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Escape of Supercritical-CO_2 Fluids Trapped in Calcite Nano-metric Pores

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Abstract. Flow of supercritical CO_2-bearing fluids through a rock is a fundamental phenomenon which acts upon a great many geological processes ranging from seismic activity to formation of ore deposits. Atomic Force Microscopy scanning experiments allowed us to infer movement of supercritical CO_2-bearing fluids through calcite crystals and relate it to natural decrepitation of nanoscale fluid inclusions. Calculated velocities exceed the rate of diffusion predicated via current vacancy models by several orders of magnitude implying that CO_2-rich fluid movement through micro and nano-pore space may presently be greatly underestimated.

1 Introduction

The rheological properties of complex fluids are of paramount importance for movement gas and water through rock matrices. Earlier work [1, 2, 3, 4] suggests that fluids confined at the micrometric (or nano-metric) scale may move fast and that this movement may play a key role in solid-fluid reactivity. At the micron scale fluid movement and solid permeability at grain boundaries have often been explained in terms of interfacial energy, while when a small amount of fluid is trapped by surface tension, the capillarity pressure is sheared. At this scale, fluids must be present in the form of absorbed molecular films, non-equilibrium or wetting film, as well as isolated fluid inclusions maintained by steric forces originating from a hydrated layer at the mineral surface [5].

In this work we focused on the fate of these trapped fluids, known as fluid inclusions, by addressing experimental and theoretical considerations of displacement processes at the lower micrometric and nano-metric scale (i.e. the scale of pores and grain boundaries), which have been often neglected in continuum-scale modelling.

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2 Nano-fluid descriptions

When sequestrating carbon dioxide in subsurface reservoirs for potentially limiting atmospheric CO_2 concentration, macroscopic modification of the ground water composition has been observed at the field scale. The complete physical description able to predict the structure developing within the geological medium is however still lacking. Indeed, when CO_2 is injected into a brine-carbonate environment it can either be dissolved in water or trapped in carbonate minerals during precipitation.

Cohen and Rotthman [6] proposed a mechanism leading to a carbonate-encrusted bubble in which a single bubble of pure CO_2 surrounded by a brine develops a crust at the interface. When CO_2 dissolves into the brine, it creates charged carbonate species and reduces the pH in its vicinity. Most of the components diffuse slowly away from the interface while protons in water diffuse faster owing to structural diffusion. The concentration gradient with unequal diffusivities generates an electrical field that slows down the rapidly diffusing protons, but also attracts positively-charged minerals towards the interface. This process suggest that an isolated bubble may remain stable owing to a self-sealing mechanism.

High magnification observations of minerals has revealed that supercritical CO_2-rich fluids can be retained in microscopic cavities forming fluid inclusions along wetting grain surfaces. These inclusions form a thin, continuous film that may short-circuit transport. Fig. 1 shows natural fluid inclusions hosted in a calcite crystal.

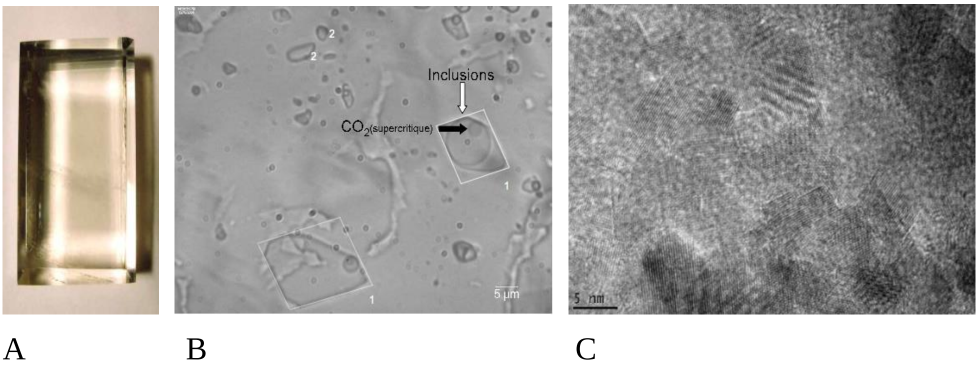

Fig. 1. Macroscopic calcite mono-crystal (A) of optical quality, observed at the micrometre scale (B) where CO_2 supercritical fluid inclusions can be easily found. When observed at the nano-meter scale (C) this crystal is in reality constituted by crystallites having 10-20 nano-metre size (grains) forming grain boundaries**.** The interface between two grains is, 2D defect, generates a polycrystalline material where nano-fluids may move very fast (Zuddas et al. 2018)

