Pressure-Solution and Crystallization Deformation

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Pressure-solution and crystallization deformation

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[Plate 10]

Pressure-solution and associated crystallization are subclasses of a diffusive mass transport process which involves diffusion in grain boundary and pore solutions.

The manner in which they give rise to permanent deformation is examined in three steps:

(*a*) A simplified reversible non-hydrostatic crystal-solution thermodynamic criterion (first order, 2-components) based on Gibbs provides a manageable basis for determining the direction in which the process will run (regions of dissolution or growth) in stressed porous, non-porous, closed and open systems.

(*b*) Considerations of irreversible diffusion and deformation indicate certain restrictions on the displacements accompanying permanent growth or dissolution and hence on the form of the solution-transfer strain rate tensor.

(*c*) The way in which the process develops, and its rate, are governed by kinetic factors, especially diffusion kinetics. As well as having an exponential dependence on stress, the displacement rate is influenced by absolute temperature, grain boundary diffusivity, initial solubility and geometric scale.

1. Introduction

Recently there seems to have been a developing interest in diffusive mass transport processes in rocks and in the structural and chemical rearrangements they produce.

This paper aims to establish some of the things that thermodynamics can and cannot tell us about the strains and displacements associated with one group of these processes – stress controlled fluid solution diffusion or solution-transfer or solution redeposition processes.

The paper starts by defining the physical geological conditions that might reasonably be expected and the types of geological process for which an explanation is sought.

2. Diffusion mechanisms

Four main types of diffusion process which may operate in polycrystalline materi 1 and its cavities, and which may involve differing contributions of self-diffusion and solution-diffusion are:

(*a*) *Intragranular (volume, lattice) diffusion* through crystal lattices, usually self-diffusion, though may involve foreign interstitial atoms;

(*b*) *Intergranular (grain boundary) diffusion* along grain boundaries, either self-diffusion or solution-diffusion or both;

(*c*) *Free surface diffusion* along crystal/free fluid interfaces, self- and/or solution-diffusion;

(*d*) *Free fluid diffusion* through a free vapour, melt or fluid solution. ('Free' is used here to signify a true fluid outside the boundary layer or the zone of influence of crystal atomic charges).

Empirically, rates of diffusion are found to increase from (*a*) to (*d*) (Barrer 1951; Jost 1952), no doubt because of the corresponding decreasing influence of crystalline forces on the diffusing species. Furthermore, the presence of a solvent phase such as water (solution-diffusion) can greatly enhance diffusion rates in ionic polycrystals. Fyfe, Turner & Verhoogen (1958) report one reaction accelerated by 10^8–10^{10} using a hydrothermal medium.

Metallurgists and physicists usually consider diffusion deformation processes in terms of self-diffusion; for example Nabarro–Herring creep (Nabarro 1948), Coble creep (Coble 1963), and grain boundary sliding/diffusion models (Gifkins 1967; Ashby & Verral 1973). In upper to middle crustal deformations, however, solution-diffusion processes are believed to be of greater importance:

Pores, cavities and fissures below groundwater level are known to normally contain an aqueous fluid.

Vacuoles within minerals always contain one kind of fluid or another (even in granulite facies rocks, where it is chiefly CO_2, Touret 1974).

Carbonate minerals, and hydrous minerals such as chlorites, micas and amphiboles, are common rock-forming minerals and presumably a carbonic or aqueous phase must be present along grain boundaries to maintain their stability.

Electron microscopy on natural quartz (McLaren & Phakey 1965; White 1973) often reveals minute bubbles (interpreted as fluid filled) strung out along grain boundaries and dislocations.

3. Grain boundaries

While the mechanical state $p = \sigma_z$† in free solutions and at free surfaces is readily understood, further discussion is required on grain boundaries especially if free pore solutions happen to be absent from the rocks. (As the rocks are being considered in a state of burial it could be assumed that micro-crack porosity, which may just be an unloading phenomenon, is often zero. Cf. Simmons & Nur (1968) and Brace (1972) for discussion on micro-cracks and pores.)

The concept of a grain boundary which is adopted here is that of a disordered zone between two separate crystal lattices containing an atmosphere of impurity ions in interatomic spaces, in lattice vacancies, holes and channels, and in sub-micrometre sized bubbles.

