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SUMMARY. Several models of pressure solution-deposition have been established by using various hypotheses: on the rate-limiting process of the deformation (kinetics of the solid/fluid reaction or rate of mass transfer); on the driving force for mass transfer (difference in normal stress or elastic, plastic or surface energies) and on the mechanism of mass transfer (diffusion or infiltration). These creep relations have been tested experimentally and in nature. In the last case the observations show that the pressure solution-deposition process is always associated with a chemical differentiation of the rocks when these rocks are initially composed of several minerals with various mobilities under stress. The aim of this paper is to discuss the development of this chemical (and mechanical) differentiation. The first part deals with the initiation and the development of the zone of dissolution (relation between stress and dissolution, effect of the initial heterogeneities, etc.) and of the zone of crystallization (effects of the nature of the rocks, processes of deposition, etc.). The second part deals with the development of chemical differentiation during the progressive deformation. The geometry and the equilibrium composition of the differentiated layer are fixed by various factors such as: the size of the dominant heterogeneities (initial or tectonically induced), the possibilities of mass transfer, the state of stress, and the nature of the solid and that of its solution. The wavelength of some stylolites could also be imposed by these various factors.

The deformation of rocks by pressure solution-deposition is one of the most common mechanisms of deformation in the upper crust from diagenetic to low-grade metamorphic environments (20–400°C) in the presence of an intergranular fluid phase which is a solvent of the solid. After Sorby (1863) and Gibbs (1877) (and considering a compressive stress as positive), we know that some minerals such as quartz, or calcite, are frequently dissolved in zones of maximum stress (with the development of pitted pebbles, stylolites, solution-cleavage seams), these minerals being redeposited in zones of minimum stress (in veins or pores of the rocks). This mass transfer leads to a change of shape (or a change of density) of the rocks. This deformation may be analysed as a creep mechanism (or a densification mechanism) by establishing the relation between the strain-rate (or the densification-rate) and the various parameters of the deformation. Several models of pressure solution-deposition have been established by using the following assumptions:

The deformation rate is dependent on the kinetics of the successive processes: the kinetics of the solid/fluid reaction (dissolution or crystallization) and the rate of mass transfer (by diffusion or by infiltration). If one of these processes is much slower than the others the rate of the deformation is imposed by the slowest process. This leads to the establishment of various models of solution-deposition. On the other hand, the driving force for the mass transfer is usually linked to the difference in normal stress between the solid/fluid interface with dissolution and the solid/fluid interface with crystallization, but may be imposed by other forces such as the difference in elastic or plastic strain energy (Paterson 1973), or the difference in surface energy (linked to the difference in the curvature of the surface, Kingery *et al.* 1976), as in the model R, Fig. 1A.

Considering only the difference in normal stress as the driving force (for simplification), the creep relation for the change of shape of a cube of a solid, by pressure solution-deposition in a closed system, is always of the following form:

$$\dot{\epsilon} = f(k, c, \Delta\sigma_n, w/d^n, T),$$

where $\dot{\epsilon}$ = strain rate, k = coefficient of transfer, c = solubility of solid in solution, $\Delta\sigma_n$ = difference in normal stress, w/d^n = geometric factors depending on the path of mass transfer, T = temperature.

More precisely: k is the coefficient of transfer, depending on the limiting process (see above) and on the path of the transfer (see Fig. 1). After Gratier (1984, 1986) k is the kinetics of the solid/fluid reaction (model R), the permeability coefficient (model I with mobile fluid), the diffusion coefficient (model D or D′ with fixed fluids). In this last case the diffusion can occur either around a continuous solid, along grain boundaries, with trapped fluid, able to support shearing stress

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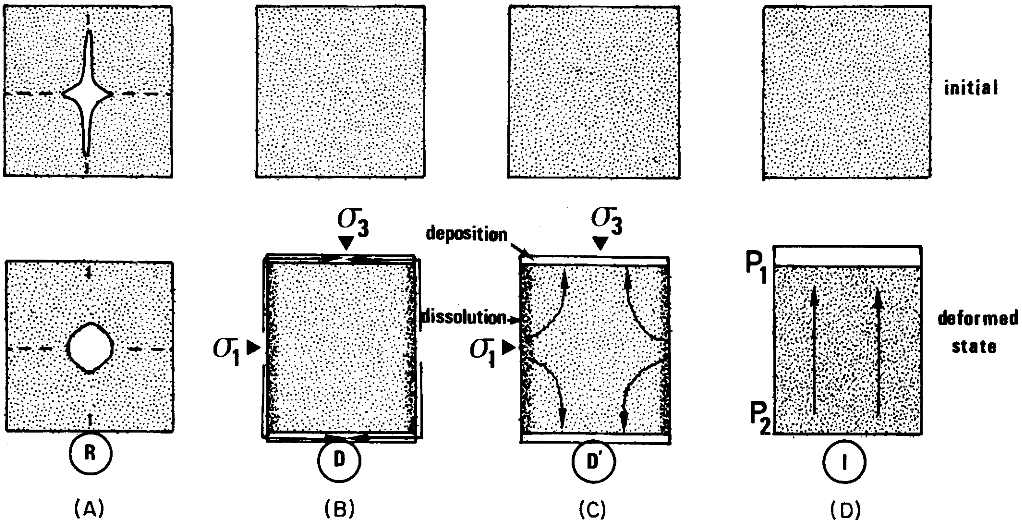


FIG. 1. Various types of mass transfer in pressure solution-deposition processes (in closed system). (A) Diffusion through free fluid in a small cavity. (B) Diffusion around a continuous solid (along grain boundaries). (C) Diffusion through a solid aggregate (along high speed diffusion paths). (D) Infiltration through porous aggregates. Depending on the limiting process (kinetics of the reaction or rate of mass transfer) various creep relations have been established and tested experimentally and in nature for these different cases (models R, D, D', I).

(model D), Rutter (1976); or through an aggregate, along high speed paths of mass transfer (model D'). These four types of models were tested experimentally and in nature: model R for the experimental change of shape of small cavities with diffusion through a free fluid phase, Fig. 1(A) (Gratier & Jenatton 1984); models D and D' for the experimental and natural deformation of compacted grains, with diffusion along grain boundaries saturated with a trapped fluid phase (Fig. 1B, C), Gratier (1984, 1986); model I for natural deformation with long distance of transfer (Fig. 1D). The mean distance of mass transfer is higher with infiltration (10–10^2 m) than with diffusion (10^{-4}–10^{-1} m).

