

Experimental pressure solution–deposition on quartz grains: the crucial effect of the nature of the fluid

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Abstract—Experimental deformation by pressure solution was performed on an aggregate of small grains subjected to deviatoric stress (50 MPa) for a long time (several weeks or months) at relatively high temperature and pressure in contact with various fluids (air, water, 0.1 to 1 N NaOH for quartz, water and 5% NH₄Cl for calcite). The change in shape of the grains by solution–deposition depended; on the duration of the experiment (with the same fluid) and on the concentration of the solid in solution (with the same duration but various fluids). Significant shape changes were obtained for quartz grains, but only with both long duration and very good solvents (1 N NaOH). By comparison with previously obtained results on the change of shape of fluid inclusions (where the kinetics of dissolution was the rate controlling process), the limiting process of the deformation of the quartz grains was inferred to be the rate of diffusion along grain boundaries saturated with trapped fluid.

INTRODUCTION

FOLLOWING Patterson (1976), the mechanisms of deformation that are possibly of importance in rocks can be conveniently grouped into three categories: cataclastic flow (with microfracturing and slipping), crystal plasticity (with glide motion of dislocations), and diffusional flow (with mass transfer). The deformation of rocks by pressure solution–deposition belongs to this last category (Elliott 1973). In comparison with the other mechanisms, this one needs an intergranular solution phase, it occurs at relatively low temperature (25–400°C), low differential stress (1–100 MPa), and very slow strain rate (10^{-11} – 10^{-16} s⁻¹) (Rutter 1976). This process is one of the most common mechanisms of ductile deformation for wet rocks in the upper crust. The mass transfer from solution zones (such as stylolites or solution cleavage) to zones with redeposition (such as veins or pores) leads to a change in shape (or a change in density) of rocks. This deformation may be analysed as a creep mechanism by establishing the relation between the strain rate and the various parameters, including driving force for mass transfer, nature of the solid and the fluid, temperature, pressure and geometry of the structure.

THEORETICAL APPROACH

The driving force for the solution–deposition process is often linked to the difference in normal stresses between the solid–fluid interface at the site of dissolution and that at the site of crystallization, but may be imposed by other forces such as the difference in elastic strain energy, in plastic strain energy or in surface energy between the two interfaces. All these forces lead to a difference in chemical potential between the dissolution zone and the crystallization zone (Paterson 1973, Robin 1978). Theoretically, the effect of a difference in normal

stresses is higher than the others. To impose such a difference in normal stresses around a solid, it is necessary to put this solid in contact with another solid. Several authors have discussed the behaviour of a fluid phase trapped in an interface between two solids under compressive stresses (Weyl 1959, Bathurst 1975, Rutter 1976, Robin 1978). The rate of mass transfer by diffusion along this interface could be drastically reduced if the fluid phase was locally expelled from the interface. To avoid this problem, Pharr & Ashby (1981) proposed that the mass transfer could occur in the free fluid phase around the solid, where there is no effect of the difference of normal stresses. Here, the driving force is the difference of surface energy linked to a difference of curvature of the solid boundaries. Gratier & Jenatton (1984) observed that a difference of curvature correlates with the amount of mass transfer around cigar-shaped microcavities (fluid inclusions) in heated synthetic quartz and calcite. It remains to make a careful investigation of the pressure solution process along solid to solid contact with a trapped solvent, between two stressed grains. The preliminary results of an experimental approach, allowing observation of significant shape changes of small grains, are given in this paper.

In all the cases (change in shape of cavities or grains), the rate of mass transfer is dependent on three successive processes: (i) the kinetics of dissolution at the solid/fluid interface; (ii) the rate of displacement of matter (by diffusion or infiltration) and (iii) the kinetics of the deposition process.

If one of these three successive processes is much slower than the others, the overall rate of mass transfer is dominated by the kinetics of the slowest process (Raj 1982). It is generally assumed that the rate of displacement is the slowest process, but it has been shown experimentally that this is not always the case: the kinetics of interface reaction may also be the limiting process (Raj 1982, Gratier & Jenatton 1984).

Consequently, for a solid cube surrounded by a fluid phase, in which the solid is soluble, various models have been constructed for mass transfer in a closed system around the cube (Gratier 1984), with the following assumptions. (i) The rate of mass transfer by diffusion within a fixed fluid phase, either around or through the solids, is the limiting process (model D or D'). (ii) The kinetics of the solid/fluid reaction (dissolution or crystallization) is the limiting process (model R). (iii) The rate of mass transfer by infiltration through a permeable solid is the limiting process (model I).

For technical reasons, the models D' and I are not easy to test experimentally, but they have been confirmed in natural deformation where the increase in volume in the deposition zone and the decrease of volume in the dissolution zone was calculated (by comparative chemical analysis), in order to estimate the size of the closed system. This size, ranging from 10^{-5} to 10^2 m (Gratier 1984); the largest values (10^{-2} to 10^2 m) are possible only with either large scale diffusion through the porous aggregate (model D') or large displacement of the fluid phase (model I).

For model D, (Raj & Ashby 1971, Elliott 1973, Rutter 1976), the creep relation is

$$\dot{\epsilon} = \frac{\alpha D_m \bar{c} w V_s \Delta \sigma_n}{RT d^3}$$

For model R (Raj 1982), the creep relation is

$$\dot{\epsilon} = \frac{\beta k' \bar{c} V_s \Delta \sigma_n}{RT d}$$

where $\dot{\epsilon}$, strain rate ($\Delta d/d \Delta t$); D_m , diffusion coefficient along grain boundaries saturated with trapped fluid; \bar{c} , solubility of the solid in the fluid (volume ratio); w , thickness of the grain boundaries; V_s , molar volume of the stressed solid; R , gas constant; T , temperature (K); d , length of the side of the cube; $k' \bar{c}$, growth (or dissolution) velocity of the face of the cube under a driving force of RT ; $\Delta \sigma_n$, difference in normal stresses between the solution surface and the deposition surface. The chemical potential $\Delta \mu$ is here considered to be proportional to the difference of normal stresses ($\Delta \sigma_n$), but $\Delta \mu$ could also be due to other driving forces (see Introduction). α and β are numerical parameters depending on the geometry and on the stress distribution.

EXPERIMENTAL APPROACH

Aims and problems of the experiment

The two models (R and D) could be distinguished by studying, firstly, the dependence of the strain rate ($\dot{\epsilon}$) on the size of the grain (d^3 or d), and, secondly, the dependence of $\dot{\epsilon}$ on the temperature (since the activation energy values are very different for the diffusion coefficient, D_m , and the kinetic coefficient, k'). However, the main problem is to obtain strain rates sufficiently high to be measured. Experimental mass transfers have been performed by several authors on