Two effects can be concluded about the impurity ions. Firstly, because of their charge neutralizing and dielectric properties they reduce interatomic bonding in the disordered zone and would thus significantly enhance ionic mobility. Secondly, they act as a dilutant for these 'mobilized' ions, and combined, they could be regarded as a solution phase (cf. 'intergranular film or fluid' (Fyfe *et al.* 1958; Orville 1962); 'solution film' (Weyl 1959); 'dispersed phase' (Gresens 1966)).

Both the mechanical properties and the spatial distribution of this 'solution' are presumably transitional between that of the crystal and a free fluid. But to use thermodynamics it is necessary to idealize the situation into a discrete crystal phase and a discrete solution phase. The most general assumption about the stresses would be that the two phases are under different non-hydrostatic stresses such that the crystals transmit a macroscopic effective stress across the grain boundary through interlattice bridging bonds:

$$\sigma^{\text{eff}} = \sigma^{\text{crystal}} - \sigma^{\text{soln}}. \tag{1}$$

† For list of symbols, see p. 239.

Given the ability to diffuse readily, it seems reasonable that the mechanical strength of the solution is low, and so the approximation follows that

$$\sigma^{\text{soln}} \simeq p. \tag{2}$$

It is noted in particular that Gibbs's assumption (1878) that p equals a principal stress on the crystal, is not required for grain boundaries and indeed poses various mechanical problems. However, the condition must be satisfied that

$$p \leqslant \sigma + |\sigma_{\text{t}}|, \tag{3}$$

where σ_{t} is probably small. The equality signifies a special and critical mechanical state and not a general state at grain boundaries. Because of low σ_{t} this is probably confined to σ_3 faces or thereabouts when it does occur. Hence, even at the critical condition, most parts of a differentially stressed crystal's grain boundary would be described by the inequality.

4. Types of geological process considered

Geological terms describing stress-controlled solution-diffusion processes are discussed below. The distinction from other solution processes, those which involve chemical reactions or bulk flow of solutions, is mainly subjective. In nature one might expect a considerable interplay of these different effects.

Pressure-solution (Sorby 1908) (Drucklösung): *the dissolution and removal of mineral substance at a grain contact subjected to 'pressure'*. The term 'pressure' is vague but its meaning should become clear in §5. 'Pressure' or 'stress' is usually regarded as 'promoting' the process. Attribution of this and the succeeding processes to specific 'principles' is deferred until further discussion. The term 'solution' is understood here to mean 'dissolution', so 'pressure-solution' does not include crystallization processes.

Cavity growth: free crystal growth from and into a free pore or cavity fluid phase (fluid inclusions wholly within a crystal are not regarded as pores in the present context).

Pressure growth: synkinematic additive overgrowth crystallization of a mineral at a grain contact subjected to 'pressure'. This is the complete reverse of pressure-solution, and logically, if one accepts pressure-solution one also has to admit this process. The process could be regarded as promoted by a deficit of 'pressure' in most cases. The term used here replaces the ambiguous and controversial 'force of crystallization' (Kristallizationskraft) which in any case is an effect and not a process. Pressure growth is independent of idioblasticity.

Solution-transfer (Lösungsumsatz) (Heim 1921): *the dissolution, transport and precipitation of crystal substance from one part of a rock interior to another via a solution medium*. In the present context the term is restricted to concomitant pressure-solution, diffusion and crystallization in any crystal-solution system where solute movements can reasonably be accounted for. Bulk solution flow may accompany the process but the term itself does not necessarily imply transport *of* solution.

5. Crystal-solution thermodynamics

As emphasized by Paterson (1973) it is important to define the system conditions before constructing or applying a thermodynamic theory. Most theories in the literature seem to be correct in themselves, but the actual situations they describe may or may not be relevant to specific geological processes.

From the foregoing discussion we are presently interested in local crystal-solution equilibrium at free surfaces and grain boundaries. So in the first instance a crystal-solution theory is required. This then belongs to the class of 'incoherent phase transformations' (McLellan 1970) which are distinct from 'coherent transformations' such as grain boundary migration. Secondly, equilibrium needs to be expressed in terms of Gibbs free energy functions inasmuch as temperature and stress are usually the long-term geological constraints. (This allows changes of shape and volume as well as isothermal heat exchange.) Thirdly, a strictly non-hydrostatic theory is required. Hydrostatically derived theories such as those of Ramberg (1947, 1952) and Correns & Steinborn (1939) lead, to ambiguity of the meaning of 'pressure' in non-hydrostatic situations.

