

Deformation by solution–deposition, and re-equilibration of fluid inclusions in crystals depending on temperature, internal pressure and stress

J. P. GRATIER and L. JENATTON

I.R.I.G.M., BP 68, 38402 Saint Martin d'Hères Cédex, France

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Abstract—Changes of shape and density of fluid inclusions in crystals were demonstrated when these crystals were subjected to temperatures and internal pressures greater than those of their growth. Experimental relations have been established between the rate of length-change of the inclusions and the different parameters of the experiment: nature of the crystal, temperature and internal pressure, state of stress on the crystal, geometric characters of the inclusion (length, width), orientation of the inclusion with respect to the optical axes of host mineral. It is essentially the effect of the variation of surface energy with the curvature around the cavity which causes a mass transfer of the host crystal by diffusion through the fluid under pressure. The rate of length-change is limited by the rate of dissolution at the median part of elongate inclusions. This change of shape and density is known to occur in naturally deformed crystals. An example of such a behaviour is given which allowed us to use the inclusions as markers of the conditions of temperature and pressure subsequent to the growth of crystal.

INTRODUCTION

FLUID inclusions are usually used as markers of the conditions of growth of crystals (e.g. Weisbrod *et al.* 1976). One of the basic postulates of these studies is that the inclusions behave as closed systems from the time they are trapped until their characteristics are measured in the laboratory. This has been shown to be the case by Roedder & Skinner (1968), when the conditions of temperature and pressure to which the crystals are subjected are less than those of their growth. However, it seemed interesting to us to test experimentally the behaviour of the fluid inclusions in the crystals when these are subjected to conditions of temperature, pressure and stress greater than those of their growth. Under these conditions, partial or complete reequilibration of the density of the fluids (Pêcher 1981), and slow but significant changes in shape of the inclusions (Gratier 1982) have been observed, in quartz and calcite.

Such changes of shape were observed clearly only in synthetic crystals heated at a temperature equal or greater than the homogenization temperature. In other cases (heating of natural crystals, and superimposition of a state of stress on synthetic crystals) no change was observed, but it is possible that this change was too slow. Hence it is necessary to establish, precisely, the relations between the rate of change of length and the various parameters involved in these changes, in order to know the mechanism or mechanisms of the 'deformations'. The objective is to determine whether the processes are involved in natural deformation, at probably much lower rates, but which are sufficient to allow the inclusions to be considered as markers of the conditions of temperature, pressure or stress subsequent to the growth of the crystals.

Another aim of this study was to conduct a preliminary experimental study on deformation of quartz and calcite by solution–deposition with mass transfer by diffusion through fluid. Theoretical models of this process (Raj &

Ashby 1971, Elliott 1973, Rutter 1976) are based on the hypothesis that the diffusion rate is the controlling factor. To compare experiments with theoretical results, we intend to determine: (a) the best experimental conditions to have the solution–deposition process measurable in laboratory and (b) the rate controlling process of this mass transfer: interface rate process (kinetics of dissolution or crystallization), or diffusion rate through fluid.

EXPERIMENTAL METHOD

Development of an internal overpressure in the inclusions by heating of the crystals

In order to subject fluid inclusions to an internal overpressure (P_i), crystals containing these inclusions were heated under a microscope with a Chaixmeca microthermometric heating stage (Poty *et al.* 1976) to a temperature T_i equal or greater than the temperature of homogenization (T_h) of the fluid in the inclusions, and kept for several weeks or months at this temperature T_i .

As long as the system remains closed, it is possible to estimate the overpressure (P_i) in the inclusion (Fig. 1a), if the nature of the fluid, the degree of filling determined from T_h (Weisbrod *et al.* 1976), and the PVT data of the fluid are known. For the natural crystals used here, the content in equivalents of NaCl in the water of the inclusions was determined from the melting point of frozen inclusions (Weisbrod *et al.* 1976). The PVT curves are known for pure water (Kennedy 1950) and for various NaCl contents (Potter & Brown 1977, Burnham *et al.* 1969, Haas 1976). These curves are less complete for the system $H_2O + NaOH$ (synthetic quartz, Regreny 1973) and for $H_2O + NH_4Cl$ (synthetic calcite, Ikornikova 1961, Lefauchaux 1974); however their use is possible without too much approximation. In this kind of test, the combined effect of temperature and fluid pressure was thus tested.

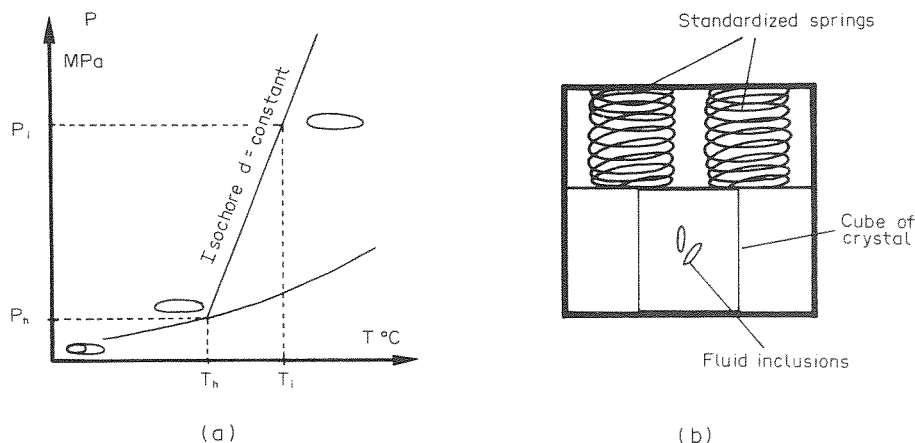


Fig. 1. Development of internal pressure within fluid inclusions in a crystal by heating of the crystal under a microscope. (a) The relation between internal pressure and temperature is given by the PVT diagram of the fluid if the system remains closed throughout the test (density of fluid constant). T_h , temperature of homogenization; P_h , internal pressure at temperature T_h ; T_i , temperature imposed for several months; P_i , internal pressure at temperature T_i . (b) Experimental arrangement for the development of a uniaxial stress state on a cube of crystal (edge = 1.5 mm) containing fluid inclusions. The whole apparatus was placed for several months in a thermostatic cell at the temperature, T_h , of the fluid in the inclusions.

If the system does not stay closed, for example, if a too strong overpressure is imposed, the inclusion fractures (decrepitation) and the fluid escapes from the cavity. In this case, there were two possibilities. (1) There was no longer any fluid in the inclusion, hence no pressure either. This was the general case when inclusions fractured. It was thus possible to test the role of temperature alone in the change of shape. (2) Some of fluid remained trapped in the inclusion. Usually the density showed a complete re-equilibration with the imposed temperature conditions. Under these conditions, the internal pressure should be practically P_h , but it was never precisely known how this pressure develops after the fracture. It is thus impossible to dissociate completely the effect of the presence of fluid from that of its pressure. It is only possible to have some indications of the effect of a certain lowering of pressure following the fracture of cavities on the rate of change of shape of inclusions.

Development of a state of stress in crystals

In order to establish a stress state around the inclusions (independent of the effect of internal pressure), a cube of crystal containing fluid inclusions was subjected to a permanent uniaxial compressive stress (with standardized springs, Fig. 1b). This device was placed in a thermostatic cell at a temperature equal to T_h , the temperature of homogenization of the fluid phase. An internal overpressure, P_h , was thus also imposed in the cavity, but its value remained very low (Fig. 1a).

