## **Supporting Information**

# Electrochemically enhanced dissolution of silica and alumina in alkaline environments

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#### S1. Approximation of the average pressure of the contact area

From the Hertz theory of contact mechanics,<sup>1</sup> the average pressure (*P*) between crossed cylinders of radius *R* is related to the contact radius (*a*) and the effective combined modulus ( $E^*$ ) by the following equation:

with

$$P = 4aE^*/3\pi R$$
$$E^* = E/(1 - v^2)$$

where *E* is the elastic modulus and v is the Poisson's ratio of the surfaces. Assuming an effective combined elastic modulus  $E^*$  of the layered mica-glue-glass composite used in these experiments of approximately 10 GPa, an approximate contact radius (*a*) of 50 µm, and a radius of curvature (*R*) of 2 cm, the approximate average pressure is 11 MPa or 110 atm, and the pressure at the center of the contact area is 165 atm.

### S2. Approximation of the local pressure at the surface of a confined nanoparticle

With one particle of diameter *d* between the mica surfaces, the mica is distorted over a lateral distance *X* from the particle given by:<sup>2</sup>

$$X = [(8dt^{3}E)/(3P(1-v^{2}))]^{1/4}$$

where t is the thickness of the mica and E is the elastic modulus of the mica. The elastic modulus of the mica rather than the effective modulus of the layered composite is used because the size of the particle is small relative to the mica thickness. A lower bound on the local pressure p between the particle and the mica is given by:

$$p = 4X^2P/d^2$$

Taking d = 200 nm, E = 70 GPa,<sup>3</sup> v = 0.25,<sup>4</sup> t = 4 µm, and P = 11 MPa the radius of the distortion caused by the nanoparticle is X = 20 µm and the local pressure at the surface of the nanoparticle is p = 500 GPa. The expression underestimates the local pressure, because the contact area between the particle and the mica will be smaller than the projected area of the particle ( $\pi d^2/4$ ). Furthermore, pressure at asperities on the particle will be higher still than the average pressure on the particle.

(a) Symmetric mica surfaces in air



**Figure S1.** Schematic of SFA experimental setup used to measure the dissolution of silica and alumina nanoparticles trapped between mica surfaces in alkaline solutions. The interference fringes show the surface profile for (a) symmetric mica surfaces in air and (b) a silica or alumina particle confined between the same mica surfaces in an alkaline solution (0.1 mM NaOH, pH 10). The particle diameter (*d*) is calculated from the shift in wavelength of the interference fringes.



**Figure S2.** Dissolution of an amorphous silica surface in close proximity to a gold electrode at different applied potentials in an alkaline solution (0.1 mM NaOH, pH 10) (black circles, data from Figure 1 in the main text) compared to dissolution of an amorphous silica nanoparticle in close proximity to mica surfaces at the same solution conditions (red circles, data from Figure 2 in the main text).

### S3. Saturation of the volume around a confined dissolving nanoparticle

Following the derivation of Perkin et al.,<sup>2</sup> a particle of diameter *d* between compressed elastic sheets distorts the sheets, with distortion extending a radial distance *X* given by:

$$X = [(8dt^{3}E)/(3P(1 - v^{2}))]^{1/4}$$

The separation between the sheets (y) is given by:

$$y = (3PX^{2}(1 - v^{2})/8Et^{3})(X^{2} - x^{4}/X^{2} + 4r^{2}\ln(x/X))$$

where x is the radial distance from the particle. Integration yields the volume between the surfaces (V) created by the particle:

$$V = \pi P X^{6} (1 - v^{2}) / 16 E t^{3} = [(2\pi^{2} d^{3} t^{3} E) / (27P(1 - v^{2}))]^{1/2}$$

Taking d = 200 nm, E = 70 GPa,<sup>3</sup> v = 0.25,<sup>4</sup>  $t = 4 \mu m$ , and P = 11 MPa (see section S1) yields  $V = 50 \mu m^3$ . The solubility limit of amorphous silica (SiO<sub>2</sub>) at pH 10 and T = 25 °C is 310 ppm = 0.31 g/L. If the silica particle (d = 200 nm) dissolves 10 nm, the dissolved volume is 0.005  $\mu m^3$ , the dissolved mass is  $1.05 \times 10^{-5}$  ng, and the concentration is 2000 g/L, assuming that dissolving species remain in the volume around the particle, well above the solubility limit. To roughly account for diffusion, Fick's law gives:

$$J = -\mathcal{D}(\mathrm{d}c/\mathrm{d}x)$$

where J is the flux per unit area,  $\mathcal{D}$  is the diffusion coefficient of the dissolving species, and c is the concentration of the species. Assuming steady state, the rate of material transport of dissolved species through the gap of cross-sectional area A, height  $h_{gap}$ , and width w between the mica surfaces outside the volume created by the particle is approximately:

$$JA = (-\mathcal{D}\Delta c/w)(2\pi Xh_{gap})$$

The radius of the contact between the mica surfaces is approximately 50 µm, and the radius of the distortion caused by the particle is approximately X = 20 µm, and therefore w = 30 µm. Assuming atomic contact between the surfaces due to the high pressure (110 atm) gives  $h_{gap} = 3$  Å. Assuming a saturated silica solution gives  $\Delta c = 0.31$  g/L = 310 g/m<sup>3</sup>. The diffusion coefficient<sup>5</sup> of dissolved silica in bulk water at 25 °C is  $1 \times 10^{-9}$  m<sup>2</sup>/s. Since the diffusion coefficients of free ions in gaps as narrow as 3 Å have been shown to be within two orders of magnitude of the diffusion coefficient for dissolved silica in the gap. These values yield a mass transport rate of  $2 \times 10^{-12}$  g/hr. This rate of mass transport is much less than the rate needed to keep the concentration of dissolved silica in the volume around the particle lower than the solubility limit, supporting the argument that transport limitations slow dissolution of confined particles.

### References

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