As a starting point we may take Gibbs's original equation 411 (1878). This is his final expression for the equilibrium relation of a stressed crystal and a multicomponent solution at a principal stress face (σ_z) at constant temperature. In his original notation this is

$$\left\{ m \left(\frac{d\mu_1}{dp}\right)^{(F)}_{t,m} - v \right\} dp + m\left(\frac{d\mu_1}{dm_2}\right)^{(F)}_{t,p,m} dm_2 + m\left(\frac{d\mu_1}{dm_3}\right)^{(F)}_{t,p,m} dm_3 + \text{etc.}$$

$$= \left(X_{X'} + p\,\frac{dy}{dy'}\frac{dz}{dz'}\right) d\,\frac{dx}{dx'} + X_{Y'}\,d\,\frac{dx}{dy'} + \left(Y_{Y'} + p\,\frac{dz}{dz'}\frac{dx}{dx'}\right) d\,\frac{dy}{dy'} \tag{4}$$

(cf. original paper for symbols) and in present day notation

$$(\bar{v}_1)^{(F)}_{T,x_i}\,dp - v_1\,d\sigma_z + \sum_i \left(\frac{\partial\mu_1}{\partial x_i}\right)^{(F)}_{T,p,x_j x_1} dx_1 = -v_1\{(\sigma_x - \sigma_z)\,de_x + \tau_{xy}de_{xy} + (\sigma_y - \sigma_z)\,de_y\}$$
$$= W' \tag{5}$$

where $\sigma_z = p$ and the superscript (F) denotes fluid phase terms.

The right hand side of this equation is the *difference* of two *second* order terms which Gibbs refers to as 'work' – one for the solid under hydrostatic pressure p and the other under non-hydrostatic pressure $\sigma_z = p$, σ_x, σ_y. Each of these terms is a small quantity and their difference is even smaller. For halite at 17 °C under a differential stress of 20 MPa uniaxial, using compliance data from Clark (1966) and solution data from Washburn (1928, p. 79* the integrated magnitude of W' is about 1/1100th that of the combined first order pressure-volume terms (l.h.s.) in equation (5) for the stressed face.

Riecke derived an analogous equation for crystal-melt systems (1895, eqn. 14) which is almost identical to Gibbs' equation 406. He then set dp and hence his $(v^{(F)} - v)\,dp$ term to zero, so *relating depression of melting point directly to the W' term* (1895, eqn. 17, $\sigma_x =$ an axial stress, $\sigma_z = \sigma_y = p$):

$$(s^{(F)} - s)\,dT = v_1\,(\sigma_x - \sigma_z)\,de_x\dagger. \tag{6}$$

Riecke's principle (1895, p. 737, lines 6–17; also proposed by Thomson in 1861), that an elastically strained crystal is more fusible or soluble than an elastically less strained crystal, was based on this restriction, equation (6). Not only is the effect small in magnitude, it applies only to those crystal boundaries showing the *same unchanged normal stress* such as the free faces ($d\sigma_z = d\sigma_y = dp = 0$) in Riecke's equation (also Riecke 1912, p. 100). It tells us nothing about the relative stability of two differently stressed faces nor about the overall relative stability of different stressed whole crystals.

* yields $v_1 = 24.2$ ml by tangent to V against $(x_1 + x_2)/x_2$ corrected to 10 MPa.
† de_x printed as de_y in original equation.

In solution-transfer processes it is essential, as was qualitatively appreciated by Sorby (1863), to retain the 1st order or 'pressure-volume' terms as variables in order to study the inter-reaction of differently stressed faces. This can be satisfactorily achieved simply by transposing Gibbs' eqn. 411 so that a *solution composition function is related to the 'pressure-volume' function plus W'.* For a binary solution (solute$_1$ and solvent$_2$) this is:

$$\left(\frac{\partial \mu_1}{\partial x_2}\right)_{T,p}^{(F)} dx_2 = \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,p}^{(F)} dx_1 = v_1 d\sigma_z - \bar{v}_1^{(F)} dp + W'. \tag{7}$$

To cover grain boundary conditions σ_z and p are now regarded as independent variables (see §3), and, following Kamb (1959), Kumazawa (1963), McLellan (1970), Durney (1972), and Paterson (1973), it can also be shown for equilibrium with respect to growth and dissolution that σ_z is replaceable by σ (together with a suitable generalization of W').

