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Compaction and porosity reduction in carbonates: A review of observations, theory, and experiments

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Abstract

Carbonates are major sedimentary materials found in many upper layers of the Earth's crust. Understanding their compaction behaviour is important for porosity prediction in sedimentary basins and to improve the knowledge about sealing of active faults at shallow depths, where the faults cross-cut limestone formations. In carbonates, as opposed to siliciclastic sediments, diagenesis starts at shallow depths (<1 km) and can contribute to the formation of a mechanically stable solid framework. Vertical stress, grain size and clay content are the main parameters influencing mechanical compaction. Mechanical compaction of unconsolidated carbonate sands in laboratory occurs mostly at low stress and is mainly controlled by mineralogy and initial packing of grains. It can explain porosity reduction down to about 30%. Conversely, very little porosity loss (< 1%) is obtained by mechanical compaction of cemented rocks under laboratory conditions. In sedimentary basins, however, much lower porosity values are usually encountered, down to zero. Given that mechanical compaction does not explain satisfactorily porosity–depth trends observed in sedimentary basins, the effect of chemical compaction on porosity must be considered. Among chemical mechanisms, pressure solution creep involves local mass transfer by dissolution, diffusion and precipitation processes at the grain scale. Subcritical crack growth is also a fluid assisted process contributing to grain fragmentation and compaction by rearrangement of particles. Pressure solution creep strain rate depends on grain size, porosity, applied stress, fluid chemistry, and temperature. Chemical compaction by pressure solution creep becomes an effective process of porosity reduction from less than one kilometer of depth, as soon as fluids are present. The main parameters controlling porosity loss then become vertical stress, temperature, diffusive flow and pore fluid chemistry. Both mechanical and chemical

compaction can lead to either pervasive compaction or localized deformation. The effect of the different parameters cannot easily be differentiated in observations of natural samples, as various deformation processes occur and interact simultaneously. However, control parameters may be separated in specifically designed theoretical studies and laboratory experiments.

So far, few experimental studies have been performed on pressure solution creep and subcritical crack growth in carbonates. Creep experiments on calcite powder and indenters experiments have shown that time-dependent compaction requires the presence of water. Even though the different controlling parameters were tested, no clear consensus exists on the rate limiting step of deformation and, consequently, on the creep law.

Individual processes leading to porosity loss in carbonates are rather well identified. However, their respective importance during burial is still debated. Even at shallow burial (<1 km) chemical compaction is needed to explain the gap between porosity loss obtained during experimental mechanical compaction and porosity-depth curves from sedimentary basins. The present study reviews various processes at work during carbonate compaction and synthesizes the current understanding on the respective importance of thermodynamic and petrophysical parameters at different stages of carbonate compaction.

Keywords: Carbonate, Compaction, Pressure-solution creep, Stress corrosion, Basin, Diagenesis, Deformation, Porosity

1 Introduction

Sedimentary materials are consolidated, or compacted, during their burial history. In sedimentary basins, the principal component of the stress field is usually the vertical stress. However, in syntectonic basins, horizontal stresses contribute to the compaction as seen by the observation of pitted grains and pebbles that dissolve against each other at some meters depths under the effect of horizontal stress (*Sorby*, 1865). Porosity loss in sedimentary basins has been widely studied especially due to the interest of the oil and gas industry in understanding accumulation of hydrocarbons. Even though 60% of the world's oil and 40% of the world's gas reserves are held in carbonates (Schlumberger market analysis, 2007), their burial compaction trends, *i.e.* porosity versus depth curves, are less well understood than for siliciclastic sediments. This situation is most likely due to the high variability of the carbonates deposition environments (*Bathurst*,

1971) as well as their great chemical reactivity (*Moore*, 2001).

Understanding processes driving porosity loss in sedimentary basins is necessary, for instance, to enable prediction of porosity in geological reservoirs. Other applications concern the geological storage of carbon dioxide and other waste materials, in which the carbonate rock can act either as a reservoir (*Le Guen et al.*, 2007) or as a cap rock, whose integrity represents a key technological challenge (*Rimmel et al.*, 2010; *Bachaud et al.*, 2011). Monitoring CO_2 storage sites from the surface by seismic imaging of subsurface is crucial, in particular to detect leakage early enough (*Wang et al.*, 1998). In active faults, compaction processes are also at work during the seismic cycle: earthquakes produce damage, and this damage is constantly healed and recovered during the interseismic period. The fragmentation process itself produces particle size distributions that follow power laws (*Storti et al.*, 2003; *Billi and Storti*, 2004) and this particle size distribution is modified during the interseismic period due to healing and sealing processes. Part of the recovery of the strength of a fault can be due to compaction and healing of the fault gouge. Due to their high reactivity, carbonate minerals are often observed to take part in the fault strengthening processes (*Labaume et al.*, 2004; *Boullier et al.*, 2004).

The accurate prediction of seismic velocities in carbonates depends on the constrained knowledge of the rock petrophysical properties and on the effect of chemical reactions on those properties. For example, predicting the decrease of bulk density with CO_2 injection is very important to CO_2 storage sites monitored via time lapse surveys. To achieve this, coupling mechanical, geochemical and seismic modelling is necessary (*Kumar et al.*, 2008) as well as a better link between fluid chemistry and the processes at the grain–to–grain contact. Principal deformation mechanisms responsible for compaction are, mechanical on the one hand, *i.e.* grains sliding and fracturing or pore collapse, and chemical on the other hand, *i.e.* intergranular pressure solution creep in association, or not, with subcritical crack growth. Various chemical processes inducing porosity loss have to be taken into account in carbonate compaction studies. These processes include dissolution (and, at shallow depth, karstification), conversion of aragonite to calcite, cementation and dolomitization.

Compaction studies based on outcrops and core materials lead to the conclusion that pressure solution creep is an important process of porosity reduction in carbonate sedimentary rocks (*Weyl*, 1959; *Schmoker and Halley*, 1982; *Rutter*, 1983; *Meyers and Hill*, 1983; *Scholle and Halley*, 1985). However, from natural observation, it is rather difficult to separate the influence of different parameters such as stress, temperature or

pore fluid composition. Thus, theoretical and experimental studies are conducted to quantify the influence of these different parameters.

This review aims to outline the state of knowledge on carbonate compaction based on natural observations, laboratory experiments and theoretical modelling. During diagenesis of carbonate sediments, changes in porosity are induced by a combination of deformation processes, dissolution and cementation. Even though this is not the focus of the present review, dissolution and cementation at shallow depth will be covered in the extent that it affects compaction processes. In the first part of this review, an overview of natural data of carbonate compaction is given. It is shown that by using natural observations, core, log and seismic data, it is possible to qualitatively separate the main deformation processes. Compaction of siliciclastic sediments is not the focus of this review but the topic will be addressed succinctly since comparison may help to the understanding of carbonate compaction. In a second part, theoretical models for mechanical and chemical compaction of carbonates are reviewed. These models are usually calibrated based on laboratory experiments that lead to a better quantification of the control parameters involved in natural processes. Our goal is to provide the reader with the key parameters responsible for the observed compaction trends. We rely on recent experimental studies performed in the rock physics community on limestone deformation and synthesize the observations and measurements obtained in these studies. We finally note that very few studies of carbonate compaction were published in the academic literature, most of the studies being kept confidential in internal reports in industrial companies.

2 Carbonate compaction in sedimentary basins

Compaction is a phenomenon taking place in all sedimentary basins. It involves several processes whose rates differ from one lithology to another. For instance, comparison of limestones compaction trends within the first hundred meters of burial with siliciclastic sediments shows that porosity loss is far more important in calcareous sediments (*Hamilton*, 1976). Similarly, *Ehrenberg and Nadeau* (2005) study of carbonate and sandstone petroleum reservoirs shows that, for a given depth, carbonate reservoirs have lower values of median and maximum porosity than sandstone reservoirs. Moreover, this compaction can be pervasive, where porosity reduction is quite homogeneous within the rock (*Ginsburg*, 1957), or highly localized, *i.e.* in compaction bands (*Tondi et al.*,

2006; *Rath et al.*, 2011; *Rustichelli et al.*, 2012) and stylolites (*Ehrenberg et al.*, 2003). Within carbonates, three main lithology groups may be differentiated – dolomite, limestone and chalk, with a wide range of microstructural textures (*Adams et al.*, 1984). Dolomite and chalk can be seen as two end members as far as porosity loss with depth is concerned. Porosity loss is faster in limestones than in dolomites (*Schmoker and Halley*, 1982; *Ehrenberg*, 2006), while porosity loss in chalk occurs faster than in shallow water carbonates (*Scholle and Halley*, 1985). Dolomites are chemically (*Bathurst*, 1971) and mechanically (*Hugman and Friedman*, 1979) more stable than limestones. Thus dolomitic rocks lose less volume by compaction than limestones (*Glover*, 1968). In contrast, the fine grained nature of chalk enhances mechanical reorganization. Hence high porosities and low permeabilities characteristic of chalk make them very susceptible to deform by pore collapse and hydro-fracturing (*Blanton*, 1981). These different compaction trends between various lithologies point out to the necessity to analyze them separately. In the following, the focus will be primarily on limestone and, to some extent, dolomite and chalk compaction will be addressed.

Porosity of carbonate sediments ranges from 50-70% at shallow depths (e.g. few hundreds of meters) (*Hamilton*, 1976; *Schmoker and Halley*, 1982; *Fabricius*, 2003) to nearly zero at depths greater than six kilometers (*Friedman et al.*, 1981; *Heydari*, 2000). It is, however, worth mentioning that some carbonate reservoirs preserve high porosity even though being deeply buried, a recent discovery being the deep water carbonate reservoir in the Santos basin, off-shore Brazil (*Caminatti et al.*, 2009).

Figure 1 displays some typical trends of porosity loss with depth in carbonate sediments. Those curves illustrate the large variability of carbonate compaction, especially at shallow depth, which might partly be explained by the wide variability of initial porosities, in the range 10 to 70% (Figure 1). These data represent carbonates from various environments, deep-sea calcareous sediments from DSDP leg 27 and ODP leg 131 (*Hamilton*, 1976), and near-surface sediments from the South Florida basin (*Schmoker and Halley*, 1982). Both data-sets indicate a fast compaction in the top 600 m and show that sediments with high initial porosity compact more readily. While within the first two kilometres porosity versus depth curves have various trends, below this depth compaction curves are more or less parallel (Figure 1). Although compaction trends are quite similar among the different environments represented in figure 1, at five kilometres depth a wide porosity range is still observable, *i.e.* from 5 to 15%.

Processes responsible for compaction involve both mechanical, *i.e.* stress dependent, and chemical, *i.e.* involving both stress and time-dependent fluid-rock interactions,

mechanisms. A detailed review of their effects on porosity loss is undertaken in the following part of this section. Porosity–depth trends (Figure 1) are regular, indicating that porosity reduction in carbonates is a continuous process (*Scholle and Halley*, 1985). Mechanical and chemical compaction are, therefore, expected to always act together, the first one being dominant at fast compaction rate, mainly shallow depth, while chemical compaction slowly becomes the main porosity reduction mechanism at slower compaction rate and greater depth.

2.1 Mechanical compaction in nature

Field observations, core and log data analysis (*Hamilton*, 1976; *Enos and Sawatsky*, 1981; *Scholle and Halley*, 1985; *Bassinot et al.*, 1993; *Wallace et al.*, 2002) tend to conclude that mechanical compaction is the principal mechanism of porosity loss during the first hundreds meters of burial. Empirical mechanical compaction law often describe porosity loss with depth as an exponential decay (*Athy*, 1930; *Sclater and Christie*, 1980),

$$\Phi = \Phi_0 e^{-bz}, \tag{1}$$

with Φ the porosity, which is function of the initial porosity, Φ_0, the burial depth, z, and a constant, b. These empirical laws have been used to fit porosity-depth trends of grain supported carbonates from the Cenozoic platform of West-Central Florida (*Budd*, 2001), ooze limestones in the shallow waters of the Ontong Java Plateau (*Hamilton*, 1976; *Bassinot et al.*, 1993), and cold water carbonates of the Gippsland basin, Australia (*Wallace et al.*, 2002), see also Figure 1. From these studies it seems that, even though early diagenesis and chemical compaction due to replacement of aragonite by calcite occurs, mechanical compaction is the predominant mechanism of porosity loss at shallow depth in various environments.

From microstructural studies, at least four different mechanisms involved in mechanical compaction can be discriminated, that is grain sliding, grain crushing, micro-crack propagation, and pore collapse. Pore collapse is influenced by the porosity distribution and initiates at larger pores (*Zhu et al.*, 2010; *Vajdova et al.*, 2010). Other mechanical compaction mechanisms in carbonates are affected mainly by stress, grain size and sorting, and clay content. Grain size in carbonates is related to the biological and physical origin of the carbonate (*Coogan and Manus*, 1975) and a wide variety of grain sizes and cement patterns can be observed in carbonates (*Adams et al.*, 1984). Due to the increase in friction, adhesion and bridging with decreasing grain size, compaction of

fine sediments is less effective than for coarse grains (*Coogan and Manus*, 1975). Heterogeneity in grain size distribution enhances mechanical compaction as well (*Chuhan et al.*, 2003). In carbonate sediments mixed with clays, mechanical compaction is more important in layers containing clays (*Ricken*, 1987). This can be explained by two mechanisms. On the one hand, clay particles increase the heterogeneity of the grain size distribution. On the other hand, clay trapped along carbonate grain contacts may prevent healing of these contacts and reduce the friction coefficient, allowing grain sliding (*Renard et al.*, 2001).

When localized, mechanical compaction can lead to the formation of the so-called compaction bands where individual grains rotate and crush along an interface where no shear could be identified, as observed in some poorly cemented carbonate grainstone (*Rath et al.*, 2011). The porosity is much smaller in the millimeter thick bands (for example close to 1% or even below (*Tondi et al.*, 2006; *Rath et al.*, 2011)), compared to the surrounding rock matrix. Such localization can induce large permeability decrease in the direction perpendicular to the compaction bands and may control fluid flow in reservoir rocks. The compaction bands can form near faults and are sometimes associated with chemical compaction (*Tondi et al.*, 2006; *Rustichelli et al.*, 2012).

The rate of sedimentation, or sediments loading, is also a very important control of compaction. Carbonate sediments which have undergone fast burial show more mechanical compaction patterns than those subjected to a lower sedimentation rate (*Scholle and Halley*, 1985). Within sediments compacting slowly enough time is available for chemical compaction processes to be operative. This may therefore reduce the effect of mechanical compaction. For instance the Upper Jurassic Smackover Formation (Alabama) is constituted of oolitic and pelletal grainstones, which were strongly affected by early cementation. In these reservoirs a stable framework was built (*Kopaska-Merkel et al.*, 1994), therefore very little mechanical compaction occurred and an average porosity of 17 % was preserved at about 3600 m depth. In low permeability carbonate mudstones, a little amount of cementation only is necessary to reduce drastically the permeability (*Budd*, 2001) when the percolation threshold is reached.

