Nanoscale Anisotropic Plastic Deformation in Single Crystal Aragonite

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The nanoscale anisotropic elastic-plastic behavior of single crystal aragonite is studied using nanoindentation and tapping mode atomic force microscopy (TMAFM) imaging. Force-depth curves coaxial to the c-axis exhibited load plateaus indicative of dislocation nucleation events. Plasticity on distinct slip systems was evident in residual topographic impressions where four pileup lobes were present after indentation with a cono-spherical probe and distinct, protruding slip bands were present after indentation with a Berkovich pyramidal probe. A finite element crystal plasticity model revealed the governing roles of the {110}<001> family, as well as the (100)[010], (100)[001], (010)[100], (010)[001], (001)[100], and (001)[010] systems.

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Aragonite (an orthorhombic form of calcium carbonate, CaCO₃) is a mineral that is ubiquitous in natural systems including both living organisms [1,2] and geological structures [3]. Examples of the former include micrometer-sized tablets which compose ~95% of the inner nacreous layer found in numerous mollusk shells [4, 5], nanometer to micrometer-sized polycrystalline fibers of scleratinian stony coral skeletons [6] and spicules in some sponges [2]. Geologically, aragonite is predominantly found in the upper mantle [7]. Aragonite has also shown potential for various technological applications such as bone grafting [8]. Since the identification of the orthorhombic crystal structure of aragonite by Bragg in 1924 [9], ongoing investigations have studied a range of aspects of this mineral [3] including high pressure experiments [10], which eventually led to the identification of the calcite-to-aragonite transition and the development of the CaCO₃ phase diagram [11].

Although the mechanical behavior of aragonite is a critical determinant of its many biological and geological functions, only a few reports exist in this area and a fundamental mechanistic understanding is lacking. The anisotropic elastic constants of aragonite were experimentally determined in 1910 [12], using static bending and torsion experiments, and again recently using Brillouin spectroscopy [13]. Regarding plastic deformation, a few reports exist on similar minerals; e.g. calcite [14] which is a rhombohedral form of CaCO₃ and olivine [14], which, like aragonite, has an orthorhombic structure. For olivine, transmission electron microscopy (TEM) on samples deformed under high pressure showed plastic deformation to be governed by slip on several systems [15]. Investigations into the large scale plastic flow of polycrystalline [16] and porous [17] aragonite at high temperatures and pressures using triaxial compression have also been conducted where dislocation creep was observed as the dominant mechanism for the former and a transition from localized brittle failure to cataclastic flow with increasing porosity and grain size occurred for the latter. Another
study on the Knoop microhardness of single crystal aragonite at room temperature showed anisotropic behavior when comparing the (100), (010) and (001) planes, as well as in-plane anisotropy in the (100) and (010) planes, in contrast to nearly isotropic microhardness in the (001) plane [18]. Recently, nanoindentation studies have been performed on aragonite-based scallops of the *Pectinidae* family [19] and on individual nacre tablets of *Trochus niloticus* [20] and *Haliotis rufescens* [21] showing plastic deformation and pile-up. In order to more fully understand the mechanical design principles of such natural biocomposite materials, it is essential to study the properties of the pure constituents, such as aragonite. In this paper, the anisotropic mechanical behavior of single crystal aragonite was studied using nanoindentation in conjunction with TMAFM imaging of residual indents. The use of indenter probe tips with two different geometries (pyramidal Berkovich and cono-spherical) and a finite element crystal plasticity model enabled interrogation and identification of the underlying activated slip systems which govern anisotropic plasticity.

Fig. 1(a) depicts averaged\(^1\) nanoindentation load-unload data using a Berkovich probe tip for single crystal aragonite on three mutually orthogonal planes, where one plane is normal to the orthorhombic crystal \(c\)-axis (001) and the other two planes ((\(\overline{1}10\)) and \((\overline{1}30)\)) are perpendicular to the (001) plane. The force-depth curves for the three planes revealed an anisotropic nanomechanical response. An Oliver-Pharr (O-P) [22] reduction of these data\(^2\) for a maximum load of 1000 \(\mu\)N gives (modulus, hardness) pairs of \((102.8 \pm 2.4 \text{ GPa}, 6.2\pm0.3 \text{ GPa})\), \((100.1 \pm 3.4 \text{ GPa}, 4.6 \pm 0.3 \text{ GPa})\) and \((108.1 \pm 2.3 \text{ GPa}, 4.36 \pm 0.4 \text{ GPa})\) for the (001), (\(\overline{1}10\)) and \((\overline{1}30)\) planes, respectively, and given the

\(^1\) The average is taken over a data set of \(n=20\) curves; averaging is performed on the displacement as indicated by the error bars.