With these generalizations and with $W' \simeq 0$ equation (7) becomes

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,p}^{(F)} dx_1 \simeq v_1 d\sigma - \bar{v}_1^{(F)} dp. \tag{8}$$

This reduces to the appropriate expression in the limiting case of uniform hydrostatic pressure (Turner & Verhoogen 1960, eqn. 2–47; see also Denbigh 1971, eqn. 7.7) $d\sigma_{\text{hydrostatic}} = dp$. Equation (8) shows that

(a) a positive (compression positive) increment of σ alone always increases the equilibrium solute concentration.

(b) a positive increment of p alone always reduces the equilibrium solute concentration, and

(c) positive and equal increments of both σ and p together increase the equilibrium solute concentration when $\bar{v}_1 < v_1$ and vice versa when $\bar{v}_1 > v_1$.

Ionic crystals usually go into aqueous solution with a volume decrease (Sorby 1863; Holland 1967) hence $\bar{v}_1 < v_1$. NH$_4$Cl, KI and CdI$_2$ are among the few exceptions. Furthermore, because in many instances $v_1 > (v_1 - \bar{v}_1)$, *variations of effective normal stress* $d(\sigma - p)$, (a) or (b), *often produce larger equilibrium solubility changes than uniform hydrostatic pressure variations* $d\sigma = dp$, (c). For NaCl at 17°C (a) is 9.6 times and (b) is 8.6 times greater in magnitude than (c)

All these effects (a), (b) and (c) may be possible. But if differential fluid pressures over typical solute diffusion distances are not large it should be mainly (a) which accounts for the geological notion (§4) that local increased 'pressure' (*on the solid*) promotes 'pressure-solution'. The remaining discussion will therefore explore this principle, (a).

To obtain the finite local equilibrium condition on a small surface in the simple situation where T and p are uniform and constant, equation (8) can be integrated from any reference crystal stress state σ_0 and σ_0 ($\sigma_0 = p = \sigma_0$ is most convenient). Thus

$$(\mu_1)_{T,p}^{(F)} \simeq \int_{\sigma_0}^{\sigma} v_1 d\sigma = (\mu_1^0)_{T,p}^{(F)} + v_1 \sigma - v_0 \sigma_0. \tag{9}$$

For non-ideal solutions and to the *first order* this is

$$RT \log_e \left(\frac{a_e}{a_0}\right)_{T,p} \simeq v_0(\sigma - \sigma_0). \tag{10}$$

(The approximation now signifies that all second terms apart from those at σ_0, σ_0 are approximated to zero).

Equation (10), which applies to interfaces but not to crystal interiors, provides a simplified *criterion for growth and dissolution*. The three physical possibilities are, (i) local *equilibrium* when the actual value of activity $a = a_e$ and the solution is perfectly saturated with respect to the solid for the particular T, p, σ (and $\boldsymbol{\sigma}$), (ii) local *pressure-solution or dissolution* when the solution is undersaturated, $a < a_e$, and (iii) local *pressure-growth or free growth* when the solution is supersaturated, $a > a_e$. (It has frequently been suggested that crystals are incapable of growing against a great pressure (e.g. Shearman, Mossop, Dunsmore & Martin 1972 and Phillips 1974) as this would require a prohibitively high 'supersaturation' compared with saturation at atmospheric conditions. However, 'saturation' should be defined according to the *prevailing* local conditions (eqn. 10). Clearly, a small displacement from the actual equilibrium condition could stimulate growth at any pressure.)

This criterion (10) provides the basis for finding the areas of growth and dissolution in an aggregate of crystals under any stress field. This could be done by establishing an array of criteria, one for each small surface element, and working out the steady state values of a from irreversible thermodynamics. There is no general analytical solution to this but finite element methods may hold some promise for complex cases. For the moment we can qualitatively predict the behaviour of a few simple cases. A quantitative result is briefly mentioned in §8.
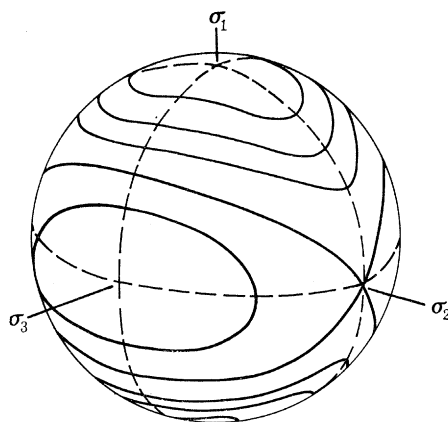

FIGURE 1. Normal stress contours on a homogeneously stressed sphere.
Contour intervals $\frac{1}{6}(\sigma_1 - \sigma_3)$; stress $(\sigma_1 - \sigma_2)/(\sigma_1 - \sigma_3) = \frac{2}{3}$.

