

The different processes involved in the mechanism of pressure solution in quartz-rich rocks and their interactions

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ABSTRACT

Pressure solution is a very efficient mechanism for rock deformation and compaction in the upper crust. It is controlled by stress, temperature, and grain size. The mechanism commonly used to describe deformation by pressure solution at a grain scale, the ‘water film diffusion’ mechanism, can be divided into three successive steps: (i) dissolution at the grain interface; (ii) diffusion of solutes along an adsorbed water film inside the contact between two grains; (iii) precipitation on the surface of the grains adjacent to the open pore. The slowest step controls the rate of the overall process.

Important geometrical variables controlling the pressure solution rate are the grain size and the geometry of the grain–grain interface. Knowledge of the geometry permits estimation of the path length for diffusion of the solutes from the contact between the grains to the pore. Physicochemical variables are important also, including: temperature, stress, chemistry of the pore water, mineralogy of the rock, and thickness of the water film trapped between the grains.

In pressure solution, different coupled variables are involved on several spatial scales: the water film thickness at a nanometre scale, the geometry of the surface of contact at a micrometre scale, and the grain size and texture of the rock at a millimetre to centimetre scale. To understand the mechanism of pressure solution, the values of all these variables must be evaluated to estimate the kinetics of the various coupled processes in which they are involved. These variables can be modelled to determine: (i) the conditions under which pressure solution is efficient in sedimentary basins; (ii) the parameters that control the rate of pressure solution and quartz cementation. The result is a model that can estimate the porosity variations and quartz cementation due to pressure solution, as a function of pressure, temperature, and rock texture.

INTRODUCTION

The deformation of rocks by a dissolution–transport–precipitation mechanism, called pressure-solution by most authors, has been observed for many years, particularly in sandstones and limestones (Heald, 1955; Weyl, 1959; see McBride, 1989 for a complete review). A common mechanistic model of pressure solution is ‘water film diffusion’ (Weyl, 1959; Rutter, 1976). In this model it is assumed that mineral dissolution takes place at the grain–grain contact area with the solutes diffusing along an adsorbed water film. The precipitation of the solutes occurs on the mineral surface facing the pore. This simple model of deformation can be described by a three-step mechanism (Fig. 1a). First, a mineral

dissolves at the contact between two grains because of a concentration of stress. Then solutes diffuse to the pore where, lastly, precipitation occurs. Thus, the whole mechanism, modifying the grain size and the volume of the pores, is a function of rock deformation. If one of the three steps in Fig. 1a is slower than the two others, it will limit the rate of deformation. When the kinetics of dissolution at the grain contacts or precipitation in the pore are the limiting step for deformation, the strain rate depends on the rate constant for dissolution (Table 1). When the slowest step is diffusion along the interface, the strain rate depends on the coefficient of diffusion inside the interface (Table 1). In these two cases, the

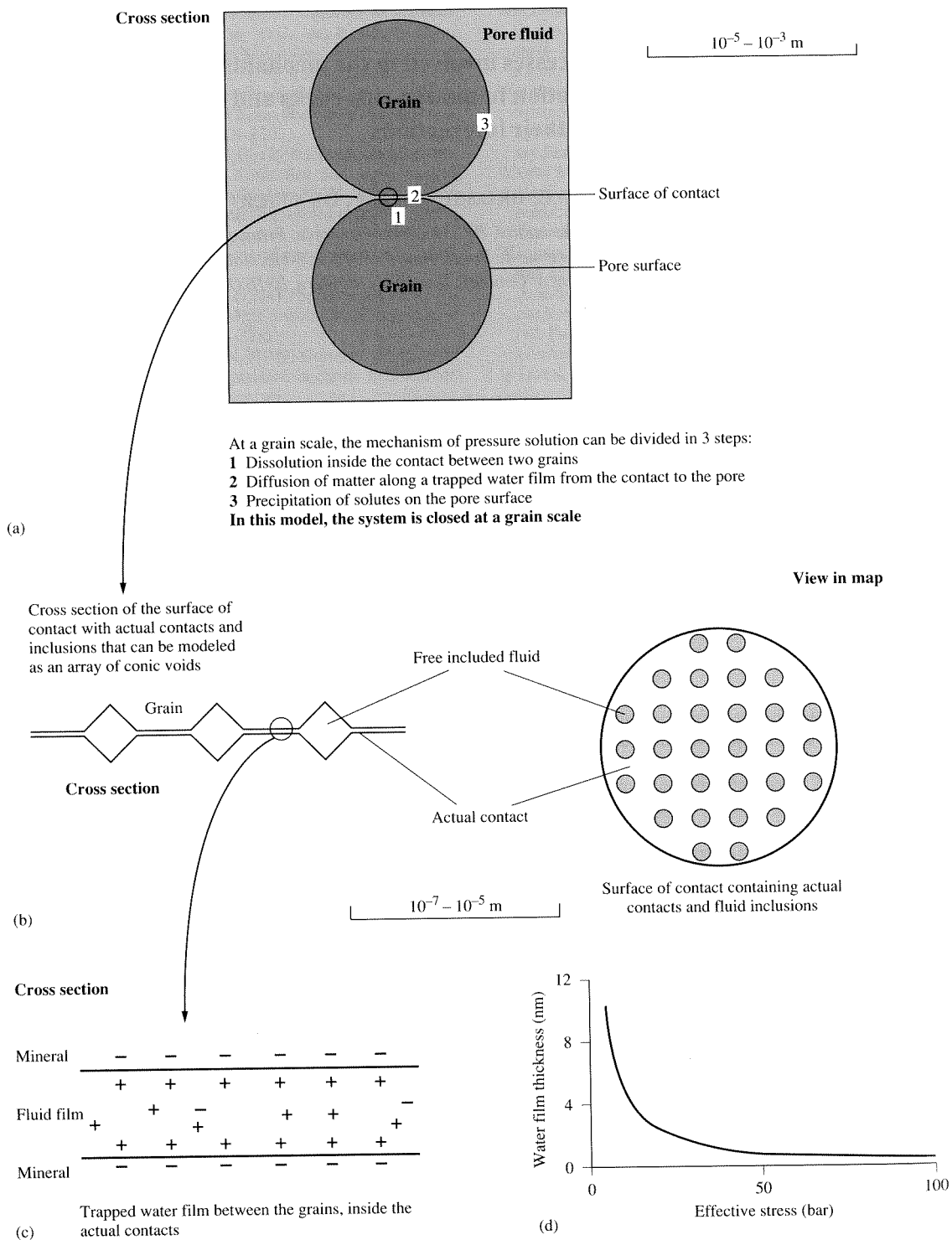


Table 1. The different variables involved in the estimation of the strain rate (Poirier, 1985). If the mechanism of pressure solution depends on diffusion or on the kinetics of dissolution at the interface (Fig. 1a), the dependence on the grain size is different. In both cases, the driving force for deformation is a difference of normal stress along the grain surface

