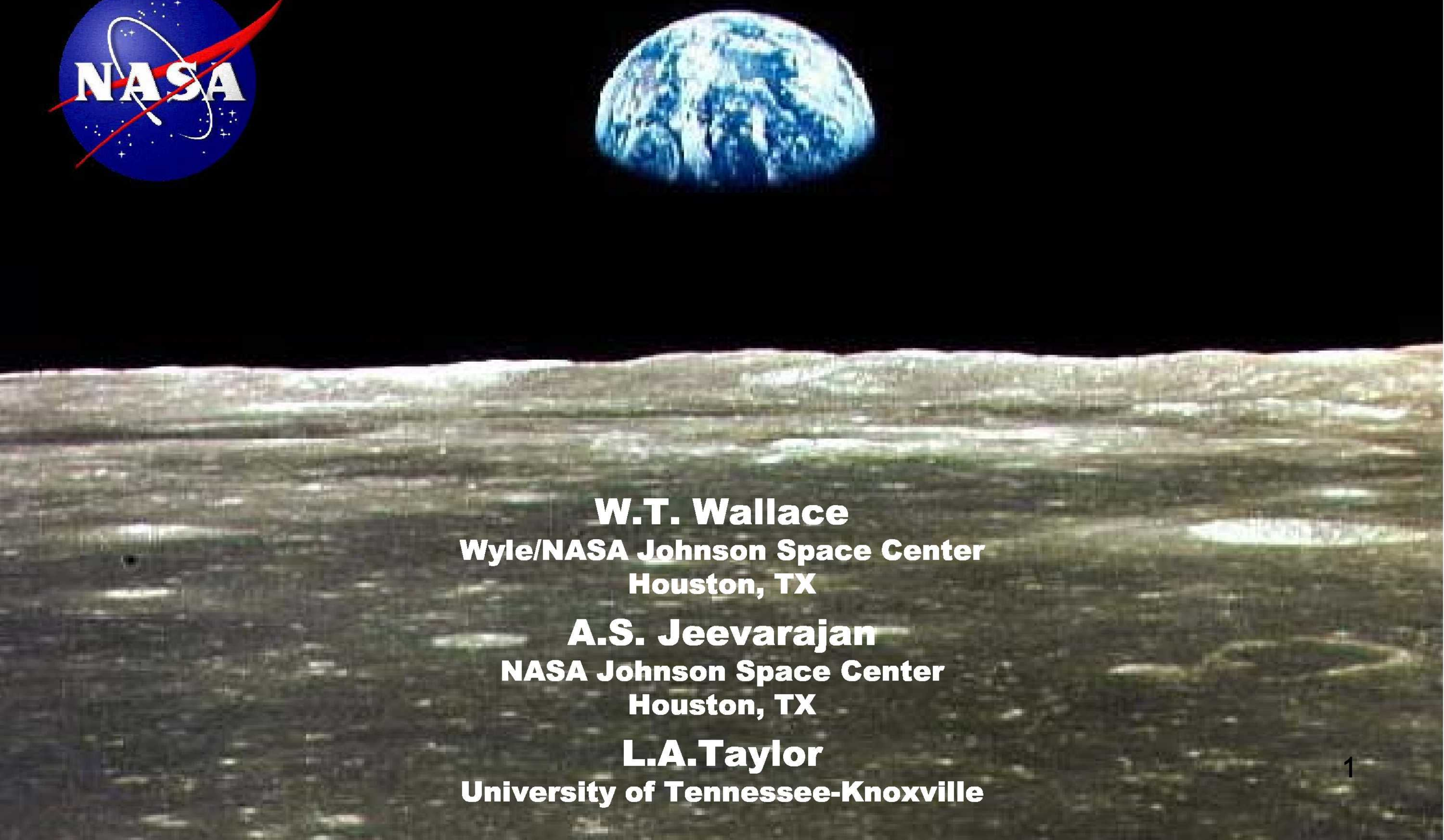
# Activation of Lunar Dust via Grinding and UV Irradiation



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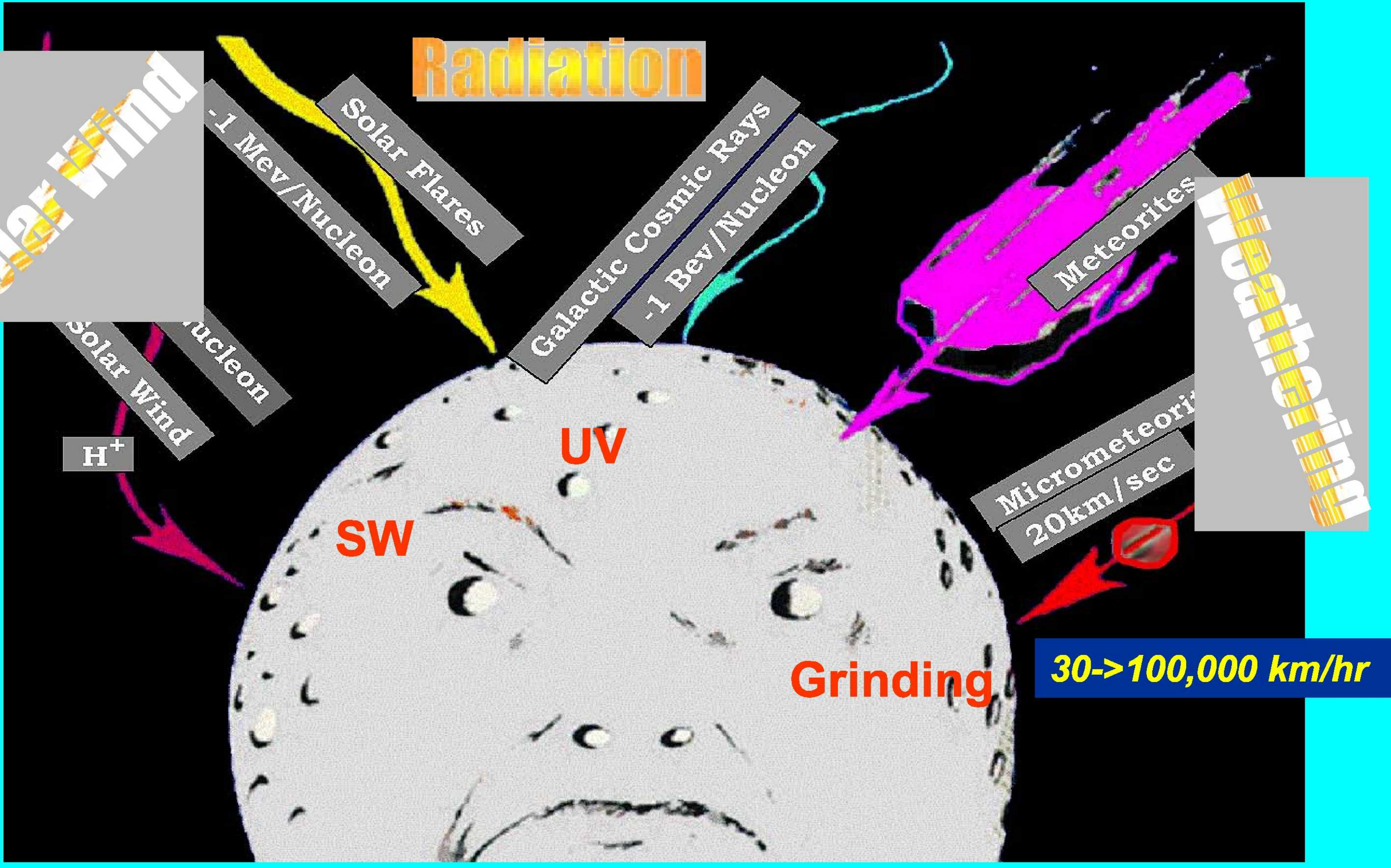
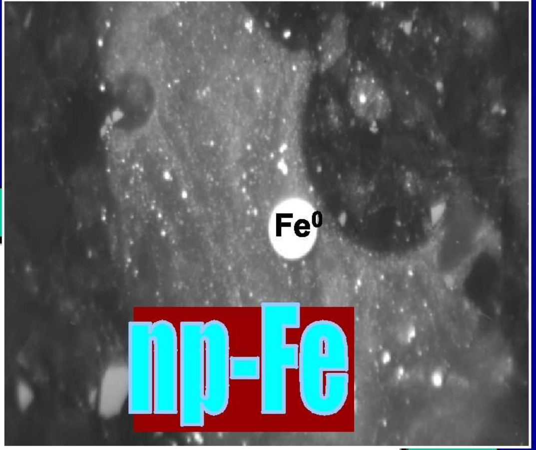
# Lunar Dust Reactivity

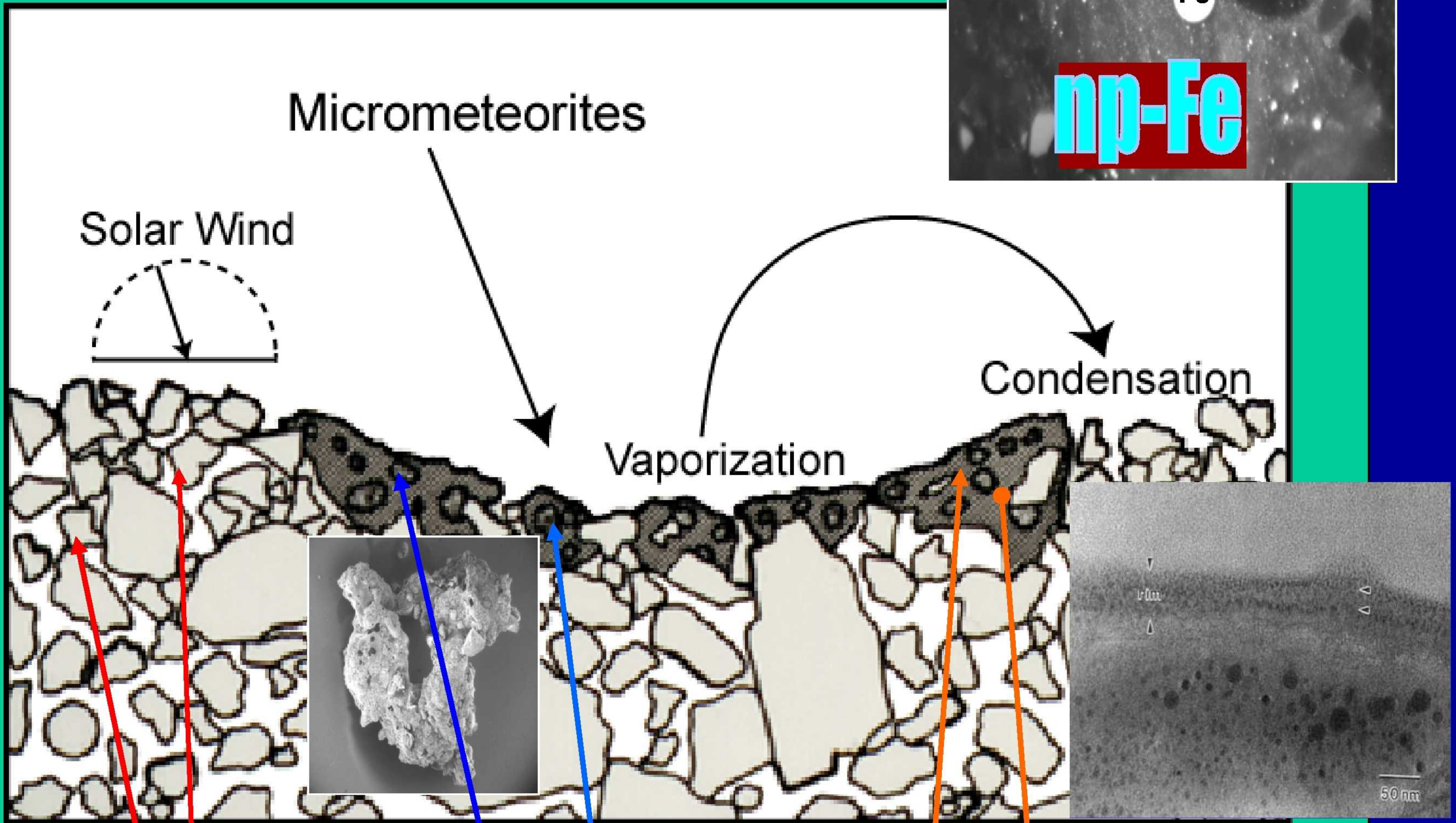
- Activation of Dust: micro-meteorite impacts; UV radiation; solar-wind particle impacts
- No passivating atmosphere;  $10^{-12}$ torr
- Active Dust: create reactive species in lungs or humid environment
- Monitor production of reactive species
- Determine methods of deactivation
- Need method to *reactivate* lunar dust on Earth
  - Lack of pristine reactive lunar soil
- Major causes of reactivity

