Stimulated Desorption of Silicates: Sources for Neutrals & Ions in Mercury's Exosphere

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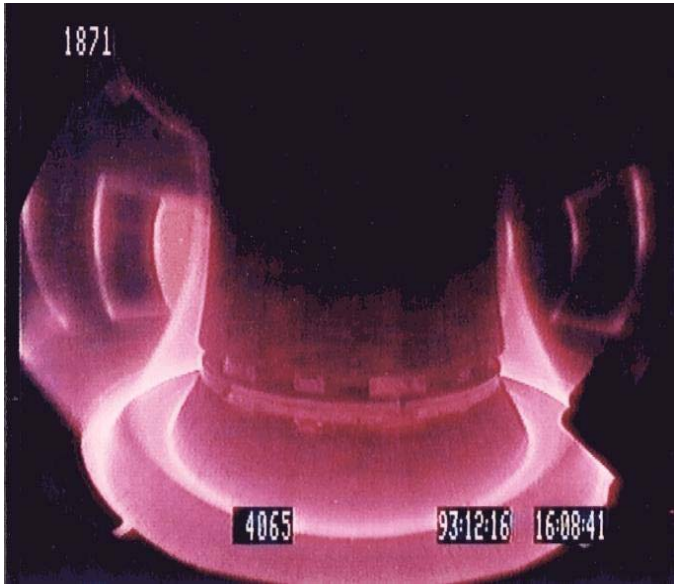
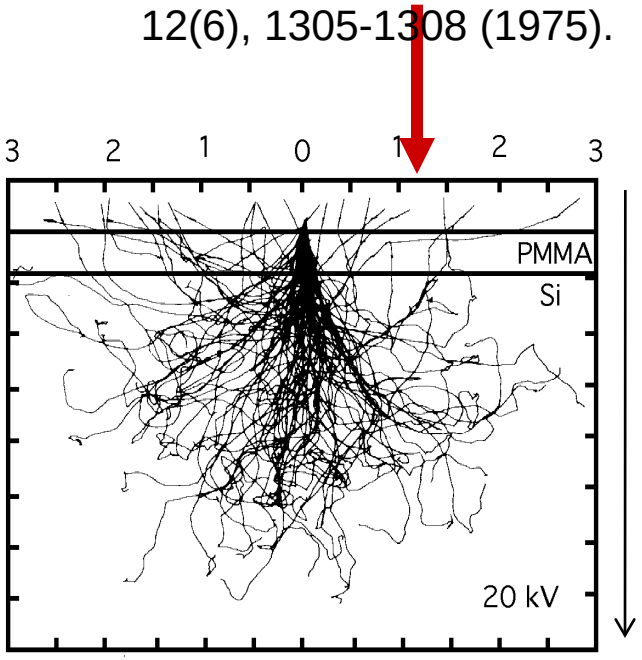
Why are electron interactions with surfaces important?



http://www.hut.fi/Units/AES/fusion.htm

X-ray or high energy electron beam . F. Kyser and N. S.Viswanathan, *J. Vac. Sci. Technol.* 12(6), 1305-1308 (1975).



100-500 nm

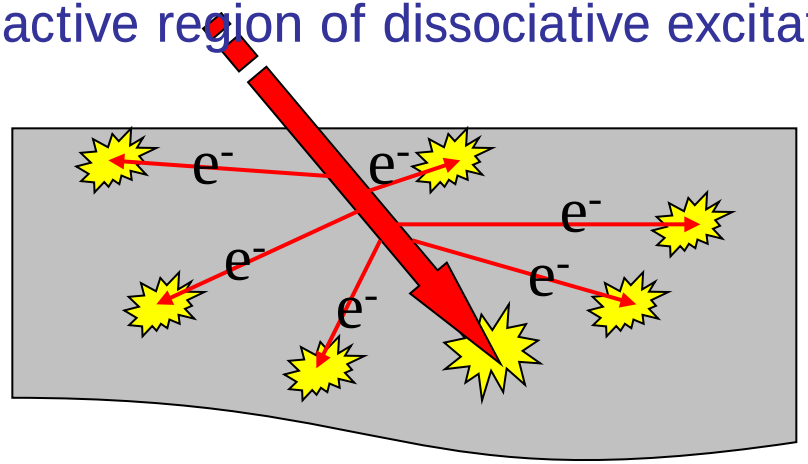
- Fusion program: Flash-over events involved electron-stimulated desorption of neutrals from the walls.