	Geometric factors	Chemical factor	Kinetic factors	Driving force
Diffusion	$\frac{w}{d^3}$	c	D	$\Delta\sigma_n$
Dissolution	$\frac{1}{d^2}$	c	k	$\Delta\sigma_n$

d: grain size; k: kinetic constant of dissolution; w: width of grain interface; D: coefficient of diffusion along the interface; c: concentration of solutes; $\Delta\sigma_n$: difference of normal stress.

dependence of the strain rate on grain size is different (Poirier, 1985).

The presence of water in the pore is necessary to obtain significant deformation by pressure solution because water is the medium of dissolution, diffusion, and precipitation of solutes (Gratier & Guiguet, 1986). A high content of oil should lower the rate of deformation since quartz solubility in oil is negligible. When oil is present in the porosity, a thin water film can be still trapped into the contact between the grains. A small amount of dissolution into the water film will saturate it, but the presence of oil in the pores will inhibit precipitation on the pore walls. Oil should decrease the rate of the third step (the precipitation on the pore surface) in Fig. 1a if the rock is oil-wet (Worden *et al.*, 1998), and therefore decrease the overall rate of deformation by pressure solution.

PHYSICAL AND CHEMICAL VARIABLES INVOLVED IN PRESSURE SOLUTION

Stability and properties of a trapped water film

A key assumption in the theory of pressure solution is the nature of the thin water film that is believed to provide the reaction and transport medium in the 'water film diffusion' mechanism (Weyl, 1959; Rutter, 1976). To facilitate pressure solution, such a film must exist for large differences between the stress applied across the grain

contact and the fluid pressure in the pore. This thin water film has a stress-dependent thickness (Horn *et al.*, 1988, 1989) and the coefficient of diffusion of solutes along this film to the pore fluid is probably higher than the coefficient of diffusion in solids.

Many authors have demonstrated that a water film can be trapped between the sheets of some minerals such as clays and micas (Low, 1992; Sposito, 1992) or sapphires (Horn *et al.*, 1988). The thickness of this film has been measured or calculated for different minerals and varies from a few tenths to several nanometres (Peschel & Aldinger, 1971; Heidug, 1995). These authors show that under most sedimentary basin conditions, its thickness decreases exponentially with stress until a lower limit of 0.5 nm is reached, which represents the thickness of two layers of water molecules (Fig. 1d).

The thin water film acts as a semipermeable membrane: the ionic concentration inside the film is higher than the concentration in the pore fluid. This difference of concentration in charged species (such as Na^+ or Cl^-) creates an osmotic pressure effect that stabilizes the water film relative to the stress on the contact. The main origin of this physical dependency is the electric surface charge, and the stability of the film is caused by an osmotic/Debye-Hückel model (Renard & Ortoleva, 1997). Most minerals have an electric charge on their surface and these charges are strongly pH-dependent. Electric charges spread on the surfaces of a mineral attract oppositely-charged ions from the pore fluid (Fig. 1c). This local

Fig. 1. (*Opposite.*) The mechanism of pressure solution at different scales. (a) At a grain scale, dissolution occurs at the contact area between grains modelled as truncated spheres (step 1), then solutes diffuse along a water film to the pore (step 2), and silica precipitates on the pore surface (step 3). (b) At a micrometre scale, the contact surface between the grains is subdivided into points of actual contact, and fluid inclusions, modelled as an array of conic inclusions. If the inclusions are connected, they can form small channels. (c) At a nanometre scale, the actual contacts contain a trapped water film. Electric charges spread on the surface of quartz (negative in our example) attract positive ions from the pore. The water film acts as a semipermeable membrane and its stability is through an electric Debye-Hückel osmotic effect. (d) The water film thickness exponentially decreases as the effective stress (pressure normal to the grain contact minus pore fluid pressure) increases. The curve is calculated for a mineral electric surface charge of $-0.1 \text{ Coulomb m}^{-2}$, like for quartz in a fluid at pH 8 (Renard & Ortoleva, 1997).

effect creates a difference of free energy between the pore fluid and the water film where ionic concentration is higher. In Fig. 1d, the thickness of the water film is given as a function of the effective pressure, i.e. the amount by which the fluid pressure acting on the fluid–solid interface exceeds the hydrostatic pressure in the bulk fluid (Renard & Ortoleva, 1997).

The diffusion coefficient within the water film controls the rate at which solutes are expelled from the stressed contact to the pore and is poorly defined. However, it may be not constant and should vary with the water film thickness such that when the film is thick enough the rate of diffusion should be similar to that in free water, and when the water film is only a few tenths of nanometre thick, the rate of diffusion is expected to be like that in solid grain boundaries.

The coefficient of diffusion of a particle in a large volume of liquid is described by the Stokes–Einstein equation:

$$D = \frac{kT}{6\pi\delta\eta} \quad (1)$$

where D is the diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), k the Boltzmann constant ($1.38 \times 10^{-23} \text{ m}^3 \text{ Pa.s}^{-1}$), δ the diameter of the diffusing particle, and η the viscosity of the liquid (Pa.s). Horn *et al.* (1989) have measured the viscosity of a 2 nm water film trapped between silica sheets and they have found a value in the order of magnitude of 10^{-3} Pa.s , an order of magnitude lower than for a free fluid. Taking the diameter of a molecule of hydrated silica (δ) to be 0.5 nm, the diffusion coefficient of aqueous silica inside a 2 nm water film at 25°C is therefore $3.5 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$; one order of magnitude less than diffusion in free water (Mullis, 1993).

