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The role of fluid inclusions in the exsolution of clinopyroxene in bustamite from Broken Hill, New South Wales, Australia

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Abstract

Rods and laths of clinopyroxene apparently exsolved in host bustamite are described from the lode rocks of Broken Hill, New South Wales, Australia. The rods are commonly oriented with *c* clinopyroxene || *b* bustamite. They are associated with fluid inclusions which may be in contact with the clinopyroxene rods (type A) or not (type B).

Freezing-point depressions recorded for the inclusion fluids range from 3° to 50°C. Although there is a region of overlap, type A inclusion fluids have salinities in the lower part of the range, whereas type B inclusions contain fluids in the higher part of the range. In bustamite samples containing only moderate numbers of clinopyroxene rods where relationships can be clearly observed, the rods are seen to be arranged within curved sheets localized along healed former fractures. Where fluid inclusions of both types are present within any one sheet, they have approximately the same salinity. Homogenization temperatures fall in the range 240–360°C, but the trapping temperatures are unknown owing to uncertain corrections for pressure.

The clinopyroxene rods are believed to have originated by a mechanism of exsolution, in which fluid inclusions act as centres of nucleation and growth in the high-temperature solid-solution phase as it cools below solvus temperatures. The rods propagate either from the solid or liquid inclusion-terminated end, but the preferred mechanism is by solution growth, the fluid inclusion advancing ahead of the rod through the host grain.

Introduction

The stratiform Pb–Zn orebody of Broken Hill, New South Wales, is one of the best known of its type. The country rocks of the area are various gneisses, amphibolites, and banded iron formation which have resulted primarily from high-grade regional metamorphism. Hornblende granulite facies was attained in the vicinity of Broken Hill, and the event is dated at about 1700 m.y. (Pidgeon, 1967). This was succeeded by a period of retrograde metamorphism which achieved its fullest expression in major shear zones, several of which either cut the orebody or are in close proximity to it. Mineral assemblages of greenschist or lower amphibolite facies are found in these rocks. Their geochronological age is approximately 500 m.y., but this date obscures what is an undoubtedly complex history of retrogression.

A carefully reasoned discussion of major problems associated with understanding the nature and origin of the Broken Hill orebody has been given by Hobbs *et al.* (1968). A major part of their analysis relates to the period of formation or emplacement of the orebody in the host rocks. Although these authors were unable to find unambiguous evidence that the orebody was present prior to the high-grade metamorphism, it nevertheless has been widely accepted since the classic work of King and Thompson (1953) that the orebody had a syngenetic sedimentary origin.

It is unlikely that a fluid inclusion study could make a meaningful contribution to the problem of

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whether the orebody was emplaced during or prior to the high-grade regional metamorphism. In either case, it is possible that the fluid associated with this metamorphic episode could have been sampled as fluid inclusions in these rocks. Owing to the general proximity of the retrograde shear zones to the orebody, it must also be expected that the associated metamorphic fluids invaded the lode rocks quite generally from time to time, and became trapped as fluid inclusions. Certainly, aqueous fluids with a wide range of salinity and temperature have pervaded the lode rocks (Wilkins, 1976), but it is not yet clear how these fluids relate to the metamorphic history of the area.

The bustamite-bearing rocks of Broken Hill are best developed in the calcitic ore of the lead lode. Bustamite also occurs sporadically elsewhere, notably in varieties of pyroxene sub-ore in the B lode (Hodgson, 1975b). During a detailed optical and X-ray crystallographic study of an extensive series of calcium-rich bustamites of the orebody (Sverjensky, 1973), fluid inclusions were noted in all samples examined. A number of these bustamites also contained an abundance of oriented solid inclusions of clinopyroxene. In similar material described in two recent papers (Mason, 1973; Hodgson, 1975a), clinopyroxene rods and lamellae have been noted in host bustamite. They are presumed to have originated by exsolution during the period of retrograde metamorphism. Our observations on the clinopyroxene inclusions show that they are commonly spatially related to fluid inclusions.

Solid inclusions

In the Broken Hill bustamites, sub-spherical inclusions of sphalerite and flat oval inclusions of quartz are common, and laths and rods of clinopyroxene are nearly ubiquitous. The clinopyroxene inclusions are elongated parallel to *c*, and they are commonly oriented parallel to the *b* axis of the host bustamite. The laths range in size up to about 40 μm in length and about 20 μm in width. The rods of clinopyroxene range in length from less than 5 μm to about 200 μm. It is unusual for them to have a width greater than 10 μm or less than 1 μm. A semi-quantitative electron microprobe analysis of a clinopyroxene lath in bustamite USGD (University of Sydney, Geology Department) 50749 gave the composition $Ca_{1.1}Fe_{0.6}Mn_{0.4}Si_{2.1}O_{5.7}$. Mason (1973) and Hodgson (1968, 1975a) analysed clinopyroxene laths in bustamite from Broken Hill, but neither reports specific analyses. Some Ca-rich bustamites contain up to an estimated 40 volume percent of clinopyroxene, whereas others, closer to the composition $CaMnSi_2O_6$, contain few clinopyroxene rods. Where the rods are attached to a fluid inclusion, they are often clearly terminated by crystal faces chiefly belonging to the forms $\{001\}$ and $\{\bar{1}01\}$.