# Our Unhappy Moon



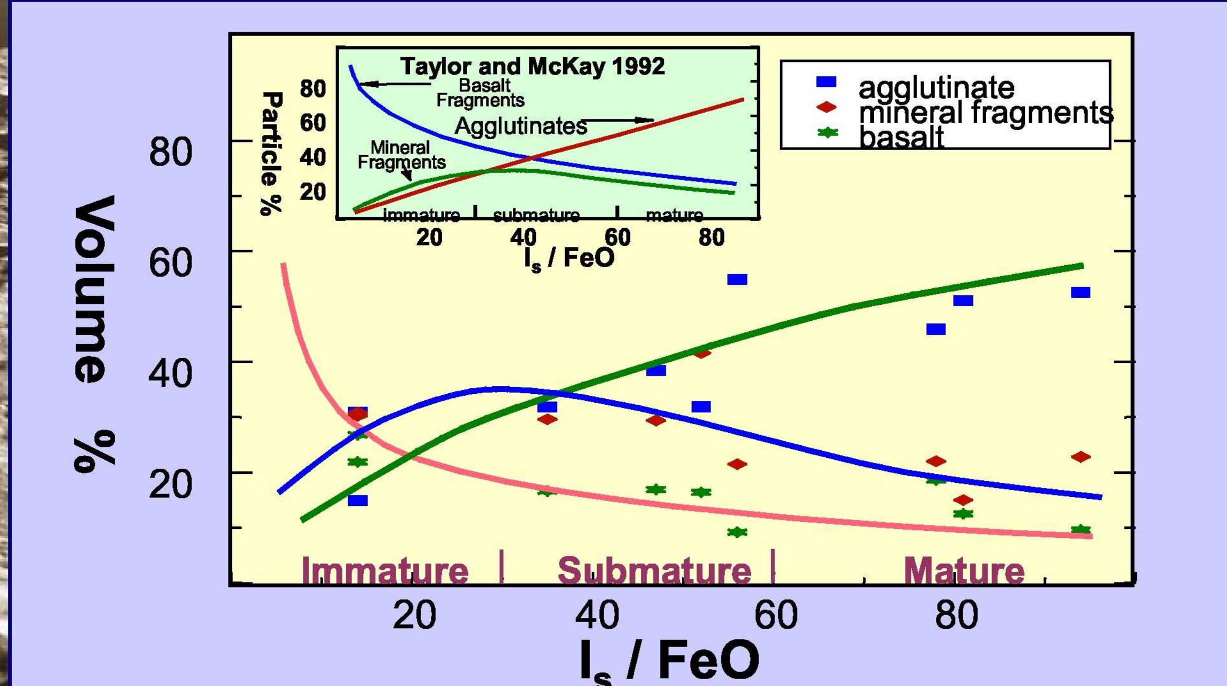
# Lunar Soil Formation




**Comminution, Agglutination, & Vapor Deposition**

# Soil Maturity

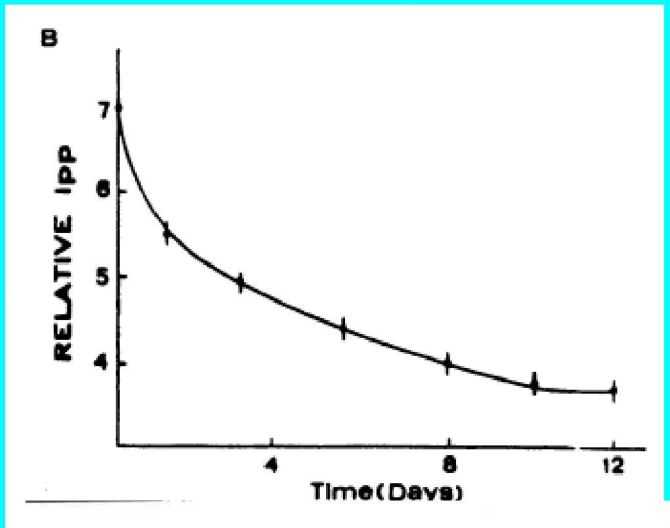



- Measurement of Single-Domain, Nanophase $Fe^0$ ($I_S$) FMR
- Normalized $I_S$ for Iron Content: $I_S$ / FeO
- $I_S$ / FeO = amount of total iron present as $Fe^o$
- $I_S$ / FeO is a Function of Agglutinate Abundance
- Agglutinate Abundance is a Function of Maturity

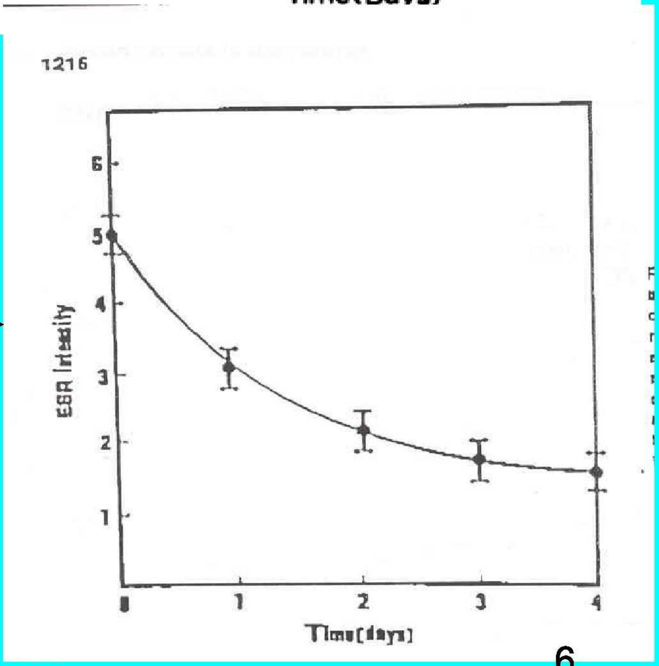
**$I_s$ / FeO = Soil Maturity**

# Quartz Activation by Grinding

- Grinding quartz: electron spin resonance (ESR) characteristic of Si· or Si-O· radicals
- Increased grinding = higher signal
- Decrease in Si-based radicals in air
- Half-life ~30 hours; at 4 weeks = still 20% signal



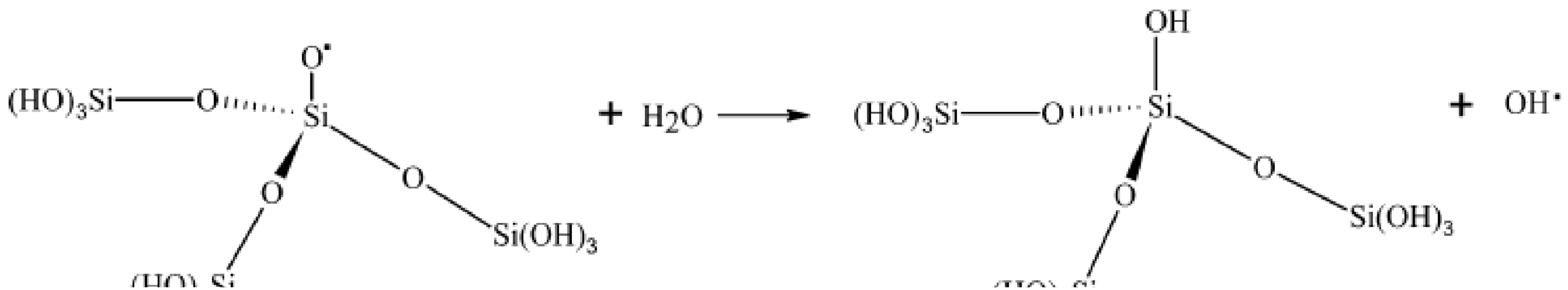

- Ground quartz + $H_2O$ = $OH^-$ in aqueous solution produces OH radicals
- Air = Decrease in Radical production
- Half life ~ 20 hours




**V. Castranova, *Environ. Health Perspect.* 102 (1994) 65-68.**
**V. Vallyathan *et al.*, *Am. Rev. Respir. Dis.* 138 (1998) 1213-1219**

# What Does "Activated" Mean?

- Presence of reactive sites on surface - Free radicals
- Ability to produce reactive species in solution




J. Narayanasamy and J.D. Kubicki, *J. Phys. Chem. B* 109 (2005) 21796-21807

## Reactive Species of Interest

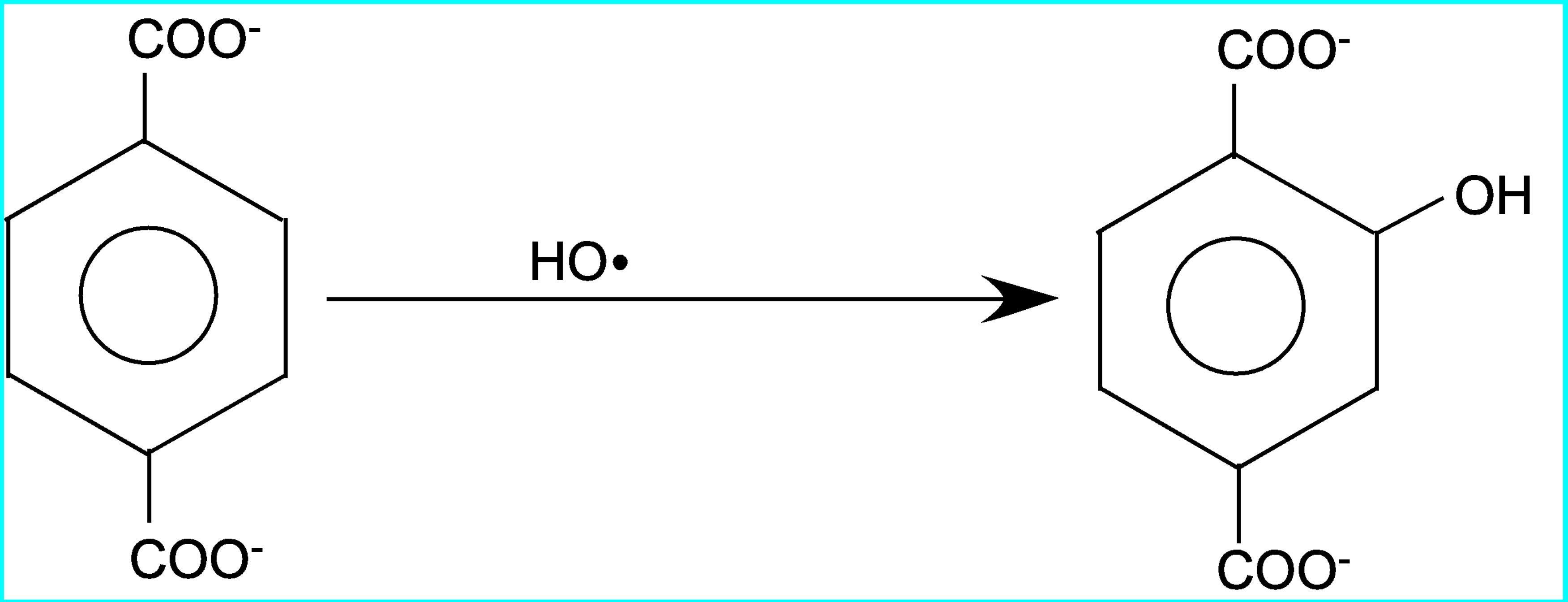
- Hydroxyl Radical, ·OH
- Highly oxidizing
- Damage & Radical species production

# How Should We Monitor ·OH?

- Fluorescence Spectroscopy
  - Can also provide quantitative analysis
  - Large number of chemical sensors already in use for other systems
  - Need to determine correct probe
- Electron Spin Resonance
  - Provides quantitative measure of radical production
  - Equipment is costly and bulky

# Fluorescence

## Monitoring Hydroxyl Radical Production




Terephthalate
(non-fluroroescent)

