Solving crystal structures of nanominerals & constructing size-dependent phase maps using transmission electron microscopy

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Wisc Nano-Geoscience
From atoms to mountain building

Nanoscience Workshop, Aug. 12-13, 2017

THE UNIVERSITY of WISCONSIN MADISON

Nano vs. Macro-

Nano-phases, nano-crystals

Nano-minerals

Photos are from web page

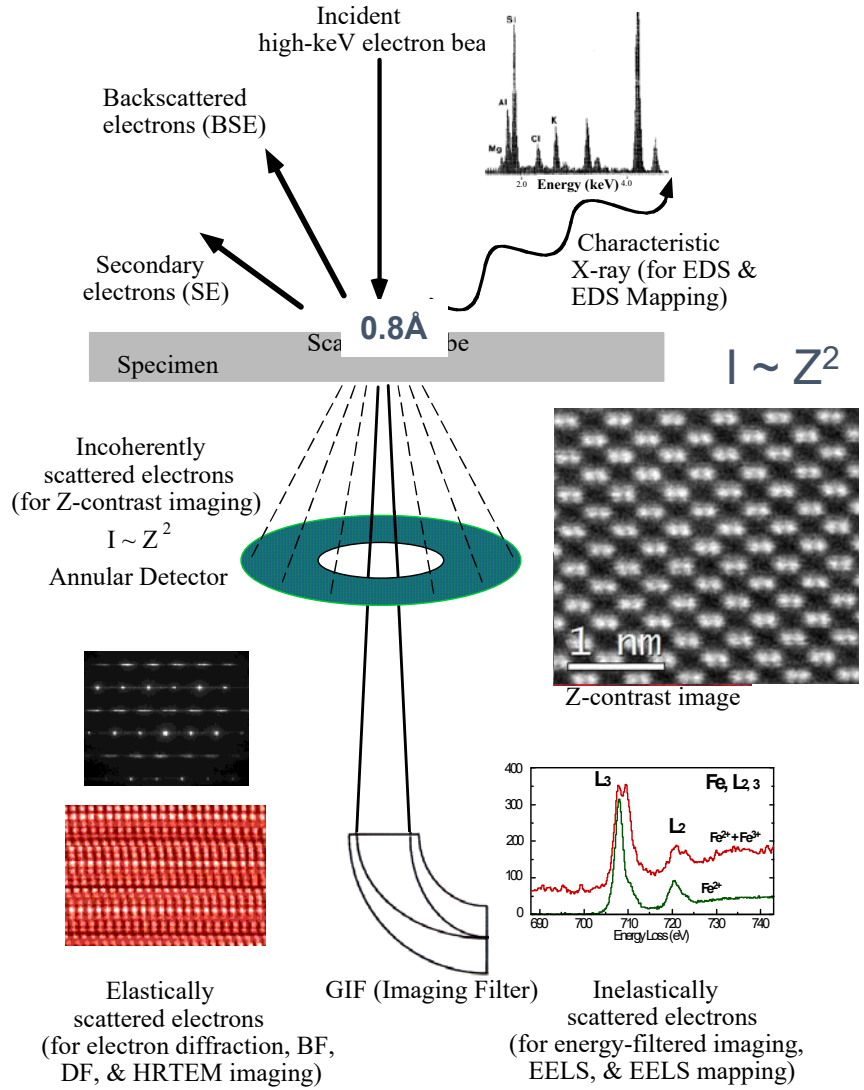
The challenge : Knowing the ‘real’ structure

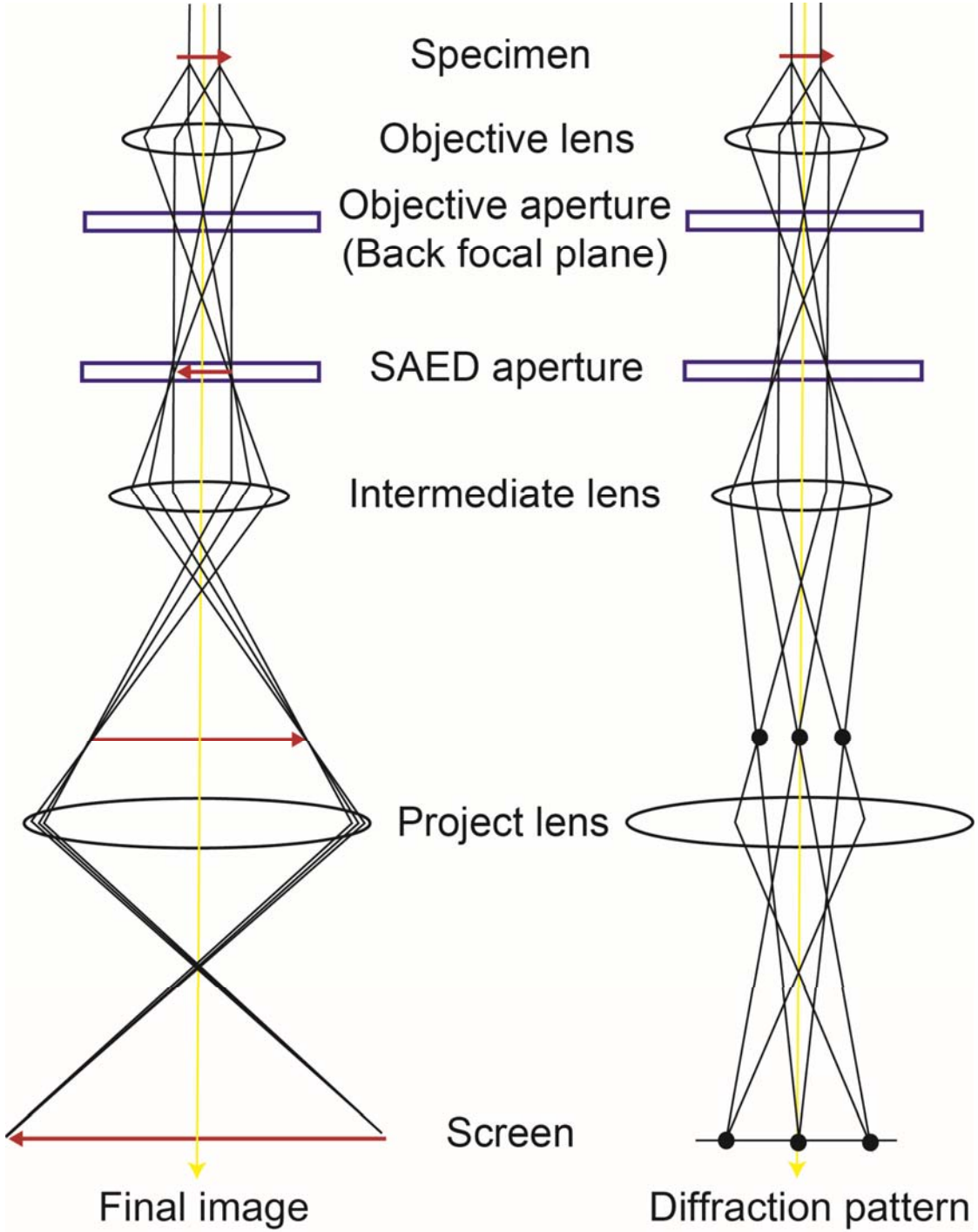
Information about the samples

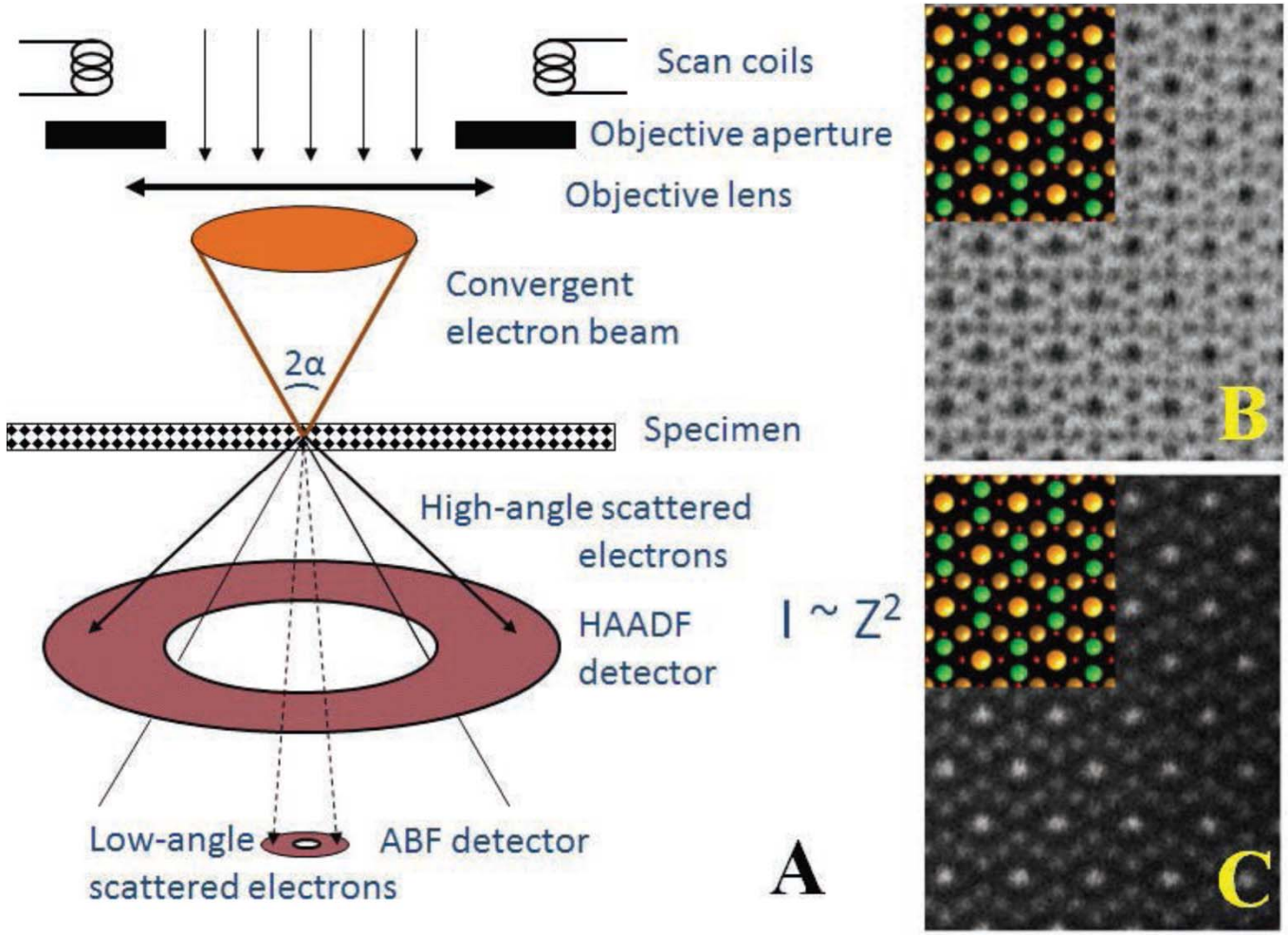
- PDF: Direct measure / Bulk
- FTIR/NMR/Raman: Indirect / Bulk
- XRD/Neutron diffraction: Direct / Bulk
- HRTEM/Z-contrast imaging : Direct / Local

Transmission electron microscope: Not just a lens, but a nano-lab

Cs-corrected FEG-STEM/HRTEM at MSC




Specimen
Objective lens
Objective aperture
(Back focal plane)
SAED aperture
Intermediate lens
Project lens
Screen
Final image
Diffraction pattern



(**a**) Schematic diagram of STEM showing formation of a Z-contrast image (or HAADF image) and annular bright-field (ABF) image. ABF image (**b**) and Z-contrast image (**c**) of magnetite (Fe_3O_4) showing position of Fe atom columns. ABF image also shows positions of oxygen atom columns (**b**). Structure model of magnetite along [110] zone-axis is also inserted in both images for comparison. (Color online.)

Xu et al., 2014

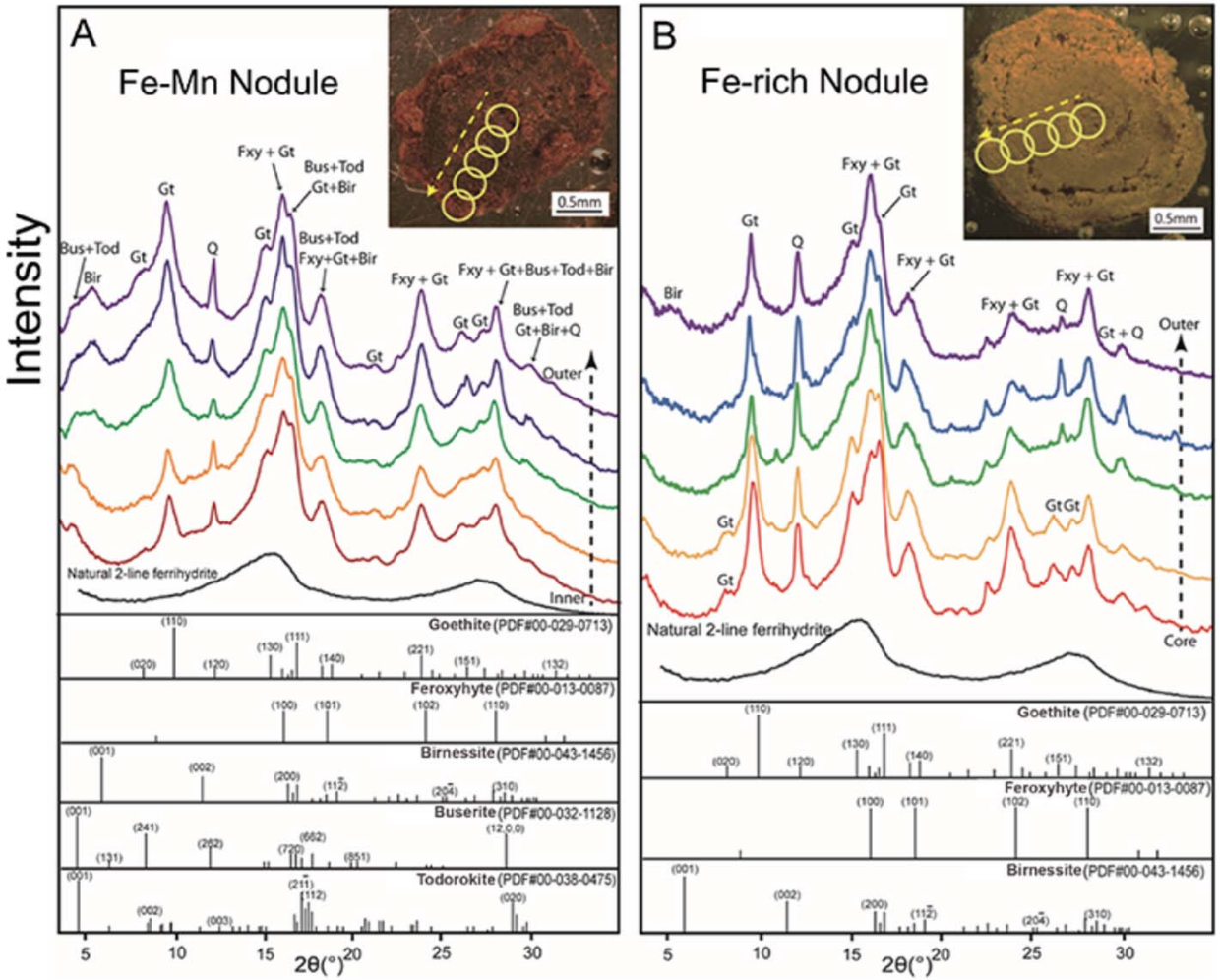
American Mineralogist, Volume 101, pages 1986–1995, 2016

SPECIAL COLLECTION: NANOMINERALS AND MINERAL NANOPARTICLES

Study on nanophase iron oxyhydroxides in freshwater ferromanganese nodules from Green Bay, Lake Michigan, with implications for the adsorption of As and heavy metals

SEUNGYEOL LEE[1], ZHIZHANG SHEN[1], AND HUIFANG XU[1,*]

[1]NASA Astrobiology Institute, Department of Geoscience, University of Wisconsin-Madison, Madison, Wisconsin 53706, U.S.A.