Other authors have deduced the product of the coefficient of diffusion and water film thickness from pressure solution experiments and found values from 10^{-18} to $10^{-21} \text{ m}^3 \text{s}^{-1}$ (Rutter, 1976; Gratier & Guiguet, 1986; Gratier, 1993a). Their experiments were performed at high effective stress, so the water film thickness should not exceed 0.5 nm, corresponding to two molecular layers of water. Their experiments were made at different temperatures, allowing an activation energy for diffusion to be estimated. The coefficient of diffusion of silica in a 0.5 nm thick water film was estimated and ranged from 8×10^{-12} to $8 \times 10^{-15} \text{ m}^2 \text{s}^{-1}$ at 25°C , with an energy of activation of 10 to 20 kJ.mole^{-1} . Despite the range in these values, they are several orders of magnitude greater than that for diffusion in solids (Freer, 1981). The activation energy is similar to that for diffusion in free liquids (Applin, 1987), but the coefficient of diffusion is 1–3 orders of magnitude smaller.

The driving force for pressure solution

The stress state of a solid has strong implications for its free energy; the effect of stress being to increase the molar free energy compared with a zero-stress state. Following the Gibbs (1961) and Paterson (1973) theory of heterogeneously stressed solids, it is possible to write the chemical potential of the solid as

$$\mu = \mu^0 + P\bar{V}_s + F\bar{V}_s^0 \quad (2)$$

where μ^0 is the chemical potential at reference state for a stress free solid at temperature T and pressure $P_0 = 1 \text{ bar}$, P is the actual normal pressure exerted by the fluid in contact with the solid, and \bar{V}_s and \bar{V}_s^0 are the molar volumes of the solid under stress and with zero stress respectively. In Equation 2, the Helmholtz free energy F contains different contributions: elastic energy induced by stress, plastic energy created by the dislocations inside the mineral, and surface free energy for particles with a very small radius of curvature. Under the conditions found in sedimentary basins, the Helmholtz free energy is one or two orders of magnitude less than the $P\bar{V}_s$ term in Equation 2 (Paterson, 1973); and to a first approximation, it can be ignored.

During pressure solution, the normal stress P is greater inside the contact between two grains, where it is approximately lithostatic-like, than in the pore where it is the fluid pressure. Thus, by reference to Equation 2, the chemical potential of a solid can be seen to vary along the surface of a grain, allowing for the chemical diffusive flux of silica from the contact surface to the free pore. In an overpressured system, the fluid pressure can reach the lithostatic pressure. In this case the gradient of chemical potential between the contact and the pore disappears and pressure solution will be inhibited.

If the Helmholtz free energy is neglected, the chemical potential of quartz is

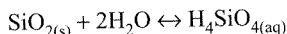
$$\mu_{qz} = \mu_0 + P\bar{V}_s \quad (3)$$

By definition $\mu_{qz} = RT \ln(K_{eq})$, where K_{eq} is the equilibrium constant for the reaction of quartz dissolution, thus

$$K_{eq} = K_0(T) \cdot \exp\left(\frac{P\bar{V}_s}{RT}\right) \quad (4)$$

where $K_0(T)$ is the equilibrium constant for an unstressed mineral of quartz, whose value depends only on temperature (Rimstidt, 1997).

The chemical reaction of dissolution or precipitation of quartz can be described by



and the equilibrium constant K_{eq} for this reaction is

$$K_{eq} = \frac{a_{\text{H}_2\text{SiO}_4}}{a_{\text{SiO}_2} a_{\text{H}_2\text{O}}^2} \quad (5)$$

At equilibrium, if one assumes that the activities of solid quartz and water are 1 (Anderson & Crerar, 1993), the equilibrium constant is related to silica solubility $c_{\text{H}_2\text{SiO}_4}$ through

$$K_{eq} = \gamma_{\text{H}_2\text{SiO}_4} c_{\text{H}_2\text{SiO}_4} \quad (6)$$

where $\gamma_{\text{H}_2\text{SiO}_4}$ is the activity coefficient, assumed to be equal to 1 because the concentration of aqueous silica is low at the low temperature of the upper crust (Rimstidt, 1997). Using Equations 4 and 6, it is possible to estimate the quartz solubility in the contact and in the pore and the corresponding gradient of concentration that facilitates deformation.

Effects on the kinetics of reactions

The rate constant for dissolution/precipitation of quartz increases with temperature and varies with pH and ionic concentrations (Dove, 1994). Some authors have evaluated the kinetics of quartz precipitation through laboratory measurements (Brady & Walther, 1990; Dove, 1994; Rimstidt, 1997) and found rates faster than in geological conditions (Oelkers *et al.*, 1996). Walderhaug (1994) has estimated precipitation rates in sandstones from the Norwegian margin and found a value much lower than derived by experiments. The kinetics of quartz dissolution can vary on one or two orders of magnitude for slight variations of the fluid composition, at constant temperature. For example, the presence of ions such as Na^+ increases the kinetics of dissolution and silica solubility (Dove, 1994).

IMPORTANCE OF ROCK GEOMETRY

Rock texture and grain size

During deformation by pressure solution, grain shape is modified while silica is dissolved at grain contacts and precipitation occurs on a grain surface facing a pore if a closed system is considered at a grain scale. A model of pressure solution should take into account dynamic variations of grain geometry and therefore the induced modifications of rock porosity. Dewers & Ortoleva (1990) proposed a model where a whole rock is described as a cubic array of grains represented as truncated spheres (Fig. 2). Four length variables facilitate the modelling of

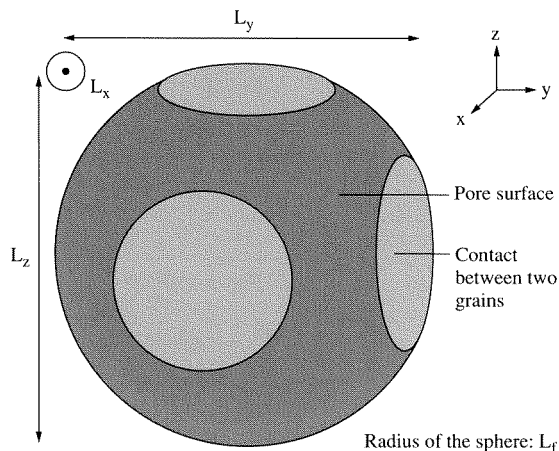


Fig. 2. Detailed description of the truncated spheres of Fig. 1a. The dark grey region is the grain surface adjacent to the pore whereas the lighter grey regions correspond to areas in contact with other grains. Each contact represents the circular composite contact of Fig. 1b. Four length variables, the radius of the sphere L_f , and the truncations L_x , L_y , and L_z , allow modifications of the grain shape, the rock texture, and the porosity to be modelled during deformation by pressure solution.

deformation by pressure solution: L_x , L_y , L_z , the truncations in the three directions in space, are characteristic of the dissolution at the grain contact; whereas L_f , the radius of the sphere, takes into account the overgrowth on the pore free surface. If the stress is not isotropic on the grain, the normal pressure perpendicular to the contacts is different in the three directions of space. In this case, the rate of dissolution of the contacts is different in these three directions and compaction is not isotropic.