In natural environments, mechanical compaction is effective to reduce porosity down to 30-40 %. To reduce further the porosity, either large differential stresses, producing pore collapse or fracturing, are needed, or chemical compaction has to play a role (*Scholle and Halley*, 1985).

2.2 Evidence of chemical compaction

Chemical compaction involves early meteoric and marine diagenesis, as well as crack propagation in presence of reactive fluid and dissolution - precipitation resulting from pressure solution creep. While early diagenesis due to precipitation of cement in open pores is not a function of stress, pressure solution creep and crack propagation are strongly dependent on stress. All these mechanisms are also strongly dependent on pore fluid chemistry.

Pressure solution creep produces characteristic microstructures such as stylolites (Figure 2A, B) or grain–to–grain indentations (Figure 2D). Cracks propagating in grains can become sealed by calcite precipitating in the veins (Figure 2C). Petrographic studies allow some quantification of the respective role of mechanical and chemical compaction in natural carbonates through microstructural observations (*Meyers*, 1980; *Gratier et al.*, 1999; *Budd*, 2002).

When localized, pressure solution creep can lead to the formation of stylolites (*Bathurst*, 1971; *Dunnington*, 1954; *Carrio-Schaffhauser et al.*, 1990; *Renard et al.*, 2004), where the dissolution occurs along a well defined interface. Only the carbonate dissolves, leaving a thin layer of insoluble material, such as clays. The destabilization of the interface gives the stylolites their peculiar morphology, due to the presence of chemical and mechanical heterogeneities in the rock that may pin the interface during dissolution (*Koehn et al.*, 2007). Moreover, the shape of stylolites can be analyzed and it was found that their fractal morphology has recorded the stress at which the stylolites have formed (*Ebner et al.*, 2009).

High permeability favours water-rock interaction. High permeability are found in coarse sands or grain supported carbonates (*Enos and Sawatsky*, 1981; *Budd*, 2001). In the case of coarse sands not yet affected by cementation, dissolution leads to compaction of sand and thus to porosity loss. If some cementation already occurred and a stable framework is on place, dissolution of shallow water carbonates may lead to porosity gain, however. Conversely, carbonate muds are highly porous but have very low permeability, thus carbonate muds are less affected by early cementation than carbonate sands (*Enos and Sawatsky*, 1981; *Goldhammer*, 1997). Nevertheless when reactive flow conditions required for early cementation are met, precipitation of matter in the pore space contributes to the formation of a mechanically stable framework which prevents further mechanical compaction.

Burial depth, or effective vertical stress applied on sediments, plays an important role

in porosity reduction of carbonate sediments. Several other parameters such as temperature, initial porosity, grain size, pore fluid chemistry and clay contact can significantly affect the rate of porosity reduction. Time is of course an important parameter for chemical compaction since it involves the chemical reaction kinetics and diffusion of material. However, considering the fast kinetics of carbonate reactions relative to geological time, this is probably not a limiting factor and therefore it is not taken into account here. In the following paragraphs, the roles of stress, temperature, water flow and pore fluid chemistry are discussed separately. A special emphasis is made on their relative importance in carbonate compaction by pressure solution creep.

2.2.1 Evidence of the effect of stress

From field observations, decrease of porosity in carbonates have been interpreted to be primarily a function of depth rather than time (*Royden and Keen*, 1980; *Schmoker and Halley*, 1982). In other words, stress appears to be the main driving force for compaction in carbonate sedimentary sequences. However, we know that when stress is applied during a long time, in case for instance of horizontal stress in some syntectonic basins, dissolution may develop at some meters depth only (*Sorby*, 1865). It remains that the vertical effective stress acting at the grain-to-grain contact is the main driving force for pressure solution creep.

In their study of Oligocene-Holocene cold water carbonates, *Wallace et al.* (2002) noticed that the amount of calcite cement increased with depth. In this same study, few signs of pressure solution were observed at depths less than one kilometer. Conversely, at greater depths, intergranular pressure solution features were well developed and was the most obvious deformation mechanism in skeletal packstones (*Wallace et al.*, 2002). Carbonate rocks from Anadarko basin (south-west Oklahoma), and ooid grainstones of the Upper Jurassic Smackover Formation (Alabama) (*Friedman et al.*, 1981; *Heydari*, 2000) experienced high vertical stresses, *i.e.* burial depth of 6 and 9 km respectively, but also to high temperatures exceeding 200°C. In these formations, a combination of mechanical and chemical compaction acted to reduce porosity. Macro- and microscopic observations of these sediments show extensive twin development on large calcite crystals, cataclastic textures, pressure solution features, cementation and grain deformation (*Friedman et al.*, 1981; *Heydari*, 2000), making it difficult to separate the effects of all these mechanisms. The combination of mechanical and chemical compaction reduced porosity to almost zero in these formations.

A common feature of the different studies is that, while very little signs of pressure solution are observed at shallow depth in basins where no horizontal tectonic compressive stress was applied, the number of pressure solution features increase significantly with depth. This is an indication that pressure solution is both stress and time-dependent. Time being no limiting factor at a geological time scale, pressure solution starts to be an efficient process of porosity reduction mostly when a significant level of stress.

2.2.2 Effect of temperature

Comparison of siliciclastic and carbonate sediments show that carbonate compaction is more sensitive to stress and to a lesser extent to temperature (*Giles*, 1997). Dissolution and precipitation processes in calcite are affected by the temperature in two manners. On the one hand, solubility of calcite decreases with an increase in temperature, on the other hand kinetics of calcite dissolution increases with temperature increase. These two effects compete with each other, and almost cancel for pressure solution creep (*Renard et al.*, 2000) (as it is considered that the flux of dissolution or precipitation is described as a kinetics rate times a chemical gradient, see Section 3.2.1). Several field observations, however, indicate that porosity loss with increasing depth can also be associated with thermal exposure. This point out that temperature also influences chemical compaction in several carbonate reservoirs (*Friedman et al.*, 1981; *Heydari*, 2000; *Ehrenberg and Nadeau*, 2005; *Bolås et al.*, 2008).

2.2.3 Effect of advective and diffusive fluid transfer

Advective flow in sedimentary basin is in general rather slow (*Bjørlykke*, 1993). However, shallow water circulation plays, in some cases, an important role for early cementation (*Enos and Sawatsky*, 1981; *Budd*, 2001) and the development of karstification patterns. From the observation that low porosity reservoirs are more often found in carbonates than in sandstones and the fact that hydrocarbons can be produced from these reservoirs, it is inferred that fractures occur more often in carbonates (*Ehrenberg and Nadeau*, 2005). This observation is significant since fracture networks can, in some cases, control fluid flow in sedimentary basin. Fractures can be either sealed by precipitation or opened by dissolution, depending both on the fluid flow and on the pore water composition (*Polak et al.*, 2004; *Yasuhara et al.*, 2006). Such evolution controls the evolution of transfer properties by diffusion or advection in the surrounding area (*Gratier*, 2011).

Diffusion of solute is an important process since it keeps pore water under-saturated with respect to calcite, allowing further dissolution and therefore compaction. The two main structures enabling fast diffusion rate are fractures and stylolites. Local dissolution along stylolites induces diffusion of matter in the surrounding media and participates to porosity occlusion (*Finkel and Wilkinson*, 1990), leading to the observation that porosity loss by cementation is actually positively correlated to the presence of stylolites (*Ehrenberg et al.*, 2006; *Bjørlykke*, 2006). Field observations also suggest that stylolitic dissolution is enhanced by the presence of clay minerals or phyllosilicates (*Weyl*, 1959; *Ehrenberg*, 2004; *Ehrenberg et al.*, 2006; *Aharonov and Katsman*, 2009).

2.2.4 Effect of pore water composition

In formation waters, concentration of dissolved elements is a function of initial pore water chemistry which tends to equilibrate with minerals present (*Bjørlykke*, 1993). The degree of saturation with respect to minerals in the shallow depth pore waters may be of importance, since it can promote or inhibit reactions. For instance the low degree of saturation of Mississippian skeletal limestones paleo-groundwater with respect to calcite is proposed to favour porosity loss by intergranular pressure solution rather than mechanical grain repacking and plastic deformation (*Meyers and Hill*, 1983). Such effect is however still debated when considering the effect of fluid saturation on the rate of pressure solution creep *Yasuhara et al.* (2006).

In Figure 3, evolution of the Mg^{2+} to Ca^{2+} ratio and of the Ca^{2+} to Sr^{2+} ratio as a function of depth are displayed for some shallow and deep carbonate formations. The Mg^{2+} to Ca^{2+} ratio decreases at shallow depth, which can be interpreted by the progressive saturation of pore waters with respect to calcite by the dissolution of carbonate. The increase of the Ca^{2+} to Sr^{2+} ratio is related to incorporation of strontium into aragonite structure. Magnesium content is also of prime importance, since it's presence is known to inhibit dissolution of calcite (*Arvidson et al.*, 2006). For instance in shallow-water carbonates rocks of South Florida, porosity is inversely related to magnesium content of pore water (*Schmoker and Halley*, 1982).

At greater depths, *i.e.* below 100 meters, pore water composition might be less important since it is already in equilibrium with the minerals present. Low variability of the Mg^{2+} to Ca^{2+} ratios at greater depths (Figure 3) demonstrates that water became saturated with respect to calcite. The lowest values of this ratio can be explained by the increase of the calcium carbonate solubility with confining pressure. The Ca^{2+} to Sr^{2+}

ratios are slightly lower in subsurface than at shallow depth, indicating that, once the substitution of Sr^{2+} into the mineral has occurred, the strontium - carbonate reaction vanishes. At these depths, the different ratios only evolve due to local dissolution by pressure solution creep.

2.3 Questions raised by the natural observations

From natural observations, several questions remain unanswered related to the dynamics of mechanical and chemical compaction. The amount of overburden necessary for pressure solution to become the dominant process of porosity loss is difficult to determine from field observations. The role of temperature on chemical processes in carbonates is rather ambiguous: increasing temperature increases the kinetics of carbonate-water interactions on the one hand, but decreases the solubility of calcite on the other hand. The rate–limiting step of pressure solution cannot be determined from field observations. Answering these questions is not easy, especially since once chemical compaction is operative, it is difficult to isolate its effects from mechanical compaction processes in the porosity-depth data sets or in microstructural observations. In order to understand the influence of the various compaction mechanisms, and their interactions, several laboratory experiments and theoretical developments were pursued. These theoretical and experimental developments are the topic of the following section.

3 Compaction of carbonate: theory and experiments

3.1 Mechanical compaction

3.1.1 Theoretical background

As sediments get buried, the vertical stress increases, which in turn leads to reduction of sediments thickness, porosity loss and in increase of bulk density. In sedimentary basins that are not associated with high compressive horizontal stress (i.e. excluding active mountain belts), the principal component of the stress field is usually the vertical stress. The reduction in sediments thickness occurs mainly without lateral strain because surrounding sediments exert lateral stresses that prevent it (*Giles*, 1997). Taking this into consideration while describing mechanical compaction in this section, the assumption is made that deformation in sedimentary basins is uniaxial.

At shallow depth, without early cementation processes, carbonate sediments compaction

can be modelled using soil mechanics approaches. At early stage of sediment deposition, when cementation has not occurred yet, the main process contributing to volumetric strain is grain rearrangement and expulsion of water. Consolidation theory, first expressed by *Terzaghi* (1925), states that an increase in effective stress leads to the expulsion of water and therefore to consolidation of soil. The effective stress, σ', is defined by,

$$\sigma' = \sigma - P_p, \tag{2}$$

where σ is the applied stress and P_p the pore pressure. Following Terzaghi's consolidation theory (*Terzaghi and Peck*, 1967), a logarithmic relation is found between the void ratio, e, and the effective stress, σ' (see dashed lines on Figure 4d),

$$e_0 - e_f = C_c \cdot log(\frac{\sigma'_f}{\sigma'_0}), \tag{3}$$

the indices 0 and f indicate the initial and final states of the sediment compaction respectively. The void ratio can be related to porosity through $\Phi = e/(1+e)$. The compression index, C_c, is a phenomenological coefficient used to characterize the different soils compaction.

If cementation occurs early, then soil strength overcomes burial stresses, and mechanical compaction processes are slowed down. Once sediments are consolidated and cemented, then their deformation may be described by a rock mechanics approach. Elastic deformation is then the main deformation process up to much higher stresses than for soils. Rock mechanics divide deformation induced by mechanical compaction into three main regions, *i.e.* linear-elastic, ductile, and brittle (Figure 5). For geological materials, the ductile phase is restricted to situations of very high temperatures and confining stresses (*Jaeger et al.*, 2007; *Baud et al.*, 2009) or for some specific low cohesion sediments (i.e. shales). Moreover, in tectonically calm sedimentary basins, most of the deformation occurs in the elastic domain and the strain is usually proportional to the applied stress and a function of the sediments intrinsic elastic properties (Figure 5).

Considering sediments to be linear–elastic, uniaxial deformation can be described by a linear stress–strain relationship function of the Young's modulus, E, and the Poisson's ratio, ν, of the sediment (*Turcotte and Schubert*, 1982),

$$\epsilon_1 = \sigma_1 \cdot \frac{(1+\nu)\cdot(1-2\nu)}{E\cdot(1-\nu)}, \tag{4}$$

where σ_1 is the applied vertical stress and ϵ_1 the vertical strain.

Poroelasticity is an extension of linear elasticity that takes into account the presence of

a diffusive fluid (*Biot*, 1941; *Rice and Cleary*, 1976). This theory is commonly used to analyze compaction of fluid saturated rocks (*Fjær et al.*, 1992; *Guéguen et al.*, 2004). The strain may then be expressed as follows,

$$\epsilon = \frac{1}{K} \cdot (\sigma_p - b \cdot P_p); \tag{5}$$

where K is the rock bulk modulus, σ_p the isotropic stress and b the Biot coefficient given by,

$$b = 1 - \frac{K}{K_s}; \tag{6}$$

with K_s the bulk modulus of the solid phase. The uniaxial bulk compressibility, β_1, and, therefore, the porosity loss are then described as a function of the effective stress and the Biot parameter (*Giles*, 1997; *Wong et al.*, 2004),

$$\beta_1 = \frac{b \cdot (1 + \nu)}{3 \cdot K \cdot (1 - \nu)}. \tag{7}$$

Typical values of the Biot parameter and bulk compressibility in limestones are given in Table 1.