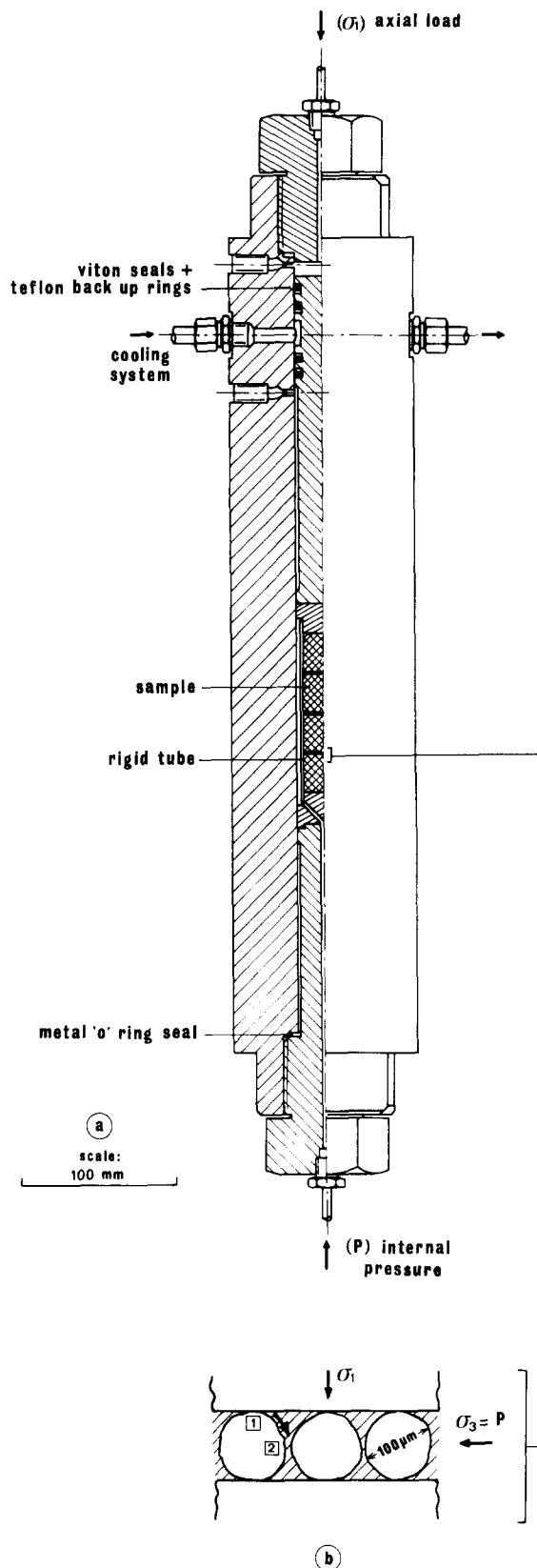


Fig. 1. (a) Schematic view of the experimental device: pressure vessel with permanent deviatoric stress on the sample provided by a difference in pressure values above (σ_1) and below ($\sigma_3 = P$) the piston (with atmospheric pressure between the two seal zones on the piston). (b) Sample assembly used in each experiment: stack of four cylindrical blocks between which were pressed three thin beds of small quartz grains. For each grain, mass transfer will occur from (1) to (2) (see Figs. 2-5).

quartz or calcite aggregates with water as the fluid phase (Maxwell 1960, Ernst *et al.* 1963, Renton *et al.* 1969, De Boer *et al.* 1977, Baker *et al.* 1980).

In these cases, the maximum deformation includes some very local mass transfer, with small pits of dissolution and small overgrowths. To test the creep relations, measurable values of deformation were needed (at least strains of several per cent). Even when taking the best conditions for the solution–deposition process (i.e. near the transition to plastic deformation) the theoretical strain rate calculated by Rutter (1976), with a D model, is about 10^{-11} – 10^{-12} s⁻¹ for small quartz and calcite grains (100 μm) in water. It is clearly impossible to measure such a deformation rate in the laboratory. Hence, it is always necessary to artificially increase the strain rate.

The temperature (with its effect on the coefficients of transfer) and the differential stress ($\Delta\sigma_n \propto \sigma_1 - P$, see Fig. 1) could not be increased above the conditions for plasticity of the mineral. The size of the grains should not be too small if we want to observe changes in shape. Thus the only parameter which can be modified is the concentration of the solid in solution (\bar{c}). High values of \bar{c} may be obtained either by using salt in water (Rutter 1976, Raj 1982) or by using quartz or calcite with respectively NaOH or NH₄Cl solutions as fluids (as is used in the experimental synthesis of these minerals, Regreny 1973, Lefauchaux 1974). Experimental mass transfers have already been observed for quartz and calcite with such fluids, but around cavities and at a low strain rate (10^{-7} – 10^{-9} s⁻¹) by Gratier & Jenatton (1984). The experiments presented here exemplify the extension of this principle of artificial activation of the pressure solution–deposition rate for grains under deviatoric stresses.

Apparatus and samples

Various types of apparatus were used to perform experimental pressure solution–deposition on quartz and calcite grains. The principle is to maintain under stress a thin bed of small solid grains, saturated with their solvent at various temperatures and pressures, for a very long time (several weeks or months, see Table 1).

The apparatus used was a pressure vessel (Fig. 1a), within which it was possible to impose a permanent

compressive uniaxial stress on the sample. Each sample comprised a stack of four cylindrical blocks of quartzite (h = 39 mm, dia. = 25 mm) which press between them three thin beds of small quartz grains (about 100 μm in diameter, Fig. 1b). Various fluids were used around these grains (air, water, 0.1 N NaOH, 0.5 N NaOH, 1 N NaOH). The temperature (T) and confining pressure values (P) could be raised to 400°C and 200 MPa. Permanent deviatoric stresses ($\sigma_1 - P$), up to 50 MPa were applied for 2–1150 days by imposing a pressure difference between the top and the bottom of a mobile piston which presses on the sample (Fig. 1a). To avoid equilibrium through leakage between the two reservoirs of high pressure and to cool the seal, the piston was sealed at two points along its length and fresh water, at atmospheric pressure, was circulated between these two seals. Each seal was produced by two Viton rubber O-rings backed up by Teflon rings. To maintain a homogeneous temperature ($\pm 1^\circ\text{C}$) all along the sample (H = 120 mm), there were three zones of independent heating around the pressure vessel. For easy manipulation of the sample, the four blocks were stacked in a tube 27 mm in diameter, freely mounted on the base and on the piston.

To avoid significant dissolution of the blocks and grains with the most corrosive solutions (with 1 N NaOH), the free space between the tube and the block was filled with a powder of amorphous silica, which is more rapidly dissolved than the quartz. At the beginning of the heating process, the solution became rapidly saturated without significant dissolution of the quartz grains. It must be noted that without this precaution in one experiment, the four blocks failed by fracture. The fractures were induced under a low deviatoric stress (50 MPa) probably due to the corrosive effect of the under-saturated solution. It may also be noted that, for all the experiments, no significant mass transfer occurred between the blocks; this confirmed the good homogeneity of the temperature in the cell.

Two types of grains were used. Quartz grains were obtained after crushing euhedral quartz crystals collected from a horizontal tectonic vein in the region of Bourg d'Oisans (Gratier & Vialon 1980); two classes of diameter were used (80–100 μm and 100–125 μm). Grains of amorphous silica were also used for one of the three thin beds. After each experiment, the sample was

Table 1. Conditions of the experiments described in this paper with reference to the photographs of Figs. 2–5

| Nature of the solid and reference to the photographs | Nature of the fluid | Axial stress (MPa) | Confining pressure (MPa) | Temperature (°C) | Duration of the experiment (days) |
|--|---------------------|--------------------|--------------------------|------------------|-----------------------------------|
| 2a, 3a–b | (quartz) air | 50 | 0.1 | 360 | 46 |
| 2b, 3c–d–e–f–g | (quartz) water | 200 | 150 | 360 | 51 |
| 4e–f | (quartz) 0.1N NaOH | 200 | 150 | 360 | 43 |
| 2g, 4a–b | (quartz) N NaOH | 200 | 150 | 360 | 2 |
| 2h, 4c–d | (quartz) N NaOH | 200 | 150 | 360 | 14 |
| 5c–d–e–f–g–h–i | (quartz) N NaOH | 187 | 150 | 360 | 44 |
| 2c–i–j, 5a–b–j | (quartz) N NaOH | 200 | 150 | 360 | 51 |
| 3h | (quartz) water | 25 | 0.1 | 20 | 1150 |
| 2d | (glass) air | 50 | 0.1 | 360 | 46 |
| 2e | (glass) water | 200 | 150 | 360 | 51 |
| 2f | (glass) 0.5N NaOH | 200 | 150 | 360 | 50 |

impregnated with an epoxy resin, and polished thin sections made across the thin beds.