On a contact surface, the normal stress approaches lithostatic stress, whereas on the pore surface, the stress is equivalent to hydrostatic pressure. During deformation, the surface area of the contact increases (Fig. 3), thus the normal stress acting on it and the rate of deformation by pressure solution decreases. This mechanism couples stress acting on the rock and rock texture during deformation.

To permit pressure solution, fluid must be able to escape from the pore during compaction to allow a difference of normal stress between the contact and the pore. The geometric model considers deformation at a grain scale. If the system is open at a pore scale and if fluids can circulate, then as compaction reduces total porosity, the fluid circulates less because of the concomitant loss of permeability. Thus fluid pressure may increase during compaction. This process also couples stress and texture because in this case, local fluid pressure can reach lithostatic pressure, thus halting pressure solution.

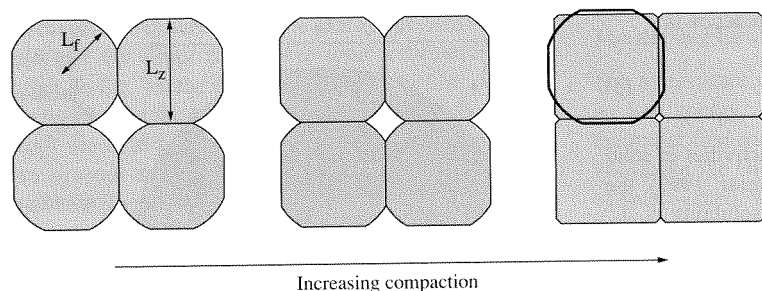


Fig. 3. A cross-section view of a cubic-packed network of truncated spheres. The grain shape evolves due to pressure solution as shown. The grain radius L_f increases, to take account of overgrowths in the pore, whereas the grain flattens (L_z decreases) resulting in a decrease in porosity and pore surface area.

Geometry of the surface of dissolution

North Sea sandstones contain quartz, micas, and potassic feldspars. Observations of thin sections of these rocks indicate the occurrence of pressure solution: detrital quartz grains dissolved at the contact with other minerals. Observations by SEM indicate that the contact surface between two grains of quartz can locally contain fluid inclusions with a hexagonal shape (Fig. 4a). These inclusions may be localized on dislocations in the mineral. Therefore the surface of contact can be rough and can be locally subdivided into contact points. Grain contacts should sustain a normal stress and should trap a water film, as well as containing inclusions where the fluid is free and where the stress is equivalent to the fluid pressure. Contacts between the grains can thus be described by geometry at two spatial scales: at a nanometre scale, a water film is trapped inside the actual contacts; at a microscale, the contact contains fluid inclusions (Spiers *et al.*, 1990).

A thick section from a sample of a metamorphic quartz vein from the Main Central Thrust in the Himalayas (Fig. 4b) also shows that an array of inclusions at the contacts between two grains can exist. These two natural examples verify that, in both diagenetic sandstones and metamorphic rocks, the contact surface between grains contains a region of actual contacts and fluid inclusions. In the case of the Himalayan sample, some of the fluid inclusions are connected and form small channels.

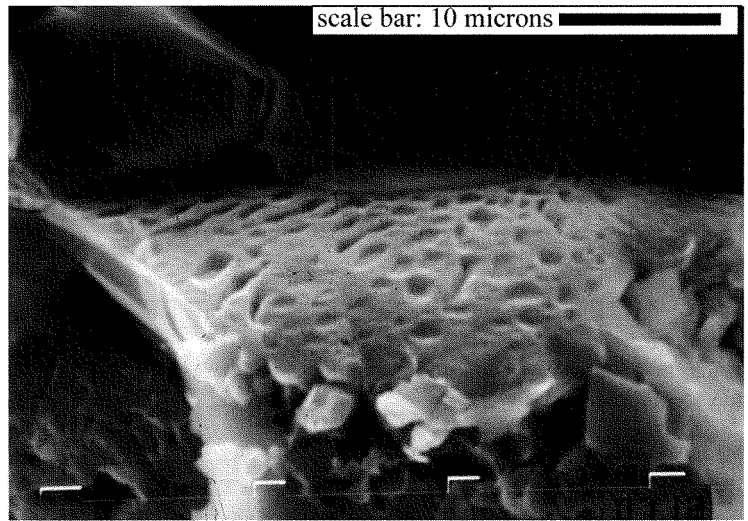
The distance of diffusion inside the contact may be the mean distance between two fluid inclusions, and not the radius of the full contact. As a consequence, a model of pressure solution should take into account the presence of fluid inclusions and regions of true contact at the interface between the grains. Grain contacts, as modelled in Fig. 2, should contain an array of fluid inclusions giving the composite contact geometry described in Fig. 1.b (Spiers *et al.*, 1990).

Consequences for the mechanism of pressure solution

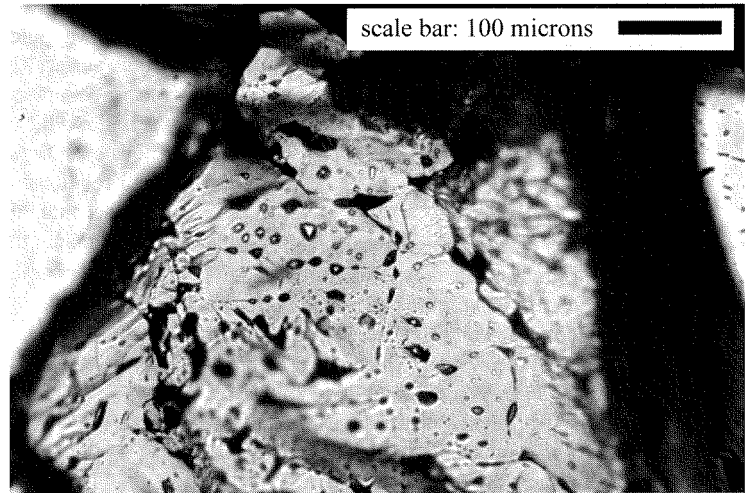
All the preceding observations indicate that there are different sites with different free energies on the grain surface and silica is exchanged between them: the pore surface where silica can precipitate, the region of true contact, and fluid inclusions. Thus, the overall mechanism of pressure solution can be described in three steps (Fig. 5). First, dissolution occurs in the regions of true contact because of a high normal stress; secondly aqueous silica is transported by diffusion along the adsorbed water film. This second step takes into account diffusion from the actual contacts to the pore fluid and diffusion from the actual contacts to the inclusions. Inside the inclusions, precipitation or dissolution can occur, decreasing or increasing their volume and their reactive surface area. Then diffusion of the solute from the inclusions to the pore occurs. This second step of diffusion is made significantly more effective if inclusions are connected and form channels. At the third step, silica precipitation can take place on the pore surface (Fig. 5).