Failure occurs when peak stress is reached (Figure 5a-b). Unconsolidated sediments first need to reach a locked state then, when the vertical stress reaches a critical value, crushing starts. Particle breakage occurs when the stress along the grain contact overcomes the yield stress of the material. As force distribution is strongly dependent on the packing structure (*Chan and Ngan*, 2005) and the geometry of the contact force network (*Mair and Hazzard*, 2007), the locking state of the grains determines the localization of breakage onset.

The stress value at which brittle failure starts in limestone is influenced by temperature and confining pressure. Increase in temperature promotes ductility and increases the strain rate sensitivity of brittle failure (*Paterson and Wong*, 2004). Additionally, up to fracture, limestone strength is relatively independent of strain rate (*Paterson and Wong*, 2004). As in other types of rocks, failure in limestone is accompanied by strain softening and strain localization (*Evans et al.*, 1997). Since, in sedimentary basins, one principal stress is mostly vertical, fracture development in nature is usually vertical or sub-vertical, unless a localized high pore pressure fluid source initiates hydraulic fracture and modifies the state of stress locally (*Rozhko et al.*, 2007). Plastic pore collapse, grain breakage and failure occur at stresses above the yield stress (*Carroll and Holt*, 1972; *Curran and Carroll*, 1979; *Baud et al.*, 2009). During compaction, changes in pore shape, structure or connection, influence fluid flow in sedimentary basin (*Evans*

et al., 1997).

In the following section, we describe some experimental studies done on carbonate sand and rocks. Initial compaction in both types of materials occurs in quite a similar, elastic fashion. However, they have different mechanical response when considering inelastic behaviours and failure modes.

3.1.2 Experimental compaction of carbonate sand

The particular response of carbonate sand to loading was, first, mainly investigated within geotechnical engineering studies. Triaxial testing of uncemented (*Coop*, 1990) and naturally cemented (*Airey*, 1993) carbonate sands were carried out at low stresses, *i.e.* below 8 MPa. Compaction studies being of geological interest, carbonate sands were also compacted at vertical stresses corresponding to greater burial depths. Hydrostatic triaxial tests on modern carbonate sediments from the great Bahamas bank (*Fruth et al.*, 1966), compression tests on sands with varying grain size and carbonate content (*Ebhardt*, 1968; *Chuhan et al.*, 2003; *Croizé et al.*, 2010a), and confined compression tests on shallow-water limestones cores from various sedimentary environments (*Shinn and Robbin*, 1983) were carried out at vertical stresses up to 100 MPa.

These tests focused on porosity decrease with increasing stress and investigated the mechanical strength of carbonate sands (Figure 4). The main results are that carbonate sands have a stiff response up to a yield point and have a higher friction angle, $\varphi \approx 40^{\circ}$, than usually encountered in soils (*Coop*, 1990). The effective angle of friction, φ', is an important parameter of the Mohr–Coulomb failure criteria which might be defined as,

$$\tau_f = c' + \sigma'_f tan\varphi' \tag{8}$$

with τ_f the shear strength at failure, c' the effective cohesion, and σ'_f the effective stress at failure. After yielding, carbonate sands become very compressible resulting in large volumetric strains. Carbonate sand compressibility can be related to the relatively high initial porosity usually encountered in these soils and to their yield stress (*Coop*, 1990; *Airey*, 1993).

Tests conducted at more than 20 MPa effective stress showed that most of the compaction occurred in the early stages of loading (effective stresses ¡ 5-10 MPa) (*Fruth et al.*, 1966; *Ebhardt*, 1968; *Shinn and Robbin*, 1983; *Chuhan et al.*, 2003). At low stress levels, 5–10 MPa , where most of the compaction occurred, the stress–strain relationship strongly depends on the grain size and stiffness. For instance, the five facies of the great Bahamas bank, *i.e.* oolite, oolitic, grapestone, skeletal and mud

facies, tested by *Fruth et al.* (1966) showed different compaction behaviour up to 25 MPa. They compacted more or less readily depending on their composition and initial porosity. Parameters controlling mechanical compaction at these stresses are the composition of the sand and its initial stiffness (*Fruth et al.*, 1966), the initial packing and therefore porosity (*Fruth et al.*, 1966; *Shinn and Robbin*, 1983), and the grain size. Finer sediments are less compressible (*Ebhardt*, 1968; *Chuhan et al.*, 2003), which is due to the fact that stress is distributed over more grain–to–grain contacts, so that, on average, grain contact stresses are lower in sands with a smaller grain size. *Ebhardt* (1968) reported that temperature had some effect on compaction as well, more intense compaction was observed in experiments conducted at 90°C than on those conducted at room temperature. However no further investigation has been done on the effect of temperature on mechanical compaction of carbonate sands. In *Croizé et al.* (2010a), mechanical compaction of bioclastic carbonate sand was found not to be affected by temperatures in the range 20 to 70 °C.

At stresses higher than 25 MPa, stress–strain curves for different carbonate sands are much more similar than at lower stresses, meaning that porosity loss in carbonate sediments is influenced mainly by initial sorting and initial compaction (*Fruth et al.*, 1966). Mechanical compaction of unconsolidated carbonate sediments is a very effective process of porosity loss at low effective stress, but once a locking state is reached the strain rate decreases substantially..

The amount of mechanical strain achieved in carbonate sands can be rather significant. *Shinn and Robbin* (1983) showed that calcareous sediments can compact by as much as 50% of their initial thickness within the first hundreds meters. However due to very large initial porosities, residual porosities higher than 30% are reported in carbonate sands and mud after mechanical compaction under effective stresses higher than 30 MPa (*Fruth et al.*, 1966; *Shinn and Robbin*, 1983). These results show that, if mechanical compaction is the only process responsible for porosity loss, one could expect porosities up to 30% in limestones buried at 3 km. However compaction curves of natural limestones show much lower porosities at this depth (Figure 1).

After mechanical compaction, microstructures observed in tested samples were very similar to those observed in naturally compacted carbonates. Grain fracturing was very common, as well as grain penetration and buckling of spalled margins (*Fruth et al.*, 1966); rotation of shells towards the horizontal, reorganization of organic material, conversion of part of the core from wackestone to packstone, obliteration of birdseyes and fenestral voids, flattening of fossils (*Shinn and Robbin*, 1983) were also observed.

Comparison of features produced experimentally and naturally may enable a better understanding of when does cementation occur in natural environment. However, features produced by mechanical compaction are certainly sites of enhanced chemical compaction in nature. And since cementation can occur very early in carbonates, effect of cement on sand mechanical behaviour has to be taken into account. Early cementation increases the shear modulus of the soil as well as its yield strength (*Airey*, 1993).

3.1.3 Experimental compaction of carbonate rock

At small stresses, experimental mechanical deformation of carbonate rock is usually characterized by a non–linear stress–strain relationship, interpreted to be related to the closure of cracks, pores and other defects (*Vajdova et al.*, 2004). This early phase can be related to *in situ* stresses to which the rock was subjected (*Couvreur et al.*, 2001). Ultrasonic P- and S-waves velocity and quality factor calculations, i.e. the estimation of how dissipative the material is, enables the monitoring of the end of the crack closure phase (*Couvreur et al.*, 2001). For brine-filled porosity, the electrical conductivity decreases at the beginning of the test, which can be related to the closure of pores and sub-horizontal cracks (*Jouniaux et al.*, 2006). Using Walsh's model (*Walsh and Brace*, 1966), the non–linear stress–strain relationship can be related to the amount of cracks and various type of pores (*Baud et al.*, 2000). After this early phase, deformation is characterized by a linear elastic stress–strain relationship. This linear elastic phase can occur at different stress stages depending on the initial porosity of the rock, the degree of cementation and the geometry of the pore space.

Vajdova et al. (2004) carried out hydrostatic triaxial tests on three different limestones, the main structural difference between them being their initial porosity. Solnhofen limestone has a porosity of 3 %, porosity of Tavel limestone is 10.4 %, porosity values of Indiana limestones are 16, 18 or 20 %. The compressibility of these limestones increases with porosity. Solnhofen limestone has a compressibility of 0.016 GPa^{-1} (*Baud et al.*, 2000; *Vajdova et al.*, 2004), Tavel limestone a compressibility of 0.033 GPa^{-1} and Indiana limestone a compressibility of 0.075 GPa^{-1} (*Vajdova et al.*, 2004). For platform limestones with an average initial porosity of 20%, uniaxial tests show that the compressibility lies in the range 0.01 to 0.2 GPa^{-1} (*Croizé et al.*, 2010b) and that early diagenesis was responsible for an over-consolidation of the rock and a good preservation of the porosity.

A major domain of investigation of experimental studies on carbonate rock compaction

is the onset of failure occurrence and the kind of failure mode (Figure 5b). Fracture propagation in rocks is an important mechanism that can induce compaction, but is also of importance for fluid flow. A failure plane creates a path for dissolution and transport of matter or can be a place of enhanced cementation and become a fluid flow barrier. This leads to sequential permeability behaviors in time, from high to low permeability flow paths.

Different mechanical parameters control failure in carbonates. These poro-elastic parameters are usually inferred from mechanical triaxial tests (*Renner and Rummel*, 1996; *Baud et al.*, 2000; *Palchik and Hatzor*, 2002; *Vajdova et al.*, 2004), compressional and shear waves propagation measurements (*Couvreur et al.*, 2001; *Eberli et al.*, 2003; *Vanorio et al.*, 2008) or electrical conductivity measurements in fluid saturated samples (*Jouniaux et al.*, 2006). These different methods allow to better constrain the mechanisms responsible for carbonate mechanical compaction. Hydrostatic triaxial tests (*Baud et al.*, 2000; *Couvreur et al.*, 2001; *Vajdova et al.*, 2004), uniaxial compression tests (*Palchik and Hatzor*, 2002; *Jouniaux et al.*, 2006; *Croizé et al.*, 2010b) and triaxial compression tests with various confining pressure (*Renner and Rummel*, 1996; *Couvreur et al.*, 2001) were performed on limestones and dolomites, some experimental data being displayed in Figure 5b-d. Carbonates tested had grain size ranging from 5 to 400 μm, various chemistry, *i.e.* calcite, aragonite, dolomite, and various pore space arrangement. Due to differences in the experimental procedures and microstructural properties of the tested samples, the different tests are difficult to compare (*Renner and Rummel*, 1996). The critical stress (i.e. peak stress) at which permanent strain is observed varies from 5 to more than 500 MPa in these different studies. Porosity seems to be the main controlling factor on the onset of failure, even though the scattering of the critical stress as a function of the porosity is rather high (Figure 6). The complexity of the pore system in carbonates (*Lucia*, 1995) might be one of the reason of this scatter. In Tavel, Indiana, Majella, Solnhofen Limestones the influence of the porosity type on the development of mechanical failure was studied. Pore collapse was found to initiate at larger pores (*Zhu et al.*, 2010). For rocks containing both macro- and microporosity, macropores determine the localization of fractures (*Vajdova et al.*, 2010). These studies point out the importance of the porosity type description when studying mechanical compaction of carbonates. When samples are saturated, water is squeezed into cracks and enhances formation of sub–vertical fractures (*Jouniaux et al.*, 2006). Therefore, critical stress is lower in water saturated samples (Figure 6).

Different failure modes were identified as a function of confining pressure (*Renner and*

Rummel, 1996; *Baud et al.*, 2000). For confining pressures lower than 50 MPa, *i.e.* equivalent to less than 3-4 km burial, dilatancy started and acted as precursor of brittle faulting. For intermediate confining pressure, an initial stage of strain hardening could be measured. And for confining pressures higher than 350 MPa, samples failed by cataclastic flow associated with shear enhanced compaction and strain hardening (*Baud et al.*, 2000). Compactive cataclastic flow was commonly observed to be a transient phenomenon which evolved with increasing strain to dilatant cataclastic flow and ultimately shear localization (*Baud et al.*, 2000). In very porous limestones a critical pressure beyond which stress-strain behaviour becomes non-linear was observed, which corresponds to pore collapse and grain crushing (*Vajdova et al.*, 2004).
Elastic, inelastic and failure properties of carbonate rocks can be related to their porosity, and carbonate compressibility increases with porosity. Critical stresses for the onset of pore collapse under hydrostatic and non-hydrostatic loading decrease with increasing porosity (*Vajdova et al.*, 2004). Mechanical twinning dominates in the most porous limestone, while dislocation slip is activated in the most compact limestone (*Vajdova et al.*, 2004). Elastic stiffness and porosity are the main parameters influencing the onset of dilatation (*Palchik and Hatzor*, 2002).

3.1.4 Conclusions on mechanical compaction

In all these experiments, small strains were obtained for rock elastic compaction. In both carbonate sands and rock compaction, the initial porosity is a crucial parameter, as the maximum compressibility was obtained for samples with the highest initial porosity. All these experiments demonstrate, that mechanical compaction plays, to some extent, a role in the loss of porosity in basin limestones. However, mechanical compaction is mainly operative for sands or high porosity limestones. For rocks with low porosities or in which a mechanically stable framework was built during early diagenesis (*Croizé et al.*, 2010b), the stresses needed to achieve grain crushing and shear fracturing are usually higher than effective stresses usually encountered in sedimentary basins (Figures 5 and 6). Finally, mechanical compaction can explain the decrease of porosity down to 20–30% at stresses equivalent to burial depths of 2 to 4 km. However, in sedimentary basins, porosity values are typically lower at these depths (Figure 1), therefore chemical compaction must play a key role in carbonate compaction.

3.2 Chemical compaction

3.2.1 Theoretical background

Pressure solution creep: Pressure solution creep is an important process of porosity elimination in sedimentary basins (*Sorby*, 1863; *Rutter*, 1983; *Tada and Siever*, 1989) or compaction and healing of active faults (*Angevine et al.*, 1982; *Hickman and Evans*, 1995; *Renard et al.*, 2000; *Yasuhara et al.*, 2003, 2005). Various types of microstructures are associated with pressure solution, *e.g.* sutured grain contacts, grain truncations, indentations, clay seams and stylolites (*Wanless*, 1979; *Buxton and Sibley*, 1981). The nature of microstructures associated with pressure solution is a function of the rock lithology and structural resistance (*Wanless*, 1979; *Buxton and Sibley*, 1981).

Pressure solution creep is a water assisted physico–chemical process occurring as a result of stress gradients along grain contacts and pore walls. Originally, an increase in solubility of minerals with pressure was measured in the laboratory, and the term pressure solution was created to describe the dissolution and diffusion processes involved (*Sorby*, 1863). The term pressure solution was later associated with three serial processes: i) dissolution at grain contacts, ii) diffusion of solute matters towards the pore space and iii) precipitation on the stress–free faces of grains (i.e. in the pore space) and/or transport by diffusion or advection (*Weyl*, 1959; *Raj*, 1982; *Rutter*, 1983; *Tada and Siever*, 1989; *Lehner*, 1990, 1995; *Gundersen et al.*, 2002). The rate of pressure solution is controlled by the slowest of the three serial steps, *i.e.* dissolution, diffusion or precipitation (*Raj*, 1982; *Rutter*, 1983).