These various coefficients of transfer k' (reaction), D (diffusion), K (permeability) are also dependent on the temperature (T), but in different ways. For example the activation energy varies from 90 to 10 kJ mol^{-1} K^{-1} between k' and D (through free fluid) (Barns *et al.* 1976; Robinson & Stokes 1959).

c is the solubility of the solid in its solution. The effect of this parameter was shown in natural deformations by comparing the relative mobility of quartz and calcite with change in temperature, since these minerals have respectively a normal and retrograde solubility. With fluid inclusion studies for the determination of pressure and temperature, (see below), we found that at about 275°C, 145 MPa quartz is more mobile than calcite, but it is the reverse at about 145°C, 80 MPa (Gratier 1984). This effect also appeared in experimental deformations when using various fluids in the deformation of quartz or calcite by pressure solution-deposition. In this case, significant values of the change of shape of small cavities, or grains, cannot be obtained without using very powerful solvents around the solid (NaOH or NH_4Cl solutions, respectively, for quartz or calcite) (Gratier & Jenatton 1984; Gratier 1986).

w/d^n are geometric factors: w is the width of the path of transfer (for example the thickness of the grain boundaries), d is the mean distance of transfer (for example the length of a cube with mass transfer in a closed system). Depending on the model, w can be equal to d (model D') and the value of the power of d^n can vary from 1 (models R, I) to 2 (model D') or 3 (model D), Gratier (1984, 1986).

$\Delta\sigma_n$ is the difference in normal stress between the zone of dissolution and the zone of crystallization. Depending on the model, this can be the difference in normal stress along the same solid/fluid interfaces (for example with mass transfer around a continuous solid, Fig. 1B), or the difference in fluid pressure (or in mean normal stress on the solid) between two zones of a porous aggregate (models D' or I).

For all these models the solid is supposed to be composed of only one soluble species. But of course this is not generally the case in natural deformations. In such cases the problem is more complicated. We shall discuss successively the initiation and development of dissolution and deposition zones in natural rocks, and a process almost always associated with the development of such zones which is the tectonic differentiation of the rocks (Soula & Debat 1976).

Initiation and development of the zones of dissolution

When a rock filled with a fluid phase, and composed of several minerals of various solubilities in this fluid, is deformed by pressure solution-deposition, a segregation of the minerals always appears. The relatively insoluble species are passively concentrated in the zone of depletion of the soluble species. Comparative chemical analyses between the zone of dissolution and the initial rock allow us to calculate the value of the volume decrease in the solution zone (Gratier 1983). For example, the distribution of various elements near such a dissolution zone, (obtained by successive profiles with a microprobe), are given in Fig. 2(A). A solution cleavage seam is marked by the zone of high content of elements

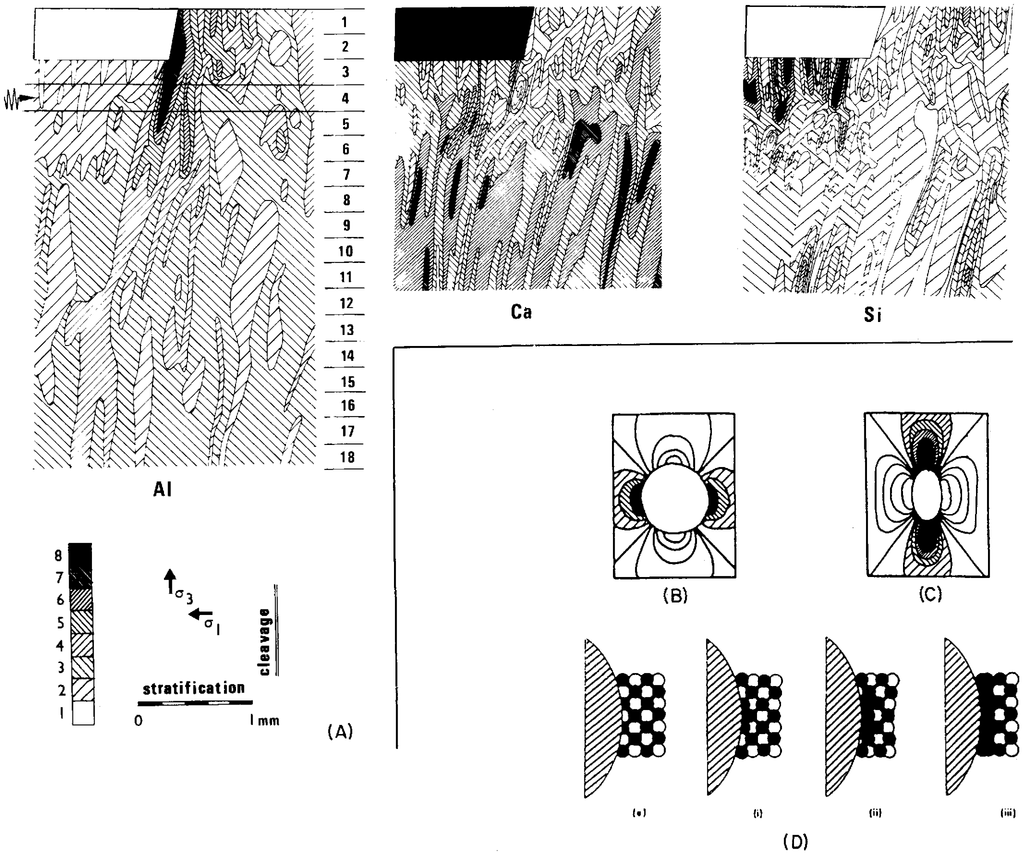


FIG. 2. (A) Chemical distribution (obtained by successive profiles with microprobe) of various elements in a slaty matrix around a rigid indentor submitted to a maximum compressive stress value (σ_1) horizontal and parallel to the initial layering. This natural deformation leads to a tectonic differentiation of the matrix: Al (in illite or chlorite) is passively concentrated in the zones of dissolution. Ca (in calcite) is removed from these zones (and not redeposited in the pressure shadow), Si (in quartz and layered silicates) has an intermediate behaviour, but the deposition of quartz in the pressure shadow sector clearly appears. (B) Theoretical distribution of mean stress values in a viscous matrix around a rigid object (after Stromgard 1973). (C) Theoretical distribution of mean stress values in a viscous matrix around a soft inclusion (after Cosgrove 1976). In the two cases the zones of maximum compressive stress are black-coloured. (D) Schematical development of a zone of dissolution near a rigid object. (i) Initiation in the zone of maximum compressive values. (ii) Development of a soft zone by the passive concentration of insoluble minerals (see B): layered silicates (black). (iii) Propagation of zone of dissolution in its own plane by preferential removal of matter in sectors with maximum compressive stress around the soft zone (see C).