RESULTS

Change of density

The density of the fluid of the inclusions was periodically examined (by measurement of the homogenization temperature, Weisbrod *et al.* 1976). The aim of these measurements was not only to know the evolution with

time of the density (which is the object of work in progress, Pêcher & Boullier *in press*), but especially to know the evolution of the internal pressure in the inclusions. An increase in T_h (thus a decrease in density) reveals a decrease in internal pressure (Fig. 1a).

Examples of the evolution of these densities with time are given in Fig. 2. A large difference in behaviour can be noted between the inclusions which can be summed up as in Fig. 3 by two types of behaviour.

(1) The density decreased suddenly by fracture of the inclusion and leakage of the fluid, when the internal pressure reached the fracture threshold of the cavity (decrepitation, Leroy 1979). Usually (see A1, A'1 in Fig. 3) the new density of the fluid corresponded to the values of the temperature and pressure imposed at the fracture (Pêcher 1981). However, in certain cases, the leakage was probably very rapidly sealed because a weak overpressure persisted in the inclusions (density of the fluid less than that of a complete re-equilibration) (see Q2 in Figs. 2a & b; C2 in Fig. 2c and A2 in Fig. 3).

The shape of the fracture surfaces is very characteristic. For quartz (Fig. 4) the orientation of fracture was always parallel to one of the three planes ($1\bar{1}00$, $10\bar{1}0$, $0\bar{1}10$) when the ellipsoidal inclusion was parallel to the 'c' axis (without external stress on the crystal, Fig. 4a). These planes were extended by a network of small inclusions organized in small channels, the whole presenting the form of a butterfly's wing around the inclusion (Fig. 4b). Such structures have been described in naturally deformed crystals (fig. 4c in Jenatton 1981, and also Swanenberg 1980, Eadington & Wilkins 1980). They show in a simple way the presence of thermic or stress effects on the crystal posterior to its growth.

(2) The density decreased very slowly with time, but these results should be confirmed in a linear fashion as a function of \sqrt{t} , t being the duration of the experiment (Q1 in Fig. 2; B, B' in Fig. 3). This decrease was probably due to very slow leakages from the cavity by diffusion (Pêcher & Boullier *in press*). Anyway, a

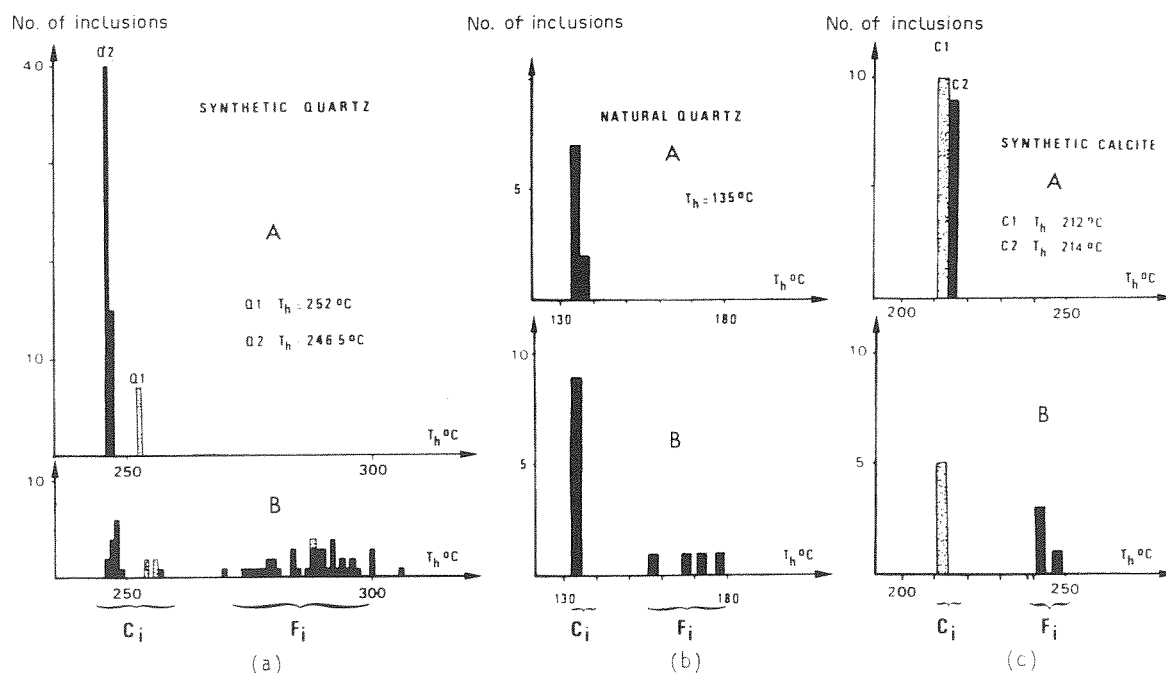


Fig. 2. Evolution of the density of fluid inclusions under internal pressure. Histograms of T_h measured for different samples before (A) and after (B) the heating of crystals. Ci, closed inclusions; Fi, fractured inclusions. (a) Quartz Q1: $T_i = 298^\circ\text{C}$, $P_i = 70\text{ MPa}$, $t = 80$ days, fluid = NaOH (0.5 N) and Q2: $T_i = 303^\circ\text{C}$, $P_i = 80\text{ MPa}$, $t = 7$ days, fluid = NaOH (0.5 N). (b) Quartz $T_i = 180^\circ\text{C}$, $P_i = 80\text{ MPa}$, $t = 90$ days, fluid = $\text{H}_2\text{O} + 1\%$ NaCl. (c) Calcite C1: $T_i = 217^\circ\text{C}$, $P_i = 5\text{ MPa}$, $t = 7$ days, fluid = $\text{H}_2\text{O} + \text{NH}_4\text{Cl}$ (5%) and C2: $T_i = 246.5^\circ\text{C}$, $P_i = 50\text{ MPa}$, $t = 7$ days, fluid = $\text{H}_2\text{O} + \text{NH}_4\text{Cl}$ (5%).

change in shape of the inclusions then occurred with an internal pressure which only decreased very slowly with time and which can be considered as constant over several weeks.

In a general way, the rate of the process of re-equilibration was affected by changes in various parameters: (a) the value of temperature and internal pressure imposed within the cavity; (b) the nature and structure of the mineral and (c) the geometric characteristics of the inclusion (form, size, orientation with relation to the optic axis, etc.).

Change of shape

Two types of change of shape appeared, one (i), very

rapid from the beginning of heating (after some hours at a maximum); the other (ii), very slow and regular during a heating of several weeks, even months.

Changes of type (i) have always very low values, and they have been neglected. These are volume changes due to elastic deformations (Eadington & Wilkins 1980) and to increases in volume due to solution of the walls of the inclusions (Leroy 1979) when the temperature is raised, since the solubility increases. To avoid these effects, all the successive measurements of length and width were made at the same temperature (T_i).

The slow type (ii) changes which appeared with time, were sufficiently large to be measured without doubt in a certain number of cases, particularly for synthetic crystals. In a general way, at the time of heating, the inclusions, initially elongate, became shorter and wider and finally rounder. The inclusions initially almost round tended to acquire the shape of a negative crystal (thus becoming slightly longer). The shortening of initially elongate inclusions was studied principally for synthetic quartz since it reaches significant and easily measurable values, and inclusions have an initially regular cigar-like ellipsoid shape. Considering that the volume of the cavity is constant, the best marker of the change of shape is the change of length of the cavity.

The change of length of the fluid inclusions was estimated by successive weekly photographs (Fig. 5), or by periodic measurements directly under a microscope with an ocular micrometer.