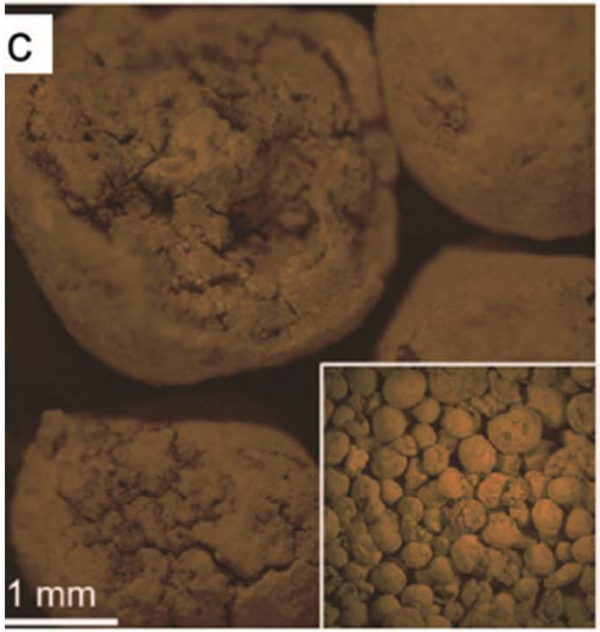
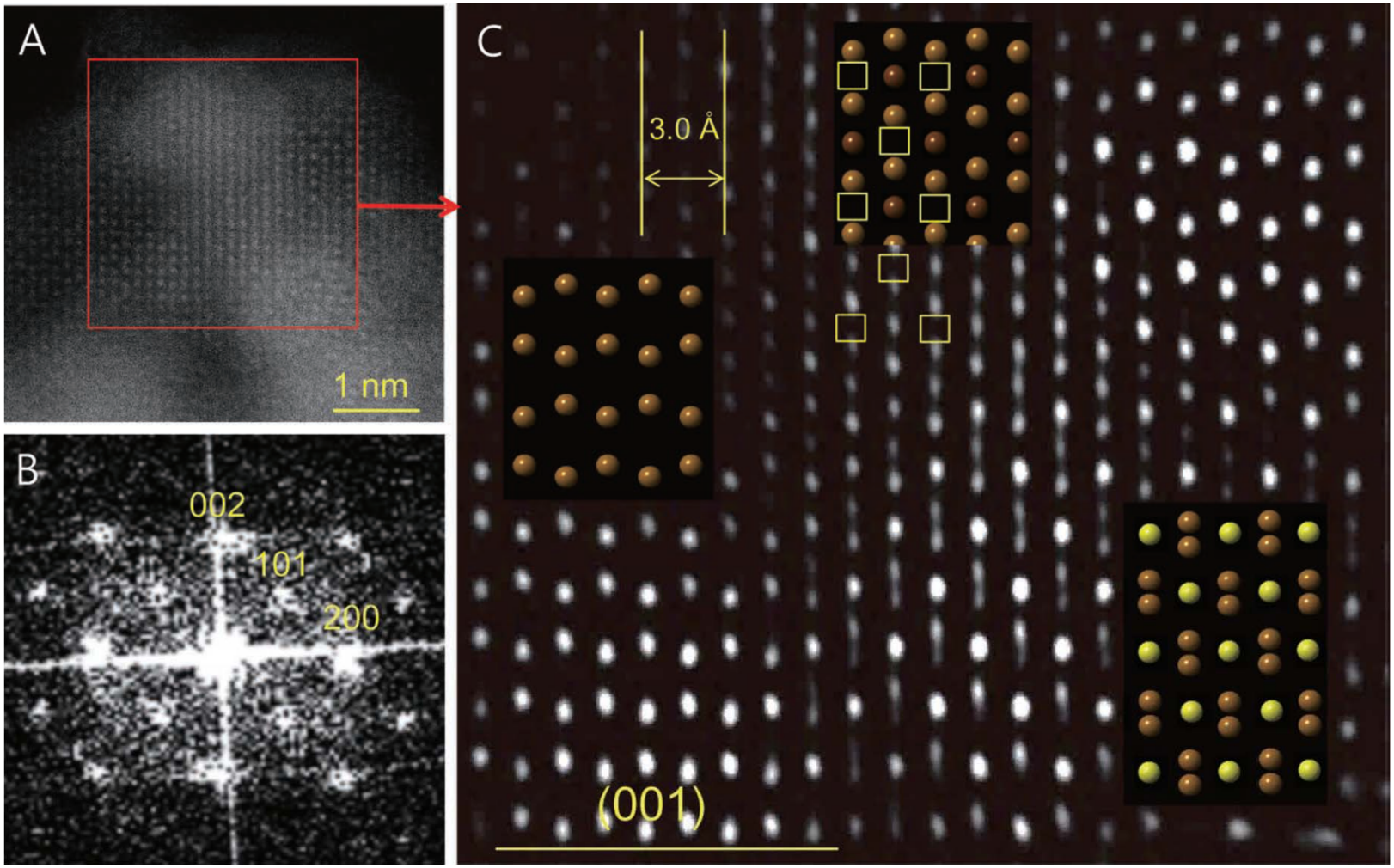


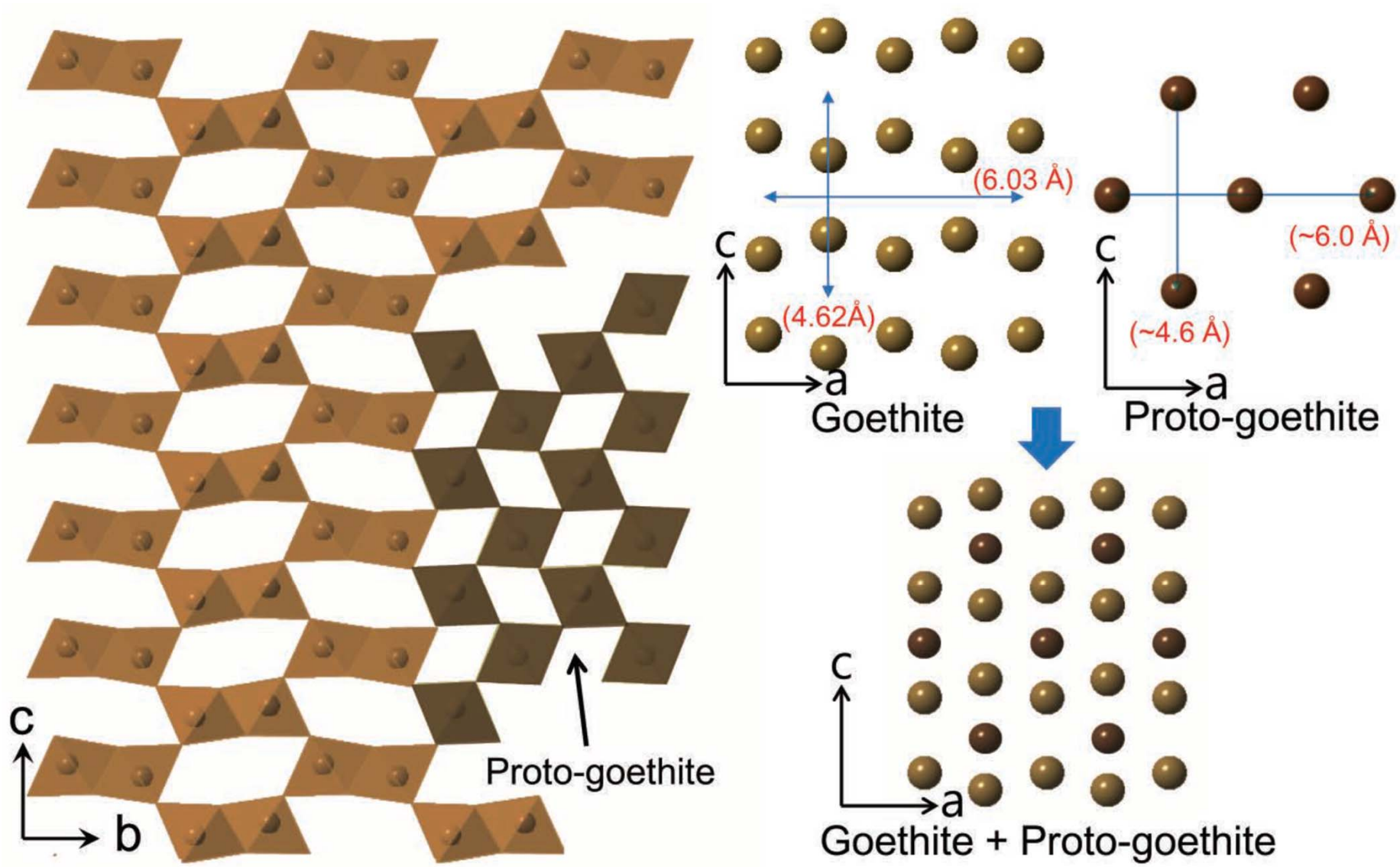
FIGURE 3. X-ray diffraction patterns of Green Bay FFN taken with 0.3 mm collimator, including natural two-line ferrihydrite, and other reference XRD patterns. Yellow circles are the spots of XRD beam. Bus = buserite; Bir = birnessite; Fxy = feroxyhyte; Gt = goethite; Tod = todorokite; Q = quartz. (Color online.)

Lee et al., 2016

Z-contrast Image of FeOOH



FeOOH: goethite and proto-goethite



DFT: Proto-goethite FeOOH

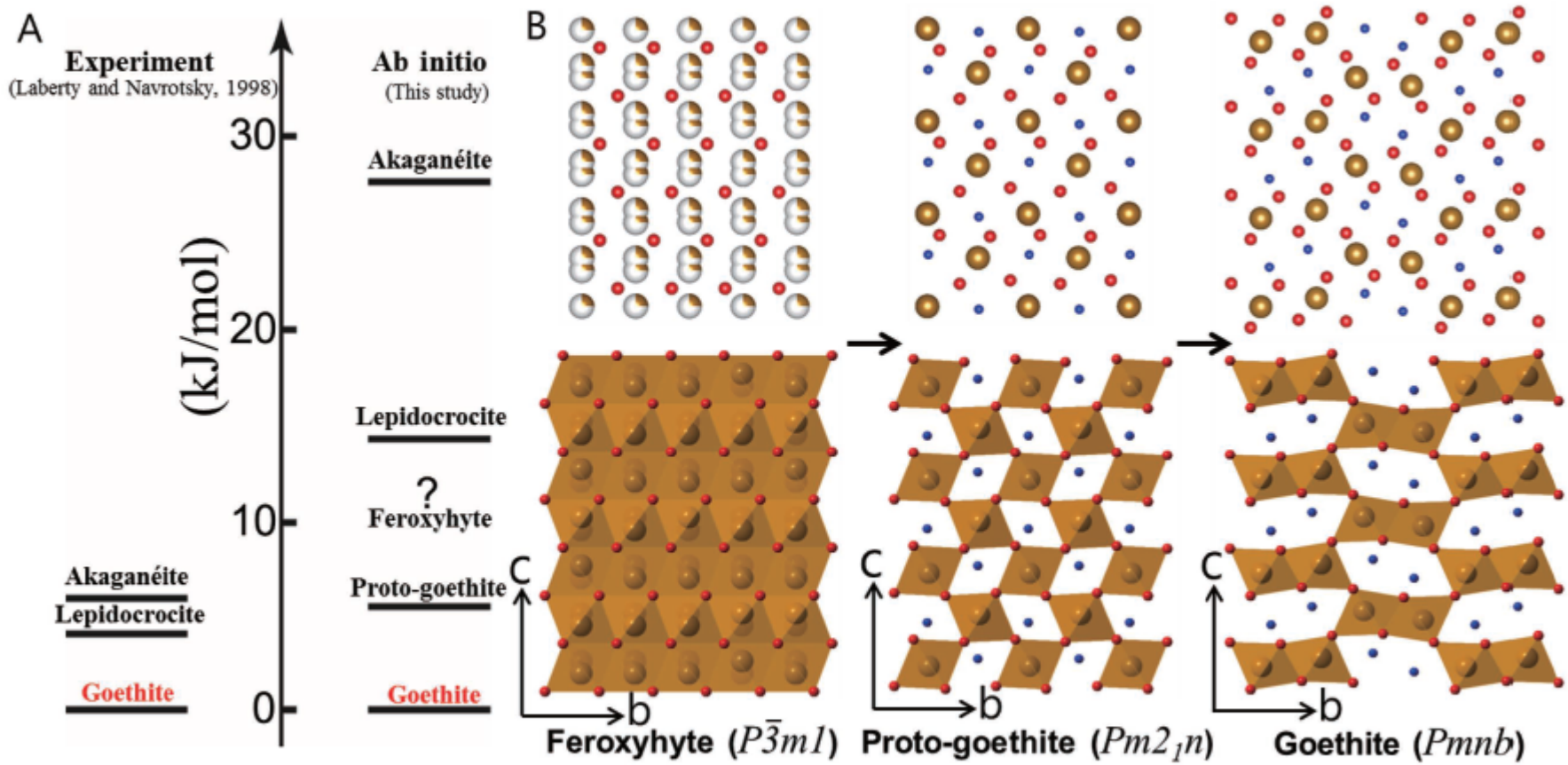
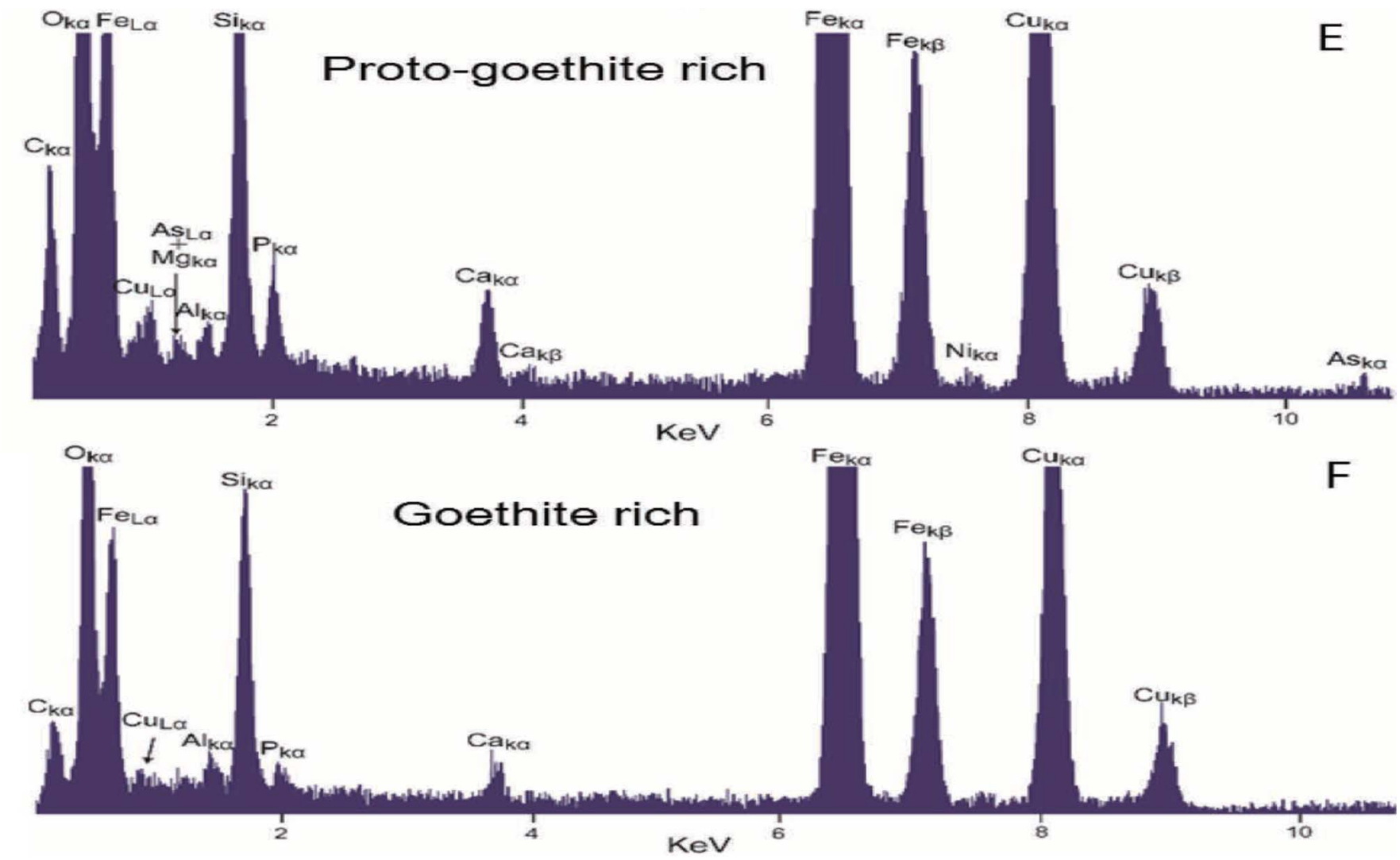


FIGURE 9. (a) Energy differences of other FeOOH polymorphs with respect to goethite, and (b) ball-and-stick models of feroxyhyte, proto-goethite, and goethite along [100] zone axis. The Fe, O, H atoms are colored in brown, red, and blue, respectively. (Color online.)