such as Al, Fe, K (belonging to insoluble minerals such as illite, chlorite, etc.) associated with a depletion in content of other elements such as Ca, Si (belonging to soluble minerals such as quartz or calcite). The rock concerned here was naturally deformed with a maximum compressive stress (σ_1) parallel to an initially horizontal layering. The zone of the maximum dissolution is localized near the top of a rigid indentor composed exclusively of Ca and embedded in the slaty matrix. With such a state of stress it is clear that the dissolution zone appeared in the sector of the matrix submitted to the maximum compressive stress, compared with the theoretical model of stress distribution around a rigid object (Fig. 2B, Stromgard 1973). But the shape of the curves of equal content in Al (which corresponds to the curve of equal values of volume decrease) has not the same shape as the theoretical curves of, for example, the mean stress values. The zone of dissolution is a very narrow seam, shaped like parenthesis, largely extended beyond the rigid indentor (Fig. 2A), in contrast with the theoretical stress distribution curves which are more rounded and with maximum values localized near the top of the indentor (Fig. 2B). Such a difference has already been observed, and explained, by an internal deformation of the rocks (Casey 1976), but it is not the case here. The rock between the solution cleavage seams is almost undeformed (spaced cleavage). The difference between volume change and stress curves arises because in such a composite fine-grained rock as soon as one or two grains are dissolved in the zone of the maximum compressive stress a localized heterogeneity is induced in the rocks. The removal of soluble grains (quartz-calcite), which constitute the skeleton of the rock, disorganizes this rock and leads to a passive concentration of the insoluble species (here layered silicates with adsorbed or free associated fluids). This induces a relative increase in fluid content and a relative softening of the rock, with both chemical and mechanical effects. Following several authors (Heald 1956; Weyl 1959) the layered silicates catalyze the process of dissolution, either by increasing the kinetics of the reaction (model R) or by constituting some high speed paths for mass transfer (model D), since the diffusivity through these silicates is relatively high (depending on the fluid content), Calvet (1973). On the other hand, with the passive concentration of the layered silicates the dissolution zone becomes relatively less competent than the initial rock (an aggregate with both soluble and insoluble minerals, e.g. slate, is always less competent than an aggregate with only soluble minerals, e.g. quartzite or limestone). By comparison with the theoretical distribution of the stress values in a viscous matrix around an elliptical soft inclusion (Cosgrove 1976), two zones of maximum compressive stress appear in this matrix near the tip of the inclusion. Consequently, as pointed out by Cosgrove, the dissolution is concentrated in these two zones with a slow but continuous propagation of the zone of dissolution in its own plane. Fletcher & Pollard (1981) named the development of such a solution zone perpendicular to the σ_1 direction 'anticrack propagation'.

The driving force for mass transfer must, however, be discussed. Following the thermodynamic analysis (see, e.g. Paterson 1973), the major driving force is the difference, in the components of the stress normal to the solid/fluid interfaces, between the solution and deposition zones. Around a void filled with a free fluid phase and surrounded by a continuous solid, the normal stress value on the solid/fluid interface is constant (whatever the stress state in the solid) and cannot be the driving force for such a propagation. In this case the driving force must be a difference in elastic, plastic, or surface energy in the solid. A difference in normal stress (on the solid/fluid interface) can only be the driving force for mass transfer around a soft zone in a rock if this rock is an aggregate filled with its solution. In such a case, it is the increase in the 'trapped fluid' pressure (equivalent to the increase in the mean normal stress on the solid/fluid limit of the grain) which increases the dissolution of some grains in the rock near the tips of the parenthesis shaped solution seams (Figs 2 and 5).

Another problem is the development of zones of dissolution on pre-existing surfaces (such as bedding, cleavage, faults etc.) oblique to the σ_1 direction. This is attested by the observation of stylolite peaks oblique to the surface of dissolution (Arthaud & Mattauer 1969), and by the observation of the relations between two successive solution cleavages. In such a case it is generally observed that when two cleavages cross each other at various angles (in heterogeneous deformations) there is a minimum value for the angle of crossing of these planes (for example 30° in the Bourg d'Oisans basin, Gratier & Vialon 1980). This means that, during the development of the second (spaced) cleavage, the dissolution had locally continued on the first cleavage plane, without slipping on this plane. This observation first confirms the assumption made by Rutter (1983) of the possibility, for a dissolution surface, to support shearing stress. Secondly, this allows us to calculate an approximate value for the deviatoric stress during the pressure solution-deposition process. By comparison with mechanical experiments on the studied rock (anisotropic slates) we have found that a low deviatoric stress value (about 10–25 MPa) is needed to avoid slipping on the cleavage when the angle between the normal to the cleavage plane and the σ_1 direction varies from 0 to 30°.

All the examples studied on various rocks have shown that it is the initial heterogeneity of the rocks which imposes the position of the zone of dissolution for both chemical and mechanical reasons. The development of such a zone (schematically shown in Fig. 5) emphasizes this heterogeneity. A tectonic differentiation is thus a normal evolution for rocks deformed by pressure solution-deposition when these rocks are composed of minerals with various solubilities in the fluid phase.

Initiation and development of the zones of deposition

The initiation and the development of the zones of deposition are very different from those of the zone of dissolution. Considering various examples of chemical differentiation around rigid objects, and observing the distribution of several minerals (by microprobe analysis), we have found that, if the dissolution zones have almost always the same shape (of parenthesis) the deposition zones have a more varied aspect, depending on the nature of the rigid object. For example, in deformed slates the cubes of pyrite have large pressure shadow overgrowths, clearly observable even with the naked eye (Fig. 3A) whereas fossils, of the same shape and size, are accompanied either by scattered microscopic overgrowths or by sealed tectonic fractures within the fossil (revealed by cathodoluminescence studies, Gratier 1984). This can be explained by comparison with experimental deformation of a viscous matrix around a rigid object. When such a rigid object is not stuck to the matrix a large void appears in the zone of minimum stress (possibly tensional stress). But if the rigid object is well stuck to the matrix either a stretching of the matrix, with associated microcavities in the zone of minimum stress, or the fracture of the rigid object can appear. The same difference can appear in nature. Usually, the deposition thus occurs in open cavities (of various size) probably filled with free fluid (see below). Another difference between deposition zones and dissolution zones is that the former rarely show a large propagation in their own plane, as do the latter. The ratio 'thickness over width' of the zone of deposition is always much higher than that of the zone of dissolution. This perhaps occurs because the development of the zones of deposition is often limited by the development of the zone of dissolution which constitutes some soft barriers perpendicular to the veins. But the sealing of a tectonic vein with the most competent mineral of the rock (quartz-calcite) also induces a hardening of the rock which facilitates the development of new veins 'en échelon' in the 'protected' zone of the first vein. We have thus commonly observed the schematical development given in Fig. 5.

Another difference between dissolution and deposition is their evolution with time. The aspect of a crystal within a sealed cavity gives some indication of the mechanism of opening of the cavity. Euhedral crystals indicate growth within a free fluid phase in permanent open cavities (Fig. 3), whilst fibrous crystals parallel to the direction of maximum elongation are developed by repeated increments of microcrack opening, followed by sealing of the microcracks by deposition of the mineral from the dissolution zone (Ramsay 1980). Each sequence of growth is expressed by a network of fluid inclusions. The study of these inclusions gives some indications about the nature of the fluid phase, its pressure and temperature. We have found that the deformation of rocks by pressure solution-deposition generally occurs between 0.1–250 MPa and 20–400°C, water (with some content of NaCl) being the fluid phase. The comparison of the P,T values between successive veins associated with successive cleavages also gives an indication of the behaviour of quartz and calcite with various P,T conditions (see in the introduction the effect of c). Jenatton (1981) has shown that even with a single vein the P,T conditions may have evolved during the progressive deposition. But all these studies give the general evolution of P,T values with time. Another interesting result, obtained by Mullis (1975), has shown that even during the growth of an euhedral crystal in a permanent open cavity the fluid pressure evolves in a relatively discontinuous manner. As the crack-seal process is also clearly discontinuous with time, it seems that in nature, and in opposition to the dissolution process, the deposition process, either with euhedral crystals, or with fibrous crystals, is rather discontinuous both in space (growth on solid/free fluid interface) and in time (periodic change of pressure values).