The rate of length change is defined as $\Delta l/\Delta t$,

$$\text{with } \Delta l = l_0 - l_1, \\ \Delta t = t_1 - t_0,$$

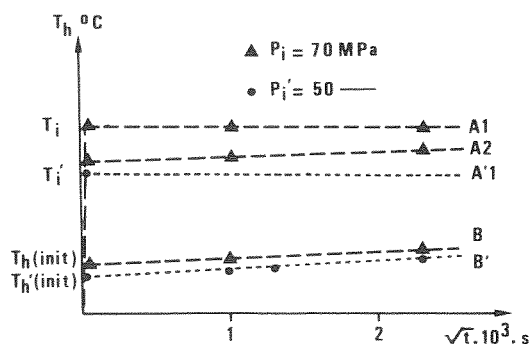


Fig. 3. Evolution of the temperature of homogenization (T_h) of the fluid in the inclusions, with the length of heating of the inclusions (\sqrt{t}). Example of synthetic quartz. A1, A'1, A2: Fracture of inclusions, complete rehomogenization T_h (after fracture) = T_i with $P = P_h$ (A1, A'1) or partial rehomogenization (A2) with, in the latter case, maintenance of a weak overpressure in the inclusion. B, B': Inclusions without apparent fracture, slow leakage of the fluid by diffusion in the solid. Permanent overpressure (P_i) in the inclusion, but slow decrease of density and P_i with time.

l_0 = length of inclusion at time t_0 , l_1 = length of inclusion at time t_1 .

This length-change was considered in relation to the various parameters operating in the experiment. It is possible to sum up the different factors operating in the experiments as follows.

(i) The behaviour of the inclusions in the different crystals were compared. These were: calcite and natural quartz, in which the fluid phase of the inclusions was constituted by H_2O plus a certain percentage of NaCl (Jenatton 1981); synthetic quartz with $H_2O + NaOH$ (0.5 N) (Regreny 1973); and synthetic calcite with $H_2O + NH_4Cl$ (5%) (Lefauchaux 1974) obtained by hydrothermal growth. The nature of the fluid influences the concentration of solid (c) and the diffusion coefficient of the species migrating in the fluid (D).

(ii) The presence of fluid and its density were checked at each series of measurements, thus fixing the internal pressure (Pi) for a temperature of heating (Ti).

(iii) Inclusions of simple initial form were selected. They varied between an ellipsoid in the form of a cigar to a cylinder terminating in two hemispherical domes. The length of the inclusions (l_0, l_1, \dots, l_n) and width (w_0, w_1, \dots, w_n) were periodically measured at t_0, t_1, \dots, t_n .

(iv) The initial orientations of inclusions with respect to the optic axes of the host mineral and with respect to the direction of the uniaxial stress were likewise noted.

Behaviour of synthetic quartz, role of the different parameters

Role of the presence of fluid in the inclusions. The inclusions only changed shape if there was a fluid phase present in the cavity; if not, for example, if there was a fracture of the inclusion and complete leakage of the fluid, no change appeared even at high temperatures (400°C maintained for several months).

Role of the geometry of the inclusions. We compared inclusions in quartz (Th = 248°C) under the same internal pressure of 50 MPa, at the same temperature Ti = $282 \pm 2^\circ C$, oriented initially with their long axes parallel to the 'c' axis of the quartz, and having similar geometric characteristics but with varied length and width. Inclusions having either the same class of length (i.e. a length between two limits), or the same class of width, are first compared: (a) for inclusions having the same initial class of width (w), the rate of length change increases linearly with the increase of the length value (Fig. 6a); and (b) for inclusions having the same initial class of length (l), the rate of length change increases linearly with the inverse of the square of width ($1/w^2$) (Fig. 6b). Using all the inclusions (with varied length and width values) a linear relation between $\Delta l/\Delta t$ and the ratio l/w^2 may be established. The slope of the line being independent of the geometry of the inclusions, all these inclusions together may be used to study the effect of the other parameters (Fig. 7a).

Role of the initial orientation of the inclusions with respect to the 'c' axis. Most of the inclusions were initially

elongated parallel to the 'c' axis, but in certain crystals we found inclusions elongate at 60 or 90° to 'c'. In these cases, it was noted that for inclusions having initially the same ratio, l/w^2 , subjected to the same temperature and internal pressure, the rate of shortening, $\Delta l/\Delta t$, was higher for inclusions oblique to the 'c' axis than for those parallel to 'c' (see Fig. 5, for the same experiment, the difference between g, h, i, and j, k).

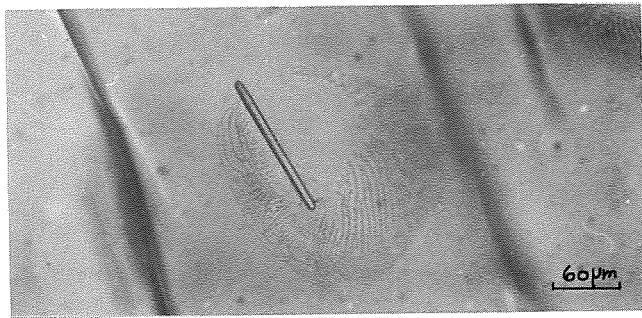
Role of uniaxial stress. No change of shape appeared clearly linked to the application of a uniaxial stress of 20–60 MPa at 265°C, applied for several months on inclusions where Th = 265°C. On the other hand, certain inclusions fractured, with at the same time the appearance of a network of secondary inclusions.

Evolution of the rate of length-change with time. This rate decreases with time for all the inclusions but the progressive change in shape of the inclusions should be born in mind. Grouping inclusions heated at the same temperature but measured after different times of heating (12 days, 1 month, 2 months), an appreciable difference was not observed (Figs. 7a & b). The slight decrease of the rate of length-change could be due to the slight decrease of the density of the fluid, since decrease of density is also accompanied by a decrease of the internal pressure, and it is shown below that the rate of length-change is dependent on the internal pressure.

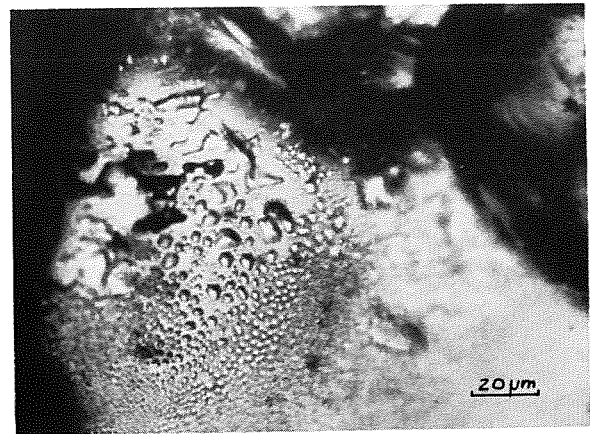
Role of internal pressure and temperature of the fluid. In a general way, a decrease in density of the fluid during heating, hence a decrease in the internal pressure in the inclusion, was accompanied by a decrease in the rate of length-change but apparently also by a difference in the equilibrium shape to which the inclusion was tending. With internal pressure, the inclusions became rounder (Figs. 5a–c) and the change of shape reached significant measurable values. On the other hand, if the internal pressure was low Ph, and when inclusions had an initial squat form, these inclusions tended rather to become angular (Figs. 5g & h). In some of these cases, inclusions showed a slight increase of length, but this process never gave a clearly measurable change of shape and was neglected since for the same experiment, initially elongate inclusions always showed a decrease in length (Fig. 5i).

Most of the time, the equilibrium shape of inclusions after long duration of heating was therefore a negative crystal shape with more or less rounded angles. In some very rare cases, the form of the cavity became extremely irregular with deep pits which were perhaps the ends of dislocations (dislocations have been indicated in these synthetic quartzes by Regreny 1973). In this last case, the rate of length-change was independent of the shape of the inclusion. The small number of inclusions showing this behaviour does not allow us to present a serious discussion of the problem.