Results of the experiments

The conditions of the experiments are given in Table 1. After these experiments, the samples were studied both under a scanning electron microscope and under an optical microscope (Figs. 2–5).

The effect of the nature of the fluid clearly appears in comparison of the two cases listed below (with $T = 360^\circ\text{C}$, $P = 150\text{ MPa}$, $\sigma_1 - P \approx 50\text{ MPa}$, $t \approx 50$ days, $\text{dia.} \approx 100\ \mu\text{m}$).

(a) With air around the grains, most preserved their initial shape, a few of them were fractured, but no compaction, nor lithification of the beds occurred (Figs. 2a, 3a & b).

(b) With water around the grains, most also preserved their initial shape, but the compaction of the thin beds was better (Figs. 2b, 3c–f). Apparently, the porosity decreased with respect to the initial state (see Fig. 2a). Very locally, in some sections, it is possible to observe some large domains composed of two or three initial grains which have been sealed together (Fig. 3g), with the long axis of the domain perpendicular to the σ_1 direction. It was also possible to see some local indentation in the grains.

(c) With 0.1 N NaOH around the grains (Figs. 4e & f), indentation and sealing were more frequent, and this phenomenon was progressively developed with increase in concentration of NaOH in the solution (corresponding to an increase in concentration of quartz in the solution, Laudise 1970).

(d) With 1 N NaOH, the porosity of the sand was completely destroyed (Figs. 2c and 5). The appearance of the thin bed was not very different from that of the host quartzite. Numerous indentations and sealing phenomena appear in all the beds (Fig. 5). This illustrates the importance of the mass transfer by solution–deposition process. We may also note that the quartzite of the blocks can be locally dissolved, especially along the grain boundary limits (Fig. 5d). Within the microcavities between the grains, some large overgrowths of quartz (new crystals up to $25\ \mu\text{m}$, Fig. 2j) were observed using a scanning electron microscope.

The crucial effect of the nature of the fluid (of the \bar{c} values) on the development of significant solution–deposition features in our experiments is represented schematically in Fig. 6. The same effect of the \bar{c} values also appeared for the change in shape of amorphous silica grains by mass transfer (Figs. 2d–f). The only test in which pressure solution–deposition appeared significantly well developed with water was a very long duration test (1150 days, Fig. 3h).

In some thin beds, it was also possible to find small grains of calcite (the powder was unfortunately badly cleaned) (Figs. 4e and 5). Other experiments were made specifically on calcite, with NH_4Cl and water as the solution. Solution–deposition also appeared with a 5% NH_4Cl solution, but the geometry of the grain did not change as clearly as for quartz. No large composite

domains appeared by the sealing of several grains, and deposition simply occurred in the voids between and around the grains.

However, the device used for the specific experiments on calcite was an adaptation of a triaxial cell, with oil as the confining medium, and with long duration experiments, infiltration of oil was observed in the sample. Consequently, the observation of the thin section was not very easy and the experiments had to be recommenced in the type of device described (Fig. 1a).

It was also observed that solution–deposition features were progressively developed during the experiments. A series of experiments on quartz was performed with the same fluid (1 N NaOH), but with various durations (2, 7, 14, 51 days). The same variation was noted with increase in time as with increase in solubility (Figs. 2g–i).

A more quantitative approach to the study of the change in shape of quartz grains was possible by counting, in thin sections, all grain boundaries crossed in traverses respectively parallel and perpendicular to the σ_1 direction (Nicolas & Poirier 1976). For equal distance, a grain size index can be defined as the ratio $R = \text{number of intersections along the directions parallel to } \sigma_1 / \text{number of intersections along the direction perpendicular to } \sigma_1$ (Fig. 6c). The measurement of the grain size index on thin sections showed a clear increase in their values depending firstly on the value of the solubility of quartz in solution (with the same duration as in the experiments, Fig. 7a), and secondly on the duration of these experiments (with the same values of \bar{c} , Fig. 7b). For example in Fig. 7(a), for the same initial grain size (100 to $125\ \mu\text{m}$) and the same duration (about 50 days), the index R varies from 1.1 (with water) to 1.45 (with 1 N NaOH). A third effect appears in Fig. 7(a), for two experiments in which the R value is inversely proportional to the initial diameter of the grain. The deformation rate is more rapid in finer grained material.

With such a deformation mechanism, the R value does not represent the exact value of the deformation. If, for example, two initially equant grains are sealed together with an ‘obliteration’ of the common boundary, an error will appear due to the neglecting of this boundary. Nevertheless, all the initial limits of grains were not obliterated, and the R value could give a maximum comparative value of the elongation: these values of R imply principal stretches of 1.13 and 0.78 under conditions of constant volume and oblate strain.

For more accurate assessment of the strain values cathodoluminescence was used to discriminate between the overgrowths and the initial mineral (Smith & Stenstrom 1965, Sippel & Glover 1965, Sprunt & Nur 1977, Amieux 1982). A difference in colour was observed between original calcite grains (orange) and their overgrowths (greenish brown). For quartz grains, the difference was less clear (original grain: greyish green and overgrowth: brownish pink). The results were not satisfactory: the elongation values were not easy to measure due to the small difference in colour. It is planned to repeat the experiments with other quartz grains with original blue cathodoluminescence colour.

