

# The Effect of Vapor-Borne Acidity on Subcritical Crack Propagation in Three Limestones

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## ABSTRACT

The propagation of cracks in solid materials can occur at stresses far below those required to cause brittle failure of the material. This type of cracking is called subcritical cracking and can be caused by both physiomechanical and chemical processes. Subcritical cracking in limestone, a sedimentary carbonate rock commonly used as a material for building and sculpting, has been studied less than cracking in other rock types. The effect of humid and aqueous environments on subcritical crack propagation have been studied in marble, the closest relative to limestone used in comparable experiments. The effect of pH on subcritical crack growth has also been studied in marble and other rock types, but always has always been introduced through liquid solutions. This study aims to examine the effect of acidity delivered by airborne moisture on the propagation of subcritical cracks in three varieties of limestone.

## I. INTRODUCTION

Limestone is one of the most abundant sedimentary rocks<sup>1</sup> on our planet (GSA 2019). It is principally composed of calcium carbonate ( $\text{CaCO}_3$ ), which for the last 540 million years has been mainly biological in origin (Boggs 2006, 177). To form,  $\text{CaCO}_3$  collected on the floor of ancient oceans, precipitated as the result of biological activity and deposited as debris from corals and tiny shell-producing animals. Buried under the weight of more recent accumulating sediment, pressure caused these deposits to be mechanically compacted and chemically cemented (GSA 2019). This process, by which loose sediment is turned into solid rock, is called diagenesis. Limestone that undergoes metamorphosis from intense heat and pressure deep within the Earth is recrystallized into marble.

Throughout history—and prehistory—limestone has been used by humans. It has been chosen as a building material and to be shaped into tools and aesthetic objects not only because of its abundance, but because of its physical qualities. Limestone is relatively soft yet hard enough to hold finely carved details. These desirable properties also make limestone susceptible to damage from sudden physical forces and gradual erosion caused by mechanical and chemical processes. For architectural and aesthetic limestone, sudden failure as the result of cracking or

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<sup>1</sup> The term “rock” is typically used to refer to the natural material in a geological context. The term “stone” is commonly used to refer to human-altered rock.

breaking is likely the most catastrophic type of possible damage. In a linear elastic solid like limestone, classical fracture mechanics predict that as long as the stress intensity factor ( $K_C$ ) at the tip of an existing defect or crack is below a critical value—defined as fracture toughness ( $K_{IC}$ ), or a material's ability to prevent crack growth—the crack is stable and will not propagate (Chau 2005, 808). The  $K_{IC}$  of a material is dependent on the inherent mechanical properties of solid materials defined by Young's modulus and Poisson's ratio (Eppes 2017, 471). Once the  $K_{IC}$  of a material is exceeded, it will rapidly fail. In a perfectly brittle material, a crack can theoretically grow at the speed of sound (Atkinson 1987, 111). Because all materials have some degree of ductility, for a propagating crack to travel at this speed, specific and uncommon conditions are required. In most occurrences, cracks in materials stressed past their critical  $K_{IC}$  still propagate at a rate instantaneous to human perception.

While brittle failure is the most dramatic type of crack growth, there is a second variety of cracking that can occur at conditions far less extreme than those necessary to cause it. This type of cracking, called subcritical cracking, develops relatively slowly and often goes unnoticed until it causes brittle failure by lowering the material's  $K_{IC}$ . Subcritical cracking can occur in stone at stresses as low as  $0.05K_{IC}$  at velocities as low as  $10^{-9}$  m/s (Chau 2005, 822; Zhao 2020, 1). It can be caused by chemical processes as well as biomechanical stresses introduced by static loading, cyclical loading, and thermal loading (Eppes 2017, 470). While all of these factors can contribute to the propagation of subcritical cracks,  $K_C$  remains the most important variable for propagation (Wachtman 2009, 152).