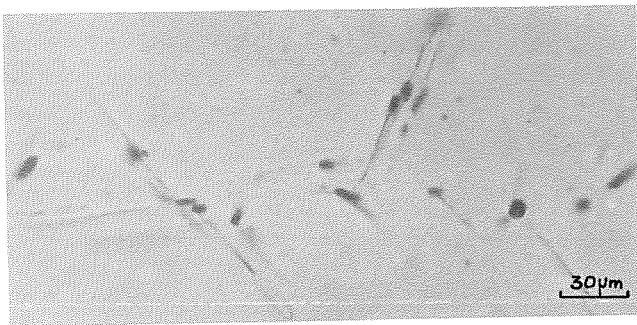
To separate the influence of pressure from that of temperature, the rate of length-change of inclusions having the same ratio, $l/w^2 = 1$, are compared (for example $l = 100 \mu m$, $w = 10 \mu m$). The measures for more than 500 inclusions are plotted on an Arrhenius plot: $\log(\Delta l/\Delta t) = f(10^3/T)$. In some experiments



(b)

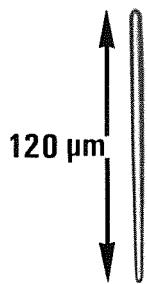


(c)

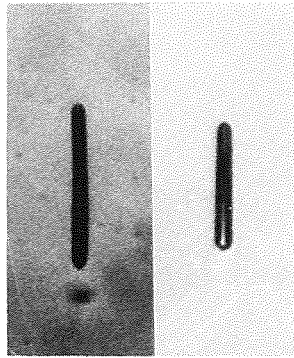


(a)

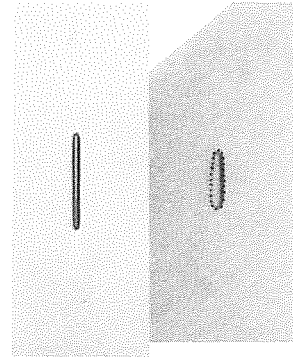
Fig. 4. Fracturing of fluid inclusions by decrepitation when developing a high internal pressure (superior to 100 MPa) in the inclusions. Example of synthetic quartz, appearance of the fracture, butterfly wing shape (a) Transverse section (b) Longitudinal section. The surface of the fracture is extended by a network of secondary inclusions. (c) Detail of a network of secondary inclusions (cluster) in naturally deformed crystals which shows a natural fracturing around an inclusion.



a

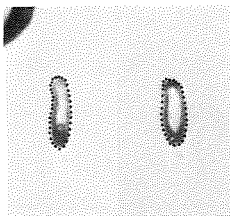


b

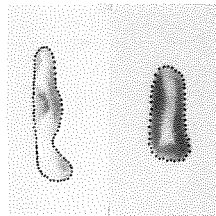


c

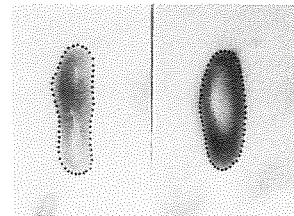
Synthetic quartz



d

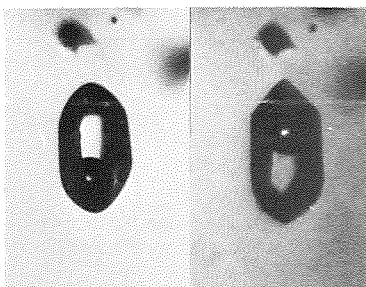


e

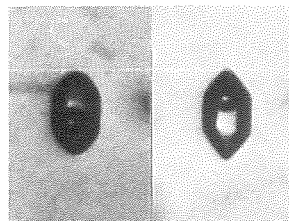


f

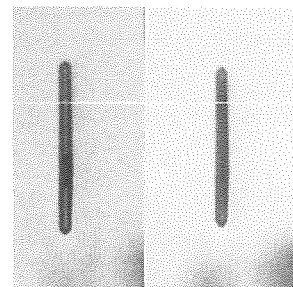
Synthetic calcite



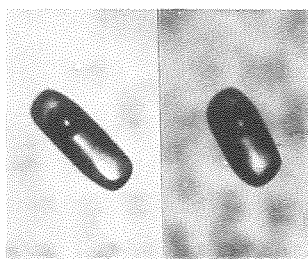
g



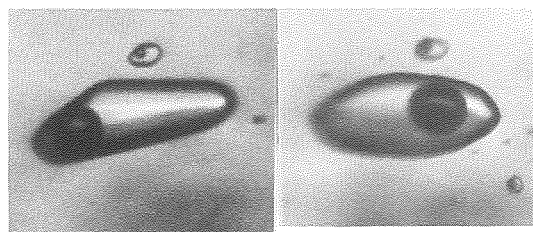
h



i



j



k

Synthetic quartz

Fig. 5. Change of shape of fluid inclusions with temperature and internal pressure: initial shape on the left, shape after permanent heating on the right. (a), (b) & (c) $T_h = 252^\circ\text{C}$, $T_i = 298^\circ\text{C}$, $P_i = 70\text{ MPa}$, $t = 80\text{ days}$, fluid = NaOH (0.5 N). (d), (e) & (f) $T_h = 212^\circ\text{C}$, $T_i = 217^\circ\text{C}$, $P_i = 5\text{ MPa}$, $t = 120\text{ days}$, fluid = $\text{H}_2\text{O} + \text{NH}_4\text{Cl}$ (5%). (g), (h), (i), (j) & (k) $T_h = 265^\circ\text{C}$, $T_i = 265^\circ\text{C}$, $P_i = 5\text{ MPa}$, $t = 40\text{ days}$, fluid = NaOH (0.5 N). T_h , temperature of homogenization of the fluid phase; T_i , temperature of heating; P_i , internal pressure deduced from PVT data (see Fig. 1), t , duration of heating.

