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Surface Site Density of Synthetic Goethites and Its Relationship to Atomic Surface Roughness and Crystal Size

Kenneth J. T. Livi,[1] Mario Villalobos[2], Quentin Ramasse[3,4], Rik Brydson[4], Hugo Slavko Salazar-Rivera[2,5]*

1. Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, MD 21218 USA

2. Environmental and Soil Science Dept., LANGEM, Instituto de Geología, Universidad Nacional Autónoma de México (UNAM), CU, CDMX, 04510 México

3. SuperSTEM Laboratory, Keckwick Lane, Daresbury, WA4 4AD UK

4. School of Chemical and Process Engineering, University of Leeds, Leeds LS2 9JT UK

5. Deceased

CORRESPONDING AUTHOR: klivi@jhu.edu

Supporting Information

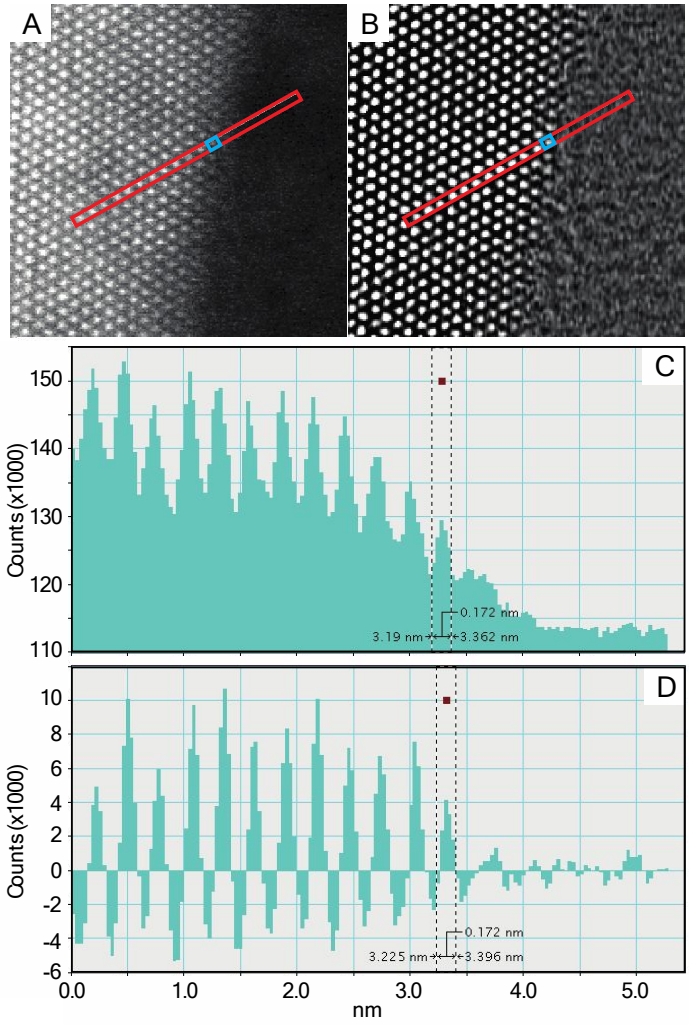

Figure S1. The effect of use of Statistically Determined Spatial Drift (SDSD) filter on AC-STEM HAADF images. A) Unfiltered manually-aligned sum of 15 images. Red box indicates area

of profile shown in C). Blue box indicates last Fe atom position. B) SDSD processed image of same area. D) Profile of red rectangle in B). Intensities of image span into negative numbers.

