# Preliminary fluid inclusion studies in a high-grade blueschist terrain, Syros, Greece

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## Abstract

Preliminary fluid inclusion measurements have been made on quartz (whole rocks and segregations) and garnet from a blueschist terrain. Although further measurements are required, the fluids apparently associated with the blueschist event are aqueous with no thermometrically detectable $CO_2$, a feature which is consistent with mineral–fluid equilibria studies. The salinity of the fluid inclusions is highly variable, from almost pure $H_2O$ to halite saturation, and a mechanism involving hydration reactions, such as proposed by Crawford *et al.* (1979), is suggested. Fluid inclusions associated with the greenschist overprint, which has affected the terrain, are also aqueous in nature.

KEYWORDS: fluid inclusions, quartz, garnet, blueschist terrain, Syros, Greece.

## Geological setting

THIS study was undertaken on the Cycladic island of Syros, Greece, which is located some 150 km to the southeast of Athens in the Aeagean Sea. The Cycladic islands form part of a regional blueschist belt known as the Attico-Cycladic massif, which stretches from mainland Greece to Turkey (Fig. 1). $^{40}Ar/^{39}Ar$ cooling ages on micas give an Eocene date for the high-pressure metamorphism (Schliestedt *et al.*, 1987; Wijbrans *et al.*, 1988). Superimposed on the blueschist assemblages is a regional greenschist event which culminated in the local development of thermal domes, such as that seen on the neighbouring island of Naxos. Rb/Sr and K/Ar age determinations on micas give late Oligocene to early Miocene dates for this second metamorphic phase (Altherr *et al.*, 1979; Schliestedt *et al.*, 1987). Although relics of the high-pressure metamorphism can be found throughout the Cyclades, the best preserved blueschists occur on the islands of Syros, Tinos and Sifnos. The rocks on Syros are predominantly metasedimentary, and comprise a continuous sequence of alternating marbles and pelitic schists with some intercalated metabasites (see Fig. 1).

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## Metamorphic evolution

The metamorphic conditions for the blueschist event are relatively well constrained. Fig. 2 is a *P–T* plot indicating the critical phase equilibria for the island (Dixon, 1969; Ridley, 1982). The assemblages jadeite and quartz, zoisite, paragonite and quartz, and the occurrence of lawsonite without jadeite, indicate temperatures between 450 and 500 °C, at a minimum pressure of 14 kbars. The static, partial greenschist overprint, associated with the uplift of the terrain, has led to the development of chlorite, calcite, albite and actinolite at the expense of glaucophane and omphacite-bearing assemblages, particularly in the south of the island.

## Aims of the fluid inclusion study

Measurements made on fluid inclusions in quartz, in both blueschist and greenschist rocks, were used to answer some specific questions about the fluid phase.

(1) Have samples of an early, synmetamorphic fluid been preserved?; and if so can they be recognized?

(2) Do the blueschist metamorphic fluid compositions predicted by mineral equilibria studies correspond to the compositions of any fluid inclusions in the rocks?

(3) Does a difference in composition exist between inclusions associated with the unaltered blueschists and those associated with the altered