Experimental pressure solution of quartz grains

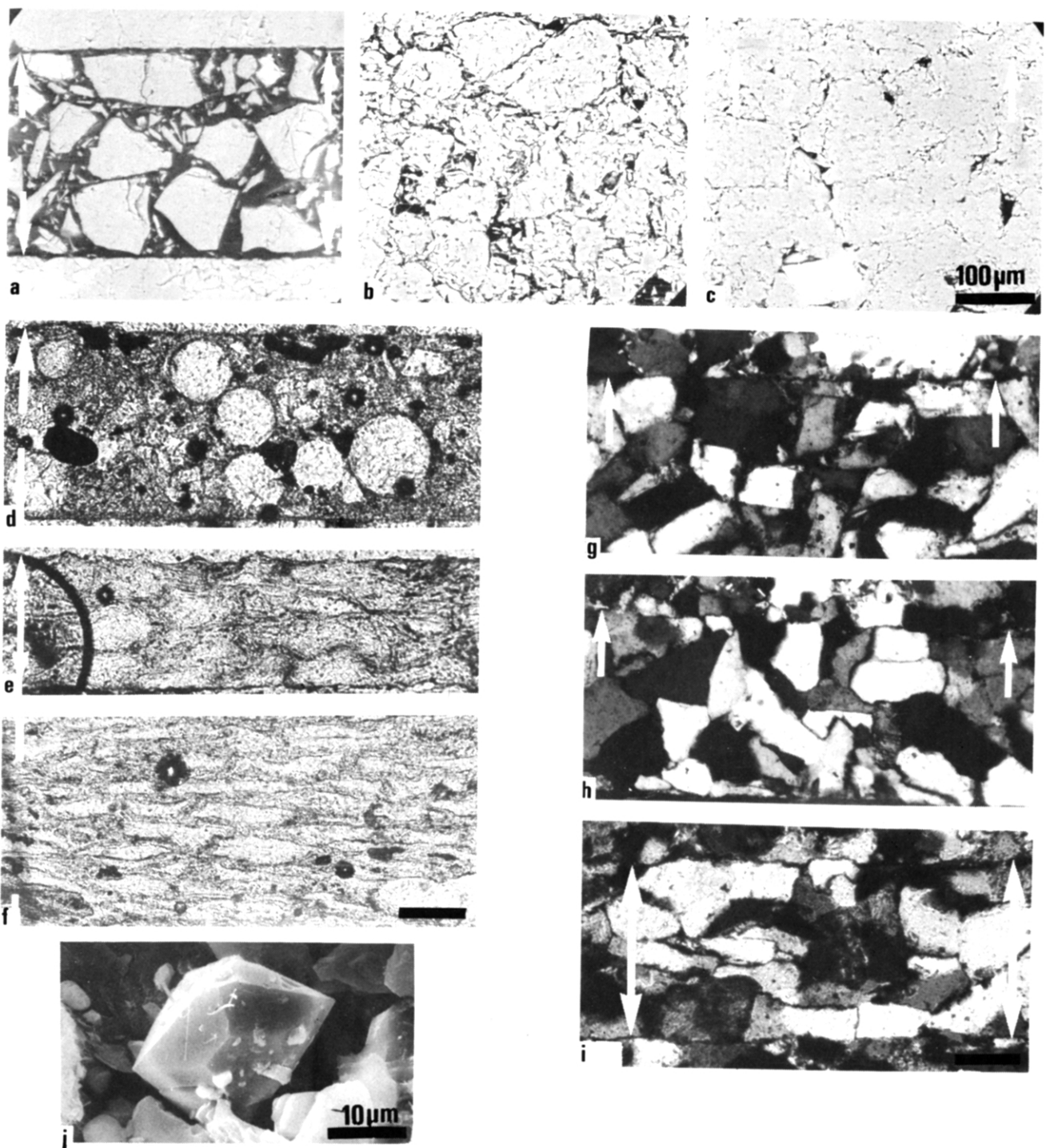


Fig. 2. Experimental deformation of quartz grains (a, b, c, g, h, i) and amorphous silica grains (d, e, f), observed in thin sections (impregnated with a resin after the experiment): back-scattered electron images from a scanning microscope (a, b, c), photographs with optical microscope (d, e, f, g, h, i), photograph of quartz overgrowths in the voids between the grains (j). The conditions of the deformation are given in Table 1. Note on figures a, b, c (with about the same 50-days duration), the crucial effect of the nature of the fluid on the development of pressure solution–deposition processes: the volume of the voids (black-coloured) between the grains decreases from experiments with air (a) to experiments with water (b) and with 1 N NaOH solution (c). The effect is even more drastic with amorphous silica: from air (d) to water (e) and 0.5 N NaOH solution (f). Note also (with the same 1 N NaOH solution), the clear effect of the duration of the experiment on the development of solution–deposition processes from 2 days (g) to 14 days (h) and 51 days (i). The arrows indicate the limit between aggregate and rigid plates (quartzites) and the direction of maximum compressive stress. In all the cases, the initial diameters of the grains ranged from 100 to 125 μm . The size of the black scale bar is 100 μm .

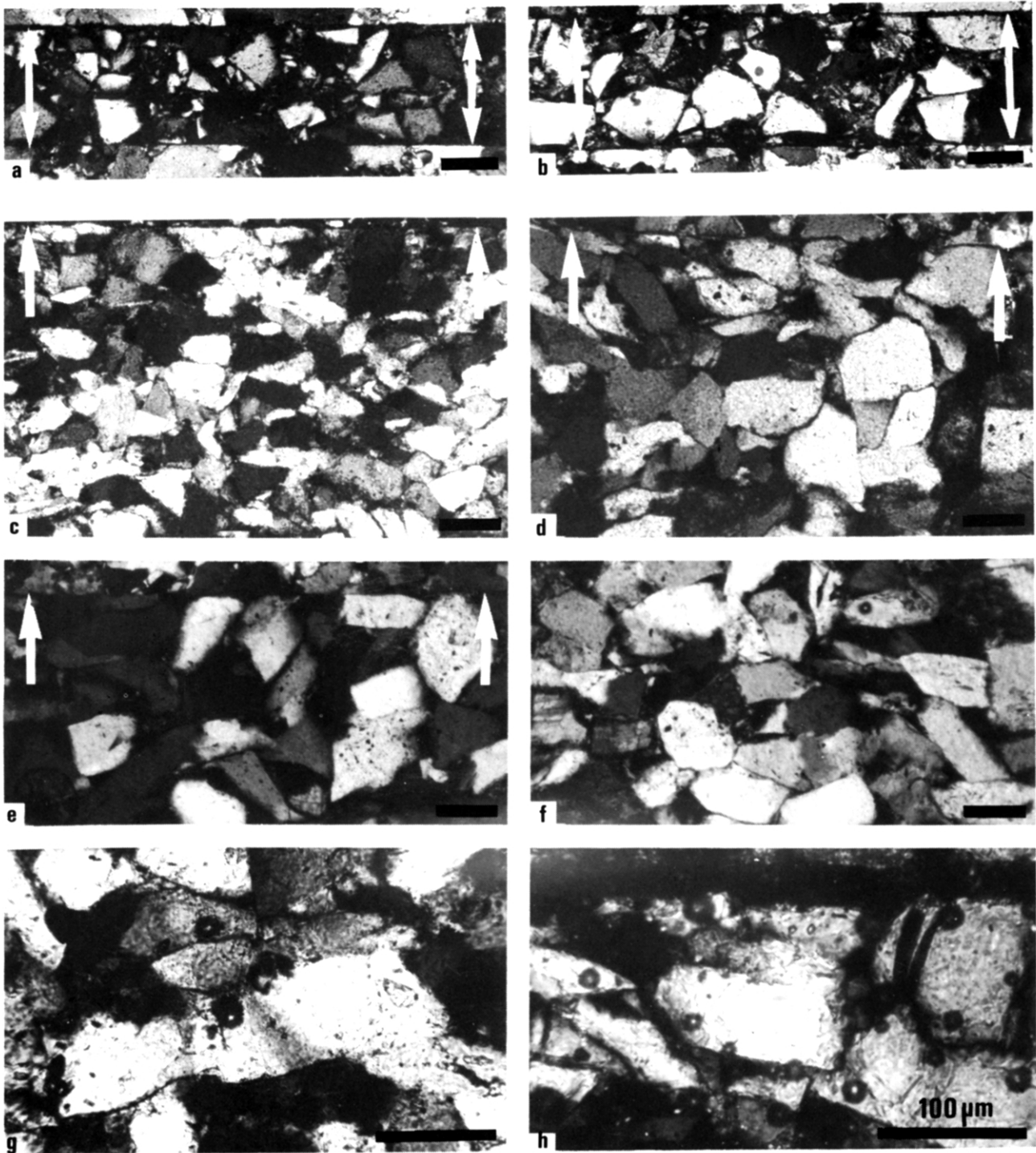


Fig. 3. Experimental deformation of quartz aggregates without solvent around the grains (a, b) or with water as solvent (c, d, e, f, g, h) with about 50 days duration (thin sections under optical microscope). With air (a, b), no densification of the aggregate nor deformation of the grain (by mass transfer) appeared. With water, densification of the aggregate but no significant deformation of the grains occurred (c, d, e, f), except in zones with very local indentation (dissolution) and sealing (deposition) (g). With very long duration experiments (1150 days), some solution-deposition was more clearly observed (h). The arrows indicate the limit between aggregates and rigid plates (quartzite) and the direction of the maximum compressive stress. The initial diameter of the grains ranged from 100 to 125 μm , except for (c): 80–100 μm . The deformation conditions are given in Table 1. The size of the black scale bar is 100 μm .