The driving force for pressure solution is the chemical potential gradient between the highly stressed grain boundary and the stress–free pore space (Figure 7A). Numerous rate laws for aggregates compacting by pressure solution have been derived. Theoretical equations for creep due to intergranular pressure solution were first derived using an equilibrium approach (*Paterson*, 1973; *Durney*, 1976; *Rutter*, 1983). In order to describe the processes in a physically more realistic way, a non-equilibrium approach was later used to develop models for creep by grain boundary diffusional pressure solution, taking also into account the role of precipitation on the overall strain rate (*Lehner and Bataille*, 1984; *Lehner*, 1990; *Spiers and Schutjens*, 1990).

The grain boundary structure must be dynamically stable (*Lehner and Bataille*, 1984), *i.e.* while continuous dissolution or precipitation occurs within a representative elementary volume in the grain-to-grain contact, the average grain boundary structure remains

constant. The equilibrium between the solid phase under stress and the solution of the component forming the solid phase at the grain-to-grain contact is given by (*Paterson*, 1973),

$$\mu_1 = f^s + \sigma_n/\rho^s; \tag{9}$$

where f^s is the mass specific Helmholtz free energy of the solid phase, ρ^s the density of the solid phase, μ_1 the chemical potential of the dissolved solid, σ_n is the stress normal to the grain to grain contact, which is considered to be equal to the fluid pressure within the grain boundary (*Lehner*, 1990; *Spiers and Schutjens*, 1990). The chemical potential of the solute in the pore space is given by $\mu_1^{eq} = f^s + p^f/\rho^s$ with p^f the pressure of the fluid in the pore space. The gradient in chemical potential between the grain contact and the pore space is then given by,

$$(\sigma_n - p^f)/\rho^s = \mu_1 - \mu_1^{eq}. \tag{10}$$

Considering the above equations (eq. 9 and 10) in the case of equilibrium, saturation in the pore space is attained. This then would lead to immediate precipitation of material as soon as it leaves the stressed grain contact and might then heal the grain boundary and thus stop pressure solution which will not be able to restart once the grain boundary is healed (*Hickman and Evans*, 1991). Since in nature a grain boundary remains permeable to fluid, therefore equilibrium cannot exist at the grain boundary and equation 9 and 10 must be considered for wet grain boundary approaching a state of equilibrium but not reaching it (*Lehner*, 1990).

Once dissolution occurred the chemical potential gradient, $\nabla\mu_1$, between the grain boundary and the pore phase will drive diffusion. Diffusion occurs following Fick's law which relates the diffusive mass flux vector, J_1, to the chemical potential gradient (*Lehner*, 1990),

$$J_1 = -\frac{l}{1 - c_1}\nabla\mu_1, \tag{11}$$

with $c_1 = \rho_1/\rho$ the mass fraction and $l > 0$ a phenomenological coefficient taking into account the geometry of the grain-to-grain contact. For diffusion to occur, the water film confined at the grain–to–grain contact needs to support shear stress and enable diffusion of solutes (*Weyl*, 1959). The transport properties of the trapped thin film are probably different from those of the pore fluid. The diffusion flux is proportional to the mean thickness of the fluid phase trapped at the grain–to–grain contact (*Durney*, 1976), which is a function of the effective stress (*Renard and Ortoleva*, 1997), and the diffusion coefficient of the thin film is typically assumed to be lower than the one of bulk

water (*Rutter*, 1983). The actual diffusion coefficient is difficult to measure, according to the literature it is 2 to 10 times lower than that for bulk water (*de Meer and Spiers*, 1999). Grain boundary structure is a critical parameter allowing diffusion of dissolved material outside of the contact area. Several types of grain boundary structures are debated in the literature (*Tada and Siever*, 1986; *Gratz*, 1991; *de Meer and Spiers*, 1999; *Dysthe et al.*, 2002; *van Noort et al.*, 2008). Pressure solution might occur as a combination of plastic deformation at the grain-to-grain contact and free face dissolution at the edge of the contact (*Tada and Siever*, 1986; *Karcz et al.*, 2006). A number of studies have assumed that water is present at the grain boundary and have discussed several geometries (Figure 7B). The first one is an adsorbed thin film which can support shear stress (*Weyl*, 1959; *Rutter*, 1983). The second proposed structure and the one mostly used in recent models, is the island–and–channel structure (*Raj*, 1982; *Lehner*, 1990). There, stresses are transmitted through solid-solid contacts. In this structure, the fluid is at hydrostatic pressure and has pore fluid transport properties. A third type of structure is a clay filled grain boundary, which is very similar to the first type of structure if the film of clays is continuous. In this structure, the presence of clays in the grain boundary support a thicker fluid film which facilitates diffusion (*de Meer and Spiers*, 1999; *Renard et al.*, 2001). The last structure, mentioned here, is a thin-film short-circuited by cracks arrays (*Gratz*, 1991; *van Noort et al.*, 2008).

Due to removal of matter by diffusion, the transport path becomes longer as the contact surface area increases. This change in the diffusion path length may then induce a change in the rate limiting step of pressure solution (*Yasuhara et al.*, 2003), from interface reaction limited to diffusion transport limited. The presence of stylolites is also important due to their role in diffusive mass transfer. The diffusive transfer activity of stylolites increases with the increasing presence of fine-grained non-diffusible debris which increase the width of the stylolite (*Hickman and Evans*, 1995; *Renard et al.*, 2001).

The solutes transported out of the contact to the pore space may be transported again out of the pore space by diffusion or advection (*Lehner*, 1995; *Gundersen et al.*, 2002). When the system is open at the grain size scale, with fluid flow, pressure solution may be associated with mass loss and compaction. When the system is closed at the grain scale, the pore fluid becomes supersaturated with respect to the solid in solution and then precipitation occurs on the stress-free face of the grains in the pore. In some cases precipitation may be inhibited; for instance the presence of a large amount of clay minerals in the sediments may retard precipitation (*Tada and Siever*, 1989). If the

pore fluid becomes largely supersaturated, the diffusion is no longer proportional to the normal stress and pressure solution becomes precipitation controlled (*Lehner*, 1990). From fundamentals thermodynamics relationships characterizing the solid, aqueous and boundary phase, taking into account the three serial processes above described, macroscopic Gibbs equations were derived for granular aggregates deforming by pressure solution (*Lehner*, 1990; *Spiers and Schutjens*, 1990; *de Meer and Spiers*, 1999). Even though some differences exist between the different rate laws, especially in the definition of the parameters characterizing the grain boundary geometry, they more or less all take the following form (*Spiers and Schutjens*, 1990; *van Noort and Spiers*, 2009),

$$\dot{\epsilon} \propto \frac{GC(T)C_{eq}}{d^m}\frac{\sigma_e \Omega_s}{RT} f(\phi), \tag{12}$$

where $\dot{\epsilon}$ is the volumetric strain rate of the aggregate, G is a geometric constant function of the grain packing, Ω_s is the molar volume of the solid, C_{eq} is the concentration of the solid into the fluid at equilibrium, R the gas constant and T the temperature. $f(\phi)$ is a dimensionless function of porosity, ϕ, taking into account the porosity dependent changes in grain contact and pore wall area. The effective stress σ_e is equal to the difference between normal stress at grain contact and pore fluid pressure and d is the grain diameter. $C(T)$ is the thermally activated rate coefficient of the rate controlling process. $C(T)$ takes different forms depending on which of dissolution, diffusion or precipitation rate is the controlling rate mechanism. m is the grain size coefficient which varies depending on the rate limiting process. Assuming that dissolution and precipitation follow linear reaction rate equations, in the case of a diffusion controlled compaction rate $m = 3$, while for an interface-reaction controlled rate $m = 1$.

As pointed out by *Rutter* (1976), the linear relationship between stress and strain rate is only valid for low value of the effective stress (below 30 MPa). Above this value the exponential relation between stress and chemical potential cannot be neglected and leads to an exponential dependence of strain rate on stress (*Dewers and Ortoleva*, 1990), which has been verified experimentally on quartz (*Dewers and Hajash*, 1995; *Niemeijer et al.*, 2002; *Gratier et al.*, 2009).

Pressure solution can also be produced by coupled mechanisms (*de Meer and Spiers*, 1999), that is plastic, elastic, brittle deformation of the grain contacts coupled with grain scale dissolution of the grain contact, diffusion and precipitation. Plasticity coupled pressure solution creep is a plastic deformation coupled with removal of material from the contact by solution transfer. In this case, the driving force is the difference in the solid's chemical potential: $\Delta\mu \approx \Delta f^s$, where f^s is the Helmholtz free energy.

In this case the compaction rate is governed by the solution transfer's kinetics and the constitutive plastic behaviour of the solid.

Various parameters such as grain size, presence of clay, stress, time, cementation, porosity and solution chemistry influence the rate of pressure solution (*Tada and Siever*, 1989). Intergranular pressure solution theory (eq. 12) states that the compaction strain rate increases with decreasing grain size (*Weyl*, 1959; *Rutter*, 1983; *Tada and Siever*, 1989; *Lehner*, 1990). In sediments with a wide range of grain size, dissolution occurs preferentially within the small grain size and solute are then transported towards areas of the sediments with coarser grain size where precipitation is easier (*Weyl*, 1959; *Tada and Siever*, 1989). However, theory does not account very well for wide grain size distribution, indeed the creep equation given above is derived assuming a pack of monodisperse spherical grains, which is not very realistic for natural and experimental aggregates(*Niemeijer et al.*, 2009).

Clay minerals are not necessary for pressure solution to take place but can certainly promote it (*Tada and Siever*, 1989). Strain rate increase due to clay mineral may be related to the increase of the water film thickness which facilitates diffusion (*Weyl*, 1959) or to the fact that clay minerals prevent grain boundary healing by maintaining the contacts open (*Renard et al.*, 2001). For stylolites, however, if the clay layer within the stylolite becomes thick compared to the grain size, then the rate of pressure solution decreases (*Weyl*, 1959). In addition, the presence of clay minerals in the pore area could potentially slow down precipitation and, if precipitation is rate-controlling, pressure solution. Finally, the presence of clay minerals might affect the pore fluid chemistry by the release of cations, which could in turn speed the dissolution process and thus pressure solution, if dissolution is the rate-controlling mechanism

The volumetric strain rate due to pressure solution is proportional to the effective stress (eq. 12). Some theoretical works also state that a critical stress is needed to initiate pressure solution and when, due to dissolution, the grain-to-grain contact becomes large enough and grain contact stress becomes smaller than the critical stress, then pressure solution will stop and grain boundary healing will start (*Tada and Siever*, 1989; *Yasuhara et al.*, 2003; *van Noort et al.*, 2008). This critical stress is a function of the mineralogy of the compacting material. In sedimentary basins, therefore, the amount of overburden pressure (i.e. burial depth) is an important factor controlling compaction by pressure solution. To predict porosity loss by pressure solution, the burial history of the sediments needs to be taken into account since dissolution, diffusion and precipitation are time dependent phenomena. The solution chemistry also plays a major

role in controlling the rate of pressure solution. In the case of an under-saturated pore fluid, free-face dissolution might occur (*Engelder*, 1982; *Tada and Siever*, 1989). In the case of supersaturation building up in the pore space then the rate of dissolution will slow down and be a function of the precipitation kinetics (*Lehner*, 1990). Another possibility that could drastically prevent pressure solution and so maintain high porosity at depth is the invasion of the pores by a fluid with a low mineral solubility (*i.e.* gas, oil), since the compaction rate is linearly proportional to the solubility of the solid in solution (see equation 12).
To summarize, critical parameters to be considered when estimating the rate of pressure solution creep are grain boundary structures (*Croizé et al.*, 2010c) and their diffusivity, as well as dissolution and precipitation kinetics of the studied mineral in different solution's composition. The experimental relationship between compaction strain rate and applied stress, grain size or strains would also give information about the process.

Subcritical crack propagation: Crack propagation is described using fracture mechanics theory and would therefore have its place in the mechanical compaction section. However, as it will be presented here, slow crack propagation in rocks is affected by the environment and the fluid chemistry and can be seen as mechanical phenomenon facilitated by chemical effects. Crack propagation may occur at low stress and is usually characterized by a slow propagation, so it is often referred to as subcritical crack propagation or stress corrosion. A short review of the fundamentals of crack propagation in linear elastic material is given, followed by a discussion on the effects of environmental conditions on propagation velocity.
To study fracture mechanics, three important variables have to be taken into account: the applied stress, the size of the initially present flaw and the fracture toughness (*Anderson*, 1995). Fracture occurs when the applied stress is sufficient to break the atomic bonds of the solid (*Anderson*, 1995; *Scholz*, 2002). Crack propagation may be described using the energy criterion theory (*Griffith*, 1920) which is based on thermodynamic and energy balance. The theory predicts that a crack will propagate in order to lower the total energy of the system, by dissipating the elastic strain energy due to loading into the creation of a new surface.
From the energy criterion theory, the crack will propagate when the energy needed for a crack to propagate is sufficient to overcome the resistance of the material. The energy release rate, G, is the change in potential energy with crack surface area for a linear

elastic material,

$$G = \frac{\pi \sigma^2 a}{E}, \tag{13}$$

with σ the tensile stress, E the Young's modulus of the considered material, and the crack's length is equal to $2a$. For a material with linear elastic properties, the fracture toughness is independent on the size and geometry of the cracked body, the theory is therefore applicable at different scales. G is the mechanical driving force for crack propagation at equilibrium and is equal to R, the material resistance (*Olagnon et al.*, 2006).

The stress intensity factor $K_I = \sigma\sqrt{\pi a}$ characterizes the crack tip stresses in a linear elastic material. K_I is also a size independent material property. The relation between the energy release rate and the stress intensity factor is,

$$G = \frac{K_I^2}{E}. \tag{14}$$

The velocity of crack propagation can be related to G or K_I leading to the so-called $v - K_I$ or $v - G$ curves (Fig 8). For cracks to propagate, the energy release rate needs to overcome the material resistance to cracking, R. In general R may be set equal to the surface energy, γ, and therefore $R = 2\gamma$ under vacuum. Thus at equilibrium in a given environment,

$$G = R_e = 2\gamma_e, \tag{15}$$

with $\gamma_e < \gamma$ (*Olagnon et al.*, 2006). The above relationships (eq. 13, 15) show that crack propagation depends on the local stress as well as on the environment. Due to pre-existence of cracks in rocks, crack propagation may occur at stresses lower than required for slip or twinning (*Atkinson*, 1982; *Olagnon et al.*, 2006). The velocity of crack propagation may also be limited by the reaction rate between the corrosive species and the material bounds.