## II. LITERATURE REVIEW

Fracture mechanics is a young field. The first rigorous paper on the subject was Alan A. Griffith's "The Phenomena of Rupture and Flow in Solids," published in 1921. The Griffith theory of fracture states that a crack will propagate if the potential energy released by the cracking of a strained material is equal to or greater than the energy needed to create new surfaces in the material by the breaking of intermolecular bonds (Griffith 1921, 165). In "Fracture, Elasticity and Plasticity" published in 1958, George R. Irwin refined Griffith's work, allowing theories of fracture mechanics to be used to solve real world engineering problems (Gross 2014, 195). In most circumstances, classical fracture mechanics theory adequately explains the fracture behavior of linear elastic solids (Atkinson 1987, 112). But in systems subjected to long-term or cyclical loading, high temperatures, or reactive environments, this framework is frequently unable to predict crack growth. The discrepancy between observed and predicted  $K_{IC}$  spurred a number of experiments in the 1970s and 1980s on materials such as rock; "Subcritical Crack Propagation in Rocks: Theory, Experimental Results and Applications" by Barry K. Atkinson, ceramic; "Reliability, Life Prediction and Proof Testing of Ceramics" by Sheldon M. Weiderhorn, and glass; "Effects of Water and other Dielectrics on Crack Growth" by Weiderhorn, Stephen W. Freiman, Edwin R. Fuller, Jr., and Joseph H. Simmons. In these papers, the phenomenon of subcritical cracking was observed and used to explain the failure of materials at  $K_C$  far below the  $K_{IC}$  predicted by classical fracture mechanics.

More recent research on the causes and effects of subcritical cracking in stone can typically be divided into two categories. In the first category, interest in the subject comes from stone's use

as an engineering material: thin slabs of stone are commonly used as cladding on the faces of buildings. Research into the growth of subcritical cracks in stone façades has received increasing attention due to the cost of replacing compromised cladding. Architectural cladding panels must resist wind pressure, daily heating and cooling by the sun, freeze-thaw cycles, and chemical weathering. Subcritical cracks in stone façades have been noticed on buildings younger than ten years old (Chau 2006, 10). Replacing a building's stone façade can cost half the total price of the original building (Chau 2006, 7).

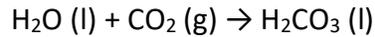
In the second category, interest in subcritical cracking in rock comes from the desire to understand the mechanics of geological processes such as weathering and deformation. The physical breakdown of in situ rock at or near the Earth's surface begins with the propagation of minuscule cracks (Eppes 2017, 471). In this way, subcritical cracking contributes to the mechanical weathering of rock, an important rate-limiting factor for a range of geologic systems (Eppes 2017, 470). While the perspectives of engineers and geologists differ in their spatial and temporal scales, both groups are concerned with the same fundamental phenomenon.

In their 2020 article "Experimental Study of Fracture Toughness and Subcritical Crack Growth of Three Rocks under Different Environments," Yanlin Zhao, Lianyang Zhang, Jian Liao, and Weijun Wang demonstrate the effects of aqueous environments on subcritical crack growth and  $K_{IC}$  in lherzolite, an igneous silicate, amphibolite, a metamorphic silicate, and marble, a metamorphic carbonate. Zhao et al. exposed samples of the three rock types to ambient air, distilled water, and acidic solutions with pHs of 6.0 and 3.0 for 60 days at 25°C (3). Samples of each rock type from each environment were then subjected to loading tests to measure changes in  $K_{IC}$  and subcritical crack growth velocity (1). Samples exposed to aqueous environments were found to have  $K_{IC}$ s lower than the corresponding samples exposed to air. Samples exposed to aqueous environments were also found to have subcritical crack growth velocities higher than the samples exposed to air (10).  $K_{IC}$ s trended downwards and subcritical crack growth velocities upwards with increasing acidity of the aqueous environment (13). The weakening effect of the acidic solutions on the marble samples was found to be much greater than that on the lherzolite and amphibolite samples (13).