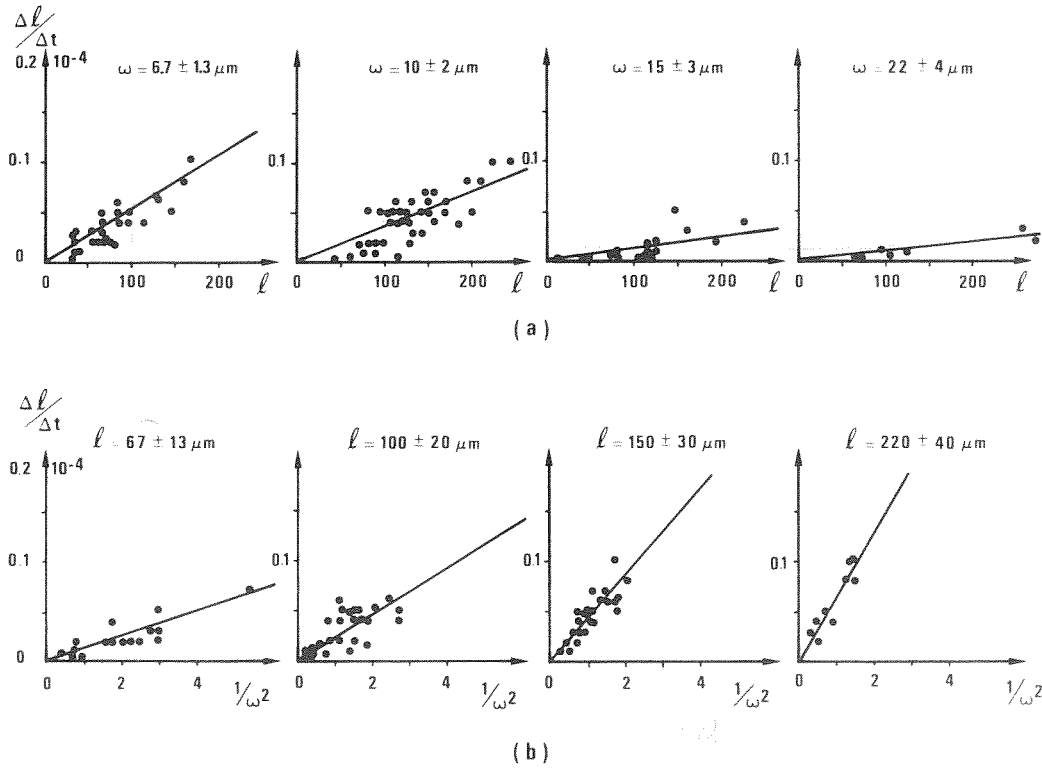


Fig. 6. Change of length of fluid inclusions in heated synthetic quartz. (a) Linear relation between the rate of change of length ($\Delta l / \Delta t$ in $\mu\text{m s}^{-1}$) and the length (l in μm) of inclusions having the same class of width (w), with $T_h = 248^\circ\text{C}$, $T_i = 282^\circ\text{C}$, $P_i = 50 \text{ MPa}$, $t = 12$ days, fluid = NaOH (0.5 N). (b) Linear relation between $\Delta l / \Delta t$ and the inverse of the square of width of inclusions having the same class of length. Same experiment as in (a).

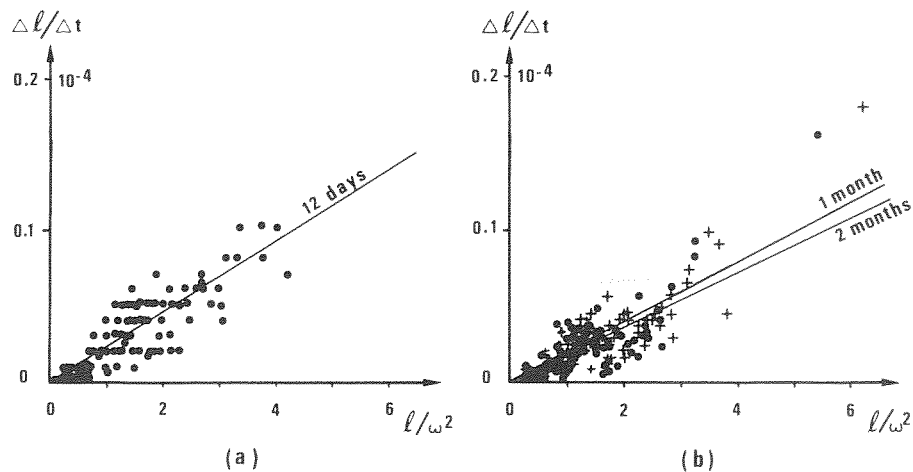


Fig. 7. Change of length of fluid inclusions in heated synthetic quartz. (a) Linear relation between the rate of length change ($\Delta l / \Delta t$ in $\mu\text{m s}^{-1}$) and the ratio: length over the square of width, l/w^2 in μm^{-1} . Same experiment as in Fig. 6(a) with $t = 12$ days. (b) Linear relations between $\Delta l / \Delta t$ and l/w^2 for the same experiment but with different duration of heating: $t = 1$ month (point), $t = 2$ months (cross). The slight decrease of $\Delta l / \Delta t$ with time is probably due to the slight decrease of density (see B' in Fig. 3) and of internal pressure (see Figs. 8–9 for the effect of internal pressure on the $\Delta l / \Delta t$ value).

(squares in Fig. 8) fluid inclusions were fractured by imposing a large overpressure in cavities. Sometimes a fluid phase remained in these cavities, then length changed. In such cases, the internal pressure could not be exactly known but we admitted that its value remained low, through the heating, as for the heating of inclusions at $T_i = T_h$ (squares with point, Fig. 8). In other experiments (circles, Fig. 8) fluid inclusions remained closed during heating at $T_i > T_h$. The slight decrease in density did not disturb the results since homogenization temperatures were measured before and after each measurement and a mean value of the internal pressure, P_i , was then estimated using PVT relations. The relative scattering of the results may be noted, especially when inclusions were fractured. This is probably because in this case the internal pressure values may have varied from one inclusion to another. In some cases, rapid sealing of the fracture may have allowed a permanent overpressure in some inclusions. This could explain some high values of the rate of length-change in experiments performed at high temperature (squares in Fig. 8).

Behaviour of synthetic calcite, natural quartz and calcite

The inclusions in synthetic calcite ($T_h = 212^\circ$, heated to 217°C , with $P_i = 5$ MPa, for 4 months) showed very definite changes of shape (Figs. 5d–f), the initially elongate inclusions tending to become round. It was difficult however to find initial regularly shaped inclusions. The rate of length-change is plotted vs the ratio l/w^2 . The slight scattering is due to the fact that inclusions initially differently oriented in the crystal were plotted together. For this reason, these results are not readily comparable with those for synthetic quartz (Fig. 10, p. 199). The inclusions in natural quartz ($T_h = 135^\circ\text{C}$, $T_i = 180^\circ\text{C}$, $P_i = 80$ MPa, fluid = $\text{H}_2\text{O} + 1\%$ NaCl, heated several months) showed no change of shape. The inclusions in natural calcite ($T_h = 196^\circ\text{C}$, $T_i = 215^\circ\text{C}$, $P_i = 35$ MPa, fluid = $\text{H}_2\text{O} + 1\%$ NaCl, heated several months) seemed to show a rounding of their angles, but this was not measurable with precision.

In conclusion to this presentation of the results, the change of shape of inclusions is considered to be a mass transfer process with, for most of the cases, dissolution at the median part (or on convex solid surface) and deposition at the extremities of each cavity (on concave solid surface). Discussion of the driving force for the mass transfer, the equilibrium shape of inclusions, the rate controlling process, and the behaviour of natural crystals, is given below.

DISCUSSION

Experimental deformation of synthetic quartz

Driving force for mass transfer and equilibrium shape of inclusions. The various effects of temperature and

internal pressure on the equilibrium shape of fluid inclusions will be discussed first. The equilibrium shape of an inclusion in a crystal depends critically upon the variation of surface energy with surface curvature and surface orientation. An inclusion in thermal equilibrium should have flat surfaces of low surface energy connected by smoothly rounded, or sharp, edges and corners, depending on the detailed variation in surface energy (Herring 1953). If such an inclusion is heated, the internal pressure increases, and a compressive elastic stress appears in the solid around the cavity. To approach equilibrium, the inclusion will change its shape, so as to increase its surface energy (Nelson *et al.* 1964). This may be achieved by developing the high-energy plane between adjacent low-energy planes, for example by rounding the cavity corners. On the other hand, a decrease in internal pressure leads to a change of shape to provide the lowest possible surface energy, tending to a negative crystallographic shape.

