Effect of Space Radiation Processing on Lunar Soil Surface Chemistry: Insights from X-ray Photoelectron Spectroscopy

Cathy Dukes
Laboratory for Atomic and Surface Physics, University of Virginia, Charlottesville, VA

Roy Christoffersen
ESCG, Code KR-ARES Directorate, NASA Johnson Space Center, Houston, TX

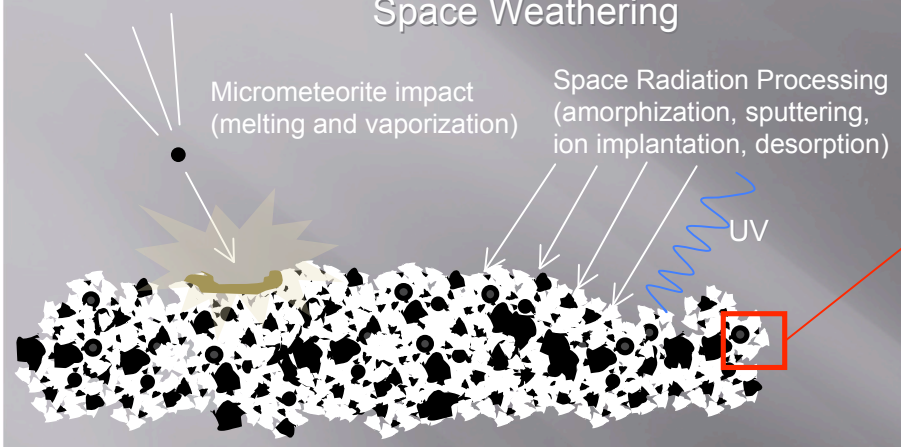
Lindsay P. Keller
Code KR-ARES Directorate, NASA Johnson Space Center, Houston, TX

Mark J. Loeffler
Laboratory for Atomic and Surface Physics, University of Virginia, Charlottesville, VA

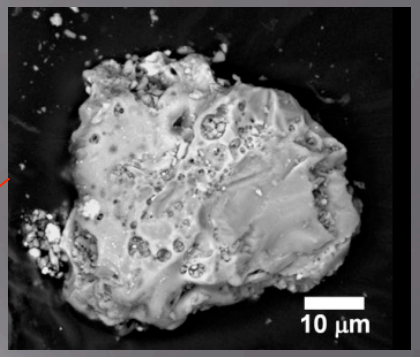
Raul Baragiola
Laboratory for Atomic and Surface Physics, University of Virginia, Charlottesville, VA