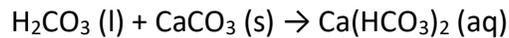
In their 2011 article "Mechanisms of Subcritical Cracking in Calcite," Anja Røyne, Jan Bisschop, and Dag Kristian Dysthe measured the effect of water on subcritical crack growth in individual calcite crystals. Calcite is the most stable polymorph of calcium carbonate. Exposing calcite crystals to glycol-water mixtures of various proportions, Røyne et al. observed subcritical crack growth velocities ranging from  $10^{-8}$  to  $10^{-2}$  m/s with crack velocity increasing by several orders of magnitude when the water concentration was raised (5). They concluded subcritical crack growth in calcite caused by exposure to water was well described using a reaction rate model (9).

The influence of water and acidic solutions on subcritical crack growth rate in stone is explained by chemophysical processes acting to break the strained bonds at crack tips (Atkinson 1987, 112). As demonstrated by Zhao et al., water is only necessary to facilitate this process, but more acidic solutions can accelerate it. The specific chemical reaction breaking bonds at the tip

of an existing crack is determined by the mineral composition of the rock. For carbonates like limestone, this process is called dissolution. In their chapter “The Theory of Subcritical Crack Growth with Applications to Minerals and Rocks” from the 1987 book *Fracture Mechanics of Rock* edited by Barry K. Atkinson, Atkinson and Philip G. Meredith outline the chemical reaction pathway for carbonate dissolution caused by water (122). First, water reacts with carbon dioxide in the air to form carbonic acid:



Carbonic acid then reacts with calcium carbonate, producing solubilized calcium bicarbonate:



Despite slower reaction kinetics, Atkinson and Meredith note that this mechanism is thermodynamically favored at low temperatures because cold water holds more dissolved carbon dioxide gas than warm water (123). Without the influence of natural or anthropogenic gases such as sulfur dioxide and nitrogen dioxide, the pH of rainwater due to carbonic acid is around 5.6 (Charlson, 1982, 683). Atkinson and Meredith also note the solubility of carbonates is greater in sea water and NaCl solutions than in fresh water (Atkinson 1987, 122). Atkinson and Meredith conclude that subcritical crack growth caused by reactions like carbonate dissolution is controlled by the chemistry of the external environment and the ability for reactive solutions from the environment to access the crack tip (123 & 124). If solid products precipitated from the dissolution process are not removed from the crack tip, subcritical crack growth can be inhibited (122).

In their 2017 article “Mechanical Weathering and Rock Erosion by Climate-Dependent Subcritical Cracking,” Martha-Cary Eppes and Russell Keanini use mathematical models and experimental data from engineering research to study the environmental dependence of subcritical crack propagation in rock. Eppes and Keanini, for the first time, show the ubiquity of water’s involvement in causing crack propagation, even in processes that do not specifically require water (470). Furthermore, they demonstrate that water in the environment does not need to be in liquid form to cause subcritical cracking. Eppes and Keanini summarize the results of preexisting experiments studying subcritical crack growth in rock exposed to environments ranging from low humidity to fully saturated conditions. They found measurable subcritical crack propagation occurs throughout the full range of relative humidity with linear increases in humidity causing exponential acceleration of subcritical cracking (470 & 476).

In their 2017 article “Influence of Surrounding Environment on Subcritical Crack Growth in Marble,” Yoshitaka Nara, Koki Kashiwaya, Yuki Nishida, and Toshinori Ii theorize about the mechanism by which water vapor from the environment is delivered to the crack tip. Since the opening of a crack near its tip is very small, Nara et al. suggest capillary condensation turns water vapor into liquid water, which can then react with the strained bonds at the crack tip (121).