Propagation of cracks occurring at stresses lower than the critical stress required for fracture is an important fracture mechanism in the upper 20 km of the Earth's crust (*Atkinson*, 1982). The presence of water at the crack tip promotes weakening reactions or locally modifies the interfacial energy of the solid, making crack propagation easier. Subcritical growth occurs at a theoretical stress intensity factor K_i, which is between K_0 and K_c (see Figure 8). K_0 is the stress intensity factor below which, theoretically, no crack growth can occur, while at K_c the cracks starts to propagate dynamically (*Atkinson*, 1982; *Scholz*, 2002). For subcritical crack growth, the crack propagation

velocity is usually described by a power law defined by *Charles* (1958):

$$v = v_0 \cdot exp\left(\frac{-\Delta H}{RT}\right) \cdot K_I^n, \tag{16}$$

with v_0 being a pre-exponential factor, ΔH the activation enthalpy and n is the stress corrosion index, which is a material property constant. Since crack propagation is a function of the reaction rate at the crack tip, it might be affected by pH (*Lawn and Wilshaw*, 1975) and the chemical activity of water (*Røyne et al.*, 2011). Itself, subcritical growth induces a degradation of the rock elastic properties, and may explain the hydrolitic weakening of chalk (*Røyne et al.*, 2011).

3.2.2 Experimental studies on carbonate chemical compaction

Experimental studies on chemical compaction by pressure solution typically aim to establish a creep equation, which can be determined by the rate limiting step of the process, *i.e.* dissolution, diffusion, or precipitation. This is done in order to determine creep laws suitable for the material studied and easily applicable to natural systems, as it was for instance proposed for quartz (*Rutter*, 1983; *Gratier et al.*, 2009).
If pressure solution is the dominant deformation mechanism, the strain rate is influenced by the manipulation of dissolution, diffusion or precipitation rates. Following the theory of grain boundary diffusional pressure solution, the influence of parameters such as grain size, stress, porosity, temperature, grain packing or the presence of clays, should be studied to discriminate which of the three steps is the rate limiting one. Experimental work was conducted on carbonate rocks (*Baker et al.*, 1980; *Le Guen et al.*, 2007), and recent studies were carried out on the one hand on fine grained (3 to 80μm) super-pure calcite powders compacted using a microœdometer (*Zhang et al.*, 2002; *Zhang and Spiers*, 2005a,b; *Liteanu and Spiers*, 2009) or on fine to medium grained sand using standard œdometer, (*Croizé et al.*, 2010a), and on the other hand on calcite crystals indented by glass or ceramic indenters (*Zubtsov et al.*, 2005; *Croizé et al.*, 2010c). In a set of experiments, the effect of the presence of carbon dioxide dissolved into the pore fluid was also studied (*Le Guen et al.*, 2007; *Liteanu and Spiers*, 2009; *Grgic*, 2011; *Liteanu et al.*, 2012). Some experimental results of chemical compaction of carbonate rocks, as well as indenter experiments are given in Table 2. If subcritical crack growth is the main deformation mechanism, rocks fail at stresses lower than their short term failure strength. The effect of temperature and water on failure due to subcritical crack growth was studied in sandstones (*Chester et al.*, 2007; *Heap et al.*, 2009) or basalt (*Heap et al.*, 2011). Relatively few data are available on subcritical

crack growth processes in carbonates. The effect of pore water and temperature on failure of limestones was studied by *Rutter* (1972) and *Røyne et al.* (2011) investigated subcritical crack growth on calcite crystals.

Pressure solution, indentation experiments: Using a micro-indenter to pressure dissolve calcite was done in a few studies (*Zubtsov et al.*, 2005; *Croizé et al.*, 2010c). The principle of the experiment is to leave a loaded rigid indenter over a single calcite crystal and let pressure solution dissolve the area under stress below the indenter (Figure 9). The depth of the hole is monitored as a function of time using either optical or high resolution displacement sensors, allowing to reach resolutions of displacement rate down to one nanometer per hour. These studies have shown that a competition between pressure solution creep and subcritical crack growth was operating and that radial cracks may develop below the indenter. When a stress perturbation was imposed to the indenter, new cracks were created and the rate of pressure solution creep was significantly enhanced (see Figure 9b).

Zubtsov et al. (2005) carried out indentation experiments at effective stresses ranging from 50 to 200 MPa and at temperatures of 27°C and 40°C. In some experiments the applied stress was constant and the deformation was measured *ex situ*. In experiments conducted with a weak acid solution, a correlation was found between the depth of the hole and the applied stress. *Zubtsov et al.* (2005) also carried out high-resolution pressure solution creep experiments with continuous recording of the deformation. In that case, indenters were glass spheres, therefore the contact area between the indenter and the crystal increases with strain while the effective applied stress decreases. In presence of a fluid in equilibrium with calcite, a direct relation between the applied stress and the deformation rate is found. Dissolution of calcite formed holes beneath indenters and dissolved calcite precipitated then around these holes (Figure 9c-d). The development of microcracks beneath the indenters shortened the diffusion transport path at the indenter/calcite interface and increased the strain rate, pleading in favor of a diffusion limited process (*Zubtsov et al.*, 2005).

Croizé et al. (2010c) also used glass spheres as indenters, but only one glass indenter was used per experiment. In those experiments the initial rate of calcite deformation was found to be linked to the presence or absence of cracks propagating from the stressed area toward less stressed parts of the crystal. In addition it was noticed that dissolution of calcite below the indenter was complex, with the formation of an empty void below the indenter (Figure 9e). Dissolution below the indenter started due to the

high normal load applied, but crack propagation occurred so that the dissolved solid was easily transported outside of the contact area. Then dissolution continued below the indenter as a combination of plastic deformation and free surface dissolution driven by strain energy. The development of microcracks beneath the indenter was found to be linked to the presence of initial flaws in the crystal, and controlled whether deformation occurred by pressure solution, *i.e.* dissolution driven by normal load, or by pressure solution and crack propagation, *i.e.* dissolution mainly driven by strain energy.

Pressure solution experiments on aggregates and rocks: Experiments on calcareous oozes were conducted at effective stresses in the range 4 to 100 MPa and temperature between 22 and 180°C (*Baker et al.*, 1980). Experiments on fine-grained calcite were carried out under effective stresses ranging from 1 to 4 MPa at room temperature (*Zhang et al.*, 2002; *Zhang and Spiers*, 2005a,b). In these studies, dry control experiments were conducted to ensure that pressure solution was the main deformation process in wet experiments. Three main aspects were studied, that is the influence of effective stress, grain size and pore fluid chemistry on carbonate compaction by pressure solution.

A wider grain size distribution enhances the compaction rate for samples with the same median grains size (*Zhang and Spiers*, 2005a,b) and decreasing the average grain size increases the strain and the strain rate at fixed strains (*Zhang et al.*, 2002; *Zhang and Spiers*, 2005b). In *Zhang and Spiers* (2005a) the strain rate is linked to the grain size by an inverse power law with an exponent equal to three, indicating that diffusion is most likely the rate limiting step of the process. Compaction of carbonate rocks lead to the conclusion that dissolution controls the rate of pressure solution (*Baker et al.*, 1980). However, the sensitivity to grain size in other experiments does not allow any conclusion on which of the precipitation, diffusion or dissolution is the rate limiting step (*Zhang and Spiers*, 2005b).

In calcite aggregates, the strain rate is decreased by the addition of Mg^{2+} into the pore fluid at concentrations ranging from 0.01 to 1 mol/l (*Zhang et al.*, 2002; *Zhang and Spiers*, 2005a). Addition of PO_4^{3-} at 0.0001 to 0.001 mol/l (*Zhang and Spiers*, 2005a), and $NaHPO_4$ with concentrations ranging from 10^{-6} to 10^{-3} mol/l (*Zhang and Spiers*, 2005b) also decreases the strain rate. Conversely, compaction creep rate increases with NaCl concentrations of 0.1 to 0.5 mol/l (*Zhang and Spiers*, 2005a). Some of these results favour precipitation as a rate limiting step for pressure solution, however the diffusion controlled hypothesis can never be completely ruled out.

In carbonate environments, where pore fluids are constituted of meteoric or organic-poor water, calcite pressure solution should be a really active diagenetic process. This process is certainly much slower in environments where pore fluids are derived from seawater or are phosphate-rich due to organic reactions or biological activity (*Zhang and Spiers*, 2005b).

These laboratory experiments of deformation of rocks or aggregates also show that strain is not linear in time (Figure 10c-d), but follows a power-law dependence with a small time exponent between 0.2 and 0.3 (*Croizé et al.*, 2010a) or a more complex shape when, for example, carbon dioxide, a reactive component, is added to the pore fluid (*Le Guen et al.*, 2007; *Liteanu and Spiers*, 2009). An intriguing observation was also made by *Le Guen et al.* (2007) who observed intermittent creep during compaction of a limestone and interpreted it as a competition, at the grain scale, of plastic and pressure solution processes (Figure 10a-b). An alternative explanation would be that subcritical crack propagation occurs and triggers dissolution (creep) rate when reaching a critical size and density and that dissolution facilitates the progressive sealing of the fracture annihilating the effect of their development.

Subcritical crack growth: Creep experiments on Solnhofen limestones showed that water enhances strength weakening of the samples more than what should expected just through a mechanical action (*Rutter*, 1972). It was then suggested that the introduction of water in the samples reduced the interfacial tension leading to dislocation at the crystals surfaces. This allowed brittle creep of the samples and failure at stresses below the rock short term failure strength.

In the same study *Rutter* (1972) showed that temperature had little influence on the strength until 300°C. *Henry et al.* (1977) also observed subcritical crack growth in a micritic limestone at 20°C. If it assumed that dissolution at the crack tip is an important part of the subcritical crack growth mechanism, then it should be expected that carbonates brittle creep is less affected by temperature than sandstones since calcite solubility increases with decreasing temperature.

The rate of subcritical crack growth in calcite was found to be dependent on water activity (*Røyne et al.*, 2011). Similarly *Heap et al.* (2009) suggested that in sandstones the rate at which species can diffuse through the samples, rather than the amount of reactive species, is the limiting control on stress corrosion.

3.2.3 Conclusions on chemical compaction

In both methods, indenter experiments, and compaction of rocks or aggregates, pressure solution creep was established as the dominant deformation mechanism. In indenter experiments, diffusion was found to be the rate limiting step for calcite pressure solution. Conversely, various limiting steps were reported for wet aggregate compaction. The deformation rate of calcite is more important when the solution contains NH_4Cl which enhances the solubility of calcite.

Overall, no consensus on the rate limiting step of pressure solution in carbonates was obtained. This is to some extent related to the absence of good agreement between macroscopic strain rate laws and experimental results. For example, macroscopic creep laws propose a linear time dependence, whereas laboratory experiments show more complex rheological behaviors. A possible explanation is that present models do not take grain–size distribution or packing of aggregates accurately into account. In addition, the grain–to–grain geometry employed in the macroscopic models might not be suitable for carbonates.

Finally, in some experimental work the combination of pressure solution and subcritical crack growth was observed both at the grain scale and at the aggregate scale (*den Brok*, 1998; *den Brok et al.*, 2002; *Liteanu and Spiers*, 2009). The effect of this combination on calcite grain contact geometry was investigated in *Croizé et al.* (2010c) and on the overall compaction behaviour of carbonate aggregates in *Croizé et al.* (2010a) and it was concluded that the presence of initial flaws controls the overall strain. These combined effects could also be an explanation of complex rheological behaviors. In these studies lateral strain was not allowed, subcritical crack growth acted as a catalyst of pressure solution leading to porosity reduction by compaction. From uniaxial stress–cycling tests on oolitic limestone *Eslami et al.* (2010) concluded that while pressure solution was certainly an active process during compaction of the samples, subcritical crack growth was certainly not dominant since no dilatant deformation of the samples was observed. However to conclude that pressure solution dominates over subcritical crack growth in the porosity loss of carbonates, more experiments are needed in which the long term effects of the competition of these two processes in carbonates are studied.

4 Applications

4.1 Applications for porosity prediction

Effect of early cementation: In carbonates, the initial porosity values show a very large variability which then decreases with increasing burial depth (Figure 1). Consequently, early cementation is an important particularity of carbonate rocks. It contributes to an early loss of porosity but also plays an important role in the stabilization and strengthening of the framework (see section 2). This process can, to some extent, inhibit or retard mechanical compaction at shallow depth (*Kopaska-Merkel et al.*, 1994; *Budd*, 2001). Initial mineralogy, *i.e.* calcite or aragonite, and saturation index of pore waters with respect to those minerals, represent crucial control parameters for early cementation at shallow depth (*Meyers and Hill*, 1983; *Bjørlykke*, 1993).

Mechanical modeling: If early cementation does not affect carbonate sediments, then soil mechanics theory can be used to model compaction within the first 200 meters of burial (*Audet*, 1995; *Goldhammer*, 1997). Porosity loss as a function of the applied effective stress can be expressed by either the consolidation theory (*Terzaghi*, 1925) or the poroelasticity theory (*Biot*, 1941; *Rice and Cleary*, 1976) if unconsolidated sediments or rocks, respectively, are to be considered. These theories involve elastic moduli that can be determined experimentally for the different sediments (see section 3.1). The determination of the elastic parameters of rocks is crucial to understand their compaction during increasing burial and therefore for porosity prediction. Mechanical compaction is also affected by the pore and grain size distributions, the clay content and the presence of different lithologies leading to differential compaction (cf. section 2).

In carbonate sands, most of the mechanical compaction occurs at low stress, *i.e.* less than 5 MPa. When a locked state is reached, compaction proceeds by grain crushing with lower strain rates. Compaction of carbonate sands depends on the initial packing, the sand composition and the grain size, with finer grain–sized samples being less compressible. The shear modulus and the yield strength both increase with cementation. Rocks tested in the laboratory show a non–linear stress–strain relationship which can be related to the amount of pre–existing cracks and various types of pores present (*Baud et al.*, 2000). Porosity seem to be the main controlling factor on rock compressibility. Overall, carbonate rocks are less compressible than sandstones (*Wong et al.*,

2004). Understanding mechanical compaction and the determination of rocks elastic moduli is important. However, these parameters are affected by chemical compaction processes that alter the grain to grain contacts and modify the grain or rock framework stiffness. Moreover, experimental mechanical compaction shows that mechanical compaction alone usually cannot explain porosity values observed in nature.

Chemical modeling: Pressure solution as the main mechanism of chemical compaction is dependent on both stress and time. Pressure solution intensity is related to the amount of applied stress or overburden (*Royden and Keen*, 1980; *Schmoker and Halley*, 1982; *Spiers and Schutjens*, 1990) and to the duration of its application. The main factors influencing carbonate pressure solution are stress, temperature, grain size and porosity, advective and diffusive transfer and the pore fluid composition (cf. section 2). At depths greater than 500–800 meters, chemical compaction becomes the main mechanism of porosity reduction in carbonates.