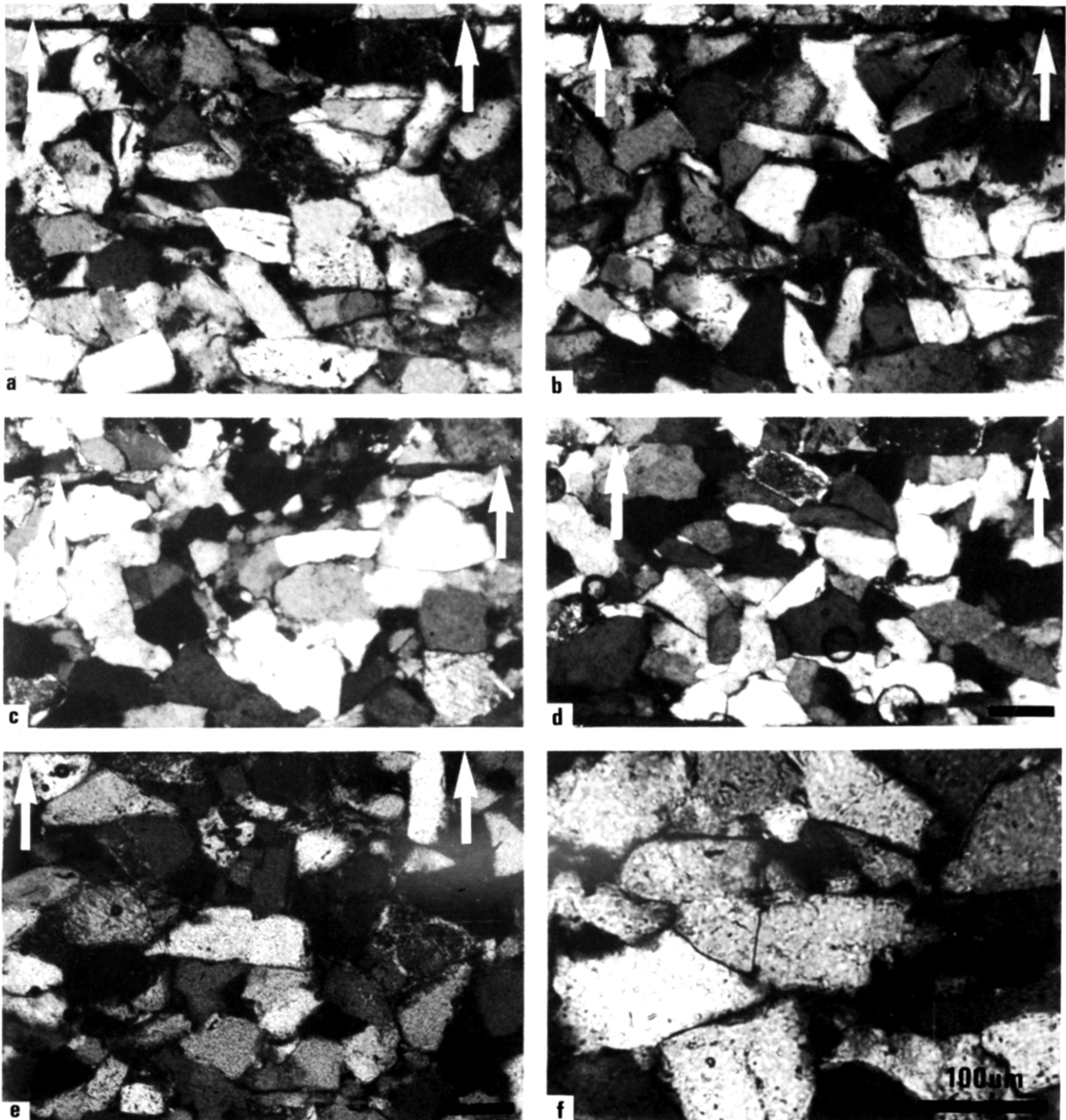


Fig. 4. Experimental deformation of quartz aggregate with good solvent (1 N NaOH solution), but short duration of the experiments (a, b: 2 days, c, d: 14 days) and with weak solvent of the quartz (0.1 N NaOH) (e, f) (thin sections under optical microscope). Densification of the aggregate occurred in all the cases. The development of pressure solution–deposition processes clearly increases with experiment duration from 2 days (a, b) to 14 days (c, d). These processes also develop more with 0.1 N NaOH (e, f) than with water (Fig. 3). Arrows indicate the limit between the aggregate and the rigid plate (quartzite), and the direction of maximum compressive stress. The initial diameter of the grain ranged from 100 to 125 μm . The deformation conditions are given in Table 1. The size of the black scale bar is 100 μm .