Surface Properties of Lunar Soil Grains: Evolving Perspectives

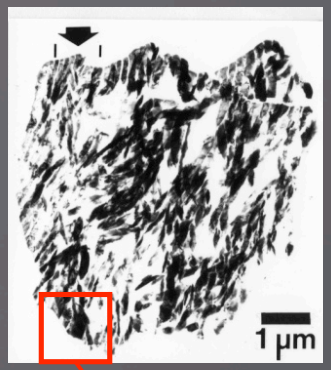
Space Weathering



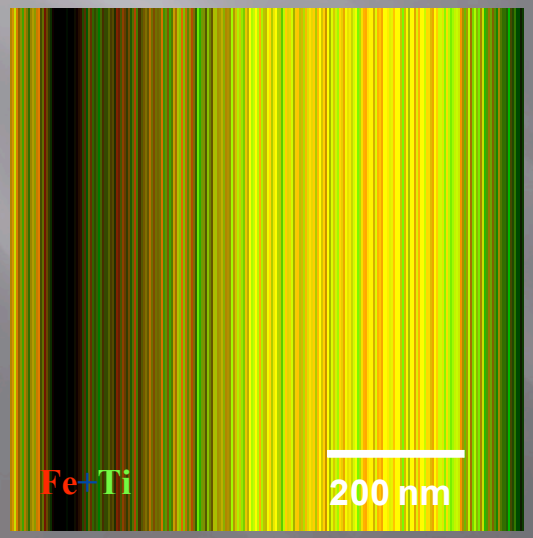
SEM



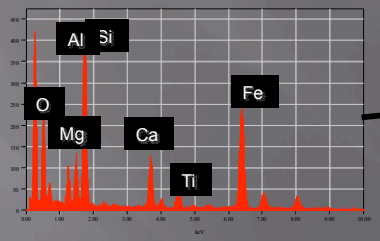
TEM + microtomy

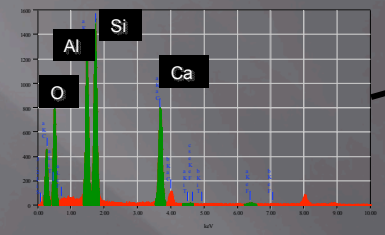


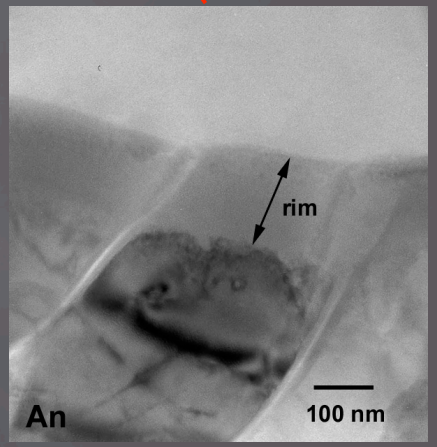
"Nanophase" Fe metal (Fe°)



Vapor-deposited Rims (Keller & McKay, 1993)



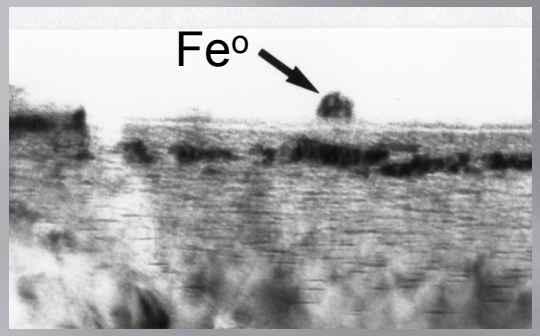




Solar ion radiation-amorphized grain "rims"

TEM-Scale "Surface" to XPS-Scale Surface (!)

TEM - ilmenite grain rim

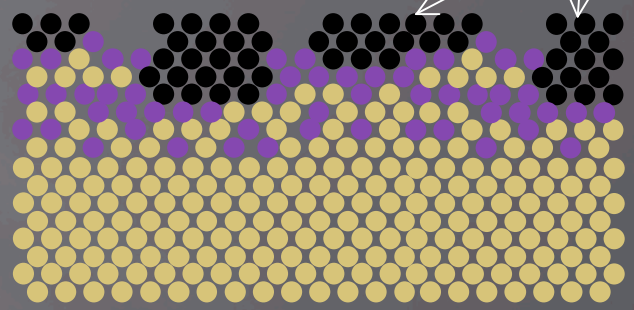


50 nm

- Imaging spatial resolution (<1 nm)
- Analytical sensitivity (~0.5 wt %)
- Surface "depth" resolution (~10 nm)