Fluid inclusions

Most bustamites had a grain size of less than 3 mm and were not entirely suitable for high-magnification microscopic study in polished thick sections. For this reason detailed work was restricted to three samples of calcium-rich bustamite (USGD 50706, 50707, and 50716) with a maximum grain size of 10 mm. It is convenient to divide the fluid inclusions into two types, which may be designated types A and B according to whether they are in contact with a clinopyroxene rod or not.

Type A fluid inclusions typically occur at one or both ends of the rods of clinopyroxene described above. The presence of a fluid inclusion at the termination of a rod is easily observed from the high negative relief of the fluid-filled cavity. This type of inclusion usually has about the same width and general cross-sectional shape of the rod to which it is attached (Fig. 1a). However, several variations exist. Some fluid inclusions have a width which is less than that of the rod (Fig. 1b), some are wedge-shaped (Fig. 1c), and, very rarely, the fluid may even fill a cavity which runs along the whole length of a rod (Fig. 1c). In grains containing a high abundance of inclusions, groups of several solid and liquid inclusions may be attached to one another. A simple variety of this type is shown in Figure 1d, where a fluid inclusion separates a rod into two parts and another fluid inclusion terminates one end of the complex.

The distribution of varieties of solid/fluid inclusion combinations in single grains is shown in Table 1. The proportion of complex inclusions varies from grain to grain, depending on the total abundance. With larger counts, the numbers of singly-terminated rods with opposed orientations in each sample are expected to be more nearly equal. Type B inclusions in these grains were not counted, since they are present in relatively large numbers and some are extremely small.

Commonly, the two ends of a rod have different widths (Fig. 2a) and may also be axially displaced. In many measured examples the fluid is found to occupy about 10 percent of the combined fluid plus solid