Once pressure solution is initiated, various factors control its kinetics. High solubility of the mineral in the fluid increases the compaction rates whereas invading fluids with impurities that lower the solubility could prevent such a compaction. Pore fluid chemistry acts as a record of the evolution of calcite dissolution, and might explain the slowdown of calcite precipitation when inhibitors, for instance magnesium ions, are present. An increase in temperature enhances dissolution and precipitation kinetics of calcite, but diminishes its solubility. The diffusion part of pressure solution can be enhanced by the presence of clay minerals which provide both high diffusivity paths and prevent healing between grains. These clays can be randomly distributed in the sediment, or concentrated along dissolution seams or stylolites (*Weyl*, 1959; *Ehrenberg*, 2004; *Ehrenberg et al.*, 2006). Diffusion is also facilitated by the presence of open fractures and micro-cracks. However, sealing of these fractures annihilates this effect, leading to non–steady state behavior. Advective flow has some importance since it can remove dissolved species keeping the pore fluid undersaturated and allowing ongoing compaction. The saturation of the fluid, under- or over-saturated, may activate or annihilate, respectively, the pressure solution creep process. Grain size and sorting is also important because the stress concentration at grain contacts depends on these parameters and controls the onset of pressure solution creep (*Heydari*, 2000).

There is no consensus yet, neither from experiment nor from natural observations, for the rate–limiting step in pressure solution of carbonates that could constrain compaction modeling. However, a general rule is that when diffusion occurs along a trapped fluid

phase, diffusion can be used as limiting process and this would give maximum values for the compaction rate which may be deduced if the reaction rates (dissolution or precipitation) are slowed down by inhibitors of dissolution or precipitation, but only if those reactions are slowed down to below the rate of diffusion.
Models for pressure solution may take into account different grain boundary structures such as thin films or islands and channels models. However, some important effects are not taken well enough into account in those theories, for instance the effect of grain size distribution (*Niemeijer et al.*, 2009). Subcritical crack propagation may promote pressure solution by shortening diffusion paths (*Croizé et al.*, 2010c). The velocity of crack propagation is found to depend on the fluid in presence, since crack propagation at low stresses is controlled by the rate of chemical reactions at the crack tip and/or by the diffusion of corrosive species to the crack tip. Most of the experimental work on carbonate has focused on trying to identify the rate limiting step of pressure solution. However, comparing experimental data with theory, no consensus has been found so far. One explanation might be that the grain contact geometry is not described well enough to be able to apply theory to experimental work. Also the effect of grain size distribution and crack propagation at the grain contact need to be accounted for.

4.2 Implications for seismic response

Various parameters required for compaction modeling may be deduced from geophysical investigations, as the velocity of seismic waves measured from the ground surface contains informations on the porosity, the nature of the fluid, and the microstructure of underground carbonate rocks.

Use of rock petrophysical models to estimate seismic velocity: Rock properties include petrophysical properties (porosity, permeability) as well as texture and fabric of the rock. Seismic wave propagation is strongly affected by porosity (*Rafavich et al.*, 1984) and the types of pores present which can be highly variable in carbonates (*Anselmetti and Eberli*, 1993). Seismic properties of rocks also depend on microstructures (*Wang*, 1997), fractures and cracks especially affecting S-wave propagation (*Dürrast and Siegesmund*, 1999; *Couvreur et al.*, 2001), and pore fluids (*Assefa et al.*, 2003). Grain size, shape and sorting are as well important factors controlling seismic properties of rocks (*Eberli et al.*, 2003). Petrophysical properties of carbonates have been proven difficult to predict, this, therefore, leads to great difficulty in understanding carbonates

seismic velocities.

To apply rock–physics models to carbonates, the complex nature of the pore system and microstructures characterizing carbonate sediments needs to be taken into account. Recent rock–physics models take better into account the complexity of the carbonates pore system (*Agersborg et al.*, 2008), the possibility of intragranular porosity (*Ruiz and Dvorkin*, 2009) or the effect of non-uniform grain contact (*Bachrach and Avseth*, 2008). Applied to various experimental data where the different parameters are well controlled, these models may enable more accurate appraisal of the rock properties in the subsurface. The effect of chemical compaction on wave propagation in carbonate is still badly constrained, however.

Effect of chemical compaction on seismic velocity: Chemical compaction leads to changes in the bulk density of sediments with an increase of the density at places of cementation and a decrease at places of dissolution. Fluid chemistry influences carbonate compaction and therefore wave propagation in carbonate (*Croizé et al.*, 2010a). Gassmann theory of fluid substitution (*Gassmann*, 1951) is widely used to predict change in seismic velocities as a function of fluid content of the pore space. This theory assumes that the pore fluid does not chemically affect the solid frame and therefore, that the shear modulus remains constant. This assumption is in most of cases not applicable in carbonates. Conversely, chemical reactions lower the grain–to–grain contact stiffness (*Assefa et al.*, 2003; *Vanorio et al.*, 2010; *Croizé et al.*, 2010a) or promote crack propagation (*Adam et al.*, 2006; *Croizé et al.*, 2010a) both leading to lower ultrasonic or seismic wave propagation velocity than the ones predicted by Gasmann theory.

Effect of heterogeneous grain contacts on seismic velocity: Rock physics models of granular media are based on elastic properties of this media, which is a function of normal and tangential contact stiffness. Different models have been developed. For instance the Hertz model considers normal compression of elastic spheres (*Johnson*, 1985), while in the Hertz-Mindlin model or the Walton model oblique compression is taken into account (*Mavko et al.*, 2009). Attempts have been made to better take into account the complexity of the grain-to-grain contact into rock physic models. *Dvorkin et al.* (1991) included the increase of the elastic modulus due to cementation at the grain–to–grain contact. The non-uniformity of grain contacts is taken into account in rock physics templates developed for sand (*Bachrach and Avseth*, 2008). However, in carbonates the interface between grains may have a complex geometry constantly

evolving due to the interaction of pressure solution and crack propagation (*Croizé et al.*, 2010c). The weakening of the grain–to–grain contact stiffness due to chemical compaction needs to be better described by rock physics model in order to better predict velocity changes during production of hydrocarbons reservoirs, and more specifically during fluid injection in reservoirs to enhance hydrocarbon recovery or to geologically store CO_2. In addition, pore occlusion by precipitation would reduce porosity and likely increase stiffness and seismic velocity, especially in fractures.

5 Conclusion

Mechanical compaction in carbonates does not play a major role on porosity loss. Already at burial depths shallower than 1 kilometer mechano-chemical processes might control the rate of sediments compaction. Therefore, unlike siliceous sediments, carbonate compaction cannot be modelled only by mechanical compaction at depths corresponding to potential hydrocarbon reservoirs or to potential storage sites of CO_2.
However, understanding mechanical compaction in carbonates is important. At shallow depth, non–cemented sediments first lose porosity by mechanical compaction and reach a locked–state. The configuration reached by sediments after initial mechanical compaction determines the amount of grain–to–grain contacts and their size and therefore further porosity loss by subsequent chemical compaction.
Natural and experimental observations agree to say that pressure solution creep and fluid-rock interactions are the main processes of porosity loss in carbonates. Theory and experiments show that pressure solution depends on effective stress, porosity, grain size and pore fluid chemistry. Although most experimental studies infer that the rate limiting step for calcite pressure solution is diffusion, no firm conclusion can be formulated. The rate limiting step might be of different nature depending on compaction conditions, but this still needs to be explored more thoroughly. Under which conditions of pressure, temperature, fluid chemistry and porosity this process starts and stops in limestones and interacts with fracture healing and the progressive change in rock composition due to mass transfer, is also not fully understood.

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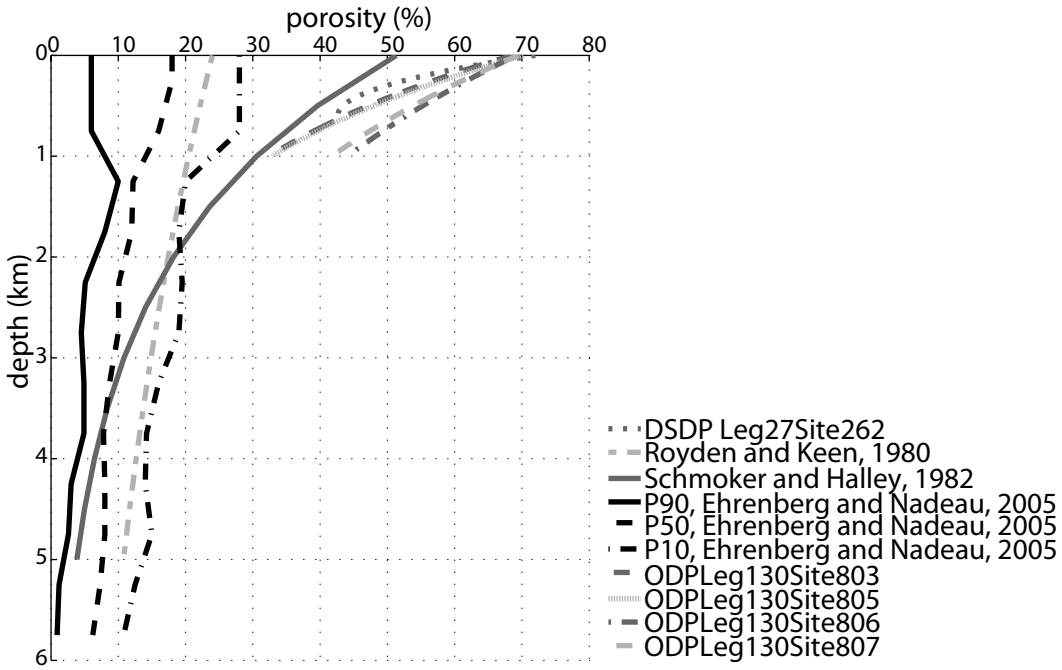


Figure 1: Porosity loss with depth in carbonates from different environments (fitting curves for DSDP leg 27 from *Hamilton* (1976), and for ODP Leg 130 from *Bassinot et al.* (1993). Usually, such data are fitted, to a first approximation, using equation 1.

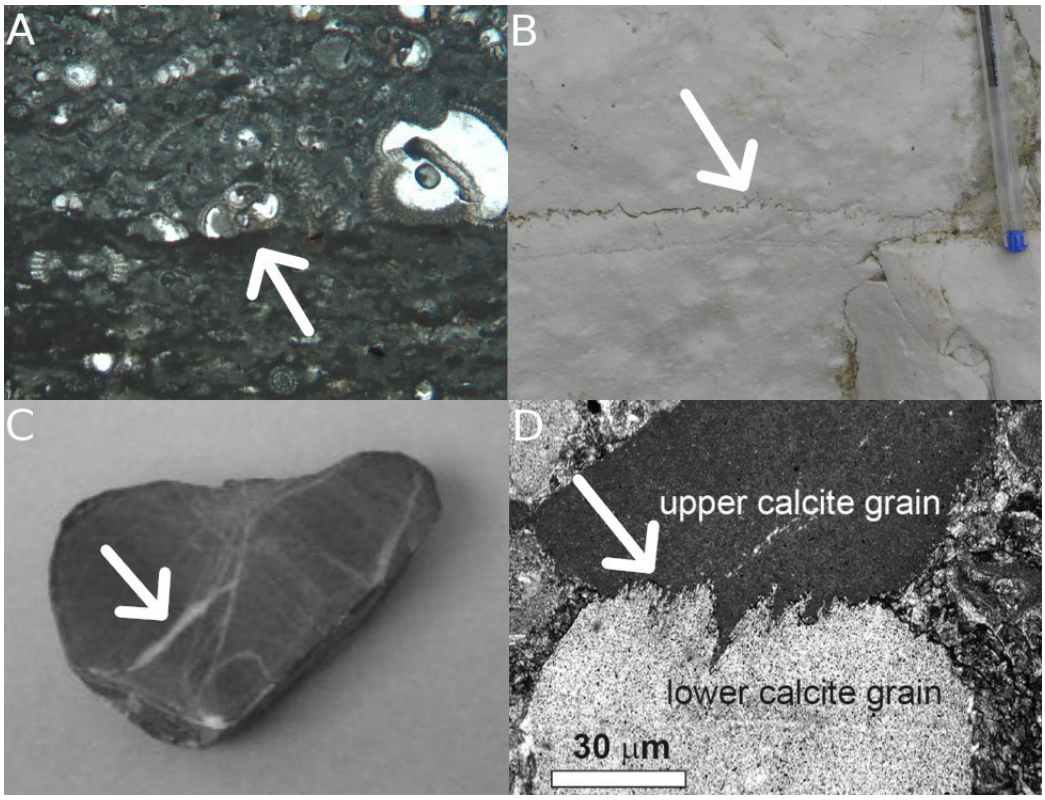


Figure 2: A) Microstylolite (white arrow), foraminifers are truncated by enhanced dissolution adjacent to a thin clay seam (picture from ODP Leg 192, Site 1183). B) Stylolite (white arrow) in Flamborough chalk, Yorkshire, UK. C) Limestone pebble fractures filled with calcite (white arrow), area of Grenoble, France (picture from *Gratier et al.* (1999)). D) Limestone from Mons, Belgium where single calcite grains (criniod fossils) show grain interpenetration (large arrow).