Lee et al., 2016

P and As associated with proto-goethite



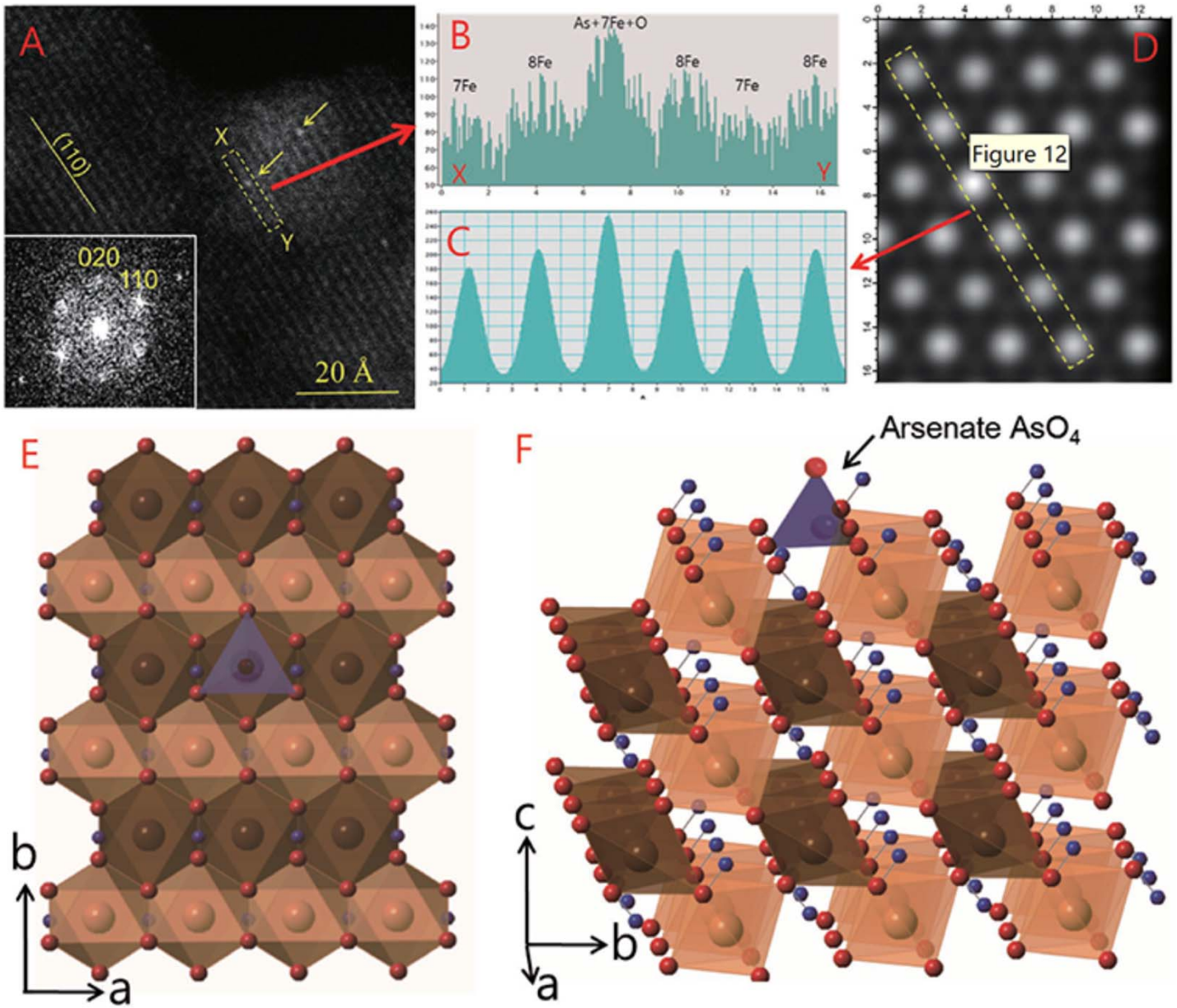


FIGURE 12. (**a**) A [001] zone axis Z-contrast image of proto-goethite; bright spots are positions of Fe atom columns. Very bright spots are As atoms on the surface right above Fe. (**b**) The intensity profile of an outlined area from X to Y. (**c**) The intensity profile of simulated Z-contrast image. (**d**) A simulated Z-contrast image; (**e–f**) polyhedral models showing arsenate adsorption on (001) surface of the proto-goethite. (Color online.)

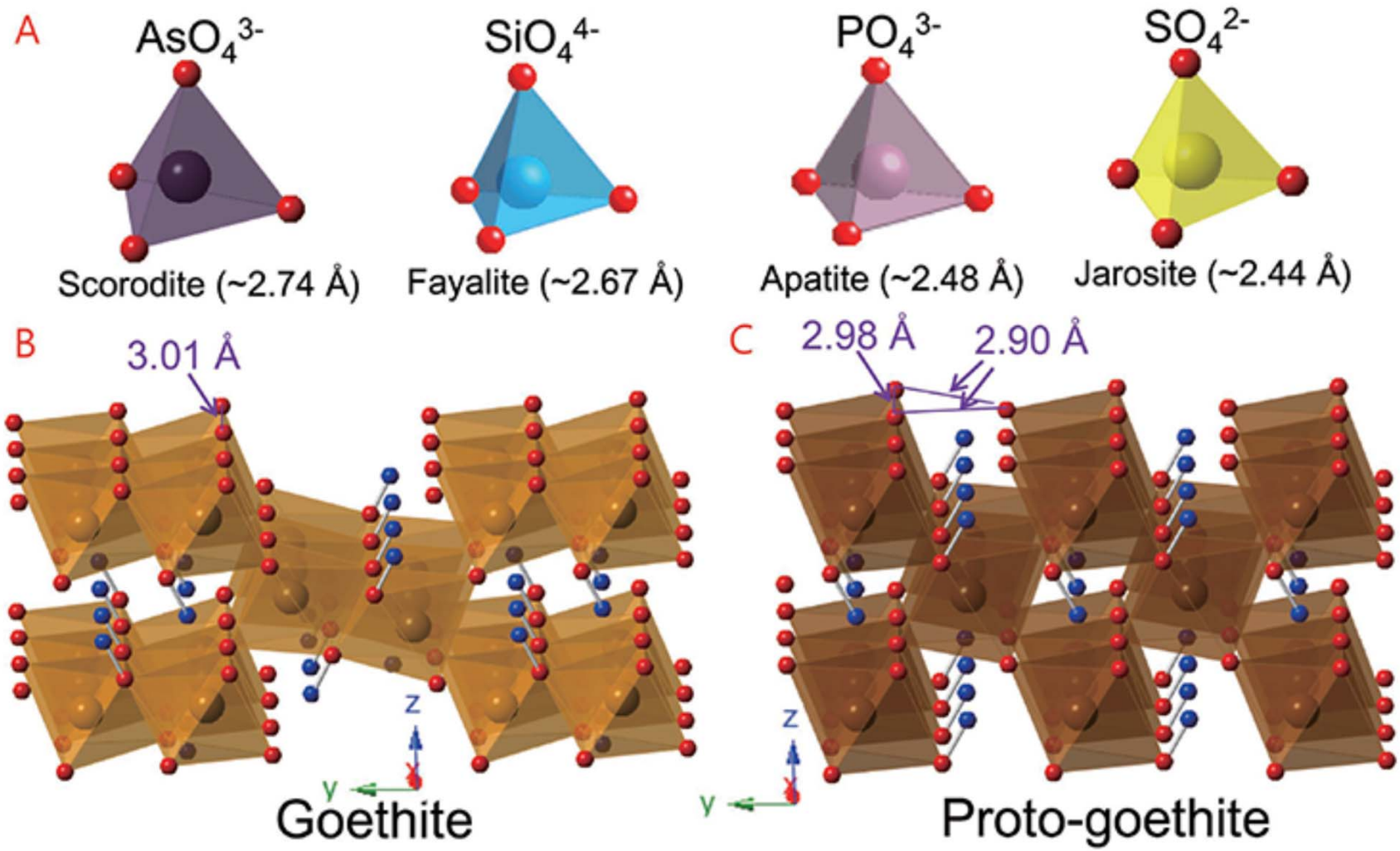
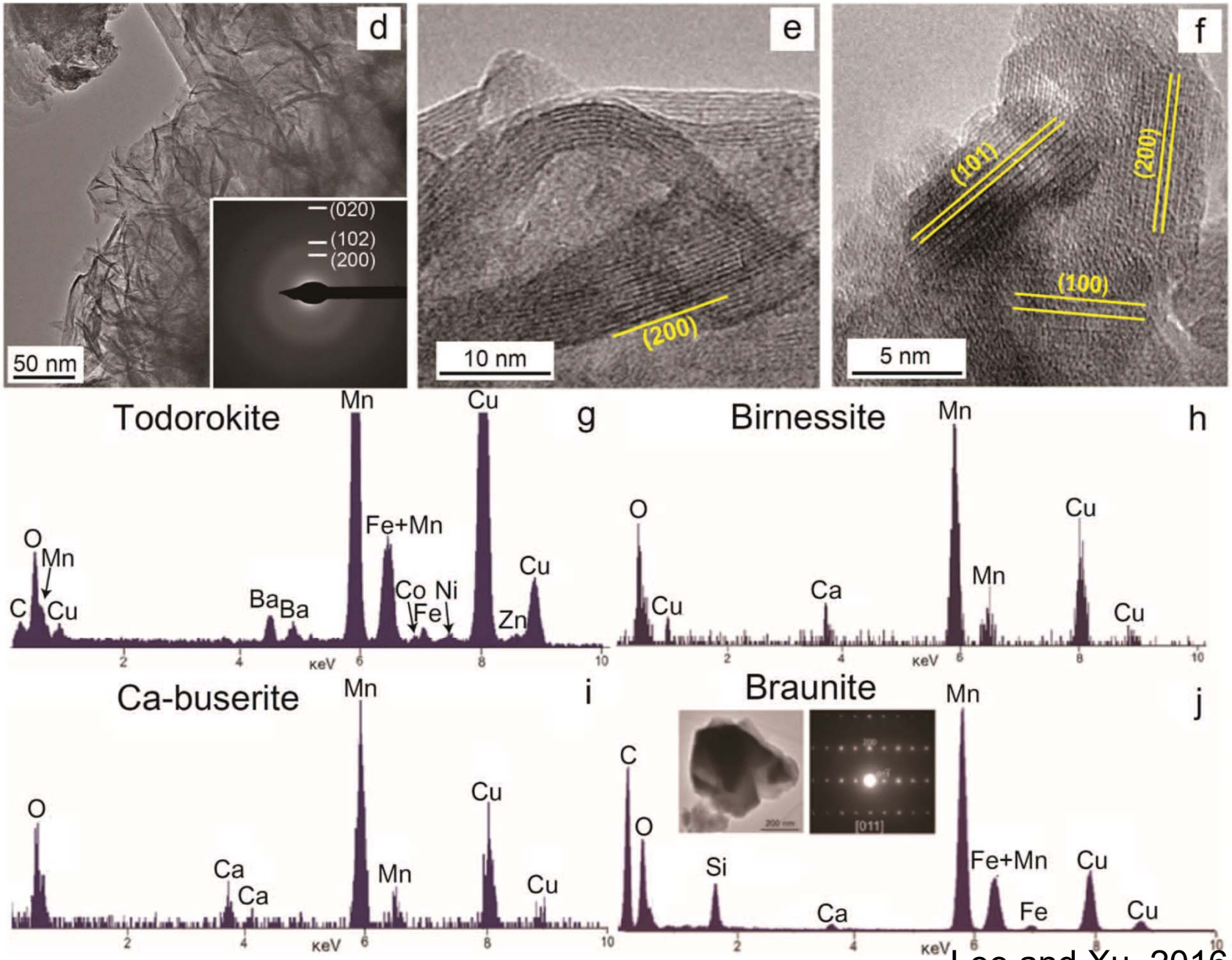


FIGURE 13. Polyhedral models of (001) surface of goethite and proto-goethite with tetrahedral models of arsenate (scorodite), silicate (fayalite), phosphate (apatite), and sulfate (jarosite). (Color online.)