Pressure solution experiments using a metallic needle that indents a crystal of quartz or halite (Gratier, 1993a, 1993b) or on compaction of aggregates (Rutter, 1976, 1983; Gratier & Guiguet, 1986; Cox & Paterson, 1991; Schutjens, 1991) indicate that the mechanism of pressure solution can be limited by diffusion of silica along the trapped water film inside the contact (step 2 in Figs 1a & 5). In such a case, the factor controlling pressure solution and deformation is the stress acting on the water film, which also controls the driving force of reaction.

However, experiments on the deformation of fluid inclusions show that the limiting process is dissolution on the walls of the inclusions. In this case, diffusion is fast because solutes are transported in a free fluid (Gratier & Jenatton, 1984). Following observations of sandstone thin-sections, it was concluded that at low temperature



(a)



(b)

Fig. 4. (a) SEM picture of the contact surface between two grains of quartz in a North Sea sandstone. The surface contains flat actual contacts and fluid inclusions. (b) Thin section in a metamorphic Himalayan quartz. The surface of contact between the grains contains fluid inclusions that can be connected and form small channels. In both examples, fluid inclusions should be localized on dislocations of the crystal.

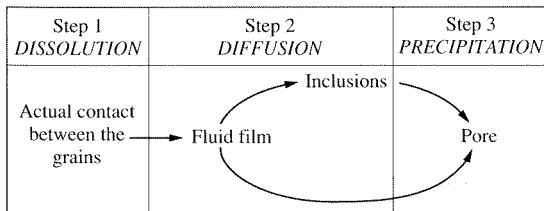


Fig. 5. The mechanism of pressure solution can be divided into three steps: (i) dissolution at grain interface; (ii) diffusion along the trapped water film from the actual contacts to the pore or to the inclusions inside the contact; (iii) precipitation on the pore surface. The slower step controls the overall rate of deformation.

(0–2500 m), the mechanism of sandstone deformation is also temperature controlled through the kinetics of quartz precipitation (step 3 in Figs 1a & 5) and that the effect of stress is not important (Bjørkum, 1996; Oelkers *et al.*, 1996). In this case, the limiting step for deformation is the rate of dissolution or precipitation of silica (steps 1 or 3 in Figs 1a & 5) for which the kinetics are slower than those for the rate of diffusion along the interface (Renard *et al.*, 1997).

All these experiments and natural observations indicate that pressure solution is complex with different processes interacting (Table 2). Depending on the conditions

Table 2. The different variables involved in pressure solution and the processes where they appear. The numbers in parenthesis correspond to the three steps of the mechanism of pressure solution described in Figs 1a & 5

Stress	Temperature	Grain geometry
Driving force for pressure solution (1 to 3)	Kinetics of reaction (1, 3)	Pore surface area (3)
Diffusion inside the water film (2)	Diffusion (2)	Porosity and permeability (3)
Water film thickness (2)	Silica solubility (1, 3)	Surface area of grain–grain contact (1, 2)
		Path length for diffusion (2)

(stress, temperature, fluid and mineral compositions, grain size, and rock texture) several domains can be defined in which these variables have a different influence on the rate of deformation.

MODEL FOR PRESSURE SOLUTION AT A GRAIN SCALE

Our model takes into account two sites (the contact area and the pore surface) on the surface of a grain and the exchange of matter between them to describe pressure solution at a grain scale (Lehner, 1995; Shimizu, 1995; Renard *et al.*, 1997).

Geometrical model and compaction

For simplicity of the presentation, we will focus on the vertically directed grain contacts (normal to the z axis) (Fig. 2). Results are identical for the horizontally directed contacts (normal to x and y contacts) because we consider an isotropic loading of the system, which is a reasonable assumption for a sedimentary basin setting. To complete the textural descriptions, different quantities are introduced:

- A_z = surface area of the contact between two grains (m^2)
- A_p = surface area of the grain facing the pore (m^2)
- P_z = lithostatic pressure (bar)
- p_p = pore fluid pressure (bar)
- p_a = normal stress across a grain contact (bar)
- Δ_a = thickness of the water film inside a grain contact (m)
- D_a = diffusion coefficient for migration along a grain contact (m^2s^{-1})
- c_p = concentration of aqueous silica in the pore fluid ($\text{mole}\cdot\text{m}^{-3}$)
- c_a = concentration of aqueous silica in a grain contact ($\text{mole}\cdot\text{m}^{-3}$).

Also, there are two distinct rates, G_a and G_p ($\text{m}\cdot\text{s}^{-1}$), for the evolution of grain texture during deformation. The rate G_a describes grain indentation by dissolution at the contacts whereas G_p takes account of the evolution of the grain radius, L_f , and represents the thickness of

overgrowth on the pore surface. Given these rates, the textural evolution of the grains can be characterized by the two equations

$$\frac{dL_z}{dt} = G_a(c^a, p_a, P_z) \quad (7)$$

$$\frac{dL_f}{dt} = G_p(c^p, p_p) \quad (8)$$

The variables G_a and G_p give the rate of change of the length variables characterizing the two sites along the grain surface (Lehner, 1995). Rates are positive/negative for precipitation/dissolution, respectively. In these two equations, the two rates G_a and G_p and the two concentrations c_a and c_p are unknown. To solve Equations 7 and 8, four relationships are necessary. The first equation takes into account the conservation of mass in a closed system: all the matter that dissolves inside the contact precipitates in the pore.

$$6A_zG_a + A_pG_p = 0 \quad (9)$$

In this equation, the factor 6 represents the six contact areas on each grain (Fig. 2). A second relationship characterizes the diffusion of aqueous silica from the contact to the pore. In this case c_a is related to c_p by a steady state assumption (Shimizu, 1995); letting l_a be the radius of a grain contact, Fick's Law gives:

$$\frac{2\pi l_a \Delta_a (c_a - c_p)}{l_a} = -\frac{A_z}{\bar{V}_s} G_a \quad (10)$$

where \bar{V}_s is the molar volume of quartz ($22.688 \times 10^{-6} \text{ m}^3\cdot\text{mole}^{-1}$) and Δ_a the thickness of the fluid film. D_a is the coefficient of diffusion of aqueous silica along the grain contact. If the fluid inclusions have connections between them and to the pore, this coefficient should be higher than in a flat grain contact.