### III. RESEARCH OBJECTIVES

The basic question guiding this study asks; “Can an existing crack in a limestone object propagate under ‘normal’ interior conditions?” The effect of aqueous and humid environments on the propagation of subcritical crack growth has been studied in varieties of andesite, amphibolite, basalt, dolerite, gabbro, granite, lherzolite, marble, peridotite, and sandstone (Zhoa 2020, 1). Limestone does yet not appear to have been studied in this way. Furthermore, while the effect of pH on crack growth in rock has been studied in fully saturated environments, it has not been studied in humid environments. Stress caused by loading is unique to every stone object, and is a function of factors like size, shape, and orientation. The proposed study eliminates these variables by focusing solely on the chemical causes of cracking in stone. The presence of water increases the rate of subcritical crack growth in virtually every rock type studied (Eppes 2017, 470). Previous studies have shown that acidic solutions have a relatively large effect on the growth rate of subcritical cracks in marble (Zhao 2020, 13). Because marble is made of recrystallized calcium carbonate grains from limestone, one would hypothesize limestone having similar sensitivities to acidic environments. Limestone’s structure, which is more porous than marble’s interlocking calcite matrix, could make it even more susceptible to subcritical cracking caused by acidic vapors. This study aims not only to determine the relative susceptibilities of three common limestone varieties, but also examine the influence of porosity, grain size, and mineral content on subcritical crack growth. The proposed study also seeks to translate existing work from outside the conservation field into a cultural heritage conservation context. The phenomenon of subcritical cracking is not discussed in the Getty Conservation Institute’s 2010 book “Stone Conservation: An Overview of Current Research , 2<sup>nd</sup> Ed.” by Eric Doehne and Clifford A. Price or in the International Council on Monuments and Cites’ (ICOMOS) 2008 book “Illustrated Glossary on Stone Deterioration Patterns.” The vulnerability of stone objects in interior environments has similarly received little attention.

### IV. MATERIALS

Three different varieties of limestone will be used in this study: micrite, travertine, and an oolitic limestone. These varieties were selected because of their varying structures and compositions, as well as the fact that all three have been frequently used for cultural heritage objects and structures. Micrite is composed of extremely fine-grained and uniform calcite particles. In this study, it represents a high-quality limestone with desirable carving characteristics. Travertine is relatively porous, with small pockets filled with coarse calcite crystals. It can be white, tan, or rust-colored, and was frequently chosen for its aesthetic properties. Oolitic limestone is composed of spherical grains made up of concentric layers. Many oolitic limestones have a dark appearance due to high organic content (GSA 2019). The micrite for this study was sourced from a retired lithography stone. The travertine and oolitic limestone were offcuts donated by a stone countertop and sculpture supplier.

### V. METHODOLOGY

#### *Petrographic Thin Section Examination*

Samples of the three limestones will be sent to National Petrographic Service, Inc., a company that prepares thin sections. Thin section examination will be useful in measuring and characterizing the grains and grain boundaries of the limestone samples. Grain size is one factor

that influences fracture toughness, with rocks with finer grains exhibiting more brittle behavior (Henry 1977, 85). Thin sections will be examined using a polarized light microscope.

#### *Indirect Measurement of Porosity by Water Absorption*

Samples of the three limestones in the form of 5cm cubes will be tested to determine their porosities using the indirect measurement of porosity by water absorption test. The protocol for this test was provided by Catherine Matsen and originally prepared for a 2001 course at the University of Pennsylvania Graduate Program in Historic Preservation. See **APPENDIX** for full test procedure. Studies have shown that mass transport to the crack tip is an important variable for subcritical crack growth in rocks with low porosities (Nara 2017, 123).

#### *X-Ray Fluorescence Spectroscopy (XRF) Analysis*

XRF, a nondestructive, quantitative test will be used to gain inorganic elemental information about the three limestones. This information will provide a broad understanding of the makeup of the samples and help focus subsequent XRD analysis. The limestones will be analyzed with a handheld BrukerTracer III-SD XRF spectrometer with a spot size of approximately 1.0 x 0.5cm.

#### *X-Ray Diffraction (XRD) Analysis*

XRD, a destructive, quantitative test will be used to determine the mineral composition of the three limestones. The calcium carbonate content of the samples will likely be a significant factor influencing chemically induced subcritical crack growth. XRD analysis will be carried out using a Rigaku D/max Rapid II diffractometer with a copper anode.