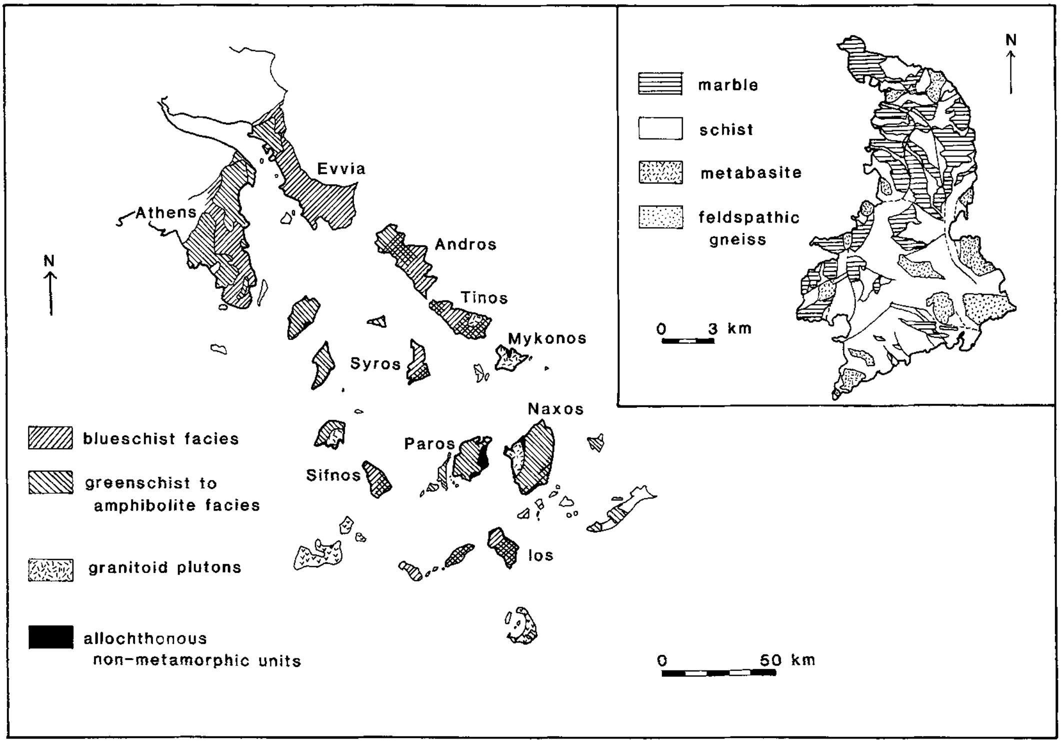


FIG. 1. Geological setting of the Cycladic blueschist belt; the inset shows a simplified geological map of Syros (from Ridley, 1982).

greenschists, either in terms of the $CO_2$:$H_2O$ ratio or the salinity fo the fluid?
(4) Does the retrograde fluid have a distinctive signature?

## Selection of study material and methodology

Inclusion studies were mainly carried out on quartz, both whole rock matrix material and segregations. As only one high-strain deformational event is documented on Syros (Ridley, 1985, 1982), the formation of deformed and boudinaged segregations, such as that shown in Fig. 3, can be confidently assigned to the blueschist event. This close age relationship between the segregations and their host blueschists was used when selecting material to fingerprint the blueschist fluid. Fluid inclusions in garnet were also studied, though to a lesser extent due to their comparative rarity.

After preliminary optical investigation with a standard petrographic microscope, samples were selected and prepared as polished wafers, with a high quality polish obtained on both sides (Shepherd *et al.*, 1985). The average thickness of the wafers was 0.3 mm. A Linkam TH600 stage attached to a general purpose Zeiss microscope was used to obtain thermometric measurements on the inclusions. Homogenisation ($T_h$) and last ice melting temperatures ($T_m$) were measured on all inclusions. The temperature of first ice melting ($T_{fm}$) was recorded when observed, and the temperature of halite dissolution ($T_{sNaCl}$) was noted for inclusions containing a daughter phase (the daughter phase was always cubic and isotropic).

## Inclusion petrography

Most fluid inclusions in the samples examined occurred in well-defined trails which crossed several grain boundaries. Rarer isolated inclusions were present, randomly distributed throughout the sample, while others occurred in short intragranular trails or clusters. 85% of the inclusions measured were under 20 $\mu$m in size, and most displayed regular, rounded negative crystal shapes. A 'relative chronology' classification was adopted. It was assumed that isolated inclusions were earlier than those outlining fractures, and intragranular trails earlier than transgranular trails.