This discontinuous process may be explained by successive changes in the volume of the cavities. A sudden opening of a vein (linked to an irregular fracture propagation) may induce a sudden decrease in the fluid pressure, which consequently induces the precipitation of the solute species and this during all the time of the re-equilibration of the pressure by the fluid flow

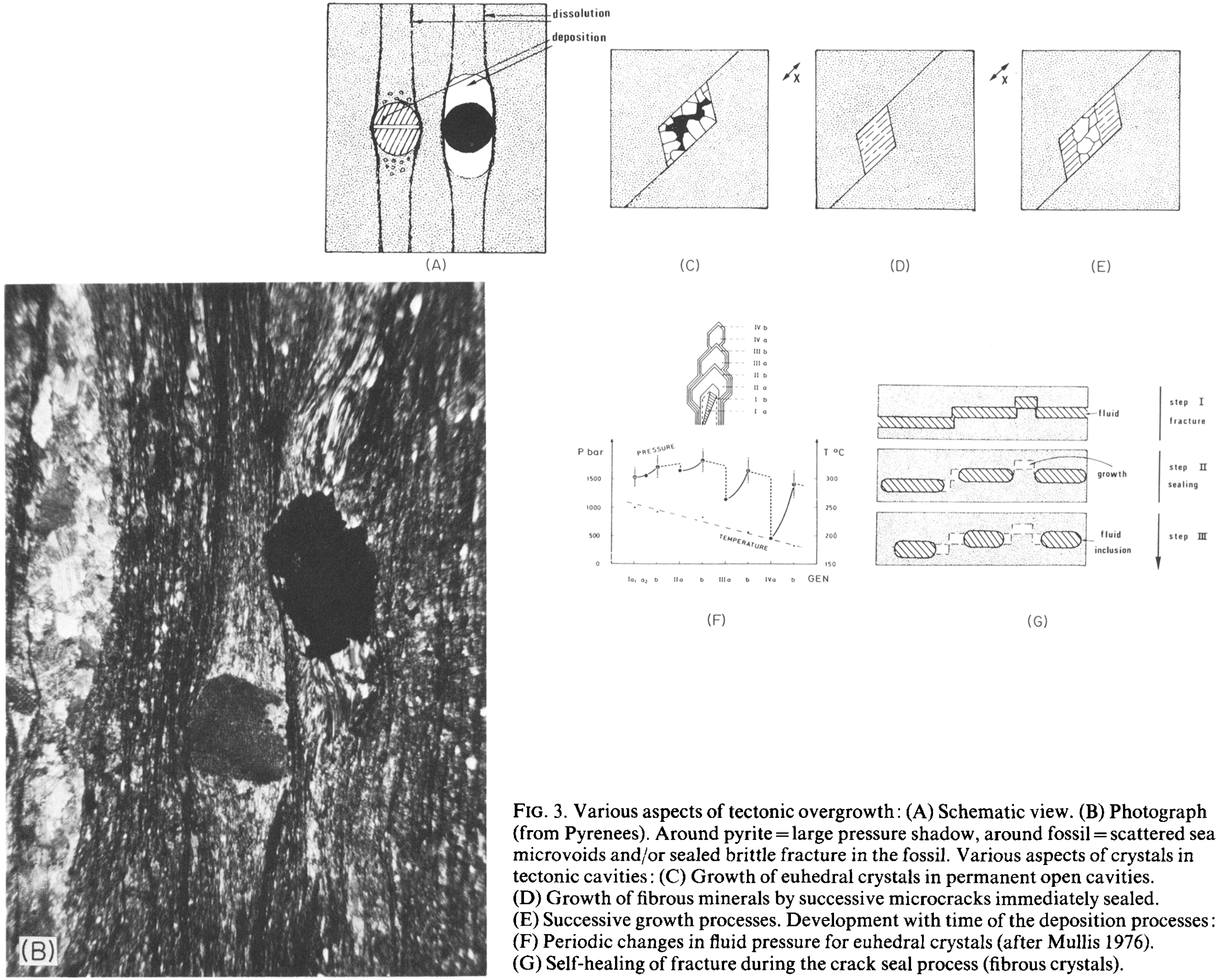


FIG. 3. Various aspects of tectonic overgrowth: (A) Schematic view. (B) Photograph (from Pyrenees). Around pyrite = large pressure shadow, around fossil = scattered sealed microvoids and/or sealed brittle fracture in the fossil. Various aspects of crystals in tectonic cavities: (C) Growth of euhedral crystals in permanent open cavities. (D) Growth of fibrous minerals by successive microcracks immediately sealed. (E) Successive growth processes. Development with time of the deposition processes: (F) Periodic changes in fluid pressure for euhedral crystals (after Mullis 1976). (G) Self-healing of fracture during the crack seal process (fibrous crystals).

into the cavity. As for dissolution, a difference in fluid pressure or, more generally, a difference in the stress components normal to the solid/fluid limit, can be the driving force for the deposition (Fig. 1B, C, D). But experimental work on the healing of fractures (Gordina & Neverov 1967; Wiederhorn & Bolz 1970) has shown that this process might be developed, even without such a difference in normal stress, by the simple effect of the surface energy reequilibration along the fracture. Such a slow process of self-healing of a fracture was reproduced on quartz at 400°C, 200 MPa in water. After several weeks a cluster of small, fluid inclusions simply marked the position of the initial fracture (Smith & Evans 1984; Wilkins *et al.* 1985).

In all the studied cases the tectonic veins developed during the pressure solution-deposition process have the aspect of a brittle fracture. Taking into account the relatively high confining pressure (up to 250 MPa) this means that the fluid pressure must remain not very different from the lithostatic pressure (Brace 1972): either a little above (hydraulic fracture) or a little below (assisted fracture). Such a brittle fracture is developed perpendicular to the σ_1 direction in initially isotropic materials (Paterson 1978). However, it is well known that such tectonic veins are sometimes developed parallel to pre-existing planes such as cleavage planes. Let us consider anisotropic rocks, with quite different tensile strength values perpendicular and parallel to the cleavage (e.g. respectively 1 and 30 MPa), submitted to low deviatoric stresses (σ_1–$\sigma_3 <$ 30 MPa, σ_1 and σ_3 being respectively perpendicular and parallel to the cleavage). With a slow increase in fluid pressure, the pressure value needed to open a fracture parallel to the cleavage ($P > \sigma_1 + 1$) is inferior to that necessary to open a fracture perpendicular to this cleavage ($P > \sigma_3 +$ 30). Fractures perpendicular to σ_1 can thus appear more easily than fractures parallel to σ_1 in such anisotropic rocks (Fig. 4). As for dissolution, the situation of the zone of deposition can thus be imposed by the pre-existing structures of the rocks.

