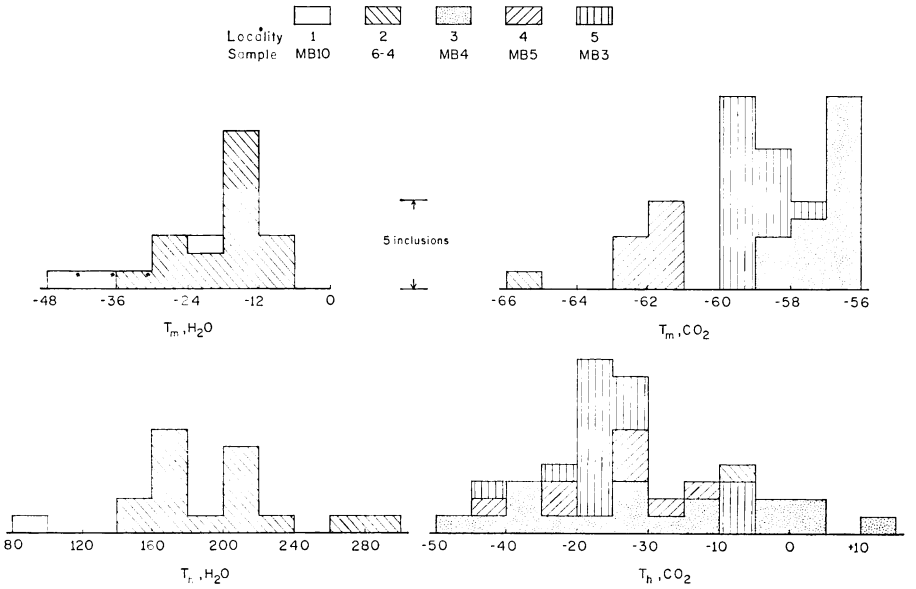


Fig. 5. Melting and homogenization data for H_2O-rich inclusions (left) and CO_2 rich inclusions (right). Note that all aqueous inclusions are from the calc–silicate assemblages at localities 1 and 2, and most of the CO_2-rich inclusions are from graphite-bearing semi-pelites at localities 3, 4, and 5.

20 μm in size and mostly equant, elongate, or pancake-shaped. In these samples no textural evidence was seen for explosive fracturing of inclusions. The inclusions lay on short fractures which did not cross grain boundaries or were scattered randomly within grains. Obvious evidence for leakage of inclusions and for trapping of late fluids is not present. Virtually all the inclusions large enough to study (>5 μm) are aqueous, with final melting points from −44.2° to −6.4°C. These melting point data show that the fluids preserved in the inclusions contain a variable, but high salt content.

Initial melting temperatures as low as −60°C suggest the brines in the inclusions are enriched in $CaCl_2$. This conclusion is based on the phase diagrams presented by Roedder (1971) for the NaCl–KCl–H_2O system, by Yanatieva (1946) for the NaCl–$CaCl_2$–H_2O system, and by Luzhnaya and Vereshtchetina (1946) for NaCl–$MgCl_2$–$CaCl_2$–H_2O. Melting temperatures below −35°C occur only in the $CaCl_2$-bearing systems. A fluid in the NaCl–$CaCl_2$–H_2O three component system should exhibit initial melting at the eutectic minimum of the system and, provided the salt content of the solution does not exceed 20 to 25 wt percent, two