Lee et al., 2016

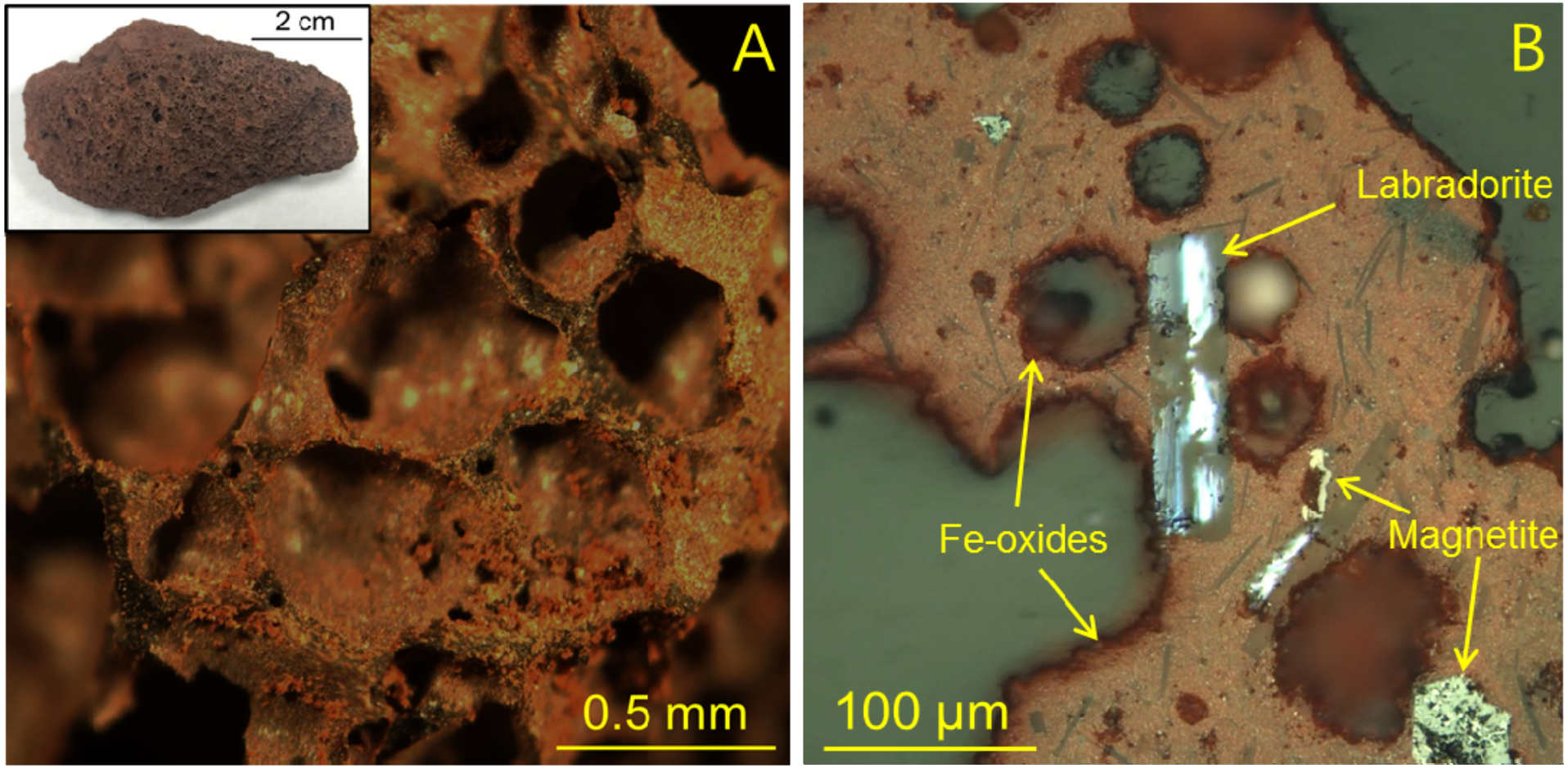
Mn-rich Nodules



Lee and Xu, 2016

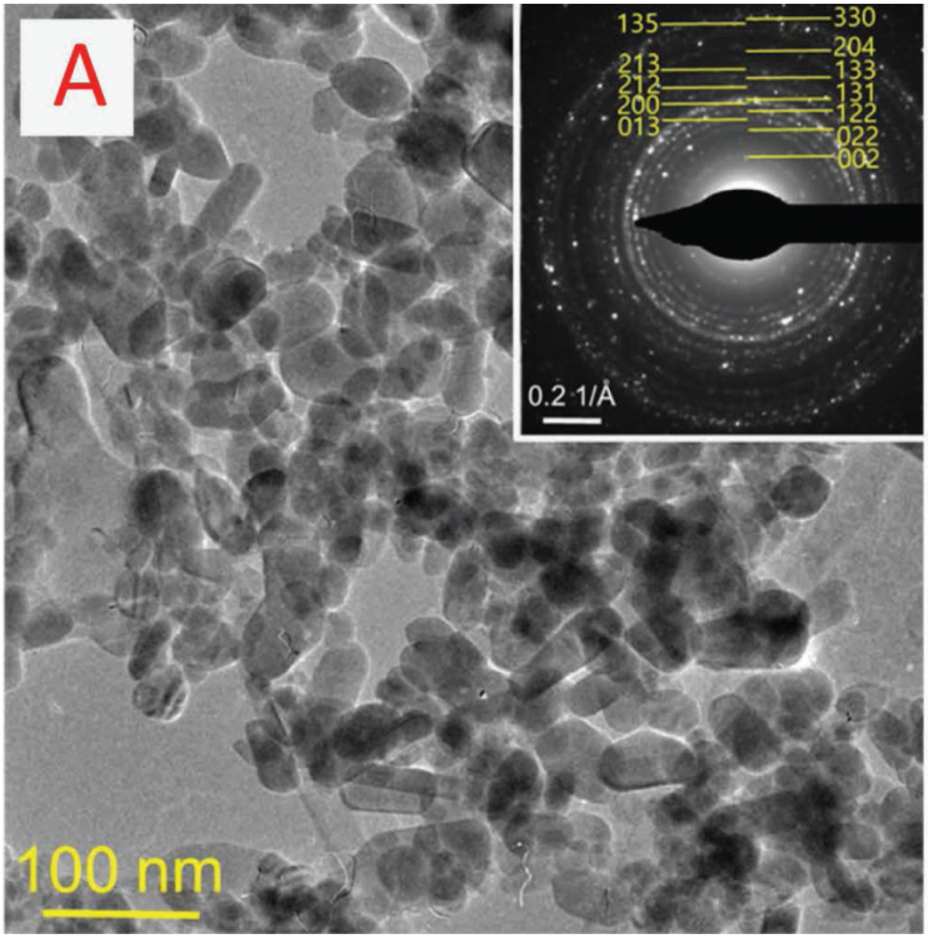
Nanomineral luogufengite from

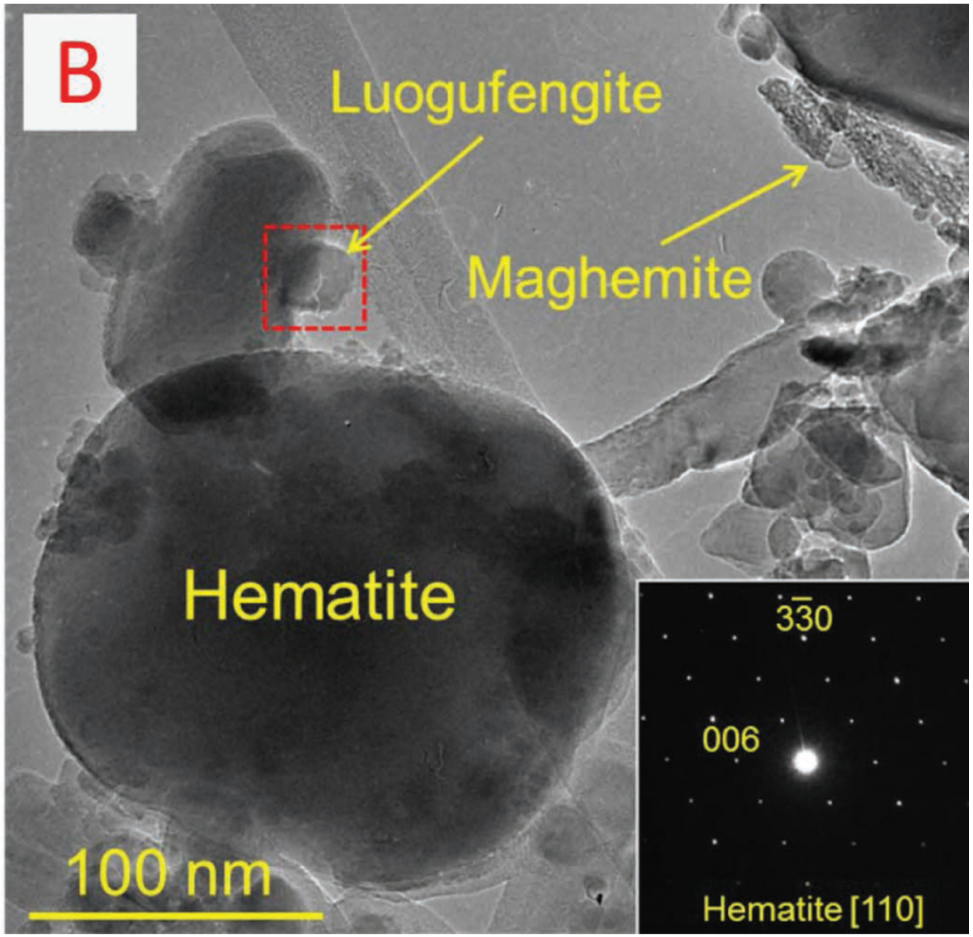
Basaltic rocks, Menan Buttes, Rexburg, ID



Xu et al., 2017a

Transmission electron microscopy





American Mineralogist, Volume 102, pages 711–719, 2017

SPECIAL COLLECTION: NANOMINERALS AND MINERAL NANOPARTICLES

Luogufengite: A new nano-mineral of Fe_2O_3 polymorph with giant coercive field

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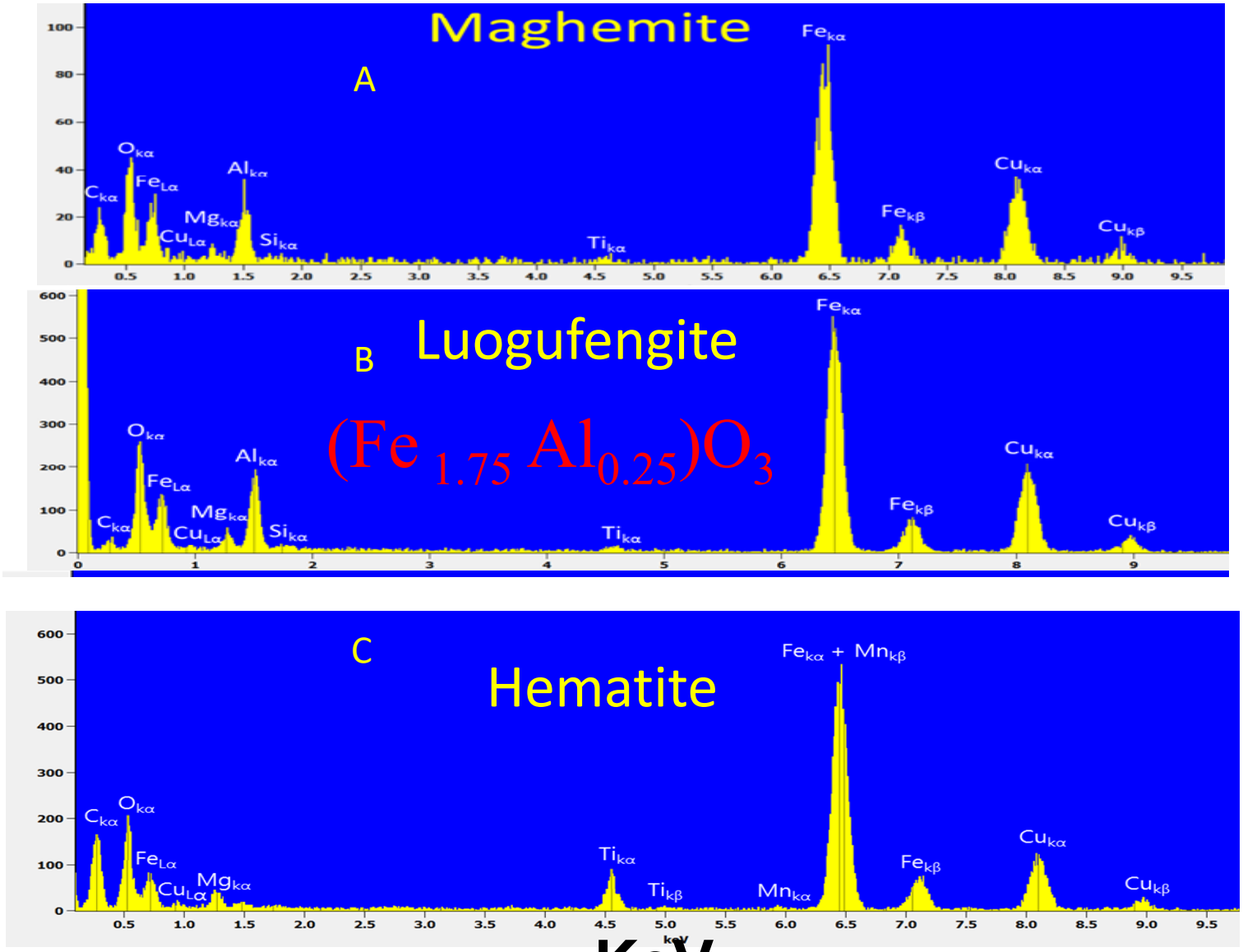
[2]Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, U.S.A.

Composition of luogufengite +



Xu et al., 2017a

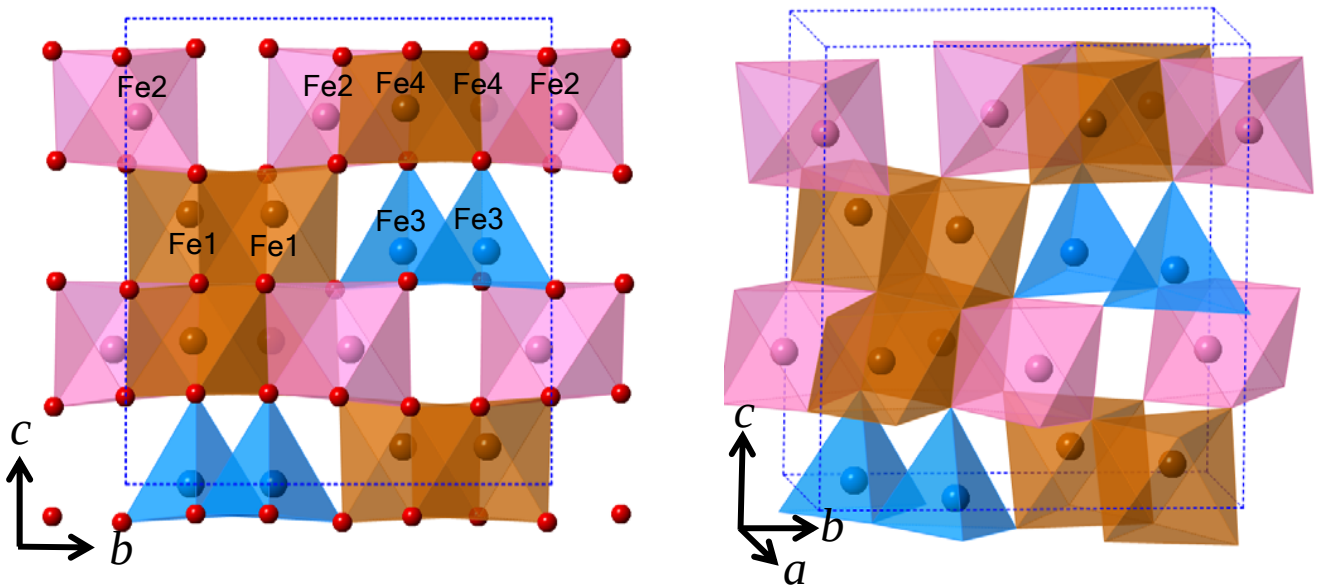
X-ray EDS of luogufengite, maghemite, and hematite

TABLE 2. Chemical compositions of luogufengite, maghemite, and hematite

	(1)	(2)	(3)	(4)	(5)	Average
Luogufengite ($Fe_{1.71}Al_{0.24}Mg_{0.02}Ti_{0.03}O_3$)						
Fe_2O_3 (wt%)	90.03%	89.74%	89.76%	90.18%	90.01%	89.94%
Al_2O_3	7.84%	8.68%	8.01%	7.62%	7.48%	7.93%
MgO	1.06%	1.06%	1.73%	0.80%	1.46%	1.22%
TiO_2	1.07%	0.52%	0.50%	1.40%	1.05%	0.91%
Fe	1.70	1.70	1.71	1.71	1.71	1.71
Al	0.23	0.26	0.24	0.23	0.22	0.24
Mg	0.02	0.02	0.03	0.02	0.03	0.02
Ti	0.05	0.02	0.02	0.04	0.04	0.03
Maghemite ($Fe_{1.69}Al_{0.25}Mg_{0.04}Ti_{0.02}O_3$)						
Fe_2O_3 (wt%)	88.04%	88.37%	89.41%	89.13%	89.54%	88.90%
Al_2O_3	9.43%	8.36%	7.87%	8.44%	8.59%	8.54%
MgO	2.14%	2.50%	2.33%	2.14%	1.62%	2.14%
TiO_2	0.39%	0.77%	0.39%	0.29%	0.25%	0.42%
Fe	1.67	1.68	1.71	1.70	1.70	1.69
Al	0.28	0.25	0.24	0.25	0.26	0.25
Mg	0.04	0.05	0.04	0.04	0.03	0.04
Ti	0.01	0.03	0.01	0.01	0.01	0.02
Hematite ($Fe_{1.76}Al_{0.02}Mg_{0.03}Ti_{0.19}O_3$)						
Fe_2O_3 (wt%)	92.85%	92.89%	92.71%	93.32%	93.04%	92.96%
Al_2O_3	1.10%	0.42%	0.29%	0.78%	0.76%	0.67%
MgO	1.28%	1.20%	1.98%	1.09%	1.53%	1.42%
TiO_2	4.77%	5.49%	5.02%	4.81%	4.67%	4.95%
Fe	1.76	1.76	1.76	1.77	1.77	1.76
Al	0.03	0.01	0.01	0.02	0.02	0.02
Mg	0.02	0.02	0.04	0.02	0.02	0.03
Ti	0.18	0.21	0.19	0.18	0.18	0.19

Note: All calculations are based on three oxygen atoms basis.