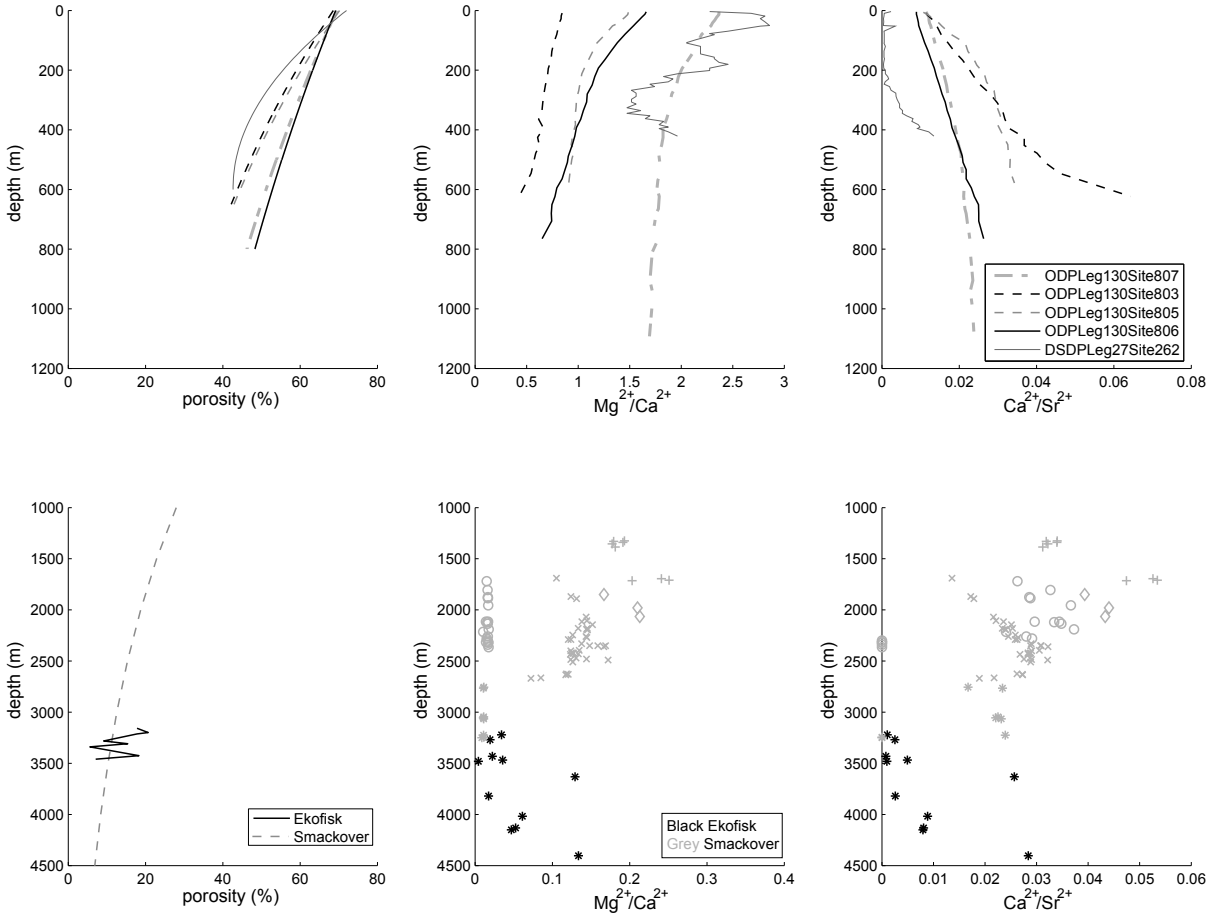


Figure 3: Comparison of porosity-depth trends with formation water chemistry. Upper graphs: shallow depth carbonates. Lower graphs: deep carbonates. (Smackover data: *Schmoker and Halley* (1982); *Moldovanyi and Walter* (1992); Ekofisk data: *Lubanzadio et al.* (2002); *Warren and Smalley* (1994).)

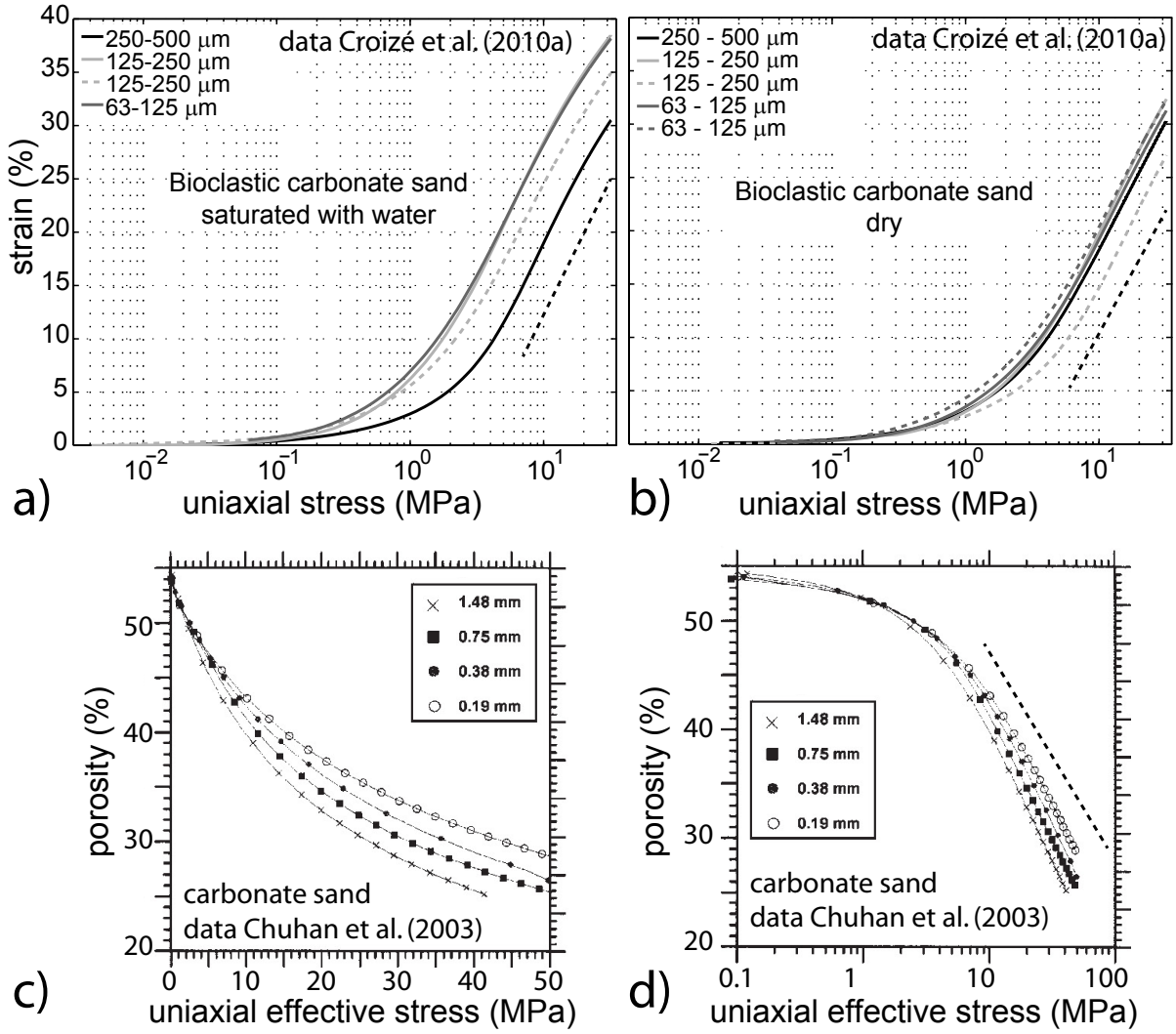


Figure 4: Mechanical compaction of carbonate sand. a-b) Compaction of bioclastic carbonate sand with different grain sizes, in presence of water or dry (*Croizé et al.*, 2010a). c-d) Porosity reduction of carbonate sand during uniaxial compaction, represented on linear plot (c) or semilogarithmic representation (d) for different grain sizes (*Chuhan et al.*, 2003). The dashed line serves as a guide for the eye to indicate where the strain–stress dependence can be approximated by a logarithmic trend.

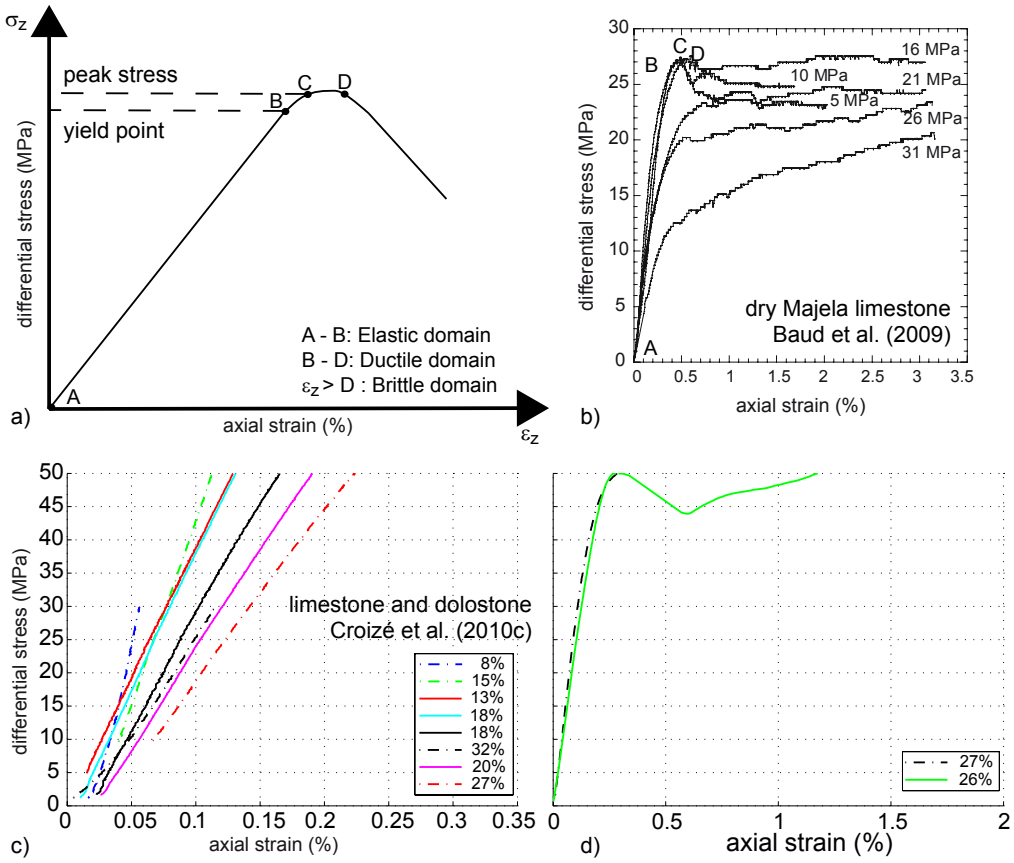


Figure 5: Mechanical compaction of carbonate rock. a) Stress–strain relationship for rock deformation. From A to B is the elastic and reversible part, B is the onset of yield and permanent deformation, C is the peak stress before the sample collapse in D due to formation of fracture. b) Triaxial conditions deformation of the Majela grainstone showing the transition from a deformation with peak stress (5, 10, 16 MPa confining stress) to more ductile deformation (pore collapse, cataclastic flow) above 20MPa confining stress. Data from *Baud et al.* (2009). c-d): Example of stress–strain relationship from uniaxial compression tests in dry limestones (solid lines) and dolostones (dashed lines), the porosity of the samples is indicated in the caption. Data from *Croizé et al.* (2010b).

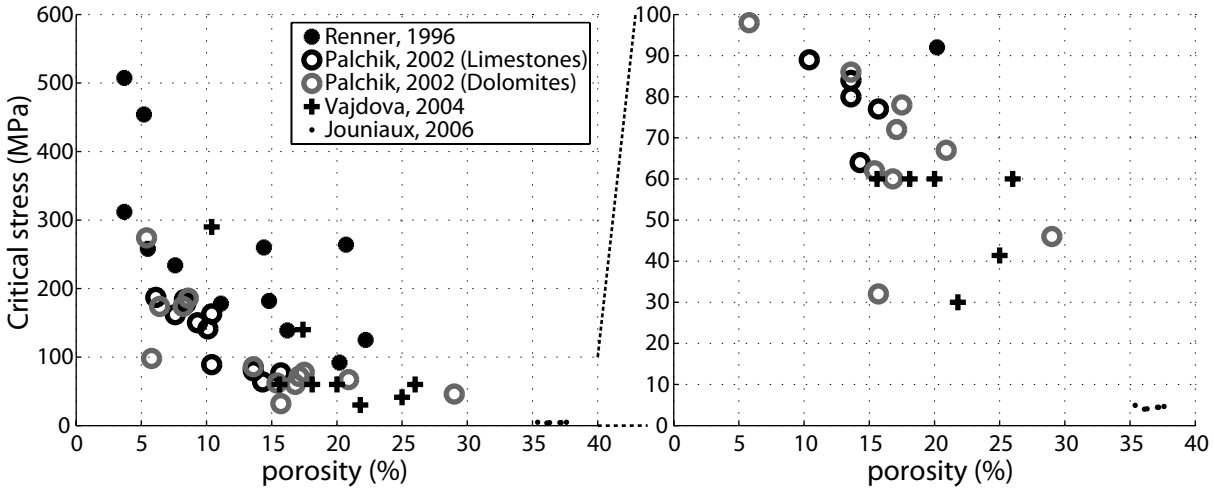


Figure 6: Critical axial stress in various carbonates as a function of porosity. The graph on the right side is a zoom of the lower stress part of the left side graph (all the tests were conducted under dry conditions, except for the data from *Jouniaux et al.* (2006).

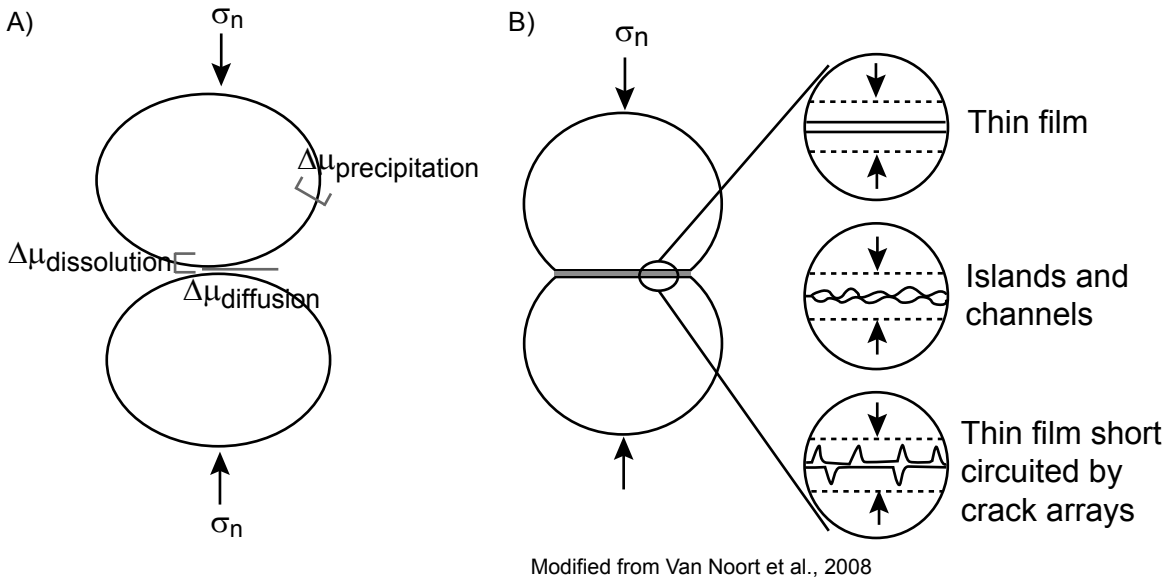


Figure 7: A) Schematic view of the three steps of pressure solution creep process. B) Three different grain boundary geometries considered in the literature.