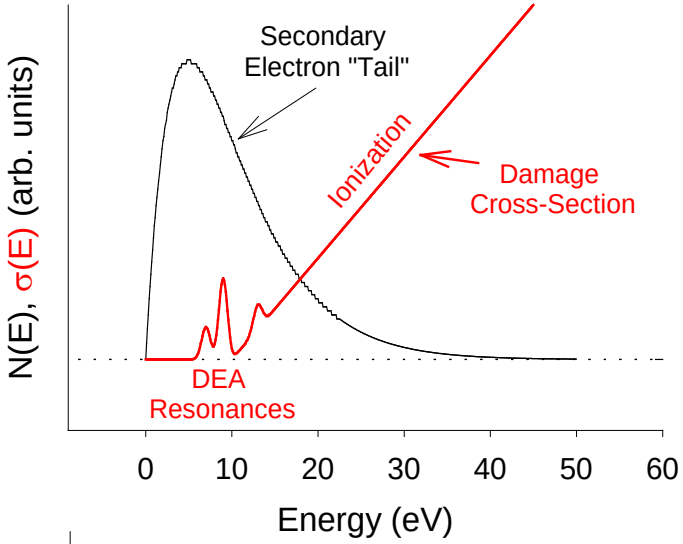
- High-energy beam processing for nano-fabrication of surfaces and interfaces
.
- Tracks are not that different in minerals

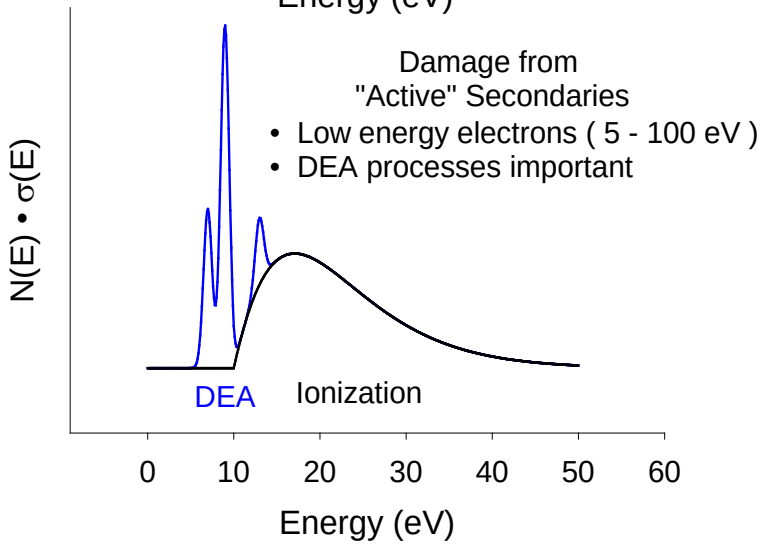
General interest in non-thermal events and “stimulated” reactions on/in materials.

Secondary Electrons

- High energy particles scatter within targets with finite stopping distance.
- Stopping power is due to inelastic scattering events.
- This results in structural damage and impact ionization yielding low energy electrons.
- Each high energy particle can produce dozens or hundreds of low energy secondary electrons.
- Energy distribution of secondary e^- peaks in active region of dissociative excitations.