Crystal Structure of Luogufengite



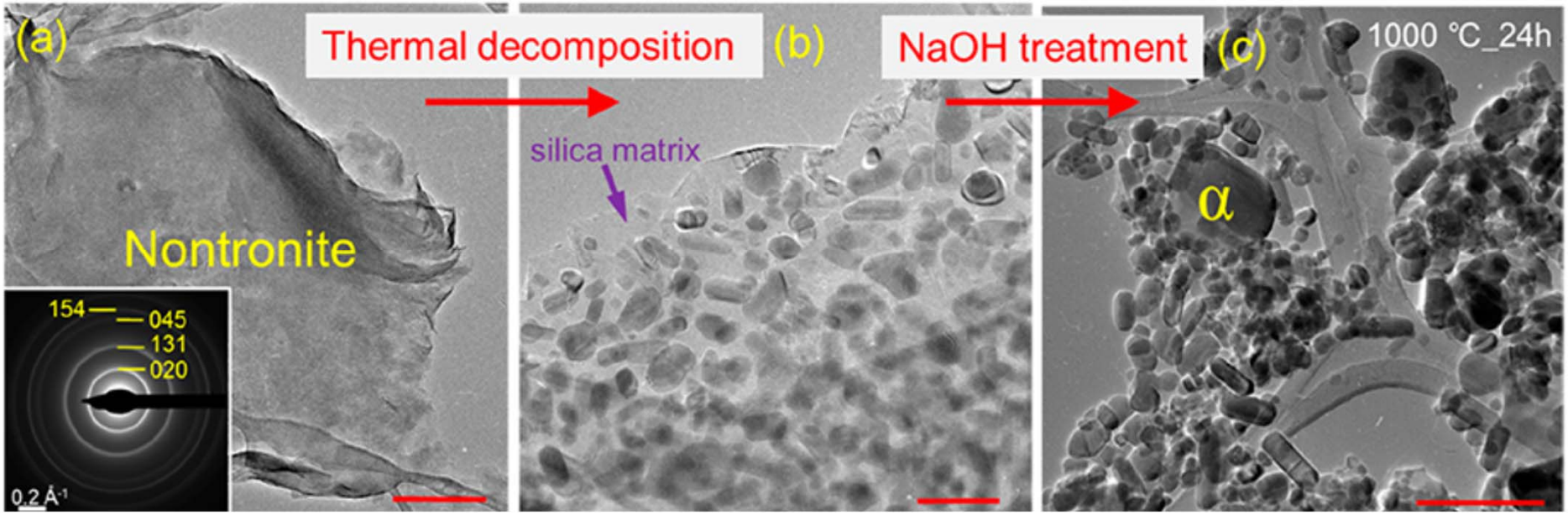
$Pnm2_1$

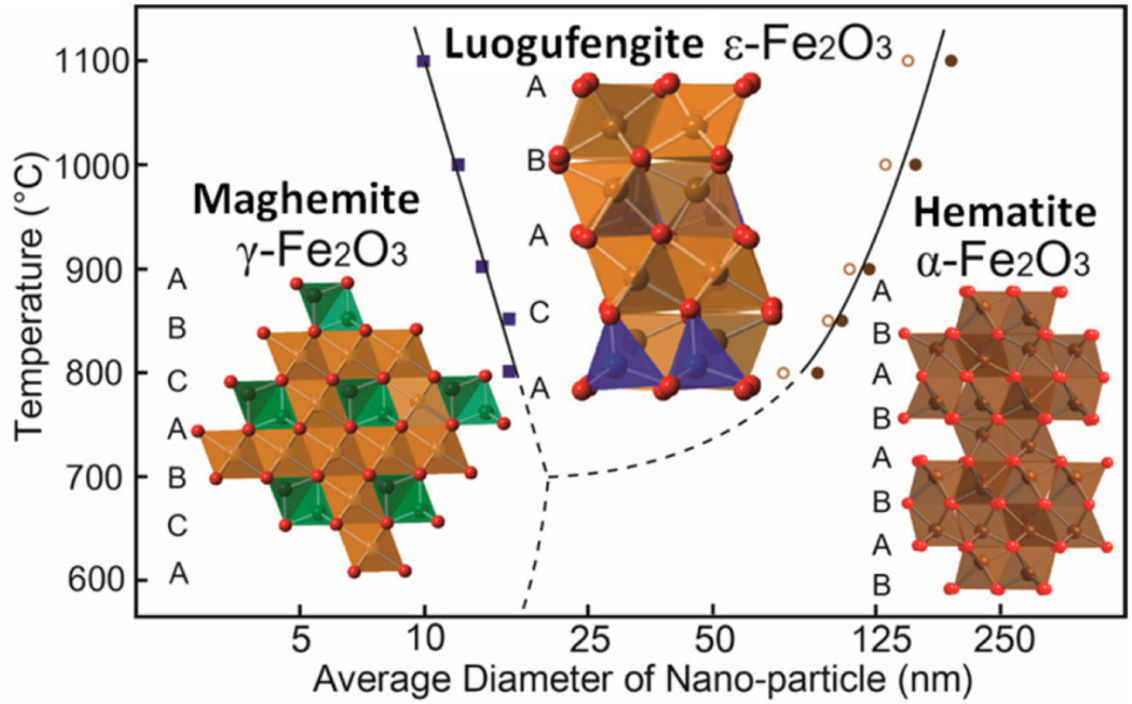
TABLE 3. Atomic coordinates of luogufengite (space group $Pna2_1$)

Atom	Occupancy	x	y	z
Fe1	Fe 1.00	0.1941(3)	0.1569(4)	0.5789(6)
Fe2	Fe 1.00	0.6844(5)	0.0228(3)	0.7893(7)
Fe3	Fe 0.73 Al 0.27	0.1878(3)	0.1531(6)	0.0000(2)
Fe4	Fe 0.80 Al 0.20	0.8081(4)	0.1602(2)	0.3044(6)
O1	O 1.00	0.9812(3)	0.3356(3)	0.4396(5)
O2	O 1.00	0.5106(2)	0.4953(3)	0.4154(5)
O3	O 1.00	0.6477(3)	0.9869(7)	0.1961(6)
O4	O 1.00	0.1569(5)	0.1568(6)	0.1902(3)
O5	O 1.00	0.8325(5)	0.1705(4)	0.6651(3)
O6	O 1.00	0.5391(4)	0.1717(2)	0.9423(6)

Notes: Lattice parameters: $a = 5.0647(3)$, $b = 8.7131(6)$, $c = 9.3842(5)$. Refinement agreement parameter: $R = 9.35\%$.

Xu et al., 2017a





Lee and Xu, 2016

THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

pubs.acs.org/JPCC

Size-Dependent Phase Map and Phase Transformation Kinetics for Nanometric Iron(III) Oxides ($\gamma \rightarrow \varepsilon \rightarrow \alpha$ Pathway)

Seungyeol Lee and Huifang Xu*

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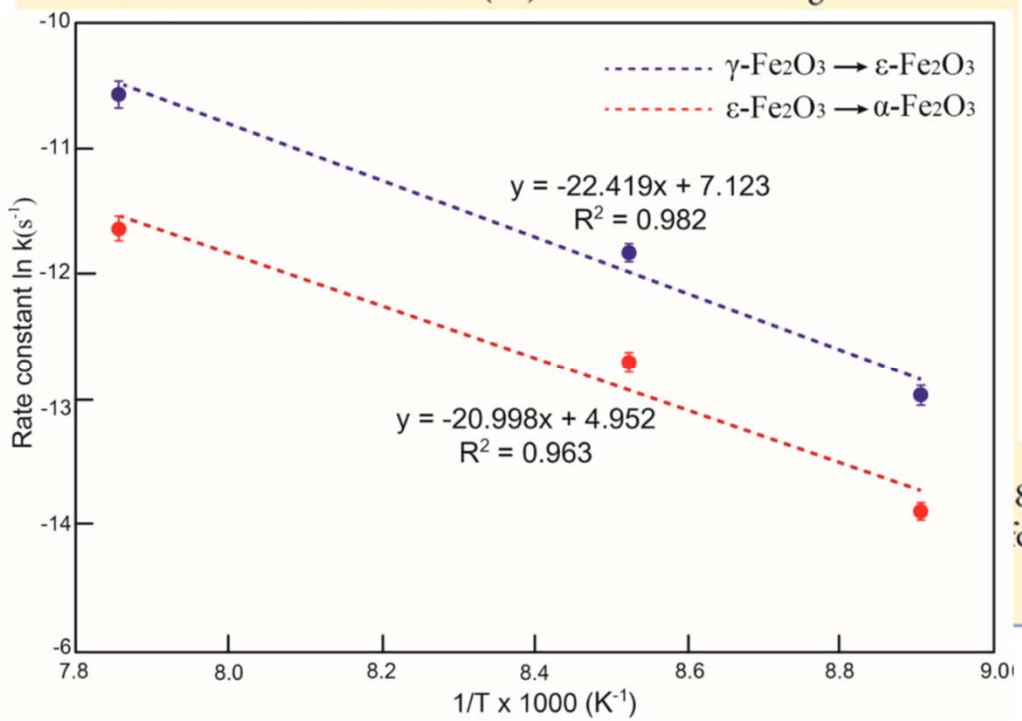
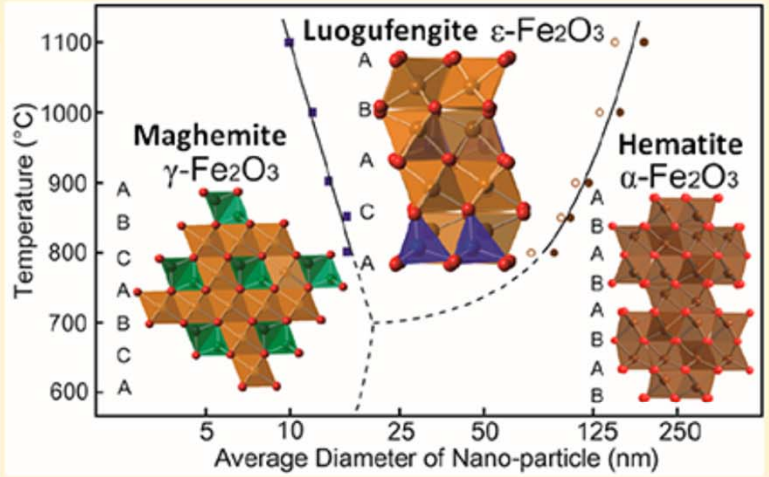
Supporting Information

ABSTRACT: Nanometric iron(III) oxide has been of great interest





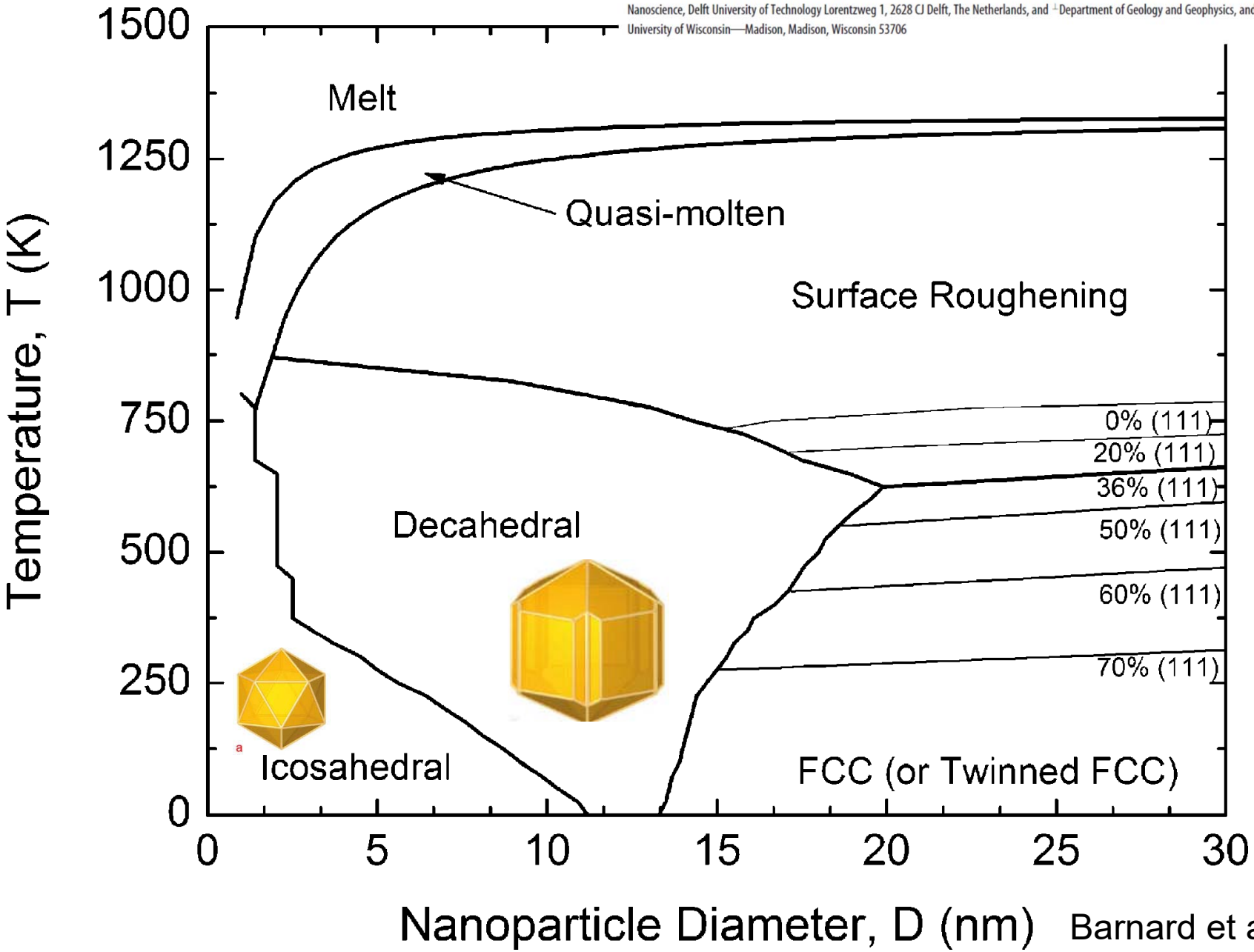
89 and 174.58 ± 2.24 kJ mol^{-1}, respectively. The results formation of the nanometric iron oxide polymorphs for

Gold nano-crystals

Nanogold: A Quantitative Phase Map

Amanda S. Barnard,[†,*] Neil P. Young,[‡] Angus I. Kirkland,[‡] Marijn A. van Huis,[§] and Huifang Xu[⊥]

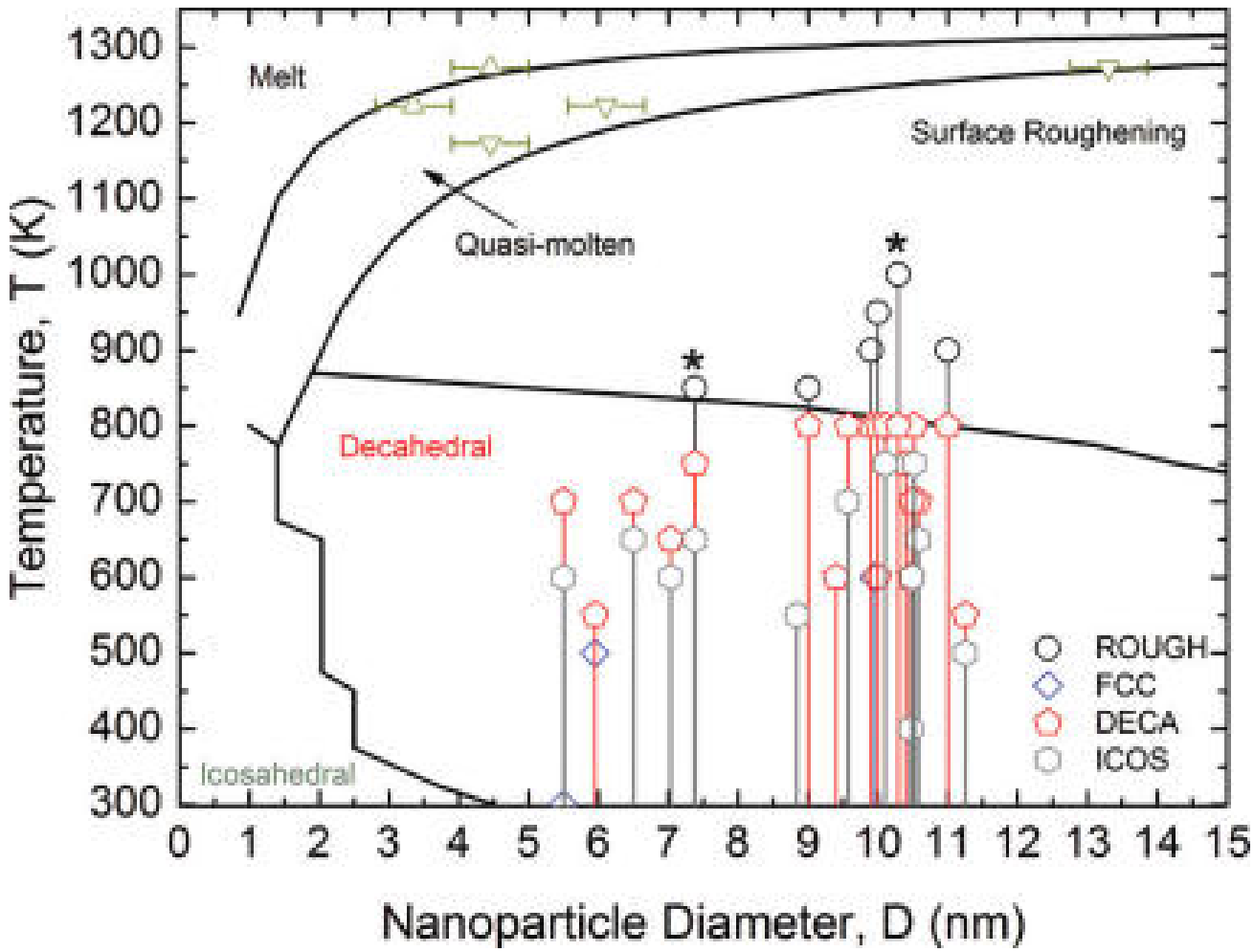
[†]CSIRO Materials Science & Engineering, Clayton, 3168, Australia, [‡]Department of Materials, University of Oxford Parks Road, Oxford, OX1 3PH, U.K., [§]Kavli Institute of Nanoscience, Delft University of Technology Lorentzweg 1, 2628 CJ Delft, The Netherlands, and [⊥]Department of Geology and Geophysics, and Materials Science Program University of Wisconsin—Madison, Madison, Wisconsin 53706