A comparison of the evolution of the zone of dissolution and deposition has shown significant differences in the paths of propagation, in their continuity with time and in their driving forces. On the other hand, the initial heterogeneity (structure) of the rocks plays a role in the two processes. In all cases the dissolution appears in the relatively less competent sector (with the highest content in layered silicates) whereas the deposition zone appears in the more competent sector (with the highest content in soluble species). Both processes emphasized the initial difference, they are self-amplified during a progressive deformation.

Processes of tectonic differentiation

Development of the processes

Considering the development of the zones of dissolution and of the zones of deposition schematically represented in Fig. 5, the process of pressure solution-deposition naturally leads to the development of a tectonic layering. Several authors have discussed the development of such differentiated layers in metamorphic environments (see Robin 1979, for a pertinent review). Several explanations have been given, based either on chemical or on mechanical effects. Following this author, the initial (or tectonically induced) heterogeneities of the rocks lead to a heterogeneous distribution of stresses. In rocks with alternatively competent and incompetent

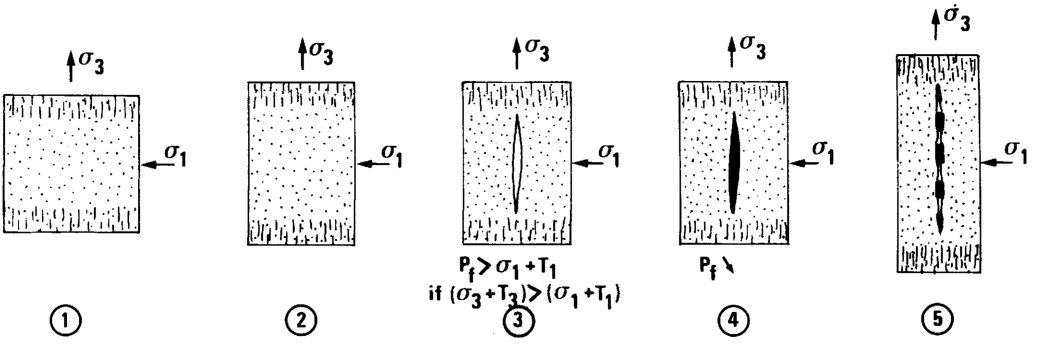


FIG. 4. In anisotropic rocks schematic development of veins perpendicular to σ_1. After the development of a cleavage (1 → 2), an hydraulic fracturing can appear (3) with particular condition for the deviatoric stress value ($\sigma_1 - \sigma_3$) and for the tensional strength values of the rock (T_1 and T_3 respectively perpendicular and parallel to the cleavage). At (4) the fracture is sealed (with a decrease of the fracture pressure P_f), and after (5) the vein is progressively boudinaged always with the same state of stress (σ_1 perpendicular to the vein).

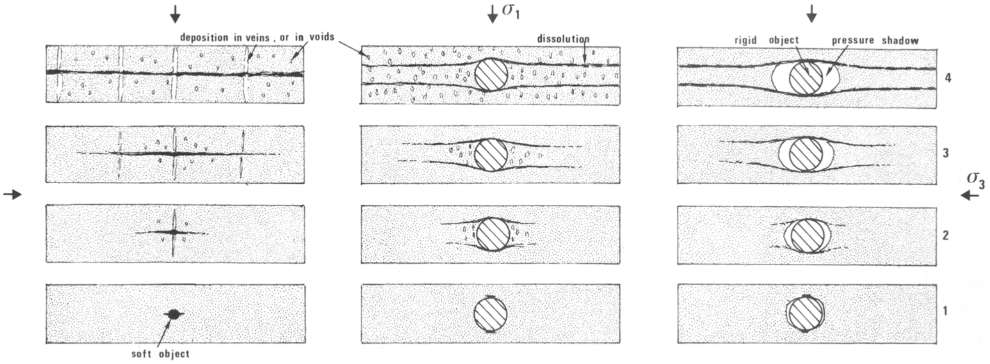


FIG. 5. Schematic comparison between the development of zones of dissolution and of zones of deposition. The propagation of the zones of dissolution can be almost infinite in its own plane, whereas the propagation of the zones of deposition is always limited in space, with induced *en échelon* veins in relatively competent sectors 'protected from dissolution and possibly hardened by scattered depositions'. This simultaneous development leads to a tectonic layering of natural rocks.

layers (or flattened domains), submitted to a compressive maximum value of stress (σ_1) perpendicular to the banding, the minimum values of stress (σ_3) parallel to the banding vary from incompetent to competent layers. Consequently a mass transfer occurs from the surfaces perpendicular to σ_1 to the surfaces perpendicular to σ_3 (see also Stromgard 1973). The driving force for the mass transfer is proportional to $\sigma_1-\sigma_3$ (Fig. 6A). Theoretical models for differentiation have been established with such a mechanical approach by Fletcher (1982) and Van der Molen (1985). These models deal with simple instantaneous cases. Of course when mass transfer proceeds for a long time, the large change of physical properties associated with the chemical differentiation must be taken into account.

The problem is more complicated when the σ_1 direction is parallel (or oblique) to an initial banding since folding of the layer is often associated with the chemical differentiation. The mass transfer occurs from limb to hinge. If the zones of removal of matter are the axial plane solution cleavage of the fold (Fig. 6B1) the problem is not very different from the preceding. But the limit of the layer (or some interstratified incompetent layers) can also be the zone of dissolution (Fig. 6B2). In this case various explanations are given based on the fact that the value of the stress component normal to the layer increases with the rotation of this layer (Fig. 6C) (Gray & Durney 1979), or on the fact that layered silicates oblique or perpendicular to σ_1 (in the limb) catalyse the pressure induced transfer of the more mobile species (Robin 1979). To test these hypotheses the mass transfer balance

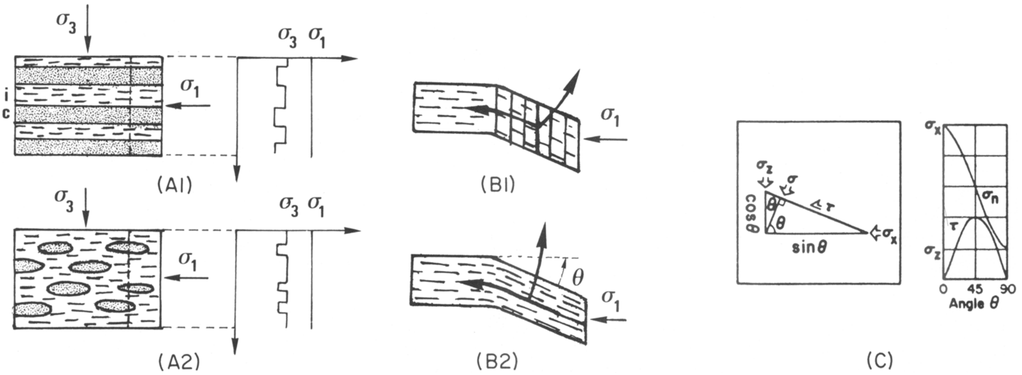


FIG. 6. (A) Distribution of principal stress values (σ_1, σ_3) in a heterogeneous material with alternately competent (c) and incompetent (i) layers (A1), or with competent domains embedded within incompetent matrix (A2), after Robin (1978). (B) Two types of dissolution seams in fold limb: axial plane cleavage (B1), or initial bedding joint (B2). (C) Evolution of the normal to bed stress values with the increase of the θ angle (after Gray & Durney 1979).