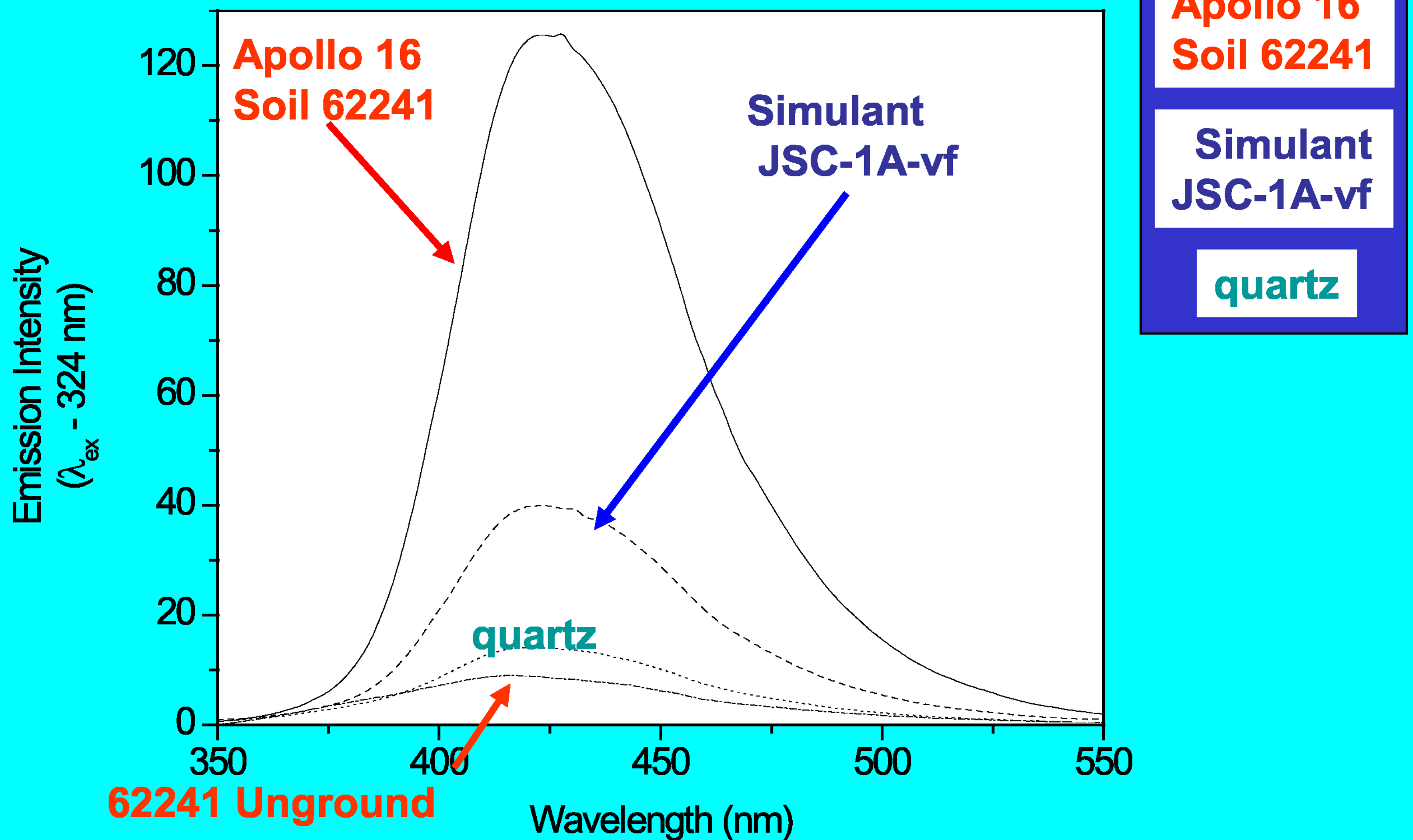
2-Hydroxyterephthalate
(fluorescent)

# Grinding Experiments

## Bulk Chemistry and Maturity

| Sample | $SiO_2$ | $Al_2O_3$ | $TiO_2$ | FeO | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ |
|---|---|---|---|---|---|---|---|---|---|---|
| JSC-1A-vf, % oxides | 48.8 | 15.7 | 1.49 | 8.88 + 1.71% $Fe_2O_3$ | 0.19 | 8.48 | 10.4 | 2.93 | 0.81 | 0.66 |
| Apollo 16 Soil (62241), % oxides $I_s/FeO = 100$ | 44.7 | 27 | 0.56 | 5.49 | 0.7 | 5.84 | 15.9 | 0.44 | 0.13 | 0.1 |
| Min-U-Sil Quartz, % oxides | 99 + | < 0.8 | < 0.1 | < 0.1 $Fe_2O_3$ | 0 | 0 | 0 | 0 | 0 | 0 |

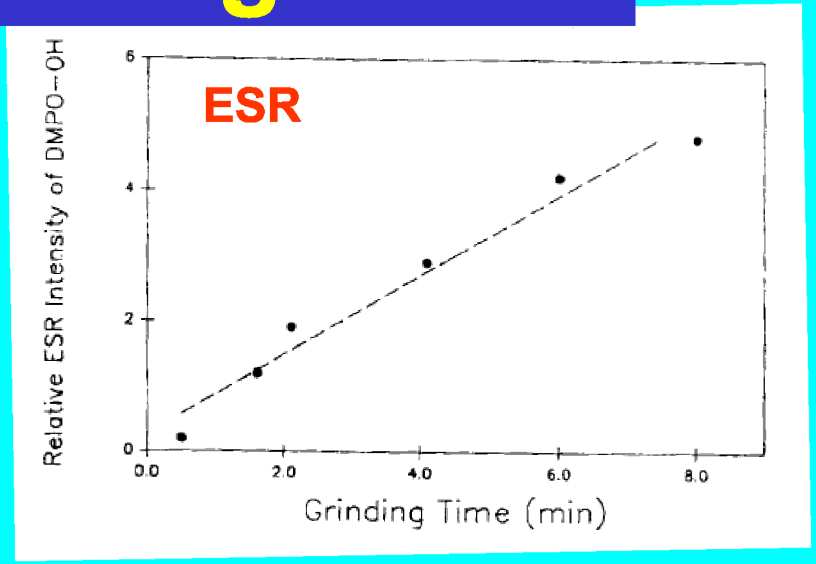
# Grinding Experiments

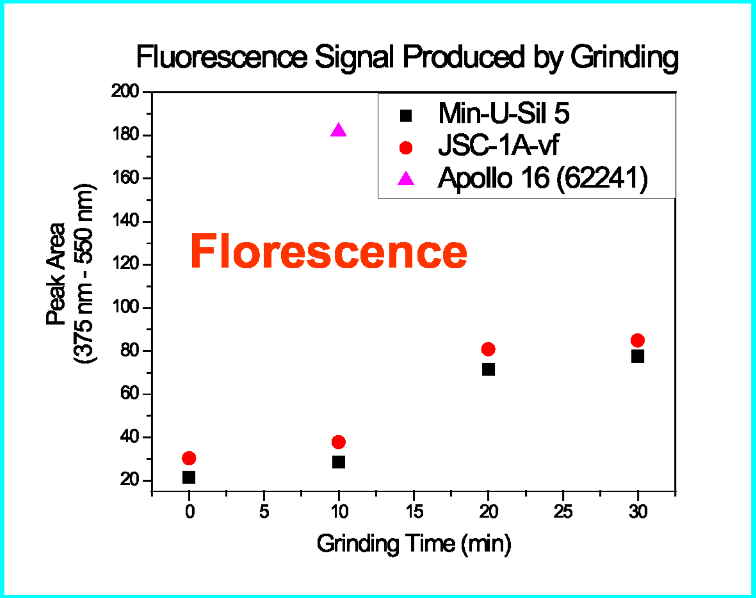



**Wallace *et al.*, (2009) Meteor. Planet. Sci. 44, 961-970**

# Effect of Grinding Time

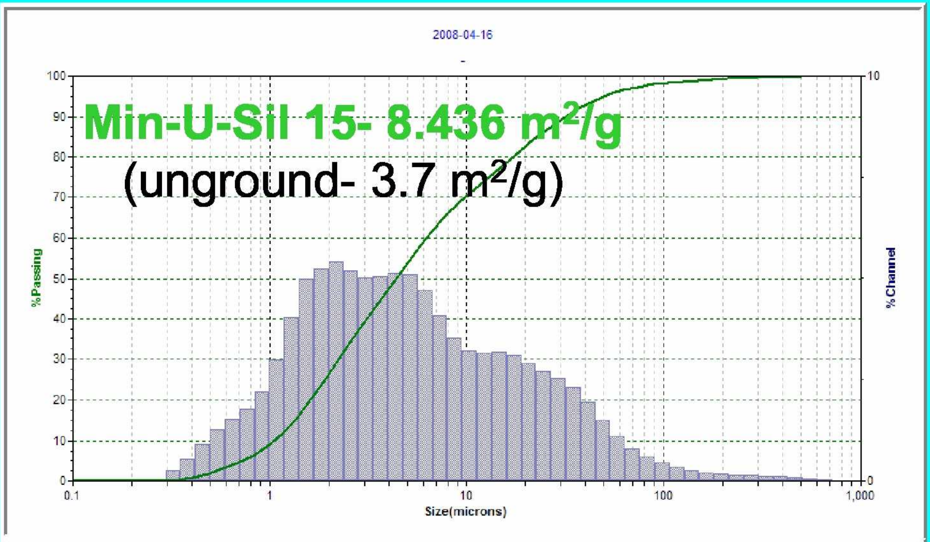
- Grinding: produces higher number of silicon-based radicals in ESR spectra
- Grinding time: direct effect on hydroxyl radicals produced
- Grinding: increase in hydroxyl production for lunar simulant and quartz with increased grinding
- **Grinding: Apollo Soil greatly increases *OH**

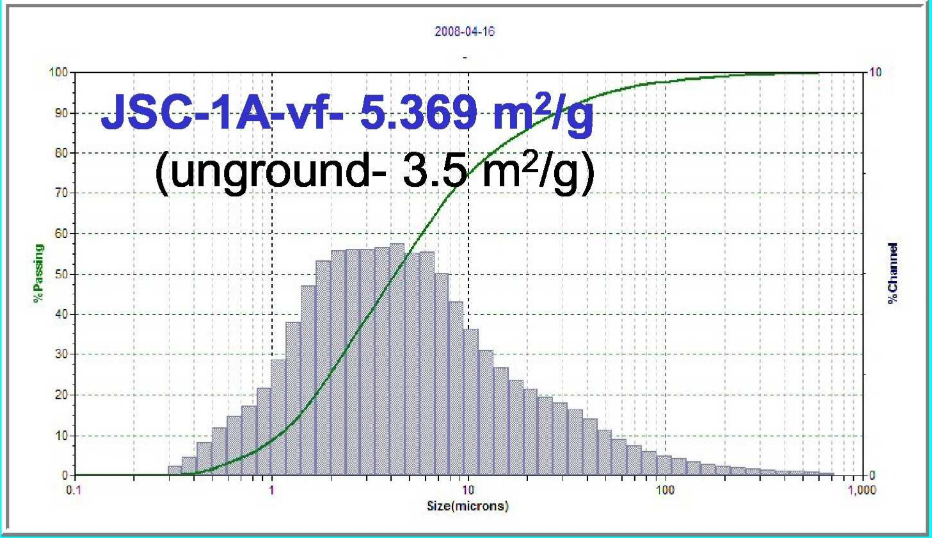


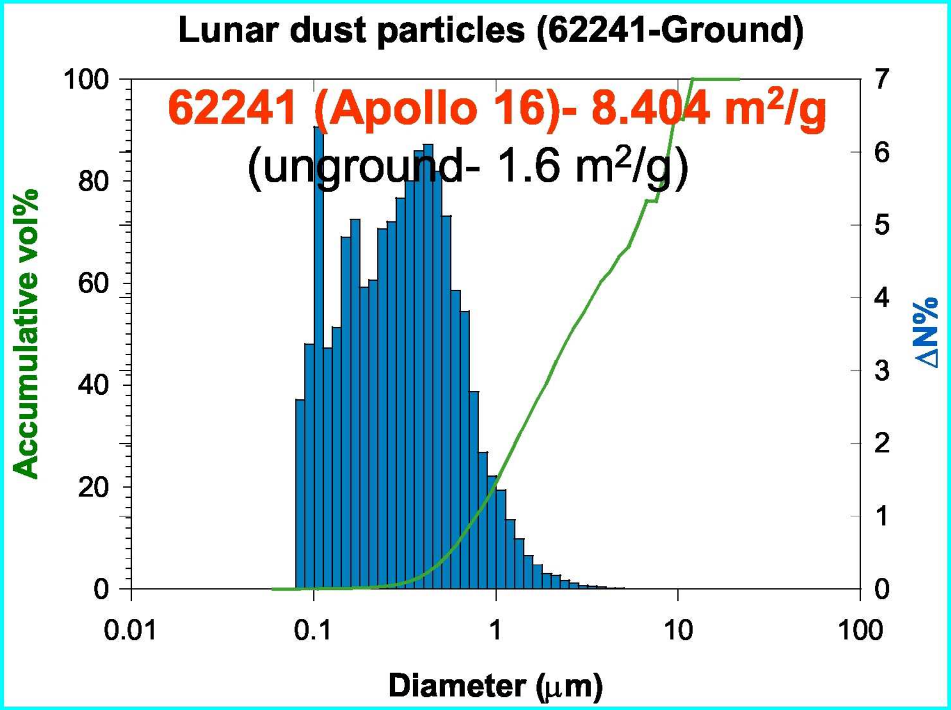




N.S. Dalal, X. Shi, and V. Vallyathan, *Free Rad. Res. Comms.* 9 (1990) 259-266.
W.T. Wallace *et al.*, *Meteor. Planet. Sci.* 44 (2009) 961-970.