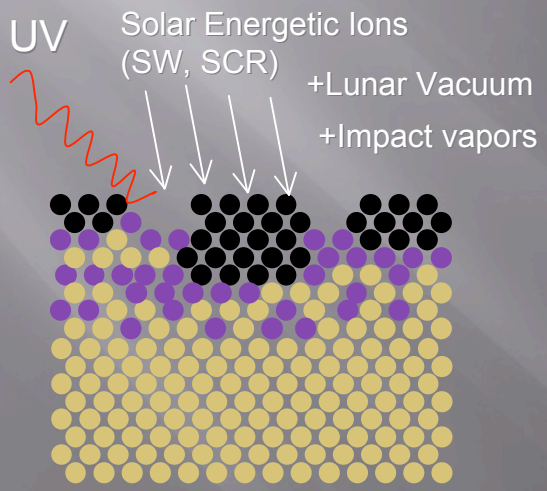
1 - 5 nm

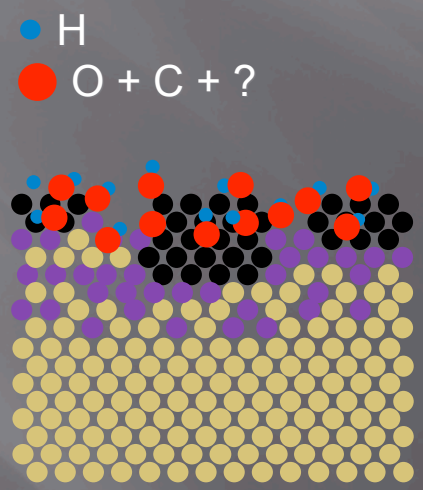
XPS

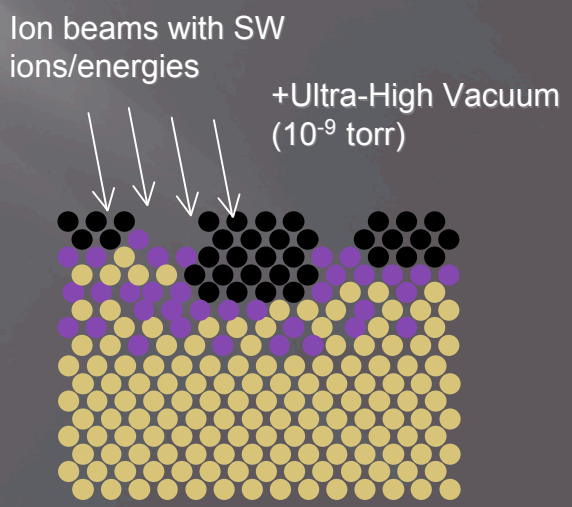


- 1 cm^2 analysis area
- Analytical sensitivity (0.1-0.3 atom %
- Surface "depth" resolution (1 – 5 nm)

From the Moon……to the Earth (ambient)….and back (via the lab)?



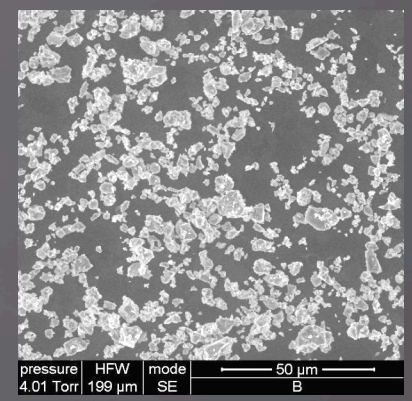


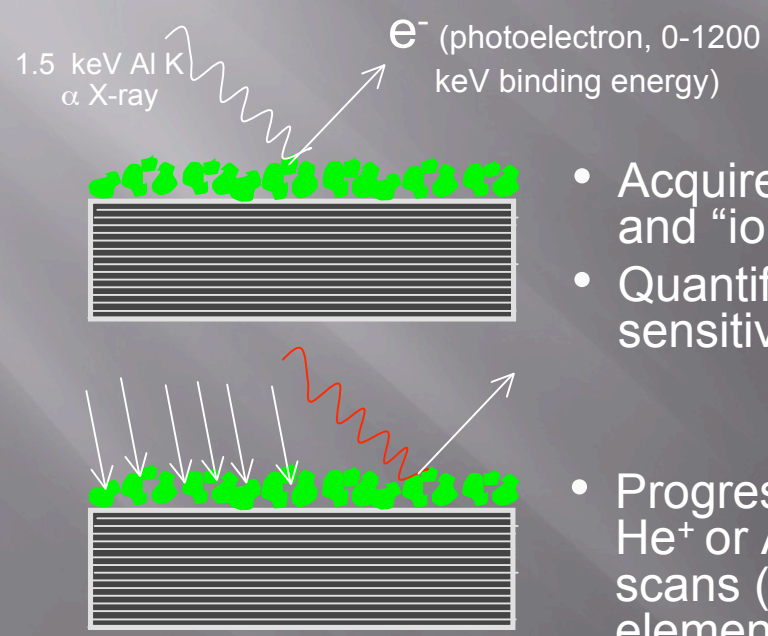


Experimental Approach

- Selected lunar soils well-characterized by SEM/TEM in previous research (e.g., LSCC publications)
- 10084 mature mare soil, (a) “bulk” < 1 mm size fraction, (b) < 20 μm dry-sieved size fraction

- “Sprinkle” coat 1 x 1 cm area of freshly cleaved oriented graphite surface (10-20 mg total sample)