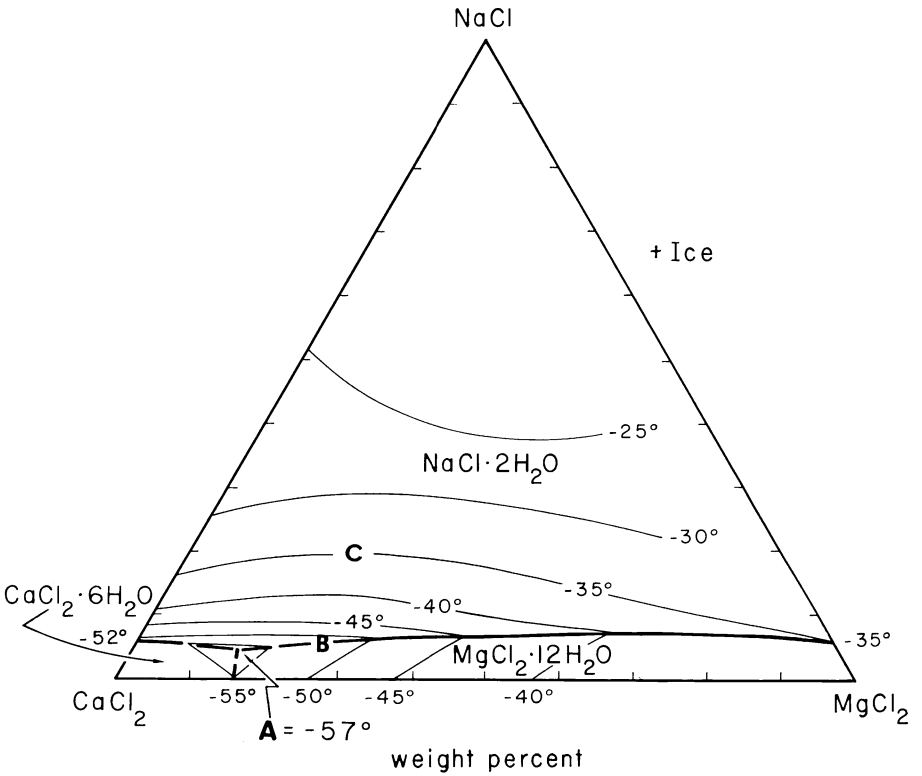
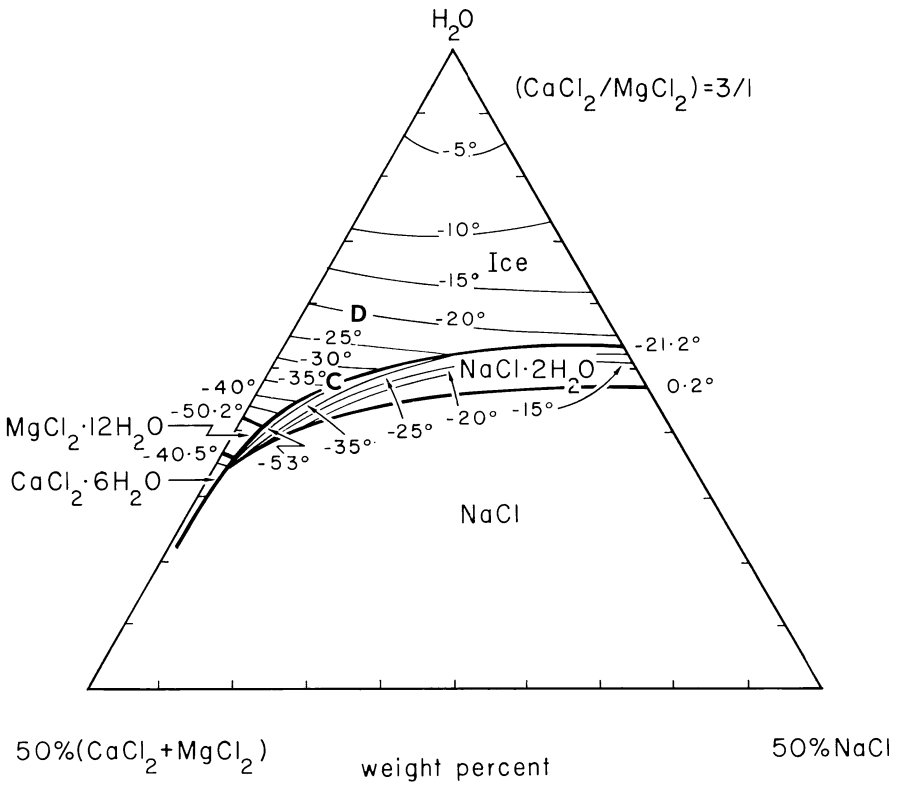


Fig. 6A. Phase relationships in the system NaCl–$CaCl_2$–$MgCl_2$–H_2O projected onto the plane of hydrate-ice equilibria.

additional melting events: one for the fusion of $NaCl \cdot 2H_2O$ in the presence of ice, liquid, and vapor, and the second for the fusion of ice. In the pure four component system (fig. 6) four separate melting episodes occur; additional components add additional phase changes. Thus careful observation of fluid inclusions in such a four component system should detect initial melting at the quaternary eutectic and three separate phase disappearances as the remaining hydrate phases melt in the presence of ice, followed by the melting of ice. Measurement of the temperatures for the disappearance by melting of each phase will provide an estimate of the composition of the trapped fluid.