6. SINGLE CRYSTAL AND AGGREGATE BEHAVIOUR

Case 1. A single crystal under homogeneous stress in a closed non-porous system. The normal stress varies around the crystal in a way such as that shown in figure 1. For irregular shaped grains the pattern would be more complex. From the r.h.s. of equation (9) the surface potential of the crystal varies in sympathy with this σ. Thus, the different parts of the crystal surface are unstable with respect to one another (figure 2a). As soon as diffusion is permitted (figure 2b) the values of μ adjust to A > B > C > D according to the coefficients of diffusion and phase change so that high σ faces go into solution and feed the growth of the low σ faces. The rate of dissolution or crystallization is related to the *divergence* of grain boundary diffusive flux:

$$J_s = \nabla . J_h = -D_h \nabla^2 c \propto -D_h \nabla^2 (a/\gamma). \tag{11}$$

Thus for a freely displaceable spherical grain boundary the maximum dissolution rate is at σ_1 faces and the maximum growth rate is at σ_3 faces. Somewhere between is a line separating the growth area from the dissolution area $(J_s = 0)$.

By this means a *differential stress produces a permanent differential strain* without affecting the interior of the crystal (figure 3, plate 10) or its volume.
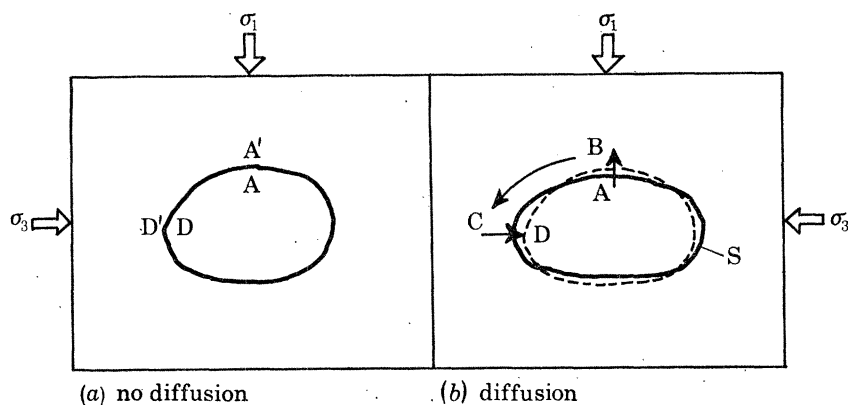

Figure 2. Case 1 system: influence of differential stress. (a) Without diffusion, crystal surface μ = fluid μ (A = A' > D' = D). (b) With diffusion, A' and D' adjust to B and C causing flux (arrows) leading to external shape change to S in given time.

Case 2. A single crystal under homogeneous stress in an open non-porous system. If case 1 is opened to allow diffusive influx or escape of solute the concentrations around the crystal will all be correspondingly upgraded or downgraded causing a shift of the lines between growth and dissolution and thus a net volume change for the whole crystal. *A permanent volumetric strain is thus superimposed* on the differential strain. In extreme cases there may be only dissolution or only growth on all parts of the crystal.

Case 3. Consider two open sub-systems inside a *closed heterogeneously stressed system* (figure 4). Each crystal undergoes its own differential strain because of the local differential stress. In addition, there is an overall μ difference between them due to the difference in mean stress. Hence material goes to B at the expense of A by a particular path or paths such as shown in figure 4. Figures 5 and 6, plate 10, illustrate migration interpreted as promoted by mean stress gradients around a hard object ($\bar{\sigma}$ assumed from P. Cobbold, personal communication 1971; Ghosh & Sengupta 1973 and Strömgård 1973).