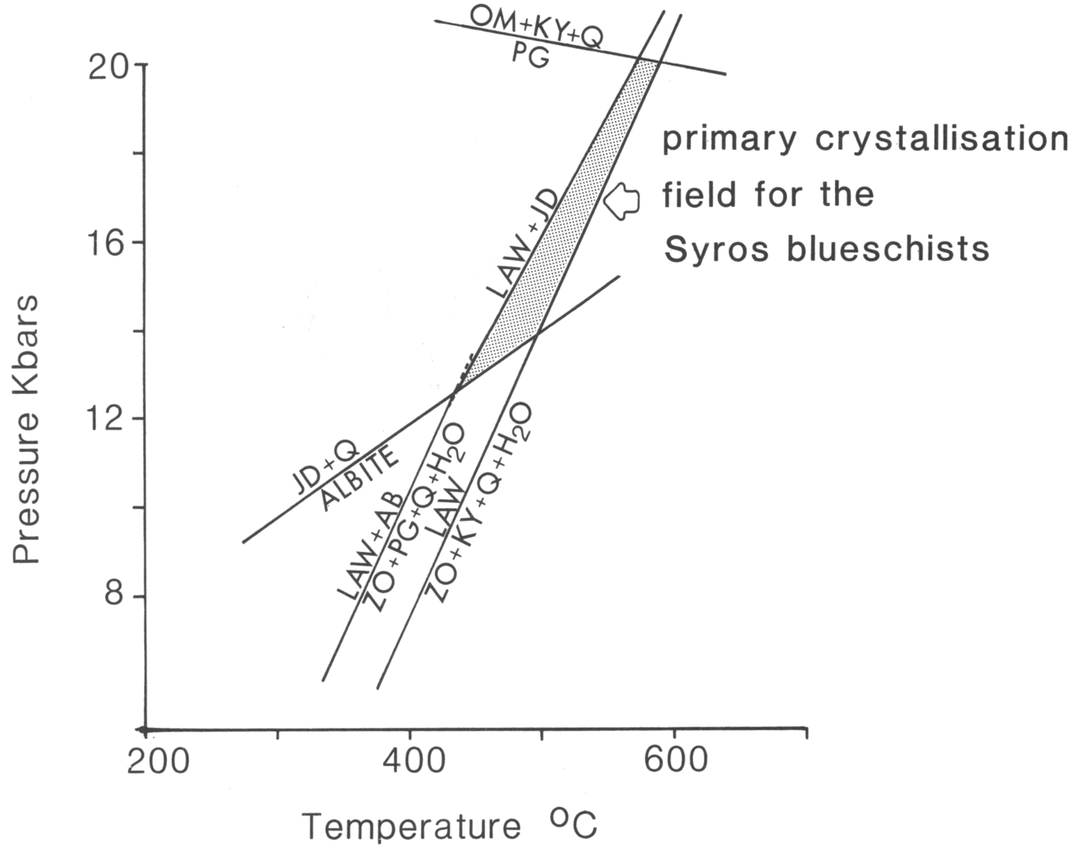


FIG. 2. Calculated equilibria defining the peak *PT* conditions for the Syros blueschists (after Dixon, 1969). All equilibria were calculated using THERMOCALC (Holland and Powell, 1985) and the extended dataset (Powell and Holland, 1988).

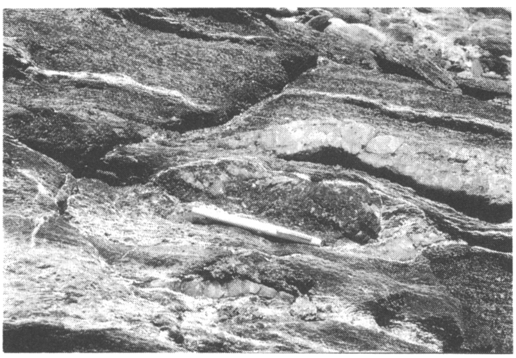

FIG. 3. Field photograph of an early boudinaged quartz segregation in blueschist metasediment.

**Mineral–fluid equilibria in the blueschists**

Detailed petrographic work has been carried out on carbonate-bearing blueschist metasediments to establish the composition of the fluid in equilibrium with the mineral assemblages. Various important reaction equilibria for the blueschist metasediments plotted in $T$–$X_{CO_2}$ space are shown in Fig. 4. Schreinemakers analysis (Schreinemakers, 1915–1925; Zen, 1966) was used to assemble the reaction curves around the invariant points, and shifts in the positions of the curves due to real mineral compositions have been calculated using appropriate activity–composition relationships.

Two important points can be made concerning the blueschist fluid. First, samples collected on a scale of centimetres from single outcrops contain mineral assemblages which equilibrated with