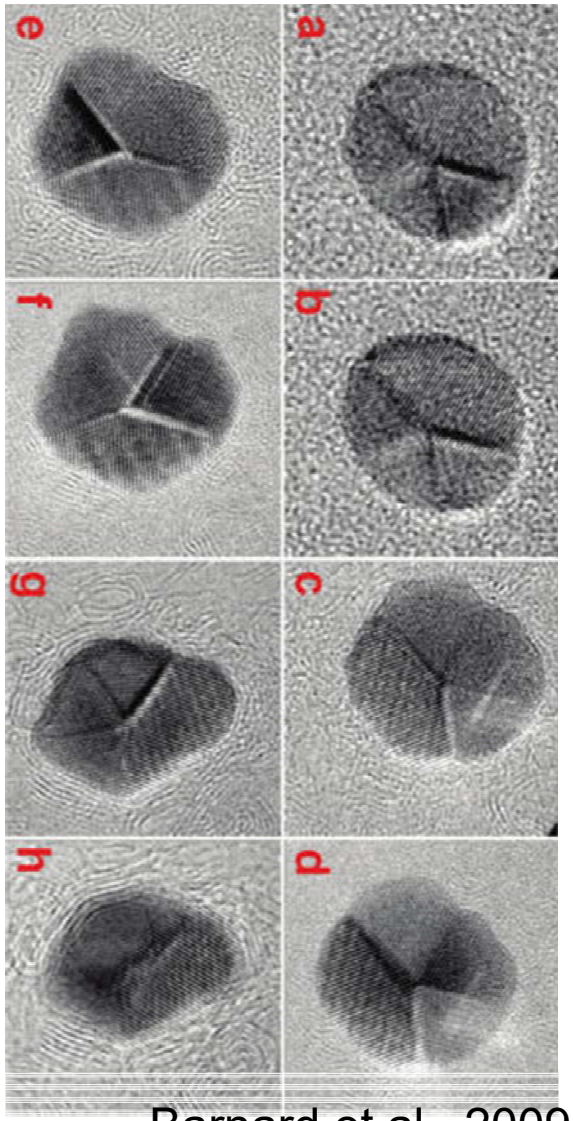


Barnard et al., 2009

Phase Map for Au Nano-crystals

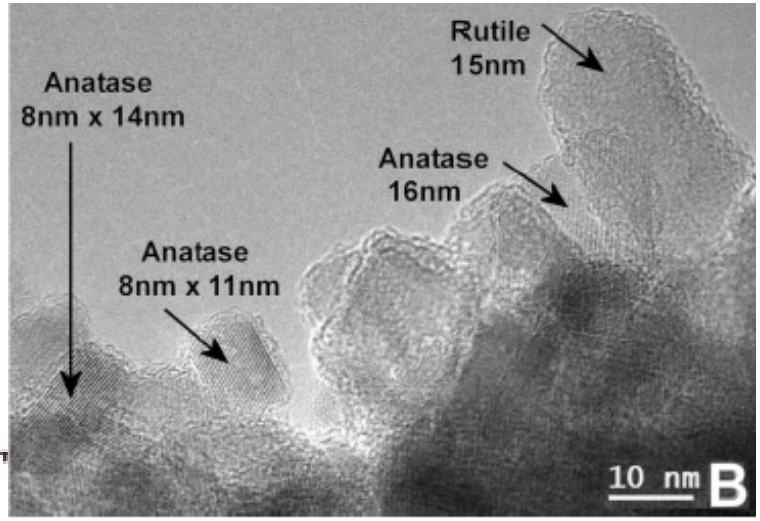
VOL. 3 ▪ NO. 6 ▪ 1431–1436 ▪ 2009 ACSNANO | 1431

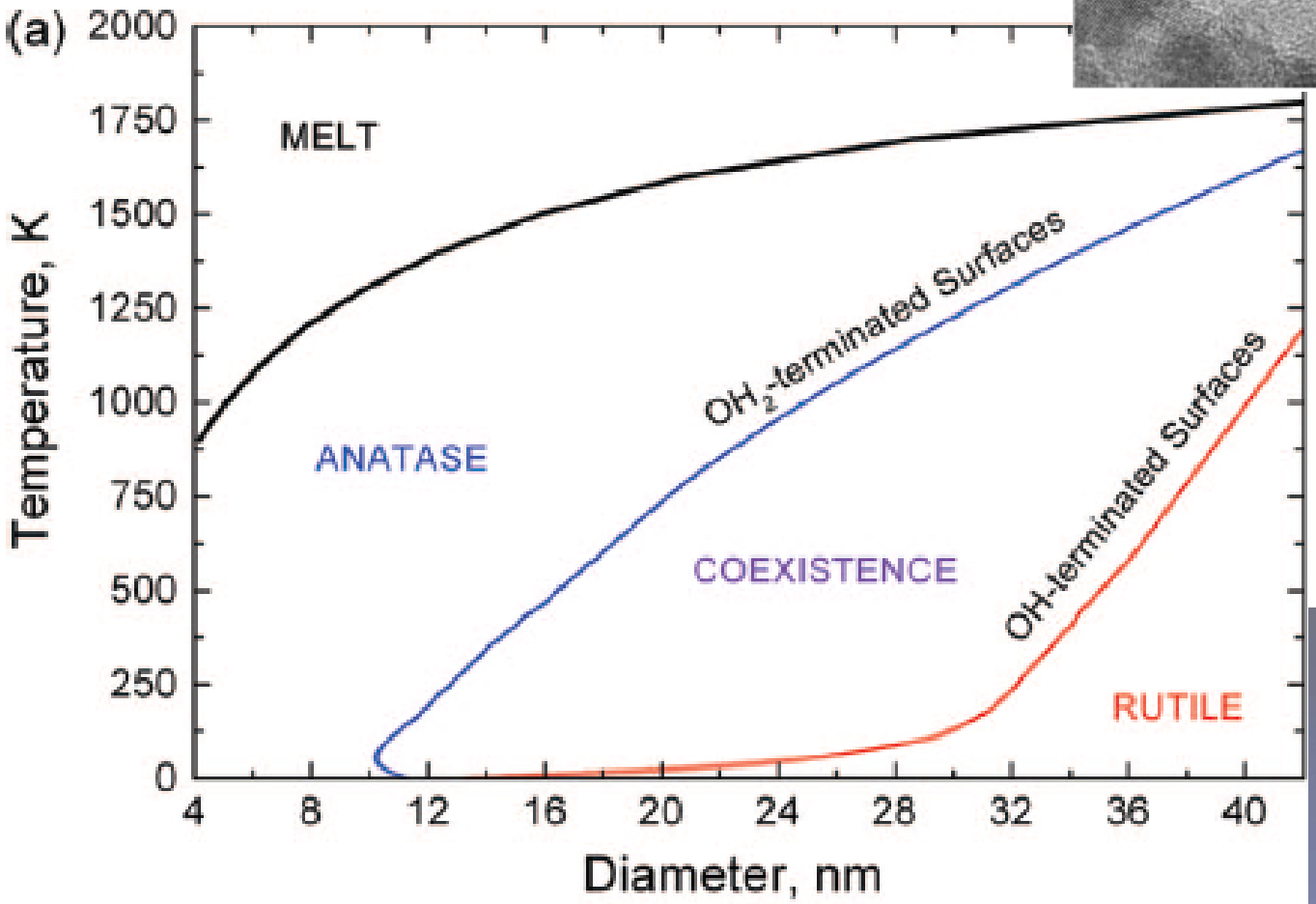




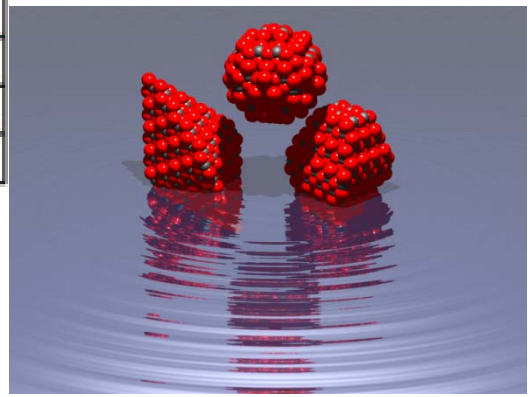
Barnard et al., 2009

Phase map for TiO_2





Barnard and Xu, 2008



Nano-crystals in Oregon Sunstones

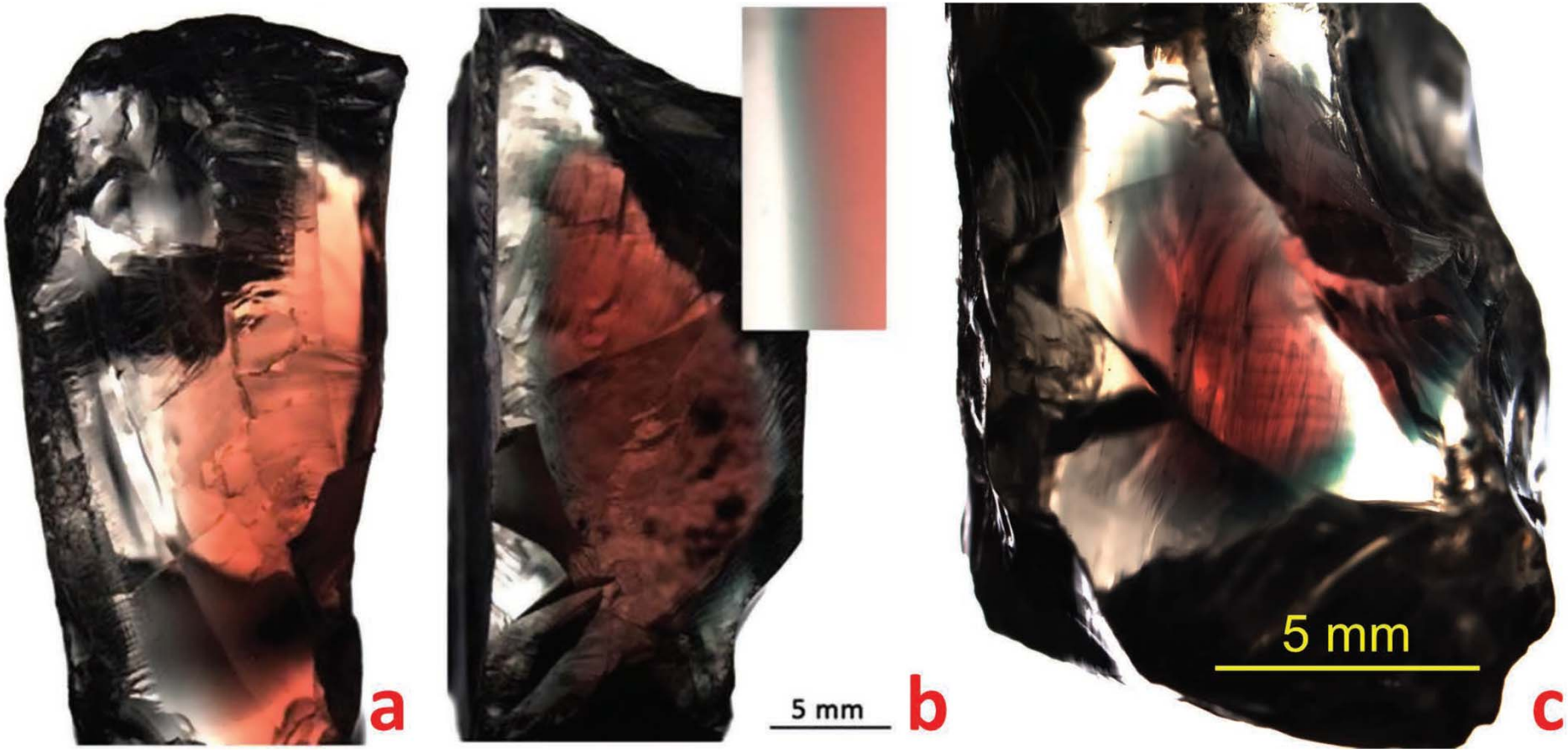
LETTER

SPECIAL COLLECTION: NANOMINERALS AND MINERAL NANOPARTICLES

Protoenstatite: A new mineral in Oregon sunstones with "watermelon" colors

HUIFANG XU[1,*], TINA R. HILL[1], HIROMI KONISHI[1,†], AND GABRIELA FARFAN[2,‡]

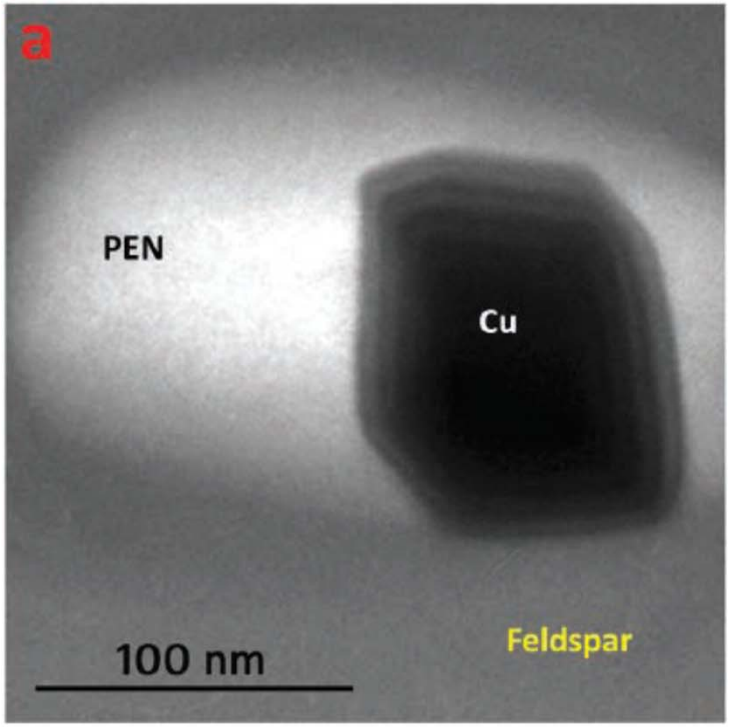
[1]Department of Geoscience, University of Wisconsin-Madison, Madison, Wisconsin 53706, U.S.A.
[2]Madison West High School, 30 Ash Street, Madison, Wisconsin 53726, U.S.A.