Although mean stress variations must be important in natural systems, as far as crystal-solution theory is concerned $\bar{\sigma}$ only operates indirectly through the ensemble of surface normal stresses. Kinetic and geometric surface factors could be just as important in determining the *effective relative stability* of two grains. For example, a rapid diffusion channel between B5 and A4 in figure 4 would produce a reverse flux. Similarly, a reversal of flux might occur if the crystals were very flat, A having a large σ_3 surface and B having a large σ_1 surface.

Case 4. A porous crystal aggregate in a quasi-homogeneously stressed and effectively semi-permeable system. ('Effectively semi-permeable' means here that the fluid is allowed to escape without carrying significant quantities of solute with it in solution. In 'open' systems significant quantities could be exchanged by transfluent solutions or by sustained diffusion gradients.)

As in case 1, there is dissolution on high σ grain contacts and growth on low σ faces in a porous aggregate. But unlike case 1 the minimum surface potential would generally be on pore

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walls rather than on a grain boundary because from equation (3): $\sigma_{pore} = p \lesssim \sigma_{3\,boundary}$. Since diffusion through a pore fluid is also much faster than along a grain boundary, it can be concluded that there is a *strong preference for growth in the pores*. Consequently pores, fissures and micro-cracks must be unstable structures prone to cementation in a rock undergoing pressure-solution. (This could to be one of the reasons for low porosity in deeply buried sediments and metamorphic rocks.)

As pressure growth would seem to be largely by-passed in porous rocks, the solution-transfer strain (excluding brittle deformation) should be dominantly uniaxial shortening increments.
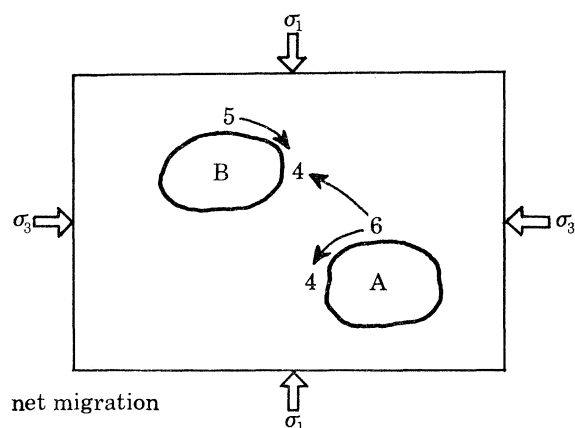

FIGURE 4. Case 3 system: influence of $\bar{\sigma}$ gradient. Numbers symbolize vaules of μ ($6 > 5 > 4$) corresponding to local principal stresses. Net migration from grain A to 1 as shown.
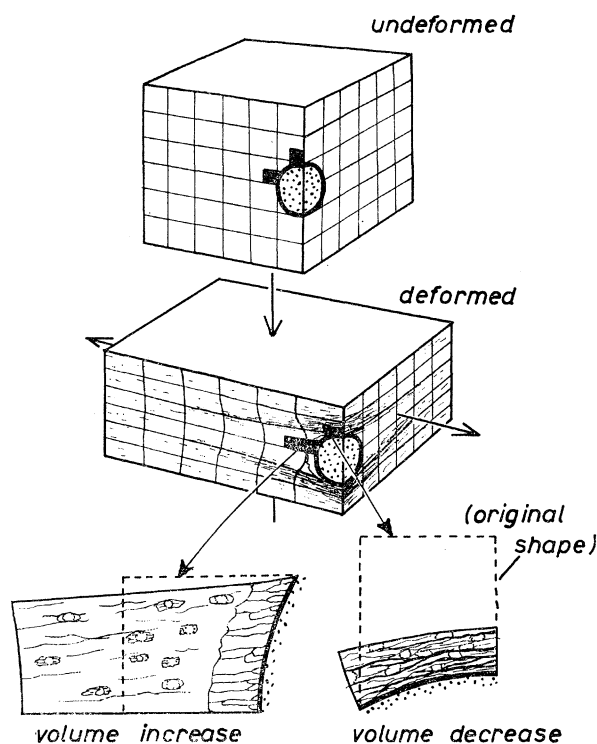

FIGURE 5. Schematic local volume increase (predominant pressure growth) and volume decrease related (predominant pressure-solution) to mean stress gradients around a hard object.

But as soon as the porosity is eliminated, the situation would revert to case 1 where pressure growth extensional strains may commence, albeit at a slower rate than cavity crystallization. This transition in behaviour may have important structural consequences in the progressive deformation of porous sediments; for example, the transition from concentric folding by inner arc shortening (Chouckrone 1969) to class $1c$ and 3 folding involving 'flattening'.