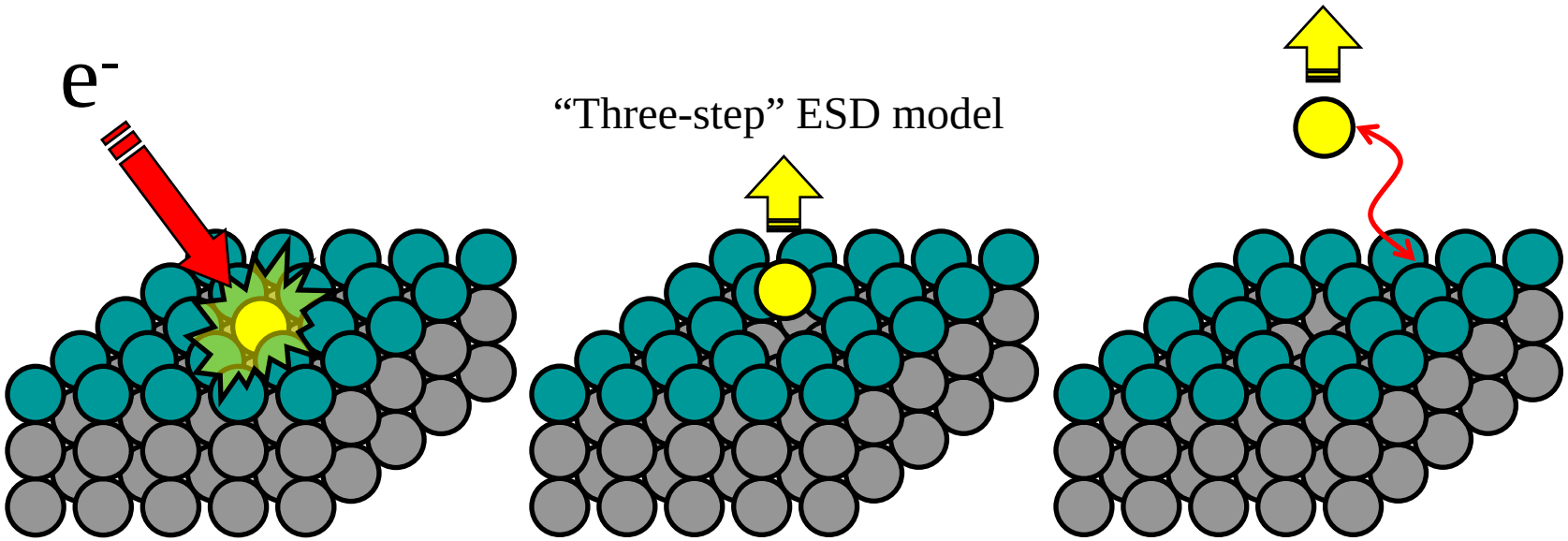






Photon- and Electron-Stimulated Desorption (PSD and ESD)

(Note: Electron-stimulated can also occur during proton irradiation. This is NOT a momentum transfer issue).



Excitation

~ 10^{-15} sec

Electron excites the target via an inelastic scattering event

Separation

~ 10^{-13} sec

Nuclear motion on the excited state potential surface

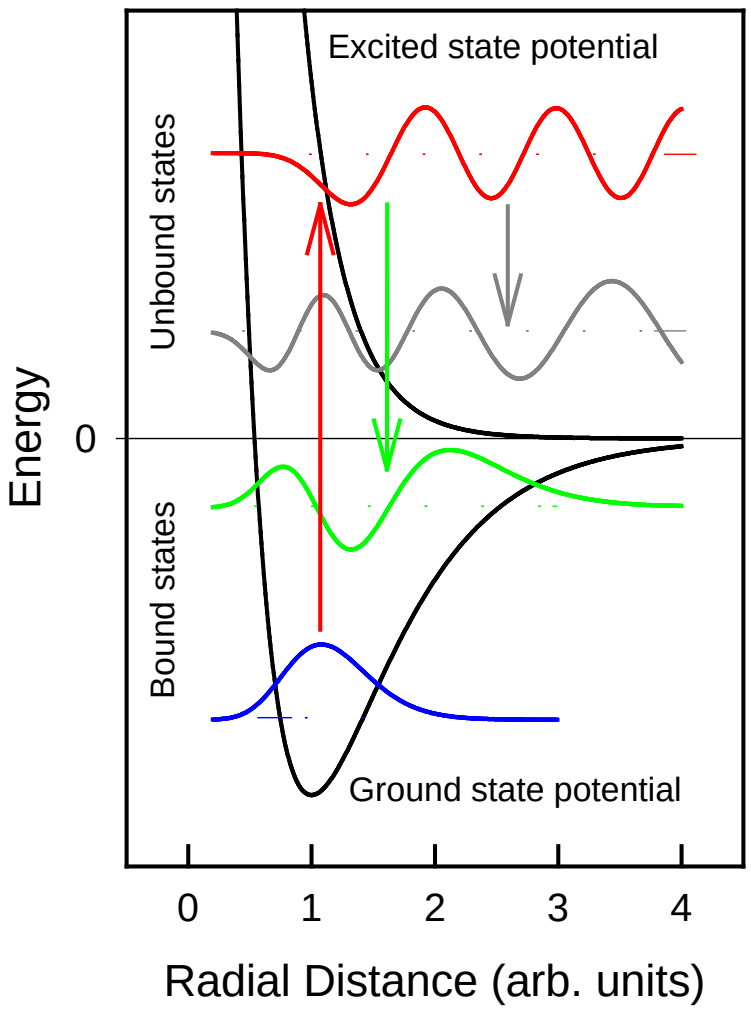
Divorce

~ 10^{-11} sec

Outgoing atom or molecule interacts with surface (energy exchange, neutralization)