# Size Distribution AFTER Grinding




**Wallace *et al.*, (2009) Meteor. Planet. Sci. 44, 961-970**

# Soil Chemistry and Maturity

| | Lo-Ti Mare | | Hi-Ti Mare | | Highlands | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Sample<br>$I_s$/FeO | 15071<br>52 | 15041<br>94 | 71061<br>14 | 79221<br>81 | 67461<br>25 | 67481<br>31 | 61141<br>56 | 62231<br>91 | 62241<br>100 |
| $SiO_2$ | 45.9 | 46.4 | 39.8 | 41.7 | 44.6 | 44.6 | 45.0 | 45.0 | 44.65 |
| $TiO_2$ | 1.81 | 1.83 | 8.76 | 6.39 | 0.35 | 0.44 | 0.59 | 0.60 | 0.56 |
| $Al_2O_3$ | 13.1 | 13.5 | 10.5 | 13.5 | 28.4 | 28.1 | 26.3 | 26.3 | 27 |
| $Cr_2O_3$ | 0.41 | 0.41 | 0.48 | 0.37 | 0.08 | 0.10 | 0.12 | 0.11 | - |
| MgO | 11.3 | 10.8 | 10.5 | 10.3 | 4.46 | 4.91 | 6.39 | 6.20 | 5.84 |
| CaO | 10.3 | 10.3 | 9.90 | 10.8 | 16.5 | 16.2 | 15.3 | 15.4 | 15.95 |
| MnO | 0.19 | 0.20 | 0.24 | 0.21 | 0.06 | 0.06 | 0.07 | 0.09 | 0.7 |
| **FeO** | **14.9** | **14.2** | **17.5** | **14.0** | **4.24** | **4.38** | **4.80** | **4.87** | **5.49** |
| $Na_2O$ | 0.37 | 0.41 | 0.41 | 0.41 | 0.40 | 0.43 | 0.43 | 0.43 | 0.44 |
| $K_2O$ | 0.13 | 0.19 | 0.09 | 0.09 | 0.06 | 0.06 | 0.11 | 0.12 | 0.13 |
| $P_2O_5$ | 0.18 | 0.21 | 0.06 | 0.07 | 0.04 | 0.04 | 0.06 | 0.07 | 0.1 |
| $SO_2$ | 0.12 | 0.13 | 0.15 | 0.19 | 0.06 | 0.04 | 0.09 | 0.09 | - |

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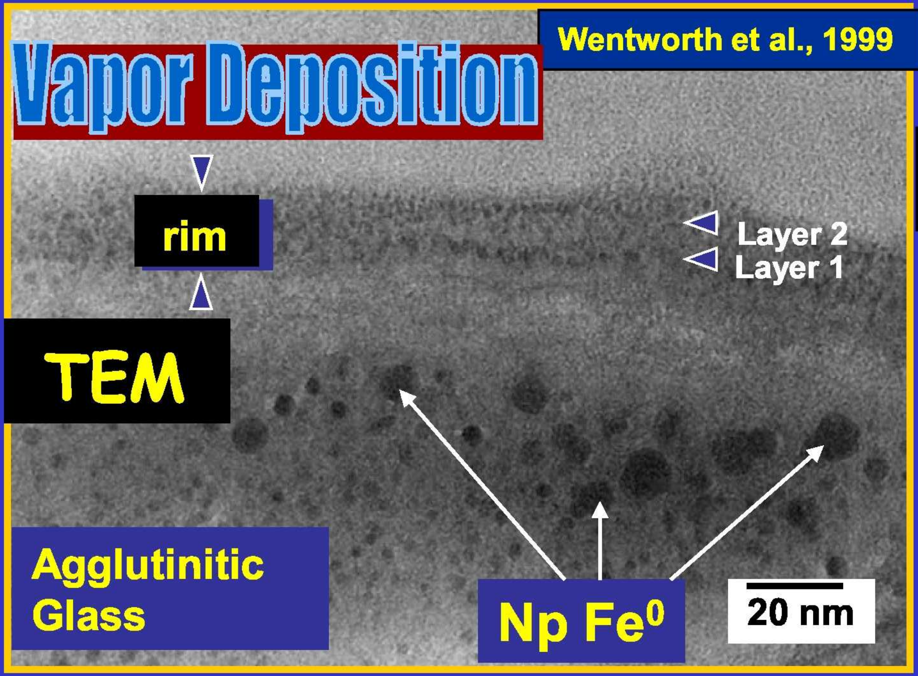
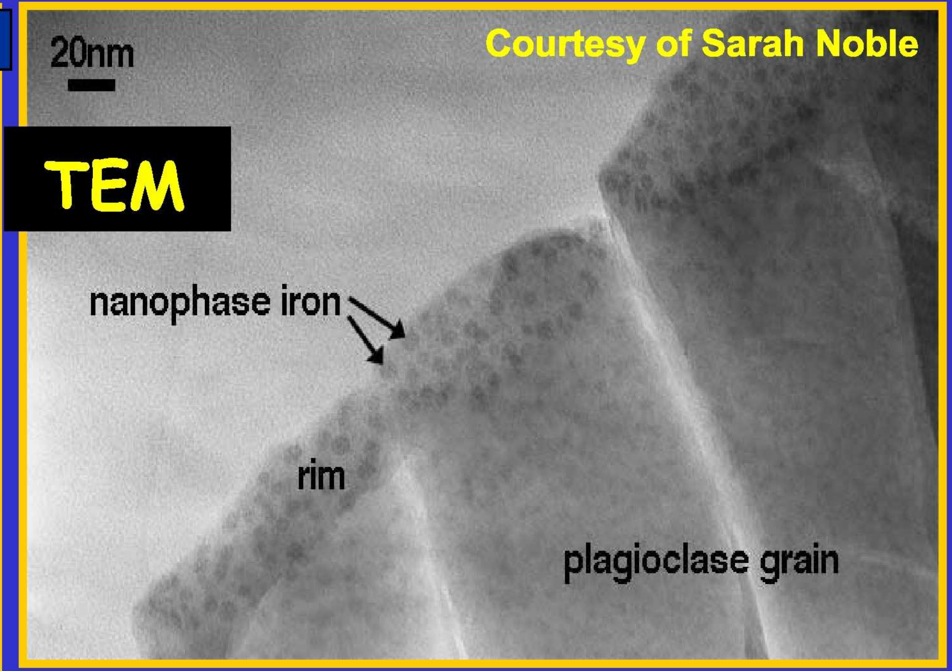
# Metallic Fe TOXICITY on Dissolution of Glass ?




**Glassy rims produced by vapor/sputter deposition**
**Single-Domain Fe = 3-33 nm nanophase Fe**

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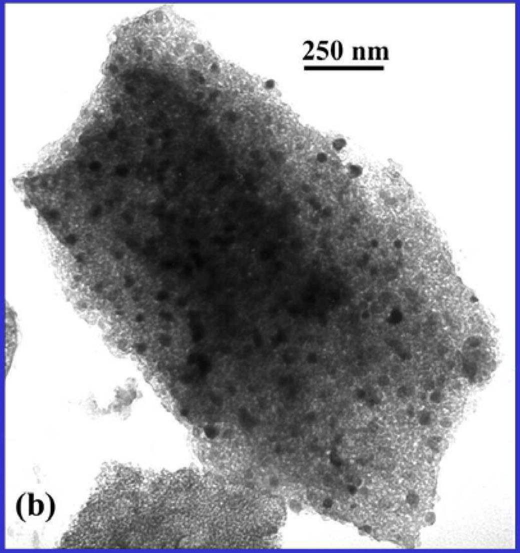
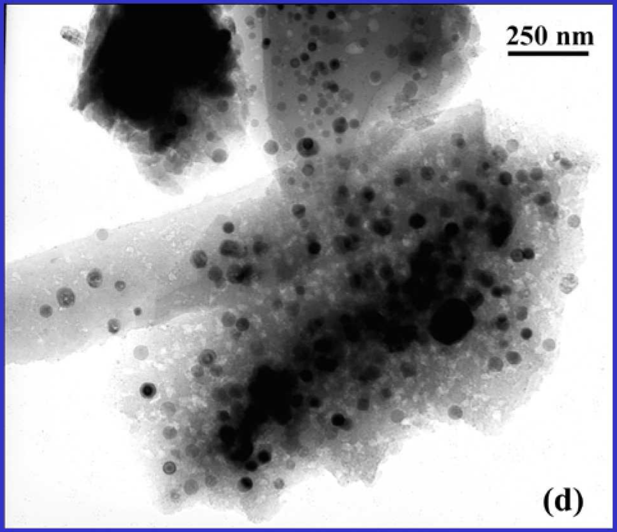
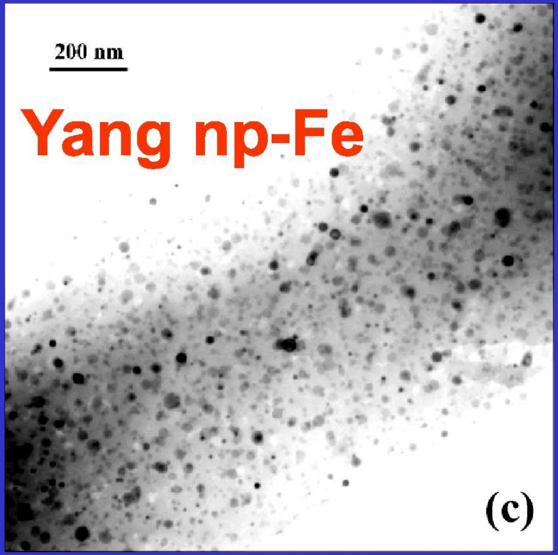
# Synthesis of NP-Fe in $SiO_2$ Glass