Two inclusions from locality 1 clearly showed phenomena associated with phase changes in a complex brine solution. The composition of the brine is unknown; however, it is likely to be composed primarily of Na^+, K^+, Ca^{+2}, and Cl^- ions dissolved in water. This assumption is made based on the observations reported by Roedder (1972), Poty, Stalder, and Weisbrod (1974), and Weisbrod and Poty (1975) who list Na^+, K^+, Ca^{+2}, and Cl^- as the most common dissolved species trapped in inclusions. The



B. Section through the $NaCl–CaCl_2–MgCl_2–H_2O$ system with a $CaCl_2/MgCl_2$ ratio of 3/1. Data are from Luzhnaya and Vereshtchetina (1946). Points A, B, C, and D are referred to in the text. Liquidus phase fields are labelled and separated by heavy lines.

similarities of properties of solutions of NaCl and KCl suggest that, in solutions containing these two components with $CaCl_2$ and possible additional species, treating them as one component will not introduce a significant error. Phase equilibrium data are available for the system NaCl–$CaCl_2$–$MgCl_2$–H_2O (Luzhnaya and Vereshtchetina, 1946), and phase transition temperatures observed in the fluids from locality 1 approximate those reported for this system. Therefore it is possible, as a first approximation, to model the phase equilibria observed in the inclusions from locality 1 using the NaCl–$CaCl_2$–$MgCl_2$–H_2O system (fig. 6), even though the presence of small amounts of Mg^{+2} or other ions cannot be confirmed.

The first observed melting at or just above −60°C does not exactly match the eutectic minimum of −57°C (A, fig. 6A). The data of Luzhnaya and Vereshtchetina (1946) suggest this temperature was determined only by extrapolation and hence may not be accurate. It is also possible that additional components (such as K^+ or Fe^{+2}) in the natural brine produce a melt below the eutectic minimum of the model system. A phase disappearance was recorded at −52°C. Referring to figure 6A, this could represent melting either of $CaCl_2 \cdot 6H_2O$ or $MgCl_2 \cdot 12H_2O$. In the former case, the system would contain virtually no $MgCl_2$ (or other analogous component), which is not likely in view of the small but visible amount of melt at the eutectic. Thus we assume this phase disappearance occurs at B (fig. 6A), which is located at about −52° on the cotectic between $MgCl_2 \cdot 12H_2O$ and $NaCl \cdot 2H_2O$. The position of this point provides an estimate of the Ca/Mg ratio in the brine. The composition of the solid portion of the system leaves the $MgCl_2 \cdot 12H_2O$–$NaCl \cdot 2H_2O$–ice–liquid–vapor cotectic and traverses the $NaCl_2 \cdot 2H_2O$–ice–liquid–vapor field as the $NaCl_2 \cdot 2H_2O$ phase melts. At approximately point C (−30°C in one case, −40°C in another) the next phase, presumably sodium chloride hydrate, disappears. The location of this phase disappearance point gives the ratio of the three chloride salts in the inclusion, provided they are the only salts present. Further heating finally melts the ice (point D, fig. 6B) and provides an estimate of the total salt content of the solution. Following this reasoning the fluids trapped in the inclusions of locality 1 could consist of brines with dissolved components having a composition of approx 67 to 57 wt percent $CaCl_2$, 20 to 23 wt percent $MgCl_2$, and 10 to 25 wt percent NaCl (or NaCl + KCl). The solution contains about 22 wt percent total dissolved salts.

Inclusions from locality 1 were particularly favorable for observations of complex melting phenomena. Even in these, however, it was not possible to identify the solid phases present due to their extremely small volume. The observations reported from other inclusions (table 3) support the conclusions from locality 1 samples: high $CaCl_2$ contents (low initial melting points) and total salt contents on the order of 20 wt percent (final melting points clustering between −20° and −12°C, fig. 5).

In addition to the fluids in the calc–silicate samples, fluids in the matrix and in quartz pods in adjacent semi-pelitic schists were also

studied (table 4; fig. 5 right). In contrast to the calc–silicate fluids, those in the semi-pelitic rocks are primarily CO_2–CH_4 mixtures. Melting points range from −61° to −56°C. Hence these contain a variable, but small amount of methane. Pure CO_2 inclusions occur only in locality 3, sample MB4, which contains no carbonaceous material. In these semi-pelites aqueous inclusions occur along well-defined fractures in quartz pods and in matrix quartz grains; we observed no isolated aqueous inclusions in these samples similar to those of the calc–silicate rocks. In every respect, therefore, the fluid compositions seem to differ markedly from those of the calc–silicates.