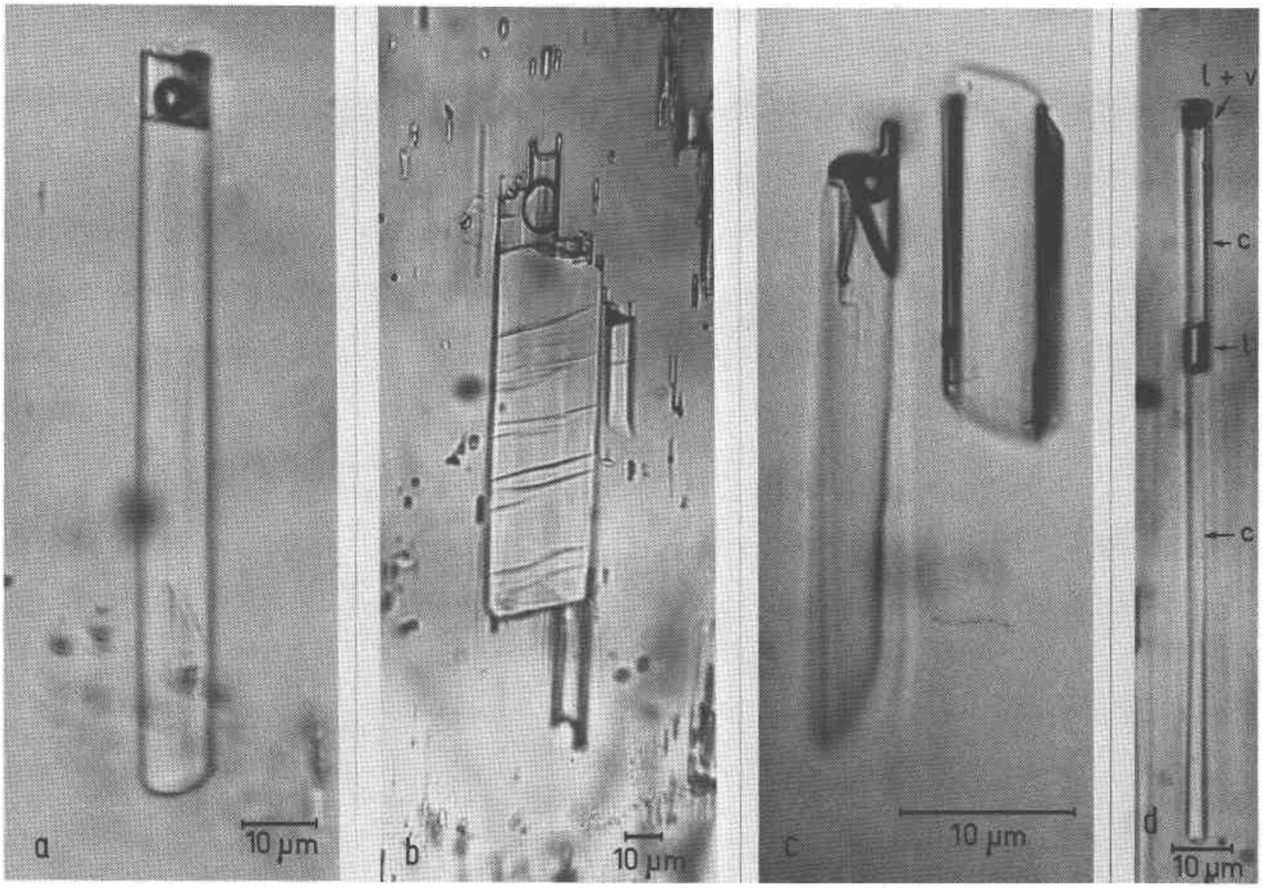

Fig. 1. Simple types of solid/fluid inclusion combinations in bustamite (USGD 50706) from the Broken Hill lode. (a) Clinopyroxene rod terminated by a fluid inclusion at one end. (b) Clinopyroxene lath terminated by fluid inclusions at both ends. The fluid inclusion at the lower end does not contain a vapor bubble, and has a width less than that of the lath. The fluid inclusion at the upper end contains a vapor bubble, and the irregular termination suggests fluid-inclusion capture by the developing complex. (c) Clinopyroxene rods, one with fluid inclusions attached to both sides, the other with a wedge-shaped fluid inclusion termination. (d) Fluid inclusion separating a clinopyroxene rod into two parts. A second fluid inclusion terminates one end of the complex. c–clinopyroxene; l–liquid; v–vapor bubble.

inclusion volume. However, examples may be found all through the series up to varieties in which a small clinopyroxene rod is attached to a large fluid inclusion which occupies as much as 90 percent of the total volume. About 10 percent of type A inclusions contain no vapor bubble. Such fluid inclusions commonly occur at one end of clinopyroxene rods which are doubly terminated by fluid inclusions, suggesting that the cavities can be interconnected along part of the bustamite/clinopyroxene grain boundary. However, even some type A fluid inclusions from singly-terminated clinopyroxene rods are without vapor bubbles.

Clinopyroxene rods and associated type A inclusions are rare in some samples, but in others they may number hundreds per cm^3. Although they have

Table 1. Distribution of inclusion varieties in single grains of bustamite from Broken Hill

Variety of inclusion	Number present	
	USGD 50706	USGD 50716
1. Rod terminated at one end with a fluid inclusion	20	35
2. Singly terminated but opposite orientation to type 1	30	44
3. Rod terminated at both ends with fluid inclusions	16	25
4. Fluid inclusion dividing rod into two parts	1	1
5. Complex solid/fluid inclusions	18	17
6. Rod with no fluid inclusion attached	1	0
Total inclusions	86	122

