

EFFECTS OF SALINITY ON THE MORPHOLOGY OF DISSOLUTION PITS IN CALCITE -IMPLICATION FOR CO₂ SEQUESTRATION IN CARBONATE ROCKS

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ABSTRACT

Fluid cell AFM (Atomic Force Microscope) dissolution experiments were carried out on cleaved {10 $\bar{1}$ 4} calcite surface to investigate the effects of fluid salinity on the Nano-scale dissolution topography. Below a critical salinity value (~0.8 M), the dissolution surface was characterized with dense deep etch pits and the dissolution was dominant by deepening of dislocations. Above the critical salinity, the dissolution surface flattened with much less dense but well-defined rhombohedral shape etch pits and the dissolution rate was dominated by lateral step retreating. Uni-axial compaction experiments on polycrystalline calcite were carried out at room temperature and 4 MPa applied stress, flooded with various saline (NaCl) solutions. The same critical salinity was found i. e. below salinity (<0.8 m/l NaCl), compaction by pressure solution were promoted by salinity in the pore fluid. However, when salinity exceeded the critical value, the increment of compaction creep rates in calcite disappeared. The combined AFM observation and compaction measurements suggest that the grain boundary structures under active pressure solution are similar to nano-scale dissolution topography seen under AFM. The roughening and flattening of grain boundary micro-structure, controlled by salinity, should play a role in controlling the nano porosity and alter the capillary pressure in carbonate rocks, which is a main factor for CO₂ sequestration.

INTRODUCTION

Carbonate rocks are the source rocks for 50% of world oil and gas reservoirs and represent the stored CO₂ from the atmosphere of our planet in geological times (1). Carbonate formations are important reservoirs for CO₂ sequestration. The dissolution and precipitation of calcite are of great importance for many geological processes such as the global carbon cycle, carbonate diagenesis, fault sealing and healing in carbonate rocks as well as CO₂ sequestration (2). One of the well known coupled dissolution and precipitation processes in carbonates is pressure solution. Pressure solution in carbonate rocks is an efficient deformation mechanism under diagenetic and low-grade metamorphic conditions (3), which controls the carbonate reservoir properties i. e. their porosity and permeability, and hence a great interest for hydrocarbon migration and storage.

Recently, experiments in polycrystalline, single calcite crystals and in natural chalk prove the occurrence of pressure solution from room to 150 °C temperatures (4), (5), (6), (7) and the importance of the chemistry of the pore fluids.

The rates of compaction by pressure solution are also a function of the grain boundary structure. However, the grain boundary microstructure of calcite under active pressure solution remains largely unknown, although it is believed to be a structure of nano scale thick. Atomic Force Microscopy provides a nano-scale observation of the topography of dissolving mineral surface. In this study, we investigate both effects of salinity on free surface dissolution of calcite (AFM) and on the compaction creep rate of polycrystalline calcite by pressure solution. Our results show that at a critical salinity value the dissolution mechanism in cleaved calcite surfaces and the compaction creep rate both changed. The correlation of the dissolution topography seen by AFM and the compaction rates in various saline solutions, suggests that there is a similarity between of the topography of free surface under active dissolution and the grain boundary structures undergoing active pressure solution. The morphology of the dissolution of calcite on the surface provides the basic information of dissolution mechanisms. The effects of salinity on the dissolution morphology in calcite infer the importance of the salinity on the generation and destruction of nano porosity in carbonate rocks.

EXPERIMENTS

Two sets of experiments were carried out, namely uni-axial compaction in polycrystalline calcite and fluid cell equipped Atomic Force Microscope (AFM) observation on cleaved calcite surfaces. The effects of salinity on the compaction rates in the polycrystalline calcite and dissolution surface morphology at the cleaved calcite surface were compared.

Uni-axial Compaction Experiments in Polycrystalline Calcite

The starting material used in our compaction experiments was super pure granular calcite (Merck 99.95% pure) with an average grain size of 15 μm . Pre-saturated CaCO_3 solutions with various salinities (NaCl) were made for individual calcite samples. The experiments were performed using dead-weight compaction set-ups. A high precision dial gauge was used to measure upper piston displacement and hence sample compaction. In all experiments, samples were first pre-compacted for 30 minutes under dry condition at applied axial stress of 8 MPa. The aim here was to obtain a well-controlled 'starting aggregate' with reproducible porosity, and to eliminate purely physical grain rearrangement and brittle/plastic deformation effects during subsequent wet compaction at a lower stress. After dry compaction, wet testing was carried out at applied axial stress of 4 MPa.