through the folds can be made with chemical comparative analyses (Gratier 1983). But we have observed that the volume of the closed system sometimes changed during the folding process (with the decrease of the hinge/limb angle α). The closed volume decreases from the size of the limb/hinge pair (low α values) to the size of the microlayers within the limb (high α values) (Gratier 1984).

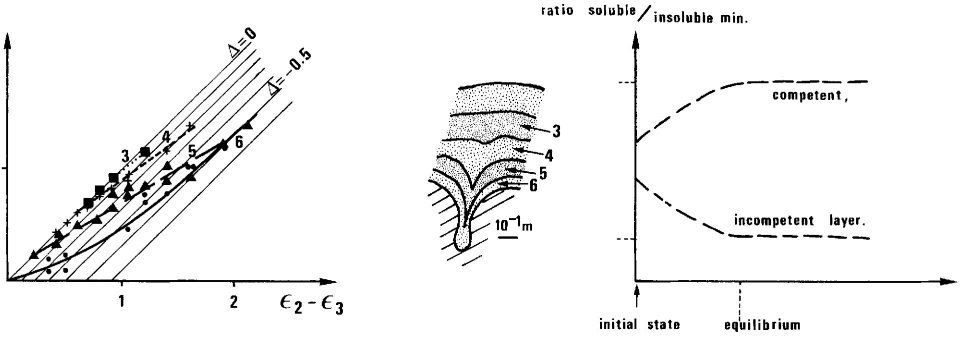
Depending on several factors such as the state of stress, the relative orientation of favourable surfaces and the possibilities of mass transfer, the mean distance of mass transfer can change during a progressive deformation. In all cases however, a rule is respected: the zone of dissolution occurs in incompetent sectors, the zone of deposition in competent sectors, as evidenced by the many examples of solution-deposition associated with boudinage, ptygmatic folding, mass transfer around rigid objects etc. This rule could seem surprising since the competent sector usually has a higher content of soluble species than the incompetent sector.

An explanation of this paradoxical behaviour is that the development of the dissolution needs the presence of both a soluble species and its solution. In competent sectors, the high content of soluble species is not usually associated with an equivalent high content of solution around the soluble grains. The fluid phase is rather localized in voids or in brittle fractures frequently perpendicular to σ_3 and then badly oriented to enhance the dissolution (but well oriented for the growth of the reprecipitated minerals). In incompetent sectors, with lower contents of mobile species, the soluble grains are well surrounded by layered silicates (micas, clays), associated with free, or adsorbed, fluid and acting as privileged paths for the mass transfer. The chemical differentiation leads to changes both in the mechanical properties and in the possibilities of mass transfer. These two variations lead to the same result: an increase of insoluble content (clays or layered silicates) softens the rocks and connects privileged paths for mass transfer normal to the σ_1 direction, then promotes the dissolution. An increase of soluble content (quartz, calcite) hardens the rocks and facilitates the development of open veins (or microcavities) normal to the σ_3 direction then promotes deposition (Fig. 5). The chemical differentiation is then self-induced. A similar feedback mechanism was proposed by Merino *et al.* (1983) between porosity and solution-rate. However we did not find a large change of porosity during the dissolution of slates (Gratier 1983).

Compositional limits of the differentiated layers

The question now is to know if the differentiation may lead to a complete partition between soluble and insoluble species or if there are compositional limits for two differentiated layers.

In the example of a heterogeneously deformed matrix around a ptygmatic fold (Fig. 7) we have been able to estimate both the volume change values (Δ) and the internal deformation values (X–Z) (Gratier 1983). When plotting the Δ and XZ values along six layers of the slaty matrix on



(A) (B) (C)

FIG. 7. (A) Evolution of values of volume decrease along several layers (of the same competence) in a slaty matrix. (B) (shaded area = open system) around a ptygmatic fold (hatched area). The layers less folded (upper layers) show a linear relation between the volume change and the internal deformation values. The layers most deformed (lower layers) do not show such a linear relation since the volume decrease value is limited (−0.5) before the complete depletion of soluble species. (C) Schematic chemical evolution of two contiguous domains, by mass transfer in closed system, from an initial state (with slight difference) to an equilibrium composition of both competent and incompetent differentiated domains.

a Flinn diagram (see also Ramsay & Wood 1974) it is possible to follow the evolution of the deformation (the path of deformation) by assuming that the spatial evolution along each layer is equivalent to a temporal evolution. We may note that a linear relation appears between volume change and internal deformation for the less deformed layers. But for the most folded, just in the vicinity of the competent strata, it seems that a maximum value of the volume change cannot be passed ($\Delta \leqslant 0.5$). This limit value is not linked to the complete removal of the soluble species, which remains about 20 and 18% respectively for quartz and calcite. It thus seems that all the soluble minerals cannot be 'extracted' from the zone submitted to the maximum compressive stress. It is observed, for example, that deformed Liassic slates of the French Alps always have the same limiting composition in the zone of dissolution. This perhaps occurs since the soluble minerals are too scattered in the matrix. This means that there is probably an equilibrium composition in the zone of dissolution which depends on the various factors influencing the rate of mass transfer (see the introduction and the following section). For the zone of deposition it is different as such zones can be completely composed of soluble species. However, if the temperature and the fluid pressure remain constant during the progressive deformation, the ratio of the quartz/calcite content is dependent on these P,T conditions since the solubility of these minerals are respectively normal and inverse with the temperature (see the introduction and Gratier 1984).

