Supporting Information

for

The role of the mineral in the self-healing of cracks in human enamel

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Supporting Methods: MD Crystal Equilibration

Calcite simulations consisted of approximately 26000 atoms and were equilibrated with NPT ensemble at 300 K, 1 atm over 20 ps. HAP simulations consisted of approximately 24000 atoms. It was found that stresses in the HAP sample remain stuck at a non-relaxed local minimum if exposed to the same equilibration procedure as calcite. Instead, the following NPT equilibration procedure includes a temporary pressure increase to fully relax stresses and reach a stable total energy.

The crystal was first subject to a 5 ps run at 300 K, 1 atm. This was followed by raising the depth-wise pressure to 1000 atm over 5 ps and lowering back to 1 atm over the next 5 ps. Then the crystal was allowed to further relax at this low pressure for an additional 5 ps at 300 K.

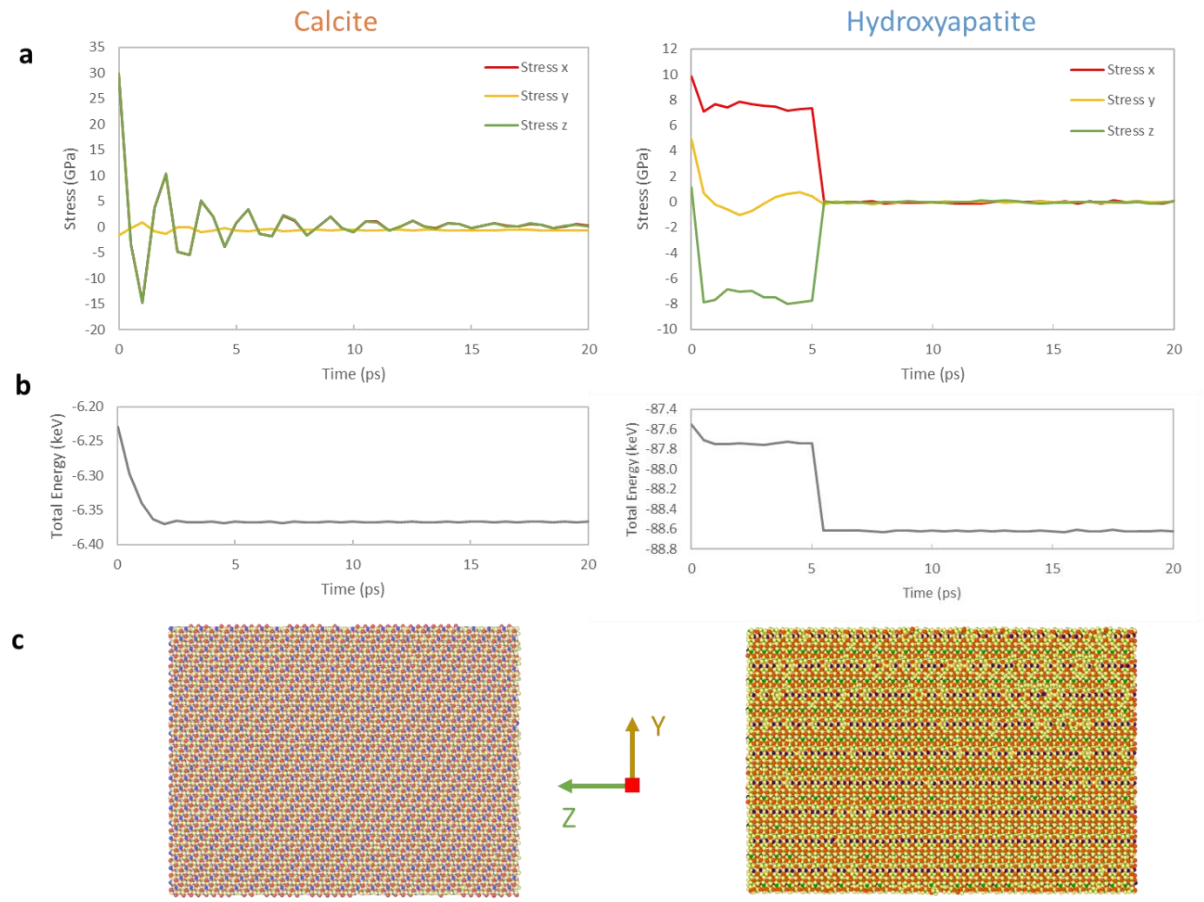

Figure S1. Equilibration of single crystal calcite and HAP in periodic boundary conditions over 20 ps, reaching **a.** relaxed stresses along all three axes and **b.** a stable potential energy minimum. **c.** Visualization after equilibration shows orderly crystal structures.