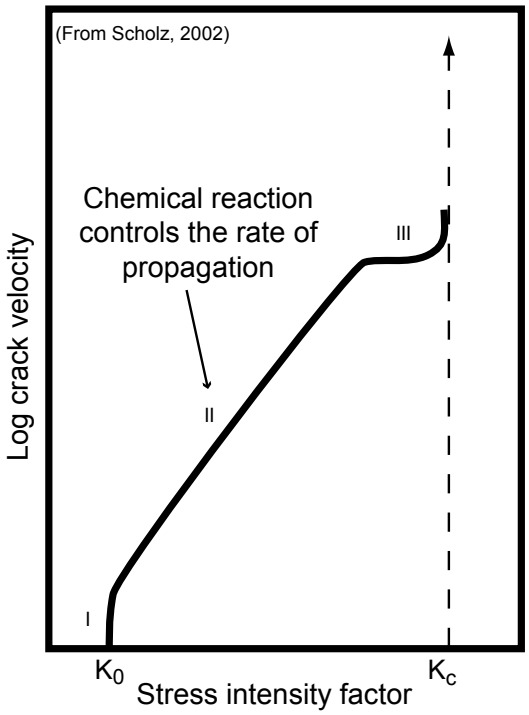


Figure 8: Evolution of the crack propagation velocity at stress intensity factor lower than the critical stress intensity factor.

Table 1: Some elastic moduli values for particular limestone and chalk rocks referenced in the literature.

Rock	ϕ	ρ	E	ν	K	b	β	σ_c[a]	ref.
	%	g/cm^3	GPa		GPa		GPa^{-1}	MPa	
Limestones:									
Solenhofen	3	2.62	64	0.29			0.016	245	1, 3
Villeperdue	6.4				36	0.41			2
Tonnerre	13				19.3	0.53	0.052	72.4	2, 3
Chauvigny	17				16.3	0.69	0.061	42	2,3
Lavoux	21.9				13.8	0.77	0.072	30.4	2,3
Majella	30							37[b]	4
Saint Maximin	37							17[b]	4
Adana/Ceyhan		2.71	26.5					78	5
Adana/Karaisali		2.43	14.4					39	5
Hatay/Iskenderun		2.96	43.1					117	5
Adana/Pozanti		2.97	45.4					121	5
Chalk:									
Lixhe	42.8				3.8	0.91	0.263	7.7	2, 3

[a] σ_c: Uniaxial compressive strength

[b] Effective pressure at the onset of grain crushing

[1] : *Fjær et al.* (1992)

[2] : *Fabre and Gustkiewicz* (1997)

[3] : *Vajdova et al.* (2004)

[4] : *Baud et al.* (2009)

[5] : *Yasar and Erdogan* (2004)

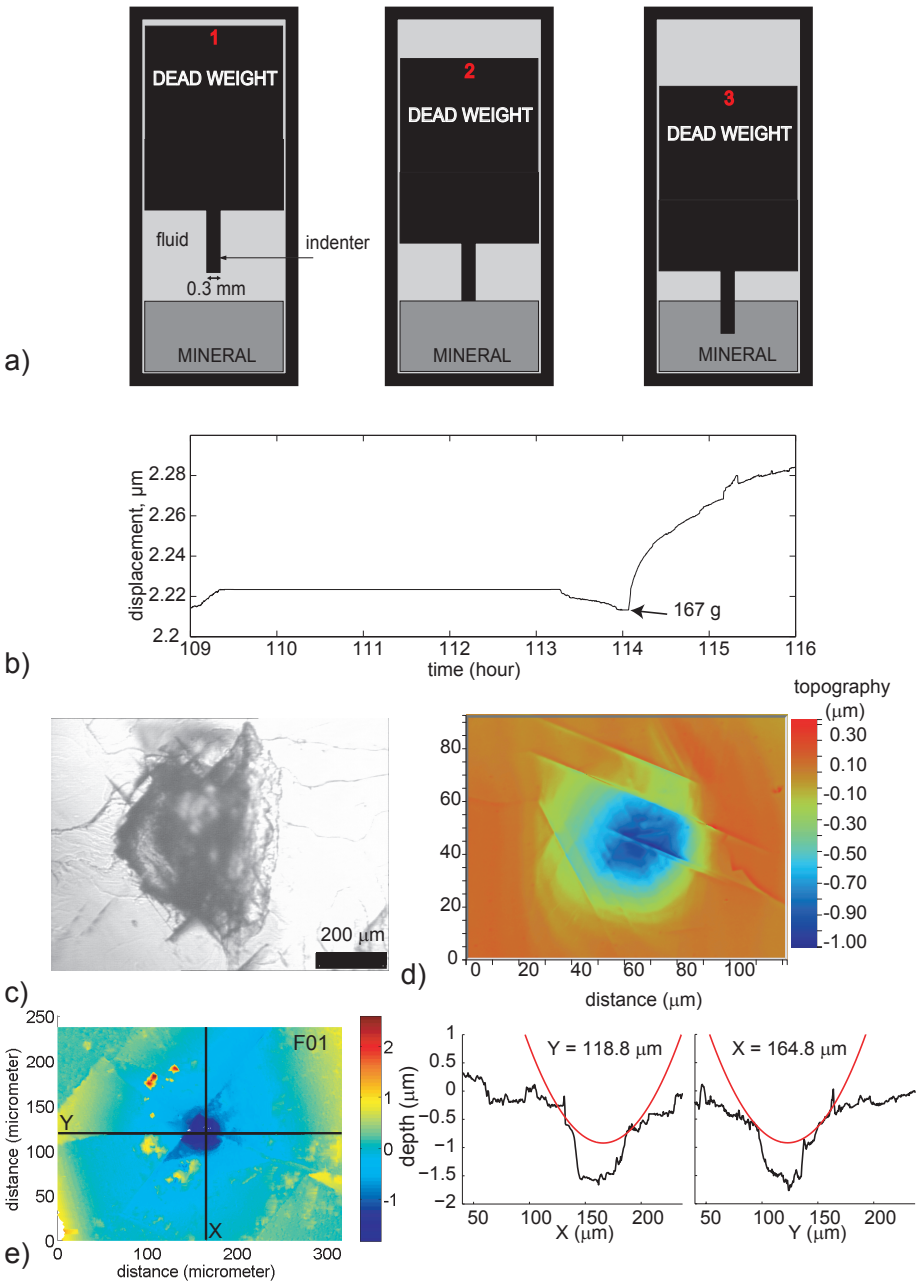


Figure 9: Indenter experiments on calcite. a) Principle of the experiment (*Zubtsov et al.*, 2005). b) Time evolution of the displacement of the indenter into a calcite crystal. At time=114h a stress perturbation was imposed, leading to enhanced deformation. c) Optical imaging of a hole obtained by indentation of a calcite monocrystal. d) White light interferometry imaging of the topography of a hole under the indenter and presence of radial cracks in the calcite. e) White light interferometry of a hole into a calcite crystal below a spherical glass indenter. The two cross-sections X and Y show that a hole has developed below the indenter represented as red curves. Adapted from *Zubtsov et al.* (2005) and *Croizé et al.* (2010c).

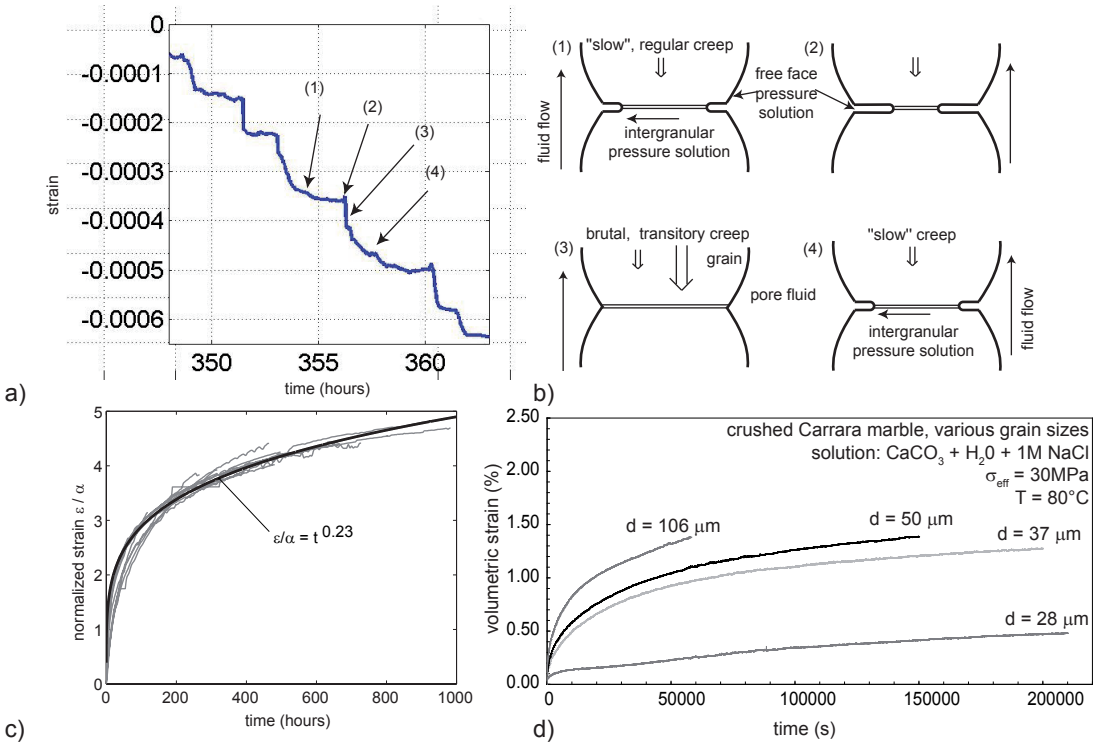


Figure 10: Non-linear time dependence of chemical compaction in carbonate rocks and aggregates during laboratory experiments. a) Time evolution of uniaxial deformation of a limestone core in the presence of CO_2dissolved into the pore fluid. b) The vertical shortening of the core sample occurs by successive increments of fast deformation and more quiet periods of slow creep. This observation illustrates the possibility of intermittent creep in carbonate rocks. This can be explained by a competition of pressure solution and plastic deformation at grain contacts (*Le Guen et al.*, 2007). c) Compaction as a function of time of a carbonate sand, showing a power law dependence in time (*Croizé et al.*, 2010a). d) Compaction creep of crushed Carrara Marble showing also a non-linear dependence in time (*Liteanu and Spiers*, 2009).

reference	material composition	load conditions	σ_{eff} (MPa)	T (°C)	grain size (µm)	duration maximum (h)	fluid composition	initial porosity	maximum compaction strain achieved	strain rate or indentation rate	strain mechanism / observations
[Rutter, 1972]	Rock: Solnhofen limestone, Carrara marble	triaxial loading	150	200 to 500	5 to 20 (limestone), 200 (marble)	-	water or air	5%, 0.1%	-	$3*10^{-5}$ s^{-1}	no effect of pressure solution creep observed in these experiments, weakening effect of water due to its action at grain boundaries, perhaps stress corrosion
[Sprunt and Nur, 1977]	Rock: Carbonate slab	uniaxial loading	up to 45	22	-	170 to 840	air or saturated/undersaturated/dilute HCl or acetic acid aqueous solution (< 0.1M)	-	30% (limestone)	-	free face dissolution and deformation of an initially circular hole due to elastic strain energy
[Baker et al., 1980]	Aggregates: carbonate sediments, calcite	triaxial compaction	4 to 100	22 to 176	62 to 300	21 to 240	sulfate-free sea water; with monitored oxygen isotope composition	10 to 49%	-	-	precipitation of carbonate driven by surface energy and strain energy
[Zhang et al., 2002]	Aggregate: calcite	uniaxial compaction	1 to 4	22	15 to 70	600	saturated aqueous solution or decane or air	50%	1%	10^{-9} to $2*10^{-7}$ s^{-1}	pressure solution creep in calcite controlled by precipitation kinetics
[Zhang and Spiers, 2005a]	Aggregate: calcite	uniaxial compaction	1 to 4	22	6 to 14	480	saturated aqueous solution + addition of 10^{-6} to 10^{-3} M phosphates	46 to 56%	2.6%	10^{-9} to 10^{-6} s^{-1}	pressure solution creep controlled by interface-reaction kinetics, phosphate ions decrease the strain rate by two orders of magnitude
[Zhang and Spiers, 2005b]	Aggregate: calcite	uniaxial compaction	1 to 4	22	2 to 68	288	saturated aqueous solution + addition of various salts (NaCl, $MgCl_2$, phosphate) or silicon oil or air or alcohol or decane	39 to 52%	2%	10^{-9} to 10^{-4} s^{-1}	diffusion-controlled pressure solution, salinity (up to 0.5 M) increases the rate of pressure solution creep for calcite. The presence of some inhibiting ions or oil reduces the strain rate
[Zubtsov et al., 2005]	Single crystal: calcite	single contact	50 to 200	40	50 to 300	1000	saturated aqueous solution or 5% NH_4Cl or air	-	-	0.05 to 50 nm/h	diffusion-controlled pressure solution, microcracks increase the strain rate for one order of magnitude at least
[Le Guen et al., 2007]	Rock: limestone	triaxial loading + fluid flow	2.2 to 8	25 to 80	-	11800	saturated aqueous solution + dissolved CO_2	16 to 30%	1%	10^{-11} to $2*10^{-9}$ s^{-1}	enhancement of creep in limestone by injection of dissolved CO_2
[Liteanu et al., 2009]	Aggregate: limestone	uniaxial compaction	30	80	28 to 106	58	saturated aqueous solution + supercritical CO_2 + salts (0 to 3M NaCl or $MgCl_2$)	25%	2%	10^{-7} to 10^{-5} s^{-1}	supercritical CO_2 or high salt content increases the compaction rate of calcite
[Croizé et al., 2010a]	Aggregate: carbonate	uniaxial compaction	10 to 30	22	63 to 500	250	saturated aqueous solution + 5% NH_4Cl or decane	28 to 48%	47%	$6*10^{-11}$ to $2*10^{-10}$ s^{-1}	pressure solution creep has power-law time dependence
[Croizé et al., 2010b]	Single crystals: calcite against glass or sapphire	single contact	430 to 830	22	40 to 80	25	saturated aqueous solution	-	-	up to 20 nm/h	nanometer resolution roughness measurements indicate that the rate of pressure solution creep in calcite is controlled by interface roughness and formation of cracks
[Zhang et al., 2010]	Aggregate: calcite or crushed limestone	uniaxial compaction	20 to 47	28 to 150	12 to 86	960	saturated solution or air or oil, intermittent flow	25 to 34%	up to 10%	10^{-8} to 10^{-4} s^{-1}	diffusion-controlled pressure solution creep at low strains; for high strains, the strain rate decreases (interface-controlled process)

Table 2: Selected experimental studies of creep in carbonate rocks.