Spacing of the tectonic layers

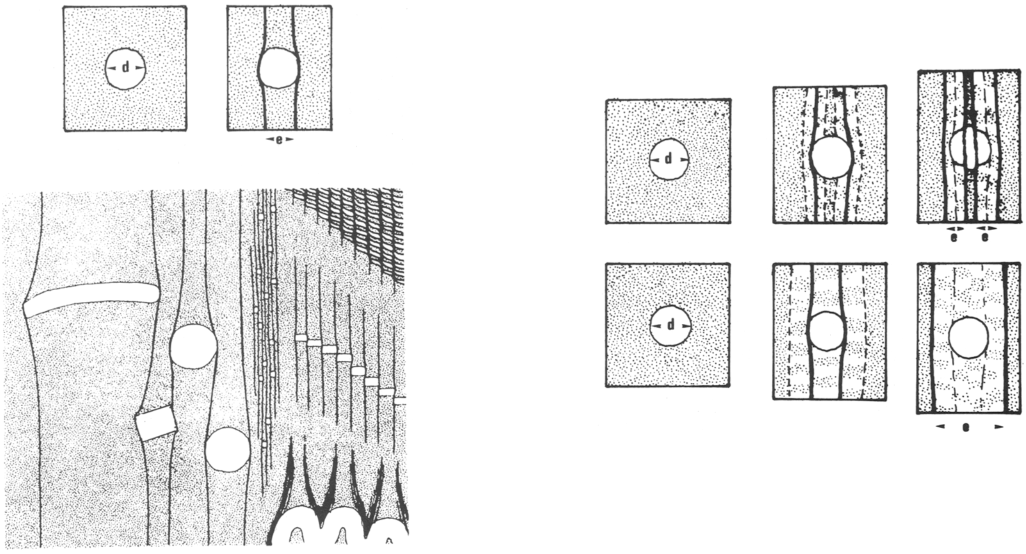
The preceding discussion can be extended to the problem of the spacing of the tectonic layers. Two cases must be distinguished: (i) when the volume of the closed system is largely superior to the spacing of the zones of dissolution, the system is said to be open, all the mobile species can move out of the studied sector; (ii) when the volume of the closed system is of the same order as the size of the tectonic layer, the system is closed, all the soluble species removed from the zones of dissolution are reprecipitated in the neighbouring deposition zone.

Open system

In all the natural examples studied, we have observed the same rule for the position of the zone of dissolution. These zones are always associated with a heterogeneity in the rocks (see the schematic relation in Figs 2–5). In slaty, fine-grained rocks, the spacing of the solution seams is clearly always linked to the size of the heterogeneity of the rocks (Fig. 8A). Usually these heterogeneities are selectively more rigid than the matrix (Fig. 2A), but they can also be relatively less rigid than the matrix (Fig. 2C–5). They can be associated with the sedimentary process (fossils, grains or polycrystalline domains with contrast of competence with the matrix), but can also be induced by some process of deformation such as the folding (with dissolution in the limb of the fold, see Fig. 6). In limestone or quartzite the problem is more complicated because dissolution markers (often stylolites) appear with the same size as the grain size (see the section on stylolites).

Closed system

If the soluble species are reprecipitated in the immediate vicinity of the zone of dissolution (with a closed system between neighbouring solution and deposition zones) the spacing of the differentiated layers is fixed by two successive effects. At the initiation of the process of differentiation the spacing of the zone of dissolution is always linked to the size of the heterogeneities of the rock (see the preceding section). However, as soon as the mobile species are reprecipitated in the zones of deposition these zones become harder than the initial rock. They then act as rigid indentors and induce, at their limits, new zones of dissolution. Depending on the mean distance of mass transfer, there are two possibilities. If the mean distance of transfer is inferior to the size of the initial heterogeneity (Fig. 8B top) this heterogeneity is progressively destroyed. If the mean distance of transfer is superior to the size of the initial heterogeneity (Fig. 8B bottom) this heterogeneity is progressively integrated within the zone of deposition. With such a closed system a regular spacing of the differentiated layers is acquired. The spacing value depends on the various factors of the rate of deformation (see the introduction). These factors are the driving force $\Delta\sigma_n$ (often proportional to the deviatoric stress value) and the nature of the solid and fluid (effect on c). Depending on the limiting process of the deformation rate (see the introduction) two other factors are probably more important: the effects of the factors of transfer (kinetics of reaction, diffusion coefficient, permeability), and the geometry of the path of transfer (or of the surface reaction). For example, the natural rate of deformation is often limited by the rate of diffusion (Gratier 1984). At, for example, 200°C,



(A) (B)

FIG. 8. Relation between spacing of zone of dissolution and size of heterogeneities in rocks. (A) In an open system with removal of the soluble species out of the studied sector: the spacing between the solution seams is fixed by the size of initial (or tectonically induced) heterogeneities (fossil, relatively rigid (or soft) domains, folds, etc.). (B) In a closed system the redeposition of the soluble species in the vicinity of the zone of dissolution hardens the sectors of deposition. This sector, becoming relatively more competent than the matrix, induces dissolution zones at their limits. Depending on the mean distance of mass transfer the spacing between the induced solution plane may be superior (bottom), or inferior (top) to the spacing between the initial solution plane.

the values of this coefficient range from 10^{-9} to 10^{-16} m^2 s^{-1} depending on the fluid content in the rocks (Fisher & Elliot 1974), whereas the deviatoric stress values probably ranged from 1 to 10^2 MPa (the maximum value being of the order of the plastic yield point for most rocks). This means that usually the possibilities for mass transfer through rocks are the crucial factors which impose the rate of deformation and the size of the regular spacing of the differentiated layers. A schematic comparison clearly illustrates this fact. The mean thickness of the differentiated layers in metamorphic environments ranges from 10^{-4} to 10^{-2} m, with high temperature and pressure but relatively low fluid content, whereas the mean thickness of the differentiated layers in tectonic environments is larger (ranging from 10^{-3} to 10^{-1} m) with low temperature and pressure but relatively high fluid content. In each domain, the scattering of the values also depends on geometric factors: the ratio between the volume of the path of transfer and the total volume which is schematically linked to the grain size value and to the content of layered silicates (with high diffusion values).

When considering the values of the mean thickness observed in naturally deformed rocks (at relatively low temperature and pressure: 100–400°C, 50–250 MPa) it is also clearly apparent that some of these values (10^{-1} m) are of the same order of magnitude as the mean thickness of many stratigraphic bandings. We may wonder if the very regular spacing sometimes described in geological formations could not be, at least partially, linked to a mass transfer by pressure solution-deposition from competent to incompetent layers, with a composition limit and equilibrium thickness for each layer dependent on the conditions of diagenesis. An accurate study of the evolution of the composition and of thickness of stratigraphic banding, with depth, for example, could perhaps answer this question.

Development of stylolites

Two characteristics of the appearance of stylolites must be discussed namely the amplitude and the wavelength of their peaks (Bathurst 1975). The amplitude of the peaks is often used to estimate the relative displacement of the blocks limited by the dissolution surface (Stockdale 1922). Yet many natural observations have shown that when the process of dissolution becomes important, the peaks tend to be destroyed (Gratier 1976). The stylolite zone becomes successively an irregular surface and then possibly a fine incompetent layer. In this case the only method of estimating the volume removed from the solution zone is to make a comparative chemical analysis of the insoluble species (between solution zone and initial rock).