## TEM Photos

## Milky Way of np-Fe°

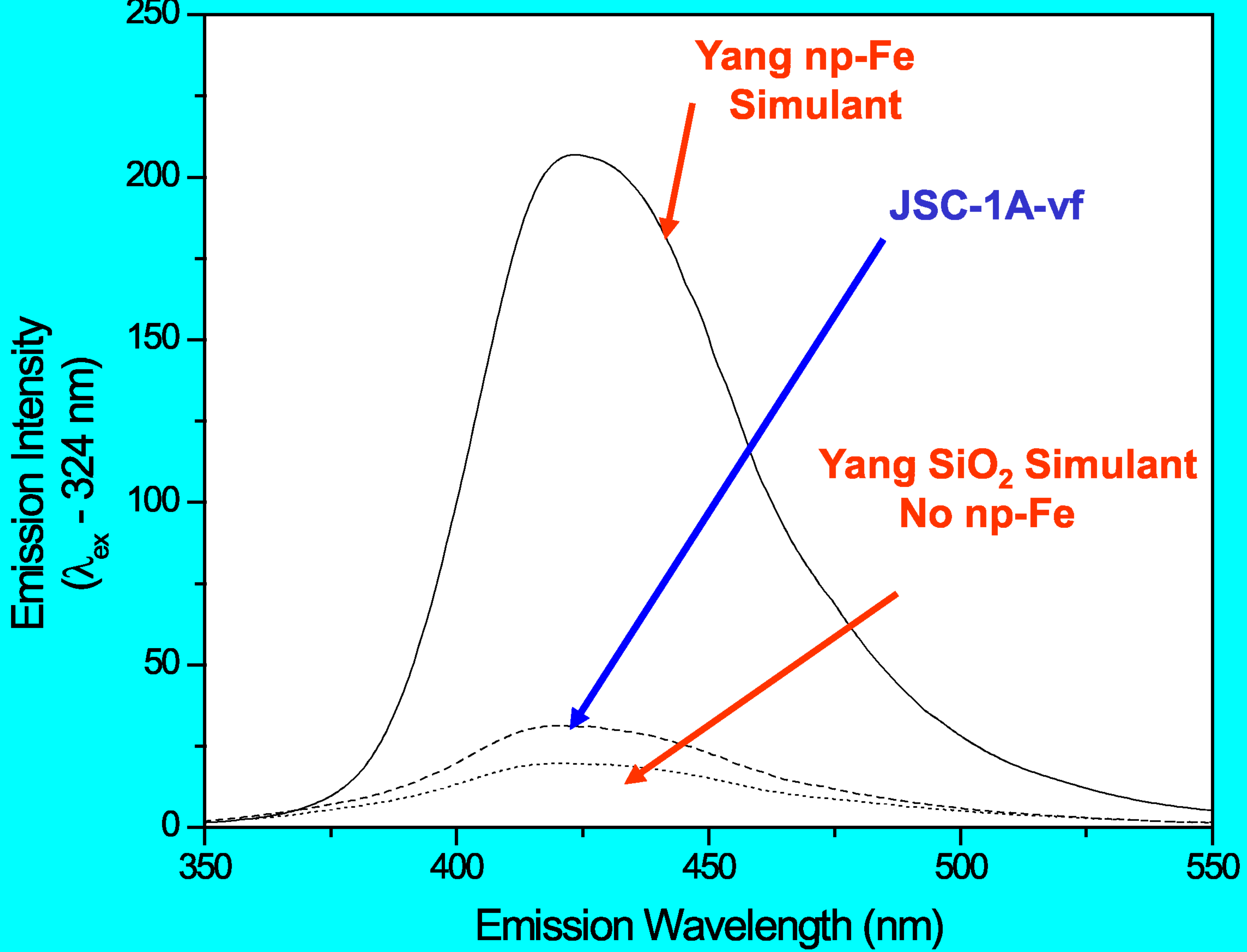




All Black Dots are Nanophase Fe

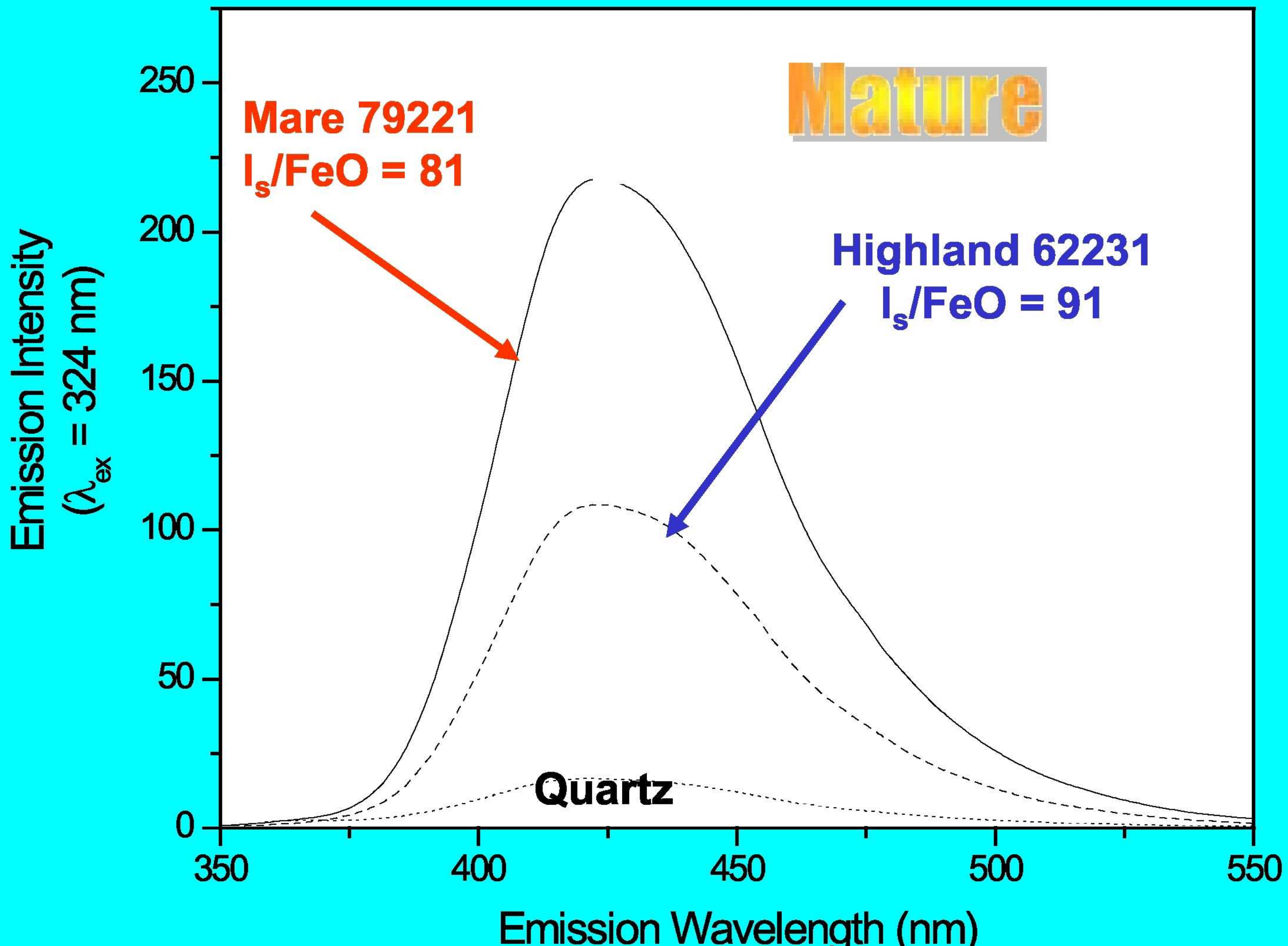
Liu et al., 2007

# Effects of Nanophase Iron




**Wallace *et al.*, *Earth Planet. Sci. Lett.* (2009) submitted.**

# Effects of Dust Source (Highland vs Mare)

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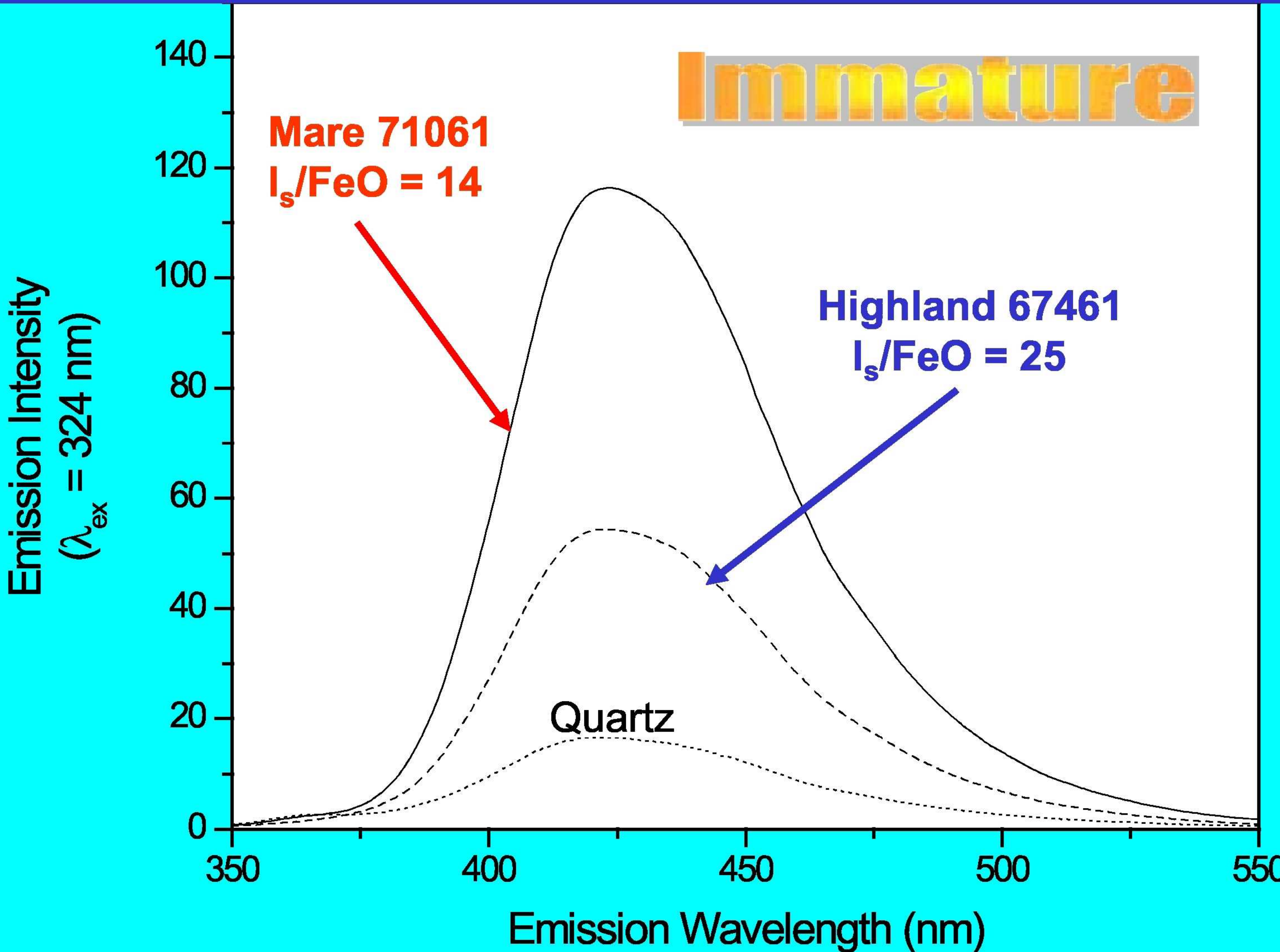
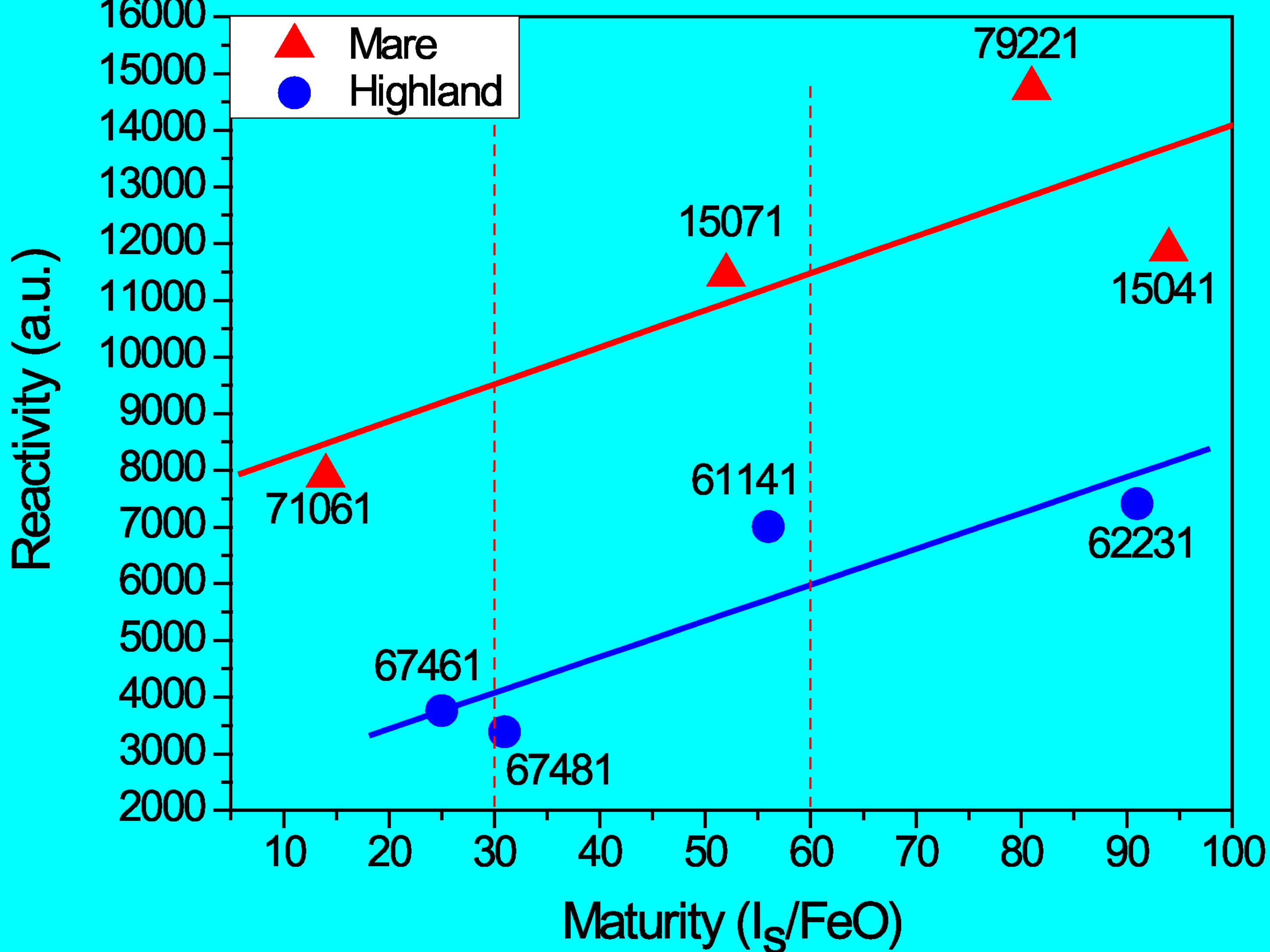


