Effect of fluid salinity on subcritical crack propagation in calcite

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A B S T R A C T

The slow propagation of cracks, also called subcritical crack growth, is a mechanism of fracturing responsible for a ductile deformation of rocks under crustal conditions. In the present study, the double-torsion technique was used to measure the effect of fluid chemistry on the slow propagation of cracks in calcite single crystals at room temperature. Time-lapse images and measurements of force and load-point displacement allowed accurate characterization of crack velocities in a range of 10^{-8} to 10^{-4} m/s. Velocity curves as a function of energy-release rates were obtained for different fluid compositions, varying NH_4Cl and $NaCl$ concentrations. Our results show the presence of a threshold in fluid composition, separating two regimes: weakening conditions where the crack propagation is favored, and strengthening conditions where crack propagation slows down. We suggest that electrostatic surface forces that modify the repulsion forces between the two surfaces of the crack may be responsible for this behavior.

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1. Introduction

Since its first developments at the beginning of the 20th century (Griffith, 1920), fracture mechanics has found many applications in different areas, be it industry or fundamental sciences (Barenblatt, 1962; Lawn, 1993). For instance, the study of damage, especially with regard to the lifetime of materials, has an important implication on the safety of buildings and civil engineering works, as well as stability of planes, boats and cars; or cliffs, mountains and seismic fault zones when considering natural hazards. Two kinds of fracturing processes have been distinguished (Lawn, 1993). The first one is dynamic fracturing, that occurs when the stress applied on a solid becomes greater than a critical value called fracture toughness. The rupture velocity is controlled by the elastic moduli of the medium and can vary depending on the material, from m/s in a soft gel, to several km/s in rocks or metals. The second type of fracturing is subcritical crack growth, characteristic of solid failure at stresses well below the short-time failure strength (Atkinson, 1984; Charles, 1958; Wiederhorn, 1967). The rupture velocity then ranges from 10^{-9} to 10^{-1} m/s, a well-known example being the slow propagation of a small crack in the glass of a car windshield.

Subcritical crack growth is a deformation mechanism with a wide range of applications, especially in Earth's systems. For instance, subcritical crack propagation may control weathering rates of surface rocks or cultural heritage monuments when coupled with crystal growth in pores (Røyne et al., 2011b). Besides, subcritical cracking is the dominant

process in brittle creep deformation of rocks, which is responsible for porosity reduction of aggregates during compaction (Chester et al., 2007) and delayed fracturing of rocks (Atkinson, 1984; Heap et al., 2009a,b). It is also seen as a key component of the damage occurring in active fault zones (Dunning et al., 1994). In geotechnics, understanding subcritical cracking has major implications for the exploitation of natural resources and the mitigation of natural hazards. Indeed, it is crucial to estimate the long-term stability of structures such as geological reservoirs, mines, or water disposal facilities (Swanson, 1984).

The theoretical study of fracturing was born with the observation that solids can break at stresses below the stress necessary to break a large number of atomic bonds in a homogeneous solid. Griffith (1920) suggested that it could be due to the presence of pre-existing flaws in the material. The profusion of submicroscopic cracks favors rupture because stress is concentrated at their tips. Griffith proposed a criterion to predict the breaking loads of solids. If G_0 (J/m^2) is the mechanical energy-release rate at equilibrium, i.e. the energy released per unit of crack length, and γ_S (J/m^2) is the surface energy of the solid in vacuum, then a crack is at the onset of propagation when the mechanical energy provided at its tip is equal to the energy needed to create two new surfaces: $G_0 - 2\gamma_S = 0$ (Griffith, 1920). Later, Orowan (1944) proposed that the presence of water or any other fluid in the medium may modify the value of γ_S, often to a lower value noted γ_S^ξ. Consequently, it requires less energy (compared to vacuum) to open a crack when a fluid is in contact with the solid. Eventually, Rice (1978) set this criterion in the framework of irreversible thermodynamics and introduced the crack velocity v: if $G \geq G_0$, then $v \geq 0$ and the crack propagates. Otherwise, the crack closes and heals. In this framework, $G = G_c > G_0$ corresponds to a discontinuity in the crack speed, where the dynamic regime may be reached (Maugis, 1985); G_0 and G_c being displayed on Fig. 1a.