With respect to initially squat inclusions, this rounding of angles seemed to appear with high internal pressure, while sharp corners developed at low internal pressures but this change of shape was not measurable. However, when inclusions are essentially elongate, another effect may be stronger, namely the difference in curvature between the extremities and the middle part of the inclusion. When heating such an inclusion, a difference of chemical potential ($\Delta\mu$) related to the difference of curvature should occur (Kingery *et al.* 1976).

$$\Delta\mu = \gamma(C_e - C_m)\Omega$$

with γ = surface energy, Ω = molecular volume of solid, C_e and C_m = principal curvatures of solid/fluid surface near extremities ($C_e = -2/w$) and middle part ($C_m = 0$), respectively of the inclusion with cylindrical shape ended by hemispherical domes. The observation that heated elongated inclusions were always transformed into ellipsoidal cavities with low l/w ratios is consistent with the effect of a driving force, due to the curvature difference around the inclusions. This curvature difference induces mass transfer from convex solid surfaces or from concave solid surfaces with large principal curvatures, to concave solid surfaces with low principal curvatures. This is the observed change of shape. The equilibrium shape is then a negative crystal shape, with more or less rounded angles, since it is the shape with the minimal surface energy. The difference in surface energy with orientation may explain the difference in behaviour between elongate inclusions parallel or oblique to the 'c' axis.

The increase of internal pressure within elongate inclusions, also increases the difference of elastic strain energy in the solid between the extremities and the middle part of the inclusions (Jaeger & Cook 1969). This could have an inverse effect on the change of shape of inclusions since the density of elastic strain energy is greater at the extremities of the cavity, the dissolution should be maximal there (Paterson 1973) and the inclusions should elongate. This elongation is not observed because the effect due to the variation of surface energy with curvature which causes a shortening, could mask

this process. This could also explain why the application of stress on the crystals did not produce change of shape of inclusions. In fact this stress simply produces a difference of elastic strain energy around the inclusions, and this difference can remain less than that due to the difference of surface energy.

Rate control of the solution–deposition process. In the general case, the driving force for mass transfer is expended partly in driving the interface reactions (dissolution or crystallization) and partly in driving diffusion through fluid (Raj 1982). A simple way to solve this problem is to write for the three cases, independently, the relation between the rate of length-change and the various parameters. One of these three processes is often much slower than the others and its rate controls the rate of the change of shape. Assuming that inclusions are of cylindrical shape, terminated by hemispherical domes, the difference of chemical potential $\Delta\mu$ is

$$\Delta\mu = \frac{2\gamma\Omega}{w} \text{ (see above).}$$

If diffusion rate is the slowest process, the rate of length change, $\Delta l/\Delta t$, must be proportional to the driving force, ($\Delta\mu$), and inversely proportional to the distance of transfer (Robin 1978)

$$\Delta l/\Delta t \propto \Delta\mu/l \propto 2\gamma\Omega/lw$$

this is not the observed relation between $\Delta\mu$ and l , w . Assume that the interface-process velocity (dissolution or crystallization rate) is linearly proportional to the driving force (Fyfe *et al.* 1975, Raj 1982) and that crystallization is the slowest process, then $\Delta l/\Delta t$ must be proportional to $\Delta\mu$

$$\Delta l/\Delta t \propto \Delta\mu \propto 2\gamma\Omega/w.$$

This is not the observed relation between $\Delta\mu$ and l , w . If dissolution is the slowest process, $\Delta l/\Delta t$ must be proportional to $\Delta\mu$ and to the ratio: surface of dissolution ($\pi w l$) over surface of deposition (πw^2)

$$\Delta l/\Delta t \propto \Delta\mu \cdot lw/w^2 \propto 2\gamma\Omega \cdot l/w^2$$

this relation between $\Delta\mu$ and l , w , is the observed relation (Figs. 7–10). Dissolution rate is then the controlling rate for solution–deposition, of course in the particular case of fluid inclusions initially elongate parallel to the 'c' axis of synthetic quartz.

Raj (1982) also found that interface rate process may be the rate controlling process in solution–deposition, with diffusion through fluid. Following this author, the term $k'\bar{c}$ may be defined as the linear dissolution velocity (m s^{-1}) of the crystal interface, under a driving force of 1 kT per molecule, (k' represents the jump frequency of the solute atom from the crystal into the fluid across the interface, \bar{c} represents the solubility of the crystal molecule in the fluid, mole fraction of the solute dissolved in the fluid). A complete relation between $\Delta l/\Delta t$ and the various parameters may then be written

$$\Delta l/\Delta t = \frac{k'\bar{c} \cdot \Delta\mu \cdot lw}{kT w^2} = \frac{2k'\bar{c} l \gamma \Omega}{kT w^2}$$

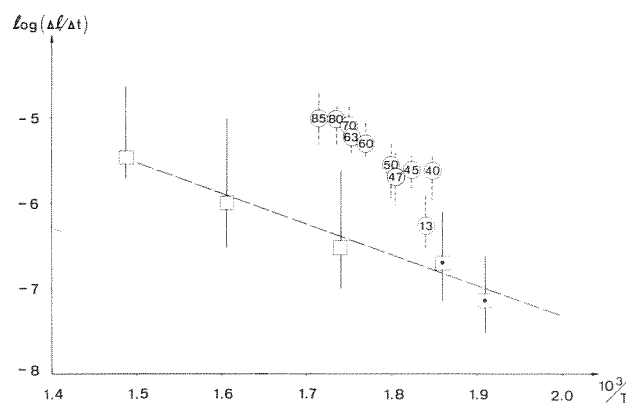


Fig. 8. Change of length of fluid inclusions in heated synthetic quartz. Relation between $\log(\Delta l/\Delta t)$ vs $10^3/T$. $\Delta l/\Delta t$ in $\mu\text{m s}^{-1}$, T in K (Arrhenius plot), for fluid inclusions with $l/w^2 = 1$. The vertical bars show the scattering of $\Delta l/\Delta t$ values for each experiment: squares = fractured inclusions; squares with point = inclusions heated at $T_i = T_h$ (in the two cases the internal pressure is supposed to be very low); $P = P_h$. As P_h increases with T_h (Fig. 1) a correction was made or some of the $\Delta l/\Delta t$ values. All the squares correspond to a pressure of 5 MPa; circles, closed inclusions heated at $T_i > T_h$ with the value of internal pressure (P_i) deduced from PVT data (see Fig. 1).

where k is the Boltzmann constant and T is the absolute temperature.

This relation is analogous to the relation defined by Raj (1982) for the change of shape of an aggregate with intergranular fluid. The difference is only on the driving force: surface energy difference here, instead of normal stress difference in his experiment. The difference of surface energy with the orientation must be taken into account. The kinetics of the interface process (dissolution or crystallization) also varied widely with the orientation in the crystal. For the case of elongate inclusions parallel to the 'c' axis, this could explain why dissolution on faces parallel to the 'c' axis is the rate controlling process, since deposition occurs on the (0001) face, and the crystallization rate is always maximal for this face (Barnes *et al.* 1976).

The effect of temperature and pressure must be considered to test the relation previously established.

Effect of temperature. Using only fractured inclusions or inclusions heated at $T_i = T_h$, thus inclusions with equal low internal pressure (Fig. 8), an activation energy value may be estimated, about $70 \text{ kJ mole}^{-1} \text{ K}^{-1}$. This is only an approximate value by reason of the imprecision of the internal pressure value. The activation energy of the kinetics of the dissolution of quartz in NaOH (0.5 N) is not known but this activation energy is known for the kinetics of crystallization: about $70\text{--}90 \text{ kJ mole}^{-1} \text{ K}^{-1}$ (Regreny 1973, Barnes *et al.* 1976). It is therefore the same order of magnitude as our estimated value. This value being much higher than the activation energy for diffusion in aqueous solutions ($13 \text{ kJ mole}^{-1} \text{ K}^{-1}$, Robinson & Stokes 1959), this also confirms the rate control by an interface process.