\(^2\)The (modulus, hardness) pairs estimated here by the O-P [22] method should be regarded as "apparent" since the O-P model assumes isotropy.
minimal difference in moduli (<7%), indicates an anisotropic yield stress. This observed plastic anisotropy is expected to result from activation of slip on preferred slip systems which depend on the indentation direction. The (001) plane indents show a noticeable change in slope in the averaged force-depth curves at ~314 and 386 μN. The origin of this slope change is clearly seen when examining individual (as opposed to averaged) load-unload curves which display distinct load plateaus (309.0 ± 27.6 μN) (Fig. 1(a) inset). Force-depth curves depicting distinct load plateaus suggesting discrete plastic flow events have been observed for nanoindentation on a number of materials (e.g. metals, semiconductors and oxides [23-25]). Consistent with the findings of other authors who have applied constitutive stability criteria to quantify such events [23,24], the plateau behavior is attributed to the onset of dislocation nucleation. This hypothesis is supported by previous work on ceramic single crystals (Al₂O₃, SiC) [25] where TEM revealed extensive dislocation activity after nanoindentation. Anisotropic behavior was also observed in nanoindentation via a cono-spherical tip (nominal tip radius <1 μm, 60° cone, Fig. 1(b)). An O-P reduction applied to these data for a maximum load of 1000 μN gives (modulus, hardness) pairs of (89 ± 1.8 GPa, 8.6 ± 0.36 GPa), (95 ± 2.78 GPa, 6.5 ± 0.13 GPa) and (85 ± 2.25 GPa, 6.36 ± 0.19 GPa) for the (001), (110) and (310) planes, respectively, which again highlights the yield anisotropy. As in the Berkovich indentation, there is a marked change in slope for the (001) plane data (at ~ 381 μN to ~439 μN) and the individual curves (Fig. 1(b) inset) depict the distinct load plateaus (424.4 ± 61.0 μN).

TMAFM images of residual indents after unloading from larger maximum loads of 10 mN for the Berkovich tip (loaded depths of ~290 nm and residual depths of ~180 nm) and 5 mN for the cono-spherical tip (loaded depths of ~420 nm and residual depths of ~300 nm) are shown in Figs. 2(a) and 2(b). Residual deformations took the form of a central impression and a surrounding pileup zone indicating extensive plastic
deformation. No microcracking was observed. Preferential pile-up patterns were observed for both probe tip geometries, indicating anisotropic plastic behavior. In the cono-spherical indent, the pile-up was localized predominantly in four lobes around the indenter. For the Berkovich tip, pile-up was typically adjacent to two sides of the indenter and showed directionally biased protruding striations within the pileup zones that appear to be slip bands. Line profiles (Fig. 2(c)) together with 3D AFM imaging of the Berkovich pile-up (Fig. 2(d)) further highlight the banded nature of the pileup.

A finite element model was employed to simulate the anisotropic plastic response of single-crystal aragonite for the two indenter geometries. Based on the clear experimental evidence of slip-dominated plastic activity described above (i.e. force plateaus and AFM images of slip bands), the overarching assumptions associated with the kinematics of plastic slip in crystals [26] are postulated as the governing deformation mechanism in single crystal aragonite and a crystal plasticity model [27,28] is adopted to describe its constitutive response. This type of model is well-established in the description of anisotropic plastic behavior in metals [29,30] where the operative slip systems, slip resistances, and hardening properties of the crystal are characterized. In this work, since the slip systems in aragonite are largely unknown, the model is used to interrogate and identify the operative systems required to explain the observed indentation slip and pile-up patterns produced by both the cono-spherical and Berkovich probe tips. Simulations assuming the \{100\}<001> family of slip systems as suggested by prior high temperature and high pressure investigations [15,16] failed to produce the observed residual topographic impressions. The four pile-up lobes observed experimentally for the cono-spherical indentation (Fig. 2(b)) exhibit a two-fold symmetry with an aspect ratio similar to the lattice constants ratio $a/b$, which suggests that the pile-ups may be rationalized as a result of slip activity on \{110\}<001> systems. Following this observation and previous work on olivine which shares with aragonite the
orthorhombic structure [15], the six systems of the \{110\}<001> family were added to the set of cubic slip systems postulated initially. When the resulting set of twelve slip systems is considered in the constitutive model, the simulation reproduces the observed pile-up pattern (Fig. 3(a)) thus indicating that the proposed slip systems provide a plausible kinematic mechanism explaining the observed anisotropic plastic behavior.