Subcritical crack growth has been studied under laboratory conditions and two types of experimental setups can be distinguished. On the one hand, experiments have been performed to study the propagation of a single crack in various single crystals or pure amorphous materials, especially glass (Wiederhorn, 1967), but also on rock-forming crystals such as mica (Obreimoff, 1930), quartz (Atkinson, 1984), calcite (Dunning et al., 1994) or fine grained mudstone and homogeneous marble (Henry et al., 1977). The most common outputs of these studies are curves of G (or fracture intensity factor, K) versus crack velocity, whose results can be summarized according to the sketch of Fig. 1b. On the other hand, several experiments were performed on the compaction by brittle creep of bulk polycrystalline rocks or aggregates. Granites, basalts and shales (Swanson, 1984), limestones (Henry et al., 1977; Rutter, 1971), quartz sands (Chester et al., 2007), and sandstones (Heap et al., 2009b) were deformed at stresses below the yield strength of the material, in the brittle creep regime. In all experiments, the crucial role of microstructural parameters such as grain size, grain boundary cohesion and heterogeneities was identified. After the experiments, all samples were crossed by a network of intra- or inter-granular cracks. Recent experimental studies underlined the effect of pore fluid chemistry on the compaction of calcite aggregates (Croizé et al., 2010; Liteanu and Spiers, 2009; Zhang and Spiers, 2005) and have shown that the concentration of NaCl and $MgCl_2$ in the pore fluid has a nontrivial effect on compaction rate. The high variability observed in the measurements of subcritical crack velocities is interpreted as related to the initial heterogeneity of flaw density and size distribution into the solid (Croizé et al., 2010). The evolution of a population of cracks has also been studied analytically and numerically (Brantut et al., 2012) using a semi-analytical approach that accounts for the propagation of individual cracks and their interactions until failure.

Most of the experimental studies aim to understand the underlying physical and chemical mechanisms of subcritical cracking. The most common model proposed is stress corrosion, which corresponds to a chemical reaction that weakens the bonds at the crack tips, for instance the hydrolysis of $Si-O$ bonds in glass (Charles, 1958). However, the mechanism responsible for cracking in calcite is much less known, despite the importance and abundance of this mineral at the surface of the Earth. All studies on calcite point to a complex and debated behavior. Atkinson (1984) suggested that the main mechanism is dissolution at the crack tips, where the crack propagates by breaking ionic bonds:

$CO_2 + H_2O + CaCO_3 = Ca^{2+} + 2HCO_3^-$; whereas Dunning et al. (1994) argued in favor of a surface energy related mechanism. Røyne et al. (2011a) used a double-torsion apparatus to study subcritical crack growth in single calcite crystals, and varied the water concentration in the fluid. Their results were consistent with the reaction rate theory that states that the bond breaking rate at the crack tip is thermally activated, with an activation energy that depends on stress (Wan et al., 1990) and an equilibrium state which depends on the chemical conditions. This suggests that the process involved was independent of water concentration. The threshold for crack growth, G_0, was, however, strongly dependent on water concentration. This was explained by a strong effect of water activity on the surface energy necessary to break calcite, as γ_S^e depends on the environment. However, other effects can explain this change in G_0 (Lawn, 1993).

In the present study, we use a newly designed double-torsion rig, with better stability than the previous one (Røyne et al., 2011a), to study crack propagation in single calcite crystals, in a certain range of chemical environments. Both ionic strength of the fluid and calcite solubility were varied by using NaCl and NH_4Cl solutions at different concentrations. The goal of this study is to quantify the effect of water chemistry and especially salinity on calcite surface energy and on the subcritical fracture process. The present article is organized as follows: In Section 2, we present the experimental set-up as well as the conditions of the experiments and data acquisition. Then, the main results are detailed in Section 3. Finally, the physical mechanisms of subcritical cracking in calcite are discussed in Section 4, as well as some geological implications.