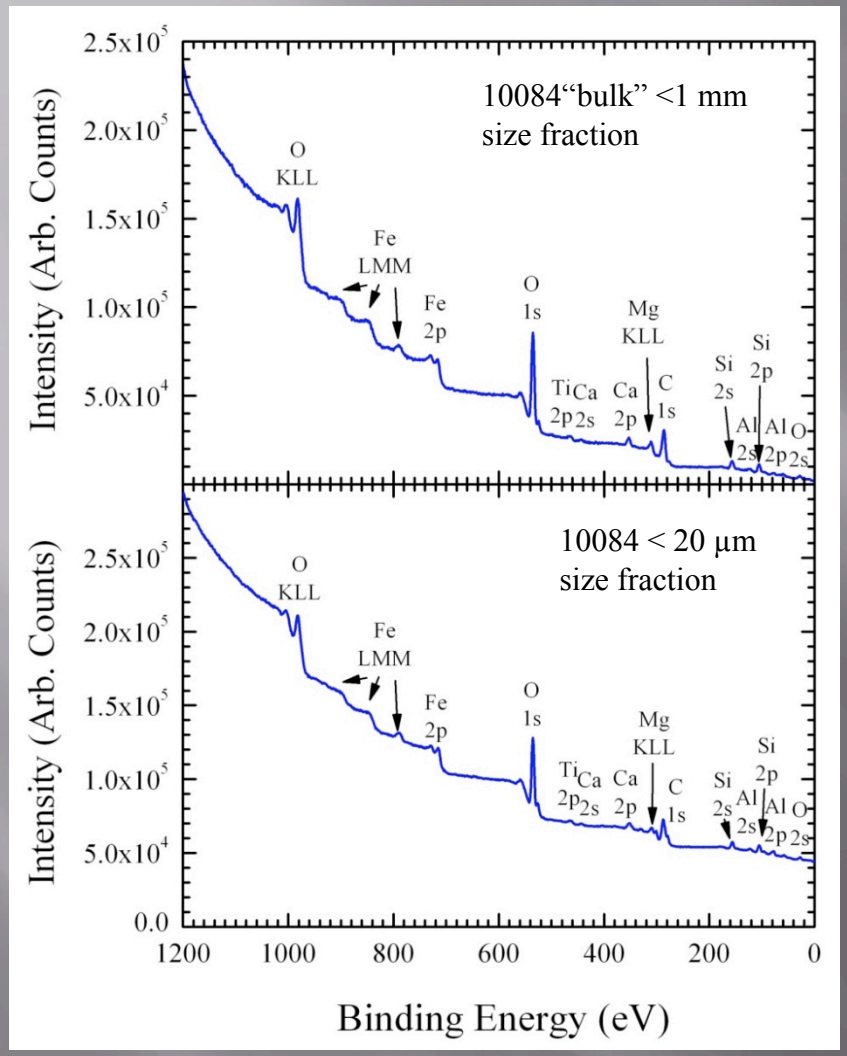




- Acquire baseline XPS spectroscopic data for “as-is” and “ion-cleaned” sample (3.2 eV analyzer resolution)
- Quantify surface element abundances using sensitivity factors.

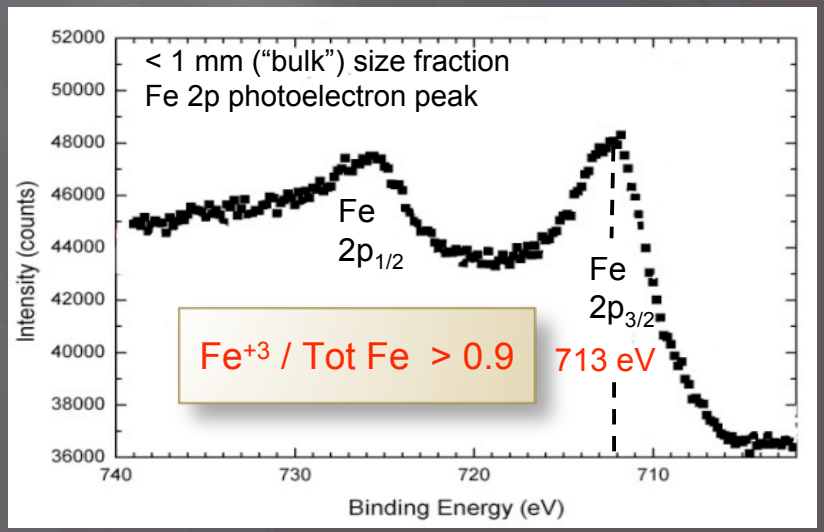
- Progressive ion irradiation with 4 keV He^+ or Ar^+ w/XPS high resolution scans (0.8 eV resolution) for selected elements