Mutihole final states if energy is high enough

Nonthermal desorption (i.e. electronic desorption)



(1) An electronic excitation changes the local arrangement of charge around the target atom, exciting the system from the ground state (blue) to an unbound state (red).

(2) The atom time-evolves in the unbound state and is pushed away from the surface.

(3) If the excitation is short-lived, the atom will be re-captured by the surface, perhaps in an excited vibrational state (green).

(4) If the excited state lives long enough, the atom can gain enough kinetic energy to escape, even if the excited state is quenched (gray).

Of course, reality is more complicated. Reference: Ramsier & Yates, Surf. Sci. Rep. **12**, 243 (1991).

Example of the MGR model: Photon stimulated desorption of neutrals....Na from Na bearing silicates.

T. Madey, R. E. Johnson, and **T. M. Orlando**, “Far-out Surface Science: Radiation-Induced Surface Processes in the Solar System”, *Surf. Sci.* **500**, 838 (2002).

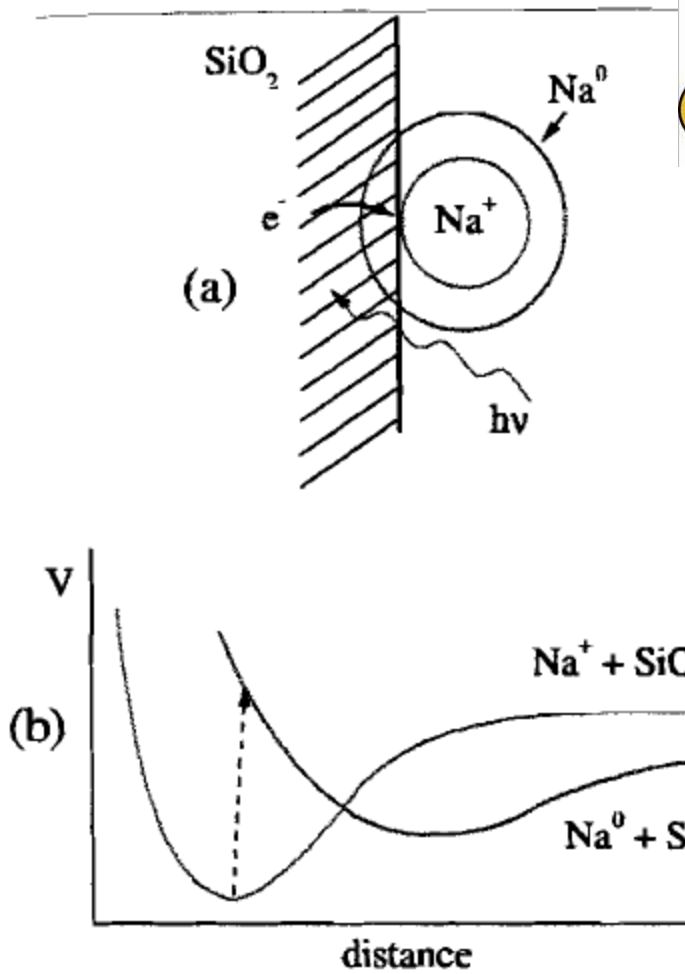


Fig. 6. Schematic mechanism for PSD of sodium from SiO_2, a model mineral for the lunar surface: (a) The sodium at the surface is ionic Na^+; a solar ultraviolet photon excites an electron in the substrate which attaches to the Na^+. This charge transfer converts Na^+ to neutral Na^o. Because Na^o has a larger radius than Na^+, the atom is in a repulsive state and can desorb (see (b) schematic of interaction potential V as a function of distance from the surface). This process is described in Ref. [21].