Supporting Methods: Visualization Cutoffs

Calcite and HAP are not regular BCC or FCC crystals. As a result, typical coordination number values cannot be used to appropriately visualize dislocation cores. Instead, a custom cutoff radius must be chosen to count number of neighbors. Too small choice of cutoff can completely miss most interatomic interactions, as in the case of 2 Å, or focus on local perturbations to the detriment of visualizing larger defect trends, as in the case of HAP 2.7 Å and calcite 2.8 Å. Too large radius ends up coloring atoms based on long range interactions which could blur the locality of dislocation positions. As a result, the cutoff radius was chosen as the boundary between distinguishable shells and more uniform distribution in the RDF. The selected values are 5.2 Å and 4 Å for calcite and HAP, respectively.

The example crystals here are subject to entirely periodic conditions, simulating bulk material with internal nanocracks rather than a nanocrystal with a surface crack. Despite this change, we observe the same remarkable fracture behavior as before: persistent crack damage with voids in calcite contrasted with crack healing in HAP.

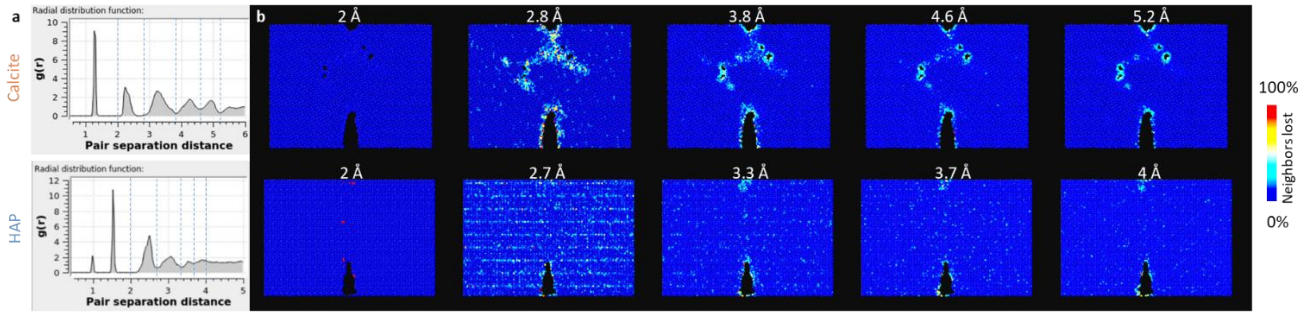

Figure S2. a. Radial distribution function of calcite and HAP crystals. Selected neighbor cutoff radii for dislocation core visualization are noted by the dashed lines. The subsequent images are of **b.** periodic calcite and HAP crystal compressed and partly healed after first fracture, colored by % neighbors lost within each choice of cutoff.

Supporting Results: Fracture Toughness and Critical Energy Release Rate

To validate HAP calculations, we present calculations of two additional material properties, fracture toughness and critical energy release rate. Fracture toughness is a measure of the energy required to fracture a material from an initial notch, with units of $MPa \cdot m^{1/2}$ and critical energy release rate is the amount of energy required to grow a crack during fracture, with units of J/m^2. Details on these calculations are provided in the Methods section of the main text. Calculated values of these material properties align directly with those from the literature. Like material toughness in the main text, the two material properties here also decrease with repeated fracture as the material accumulates damage. Additionally, the error bars tend to be larger at later fractures compared to the initial fracture of pristine crystal, due to build-up of stochastic differences during fracture.

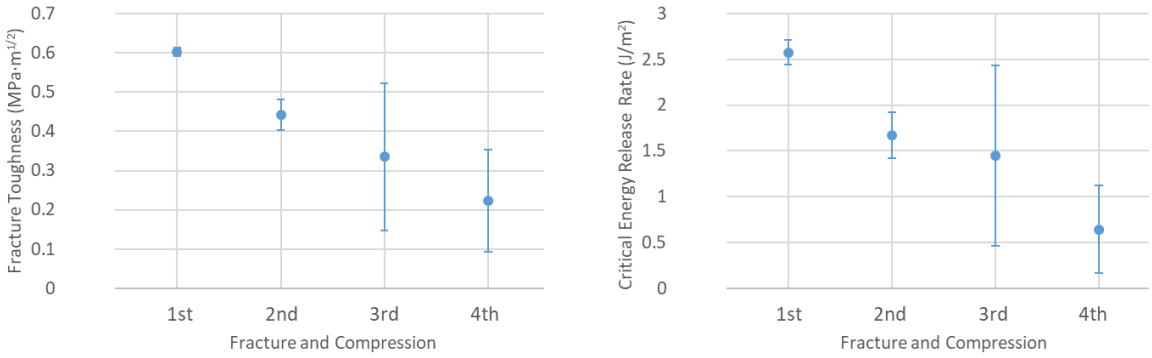

Figure S3. Calculated HAP properties have good agreement to values known in the literature. Pristine HAP properties align with historically known ranges (0.6-10 $MPa \cdot m^{1/2}$ and 2.3-20 J/m^2). Subsequently, all measures of material toughness decrease as the crystal accumulates damage with repeated fracture. Average fracture toughness values align with literature reports of around 0.37 $MPa \cdot m^{1/2}$.