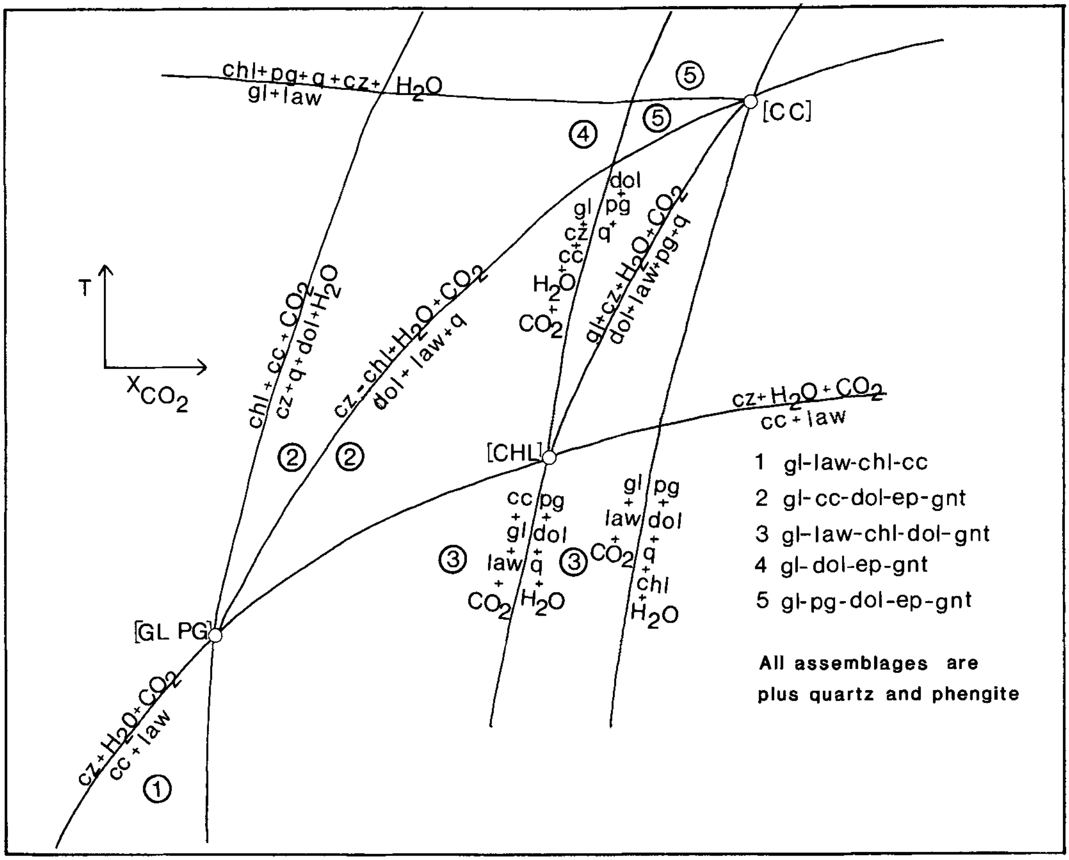


FIG. 4. A portion of the $T$–$X_{CO_2}$ diagram for the system $Na_2O$–$CaO$–$Al_2O_3$–$MgO$–$SiO_2$–$H_2O$–$CO_2$ calculated at 14 kbars. The temperature range covered by the diagram is approximately 10 °C (390–400 °C) and $X_{CO_2}$ values range from 0–0.0015 mol. %. Various reaction equilibria are shown, and the mineral activities and abbreviations are given below. Also illustrated on the $T$–$X$ grid are the locations of five mineral assemblages collected from a sequence of layered beds at one locality. Although not every assemblage is uniquely defined in $T$–$X_{CO_2}$ space (i.e. 2, 3 and 5), the mineral assemblages from different rock layers still plot across a real range of divariant volumes, indicating that the individual layers have equilibrated with fluids of different compositions. No temperature difference is implied between the mineral assemblages. Mineral abbreviations: gl = glaucophane ($a_{gl}$ = 0.055 a); pg = paragonite ($a_{pg}$ = 0.900 b); law = lawsonite ($a_{law}$ = 0.954 a); chl = clinochlore ($a_{clin}$ = 0.051 c); cz = clinozoisite/epidote ($a_{ep}$ = 0.136 b); cc = Ca-carbonate ($a_{cc}$ = 0.995 d) and dol = dolomite ($a_{dol}$ = 0.678 d). Source of activity formulations; a = ideal mixing on sites; b = Powell (1978); c = Powell and Evans (1983); d = Bickle and Powell (1977).

different fluid compositions. In terms of the $T$–$X_{CO_2}$ diagram, this means that fluid compositions in equilibrium with different rock layers plot in separate areas of the $T$–$X_{CO_2}$ reaction net (Fig. 4). Differences in fluid composition existing on such a small scale suggest that the rock layers have controlled, or buffered, the composition of the coexisting fluid, and the volume of any external fluid involved was probably low.

The second point is that the fluids in equilibrium with the blueschist assemblages are very water-rich, with considerably less than 0.1 mol. % $CO_2$ present (see Fig. 4).

## Fluid inclusion results

### *Blueschists—inclusions in quartz*

Fig. 5 shows the thermometric data collected from a small quartz segregation in a glaucophane–garnet metabasite. The $T_h$ and $T_m$ histograms show one clear peak, and it appears that a single fluid event has been sampled. Salinity, deter-