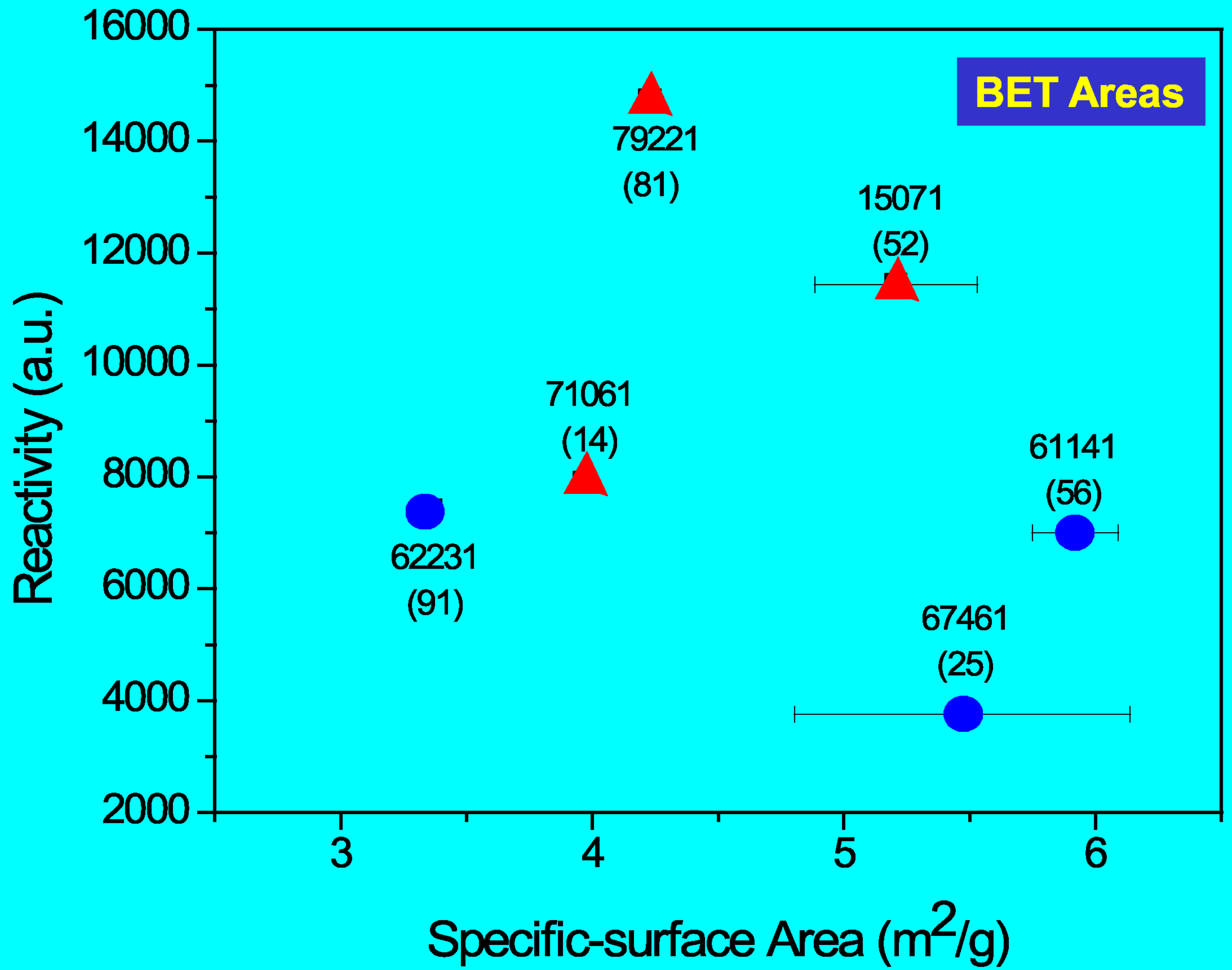

**Wallace *et al.*, *Earth Planet. Sci. Lett.* (2009) submitted.**

# Effects of Maturity on Reactivity



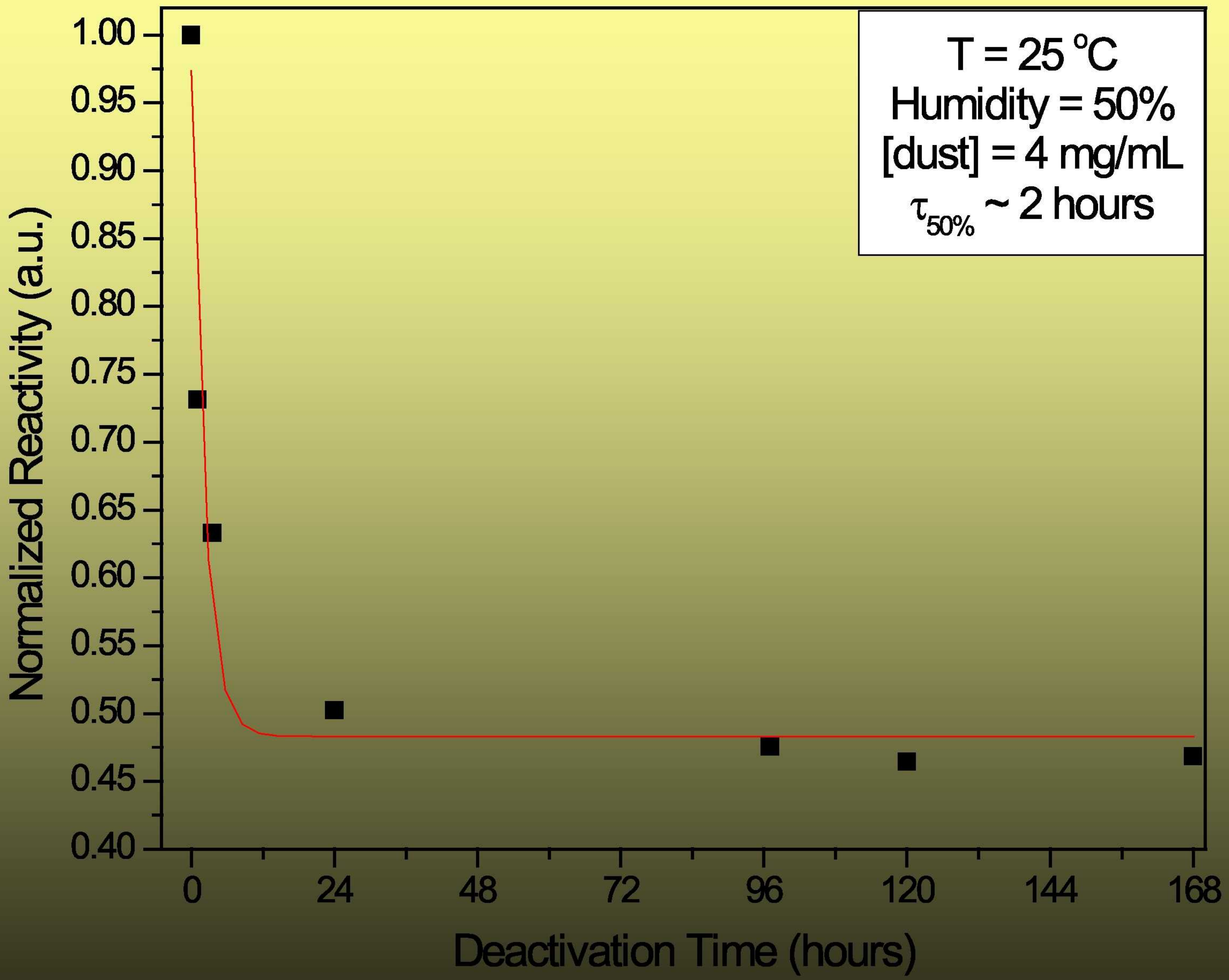

**Wallace *et al.*, *Earth Planet. Sci. Lett.* (2009) submitted.**

# REACTIVITY: Effects of Surface Area

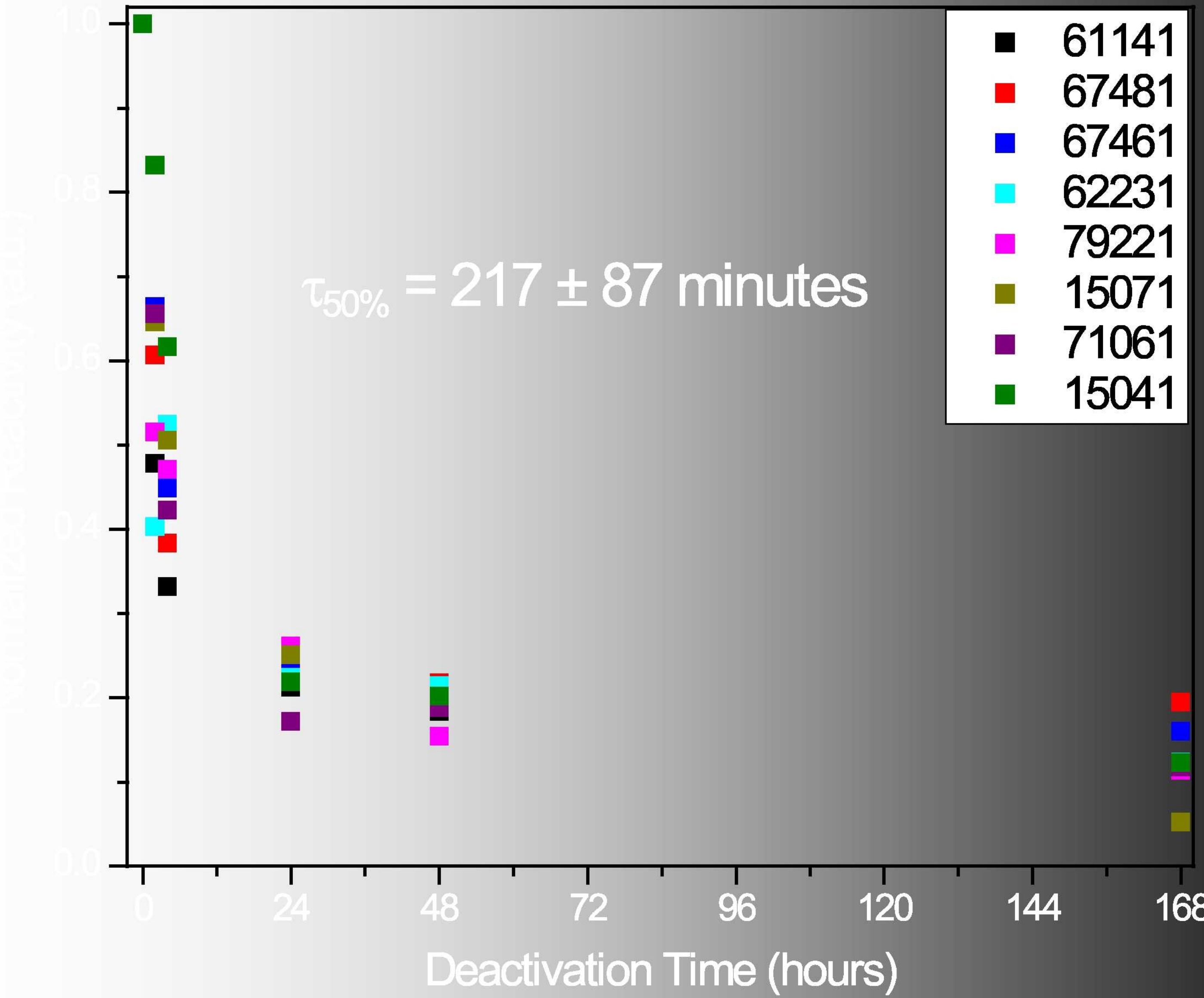



**Wallace *et al.*, *Earth Planet. Sci. Lett.* (2009) submitted.**

# Deactivation of JSC-1A-vf



# Deactivation of Lunar Soils



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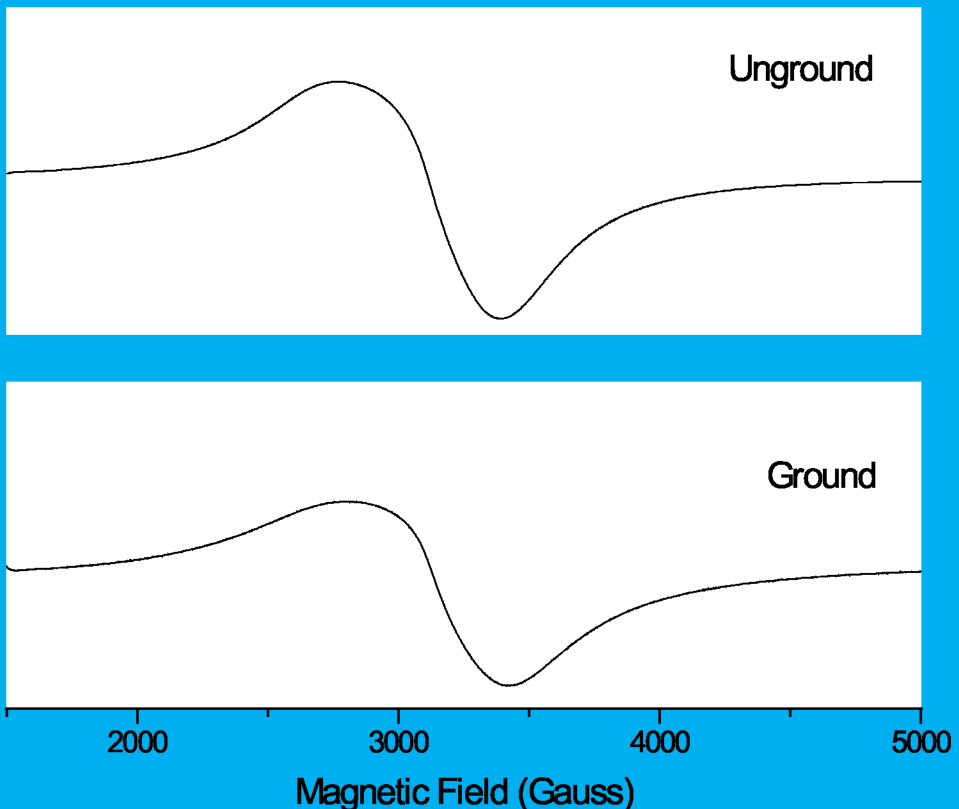
# TAKE - HOMES

- **Lunar Soil is Highly Activated by Grinding; Dependent upon Soil Maturity and Locale.**
- **RECALL: $I_s$/FeO is Measure of the Amount of NP-Fe in a Soil Relative to the Total Iron as FeO.**
- **LUNAR SOIL ACTIVITY IS A DIRECT FUNCTION OF AMOUNT OF NP-Fe PRESENT.**
- **Fluorescence and EPR can Measure Soil Activity; Fluorescence can be Quantified.**