The wavelength of tectonic stylolites is often of the same order of magnitude as that of the grain size of limestones or quartzite. In this case we may think that the relative difference in competence of neighbouring grains induces localized dissolution, the mean wavelength being fixed by the mean size of the heterogeneities (the grains) (Fig. 9). On the contrary, diagenetic stylolites often have a wavelength value largely superior to those of the mean grain size. This can be explained if the pressure solution-deposition occurs in rocks with an initial porosity and on pre-existing surfaces of stratigraphic origin. If zones of dissolution appear along such a surface, and if the matter removed from these zones is reprecipitated in the immediate vicinity of the initial surface, the sealing of the voids of the rocks will tend to consolidate these zones with deposition (Fig. 9). These zones, becoming progressively harder than the initial rock, will act as rigid indentors and induce localized zones of dissolution at their limits, i.e. on the initial surface (Fig. 9). With such an evolution the mean wavelength of the stylolite is of the order of magnitude of the size of the consolidated zones of deposition. It is a process of differentiation not very different from the process which leads to a tectonic layering, but it is rather a tectonic differentiated cementation. In this case, the wavelength of the stylolites gives an indication of the possibilities for mass transfer at the moment of their development.

Conclusion

The deformation of rocks by pressure solution-deposition is always associated with the development of a tectonic layering when the rocks are initially composed of minerals with various mobilities.

A feedback mechanism is proposed between clay- (or layered silicate-) content (insoluble species) and the solution-deposition rate. The mechanical properties and the possibilities for mass transfer both evolve with the change of insoluble content, the major effect being given by the second factor in most natural large deformations.

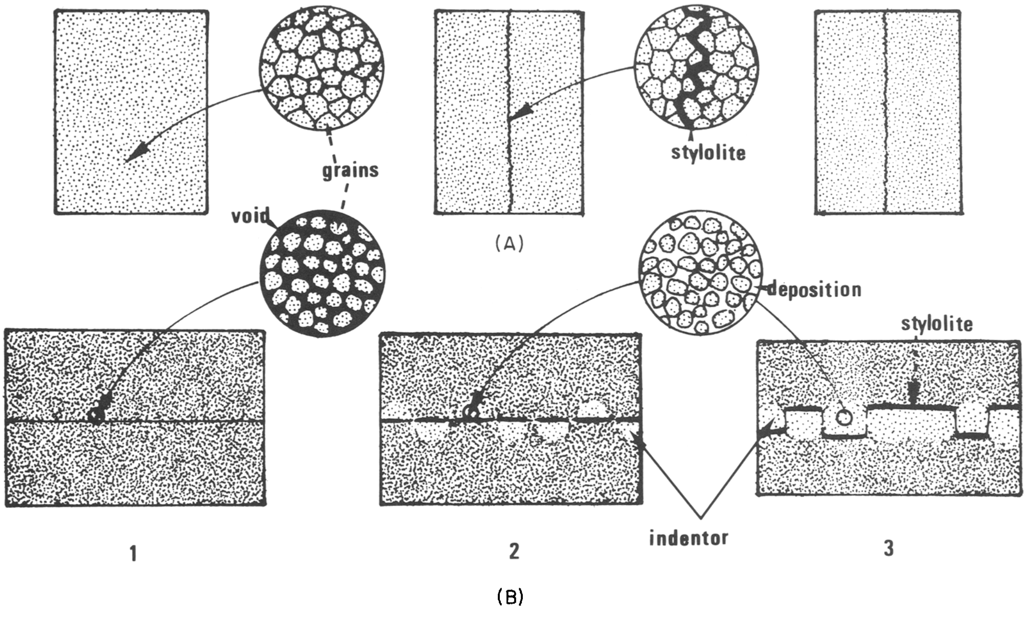


FIG. 9. Development of peaks of stylolites and acquisition of their characteristic wavelength. (A) Effect of the shape of the limit of the grain for tectonic stylolites. (B) Effect of the size of the heterogeneities along an initial surface for diagenetic stylolite. These heterogeneities could be linked to the local hardening of the initial rocks by localized deposition in the vicinity of the initial dissolution. The mean size of the hardened sector depends on the possibilities of mass transfer through the rocks, and imposes the mean wavelength of the stylolites.

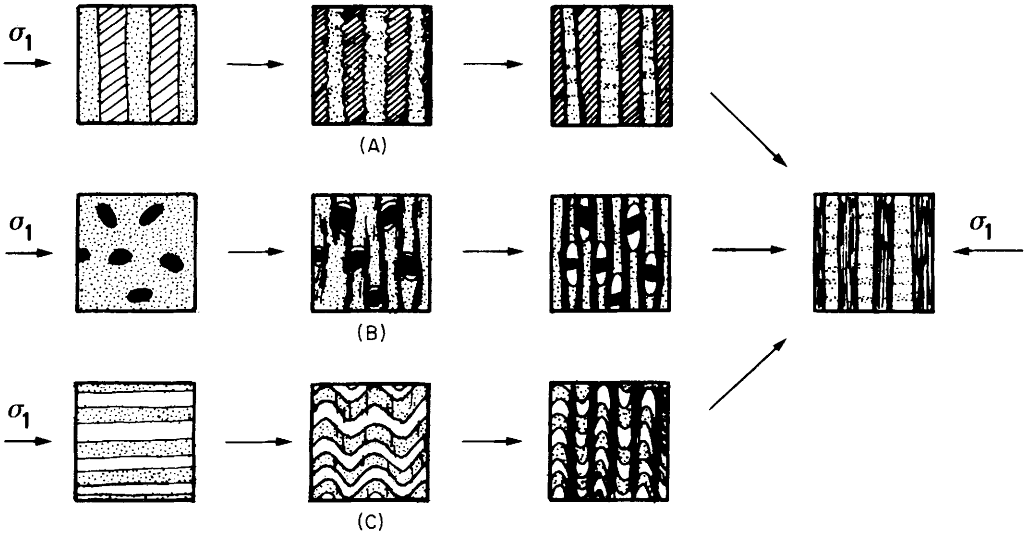


FIG. 10. Mechanical and chemical differentiation of rocks under stress by pressure solution-deposition. The paths of the transformation depends on the initial arrangement of the rocks. From an unstable initial state (initial layers perpendicular to σ_1, scattered heterogeneities or initial layers parallel to σ_1) we may obtain, under a deviatoric stress, an equilibrium state (both in the composition and the size of the differentiated layers) for given conditions of deformation (possibilities of mass transfer, nature of the solid/fluid phases, state of stress, temperature and pressure, etc.).

Depending on the geometry of the initial heterogeneities of the rocks and of the orientation of favourable surfaces to the σ_1 direction, various progressive developments of the differentiated layers are possible such as transformation of an initial layering (Fig. 10A), development of successive layers around dispersed heterogeneities (Fig. 10B), differentiated layering associated with folding (Fig. 10C). In all cases the differentiated layers tend to an equilibrium composition and thickness depending on the possibilities of mass transfer, the driving force of this mass transfer, the nature of the soluble and solvent matter and the temperature and pressure conditions.

As the same type of differentiation could appear along an initial well-oriented surface leading to differentiated cementation of the rocks, this process could control the size of diagenetic stylolites.

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