The rate G_p represents the precipitation on the pore surface and can be described by a kinetic law:

$$G_p = k_p \left(1 - \frac{c_p}{K_{eq}} \right) \quad (11)$$

where k_p is the rate of quartz precipitation, as measured in laboratory conditions (Brady & Walther, 1990; Dove, 1994; Rimstidt 1997) or estimated by Walderhaug (1994) from fluid inclusions microthermometry, and K_{eq} is the equilibrium constant for quartz in the pore. The ratio in Equation 11 represents the degree of saturation.

The kinetic constant for quartz dissolution–precipitation can vary by several orders of magnitude depending if the rates are estimated under laboratory conditions or in nature. We have chosen to use the kinetic data measured by Brady & Walther (1990) because they give intermediate values.

The last relationship is based on an assumption about the limiting step of deformation. If diffusion inside the contact is the limiting step, the concentration in the contact c_a is equal to the equilibrium constant at the contact. If the limiting step is precipitation in the pore, the concentration in the pore c_p is equal to the concentration at the contact. In the numerical model, the diffusion step and the precipitation step are estimated and the slowest is chosen to be the limiting step for deformation. Depending on depth, the limiting step can vary (see Fig. 7): kinetics of precipitation at shallow depth, kinetics of diffusion under 2.5 to 3 km for geological conditions similar to the Norwegian margin.

Normal stress inside the grain contacts

For the monomineralic system modelled as a periodic array of truncated spheres, the following relationship between the macroscopic vertical pressure P_z (equivalent to a lithostatic pressure), the normal stress on a grain contact, p_a , and the pore pressure, p_p , allows a feedback between pressure and rock texture (Dewers & Ortoleva, 1990).

$$-L_x L_y P_z = A_z p_a + (L_x L_y - A_z) p_p \quad (12)$$

Pressure solution and porosity variation with depth

Ramm (1992) has pointed out that mechanical compaction, due to grain rearrangements for example, is not sufficient to explain the porosity–depth trend in sandstones of the Norwegian continental shelf. We have applied our model of compaction due to pressure solution (Fig. 3; Equations 9–11) in the case of a subsiding sandstone, with similar conditions as those that have been found in the Norwegian shelf, namely, temperature gradient of $40^\circ\text{C}\cdot\text{km}^{-1}$; lithostatic and hydrostatic pressure gradients and sedimentation rates varying from 20 to 100 m per million years (Fig. 6). For simplicity we

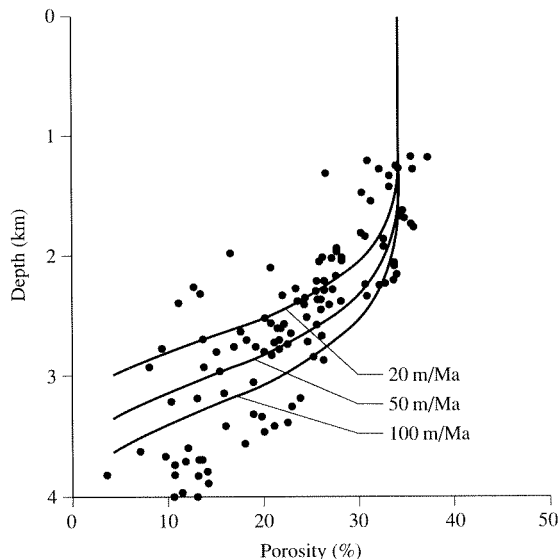


Fig. 6. Porosity–depth variation due to pressure solution. The porosity data are given in Ramm (1992). In the numerical model, initial grain size is 600 μm ; the temperature gradient is chosen to be $40^\circ\text{C}\cdot\text{km}^{-1}$, and a hydrostatic pressure gradient is assumed. The calculations were done for three sedimentation rates, 25, 50, and 100 m per million years. These conditions are similar to those for Jurassic sandstones of the Norwegian margin (Ramm, 1992). The theoretical curves fit the data at depths greater than 2 km. Between 0 and 2 km, porosity variations are essentially due to mechanical deformation. Below 2 km, pressure solution could be the dominant mechanism of porosity decrease.

consider that there are no overpressured compartments in the sediment, even if this assumption is far from reality (Ortoleva, 1994).

The following scenario seems to emerge. At shallow depth (lower than 2500 m in a sandstone), porosity variations are essentially due to grain sliding and rearrangement and brittle deformation. At greater depth, pressure solution becomes more efficient because of an increase of temperature and stress. Most of the compaction can be described by this mechanism of deformation.

The limiting step for deformation: diffusion or precipitation

We have calculated the slowest step for deformation in conditions identical to Fig. 6. Between 0 and 2.5 to 3 km, the slowest step is quartz precipitation (Fig. 7). At these depths, the water film inside the grain contacts is thick and diffusion is fast, whereas kinetics of precipitation are

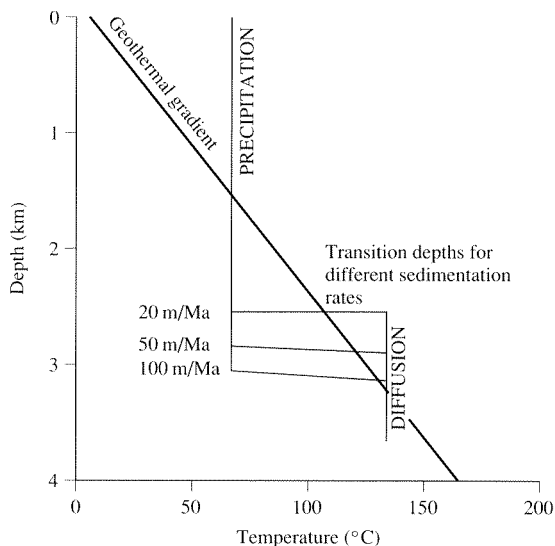


Fig. 7. The limiting step for pressure solution. The physical and textural conditions are the same as in Fig. 6 (the bold line represents a temperature gradient of $40^{\circ}\text{C}\cdot\text{km}^{-1}$). Between 0 and 2.5 km the slowest step is precipitation in the pore. Below this limit, diffusion at the contact becomes the slowest step and controls the deformation.

slow because of a low temperature. Under the transition depth, kinetics of quartz precipitation are activated by an increase of temperature and the limiting step becomes silica diffusion along the grain contacts.