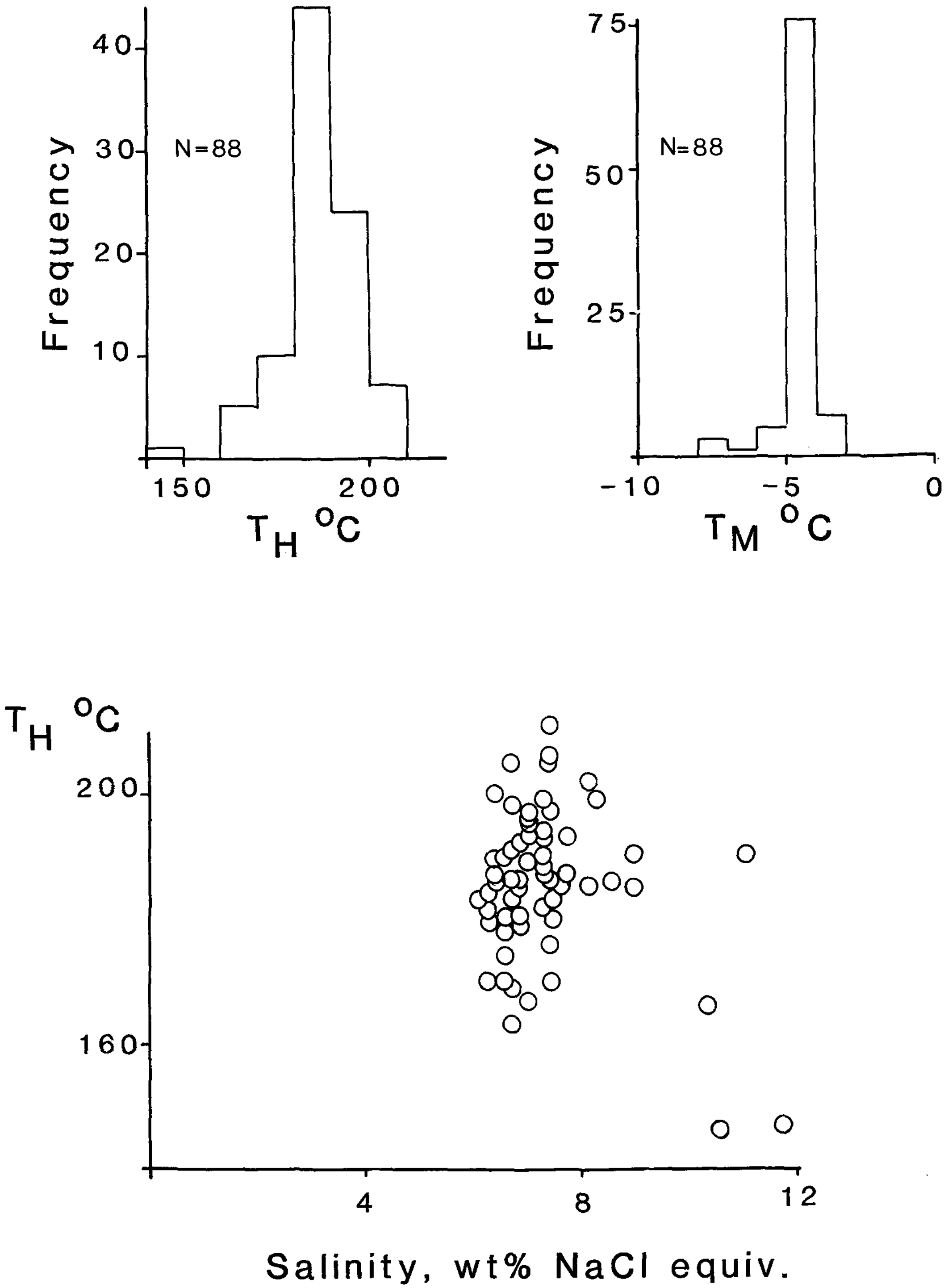


FIG. 5. Thermometric data for sample #190. A fuller description of the samples studied is given in the appendix.

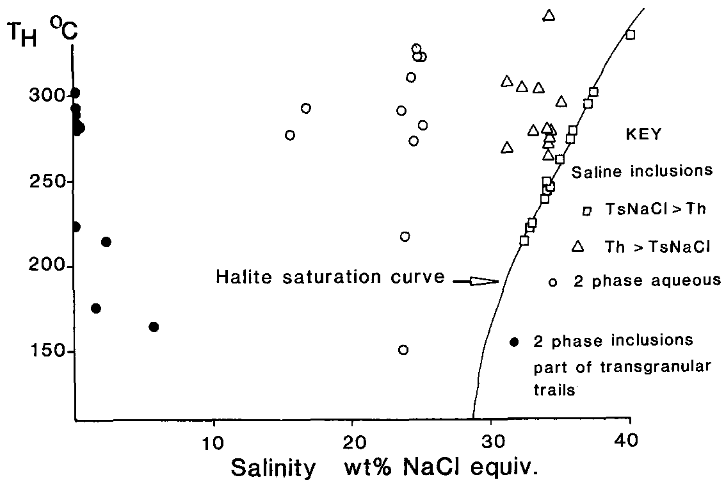


FIG. 6. Thermometric data for sample #77. Fluid inclusions were studied in both matrix quartz and a small quartz segregation but no significant compositional or density differences were detected between the inclusion populations in the two settings.

mined from $T_m$ ice, ranges from 6–9 eq. wt. % NaCl, and homogenization temperatures ($T_h$) from 170–210 °C were recorded. The spread of homogenization temperatures associated with a reasonably constant salinity value probably indicates necking down of the inclusions during uplift (Pêcher 1981; Yardley 1983).