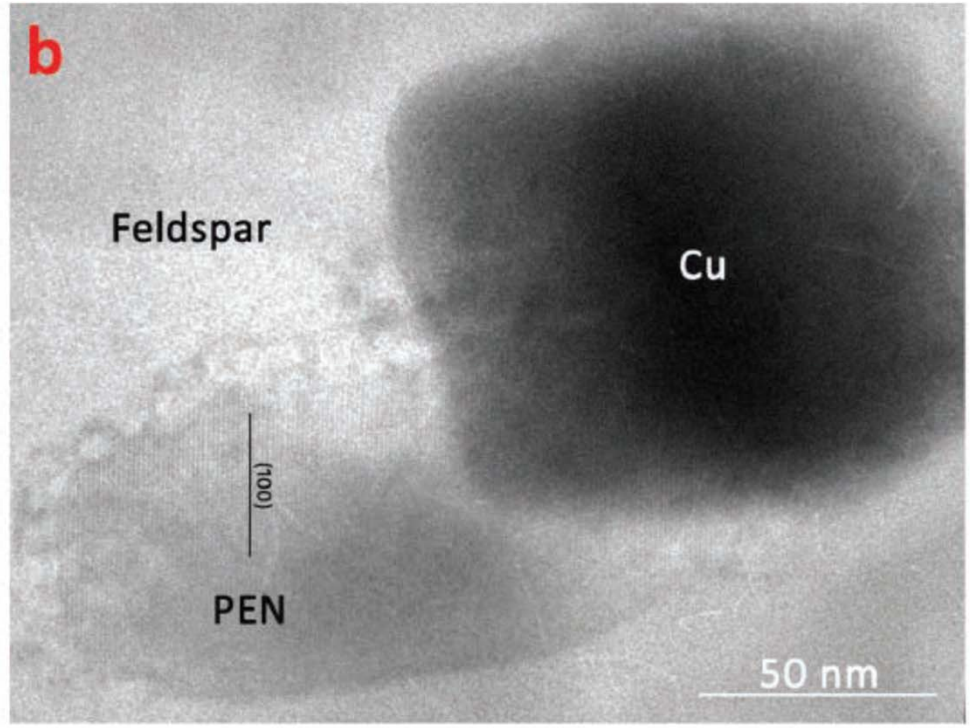


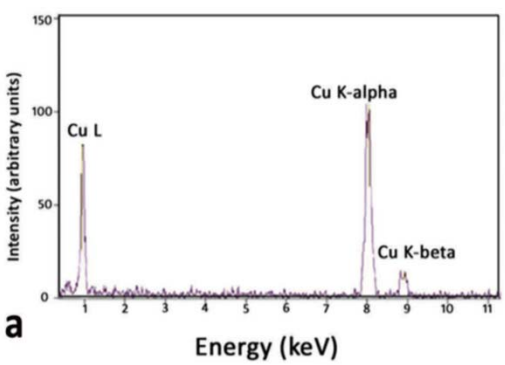
Oregon Sunstones

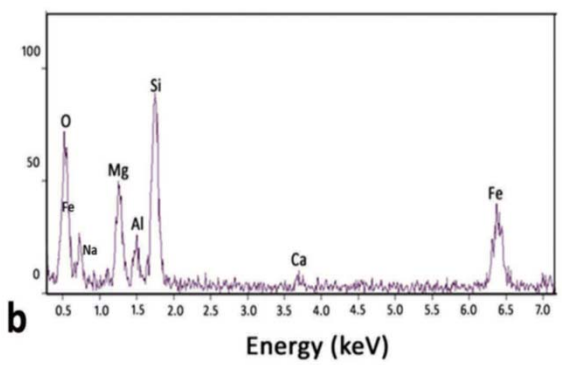
Xu et al., 2017b

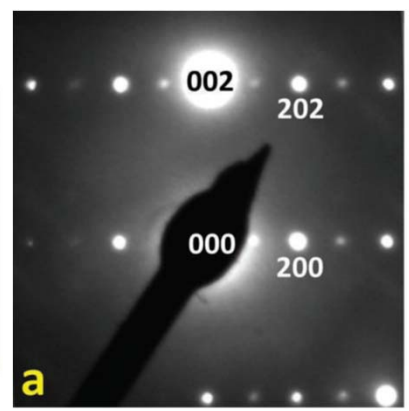
Nano-crystals in Oregon Sunstones

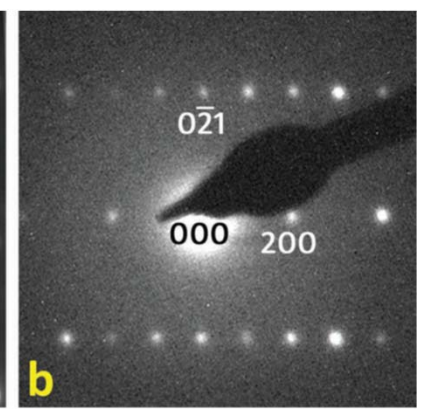










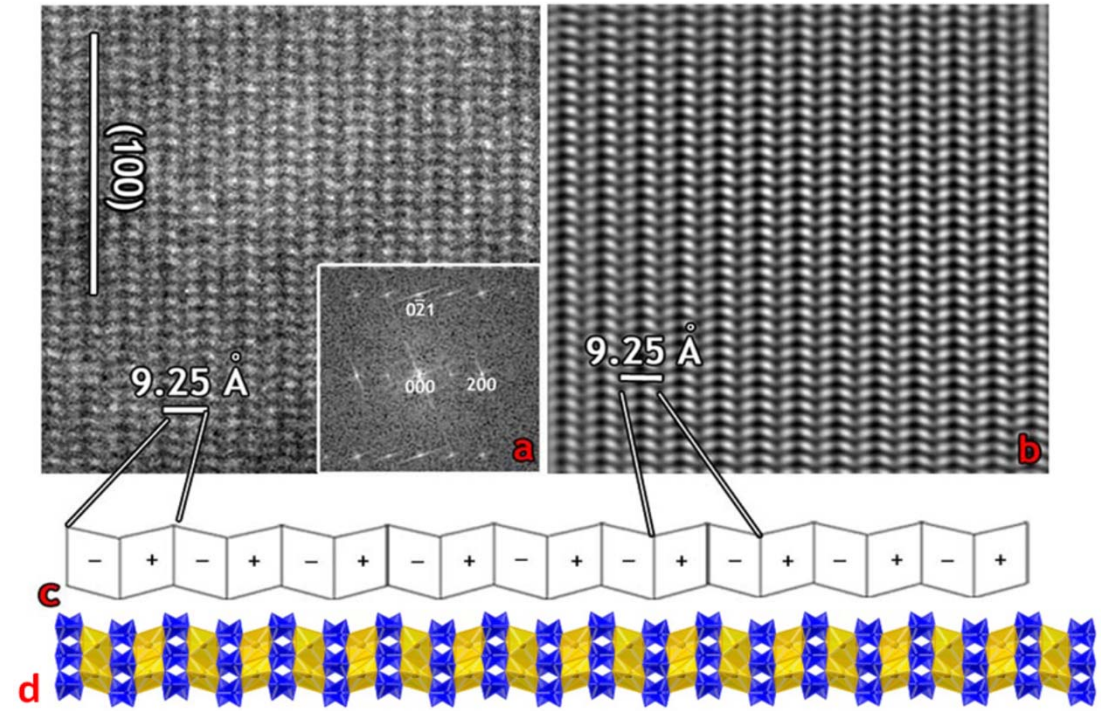


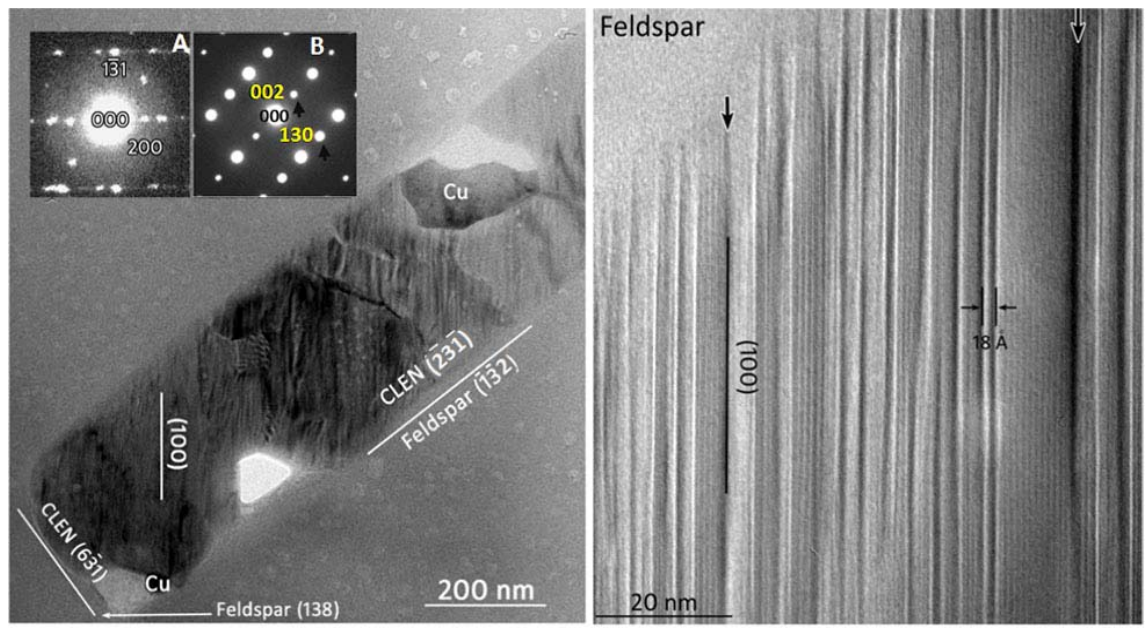
Xu et al., 2017b

Size effect:

Protoenstatite
< 200 nm
quenchable

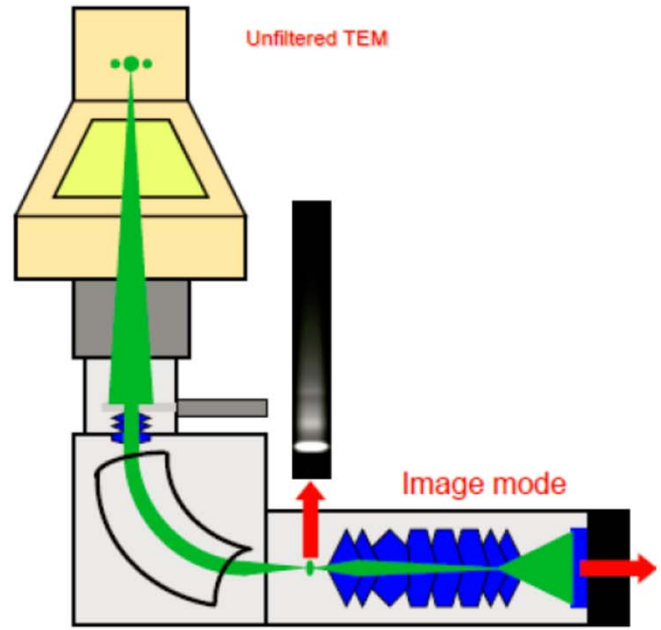
Clinoenstatite
> 200 nm
un-quenchable

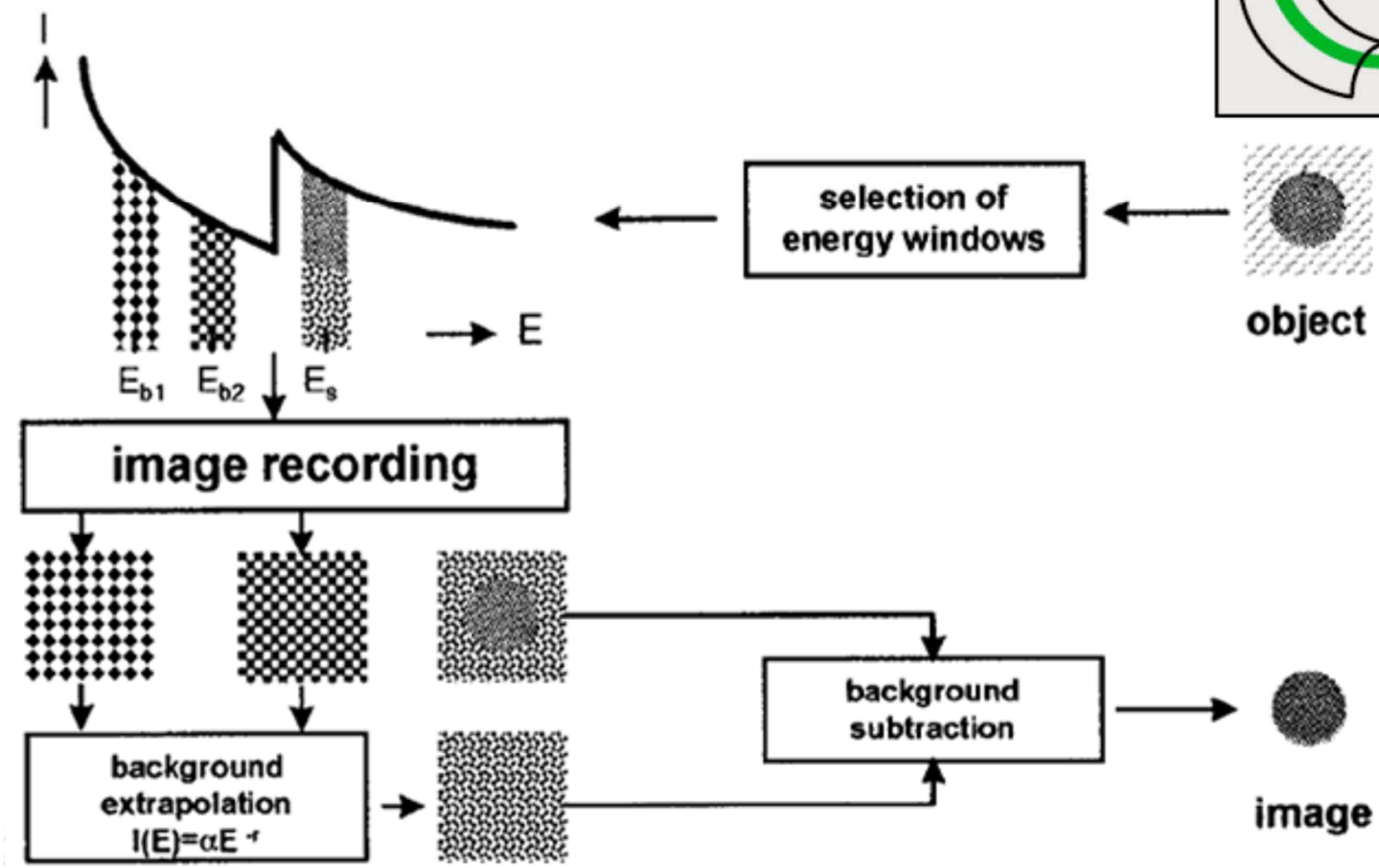




Xu et al., 2017b

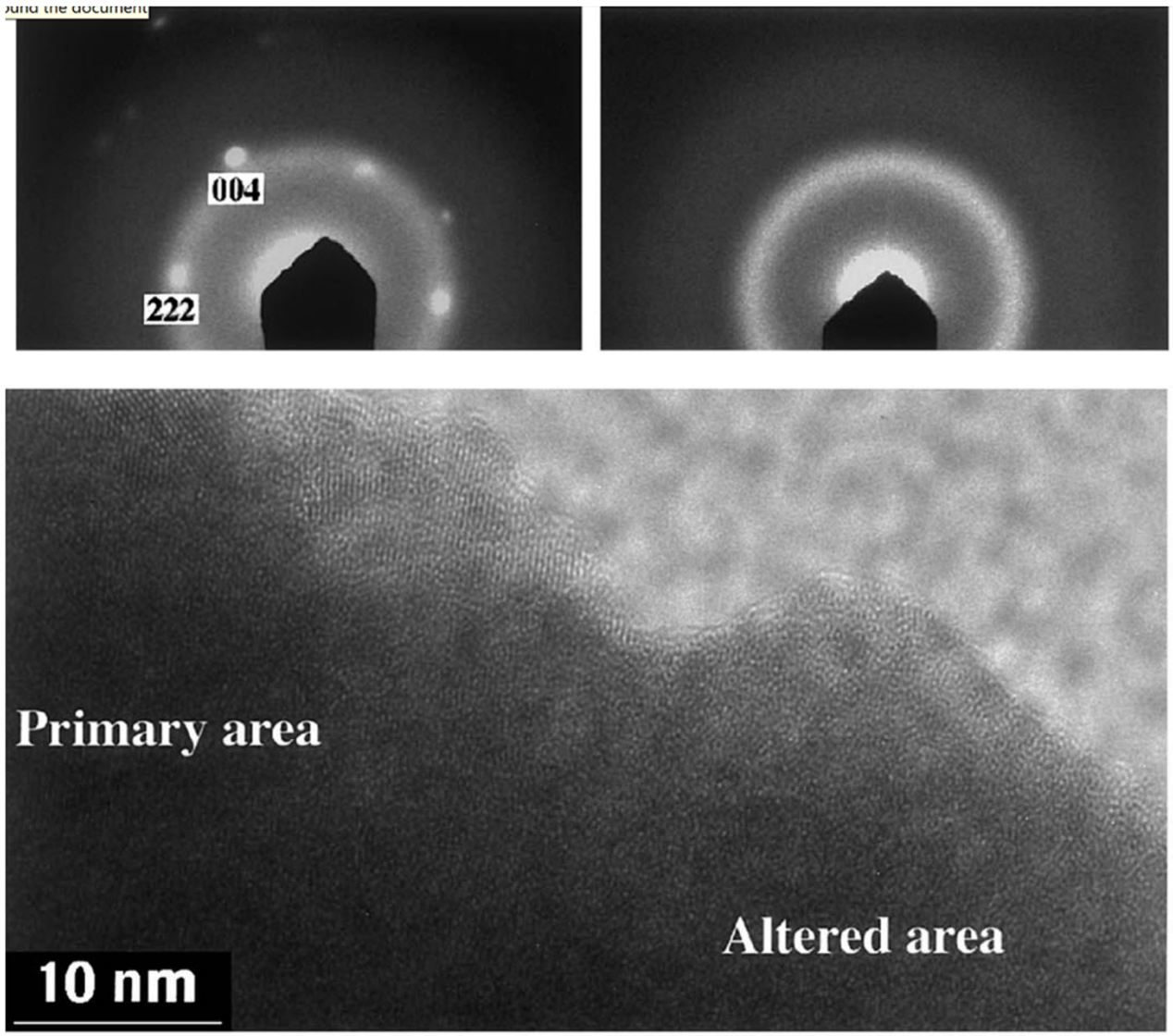
Energy-filtering TEM





Electron energy-loss spectroscopy (EELS) study of oxidation states of Ce and U in pyrochlore and uraninite – natural analogues for Pu- and U-bearing waste forms

Huifang Xu [a,*], Yifeng Wang [b,1]