AFM Observation

Rhombohedral calcite fragments were cleaved from single crystals of optical quality Iceland Spar (Chihuahua, Mexico) with a knife blade. The fragments were examined by optical microscopy to ensure that the cleaved surfaces were free from macroscopic steps and small particles. The calcite $\{10\bar{1}4\}$ surfaces with ca. $3\times 3\times 1$ mm in size, freshly cleaved prior to each experiment, were used. *In situ* observations and measurements of the calcite surfaces during dissolution were performed using Atomic Force Microscope (AFM) equipped with a fluid cell, working in contact mode. The scanning frequency was 3 or 5 Hz, and the areas scanned were 5×5 and 10×10 μm . Saline solutions in concentrations ranging from 0.1 m/l to saturation flowed continuously at 50 ml/h⁻¹ through the fluid cell containing the sample crystal.

RESULTS

Compaction Experiments

The compaction experiments carried out in this study are listed in Table 1. Dry pre-compaction at 8 MPa produced a few percent of instantaneous strains in all cases. Samples subsequently loaded at 4 MPa and then flooded with chemically inert decane, or loaded dry, showed no measurable compaction creep. However, those flooded with pre-saturated CaCO_3 solutions containing various salinities compacted by 0.5-1.0 % within 7 days, as illustrated in Figure 1. It is noticeable that the samples with salinity of 0.1 and 0.5 m/l reached largest strains. The samples with low salinity (< 0.1 m/l) and high salinity (> 1 m/l) reached nearly the same strain.

AFM Observation

Calcite crystal surfaces flushed with pure water and brine show different morphology under AFM. Figure 2a shows the dissolution surface of calcite contact with pure water. The dissolution pits were characterized by a shallow rhombohedral shape. With increasing salinity, the same surface became rough. Figure 2b shows an image of sample contacted with salinity of 0.2 m/l NaCl, the dissolution etch pits became deeper and had the shape of an inverted pyramid. The density of the etch pits increased with increasing salinity. In some cases, the etch pit obtuse edges became curved and even disappeared so the pits became triangular (Figure 2c). When the salinity exceeded a critical value (0.8-1 m/l), the etch pits became very-well developed rhombohedral shape with straight edges. Big dissolution pits with flat bottoms, and with straight edges were developed in high salinity fluid (Figure 2d). In the mis-cut areas where steps were very well developed, the steps were bounded and the terraces were flattened. The density and shape of the dissolution etch pits were controlled by the solution salinity.

DISCUSSION

The effects of salinity on the creep rate of polycrystalline calcite

The mechanism for compaction in wet polycrystalline calcite under our experimental conditions is dominated by pressure solution (4), (5), (6). The rate limit step for the pressure solution is diffusion process of the dissolved material through grain boundary. It is well established that the creep rate of pressure solution in the diffusion control case is a function of diffusion product DCS . D is the diffusion coefficient, C is the solubility of calcite, and S is the average thickness of the grain boundary film under active pressure solution.

In the range of 0-0.5 m/l salinity, the effects of salinity on the rate of creep in calcite is consistent with the theoretical prediction i. e. creep rate increases with increase of calcite solubility as a result of increase of pore fluid salinity. However, in the high salinity range, the solubility of calcite continues to increase with increasing salinity, while the compaction creep rate does not increase. This means that the rest of the diffusion product DCS , i. e. the diffusion coefficient or grain boundary (effective) thickness, changed in high salinity.

Effects of salinity on the dissolution etch pits

It is well established that the bulk solubility of calcite increases with increase of salinity. For the intermediate salinity, the observation of the deepening of dissolution etch pits and increase of density of pits under AFM is consistent with the bulk experimental

results and the thermodynamic modeling. In high salinity conditions (>0.8 -1 m/l), the dissolution mechanism changed the dominant morphology into the lateral retreat of steps (edges of dissolution pits). The mechanism change results in forming of shallow well-defined rhombohedral dissolution etch pits with much less density.