Other samples contain inclusions which are much more saline than those previously described. Fig. 6 presents thermometric data for one such sample which contains several generations of inclusions. One group of inclusions are highly saline (>20 eq. wt. % NaCl), and some contain an isotropic daughter phase thought to be halite. These inclusions occur either as isolated groups, or along short intragranular fractures. A second group of much less saline inclusions is also present, occurring in apparently randomly-oriented trails which transect several grain boundaries, and these are clearly later. Two types of homogenisation behaviour were observed in the halite-bearing inclusions, and these are indicated in Fig. 6. First-melting temperatures in the highly saline inclusions were observed at −50 °C, which suggests the presence of $CaCl_2$ (Crawford, 1981; Shepherd *et al.*, 1985). Transitions in addition to $T_{fm}$ and $T_m$ must have occurred in these highly saline inclusions, although they were not directly observed. The final melting temperatures observed (usually around −24 °C) probably refer to the melting of hydrohalite, and should be referred to as $T_{mhy}$ (Roedder, 1984; Shepherd *et al.*, 1985). The overall salinity of halite-bearing inclusions was determined from the dissolution temperature, $T_{sNaCl}$. The possible significance of these early high-salinity inclusions is discussed more fully later.

*Fluid inclusions in garnet.* Almost all the fluid inclusions studied in the blueschist rocks occur in quartz, but some rare fluid inclusions were also found as small irregularly-distributed clusters in garnet cores. As these almandine–grossular garnets developed under blueschist conditions, there is a good chance that these inclusions are trapped samples of the primary fluid.

The inclusions are relatively large, up to 15 μm long, and they tend to be elongate and flat. Their habit is quite different from the negative crystal inclusion shapes described by Berglund and Touret (1976) from garnets in Madagascar, yet there is no reason to suspect that these inclusions are secondary.

The salinity of the garnet fluids is quite low at around 4 eq. wt. % NaCl. Homogenization temperatures range from approximately 200–270 °C, a similar spread to that seen in the other blueschist samples. Also shown on Fig. 7 are measurements made on isolated inclusions present in the matrix quartz associated with the garnet. Interestingly, a proportion of these early inclusions are highly saline, similar to the inclusions seen in the previously described quartz sample.

## *Greenschists*

Four samples showing the greenschist overprint were studied in order to make comparisons with the blueschist samples. Quartz veins or segrega-