Results: XPS "Baseline" Scans



Element	XPS This Study 10084 < 20 µm (ion cleaned)*	XPS "ESCA" Housley & Grant (1976) 10084 < 20 µm	10084 bulk soil (Lucey et al., 2006)
O	65.1 (at.%)	61.8 (at.%)	60.6 (at.%
Si	18.3	19.8	16.1
Al	4.8	5.4	6.1
Fe	4.2	5.0	5.1
Ca	3.4	3.8	4.9
Mg	2.8	3.0	4.5
Ti	1.5	1.2	2.2

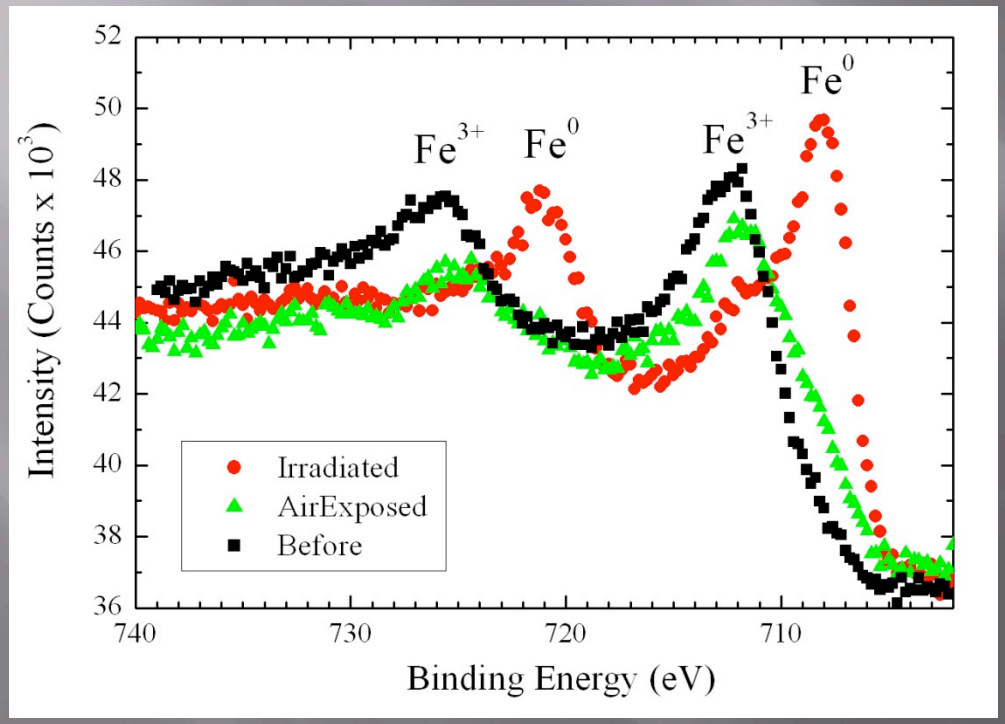
- Si surface enrichment relative to bulk – consistant with TEM grain rim studies and Housley & Grant XPS results.
- Enrichment / depletion pattern for other elements similar to Housley and Grant (1976)
- Except for Oxygen!



*low dose (1.3 x 10^{15} Ar+/cm^2) to removed adventitious C (hydrocarbon)