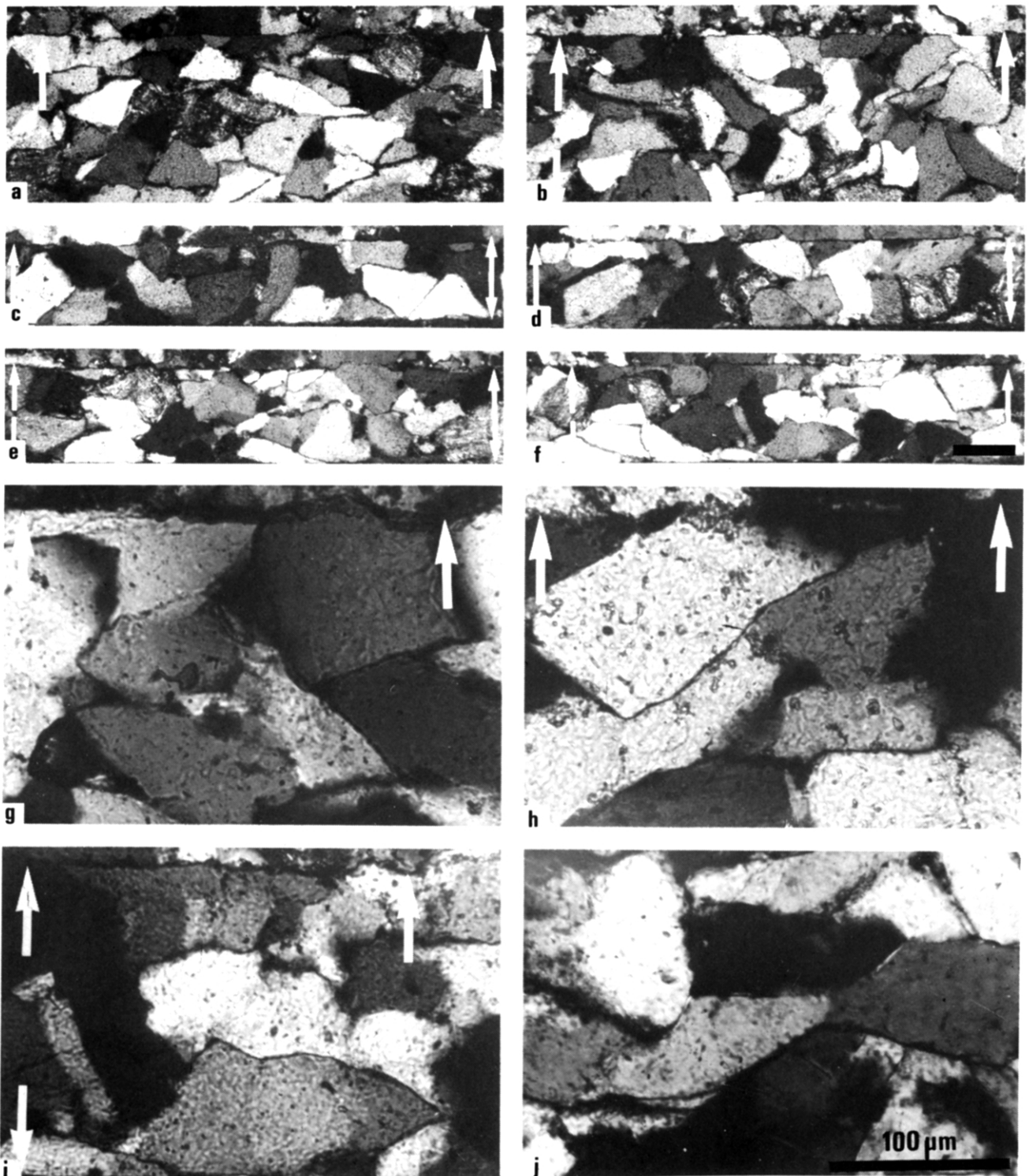


Fig. 5. Experimental deformation of quartz aggregate with good solvent of quartz (1 N NaOH solution) and long duration of the experiment (about 50 days) (thin sections under optical microscope). Pressure solution–deposition processes are well developed in all the thin sections. The grains of the aggregate are clearly indented and so is the rigid plate (quartzite) especially along the grain boundary (d). These indentations look like the tectonic stylolites frequently observed in natural deformation. Sealing between the grains also appeared clearly in all the thin sections. The grain size index (Figs. 6 and 7) indicates significant change in shape of the grains. Very local undulose extinction may be observed within some grains (g). Arrows indicate the limit between the aggregate and the rigid plate (quartzite) and the direction of maximum compressive stress. The initial diameter of the grains ranged from 100 to 125 μm . The deformation conditions are given in Table 1. The size of the black scale bar is 100 μm .

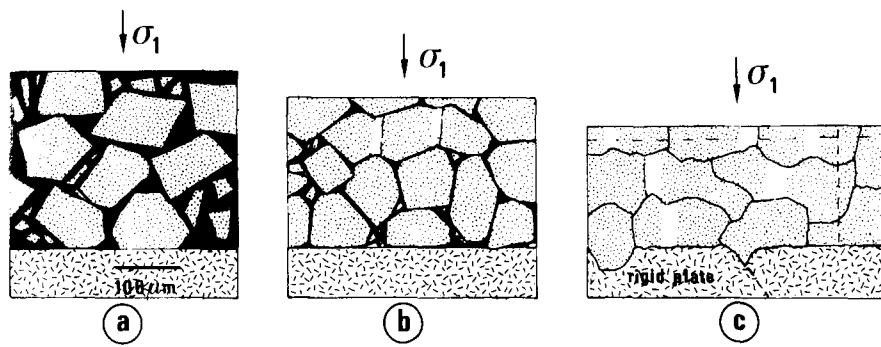


Fig. 6. Schematic view of the transformation of quartz grains in thin beds subjected to a permanent deviatoric stress; (a) initial state as in Figs. 3(a, b); (b) densification as produced very rapidly with NaOH solution (Figs. 4a & b) or slowly with water (Figs. 3c-f). The change in shape of the grain by solution-deposition depended on the duration of the experiment and the nature of the fluid; (c) significant values of this deformation which appeared only in experiments with both long duration and good solvent of the solid, as in Fig. 5. Dotted area, initial grain; white area, experimental deposition.

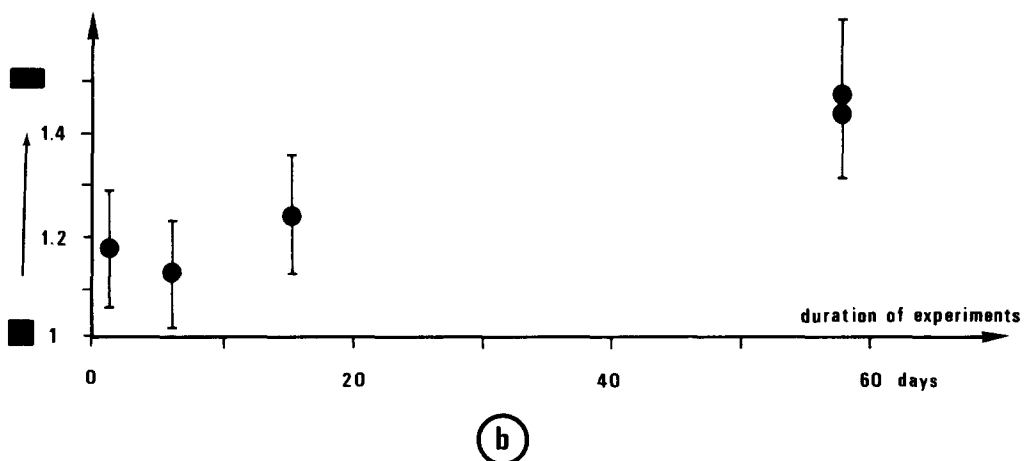
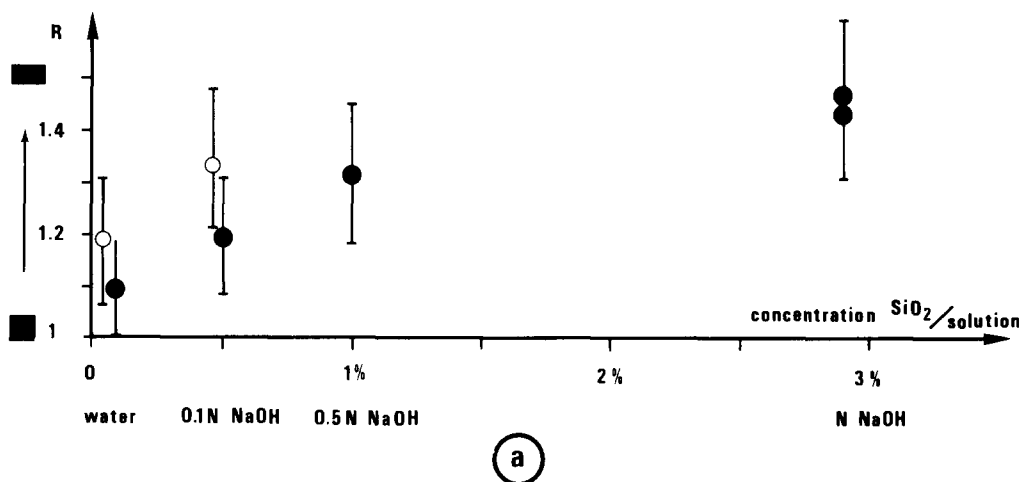


Fig. 7. Plot of the grain size index R vs (a) the concentration of SiO_2 in the solution with same experimental duration, (b) the duration of the experiments, with the same 1 N NaOH solution. The open circles represent the aggregate with grain diameters ranging from 80 to 100 μm , the closed circles represent the aggregate with grain diameters ranging from 100 to 125 μm .