VOLUME 86, NUMBER 3 PHYSICAL REVIEW LETTERS 15 JANUARY 2001

Role of Excitons in Electron- and Photon-Stimulated Desorption of Neutrals from Alkali Halides

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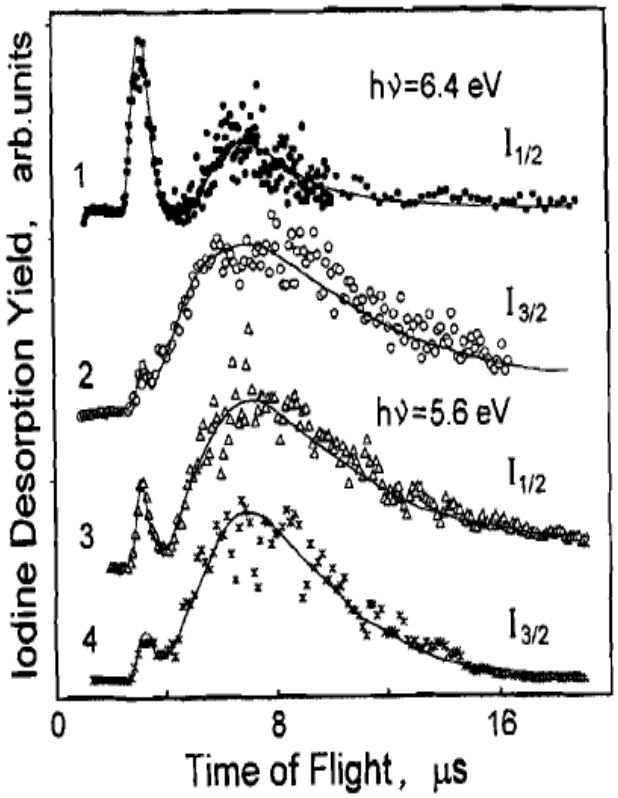


FIG. 1. Time-of-flight (TOF) distributions of emitted iodine atoms in the $^2P_{1/2}$ and $^2P_{3/2}$ states. Curves 1, 2 were obtained using 6.4 eV photons, curves 3, 4 using 5.57 eV photons. Irradiation energy flux is 1.9 $\mu J/mm^2$ per pulse. The sample temperature was maintained at 470 K and all TOF spectra are scaled to approximately equal intensities of the thermal yield.

PSD at two different photon energies yields different velocity distributions.
(The exciton spin is preserved.)

ESD and PSD involve the same physics but ESD does not have to follow dipole selection rules.

ESD can have much higher cross sections and involves secondary interactions and multiple scattering.

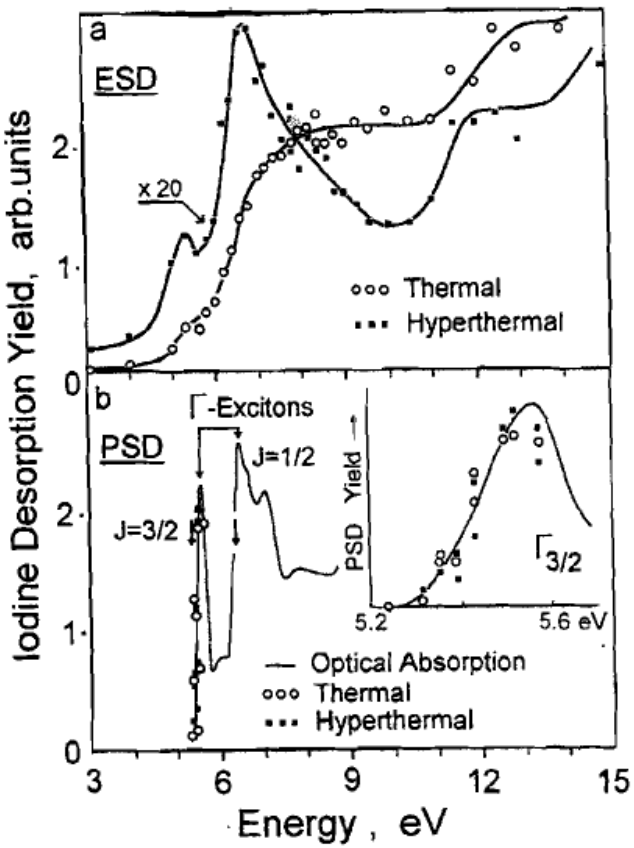


FIG. 2. Desorption yields of thermal (○) and hyperthermal (■) $I^2P_{3/2}$ as a function of incident electron energy (a) and photon energy (b). The points correspond to the gated integrated signal of the hyperthermal and thermal TOF peaks obtained at each incident energy. The data in (b) are compared to the exciton structure of KI [15]. The inset is an enlargement of the comparison to the $\Gamma_{3/2}$-exciton long-wavelength edge.