- **CAUTION: Keller has Stated that in Mature Soils Most Soil Particles are Glass + NP-Fe Coated; Passifier of Grinding-Produced Dangling Bonds??**


EPR

# EPR Spectra of Apollo 62241

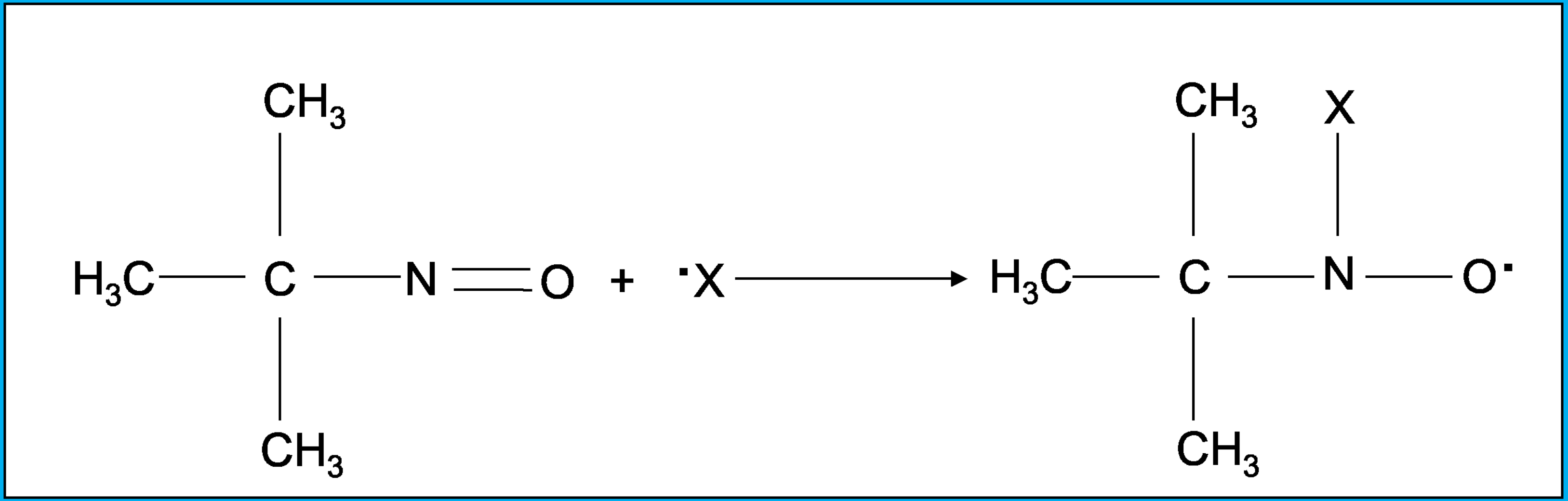



- Same grinding conditions as fluorescence studies
- Broad peaks
    - Si· or Si-O· ?
- g-values: 2.11 ⟶ 2.09 (unground ⟶ ground)
- Similar to previous results*



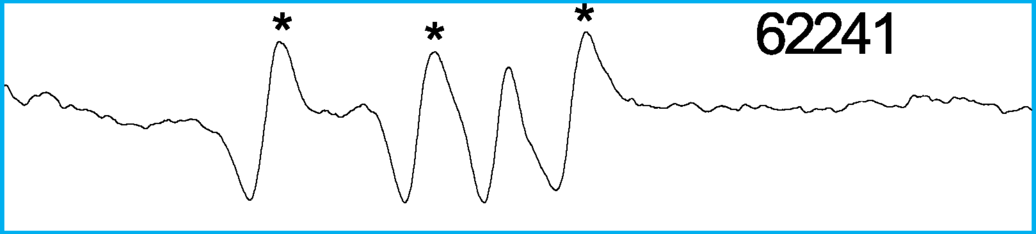
*: D. Haneman and D.J. Miller, *Proc. Second Lunar Sci. Conf.* **3** (1971) 2529-2541.

# Testing for Radicals Using Spin Traps

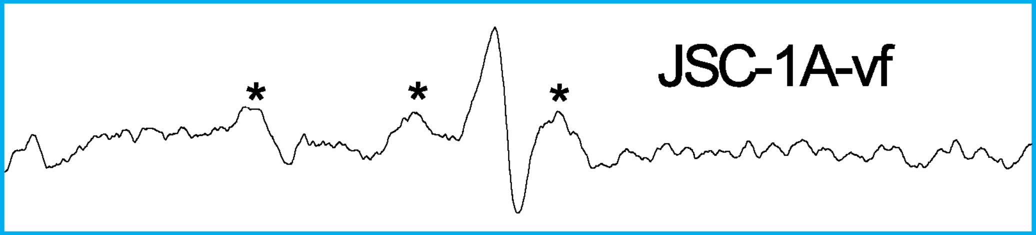



2-methyl-2-nitropropane (MNP)

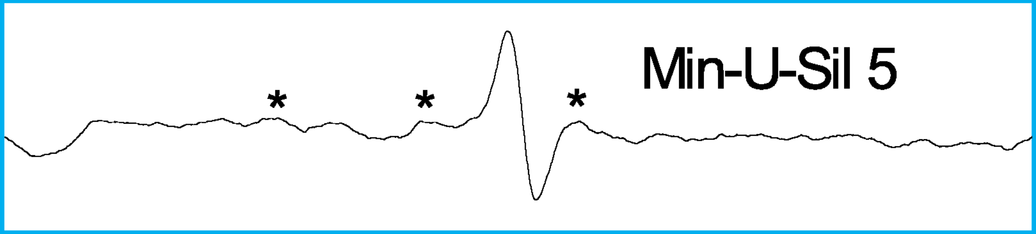
# Spin-trapping of Radicals




10 minute grinding




10 minute grinding




30 minute grinding

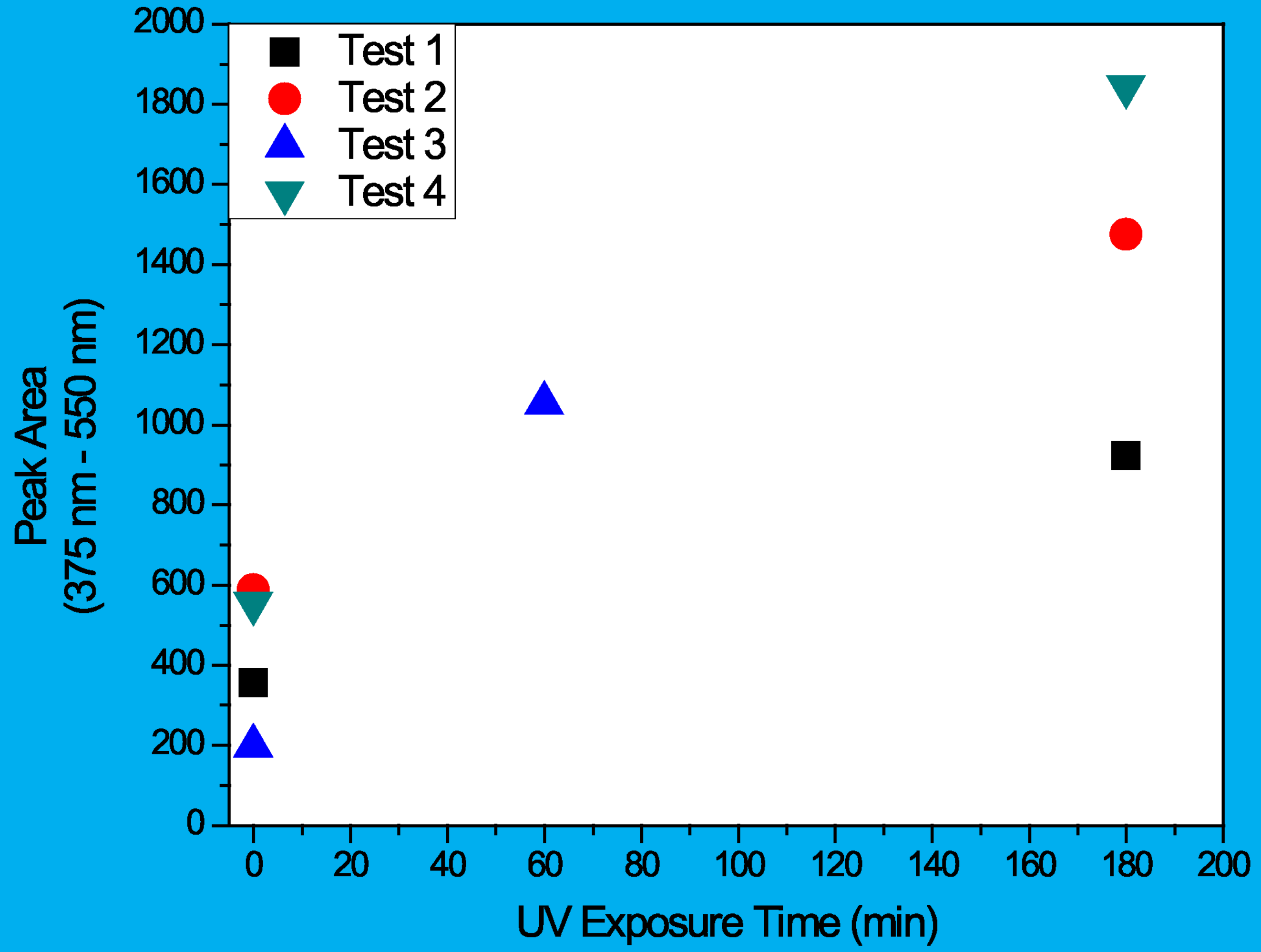
* : spin-adduct triplet

100 mM MNP/acetonitrile

- Activity: quartz < lunar dust simulant < lunar dust
- Activated species + acetonitrile = radicals
    - Radical has no H (no hyperfine coupling peaks)
- Future testing: DMPO in water