Recently, Atomic Force Microscopy observations [7] provided evidence for stress-induced fluid leakage from micrometric and nanometric fluid inclusions, and that this phenomenon took place in a very short time even at standard conditions. These experiments could show that even a stress lower that the Shear Modulus (modulus of rigidity measuring the stiffness of calcite macroscopic crystals) can produce disruptions responsible for fast fluid movement through a calcite crystal. The rate of fluid transport has been estimated to be ~ $5 \times 10^{-10 \pm 0.5}$ $m \cdot s^{-1}$, a value 4 to 5 orders of magnitude higher than that resulting from diffusion, extrapolated at low-temperature conditions. These results highlight the extreme mobility of fluids at the micro-nano fluidic scale in calcite crystals even at standard pressure and temperature.

3 Interfacial transport at the nano-fluidic scale

A question that remains to be addressed concerns the limiting conditions of fluid mobility and in what case could it represent a dominant transport mechanism. The liquid resistance to driving forces increases when flow channel size decreases [13]. However, in case of micrometric or nano-metric channel sizes, calculations of transport coefficients must take interfacial properties into account [8, 9].

For a simple fluid/solid interface with pressure flow represented by a slit of thickness h and slip length b, the mean velocity increases by a factor 1+ 6b/h as compared to the no-slip surfaces, suggesting that the size of the channel h drives the flow. The structure of the solid-liquid interface could be an alternative way to generate flow. The electrical interaction between tip and surface atoms may stress the mineral surface. Applying a stress E, the fluid acquires a plug flow comparable to a velocity profile, with a velocity ν_{EO} proportional to E following the Smoluchowski equation[8]:

$$\nu Eo = - \varepsilon\zeta E / \eta \tag{1}$$

where ε is the dielectric permittivity of the solvent, η its viscosity, and ζ is the Zeta potential of the surface, which is traditionally assumed to match the electrostatic potential at the position where the velocity profile vanishes.

The interface transport originated with the Debye layer, of size λ_D at the interface represents the width of the interfacial region at the charged surface. The size of the Debye layer results from the competition between ion attraction at the charged surface and the entropic effects. The fluid exodus results from the balance between the electrical driving force in the Debye layer and the viscous stress at the surface. If slippage is exhibited at the surface, the velocity varies on the size $\lambda D + b$ and the viscous stress becomes

$$v \frac{v_{EO}}{\lambda_D + b} \approx -\varepsilon \frac{V0}{\lambda_D} E \tag{2}$$

where E is the applied stress, V0 is the surface potential, $v_{EO}$is the acquired fluid velocity resulting from the stress aplication , $v_{EO}$is the velocity and λ_D the size of the Debye layer. This leads to the Smoluchowski formula and provides an expression for the zeta potential in the form:

$$\zeta = V_0 \, (1+ b/\lambda_D) \tag{3}$$

Equation 3 shows that for a non-slipping surface, V_0 can be identified as the potential at the plane of shear V0 = $V(_{Zs})$, with Zs being of the order of one liquid layer. As expected, a strong amplification of charge transport is therefore demonstrated on a slipping surface. Generalizing this behaviour to all interfacial transport phenomena, the flow fluid velocity in confined media is proportional to the applied gradient (stress, electrical potential) and depends on the size L, of the interface where the fluids interacts specifically with the mineral surface.

We propose that slippage amplifies the transport according to the ratio b/L, which in turn controls the interfacial transport of fluids at the micro and nano-meter scale. While structural defects at the external surface of minerals have been identified as limiting steps in transport and reactivity in non-confined fluids [10], fast movement of CO_2-rich fluids are related to fluid-fluid and fluid-calcite interfaces. These small-scale phenomena, interpreted as interfacial processes, have been often neglected in continuum-scale modelling such a viscous fingering [11] and wetting alteration by CO_2-rich fluids [12, 13].

4 Conclusions

Contrary to classical reasoning that assumes local equilibrium at the fluid-solid interface, or, equivalently, a continuity of the chemical potential, the nanometric observations and the approach outlined above indicate that it would be more consistent to consider a discontinuous flux across the interface. The magnitude of this discontinuity characterizes the kinetics of pressure solution rather than inter-granular diffusion, affecting anisotropy in fluid-bearing rock systems during geological CO_2 sequestration or fault lubrication processes. Rapid fluid mobility also has important implications for fluid-mediated metal transport: the origin of native gold grains observed at the surface of sulphide grains in orogenic-type deposits [14] could be explained by movement of micron-size fluid inclusions commonly observed in sulphides rather than by dissolution/precipitation processes involving external fluids [15].

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