DISCUSSION — FLUID COMPOSITIONS

The occurrence of aqueous inclusions in the matrix quartz grains of the calc–silicate samples was surprising to us at first because most metamorphic rocks studied have contained a considerable amount of CO_2 in one or more types of inclusions (Touret, 1974; Hollister and Burruss, 1976; Wood, ms; Rich, ms; Burrus, ms; Kreulen, ms). Petrologic inferences about fluid compositions in calc–silicate assemblages have also predicted variable but significant amounts of CO_2 (Hewitt, 1973; Kerrick,

TABLE 4

Melting and homogenization temperatures of CO_2-rich inclusions

Sample (Locality)	T_m	T_h	T_m	T_h
MB4	-58.8	-36.6	-56.6	-16.9*
(3)	-57.2	-37.4	-56.6	-21.8*
	-56.4	- .4.0	-56.6	-36.6*
	-56.4	+ 2.6	-56.6	-45.4*
	-56.9	+ 1.9	-56.7	-20.1*
	-56.8	- 3.3*	.56.9	-11.3*
	-57.1	+15.0*	-58.0	-22.7*
	-57.8	-13.5*	-58.3	-34.6*
	-57.2	-22.1*	-56.3	-40.8*
MB5	-61.7	-15.1	-61.7	-22.5
(4)	-62.1	-42.0	-61.7	-24.7
	-61.5	-11.5	-62.1	-34.7
	-61.6	-22.9	-62.1	-32.7
MB3	-59	- 5.1	-59.9	-41.3
(5)	-58.8	- 5.1	-59.7	-27.8
	.58.9	-20.7	-59.7	-26.9
	-59.0	-26.6	-59.7	-30.8
	-58.9	-27.9	-59.0	-23.8
	-59.3	-27.2	-59.7	-26.9
	-57.6	- 7.4±0.5	-59.1	-26.4
	-59.3	-24.6	-58.6	-26.2
	-58.6	-25.4		
6-4	-66.0±1.0	-. 9.7±0.3		

Notes: All temperatures ± 0.2°C unless otherwise indicated.
* All inclusions in matrix except *, which are in a quartz vein.

1974; Ferry, 1976a). However, the calculated compositions of the fluids shown in figure 4 do predict fluids with less than 5 mol percent CO_2.

We should be able to observe as little as 2.3 mol percent CO_2 in a CO_2–H_2O inclusion, assuming a high CO_2 density similar to that observed in the adjacent semi-pelitic samples and also assuming no CO_2 is dissolved in the aqueous phase. The latter assumption seems reasonable based on the observed solubilities of CO_2 in chloride solutions (Malinin and Kurovskaya, 1975).

We cannot say that the fluid inclusions from the calc–silicate rocks of this study precisely reproduce the composition of the fluid that, according to our calculations, would have equilibrated with the minerals at the temperature and pressure of metamorphism. We can conclude from the near absence of an observed CO_2 phase, except for one inclusion, and the abundance of aqueous fluid in the inclusions, that the fluid composition observed in the calc–silicate assemblages is close to the fluid composition predicted. This contrasts with the paucity of aqueous inclusions and abundance of CO_2-rich inclusions in the immediately adjacent graphite-bearing semi-pelitic schists.

The discussion of correspondence between predicted and observed fluid compositions must be tempered by the lack of information on the effects of the high salinity of the aqueous phase on the fugacities of the components of the fluid. In addition, the C-bearing fluid phase, where present, appears to contain methane. (The calculations assumed pure H_2O and CO_2 as components of the vapor phase). In a CH_4–CO_2–H_2O mixture, methane will preferentially partition into the CO_2-rich phase which would cause the CO_2 to behave more ideally and the H_2O less ideally than predicted by the H_2O–CO_2 fugacities of Holloway (1977). The salinity of the aqueous phase will also affect the fugacity calculations, producing further adjustments in the final result.