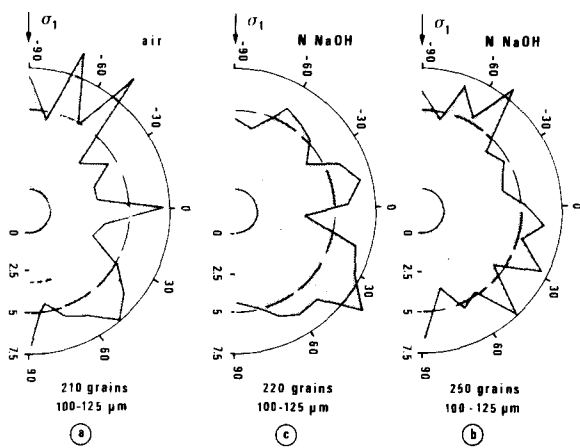


Fig. 8. Angular distribution of the trace of the (0001) plane of the quartz grains, on thin sections parallel to the σ_1 direction, in various deformed thin beds with either air (a), or 1 N NaOH solution (b, c). No clear difference appeared between the two kinds of experiments. The major deformation of the grain surrounded by 1 N NaOH solution (Fig. 5) was not linked to major plastic deformation.

Figure 5(g) shows that inside a grain which acted as an indenter an undulose extinction appears locally, but most of the change in shape of the grains was not linked to plastic deformation. Measurement of the orientation of the trace of the "c" axis on several thin sections (parallel to the σ_1 direction) showed that no clear preferred orientation appeared, and no clear difference was observed between aggregates without deformation (Fig. 8a with air around the grains) and aggregates with a relatively large amount of deformation (Figs. 8b & c, with 1 N NaOH around the grains).

DISCUSSION

The schematic representation given in Fig. 6 can be considered as a kinematic evolution of an aggregate of quartz, filled with its solution, and subjected to a permanent uniaxial compressive stress. The initial state is shown in Fig. 6(a). A first stage of densification always occurred with grain boundaries sliding, either by local mass transfer or by local plastic or cataclastic deformation. This stage was indicated by a relatively fast displacement of the piston during the first two days of the experiment. The pressure above and below the piston had to be readjusted frequently during this time to keep a constant difference in pressure values (given $\sigma_1 > P$). After this stage, the grain stacking geometry might be as in Fig. 6(b) (or in Fig. 2b). Maximum densification was reached without any significant change in the initial equant shape of the grain. After this stage, measurable change in shape (deformation) of the grains depended on the duration of the experiment and the nature of the solvent. With water, shape change is very slow, as in natural deformation, and no measurable values were obtained after several months. With NaOH solution, the grains presented a clear change in shape after some weeks or months.

The principal aim of this study, which was to obtain a

significant experimental deformation of quartz (or calcite) grains by pressure solution–deposition, was thus achieved by the use of a corrosive fluid which was a very good solvent of the mineral. We will now discuss, firstly, the driving force of the mass transfer and, secondly, the question of the process which limits the rate of deformation: kinetics of the reaction (model R) or rate of mass transfer (model D).

(i) The effect of a difference between the axial load value (σ_1) and the confining pressure value (P), ranging from 31 to 50 MPa for two experiments with 1 N NaOH, was not clearly shown (Fig. 5). The experimental equipment described here was not well adapted to a quantitative study of the effect of stress for two reasons: firstly, the geometry of the grains changed during the experiment and so changed the stress state on each grain and, secondly, even if we know exactly the $\sigma_1 - P$ value, we do not know exactly the proportion of load supported by friction at the seals. It remains clear that, as dissolution took place at the grain-to-grain contacts perpendicular to the σ_1 direction, and deposition occurred on surfaces parallel to σ_1 , the driving force for mass transfer was linked to the $\sigma_1 - P$ value which imposes a difference in the normal stress (σ_n) around each grain. To test accurately the stress to strain rate relation during the pressure solution process, another type of device is needed, allowing constant geometry of the grain-to-grain contact and constant σ_n value during deformation. This device is currently being constructed.

(ii) One way to deduce the limiting process of deformation (and thus to distinguish between models R and D) is to determine the effect of the size of the grain (Raj 1982) and of temperature (see the theoretical approach) on the value of the strain rate at constant stress and state of microstructural evolution.

Because the apparatus used for the present study does not give these conditions, this work will have to be done in the future in a new apparatus (see above). Another approach is to use the numerical values of the term $k'\bar{c}$ obtained by the study of the change in shape of fluid inclusions by a solution–deposition process (Gratier & Jenatton 1984). The kinetics of the reaction (dissolution on faces of the quartz parallel to the "c" axis) was found to be the limiting process in the latter case. The change of length of an initially elongated inclusion $\Delta l/\Delta t$ was found to be proportional to several factors as follows:

$$\frac{\Delta l}{\Delta t} = \frac{2k'\bar{c}l\gamma V_s}{RTW^2},$$

where l , length of the inclusion; γ , surface energy and W , width of the inclusion.

With $\gamma = 0.36 \text{ J m}^{-2}$ (Parks 1984), the $k'\bar{c}$ values, calculated at the temperature and pressure used, were $2 \times 10^{-8} \text{ m s}^{-1}$ for 0.5 N NaOH and $6 \times 10^{-8} \text{ m s}^{-1}$ for 1 N NaOH. These values must be compared with the experimental observations on grains. When using the maximum scattering of the measured strain values for aggregates with 1 N NaOH (1 to 10%), the values of the terms $k'\bar{c}$ and D_m may be calculated and compared with the known values. The numerical application of models

D and R (with $\dot{\epsilon} = 2.3 \times 10^{-9}$ to $2.3 \times 10^{-8} \text{ s}^{-1}$; $\alpha = 44$; $\beta = 2$; $\Delta\mu = \Delta\sigma_n V_s = 1.1 \text{ kJ}$; $w = 0.1 \text{ }\mu\text{m}$; $\bar{c} = 0.01$) give the following results: $D_m = 2.5 \times 10^{-12}$ to $2.5 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ (with the D model) and $k'\bar{c} = 5.5 \times 10^{-12}$ to $5.5 \times 10^{-13} \text{ m s}^{-1}$ (with the R model).

The value of $k'\bar{c}$ is very different from that calculated from the change in shape of fluid inclusions. If the strain rate was imposed by the kinetics of the reaction, its value would be higher ($\dot{\epsilon}$ could be equal to $2.5 \times 10^{-4} \text{ s}^{-1}$ with $k'\bar{c} = 6 \times 10^{-8} \text{ m s}^{-1}$). On the contrary, the calculated values for D seem reasonable, especially the lowest value (Fisher & Elliott 1974, Rutter 1983). Hence D model is probably the best model for the change in shape of an aggregate unfilled by its solution. In this case, the mass transfer by diffusion along grain boundaries with trapped fluid could be the limiting process. It must be kept in mind that this model is applicable to the second stage of the deformation (the deformation of the grain, Figs. 6b & c) and not to the first stage of densification. During densification, the high content of free fluid may radically increase the rate of mass transfer, since the diffusion coefficient through a free fluid is about five orders of magnitude higher than that along a trapped fluid phase (Rutter 1983). The kinetics of the reaction could be the limiting process for densification, as found by Raj (1982) for polycrystalline aggregates of salt, or by Gratier & Jenatton (1984) for the change in shape of fluid inclusions. The high early deformation rate is also linked to the high value of interfacial normal stress due to point contacts between grains, but this effect is probably the same in the two models R and D.

