

## THE ROLE OF ANNEALING AND GRAIN BOUNDARY CONTROLS ON THE MECHANICAL PROPERTIES OF LIMESTONES AND MARBLES

Lawrence M. Anovitz<sup>1</sup>, Rui Zhang<sup>1</sup>, Paul A. Bosomworth<sup>2</sup>, Juliane Weber<sup>1</sup>, Jan Ilavsky<sup>3</sup>, Si Athena Chen<sup>1</sup>, Alexis Flores-Betencourt<sup>4</sup>, Elliot Paul Gilbert<sup>5,6</sup>, Jitendra Mata<sup>5,7</sup>, Mark L. Rivers<sup>8</sup>, Peter J. Eng<sup>8,9</sup>

<sup>1</sup>Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States

<sup>2</sup>BuzzMac International LLC, Portland, ME 04101, United States

<sup>3</sup>X-ray Science Division, Argonne National Laboratory, Lemont, IL 60439, United States

<sup>4</sup>Material Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

<sup>5</sup>Australian Centre for Neutron Scattering, Australian Nuclear Science and Technology Organisation, Lucas Heights, NSW 2234, Australia

<sup>6</sup>Australian Institute for Bioengineering and Nanotechnology and Queensland Alliance for Agriculture and Food Innovation, The University of Queensland, Brisbane, QLD, Australia

<sup>7</sup>School of Chemistry, University of New South Wales, NSW 2052, Australia

<sup>8</sup>Center for Advanced Radiation Sources, The University of Chicago, Chicago, IL 60637, United States

<sup>9</sup>James Franck Institute, The University of Chicago, Chicago, IL 60637, United States

### ABSTRACT

Chemical and mechanical processes are coupled in many geological and geochemical environments. Reactive processes anneal defects and restructure grain boundaries, modifying their elastic properties, levels of internal friction, wave propagation rates and fracture behaviors. The nature of these changes is, however, contingent on the initial state of the rock. In this study, impulse excitation was used to measure changes in mechanical properties as a function of dry and steam heating time at 300 °C for three carbonate rocks: Carrara marble, Carthage marble (Burlington Limestone), and Texas Cream limestone (Edwards limestone), with initial porosities of about 1 %, 3 %, and 27 %, respectively. Frequency-dependent phenomena along with orientation-dependent mineral recrystallization were observed. This was coupled with small-angle X-ray and neutron scattering analysis to determine the relationship between changes in bulk mechanical and microstructural properties. An observed decrease in both the Young's and shear moduli in the experimental limestones as a function of heating time reflects and quantifies a reduction in the stiffness of the rock due to annealing. The internal friction of the samples first increases then decreases with reaction time, reflecting defect annealing, but this was balanced against grain boundary dissolution apparently driven by condensation of steam in the confined grain-boundary environment. This implies an increase in the boiling point under confinement leading to dissolution, increased porosity and widening of the grain boundaries. In addition, comparison of small-angle X-ray and neutron results suggests that it is inappropriate to assume that pores are empty for quantitative analysis of typical small-angle scattering samples