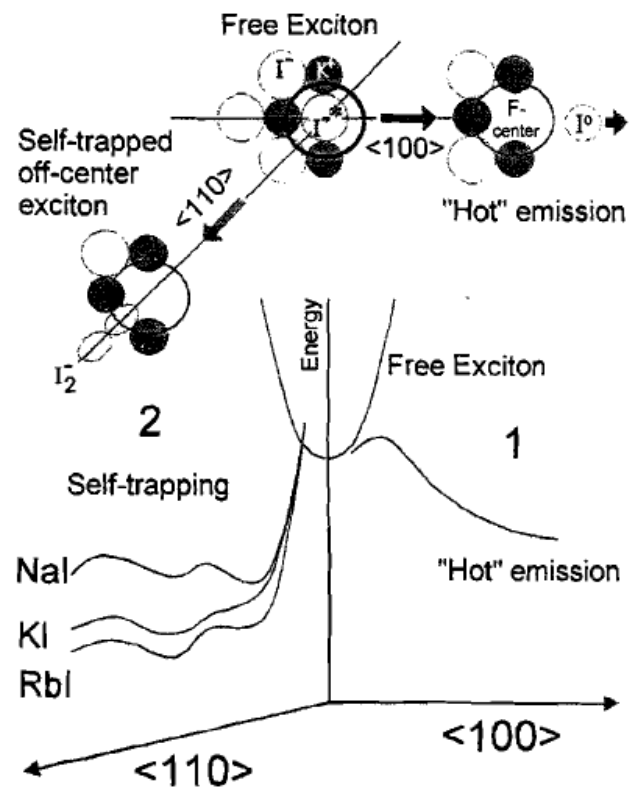
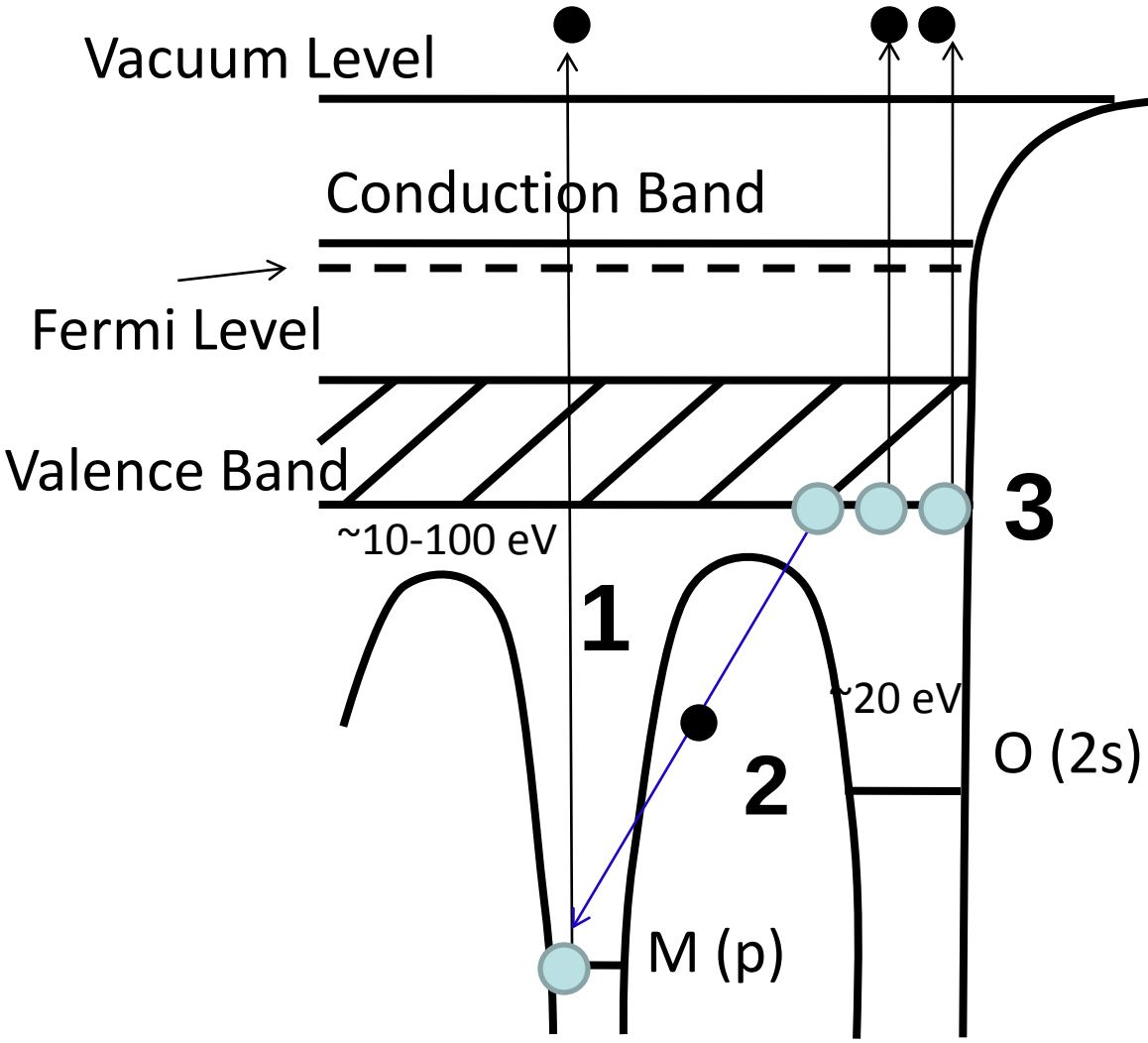