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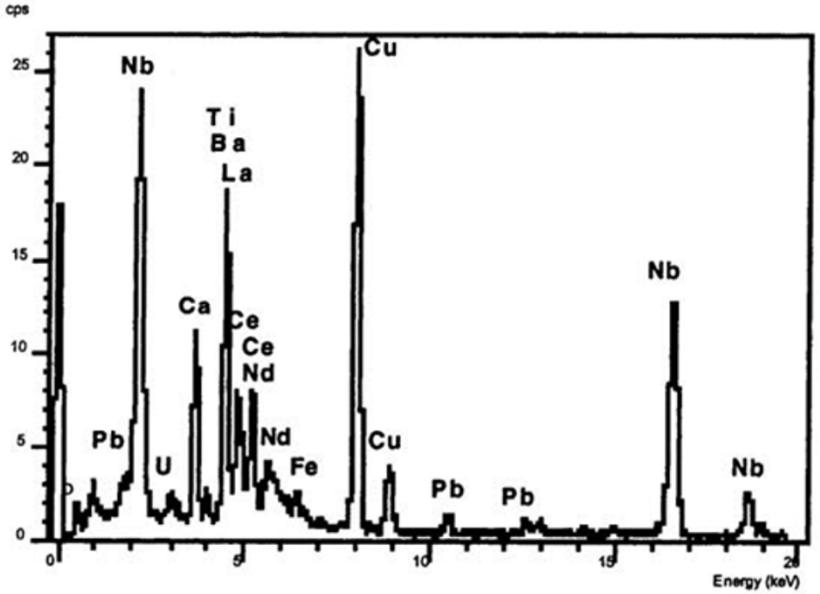

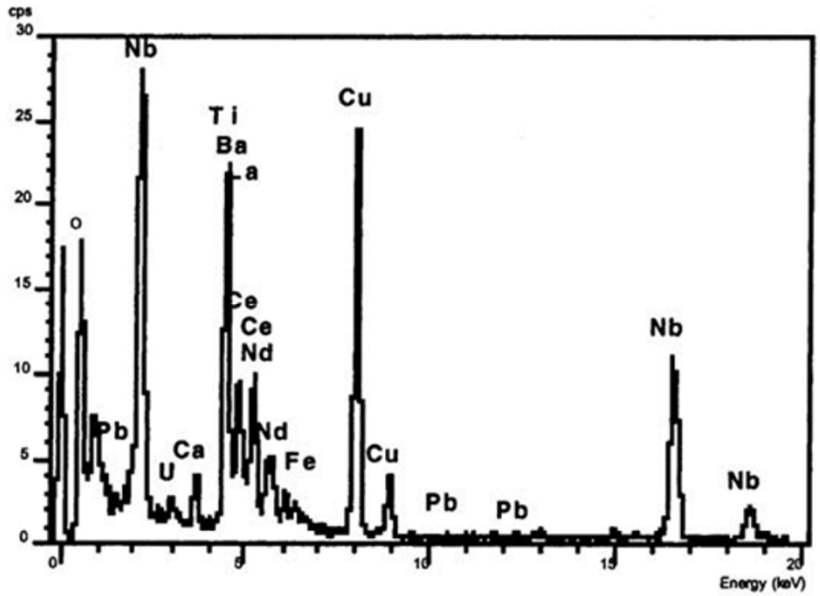

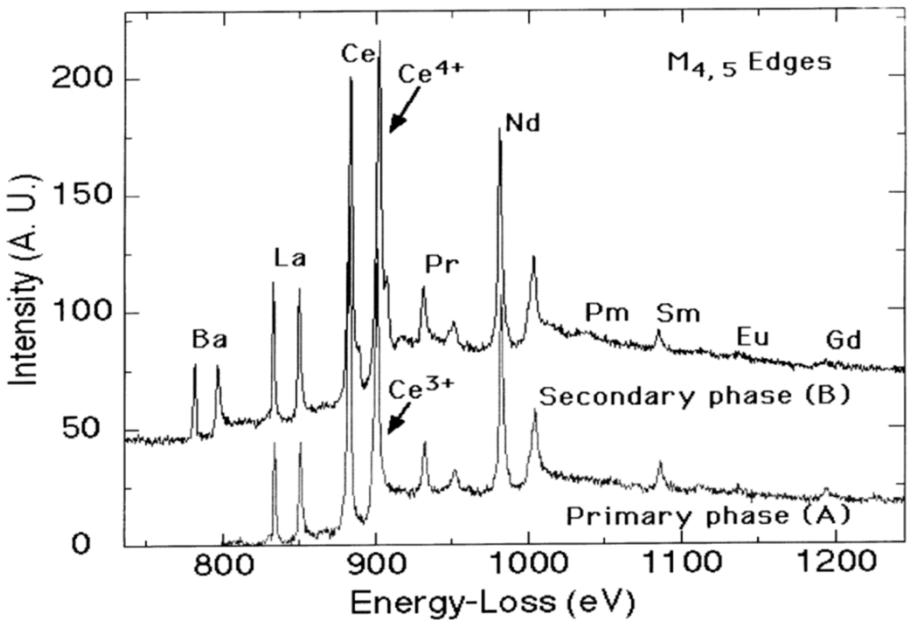

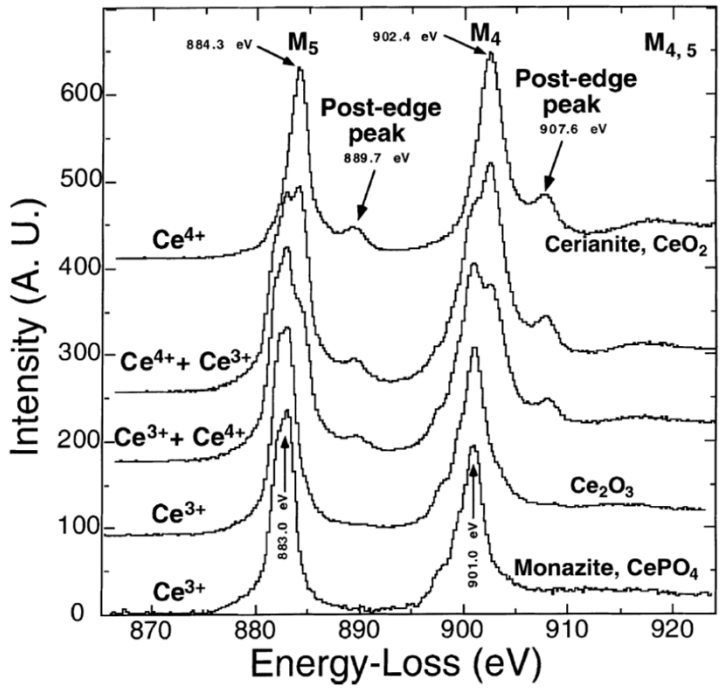

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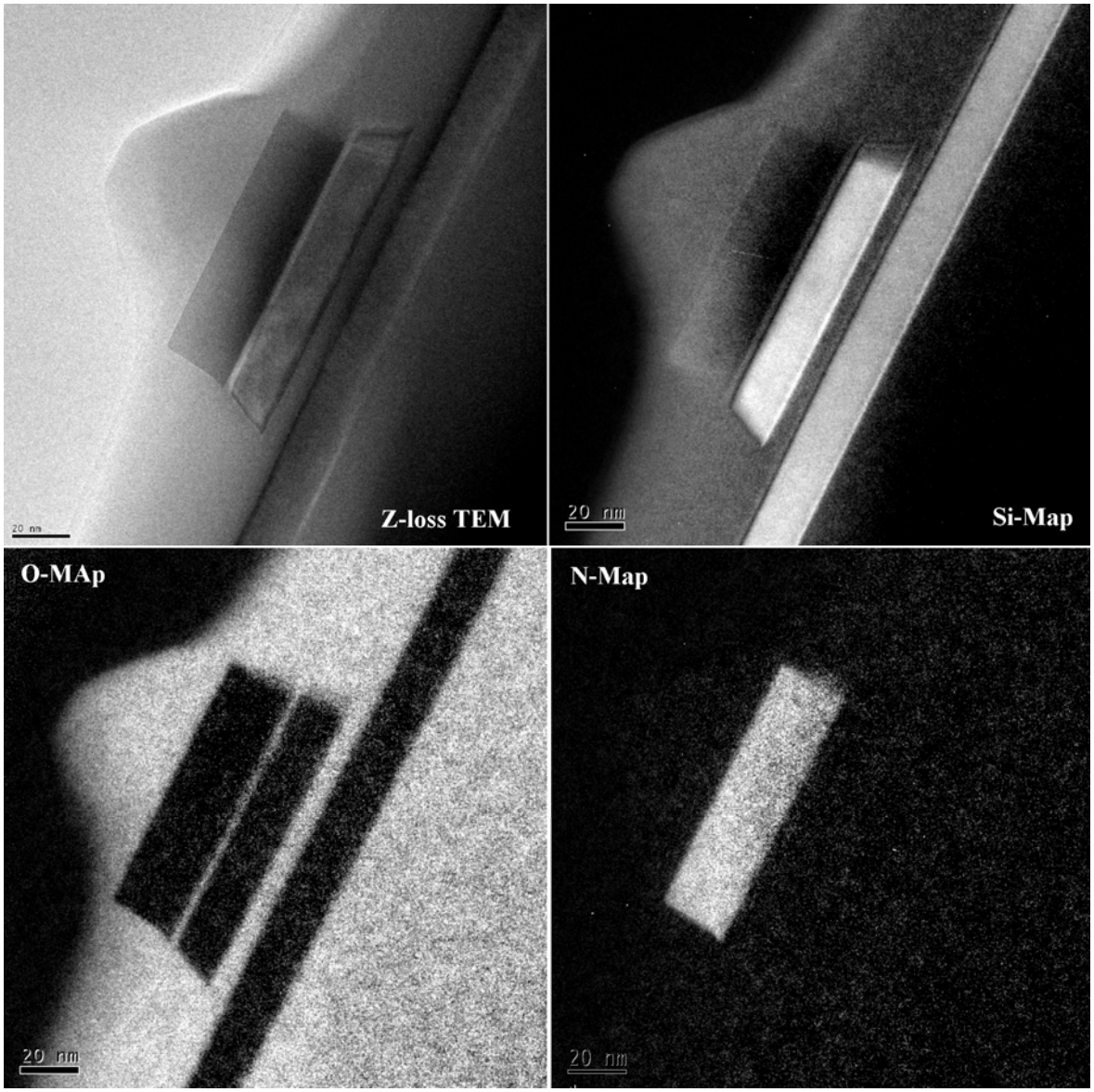
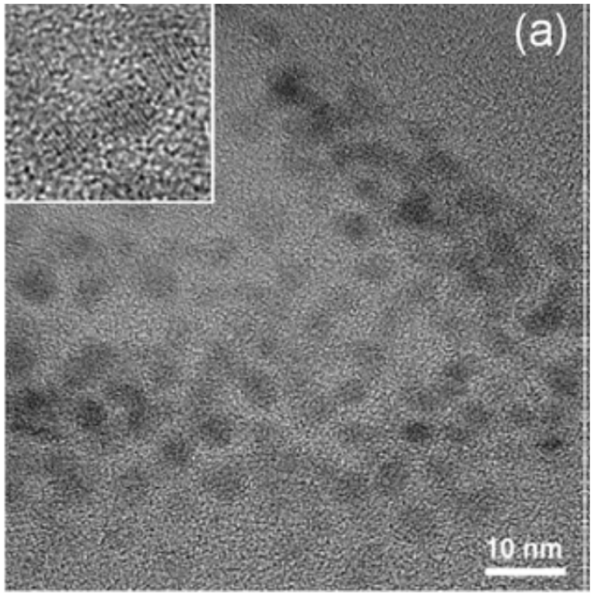
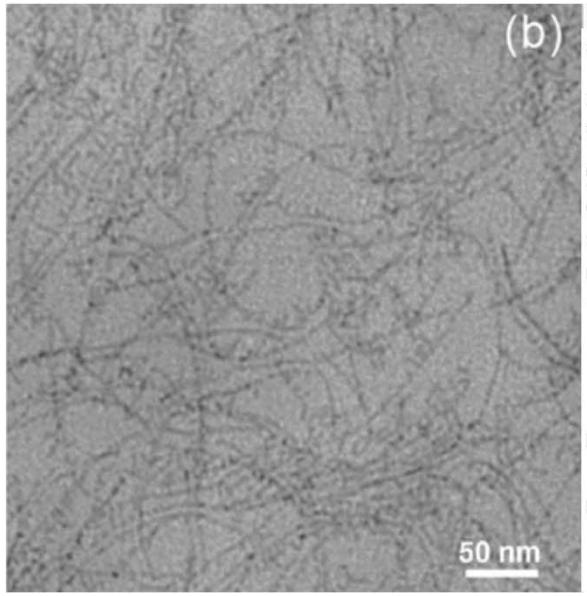
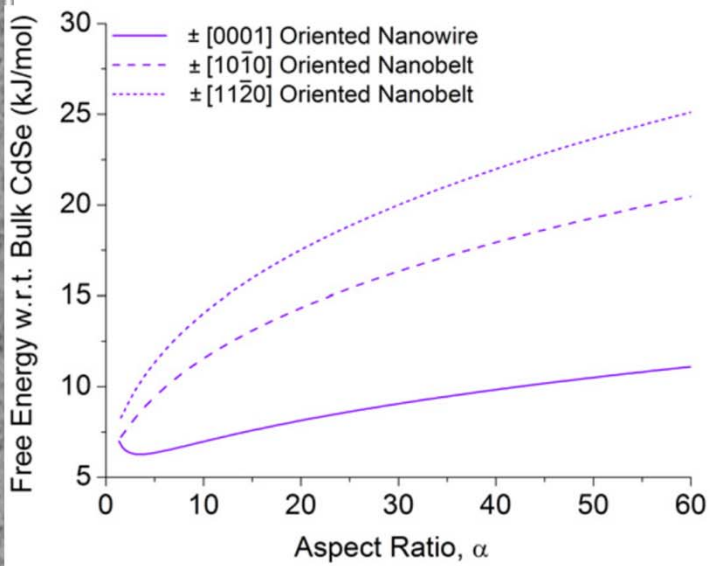
Energy-filtered images

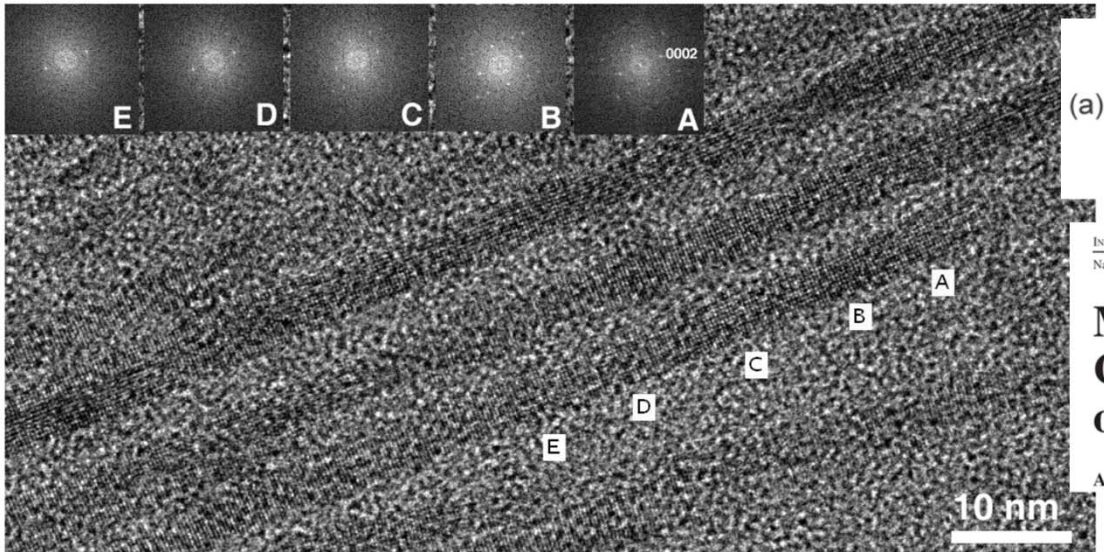


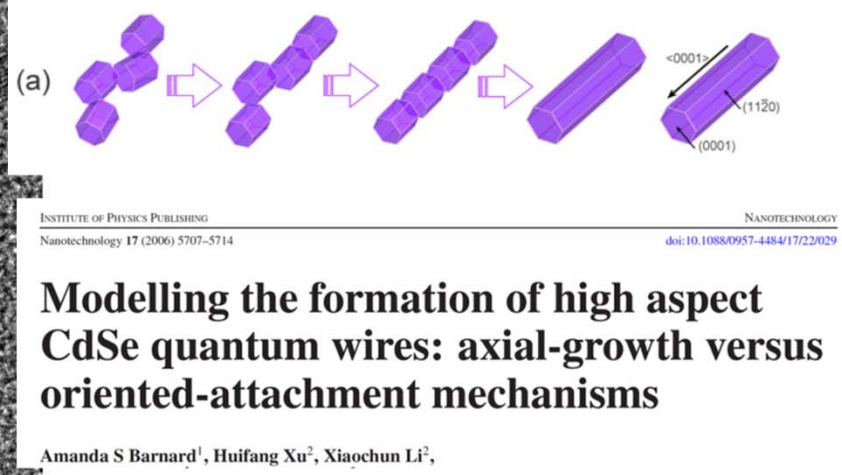
Growth / assembly: CdSe case study











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