DISCUSSION — FLUID DENSITIES

PVT data on highly saline solutions are, at present, limited to measurements at low pressures (Lemmlein and Klevtsov, 1961; Potter and Brown, 1977). Any interpretations must be based on straight line extrapolations of these data to the temperature and pressure of the metamorphism inferred for these samples. Figure 7 shows a plot of extrapolated isochores for 25 wt percent NaCl solutions. To use this diagram, the specific volume at room temperature and pressure is deduced from the temperature at which an inclusion is homogenized to liquid from vapor plus liquid. That specific volume and the composition of the fluid derived from the melting point studies determine a unique isochore (equal density line) in T–P space. If the specific volume of the fluid phase has not changed since it was trapped in the inclusion, the isochore will pass through the point in T–P space that corresponds to the temperature and pressure of fluid entrapment. As shown in figure 7, none of the isochores predicted from the estimated compositions and observed homogenization temperatures passes close to the inferred metamorphic conditions.

The discrepancy between the T–P regime predicted by the location of the isochores and that predicted from the mineral assemblages can be interpreted either

1. as an indication of the uncertainty in the position of the extrapolated isochores;
2. as a lack of enough measurements of homogenization temperature to identify the densest fluids;
3. an error in the determination of metamorphic T and P;
4. as suggesting the fluids observed were not, after all, trapped during the peak of the metamorphism and hence are not directly related to the primary metamorphic fluid; or

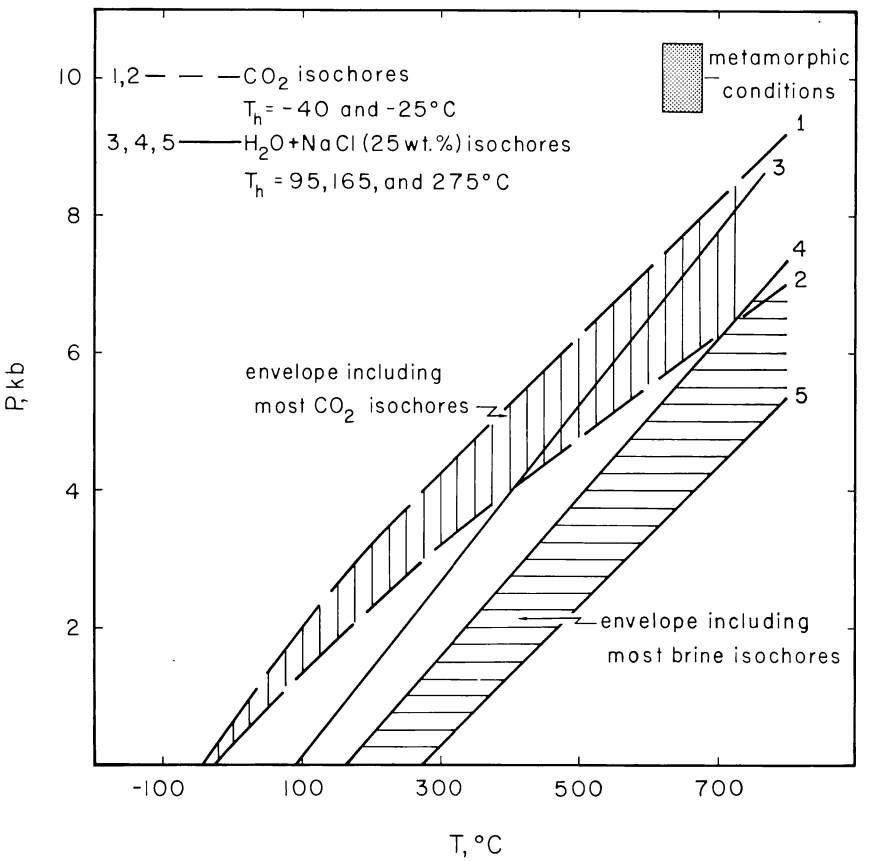


Fig. 7. Isochores for brines containing 25 wt percent NaCl (Potter and Brown, 1977) and for CO_2 (Juza, Kmonicek, and Sifner, 1965; Holloway, 1977). The shaded areas represent the ranges of conditions of entrapment for the majority of the inclusions of each type. The isochore for the densest aqueous inclusion measured (isochore 3) projects to 7 kb at 640°C. The isochore for the densest CO_2 inclusion (isochore 1) projects to 7.75 kb at 650°C. The range for approximate metamorphic conditions is from figure 2.

5. that the fluids are the primary metamorphic fluids, but that specific volume changes have occurred subsequent to entrapment.