FIG. 3. Schematic of the general desorption mechanism for alkali halides which involves FE or surface exciton decay. The decay at the surface, which directly produces the hyperthermal atoms in the ⟨100⟩ direction, is in competition with formation of the self-trapped dihalide exciton (STE).

- **Surface excitons decay to produce a "hot" and slow (thermal) fragments.**
- **Surface excitons are active in removing neutral atoms such as K, Na, H_2O, etc. from minerals.**
- **For minerals with defects, surface excitations can also remove oxygen.**
- **Ionizing transitions can lead to ion desorption**.

Knotek-Feibelman mechanism for desorption of ions directly from metal-oxide surfaces



Step 1: Direct ionization of metal core level.

Step 2: Auger decay of core hole.

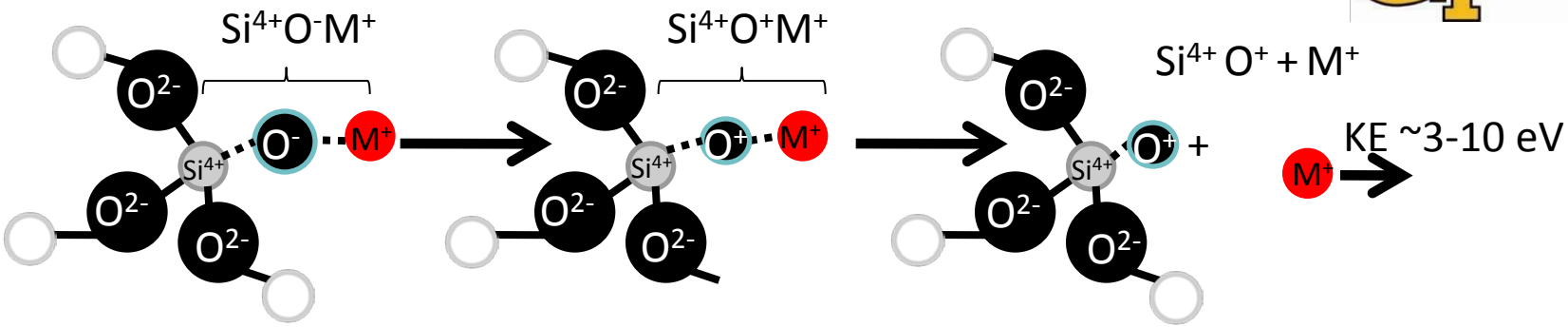
Step 3: Electron correlation and ejection from top of the valence band. (Formation of O^+)