Table 1. List of compaction experiments.

| ID | Grain size (μm) | Pore fluid | stress (MPa) | initial porosity (%) | Final strain (%) |
|------|------------------------------|------------|--------------|----------------------|------------------|
| Tb19 | ~14 | Dry | 4 | 51.8 | 0 |
| Tb20 | ~14 | Solution | 4 | 50.01 | 0.92 |
| Tb24 | ~14 | Solution | 4 | 49.5 | 1.1 |
| Tb36 | ~14 | Solution | 4 | 50.9 | 1.5 |
| Tb38 | ~14 | Decane | 4 | 52.2 | 0 |
| Tb40 | ~14 | Solution | 4 | 49.6 | 1.5 |
| Tb66 | ~12 | Decane | 4 | 46.7 | 0 |
| Tb67 | ~14 | Solution | 4 | 50.4 | 0.84 |
| Tb69 | ~6 | Solution | 4 | 45.96 | 1.48 |
| Tb70 | ~22 | Solution | 4 | 46.96 | 1.19 |
| Tb71 | ~22 | Solution | 4 | 50.77 | 0.92 |
| Tb78 | ~12 | Solution | 4 | 47.46 | 1.08 |
| Tb88 | ~14 | Solution | 4 | 53.68 | 2.81 |
| Tb98 | ~14 | Decane | 4 | 53.2 | 0.05 |

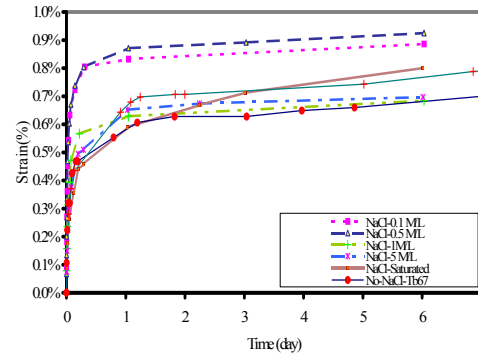


Figure 1. Creep curves of polycrystalline calcite filled with various saline solutions.

When increasing the salinity in the fluid (below ~ 0.8 m/l), chemical potential in the fluid is lowered with respect to the solid surface, the dislocations can be opened. The sudden increasing of dissolution etch pits density seen in AFM when salinity is increased can be interpreted as the opening of screw dislocations. When salinity increases to a critical point (~ 0.8 M), the etch pits are strictly rhombohedral shapes with very straight edges and with very flat bottoms. The density of etch pits is very much less than those showed in the low salinity case. These etch pits can develop into a very large size, normally much larger than those developed in the low salinity solution. Also the lateral spread of steps or the edges of dislocation is very fast. This fast retreat of the edges of the big pits causes the shallow pits to be easily swept out and the new potential sites of screw dislocations cannot be generated, the screw dislocations were swept out before growth could be seen. With the development of very few big sized etch pits, the total surface of the dissolution surface was smoothed.

Integration of compaction rate measurements and AFM observations

The fact that the compaction creep rates changed at the same salinity as the dissolution of cleaved surfaces (observed under AFM) suggests that there is a relationship between the creep rate and dissolution observations (mechanisms). Our explanation is that the flattening seen in the cleaved surface at high salinity also happened in the polycrystalline calcite sample i. e. the grain boundary where dissolution occurred during pressure solution. The flattening of the grain boundary will thin the grain boundary water film. The thinning of grain boundary water film will thus reduce the diffusion of dissolved material out of the grain contacts. In the case of grain boundary diffusion controlled pressure solution, the rate will be reduced. This implies that the surface dissolution at the nano scale has a similar character with the dissolution at the grain boundary confined water film. The effects of salinity on the dissolution etch pits may provide an explanation for the nano porosity in carbonate rocks (1).