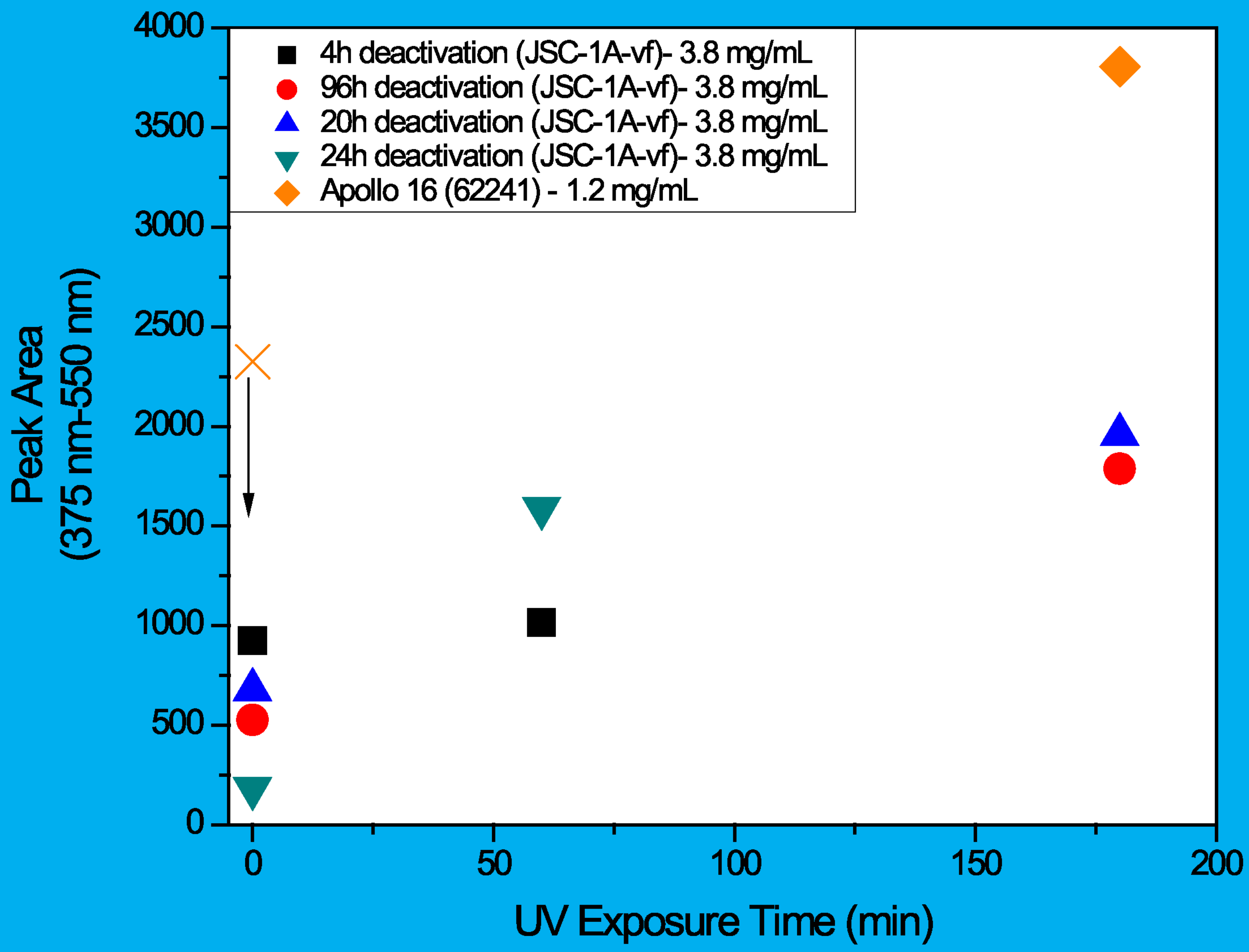
# Activation by UV Exposure

# UV Activation of Unground Lunar Simulant




- 3.8 mg/mL JSC-1A-vf
- 10 mM Terephthalate
- 800 W UV
- ~ 5 X $10^{-4}$ Torr

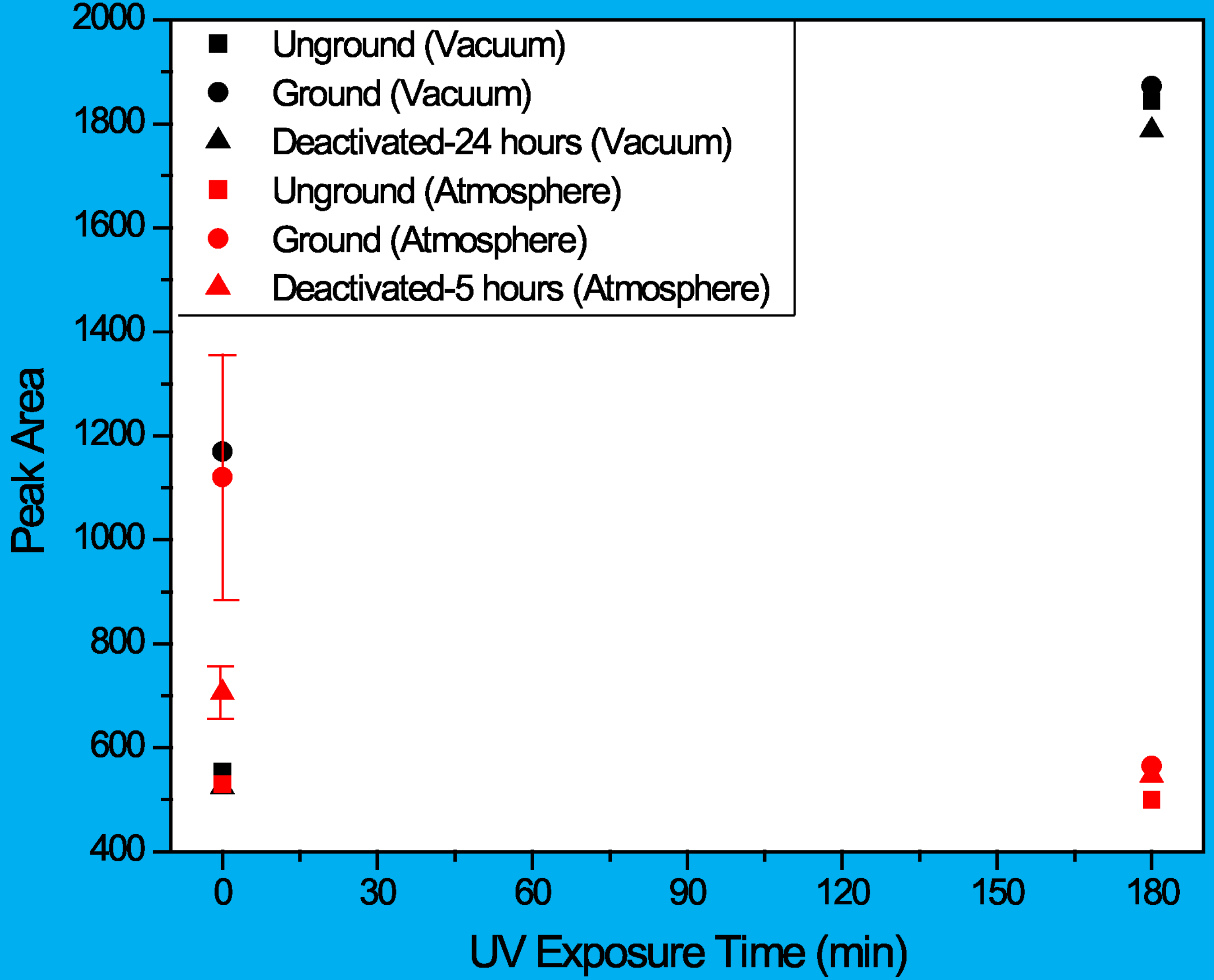
# UV Reactivation of Ground, Deactivated Lunar Dust and Simulant




X

Final deactivation point from initial lunar dust testing (> 1 month further deactivation; upper limit for activity)

# Effects of Vacuum on UV Activation/Deactivation of Lunar Simulant



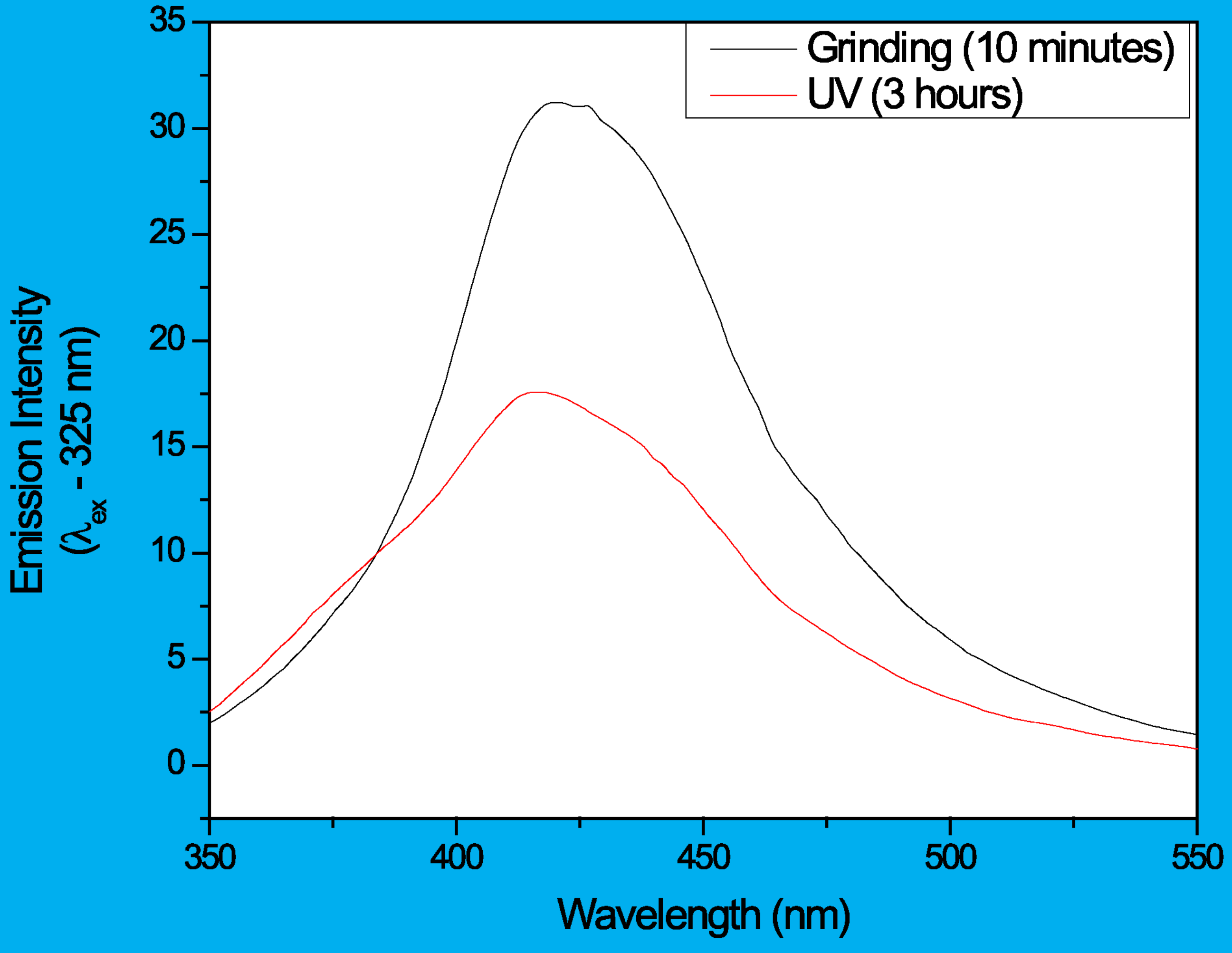

- 3.8 mg/mL
- 10 mM

Terephthalate

- 800 W UV

**Exposure of active simulant to UV in air leads to deactivation!**

# Comparison of Activation by Grinding and UV Exposure




- JSC-1A-vf
- 4 mg/mL
- 800 W UV
- ~ 5 X $10^{-4}$ Torr

# Summary

- Hydroxyl radical production in solution a measure of reactivity
- Both EPR and fluorescence used
  - Further EPR – 02/10
- Reactivity by grinding: lunar dust > simulant > quartz
- Reactivity: Mare > Highland
- Reactivity correlated with maturity (np-Fe concentration)
- Deactivation tested (50% RH, 25 $^{o}$C)
  - 50% of initial reactivity ~ 2 hours for lunar dust simulant and ~ 3-4 hours for lunar soils
- UV radiation leads to hydroxyl radical production
  - UV less efficient than grinding

# Acknowledgements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