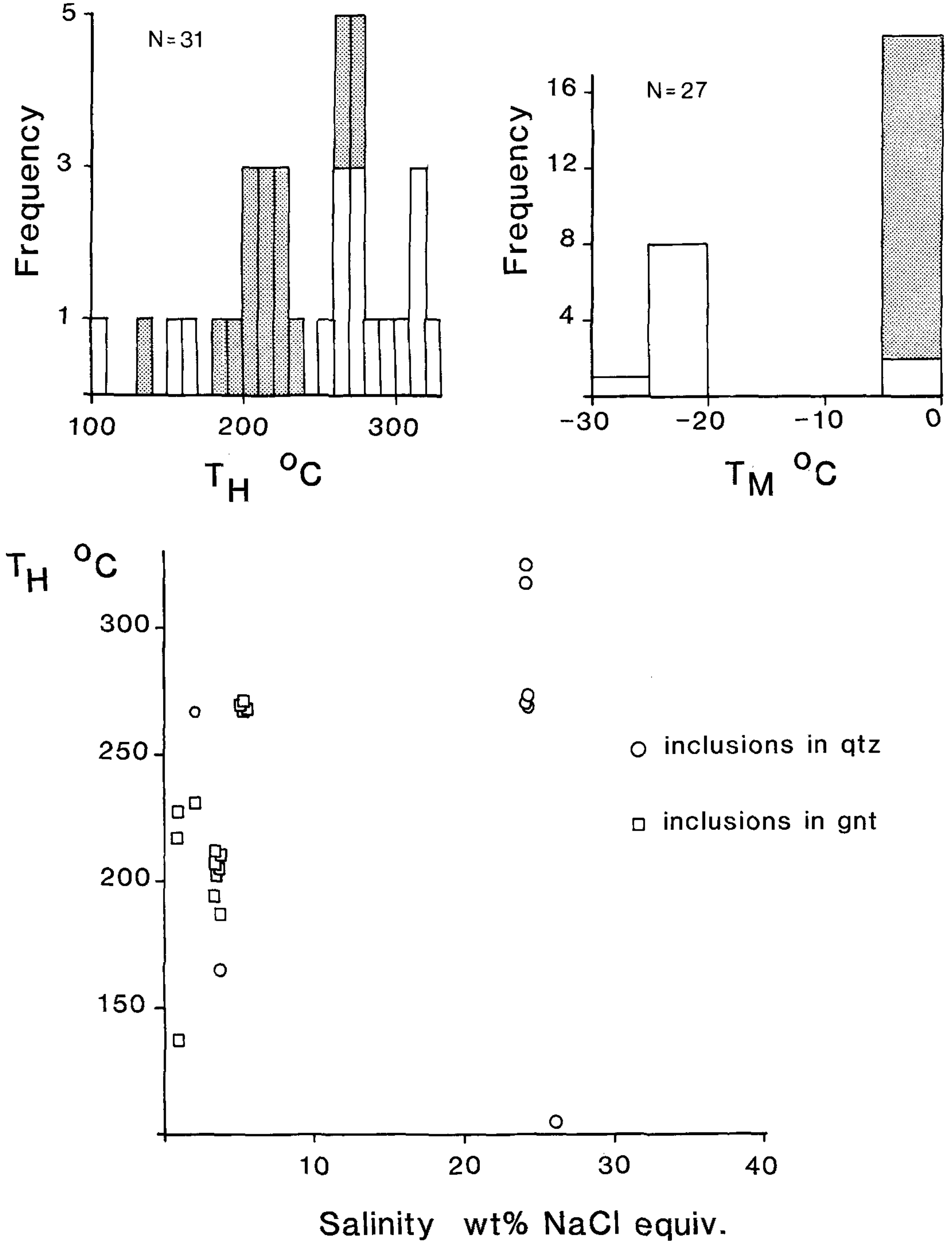


FIG. 7. Thermometric data for sample #76. The shaded blocks in the frequency histograms refer to the thermometric data collected from inclusions in garnet, rather than those from the surrounding matrix quartz.

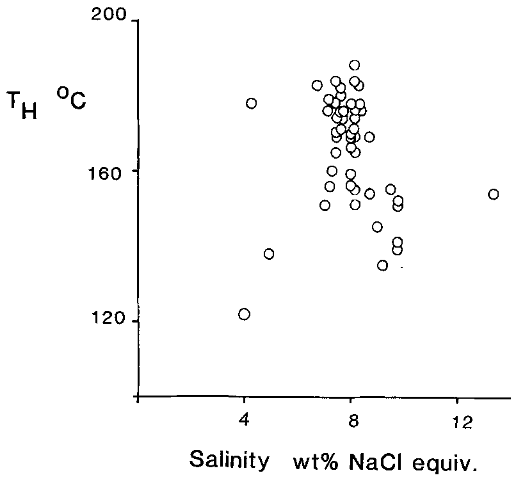


FIG. 8. Thermometric data from a quartz–ankerite segregation in altered blueschist metasediments, sample #32.

tions were studied from samples which showed partial or complete development of the greenschist facies overprint, and it was hoped that these might contain samples of the fluid responsible for the retrogression.

Fig. 8 presents data collected from a quartz segregation in altered blueschists. The inclusions in this sample are large and abundant, and nearly all of them are part of transgranular trails. All the inclusions seen are aqueous and, as is indicated in Fig. 8, they appear to be recording a single fluid event, with salinities in the range 6–9 eq. wt. % NaCl, and homogenization temperatures from 150–190 °C. Other greenschist samples studied show a clear bimodal grouping of salinities, with values up to 20 eq. wt. % NaCl being measured. Such a bimodal grouping indicates the presence of at least two distinct fluid populations, and the more saline inclusions may be a 'memory population' related to the earlier blueschist event.

## Summary of results

The properties of the inclusions in quartz and garnet measured in the blueschists are summarized below.

All the inclusions observed were two-phase (l + v) inclusions.

V/L homogenization temperatures are in the range 110–370 °C.

First melting temperatures, when observed, were lower than the eutectic temperature for the NaCl–$H_2O$ system ($Te = -20.8$ °C; Crawford, 1981). Values obtained clustered around −35 °C, indicating the presence of other salts ($MgCl_2$?) in addition to NaCl. Melting was observed in some of the highly saline inclusions at temperatures as low as −50 °C, pointing to the presence of $CaCl_2$.

Final melting occurred in the range −12–0 °C, except for the highly saline inclusions, where final melting occurred at much lower temperatures, around −25 °C, and these measurements refer to the melting of hydrohalite rather than ice.