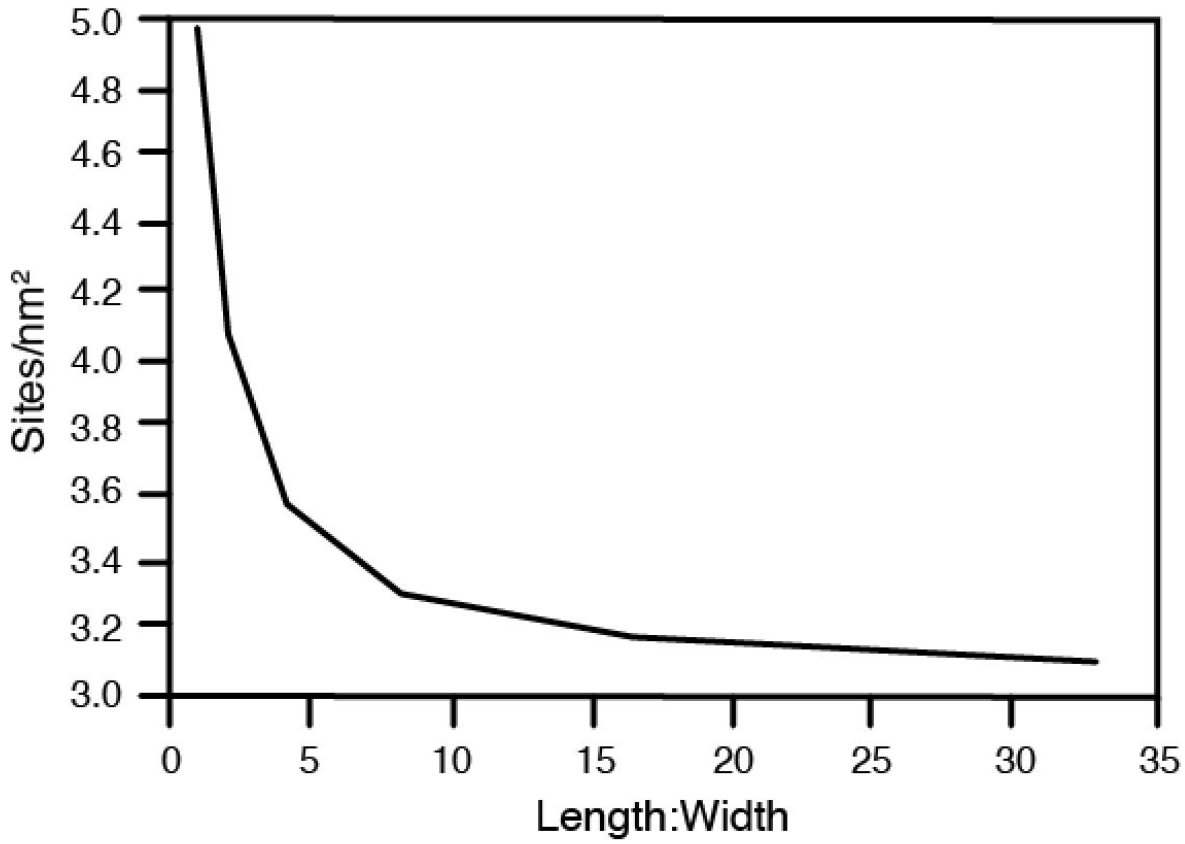

Figure S2. Calculated relationship of bulk singly-coordinated site densities of ideal goethite crystals with changing aspect ratios. Length = dimension of the **b** axis, width = dimension of the **a** axis.

Figure S3. Surface proton charging behavior of 82 m^2/g and 94 m^2/g goethites at three different ionic strengths imposed with $NaNO_3$.

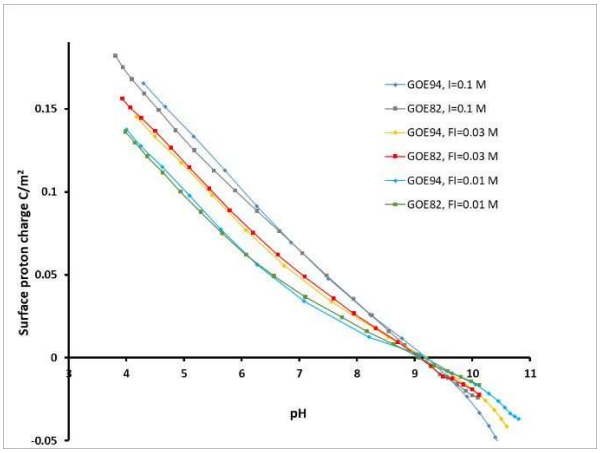

Table S1 includes the calculated number of sites for the singly, doubly and triply coordinated binding models for each sample. From these values, the calculated total site densities for GOE76 are: singly coord. = 4.26, doubly coord. = 1.03, triply coord. = 2.20 sites/nm^2; and for GOE53: singly coord. = 4.50, doubly coord. = 1.24, triply coord. = 2.03 sites/nm^2. These values together with the estimated SSAs from the TEM models are necessary for adequate surface complexation modeling: for proton charging both singly- and triply-coordinated site densities are required, while for ion binding singly-coordinated site densities are crucial and perhaps in some cases doubly-coordinated sites may be required. The labor-intensive measurements performed in the present work will require finding adequate correlations of parameters for a simpler way to predict the SSAs and site densities for goethite preparations of different SSAs, especially for those below *ca.* 80 m^2/g as measured by BET.

Table S1. Summary of calculated sites per representative crystal.

Sample GOE76	Step Type	Percent of Face	Area of Steps ($x10^4$ nm^2)	# Singly Coord Sites ($x10^4$)	# Doubly Coord Sites ($x10^4$)	# Triply Coord Sites ($x10^4$)
Prism	{210}	24 ± 1	0.30 ± 0.02	2.23 ± 0.22	1.12 ± 0.01	0
Prism	{101}	76 ± 4	0.94 ± 0.04	2.86 ± 0.29	0	2.86 ± 0.29
Tip	{210}	74 ± 4	0.068 ± 0.003	0.51 ± 0.05	0.25 ± 0.03	0
Tip	{101}	26 ± 1	0.024 ± 0.001	0.072 ± 0.007	0	0.072 ± 0.007
Total	{210}	27 ± 2	0.37 ± 0.02	2.74 ± 0.51	1.37 ± 0.28	0
Total	{101}	73 ± 5	0.97 ± 0.05	2.93 ± 0.59	0	2.93 ± 0.59

Sample GOE53	Step Type	Percent of Face	Area of Steps ($x10^4$ nm^2)	# Singly Coord Sites ($x10^4$)	# Doubly Coord Sites ($x10^4$)	# Triply Coord Sites ($x10^4$)
Prism	{210}	30 ± 2	3.66 ± 0.18	27.5 ± 5.0	13.7 ± 2.4	0
Prism	{101}	70 ± 2	8.54 ± 0.43	25.9 ± 4.3	0	25.9 ± 4.3
Tip	{210}	84 ± 2	0.59 ± 0.03	4.43 ± 0.69	2.21 ± 0.36	0
Tip	{101}	16 ± 2	0.11 ± 0.01	0.34 ± 0.07	0	0.341 ± 0.07
Total	{210}	33 ± 2	4.25 ± 0.21	31.9 ± 6.5	15.9 ± 3.2	0
Total	{101}	67 ± 2	8.65 ± 0.43	26.2 ± 4.8	0	26.2 ± 4.8