#### *Microscopy*

Cracks in the samples will be imaged before and after exposure inside the vapor chambers using a Zeiss Axio Imager M2m Binocular microscope. Subcritical crack propagation will be measured by comparing before and after images. If visualization of the cracks is difficult under magnification alone, nonparticulate fluorescent dyes, as outlined by R. D. Gardner and H. J. Pincus in "Fluorescent Dye Penetrants Applied to Rock Fractures," could be used. The dyed samples would be examined using a microscope with ultraviolet fluorescence capabilities.

#### *Vapor Chambers*

Vapor chambers will be used to expose the samples to a spectrum of environments. The chambers will consist of glass containers with tight-fitting silicone lids. In the chambers, the samples will be suspended over solutions. One chamber will contain deionized water. A second chamber will contain a glacial acetic acid/deionized water solution with a pH 5.7 to emulate moisture in the ambient air. The final chamber will contain pure glacial acetic acid with a pH of around 2.4. This chamber will be an analogue for extended exposure to the pH 5.7 vapor. The relative humidity in the chambers will be measured with humidity indicator cards. Heating blankets will be used to ensure the temperatures in the chambers remain constant and above their dew points so that condensation does not form. Samples will be left in the chambers for two months. A set of samples—three of each limestone variety—will be exposed to ambient room conditions as a control.

## VI. PROCEDURE

### 1. Prepare samples:

- Cut twelve samples of each variety of limestone so that tests in each of the four environments outlined above can be run in triplicate.
  - Samples will be 80mm x 50mm x 4mm.
    - No original surfaces of the lithography stone will be preserved in the samples to ensure ink or oil residues do not interfere with the tests.
  - Samples will have a groove, approximately 1mm wide and 2mm deep, running along their lengths. This groove will direct the growth of the cracks, ensuring they propagate linearly down the center of the samples. [See figure.]
- Pre-crack the samples. See **APPENDIX** for more information on the pre-cracking process.
- Cut 5cm cubes of each limestone variety for porosity testing.

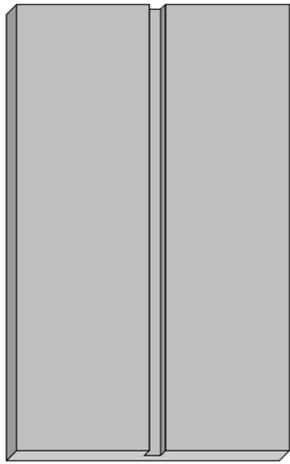


Diagram of generic sample before pre-cracking. The groove down the middle of the sample's face will keep the crack propagating in a straight line as it travels the route of least resistance. (Diagram not drawn to scale.)

2. Image the samples and measure crack length before samples are exposed to vapor chamber environments.
3. Analyze limestones:
  - Conduct XRF and XRD analysis and test the porosity of the three limestones as outlined in the **METHODOLOGY** section of this proposal.
    - These analytical techniques will use different materials than the samples used in the vapor chambers and so can be conducted concurrently with the exposure tests.
4. Set up vapor chambers as described in the **METHODOLOGY** section of this proposal.
5. Expose the samples to their respective test environments for two months.
6. Examine the samples for crack growth.

## VII. APPENDIX

### *Pre-Cracking Procedure*

Pre-cracking will be performed using a loading indenter or an equivalent instrument at the University of Delaware's Center for Composite Materials. In a study utilizing similarly prepared samples, Nara et al. applied a displacement of 4 $\mu$ m at the loading point to create a crack in samples of Carrara and Macedonian marble (Nara 2017, 118). While the size of the samples is

the same, the  $K_{ICs}$  of the three limestone varieties used in this study will likely be different than the  $K_{ICs}$  of the marble varieties used by Nara et al. More limestone samples will be prepared than are needed, in anticipation of losing usable samples as the appropriate displacement to create a crack is determined.