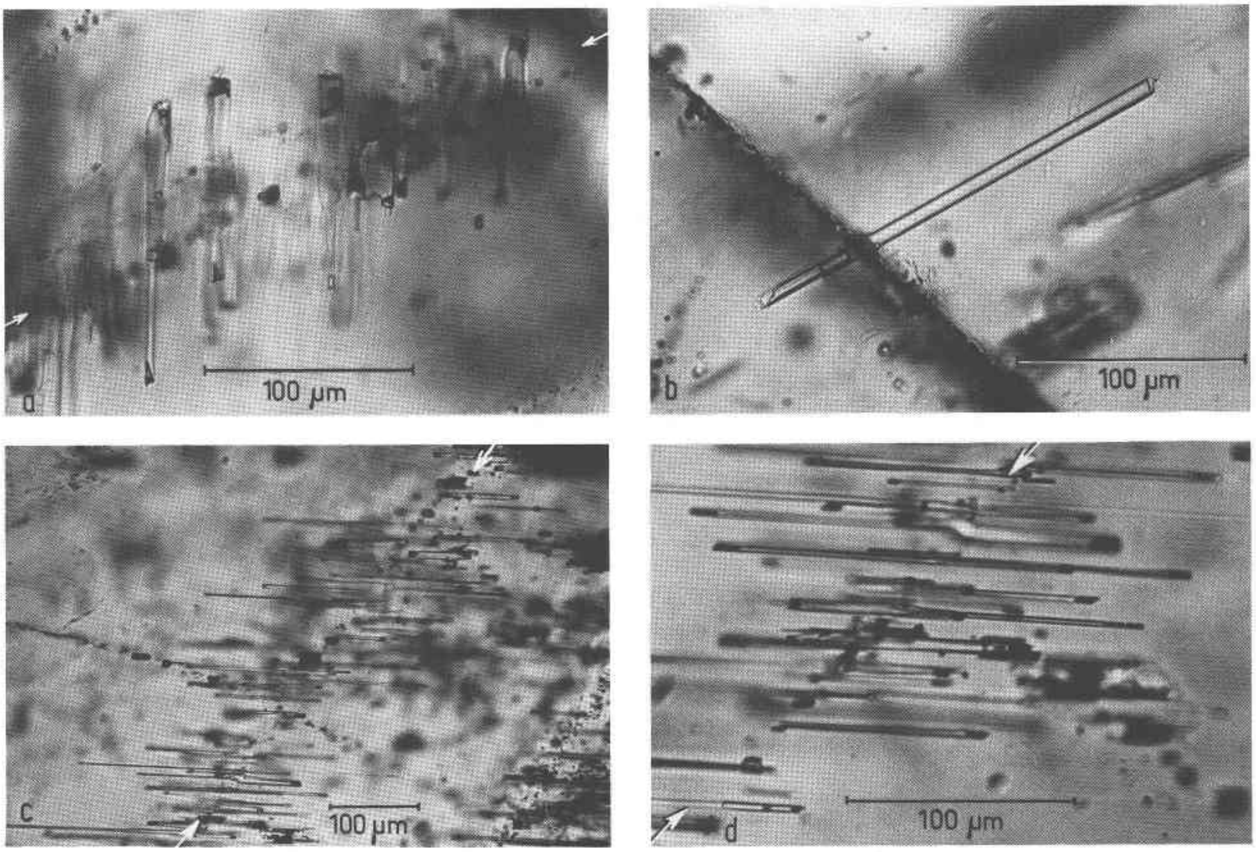

Fig. 2. Fluid and solid inclusions in bustamite from Broken Hill. (a) Portion of a sheet containing clinopyroxene rods terminated at one or both ends by fluid inclusions. A number of small fluid inclusions are visible which are not attached to clinopyroxene rods. (USGD 50716). (b) Rod-shaped fluid inclusion which has been intercepted by a subsequent fracture. Anomalous degree of fill of this inclusion suggests that original fluid has been replaced by fluid which healed this fracture plane. (USGD 50738). (c) and (d) Details of sheets containing clinopyroxene rods and fluid inclusions. Arrows indicate the approximate position of original fracture plane. Fluid inclusions, visible as black tips, are present at both ends of rods which terminate at a distance from the fracture plane. (USGD 50716).

parallel orientation, they are not coplanar. The inclusions occupy intersecting curved sheets. Portions of sheets of inclusions are illustrated in Figures 2a, c, d. If a host bustamite grain contains large numbers of these intersecting sheets, the rods appear to be randomly distributed. In samples with fewer inclusions, individual sheets are separated by bustamite free of inclusions, and their true disposition is more clearly evident.

In most bustamites the distribution of type B inclusions appears to be random, but in material with a low abundance of inclusions it is clear that they either have a roughly coplanar distribution or are distributed within the sheets containing the clinopyroxene rods. Quite spectacular rod- and needle-shaped fluid inclusions having orientation and arrangement identical to that of the rod-shaped clinopyroxene inclusions are present in sample USGD 50738, which has a composition close to $Ca(Mn,Fe)Si_2O_6$. Clinopyroxene rods are rare in this specimen, but an example of the type B inclusions is shown in Figure 2b.

Crystals, often only 1–2 μm in length, are found in some of the type B fluid inclusions. No isotropic crystals of cubic form have been seen, and it is therefore unlikely that any of the common crystals are halite. Acicular and rectangular-shaped crystals with low birefringence are most frequent, but because of their size, they cannot be easily identified. Rare inclusions with up to five crystals have been observed. The fact that these crystals are frequently attached to the side walls of the cavities and oriented with their long axis parallel to the *b* axis of the host bustamite suggests that some, or all, of these crystals are clinopyroxene. As subsequent discussion will show, the term 'daughter' may not properly be applied to them.

Freezing and heating stage examination

Samples were examined using a freezing stage in which a sample chamber filled with propanol is cooled by a flow of nitrogen gas from a liquid-nitrogen heat exchanger. The precision of measurement was not high—somewhat greater than 1°C depending upon the visibility of ice in the inclusion, which was often poor. It was not considered necessary to correct the data, since calibration of the stage by the method described by Roedder (1962) established that the correction is only 0.6°C at −20°C and values applicable to lower temperatures are unknown.

The results of freezing-stage measurements on three samples are displayed in histograms in Figure 3. By obtaining data on many inclusions within clearly-defined curved sheets, it was established that each individual sheet is characterized by salinities within a small range of two or three degrees of freezing-point depression. Although there is a region of overlap, type A inclusions contain less-saline fluids. The salinity data on type B inclusions is undoubtedly biased. One plane in specimen USGD 50716 containing fluid inclusions of both A and B types yielded closely-similar freezing-point depression data (A 31.8, 31.8, 29.5°C; B 30.5, 31.0°C). There is no reason to suppose that the unattached fluid inclusions in the low-salinity planes have solution compositions different from the attached inclusions in the same sheet, but the numerous type B inclusions within these sheets are too small for freezing-stage study. The larger the inclusion and the lower the salinity, the greater the probability that a clinopyroxene rod is attached to it.