DISCUSSION

Effects of stress and temperature on deformation

An increase in effective stress on the grains has two consequences. First it decreases the water film thickness; second it increases the driving force for diffusion (Rutter, 1976; Renard *et al.*, 1997) (Table 2). The first factor decreases the pressure solution rate, whereas the second factor increases it.

Temperature plays a key role in quartz solubility and the rate of dissolution, both of which increase with temperature. Kinetics of the surface reactions are the limiting processes when there is a small effective stress because the water film is thick enough to allow the solute to diffuse easily (Fig. 5 & Table 2). In contrast, at high effective stress diffusion becomes the slowest process that limits the rate of the whole mechanism of deformation.

Note that for burial depths between 0 and 3 km, the precipitation rate is so slow that regardless of the stress, the limiting factor would be the kinetics of quartz dissolution/precipitation (Oelkers *et al.*, 1996).

Effect of clays on the rate of pressure solution

Clay minerals can promote mineral dissolution through 'water film diffusion' because a thick water film can be preserved at their surface. Clays can have structural electric charges spread on their surface which stabilize the water film (Fig. 1c), allowing the solutes to diffuse easily to the pore (Renard & Ortoleva, 1997).

In contrast, some authors have shown that clay coatings can retard pressure solution (Tada *et al.*, 1987; McBride, 1989; Ramm, 1992). In this case, quartz precipitation on the pore surface is hindered because of the loss of clean grain surfaces (step 3 in Fig. 5). The pore fluid at the site of precipitation becomes supersaturated in aqueous silica, so that the gradient of concentration between the contact and the pore should disappear thus diminishing the driving force for pressure solution.

Case of an open system

In the model presented here, it is assumed that aqueous silica that goes outside the grain contact precipitates on the local grain surface opposite an open pore; the system being closed at a grain scale. If one considers a closed system at a decimetric to metric scale, transport phenomena should not be neglected. Silica can diffuse from a region where pressure solution is inhibited due to coating effects to a region where grains are cleaner and overgrowths can occur. Such a process could operate in sandstones where beds with abundant precipitated silica alternate with stylolite-rich regions where quartz dissolves (Oelkers *et al.*, 1996). In such systems, the driving force for pressure solution is the same in the clean layers and in the stylolites, whereas in the latter, precipitation is slower, due to clay coatings.

In the case of an open system at a grain scale where an aqueous fluid can circulate in the pores, fluid saturation is an important parameter. If the fluid is undersaturated with respect to silica, dissolution can occur directly from the grain surface adjacent to an open pore and not only at grain contacts. In contrast, if the fluid is supersaturated with respect to silica, the gradient of concentration between the contact and the pore decreases and the rate of pressure solution is diminished. And if the supersaturation is greater than a nucleation threshold, precipitation can occur directly in the pore.

CONCLUSIONS

1 The difference of silica solubility at a grain contact and in the pore fluid creates a concentration gradient, allowing solutes to diffuse along the grain-grain interface and precipitate in the pore. This overall process consists of several steps, the slowest of which controls the rate of deformation and quartz cementation. In laboratory pressure solution experiments, the effective stress is high and the water film trapped between the grains is very thin. Therefore, the rate limiting step is diffusion, especially at high temperature where the kinetics of dissolution and reaction are high. In contrast, geological observations suggest that when the effective stress is lower, diffusion is relatively faster than dissolution or precipitation, even if the driving force for solute transport is lower. Therefore, the limiting step can be the rate of precipitation on the pore free face. In clay-rich sandstones, especially at low temperatures, the kinetics of precipitation of quartz can limit the rate of deformation (Oelkers *et al.*, 1996), whereas at greater depths, diffusion controls the rate of deformation (Rutter, 1976).

2 In some conditions, the pressure solution rate can be diminished. When the pore pressure reaches the lithostatic pressure, in an overpressured compartment for example (Ortoleva, 1994), the gradient of solubility between the grain contacts and the pore disappears. Fluid composition can also modify the rates of quartz dissolution, precipitation and transport. For example, an elevated concentration in Na^+ of the pore fluid, as well as a basic pH, activate quartz dissolution and increase quartz solubility (Dove, 1994).

3 Finally, a crucial variable is rock fabric (grain shape and size, contact geometry, porosity and permeability). This variable has the same properties as a tensor: it can vary in the three directions of space. Therefore, a macroscopic model of pressure solution must take into account the evolution of rock texture to estimate the rate of compaction.