2. Material and methods

2.1. Double-torsion test apparatus

The double torsion technique was introduced by Evans (1972) and is used to study stable crack propagation. It consists in imposing an elastic torsional deformation in the middle of a rectangular plate that lies on three contact points (Fig. 2a). The experimental setup used here is a modification of that used by Røyne et al. (2011a). A load is applied on an initial notch with the tip of a linear piezo-actuator (PI, N-381), which offers a precisely controlled velocity and position. The specimen is thus bent by torsion on the three contact points, allowing the propagation of a mode I crack along a well-defined direction. An important feature is the stiffness of the rig that controls the energy-release rate at the crack tip. That is why we used a rig, which is stiffer than in a previous study (Røyne et al., 2011a), allowing to achieve a wider range of crack velocities and a better stability. The double torsion method requires much care in the alignment of the sample (Shyam and Lara-Curzio, 2006), because the crack must remain straight in order not to lose energy by forming new cleavage steps (Gilman, 1959). In the present study, the sample was placed in a Plexiglas cell (Fig. 2b) in which a fluid with controlled composition and atmospheric pressure was introduced before loading the sample and propagating the crack.

2.2. Sample preparation and experimental conditions

Rectangular single crystals of pure and homogeneous natural calcite, with dimensions $30 \times 10 \times 1$ mm, were provided by Photox Optical Systems Ltd. The 1×30 mm face was cut parallel to the $\{10\bar{1}4\}$ cleavage surface, the other faces being perpendicular to that plane. On each crystal, a starting notch, 4 to 5 mm long, was manually initiated by scratching one edge of the sample, allowing the crack to propagate from a pre-defined cleavage plane (Fig. 2a).

All experiments were run in a room with controlled temperature of 23 ± 1 °C and we used LED cold light to avoid heating when using the camera. The solutions were prepared with double deionized water. Sodium chloride was provided by Sigma Aldrich and a range of concentrations was tested. The effect of calcite solubility was also tested by preparing
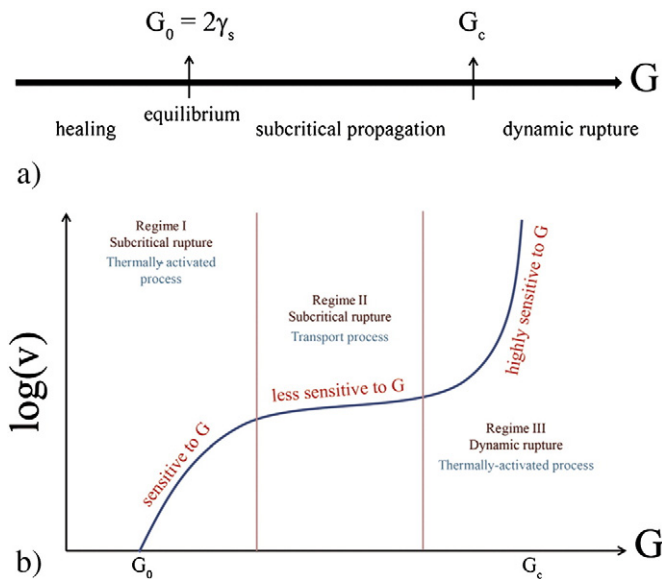
Fig. 1. a) Crack propagation behavior depending on the energy-release rate G. G_0 is the limit above which a crack propagates in a subcritical manner; G_c corresponding to the onset of dynamic rupture. b) Schematic diagram of crack velocity v versus mechanical energy-release rate G. Three regimes can be distinguished, depending on the load applied. In the present study, crack propagation in regime I is studied.