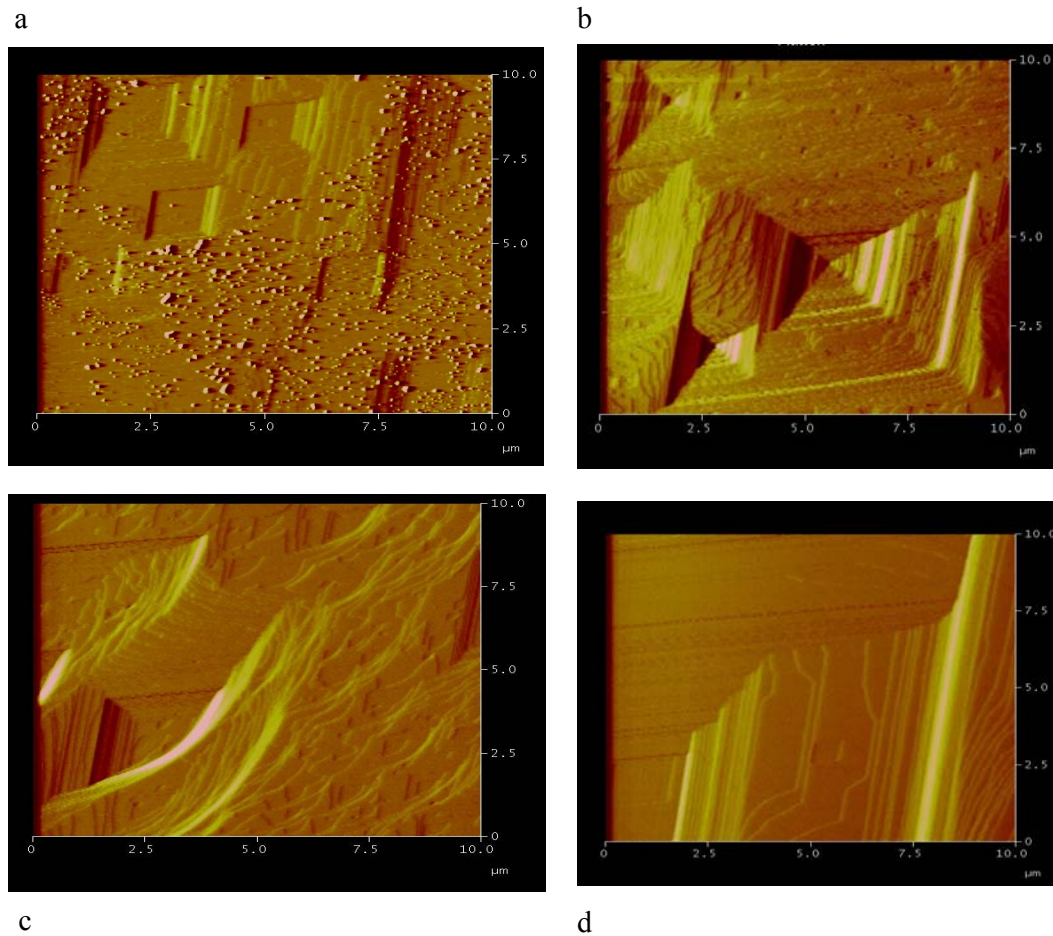


Figure 2. Microphotography of AFM image of dissolution pits developed on the surface of calcite with various salinity (NaCl) in fluids. a) Zero salinity; b) 0.2 m/l salinity, note the inverse pyramid shape of the pits; c) 0.5 m/l salinity, note the curved edges of the deep etch pits and the roughness of the surface (dense etch pits); d) salinity higher than 1 m/l, etch pits become very well-defined rhombohedral shape.

Implications

The effects of pore fluid salinity on the dissolution pits and compaction creep observed in our study may have significant implications for many geological processes in carbonate rocks. First salinity control of the density of dissolution pits affects the grain surface areas hence may affect the reaction/adsorption related processes such as in the CO₂ sequestrations. Secondly, the grain boundary microstructure in the carbonate rocks is influenced by the pore fluid salinity. The geological processes, which occur at the grain boundaries such as diagenesis, pressure solution and re-crystallization via grain boundary migration should be influenced by the pore fluid salinity. Modeling of such processes should take into account the effects of pore fluid salinity.

CONCLUSIONS

Pressure solution was the dominant compaction creep mechanism under these testing conditions. At low salinity (< 0.8 m/l), the NaCl in the pore fluid solution increased the compaction rate in the polycrystalline calcite, as a result of increasing calcite solubility and roughening grain boundary structure. However, when salinity exceeded the critical value (about 0.8 m/l), the increment of compaction creep rates in calcite by increasing

pore fluid salinity disappeared. Below the critical salinity value (~ 0.8 m/l), the dissolution surface was characterized with dense deep etch pits and the dissolution was dominant by deepening of dislocations. Above the critical salinity, the dissolution surface flattened with fewer but better-defined rhombohedral shaped etch pits and the dissolution (rate) was dominated by lateral step retreating. The combined observations suggested that the grain boundary structures under active pressure solution are similar to nano-scale dissolution topography seen under AFM. The roughening and flattening of grain boundary microstructure, which is controlled by salinity, should play a role in controlling the nano porosity. The induced nano porosity will alter the capillary pressure in carbonate rocks, which is a main factor for CO₂ sequestration.

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