Having summarized the findings for the blueschist samples it can be stated that those inclusions which are thought to be primary, or at least early, are dominantly aqueous with a variable salinity from almost pure water to halite saturation. Comparing the data for inclusions measured in blueschist and greenschist samples a number of similarities are apparent. In both cases the inclusions are of the two-phase aqueous type, and the two groups show a very similar range of homogenization temperatures, from 110–370 °C. The main difference is that the blueschist samples contain inclusions which are much more saline than anything found in the greenschists.

## Discussion

### *The saline inclusions (>20 eq. wt. % NaCl)*

The saline inclusions in the blueschists appear to be some of the earlier fluids preserved. Until recently the sporadic occurrence of highly saline and halite-saturated inclusions in metamorphic veins and whole rocks tended to be dismissed as an enigmatic curiosity unless they could be directly related to the presence of nearby evaporitic sequences (Rich, 1979). There is certainly no evidence for the presence of an evaporite deposit at depth on Syros, but the presence of Na-bearing phases in the blueschists glaucophane, paragonite, omphacite) means that the synmetamorphic fluid was probably saturated with respect to sodium. However, it would be the availability of the chloride ion, presumably inherited from the original pore fluid, which would ultimately determine whether or not the fluid became saturated in NaCl.

Participation in hydration reactions could cause low-salinity fluids to become more saline, as was suggested by Crawford *et al.* (1979), and given that sufficient chloride ions were present, highly saline and halite-saturated inclusions could be produced by such a mechanism. A process of evolving salinity with time could explain the occurrence of low salinity fluids in the garnet core of sample #76, and saline fluids in the external matrix quartz. An early sample of the fluid is thus preserved within the garnet, while subsequent hydration reactions modify the salinity of the remaining fluid which is later trapped in the quartz.

## Conclusions

On the amount of data gathered so far, it is not possible to state conclusively that the fluid inclusions present in the blueschists represent samples of the high-pressure synmetamorphic fluids. However, the absence of $CO_2$-bearing inclusions is compatible with the results of the mineral–fluid equilibria studies on the stable phase assemblages. There are very few documented cases of aqueous inclusions in high-grade metamorphic rocks, largely because much of the fluid inclusion work on metamorphic rocks has concentrated on $CO_2$-dominated granulite terrains, where $H_2O$-bearing inclusions are invariably dismissed as being secondary. However, examples of very early $H_2O$ inclusions are now being reported from granulite terrains, and there are indications that these could be contemporaneous with the early $CO_2$-rich fluids. The recent discovery of halite cubes in decrepitated inclusions in granulites is also being interpreted as evidence for the presence of very early high saline aqueous fluids (J. Touret, pers. comm., 1989).

Unfortunately it is not possible to calculate meaningful isochores for the blueschist samples. The relatively low homogenisation temperatures, compared to the metamorphic temperatures estimated from the phase equilibrium studies (450 °C) suggest that the inclusions have necked-down during uplift. The available *PVT* data on aqueous saline solutions are limited to measurements made at low pressure, up to 2 kbars (Haas, 1976; Potter and Brown, 1977) and the linear extrapolation of these isochores up to pressures of 14 kbars is not justifiable. The inclusions present in the greenschist samples are largely of secondary origin, but whether these represent samples of the infiltrating greenschist fluid is debatable. In terms of a relative chronology these fluids definitely appear to be later than the fluids sampled in the blueschists, but the greenschist samples are probably recording several fluid events which occurred during the later history of the rocks.

Although the preliminary nature of this study means that no definite conclusions can be reached at this stage, it illustrates the potential for future studies in blueschist terrains, an environment in which previous work on fluid inclusions is noticeably lacking.

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## Appendix: description of samples mentioned in the text

*Sample #32.* Quartz segregation in an altered blueschist metasediment. Mineralogy of host rock: qtz–dol–cc–chl–w.mica–rutile.

*Sample #76.* Matrix quartz and garnet porphyroblasts in a blueschist metasediment. Mineralogy: gl–w.mica–qtz–gnt–law(psd)–cc–rutile.

*Sample #77.* Matrix quartz in a blueschist metasediment. Mineralogy: law(psd)–qtz–w.mica–gl–gnt–cc–dol–titanite.

*Sample #190.* Quartz segregation in a gl–gnt metabasite. Mineralogy of host rock: gl–epid–omphacite–gnt–qutz–w.mica–rutile.

*Mineral abbreviations.* cc = calcite; chl = chlorite; dol = dolomite; epid = epidote; gl = glaucophane; gnt = garnet; law(psd) = lawsonite pseudomorph; qtz = quartz; w.mica = phengite.

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