The depressions of freezing point indicate that fluids with a very wide range of salinity have pervaded the Broken Hill lode rocks. Since the maximum depression which can be obtained with NaCl as the only solute is 21.1°C, the solutions with lower melting points must contain other salts (Roedder, 1963). A high content of calcium, manganese, and chloride is suspected in these solutions.

Homogenization temperatures were determined with a Leitz heating stage, calibrated to 400°C and modified to take 6 mm diameter pieces cut from doubly-polished thick sections. Most heating-stage determinations were carried out on the same inclusions from which freezing data had been obtained previously. However, for inclusions in samples other than USGD 50706, a tendency towards leaking was noticed, indicated by non-repeatability of some homogenization runs. In USGD 50706, 13 type A inclusions homogenized in the range 246–352° C, and eight type B inclusions homogenized in the range 254–281°C. The temperatures have little absolute significance, because large and uncertain corrections due to pressure at the time of trapping must be applied. In general, the more saline the fluid, the higher the homogenization temperature.

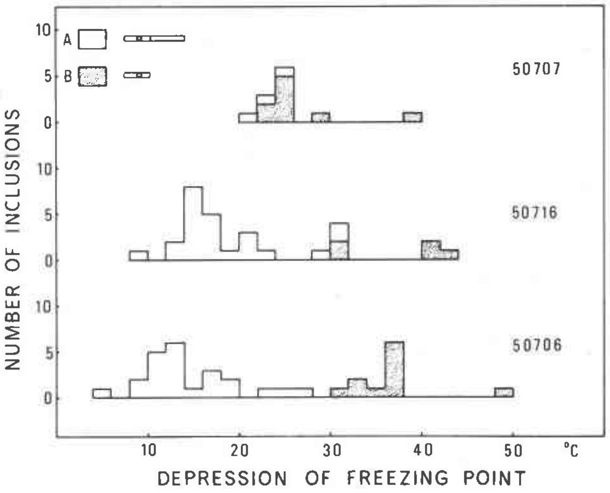

Fig. 3. Freezing-stage data on fluid inclusions in three bustamites from Broken Hill. Type B inclusion data are indicated by shading.

Discussion

Liquid inclusions formed by imperfect closure of a growing crystal around a solid impurity on a growth surface provide one of the most positive criteria for primary origin of the fluid (Roedder, 1967; 1972, Fig. 1). The phenomenon is well known, and the fluid cavity may possibly form in either anterior or posterior positions relative to the impurity particle (Safronov, 1965).

Problems arise if an attempt is made to apply this mechanism to the formation of type A fluid inclusions in the Broken Hill material. The bustamite has clearly developed early during the metamorphic history of the area, not by growth in free space, but by a process of replacement. Nevertheless, the clinopyroxene is in a not-unlikely orientation for epitaxial growth, and it is conceivable that, if the rods and laths grew at an advancing bustamite crystal surface, intergranular fluids could have been trapped by imperfect closure.

A mechanism of imperfect closure requires that within growth sectors of a crystal there should be a consistent directional relationship between solid inclusions and their associated fluid inclusions. Nowhere has this been observed. All distinguishable fluid/solid inclusion relationships are seen throughout each host bustamite grain. It is also very difficult to explain the existence of fluid inclusions in the middle of clinopyroxene rods by imperfect closure.

The distribution of the clinopyroxene rods within curved sheets through the bustamite grains must be recognized as having fundamental significance. Careful examination reveals that each sheet contains a secondary fluid inclusion plane, the result of fracture and healing. The relationship of the rods to the secondary fluid-inclusion planes is not obvious at first sight, because the type B fluid inclusions are developed along healed fracture surfaces which have a general orientation across the cleavages of the bustamite. The clinopyroxene rods within the sheets, however, are greatly elongated in the direction of the cleavage zone axis of the bustamite. Where there are numerous secondary fluid inclusion planes the associated clinopyroxene rods extend and interfinger. This is the usual mode of occurrence, and the liquid and solid inclusions are so numerous that it is virtually impossible to determine whether the fluid-inclusion-terminated rods are, or are not, related to the type B fluid inclusions.

Not all the secondary fluid inclusion planes are associated with the development of clinopyroxene rods. It is, of course, possible that these planes originated after the period of rod formation. However that may be, it is clear that much of the clinopyroxene has been initiated in the vicinity of secondary fluid inclusion planes, in particular, those which are associated with a fluid composition in the range 5 to 32°C depression of freezing point.

One may speculate on the possibility that the fractures remained unhealed for a sufficient period to allow iron-rich solutions access to sites of clinopyroxene crystal growth along the planes. There is a lack of experimental evidence on how long such fractures could exist in an aqueous environment at elevated temperature. Experimental studies at low temperature by Laemmlein (1929) show that hairline fractures in such materials as NaCl and $NaNO_3$ heal in a period of hours or days in aqueous media. It seems unlikely that fractures could remain open while some process of replacement of bustamite by clinopyroxene occurred, but the major difficulty is that of explaining the association of fluid inclusions with the clinopyroxene rods.