Surface Response to Ion Irradiation

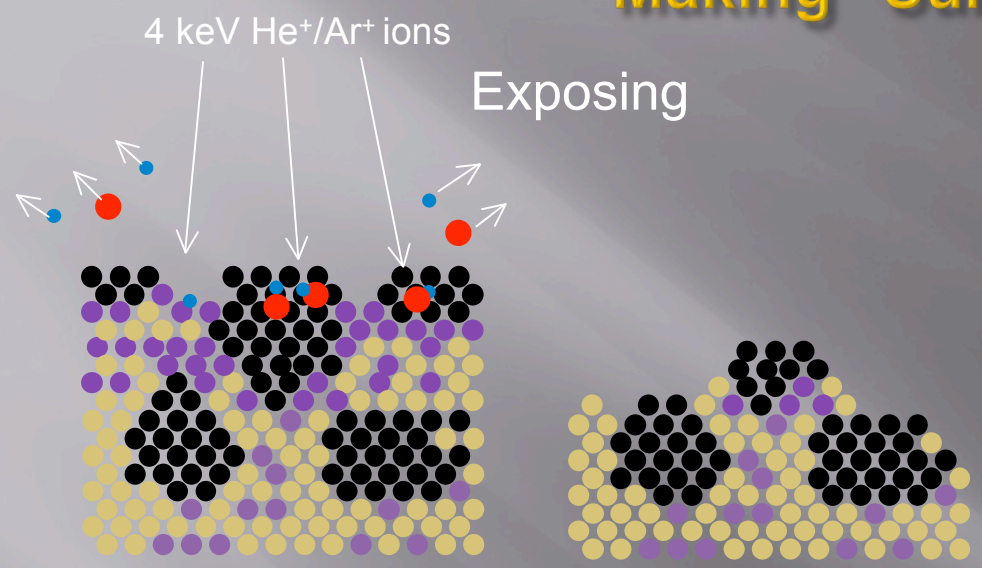
- Sample: < 1 mm "bulk" size fraction 10084 soil
- *In-situ* ion irradiation with 4 keV He^+ ions (following baseline scans)
- Fe 2p high-resolution scans at fluence (dose) = 2×10^{17} He^+ ions/cm^2
- Remove from XPS chamber, expose to room atmosphere – 5 minutes
- Re-scan Fe 2p peak

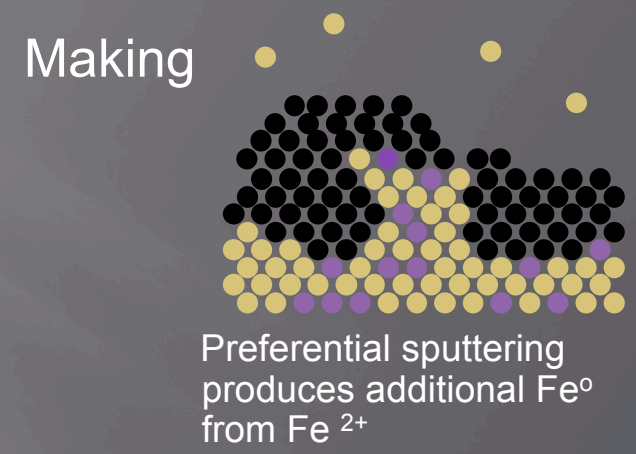


Results

- Fe 2p peak at 707 eV following irradiation
- Predominantly metallic-state Fe (Feo) on surface
- Reduction "mechanism"?
- Fe 2p peak very close to original Fe3+ energy after 5 minute exposure to room air
- Rapid surface oxidation at the monolayer level

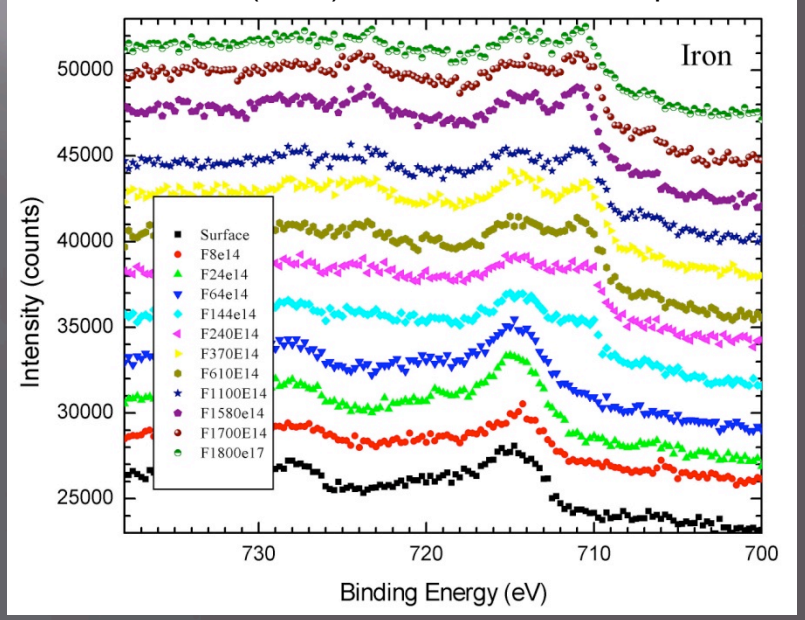
Ion-induced Fe reduction: "Exposing" or "Making" Surface Fe°?