Moderately open porous systems should behave in a similar manner except that the volumetric strains are not limited by the initial porosity as they would be in 'semi-permeable' systems.

7. DISPLACEMENTS AND STRAINS

It is not obvious from reversible thermodynamics what the displacements are that accompany growth or dissolution at grain contacts. The theory used so far is concerned only with normal components of displacement.

Three different approaches have been attempted in an effort to solve this problem. The one described here borrows the minimum potential energy theorem from finite element methods. For stable time dependent flow, this theorem states that $\dot{U}_p - \dot{V}_p$ is minimized, where $\dot{U}_p$ is the internal deformation energy rate and $\dot{V}_p$ is the energy rate supplied by the environment during displacement of the system (Voight & Dahl 1970; Stephansson & Berner 1971).

A closed steady state diffusion situation like that in figure $2b$ is assumed but it is envisaged in three dimensions ($\sigma_1 > \sigma_2 > \sigma_3$) and with the system boundary just enclosing the grain and its intergranular fluid. The total rate of steady diffusive work, corresponding to a minimum $\dot{U}_p$, is assumed to be predetermined by the surface chemical potential gradients and by the kinetic coefficients through the irreversible internal entropy production criterion. Minimization of $\dot{U}_p - \dot{V}_p$ then depends on maximization of $\dot{V}_p$; that is, maximization of collapse energy and minimization of expansion energy. Since the local rates of volume addition or removal ($\delta \dot{V}_1$) around the crystal are also predetermined by the diffusion process it is obvious in this situation that $\dot{V}_p$ *is maximized when all dissolution displacements parallel the σ_1 axis* ($\Sigma \sigma_1 \delta \dot{V}_1$) *and when all growth displacements parallel the σ_3 axis* ($\Sigma \sigma_3 \delta \dot{V}_1$). Unless $\sigma_2 = \sigma_3$ or $\sigma_2 = \sigma_1$, $\dot{V}_p$ can furthermore only reach its maximum possible value when there is *no growth or dissolution in the σ_2 direction*. Steady state normal displacements on small σ_2 faces also seem unlikely when all other displacements are taking place at right angles to σ_2.

Similar arguments apply to moderately open systems. In strongly open systems (those where some growth has to occur on σ_1 faces as in the experiments of Becker & Day (1905), or some dissolution on σ_3 faces) some of the displacements will have to take place in directions other than those stated above. Maximization of $\dot{V}_p$, however, requires such displacements to be kept to a minimum rate.

In closed to moderately open systems at steady state, the local displacements at grain boundaries should therefore approach $x, y, z \rightarrow (x + \delta u), y, z$ on a growing face,

$$x, y, z \rightarrow x, y, (z + \delta w)$$

on a dissolving face (δw negative), and $x, y, z \rightarrow x, y, z$ in the interior of the crystal and on σ_2 faces $\neq \sigma_3$ or $\neq \sigma_1$ (x, y, z axes being parallel and rotating with local stress axes σ_3, σ_2, σ_1 in the crystal). Geological examples of parallel pressure-solution and pressure growth displacements are shown in figures 7 and 8 respectively, plate 10.

Strains

In an aggregate of crystals the accumulated displacements over a series of grain boundaries tend to smooth out the displacement discontinuities (see, for example, Ramsay 1976) and it becomes possible to define a homogeneous *solution-transfer bulk strain rate tensor* which is coaxial with the stress axes:

$$\dot{e}_{\text{soln-trans}} = \frac{\mathrm{d}e_{\text{soln-trans}}}{\mathrm{d}t} = \begin{pmatrix} \dot{e}_1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \dot{e}_3 \end{pmatrix}. \tag{12}$$

Thus, small solution-transfer pure strains should commonly be plane strain: *pure shear strain* in closed non-porous systems, *general plane strain* (with a volumetric component) in moderately open non-porous systems, and *uniaxial shortening* in 'semi-permeable' or moderately open porous systems. Superimposed on this, of course, there may be contributions from brittle and dislocation deformation mechanisms. Usually, the *finite solution-transfer bulk strain*, which depends on the sum of the infinitesimal increments, will *not* be plane strain unless the strain path is irrotational about the initial x and z axes.