For these reasons, an exsolution origin of the clinopyroxene must be favoured. Mason (1973) has summarized evidence which shows the considerable extent of solid solution in the system $CaSiO_3$–$MnSiO_3$–$FeSiO_3$ at temperatures appropriate to hornblende–granulite facies metamorphism. For minerals in this range of composition formed during high-grade regional metamorphism, exsolution is believed to have occurred during cooling.

Nucleation of particles of an exsolving phase will only exceptionally take place at random sites; normally it is expected that grain boundaries, stacking faults, dislocations, other inclusions and possibly point defects will form the sites of preferred nucleation. A fracture surface will normally heal to a low-angle boundary. Carstens (1969) has shown that such planes are characterized by arrays of dislocations which adjust the mismatch between the structure on either side of the crack, so that it is a region where nucleation would be anticipated. Most of the rods, however, are attached to fluid inclusions at one or both ends. It is difficult, therefore, to escape the conclusion that the fluid inclusions which remained along the former plane of fracture have acted as the preferred sites of nucleation.

There are good reasons why this should be so. First, if nucleation occurs at or near the fluid/solid interface, the probability of deriving the nucleation configuration is enhanced owing to the hydrolytic effect of water in promoting bond breaking. Secondly, during the cooling of a metamorphic rock, a region of strain rich in dislocations will develop around the sites of the fluid inclusions (Carstens, 1968). This in itself creates a preferred region for nucleation of the exsolving phase. Alternatively, on cooling, the clinopyroxene could be nucleated on the liquid side of the interface by growth from the solution in an epitaxial or oriented relationship with the surrounding bustamite. Owing to a tendency for excess strain to be minimized by the formation of coherent interfaces, an orientation of the clinopyroxene so that its chain structure is parallel to the chain structure of the bustamite is evidently favoured.

The possibility therefore exists of two distinct mechanisms of rod growth, according to whether the rod propagates from an end with no attached fluid inclusion, or from an end which is terminated by a fluid inclusion. The basic difference is that, in the first mechanism (Figs. 4a–c), the structure probably remains partly intact, and loss of excess Mn and gain of Fe and Ca in the region of rod propagation is accomplished only by solid-state diffusion. In this case the fluid inclusion effectively anchors that end of the rod to which it is attached. In the second mechanism (Figs. 4d–f), the clinopyroxene is completely constructed through the medium of the fluid phase.

Components for growth of the rod are provided to the aqueous fluid by dissolution of the host crystal at the end of the cavity which is distant to the rod, augmented by gain of Fe by solid-state diffusion from the surrounding bustamite. As a result, the pool of fluid is effectively pushed ahead of the growing rod. The process of dissolution of strained bustamite from walls of the fluid-inclusion cavity, and the precipitation of clinopyroxene at the unstrained clinopyroxene interface which is advancing by solution growth is reminiscent of the manner in which fluid inclusions have been supposed to move through disturbed regions of structure by dissolution and reprecipitation at opposite ends of a cavity (Roedder, 1971, Fig. 11).

Steep Mn concentration gradients in bustamite away from the included clinopyroxene rods, as shown by electron microprobe traverses (Hodgson, 1975a), are consistent with either mechanism of exsolution. Since some rods are apparently without fluid-inclusion terminations at either end, and some rods are terminated at both ends with fluid inclusions, there can be little doubt that growth of the rods occurs by both mechanisms. Examination of the clinopyroxene rods and type A inclusions within individual sheets in sample USGD 50716, where they can be best observed, shows that the preferred method of propagation is through the solution growth mechanism. This can be readily inferred from the fact that almost invariably the ends of the rods which are furthest from the secondary fluid inclusion plane are capped by fluid inclusions (Figs. 2c,d).

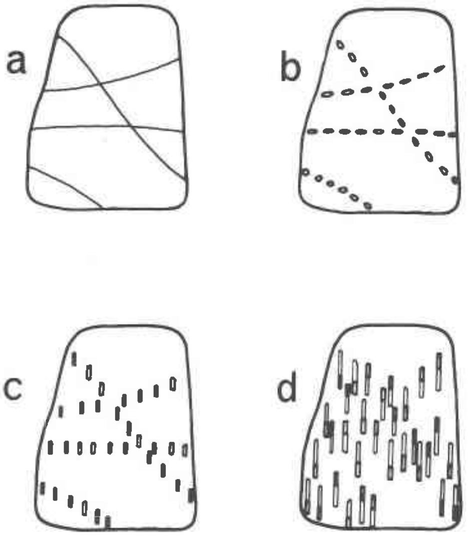

Fig. 5. Steps in process of exsolution of clinopyroxene from bustamite. (a) Fracture of bustamite grain. (b) Secondary fluid-inclusion planes form by healing of fractures. (c) Fluid inclusions develop a stable rod shape. (d) On cooling to exsolution temperatures, fluid inclusions initiate growth of clinopyroxene exsolution phase. Interfingering of rods derived from different planes makes their distribution appear to be random.