In the subsequent discussion we assume the locations of the aqueous fluid isochores are not significantly in error. Figure 5 shows the lowest homogenization temperatures (= densest inclusions) occur in a definite cluster. Our observations suggest further measurements will mainly add points in the observed range of homogenization rather than locating denser inclusions.

The metamorphic temperatures are deduced from the calc–silicate assemblages using a pressure estimate based on the assemblage containing zoisite, margarite, and kyanite. If the assumed pressure is too high, a lower temperature would also be predicted, and the fluid in the calc–silicate assemblages should be more water-rich than 0.5 mol percent (fig. 2B). However, the low slope of the margarite + anorthite = kyanite + zoisite curve which defines the minimum pressure would also require a higher density fluid at lower temperatures. As discussed above, it is unlikely that the postulated metamorphic temperatures or pressures are too high.

We cannot absolutely preclude the possibility that no fluids were trapped in matrix quartz in the rocks at the peak of the metamorphism, but this seems unlikely. We have already suggested that the compositions of the fluids permit the interpretation that they do represent the primary metamorphic fluid. The contrast between the CO_2-rich fluids in the noncalcareous rocks and the $CaCl_2$-rich saline aqueous fluids in the calc–silicate assemblages appears to rule out a flushing of the metamorphic terrane by a fluid derived from an external source and not equilibrated with the mineral assemblages. If an aqueous fluid had been introduced and had reacted with the samples following the peak of the metamorphism, we would expect considerable evidence of retrograde alteration in the minerals. We also know that other metamorphic terranes contain fluids with the appropriate specific volume for the inferred metamorphic conditions (Bilal and Touret, 1976; Burruss, ms; Rich, ms; Wood, ms). This is evidence that primary metamorphic fluids may be trapped during peak metamorphic conditions and preserved. Discrepancies between estimated metamorphic conditions and fluid densities have also been observed elsewhere (Kreulen, ms).

We suggest that the possibility of changes in specific volume after initial entrapment cannot be ruled out despite a lack of textural evidence for leakage from inclusions. The uplift of the metamorphic terrane which includes these samples probably followed a path that crossed lines of constant specific volume (isochores) for the fluid. Calculated uplift and cooling curves for several metamorphic terranes are shown in figure 8. For an uplift and cooling history similar to the one described by curve 1 of figure 8, the pressure will first drop with a small decrease in temperature. Later, as the terrane nears the surface, the change of temperature for a given change in pressure becomes larger. Should the rocks be uplifted in this fashion, without significant cooling during the initial uplift, the

volume of the fluid will increase, and, if the strength of the quartz enclosing the inclusions is exceeded, fluid will leak out. This will cause the specific volume of the remaining fluid to increase.

At room pressure, about 850 bars pressure differential between the pressure exerted by the fluid and the confining pressure on the quartz grains appears to be sufficient to rupture most aqueous inclusions in quartz larger than 12 μm, causing them to leak (Leroy, personal commun., 1978; Naumov, Balitskii, and Khetchikov, 1966). Quartz will probably be less strong at the temperatures and pressures inferred for these rocks, especially in the presence of an aqueous fluid (Griggs and Blacic, 1965; Griggs, 1967), so leakage may be considered a likely possibility if uplift crosses isochores along a path similar to 1 of figure 8. This explanation would also account for the observation that a few of the aqueous fluid inclusions lie along healed fractures in the quartz grains. In some terranes fluid inclusions show evidence of "explosive" fracturing (Touret, 1976; Hollister and Burruss, 1976; Kruelen, ms). In others, as in this case, there is no visible rupture of inclusions, but low densities suggest leakage (Rich, ms). The leaking of the primary inclusions may, in addition, be related to