8. DISPLACEMENT RATE

Finally, equation (13)†, which has been derived for pressure solution or pressure growth on a circular plane interface:

$$\frac{\mathrm{d}n}{\mathrm{d}t} \simeq -\frac{6c_0 D_\text{h}}{\rho r^2}\left(\exp\left(\frac{4(\sigma_\text{a}-\sigma_0)\,v_0}{3RT}\right) - 1\right) \tag{13}$$

shows that the displacement rates are *directly proportional to c_0 and D_h and inversely proportional to contact area*. They are also an *exponential* function of stress, rather than a linear function as suggested by Coble (1963) and Green (1970), because of the exponential dependence of solute activity (and vacancy concentration) on stress.

Equation (13) is a series approximation for an exact solution based on equation (10) and assumes radial diffusion, virtual equilibrium and constant activity coefficient. The approximation holds when

$$\tfrac{5}{3} > \exp\left[4(\sigma_\text{a}-\sigma_0)\,v_0/3RT\right] > \tfrac{1}{3}.$$

DESCRIPTION OF PLATE 10

FIGURE 3. Differential pressure-solution and growth strain around crinoid calcite single crystals. Dogger, Morcles Nappe, Saillon, Switz.; XZ sect. (magn. × 36).

FIGURE 6. Strong migration of quartz around hard andalusite porphyroblast. Biotite-garnet residue trails in matrix: garnet residue in appressed microstylolitic contact between porphyroblasts. Andalusite schist, Kanmantoo Mine, S. Australia; XZ sect. (magn. × 11).

FIGURE 7. Unidirectional contractile pressure-solution displacements shown by parallel sided stylolite teeth and sockets. Late tectonic stylolite (and coeval calcite stretch veinlets) overprinting strong S_1 fabric. Malm, Wildhorn – Diablerets root zone, Ardon, Switz.; late XZ sect. (magn. × 30).

FIGURE 8. Unidirectional instantaneous extensile pressure growth displacements as shown by parallelism of quartz–calcite fibres at various growth stages. Syntectonic pressure-shadow around concretionary pyrite, Lias, Autochthon, Arbignon, Switz.; XZ sect. (magn. × 36).

† Comparable equations for an identical situation have been worked out independently by Dr E. Rutter.

FIGURES 3 AND 6–8. For description see opposite.

Symbols

a	activity of solute
a_e	local equilibrium activity
a_0	reference equilibrium activity at σ_0, $\boldsymbol{\sigma}_0$, p, T
c	concentration, mass %
c_0	reference concentration at σ_0
D_h	grain boundary diffusion coefficient times effective grain boundary thickness
e	base of Naperian logarithm
$e_{1,3}$	maximum and minimum principal extensional strains
e	small strain tensor
J_h	grain boundary diffusive flux, equal to $-D_h \nabla c$
J_s	dissolution rate ($\mathrm{g\ s^{-1}\ cm^{-2}}$)
n	normal displacement component, dissolution negative
p	'fluid' hydrostatic pressure
r	contact radius
R	universal gas constant
s	molar entropy
t	time
T	absolute temperature
u, w	displacements in x and z
U_p	internal energy
v	molar volume
v_1	molar volume of crystal at σ, $\boldsymbol{\sigma}$, T
v_0	crystal molar volume at σ_0, $\boldsymbol{\sigma}_0$, T
$\bar{v}_1$	partial molar volume of solute
V_p	external energy
V_1	extensive crystal volume
W'	Gibbs' work difference
x, y, z	coordinate axes
$x_{1,2,i}$	mole fractions of solute and solvent or ith component
γ	solute activity coefficient
ρ	density
μ_1	solute chemical potential
μ_1^0	reference μ_1, at σ_0
σ	normal stress on the solid
σ_0	reference normal stress
$\sigma_{1,2,3}$	max., int. and min. principal compressive stresses
σ_z	a principal stress
$\sigma_{x,y,\tau xy}$	stress components perpendicular to σ_z
σ_a	average normal stress on a surface
σ_t	long term grain boundary tensile strength at $\boldsymbol{\sigma}$
$\bar{\sigma}$	mean stress $(\sigma_1 + \sigma_2 + \sigma_3)/3$
$\boldsymbol{\sigma}$	stress tensor
$\boldsymbol{\sigma}_0$	reference stress tensor

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FIGURES 3 AND 6–8. For description see opposite.