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REFERENCES

- ANDERSON, G.M. & CRERAR, D.A. (1993) *Thermodynamics in Geochemistry. The Equilibrium Model*. Oxford University Press, 588pp.
- APPLIN, K.R. (1987) The diffusion of dissolved silica in dilute aqueous solution. *Geochimica et Cosmochimica Acta* **51**, 2147–2151.
- BJØRKUM, P.A. (1996) How important is pressure in causing dissolution of quartz in sandstones? *Journal of Sedimentary Research* **66** (1), 147–154.
- BRADY, P.V. & WALTHER, J.V. (1990) Kinetics of quartz dissolution at low temperatures. *Chemical Geology* **82**, 253–264.
- COX, S.F. & PATERSON, M.S. (1991) Experimental dissolution-precipitation creep in quartz aggregates at high temperatures. *Geophysical Research Letters* **78** (8), 1401–1404.
- DEWERS, T. & ORTOLEVA, P. (1990a) A coupled reaction/transport/mechanical model for intergranular pressure solution stylolites, and differential compaction and cementation in clean sandstones. *Geochimica et Cosmochimica Acta* **54**, 1609–1625.
- DOVE, P.M. (1994) The dissolution kinetics of quartz in sodium chloride solutions at 25°C to 300°C. *American Journal of Science* **294**, 665–712.
- FREER, R. (1981) Diffusion in silicate minerals and glasses: a data digest and guide to the literature. *Contributions to Mineralogy and Petrology* **76**, 440–454.
- GIBBS, J.W. (1961) *The collected works of J. Willard Gibbs. Volume 1: Thermodynamics*. Yale University Press.
- GRATIER, J.P. & JENATTON, L. (1984) Deformation by solution-deposition and reequilibration of fluid inclusions in crystals depending on temperature, internal pressure, and stress. *Journal of Structural Geology* **6**, 189–200.
- GRATIER, J.P. & GUIGUET, R. (1986) Experimental pressure solution-deposition on quartz grains: the crucial effect of the nature of the fluid. *Journal of Structural Geology* **8**, 845–856.
- GRATIER, J.P. (1993a) Experimental pressure solution of halite by an indenter technique. *Geophysical Research Letters* **20**, 1647–1650.
- GRATIER, J.P. (1993b) Le fluage des roches par dissolution-cristallisation sous contrainte dans la croûte supérieure. *Bulletin de la Société Géologique de France* **164**, 267–287.
- HEALD, M.T. (1955) Stylolites in sandstones. *Journal of Geology* **63**, 101–114.
- HEIDUG, W.K. (1995) Intergranular solid-fluid phase transformations under stress: the effect of surface forces. *Journal of Geophysical Research* **100** (B4), 5931–5940.
- HORN, R.G., CLARKE, D.R. & CLARKSON, M.T. (1988) Direct measurements of surface forces between sapphire crystals in aqueous solutions. *Journal of Materials Research* **3** (3), 413–416.
- HORN, R.G., SMITH, D.T. & HALLER, W. (1989) Surface forces and viscosity of water measured between silica sheets. *Chemical Physics Letters* **162**, 404–408.
- LEHNER, F.K. (1995) A model for intergranular pressure solution in open systems. *Tectonophysics* **245**, 153–170.
- LOW, P.F. (1992) Interparticle forces in clay suspensions: Flocculation, viscous flow and swells. In: *Clay-Water Interface and its Rheological Implications*, Vol. 4. (eds Guven, N. & Pollastro, R.M.) pp. 158–186. Clay Minerals Society Workshop Lectures.

- MCBRIDE, E.F. (1989) Quartz cement in sandstones: a review. *Earth Science Reviews* **26**, 69–112.
- MULLIS, A.M. (1993) Determination of the rate-limiting mechanism for quartz pressure dissolution. *Geochimica et Cosmochimica Acta* **57**, 1499–1503.
- OELKERS, E.H., BJØRKKUM, P.A. & MURPHY, W.M. (1996) A petrographic and computational investigation of quartz cementation and porosity reduction in North Sea sandstones. *American Journal of Science* **296**, 420–452.
- ORTOLEVA, P.J. (1994) *Geochemical Self-organization*. Oxford University Press, 412pp.
- PATERSON, M.S. (1973) Nonhydrostatic thermodynamics and its geologic applications. *Reviews of Geophysics and Space Physics* **11**, 355–389.
- PESCHEL, G. & ALDFINGER, K.H. (1971) Thermodynamic investigations of thin liquid layers between solid surfaces. *Zeitschrift für Naturforschung* **26**, 707–715.
- POIRIER, J.P. (1985) *Creep of Crystals*. Cambridge University Press, 260pp.
- RAMM, M. (1992) Porosity–depth trends in reservoir sandstones: theoretical models related to Jurassic sandstones offshore Norway. *Marine and Petroleum Geology* **9**, 553–567.
- RENARD, F. & ORTOLEVA, P. (1997) Water film at grain–grain contacts: Debye–Hückel, osmotic model of stress, salinity and mineralogy dependence. *Geochimica et Cosmochimica Acta* **61**, 1963–1970.
- RENARD, F., ORTOLEVA, P. & GRATIER, J.P. (1997) Pressure solution in sandstones: influence of clays and dependence on temperature and stress. *Tectonophysics* **280**, 257–266.
- RIMSTIDT, J.D. (1997) Quartz solubility at low temperature. *Geochimica et Cosmochimica Acta* **61**, 2553–2558.
- RUTTER, E.H. (1976) The kinetics of rock deformation by pressure solution. *Philosophical Transactions of the Royal Society of London* **283**, 203–219.
- RUTTER, E.H. (1983) Pressure solution in nature, theory and experiment. *Journal of the Geological Society of London* **140**, 725–740.
- SCHUTJENS, P.M.T. (1991) Experimental compaction of quartz sand at low effective stress. *Journal of the Geological Society of London* **148**, 527–539.
- SHIMIZU, J. (1995) Kinetics of pressure solution creep in quartz: theoretical considerations. *Tectonophysics* **245**, 121–134.
- SPIERS, C.J., SCHUTJENS, P.M., BRZESOWSKY, R.H. *et al.*, (1990) Experimental determination of constitutive parameters governing creep of rocksalt by pressure solution. In: *Deformation Mechanisms, Rheology and Tectonics* (eds Knipe, R.J. & Rutter, E.H.) pp. 215–227. Special Publication of the Geological Society of London 54.
- SPOSITO, G. (1992) The diffuse-ion swarm near smectite particles suspended in 1:1 electrolyte solutions: Modified Gouy–Chapman theory and quasicrystal formation. In: *Clay–Water Interface and its Rheological Implications, Vol. 4*. (eds Guven, N. & Pollastro, R.M.) pp. 128–152. Clay Minerals Society Workshop Lectures.
- TADA, R., MALIVA, R. & SIEVER, R. (1987) A new mechanism of pressure solution in porous quartzose sandstone. *Geochimica et Cosmochimica Acta* **51**, 2295–2301.
- WALDERHAUG, O. (1994) Precipitation rates for quartz cement in sandstones determined by fluid-inclusion microthermometry and temperature-history modeling. *Journal of Sedimentary Research* **A64** (2), 324–333.
- WEYL, P.K. (1959) Pressure solution and the force of crystallization—a phenomenological theory. *Journal of Geophysical Research* **69**, 2001–2025.
- WORDEN, R.H., OXTOBY, N.H. & SMALLEY, P.C. (1998) Can oil replacement prevent quartz cementation in sandstones? *Petroleum Geoscience* **4**, 129–138.