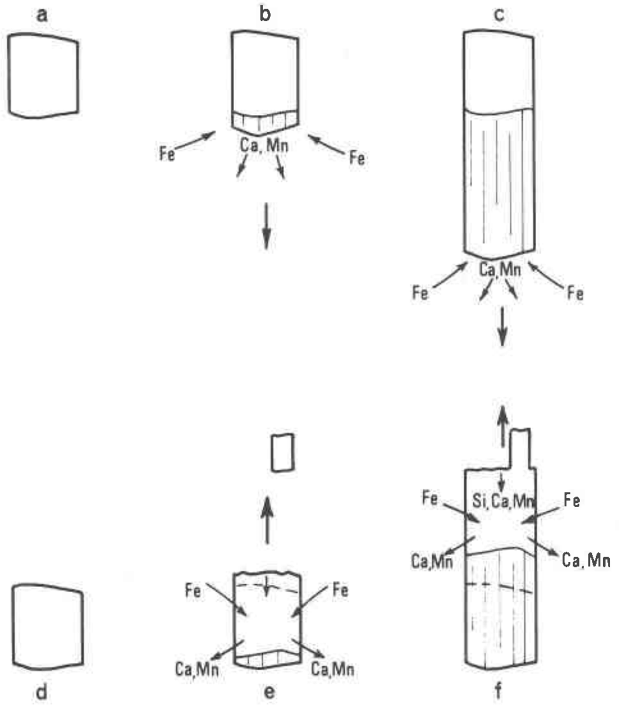

Fig. 4. Alternative mechanisms of rod propagation in exsolution of clinopyroxene from bustamite. (a)–(c) solid-state mechanism; (d)–(f) solution-growth mechanism. Bold arrows indicate direction of propagation of the rod.

The steps in the process of exsolution are diagrammatically illustrated in Figure 5. With brittle deformation, simple fractures develop in the bustamite. At this time, the rock texture is already maturely developed. Fluids invade and heal the fractures, and some fluid is trapped as inclusions. A period of time ensues during which the fluid inclusions tend to develop a stable rod-shaped form. Simultaneously or subsequently, as the rock cools, the components for the clinopyroxene rods and laths exsolve from the bustamite and crystallize chiefly by the solution-growth mechanism.

The range of complex solid/liquid inclusions requires explanation. The simplest combination form is the rod terminated by a fluid inclusion at one end. Starting at the secondary inclusion planes, the rods may propagate to either side. As illustrated in Figure 4, during propagation other immobile or less-mobile fluid inclusions from other planes may be captured. This is a possible explanation of the irregular shape

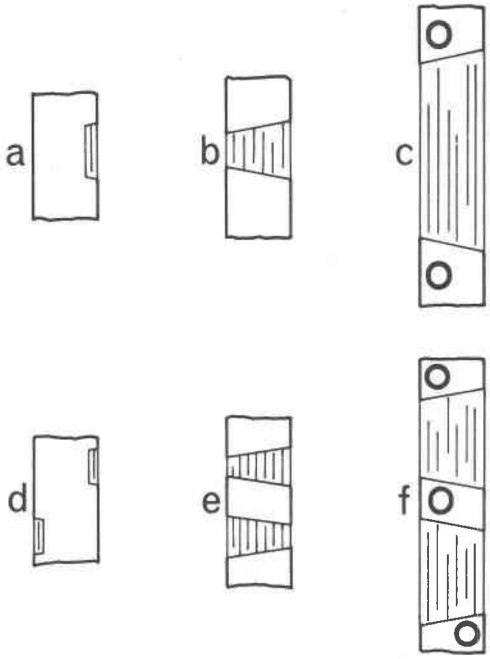

Fig. 6. Development of some solid/fluid inclusion complexes. (a)–(c) A clinopyroxene crystal nucleates on a side wall of the fluid inclusion and grows laterally dividing the fluid cavity. The rod then propagates in both directions by the solution-growth mechanism. (d)–(f) Two clinopyroxene nuclei developing simultaneously isolate a volume of fluid, then continue to extend in both directions by solution-growth mechanism.

acquired by some rod-terminating fluid inclusions (Fig. 1b). Actual collisions between propagating rods must account for the complex solid/fluid inclusion aggregates commonly found in regions of high inclusion abundance.

Rods doubly terminated with fluid inclusions and rods which contain a fluid-inclusion segment dividing them into two parts can be envisaged as originating in fluid inclusions in which the growth of the clinopyroxene rod was initiated on the side walls rather than the ends of the fluid-inclusion cavity. The process is diagrammatically illustrated in Figure 6. The type of complex inclusion which develops depends upon the number and position of the clinopyroxene nuclei in the initial fluid inclusion. Strictly speaking, the clinopyroxene nuclei are not daughter crystals, since they result from breakdown of the bustamite solid solution as temperature falls below the solvus. This is also obvious from the observation that they may continue to grow into rods which have many times the volume of the original fluid inclusion.