#### *Indirect Measurement of Porosity by Water Absorption Test Procedure*

The following procedure has been copied virtually verbatim from a handout for the class “Introduction to Conservation Science” taught by Frank G. Matero during the 2001 fall semester as part of the University of Pennsylvania Graduate Program in Historic Preservation.

#### Preparation

Dry samples for a minimum of 24 hours at 60° (±5°C).

#### Procedure

Water Absorption by Total Immersion:

1. Weigh dry, cooled samples. Record weight ( $M_0$ ).
2. Place weighed samples on glass rods or beads in the immersion container. Slowly fill the container with deionized water until the samples are immersed and covered by at least 2cm of water.
3. At predetermined time intervals (see below), remove each sample from the water, quickly blot with a damp cloth to remove surface moisture, and weigh. Record results ( $M_N$ ). Re-immerses sample.
  - a. Stone should be weighed after the first five minutes of immersion and then every hour for the first three hours.

All samples should then be re-weighed eight hours from the start of the test and then every twenty-four hours until the quantity of water absorbed in two successive weighings is not more than 0.1% of the dry mass. At this point the mass of the object is referred to as the “saturated mass” ( $M_{sat}$ ).

4. At each interval, calculate the quantity of water absorbed (WA) as a percentage with respect to the dry sample:

$$WA, \% = [(M_N - M_0) / M_0] \times 100\%$$

5. When relative equilibrium is reached as described in Step 3, remove the samples from the water and proceed to Indirect Measurement and Hydrostatic Weighing (see below). After these tests are complete, dry the samples at 60°C until they have reached constant mass. Record this value ( $M_d$ ).

#### Indirect Measurement of Porosity by Water Absorption

1. Using the data recorded in the total immersion test for the saturated sample, the mass of water in the pores at the saturation point ( $M_p$ ) can be found:

$$M_p = M_{sat} - M_0$$

Since the density of water is  $1\text{g/cm}^3$  at  $24^\circ\text{C}$ , the mass of the water in the pores (in grams) can be considered to be the volume of the pores ( $V_p$  in  $\text{cm}^3$ ).

$$M_p = V_p$$

2. Measure the apparent volume of the saturated sample by placing it in a beaker containing a known volume of water. According to Archimedes' Principle, the quantity of water displaced is equal to the apparent volume ( $V_a$ ).
3. An estimate of the percent porosity can be obtained (assuming that all pores are accessible and that the sample is saturated; that is assuming a good relationship between porosity and permeability):

$$\% \text{ porosity} = \% \text{voids} = (V_p/V_a) \times 100\%$$

### Hydrostatic Weighing

1. Suspend **saturated sample** from a wire hook, immersed in container of water on the plate of the hydrostatic balance. Record the results ( $M_1$ ), being sure to subtract the mass of the wire used.
2. Quickly wipe the saturated sample with a damp cloth and weigh it in air on the plate of the hydrostatic balance. Record the results ( $M_2$ ).
3. The volume of water in the pores in  $\text{cm}^3$  is equal to the mass of the water in the pores (in grams), and is expressed by:

$$V_p = M_p = M_2 - M_0$$

The **apparent volume** in  $\text{cm}^3$  is expressed by:

$$V_a = M_2 - M_1$$

One may also determine this, with less accuracy, by measuring the dimensions of the sample with a gauge of 0.1mm precision.

The **real volume** is expressed by:

$$V_r = M_0 - M_1$$

The **real density** is expressed in  $\text{kg/m}^3$  by:

$$\rho_r = (M_0/V_r)$$

$$\rho_r = [M_0/(M_0 - M_1)] \times 10^3$$

The **apparent density** is expressed by:

$$\rho_a = [M_0/(M_2 - M_1)] \times 10^3$$

**Porosity** is expressed by:

$$\varepsilon = 1 - (\rho_a/\rho_r)$$

$$\% \varepsilon = 1 - (\rho_a/\rho_r) \times 100\%$$

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