For the two models, if the strain rate is proportional to the applied stress, the deformation is equivalent to that of a Newtonian fluid (Laubscher 1975, Fletcher 1982) with a viscosity $\eta = \Delta\sigma_n/3\dot{\epsilon}$. From our experimental results, this means that the viscosity is about 7×10^{15} to 7×10^{14} Poise for a polycrystalline aggregate of quartz in a NaOH solution. This value could be extrapolated to about 5×10^{16} – 5×10^{17} Poise for a polycrystalline aggregate of quartz in water (taking into account the difference in the \bar{c} value).

This value of viscosity would seem to be relatively low, but the natural observations show that solution–deposition creep is one of the most frequent mechanisms of deformation in wet, upper crustal rocks, at low strain rate and low deviatoric stress (below the yield strength). The effect of stress seems to be less important than that of the geometry (size of the closed system) and of the mass transfer condition (through free or trapped fluid) (Gratier 1984). This also means that significant viscous deformation in the wet, upper crust could appear with a deviatoric stress much less than the “tectonic strength value” estimated by Molnar & Tapponnier (1981).

CONCLUSIONS

Experimental deformation by pressure solution–deposition was produced and measured on small grains

maintained under deviatoric stress (50 MPa) for a period of several weeks or months, in contact with a very good solvent: solution of NaOH (quartz) or NH_4Cl (calcite), at relatively high temperature and pressure.

For an aggregate of small quartz grains (dia. $\approx 100 \text{ }\mu\text{m}$), the limiting process controlling the rate of grain shape change is probably the rate of mass transfer by diffusion along grain boundaries saturated with the trapped solution (model D). The estimated diffusion coefficient values were about 2.5×10^{-12} – $2.5 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ at (360°C, 150 MPa).

As the kinetics of the reaction was found to be the limiting process (model R) for the densification rate of salt aggregates (Raj 1982) and for the change in shape of fluid inclusions in quartz (Gratier & Jenatton 1984), it is now necessary to establish the conditions of transition between the two models for solution–deposition. For example, when the possibilities of mass transfer change, from high contents of free fluid (early diagenesis) to low contents of trapped fluid (tectonic), the type of model could change from model R to model D. Future tests will be carried out using the present device if the proposed method for estimating the redeposited matter by cathodoluminescence examination can be improved.

To test accurately the stress to strain rate relation, another device is needed to keep both the geometry of the deformed structures and the load on these structures constant during long experiments. This device is currently being constructed.

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REFERENCES

- Amieux, P. 1982. La cathodoluminescence: méthode d'étude sédimentologique des carbonates. *Bull. Centres Rech. Elf-Aqu.* **6**, 437–483.
- Baker, P. A., Kastner, M. & Byerlee, D. A. 1980. Pressure solution and hydrothermal recrystallization of carbonate sediments: an experimental study. *Mar. Geol.* **38**, 185–203.
- Bathurst, R. C. G. 1975. *Carbonate Sediments and their Diagenesis*. Elsevier, Amsterdam.
- De Boer, R. B., Nagtegaal, P. J. C. & Duyvus, E. M. 1977. Pressure solution experiment on quartz sand. *Geochim. Cosmochim. Acta* **41**, 257–264.
- Elliott, D. 1973. Diffusion flow laws in metamorphic rocks. *Bull. geol. Soc. Am.* **84**, 2645–2664.
- Ernst, N. G., Blatt, H. G. & Harvey, A. 1963. Experimental study of quartz overgrowths and synthetic quartzites. *J. Geol.* **72**, 461–469.
- Fisher, G. W. & Elliott, D. 1974. Criteria for quasi-steady diffusion and local equilibrium in metamorphism. In: *Geochemical Transport and Kinetics* (edited by Hofmann, Gilletti, Yoder & Yund) Carnegie Institute, Washington.
- Fletcher, R. C. 1982. Coupling of diffusional mass transport and deformation in tight rocks. *Tectonophysics* **83**, 275–292.
- 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.
- Gratier, J. P. & Jenatton, L. 1984. Deformation by solution–deposition and re-equilibration of fluid inclusions in crystals depending on temperature, internal pressure and stress. *J. Struct. Geol.* **6**, 189–200.
- Gratier, J. P. 1984. La déformation des roches par dissolution–cristallisation: aspects naturels et expérimentaux de ce fluage avec

- transfert de matière dans la croûte supérieure. Thèse d'Etat, Université de Grenoble.
- Laubscher, H. B. 1975. Viscous components in Jura. *Tectonophysics* **27**, 239–254.
- Laudise, R. A. 1970. *Hydrothermal Synthesis of Single Crystals*. Prentice Hall, Englewood Cliffs, New Jersey.
- Lefaucheur, F. 1974. Contribution à l'étude de défauts présentés par des calcites hydrothermales de synthèse. Thèse d'Etat, Université Paris VI.
- Maxwell, J. C. 1960. Experiment on compaction and cementation of sand in rock deformation. *Mem. geol. Soc. Am.* **79**, 105–132.
- Molnar, P. & Tapponnier, P. 1981. A possible dependence of tectonic strength on the age of the crust in Asia. *Earth Planet. Sci. Lett.* **52**, 107–114.
- Nicolas, A. & Poirier, J. P. 1976. *Crystalline Plasticity and Solid State Flow in Metamorphic Rocks*. Wiley, New York.
- Parks, G. A. 1984. Surface and interfacial free energies of quartz. *J. geophys. Res.* **89**, 3997–4008.
- Paterson, M. S. 1973. Non hydrostatic thermodynamics and its geological applications. *Rev. Geophys. Space Phys.* **11**, 355–390.
- Paterson, M. S. 1976. Some current aspects of experimental rock deformation. *Phil. Trans. R. Soc. Lond.* **A283**, 163–172.
- Pharr, G. M. & Ashby, M. F. 1981. On creep enhanced by a liquid phase. Cambridge Univ. Eng. Dept. Research Report CUED/C/MATS/TR.69.
- Raj, R. & Ashby, M. F. 1971. On grain boundary sliding and diffusional creep. *Metall. Trans.* **2**, 1113–1128.
- Raj, R. 1982. Creep in polycrystalline aggregate by matter transport through a liquid phase. *J. geophys. Res.* **87**, 4731–4739.
- Regreny, A. 1973. Recristallisation hydrothermale du quartz. Thèse Doct.-Ing., Université de Paris VI.
- Renton, J. J., Heald, M. T. & Cecil, C. B. 1969. Experimental investigation of pressure solution of quartz. *J. sedim. Petrol.* **39**, 1107–1117.
- Robin, P. Y. 1978. Pressure solution at grain to grain contacts. *Geochim. Cosmochim. Acta* **42**, 1383–1389.
- Rutter, E. H. 1976. The kinetics of rock deformation by pressure-solution. *Phil. Trans. R. Soc. Lond.* **A283**, 43–54.
- Rutter, E. H. 1983. Pressure solution in nature, theory and experiment. *J. geol. Soc. Lond.* **140**, 725–740.
- Sippel, R. F. & Glover, F. D. 1965. Structures in carbonate rocks made visible by luminescence petrography. *Science, Wash.* **150**, 1283–1287.
- Smith, J. V. & Stenstrom, R. C. 1965. Electron excited luminescence as a petrological tool. *J. Geol.* **73**, 627–635.
- Sprunt, E. S. & Nur, A. 1977. Experimental study of the effects of stress on solution rate. *J. geophys. Res.* **82**, 3013–3022.
- Weyl, P. K. 1959. Pressure solution and force of crystallization, a phenomenological theory. *J. geophys. Res.* **64**, 2001–2025.