In order to provide further support for the postulated operative slip systems, the same model was used to simulate the indentation with the Berkovich probe tip. The nonsymmetric geometry of the Berkovich tip further exposes the anisotropy of plastic deformation and provides a stringent test for the ability of the model to describe the basic mechanisms of anisotropic plastic flow. Fig. 3(b) compares the pile-up patterns obtained numerically with the corresponding experimental observations (TMAFM image of residual indent). The (110)[001] and (\overline{1}10)[001] slip systems are found to provide the kinematic mechanisms of plastic slip necessary to produce the pileup bands observed in the Berkovich residual impression, thus supporting the postulated slip systems in aragonite. Furthermore, the gradient in magnitude of slip activity is consistent with the slope of the banded region observed in the line profile.

The mechanisms governing the formation of the pile-ups for the cono-spherical probe tip indentation are described in more detail in a series of cross-sectional views plotted in Fig. 4 which document the theoretical predictions for the through-thickness distribution of slip activation within the indentation zone. The (100) plane cross sections shown on the top right figures exhibit activation of slip on the (101)[010] and (001)[010] systems whereas the (010) plane cross sections shown on the bottom right figures exhibit activation of slip on the (011)[100] and (001)[100] systems. The activation of these sets of slip systems shear the material away from the indentation zone along the [010] and [100] directions, respectively. This slip activity is kinematically compatible with the
activation of the (110)[001] and (1 10)[001] slip systems which are responsible for the pile-up tendency along the [001] direction.

This previously unreported detail of the nanoscale anisotropic plastic behavior of aragonite may be of substantial relevance to understanding mechanical design of biological composites, geological behavior and development of biomimetic materials. In particular, given that brittle failure is averted in micron and sub-micron scaled biological composite structures due to the small length scale effect [2, 5], the hardness values reported here indicate that natural composites containing small-scale aragonite structures (e.g., tablets in the nacre of seashells) are able to withstand high stress prior to yield. Furthermore, this study details specific aspects of aragonite anisotropic plasticity where the preferentially oriented crystallographic structure of biological composites is considered to play an important functional role [31].

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References


FIG. 1. Averaged force-depth data on loading and unloading for nanoindentation normal to three mutually orthogonal planes of single crystal aragonite (each averaged curve considers a dataset of 20); loading rate of 50 μN/s; error bars indicate one standard deviation for dataset with averaging of displacement at a given force level. **Insets:** three representative individual load-unload curves from the (001) datasets using a (a) Berkovich tip, (b) cono-spherical tip.
FIG. 2. TMAFM images of residual indents, (a) amplitude image, 10000μN maximum load, Berkovich tip, load/unload rate 1mN/s, (b) amplitude image, 5000μN maximum load, 1μm, 60° cono-spherical tip, load rate 1mN/s, ○ indicates c-axis is out of the page, (c) Line profiles of Berkovich indent depicted in (a); and (d) 3D height image of Berkovich indent.
FIG. 3. Simulated pile-up pattern compared to experimental TMAFM amplitude images. Blue color is minimum, red is maximum (a) cono-spherical tip, (b) Berkovich tip, pile-ups take place at two sides with (110)[001] and (1\overline{1})0[100] dominant.

FIG. 4. Theoretical predictions from finite element crystal plasticity model of through thickness cross sections showing contours of amount of slip activity in indicated individual slip systems for nanoindentation (red color is maximum positive slip and blue color is maximum negative slip, green color is unslipped region).