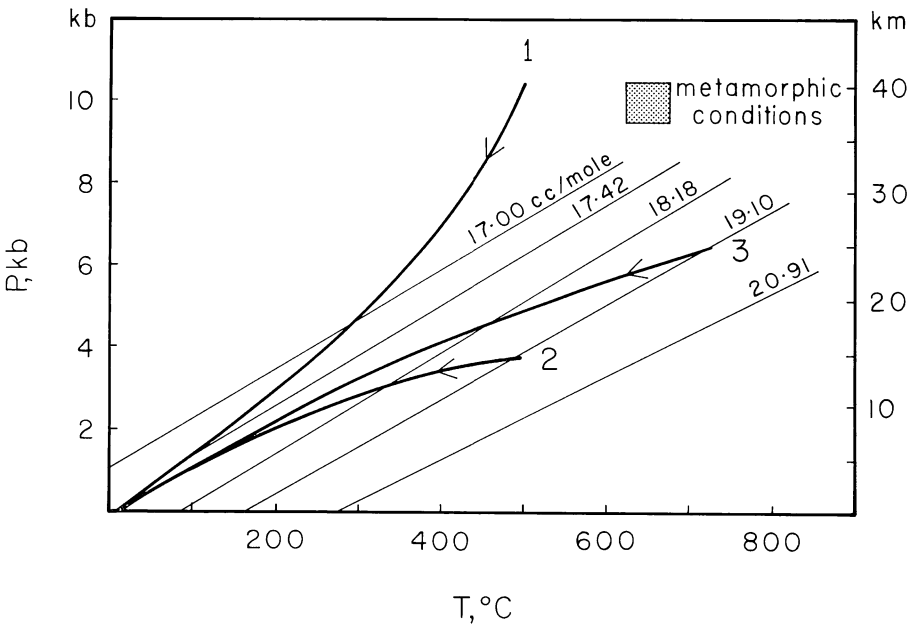


Fig. 8. Uplift paths calculated for the Alps (Clark and Jager, 1969, curves 1, 2) and for the southern Appalachians (Dallmeyer, 1978, curve 3). Uplift rates: curve 1 = 0.74 mm/yr; curve 2 = 0.47 mm/yr; curve 3 = 0.1 mm/yr. Isochores are for 25 wt percent NaCl brines, values are cc/mole. Limiting assumptions for Alpine uplift curves (surface heat flow, mineral ages, P, T conditions of metamorphism) give rise to considerable variation in calculated uplift trajectories. The curves illustrated represent high (curve 1) and low (curve 2) uplift rates. Clark and Jäger (1969) favor the high uplift rate curve. The Appalachian uplift trajectory is constrained by two thermal events and the P, T conditions prevailing during each event.

stresses acting on the grains during uplift (Kerrich, 1976; Wilkins and Barkas, 1978). Leakage or redistribution of fluids in quartz may have been accompanied by partial or substantial recrystallization of the host grain. Even a slight amount of recrystallization could obliterate visible cracks or "explosion" features.

Changes in molar volume of inclusions by leakage is not an ubiquitous phenomenon as attested by those cases where the isochores for the fluids do extrapolate to the predicted metamorphic conditions. Experimental work by Roedder and Skinner (1968) at lower pressures and temperatures (max 4 kb, 400°C) suggests that inclusions do not leak. However, their experiments did not take into account the stresses that would be operating in the natural system and the properties of quartz at the temperature and pressure conditions of this study. Other uplift paths (curves 2 and 3, fig. 8) cross isochores in a direction that will not result in buildup of excess pressure in entrapped inclusions. In such cases and in the absence of deformation, fluid inclusions may not leak during uplift.

CONCLUSIONS

The study of fluid inclusions in a series of calc–silicate metamorphic rocks confirms the observation on graphite-bearing pelitic metamorphic rocks (Burruss, ms) that fluid compositions predicted from metamorphic mineral assemblages are represented by fluid inclusions in the samples. The lack of complete and accurate data on fugacities of components in the fluids involved and on activities of various components in the metamorphic minerals limits our ability to specify precisely the fluid compositions expected. However, the agreement between predicted fluid compositions with those observed in fluid inclusions is good enough to conclude that calculations of calc–silicate equilibria give a close estimate of true fluid compositions if they are based on: (1) good experimental data, (2) an independent estimate of metamorphic conditions, and (3) the fugacities of CO_2 and H_2O calculated by Holloway (1977).

The contrast between fluid compositions in matrix quartz grains in calcareous and in semi-pelitic schists suggests that the fluid composition was buffered independently in each rock type. This observation reinforces the concept originally proposed by Hewitt (1973) and Greenwood (1975) of the buffering capacity of low variance mineral assemblages. There is no evidence for introduction of fluids from an external source. In the Morse Basin terrane, where metamorphic pressure was high, the specific volume data for aqueous inclusions apparently underestimates the pressure by at least 3 kb, assuming the extrapolation of fluid density data from low T, P conditions are valid. Our results may serve to outline some of the steps in the uplift history that control the final densities of the fluid inclusions preserved when the samples reach the surface.

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