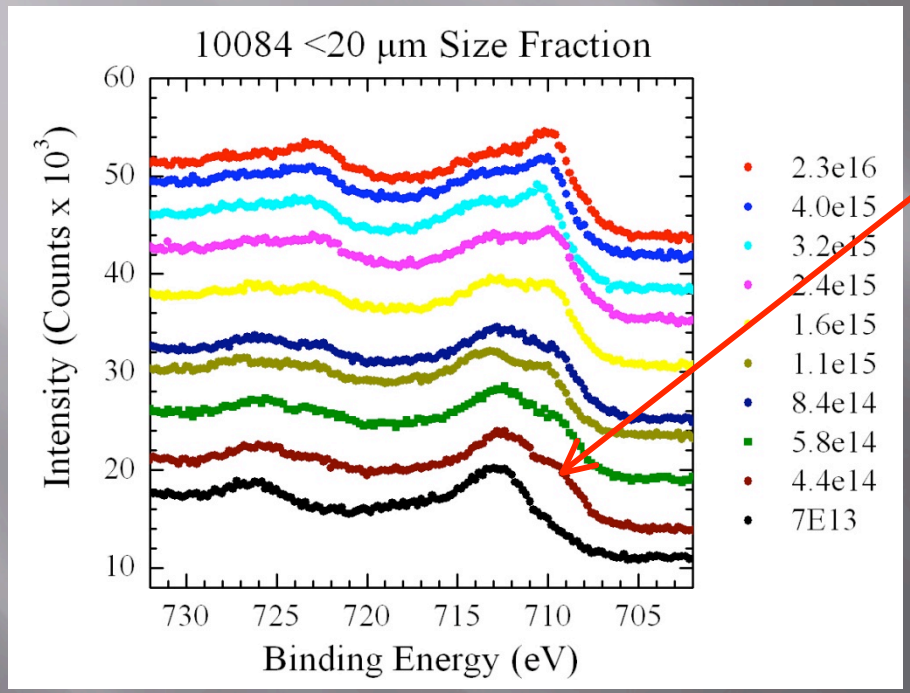
- "Making" has precedence
  - Surface metallic-state Fe produced on olivine $(Fe,Mg)_2SiO_4$ under 4 keV Ar ion irradiation (Loeffler et al., 2009)
  - Metallic-state Fe appears in XPS Fe 2p scan at ~ 1 x 10^{16} Ar ions/cm^2

Loeffler et al. (2009): 4 keV Ar+ on olivine powder



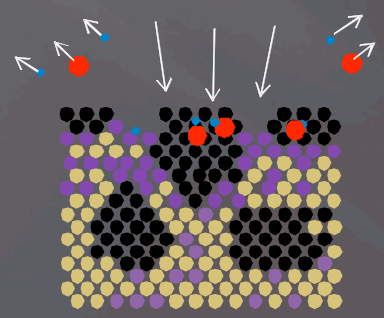
Duplicate "Olivine" Experiment with Lunar Soil

- Sample: < 20 μm dry-sieved size fraction 10084 soil
- *In-situ* ion irradiation with 4 keV Ar^+ ions (following baseline scans)
- Fe 2p high-resolution scans at incremental Ar^+ fluence (dose) levels



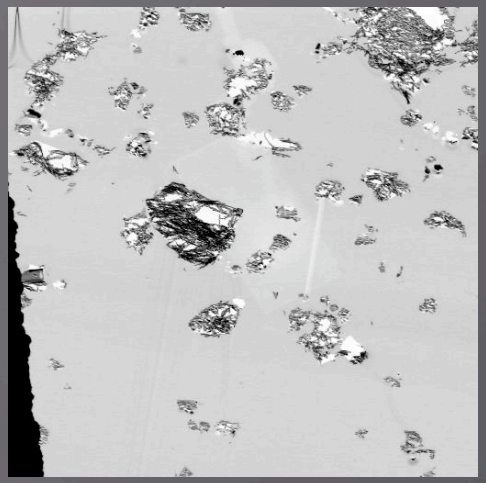
Results

- Metallic-state Fe appears 4.4 x 10^{14} Ar+/cm2
- Estimate sputtering depth at only 1-2 atomic monolayers
- 100 times lower dose than olivine (~ 1 x 10^{16} Ar+/cm^2)
- Likely insufficient dose to "evolve" surface to strongly altered O/Fe ratio by preferential sputtering
- Supports "Exposure" hypothesis