Support for this mode of development of the complex inclusions is obtained from salinity data on pairs of fluid inclusions from four doubly-terminated rods suitable for precise measurements. The fluids at both ends of these rods had identical freezing-point depressions, suggesting that, in agreement with the proposed model, they were ultimately derived from the same volume of fluid.

The significance of an intergranular film of water in metamorphism has been widely accepted (Fyfe *et al.*, 1958), although Kretz (1966) has noted that its presence causes difficulties in understanding the development of observed grain-shape relationships in metamorphic rocks. Experimental studies have confirmed the importance of quite small concentrations of water, in one form or another, in such different processes as the plastic deformation of quartz (Griggs and Blacic, 1965), Al/Si ordering in feldspars (Wyart and Sabatier, 1956), and rates of reaction such as the formation of forsterite from oxides. In the last case, for example, minute concentrations of water have been found to increase the reaction rate by a factor of 10^8–10^{10} (Fyfe *et al.*, 1958). The effect of water in such processes has usually been ascribed to the ability of water to break bonds in the reacting materials (*e.g.* Donnay *et al.*, 1959).

That the intergranular fluid can play an important role in the process of unmixing of high-temperature solid solutions does not appear to have been sufficiently appreciated, though Goldsmith and Newton (1974) have shown experimentally that high water pressures greatly enhance the rates of unmixing of alkali feldspars. The solution-growth exsolution mechanism has something in common with the process of cation exchange in feldspars in an aqueous medium. Oxygen isotopic studies of this reaction led O'Neil and Taylor (1967) to propose that their results could be best explained by the occurrence of a solution and redeposition step at the boundary between exchanged and unexchanged feldspar, *i.e.* a replacement process.

Leaving aside spinodal decomposition, which does not seem to be involved in this case, the unmixing of solid solutions as they cool from high temperature is usually supposed to proceed by solid-state diffusion (Yund and McCallister, 1970). In the present example, fluid promotes nucleation and growth of the new phase, but the essential features of the process of exsolution remain unchanged. The same amount of inclusion water is present within each bustamite grain before and after precipitation of clinopyroxene. There is neither gain nor loss of components from individual bustamite grains. Fe (and Ca) must still be provided to and Mn removed from the sites of clinopyroxene growth by solid-state diffusion.

There is an interesting problem of scale implicit in mechanisms involving a solution step. The effects we have described occur on a micrometer to tens of micrometer scale, but they could also develop on a smaller scale. Fluid inclusions seen with the optical microscope are often extremely small, and it is not surprising that they have also been revealed in some electron microscopic studies (McLaren and Phakey, 1966; Christie and Ardell, 1974; Green and Radcliffe, 1975). They are probably widespread and even present in large numbers in some minerals. Possibly these fluid inclusions could sometimes initiate the nucleation and growth of an exsolved phase, though, as the present example shows, smaller inclusions may be less effective in this regard. Even if the exsolving phase is not nucleated at the site of a fluid inclusion, it could still propagate through the structure by a solution step facilitated by the capture of sub-microscopic fluid inclusions coalescing to form a fluid film at the growing end of the exsolving phase. The thin fluid film would not be visible under an optical microscope, and it is possible that growth by an entirely solid-state mechanism would be mistakenly inferred.

Conclusion

Fluid inclusions have much promise in providing a new approach for investigating the somewhat enigmatic period between the dates of high-grade metamorphism (1700 m.y.) and retrograde metamorphism (500 m.y.) at Broken Hill. The inclusions in the lode rocks appear to be samples of fluids which were available throughout this period.

The relationship between the exsolved rods of clinopyroxene and the fluid inclusions provides the first evidence relating to the age of specific fluids. On the simplest, and probably inadequate, model of the metamorphism, consisting of two discrete events which attained their peaks at the geochronological ages, the exsolution probably belongs to the period of cooling following the former or high-grade event. The available experimental data on the system $CaSiO_3$–$MnSiO_3$–$FeSiO_3$ (summarized by Mason, 1973) is inadequate to appeal to for support, but the fact that clinopyroxene is the exsolved phase, together with its sheer percentage volume, suggests that the exsolution is related to the high-grade metamorphism.

The conditions of high-grade metamorphism followed by a period of retrogression under which the Broken Hill bustamites developed thir exsolution features cannot be considered as unusual. Consequently, minerals such as pyroxenes, amphiboles and feldspars from related environments deserve careful microscopic examination for evidence of features similar to those in the Broken Hill bustamites.

Care should be taken when inferring a primary origin for inclusions attached to solid impurity particles within a mineral. This is especially important where the composition of impurity particles is such that they could have been derived by exsolution. There seems to be no good reason why primary fluid inclusions, if present, should not be just as effective in initiating the nucleation and growth of an exsolution phase; however they must be identified as such on other criteria.

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