Effect of internal pressure. This effect appears in Fig. 8. For the same temperature, the $\Delta l/\Delta t$ value for closed inclusions (with internal pressure) is always higher than the $\Delta l/\Delta t$ value for fractured inclusions or inclusions heated at $T_i = T_h$ (low internal pressure). To present this effect more clearly, the internal pressure is plotted

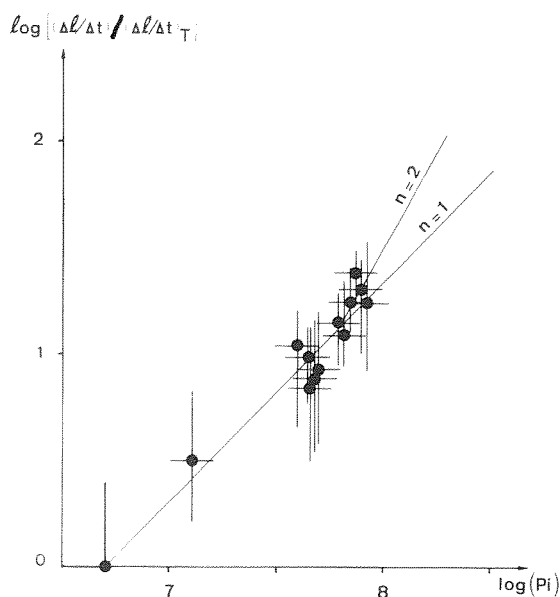


Fig. 9. Change of length of fluid inclusions in heated synthetic quartz. Relation between internal pressure (P_i in Pa) and the difference between the observed rate of length change ($\Delta l/\Delta t$) and the rate of length change ($\Delta l/\Delta t$) $_T$ at the same temperature with 5 MPa of internal pressure (square line in Fig. 8). The relation is linear for almost all the range of pressure except perhaps for high pressure, $P_i > 70$ MPa (see the text for discussion).

vs the difference between the $\Delta l/\Delta t$ values for inclusions with internal pressure and the $(\Delta l/\Delta t)_T$ values for inclusions for which internal pressure is low (5 MPa) (for the same temperature of heating).

The relation $\log(\Delta l/\Delta t) - \log(\Delta l/\Delta t)_T = f(P_i)^n$ is obtained (Fig. 9) with a value for n equal to 1 for most of the experiments, and a value tending to 2 for high internal pressure ($P_i > 70$ MPa). Linear dependence of the kinetics of growth of synthetic quartz vs the pressure was also observed by Regreny (1973) for an equivalent range of pressure in the same solution of NaOH (0.5 N). At least two explanations may be advanced for the apparent non-linear behaviour at high pressure. (1) The rate of length change is dependent on the concentration of the solution which is also pressure dependent with the following relation (Kern & Weisbrod 1964)

$$c = c_0 e^{-p\Delta V/kT}$$

with p = pressure, ΔV = difference in the partial molecular volume of the solute in the fluid and the crystal phase. (2) The high internal pressure may induce plastic deformation around the cavity, especially for synthetic quartz with hydraulic weakening, the n value could then tend to 3–4 (Balderman 1974).

Experimental deformation of natural minerals

Contrary to synthetic quartz, no change of shape clearly appeared for natural minerals. Several explanations may be advanced. We shall consider only the case of quartz since the results for synthetic calcite are not sufficient for discussion. The first difference between natural and synthetic quartz is the temperature of heat-

ing. Because of the relatively low temperature of homogenization of natural quartz, the heating temperature for our experiments did not exceed 180°C (above this temperature, the inclusions fractured). The behaviour of synthetic quartz may be extrapolated to this temperature. At 180°C without pressure, the $\Delta l/\Delta t$ value is about $10^{-8} \mu\text{m s}^{-1}$ (Fig. 7). With the effect of a 80 MPa pressure, $\Delta l/\Delta t$ could rise to $2 \cdot 10^{-7} \mu\text{m s}^{-1}$ for an inclusion with $l/w^2 = 1$ (Fig. 8). The second difference is in the concentration (c) of the solution. We do not know exactly the c value at 180° for synthetic quartz but at 310°C and 80 MPa, the ratio of concentration in NaOH (0.5 N) and in water is equal to $2.17/0.094 = 23$ (Regreny 1973, Kennedy 1950). Admitting the same ratio at $T_i = 180^\circ\text{C}$ and $P_i = 80$ MPa (with $T_h = 135^\circ\text{C}$), the rate of length change could be $8.7 \cdot 10^{-9} \mu\text{m s}^{-1}$. The lower limit of measurement being $1 \mu\text{m}$, it would take at least 3.6 years to observe a change of shape! The effect of these two factors (T_i and c) are sufficient to explain the fact that natural fluid inclusions did not apparently change shape after several months of heating.

Of course other factors may also affect the differences in $\Delta l/\Delta t$ values between natural and synthetic minerals such as the difference of the kinetics of dissolution. Very little is known about this problem for the temperature-pressure conditions used here (Fyfe *et al.* 1975). For these reasons, no attempt is made to directly extrapolate the behaviour of synthetic minerals to natural minerals. The established relation for the former must be experimentally confirmed for the latter. This experimental change of shape could perhaps be observed when heating at a high temperature natural elongate inclusions with a high temperature of homogenization. However the problem is that this kind of elongate inclusion is very rare. With such a high temperature of trapping, the natural inclusions perhaps always change shape and tend to an equilibrium shape.

Natural deformation

The rates of shape-change by solution-deposition which could be expected for natural quartz and calcite, if they are not measurable in the laboratory, could be significant for natural deformations. Crystals having been subjected to natural heating after their growth should have both rounded and fractured inclusions. Such research has been carried out on crystalline fillings of quartz and calcite in tension gashes in the sedimentary cover of the Pelvoux massif, French Alps (Bernard *et al.* 1977, Jenatton 1981).

Rounded inclusions, having T_h less than those of fractured inclusions (Fig. 4c), were observed in the same crystals, with all the intermediate values of T_h between rounded and fractured inclusions. Classically, these rounded inclusions are interpreted as primary inclusions which mark the conditions of growth of the crystals. Because generally the density increases after growth, the T_h of these rounded inclusions should be greater than those of the inclusions of irregular shape, which are

usually interpreted as secondary inclusions linked to tectonic effects. With the hypothesis that inclusions both changed shape and density, this association was interpreted as a marker of a thermal effect after the formation of the veins. The rounded inclusions would be inclusions which have preserved their fluid under pressure; thus their shapes have been changed. Their densities have also come back into equilibrium, but at different rates as observed in laboratory tests (Fig. 2). The densities of the fractured inclusions are completely in equilibrium with the thermal effect; they have angular shapes as observed in the laboratory, when there is low pressure in the inclusions. This thermal effect has been confirmed by a geological study. The sedimentary cover was in the proximity of a hotter basement, caused by thrusting of the basement onto the sedimentary cover (Gratier & Vialon 1980). In the case of crystals subjected to conditions of temperature and internal pressure greater than those of their growth, the inclusions not only marked the conditions of growth, but could also mark the conditions subsequent to the formation of the crystals.

CONCLUSIONS

Experimental solution–deposition may be studied by observing the change of length ($\Delta l/\Delta t$) of elongated fluid inclusions in heated synthetic minerals (quartz or calcite obtained by hydrothermal synthesis).

The driving force for mass transfer is the difference of surface energy around the cavity, linked to the difference of curvature (mass transfer from median part to extremities of inclusions). Consequently no apparent effect of an imposed state of stress on crystals was observed on the $\Delta l/\Delta t$ values. But theoretical and experimental work is in progress for the effect of high stress values.

The kinetics of dissolution is the rate-controlling process for elongate inclusions parallel to the 'c' axis of synthetic quartz. A relation is proposed between $\Delta l/\Delta t$ and the other parameters.