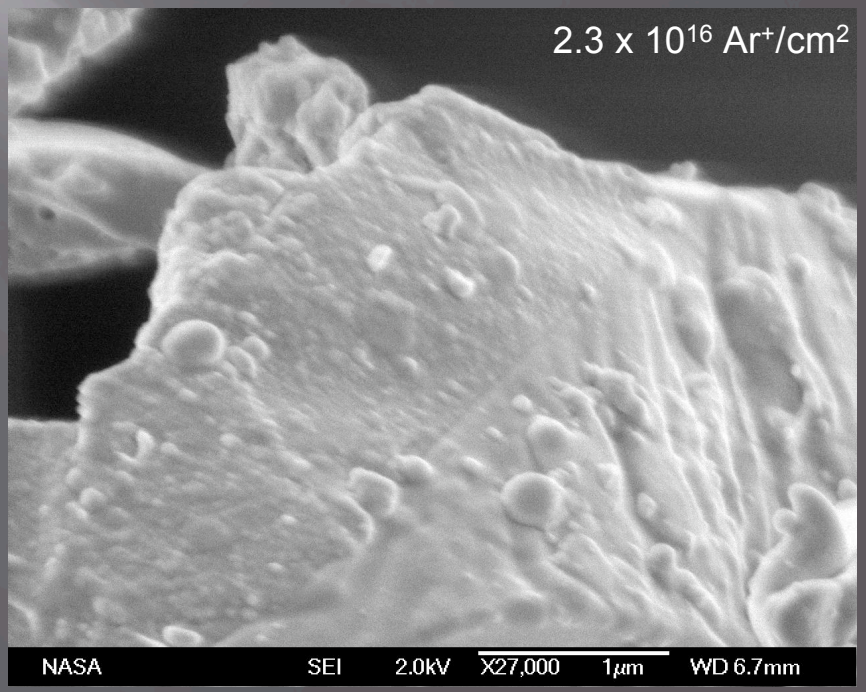
SEM / TEM Observations

- Currently following up XPS experiments with detailed SEM / TEM characterization of in-situ irradiated XPS samples

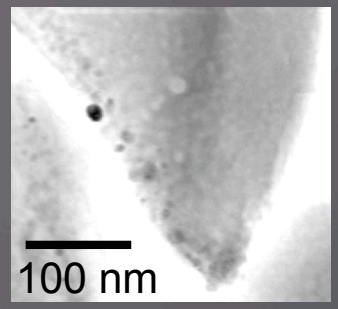


- Challenge: Correlating XPS data integrated over bulk soil sample with grain-by-grain SEM / TEM observations (use of non-soil lunar mineral "standards" and other approaches)

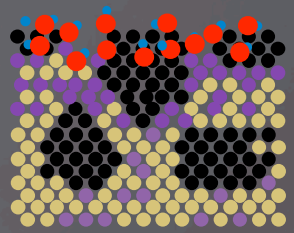
- Preliminary field-emission SEM examination of Ar+ ion irradiated grain surfaces in <20 μm sample shows clear evidence for surface roughening / modification

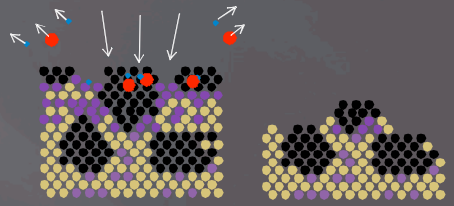


Overview and Conclusions



- Prior TEM-scale findings of ubiquitous nanophase metallic Fe on outer margins / “surfaces” of lunar soil remain established
- BUT..on the XPS-scale the majority of Fe (metallic or Fe2+) on surfaces is oxidized to the 3+ state, likely by reaction with atmospheric species (“passivated”; “non-lunar” surface oxidation state)
- Ion irradiation at solar-wind energies produces outer monolayers dominated by metallic-state Fe (“back to the Moon”; “lunar” surface oxidation state?)
- Metallic-state Fe appears at ion doses consistent with “exposure” of <u>previously-existing</u>, passivated, Fe metal on grain outer margins; ions likely “make” little additional metallic Fe





- TEM / SEM characterization work on XPS samples is proceeding