No change of shape was observed when heating (at relatively low temperature) natural crystals with fluid inclusions. The $\Delta l/\Delta t$ values being proportional to the

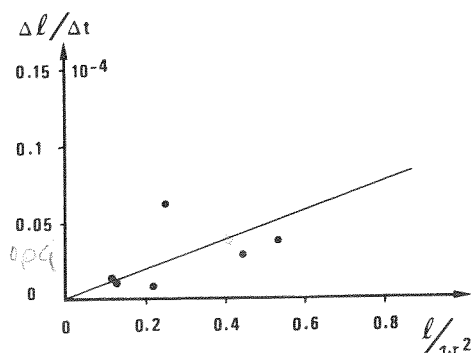


Fig. 10. Change of length of fluid inclusions in heated synthetic calcite. Relation between $\Delta l/\Delta t$ (in $\mu\text{m s}^{-1}$) and the ratio l/w^2 (in μm^{-1}). The inclusions did not have the same initial orientation in the crystal. Th, 212°C; Ti, 217°C; Pi, 5 MPa; $t = 60$ days; fluid, $\text{H}_2\text{O} + \text{NH}_4\text{Cl}$ (5%).

concentration of the solution, corrosive fluid must be used to have observable change of shape by solution–deposition. Such an activation of the solution–deposition process is also necessary for the experiment on pressure solution–deposition of an aggregate with intergranular fluid (Gratier 1984).

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REFERENCES

- Balderman, M. A. 1974. The effect of strain rate and temperature on the yield point of hydrolytically weakened synthetic quartz. *J. geophys. Res.* **79**, 1647–1652.
- Barns, R. L., Kolb, E. D., Laudise, R. A., Simpson, E. E. & Kroupa, K. M. 1976. Production and perfection of "z face" quartz. *J. Crystal Growth* **34**, 189–197.
- Bernard, D., Gratier, J. P. & Pêcher, A. 1977. Application de la microthermométrie des inclusions fluides des cristaux syn-cinématiques à un problème tectonique. *C. r. Somm. Soc. geol. Fr* **5**, 284–288.
- Burnham, C. W., Holloway, J. R. & Davis, N. F. 1969. Thermodynamic properties of water to 1000°C and 10,000 bar. *Spec. Pap. geol. Soc. Am.* **132**.
- Eadington, P. J. & Wilkins, R. W. T. 1980. The origin, interpretation and chemical analysis of fluid inclusions in minerals. Technical Communication No. 69, Institute of Earth Resources, CSIRO, North Ryde, Australia.
- Elliott, D. 1973. Diffusion flow laws in metamorphic rocks. *Bull. geol. Soc. Am.* **84**, 2645–2664.
- Fyfe, W. S., Price, N. J. & Thompson, A. B. 1975. *Fluids in the Earth's Crust*. Elsevier, Amsterdam.
- Gratier, J. P. 1982. Approche expérimentale et naturelle de la déformation des roches par dissolution–cristallisation avec transfert de matière. *Bull. Mineral. Cristallogr.* **105**, 291–300.
- Gratier, J. P. 1984. Dissolution–cristallisation et transfert de matière dans la déformation des roches en présence de fluides: aspects naturels et expérimentaux. Thèse Doctorat d'Etat, Grenoble.
- Gratier, J. P. & Vialon, P. 1980. Deformation pattern in a heterogeneous material: folded and cleaved sedimentary cover immediately overlying a crystalline basement (Oisans, French Alps). *Tectonophysics* **65**, 151–180.
- Haas, J. L., Jr. 1976. Physical properties of the coexisting phases and thermochemical properties of the H_2O component in boiling NaCl solutions. *Bull. U.S. geol. Surv.* **1421a**.
- Herring, C. 1953. *Structure and Properties of Solid Surfaces*. University of Chicago Press, Chicago.
- Ikornikova, N. Y. 1961. The process of solution of calcite in aqueous solutions of chlorides at high temperatures and pressures. *Soviet Phys. Crystallogr.* **5**, 726–733.
- Jaeger, J. C. & Cook, N. G. W. 1969. *Fundamentals of Rock Mechanics*. Chapman & Hall, London.
- Jenatton, L. 1981. Microthermométrie des inclusions fluides des cristaux associés à l'ouverture de fentes alpines. Thèse 3ème cycle, Grenoble.
- Kennedy, G. C. 1950. A portion of the system silica–water. *Econ. Geol.* **45**, 6–29.
- Kern, R. & Weisbrod, A. 1964. *Thermodynamique de Base pour Minéralogistes, Pétrographes et Géologues*. Masson, Paris.
- Kingery, W. D., Bowen, H. K. & Uhlmann, D. R. 1976. *Introduction to Ceramics*. Wiley, London.
- Lefaucheur, F. 1974. Contribution à l'étude de défauts présentés par des calcites hydrothermales de synthèse. Thèse Doctorat d'Etat, Paris.
- Leroy, J. 1979. Contribution à l'étalonnage de la pression interne des inclusions fluides lors de la décrépiation. *Bull. Mineral. Cristallogr.* **102**, 584–593.
- Nelson, R. S., Mazey, D. J. & Barnes, R. S. 1964. The thermal equilibrium shape and size of holes in solids. *Phil. Mag.* **11**, 91–111.
- Paterson, M. S. 1973. Nonhydrostatic thermodynamics and its geologic applications. *Rev. Geophys. Space Phys.* **11**, 355–389.
- Pêcher, A. 1981. Experimental decrepitation and re-equilibration of fluid inclusions in synthetic quartz. *Tectonophysics* **78**, 567–584.

- Pêcher, A. & Boullier, A. M. in press. Experimental evolution of fluid inclusions under high confining pressure. *Bull. Mineral. Cristallogr.*
- Potter, R. W. & Brown, D. L. 1977. The volumetric properties of aqueous chloride solutions from 0°C to 500°C at pressures up to 2000 bars based on a regression of available data in the literature. *Bull. U.S. geol. Surv.* **1421c**.
- Poty, B., Leroy, J. & Jachimowicz, L. 1976. Un nouvel appareil pour la mesure des températures sous microscope: l'installation de microthermométrie Chaixméca. *Bull. Mineral. Cristallogr.* **99**, 182–186.
- Raj, R. 1982. Creep in polycrystalline aggregates by matter transport through a liquid phase. *J. geophys. Res.* **87**, 4731–4739.
- Raj, R. & Ashby, M. F. 1971. On grain boundary sliding and diffusional creep. *Met. Transl.* **2**, 1113–1127.
- Regreny, A. 1973. Recristallisation hydrothermale du quartz. Thèse Doc ing., Paris VI.
- Robin, P. Y. 1978. Pressure–solution at grain to grain contacts. *Geochim. Cosmochim. Acta* **42**, 1382–1389.
- Robinson, R. A. & Stokes, R. M. 1959. *Electrolyte Solutions* (2nd ed.) Butterworth, London.
- Roedder, E. & Skinner, B. J. 1968. Experimental evidence that fluid inclusions do not leak. *Econ. Geol.* **63**, 715–730.
- Rutter, E. H. 1976. The kinetics of rock deformation by pressure–solution. *Phil. Trans. R. Soc.* **283**, 203–219.
- Swanenberg, H. E. C. 1980. Fluid inclusions in high grade metamorphic rocks from S.W. Norway. Ph.D thesis, Utrecht.
- Weisbrod, A., Poty, B. & Touret, J. 1976. Les inclusions fluides en géochimie-pétrologie: tendances actuelles. *Bull. Mineral. Cristallogr.* **99**, 140–152.