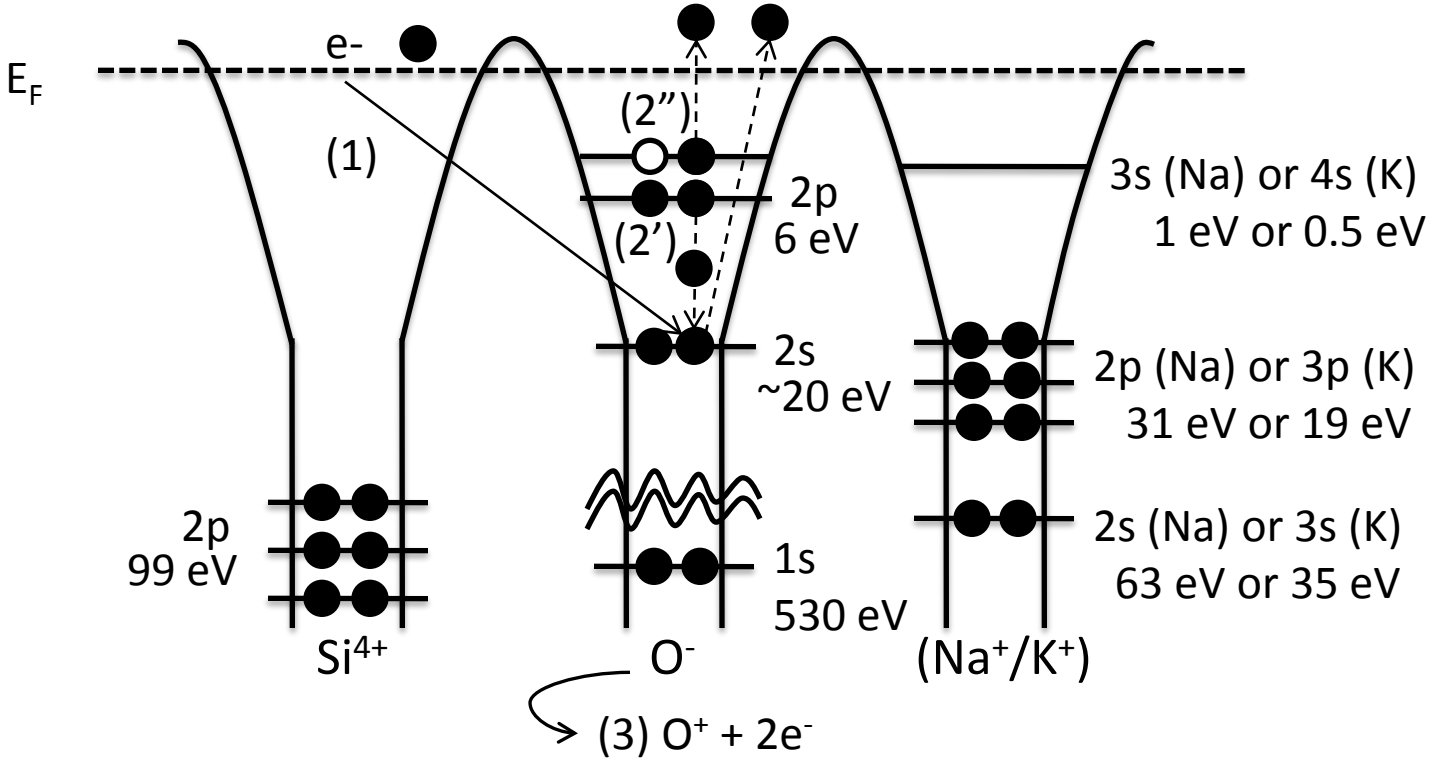
Step 4: O^+ desorption due to Coulomb explosion.

M. L. Knotek, P. J. Feibelman, PRL, 1978, (40), 14.

Knotek-Feibelman mechanism for ESD of Ions

Intra-atomic Decay





Electron and Photon Stimulated Desorption Summary

Desorption Cross-sections:

Ions: (10^{-19} – 10^{-23} cm^2)

Neutrals: (10^{-18} – 10^{-20} cm^2)

Typical gas-phase dissociative ionization: (10^{-18} cm^2 at 100 eV)

ESD ion Yields: 10^{-6} per electron at 100 eV but are as high as 10^{-3}/electron or 10^{-4}/electron for minerals

Standard PSD does NOT yield ions. PSD with x-rays does.

Threshold Energies:

Neutrals: ~ 5 eV (One-electron valence level excitation- MGR)

Ions: > 5 eV (Shallow core-excitation followed by Auger decay)

Lifetimes:

Core-holes: 10^{-16} seconds

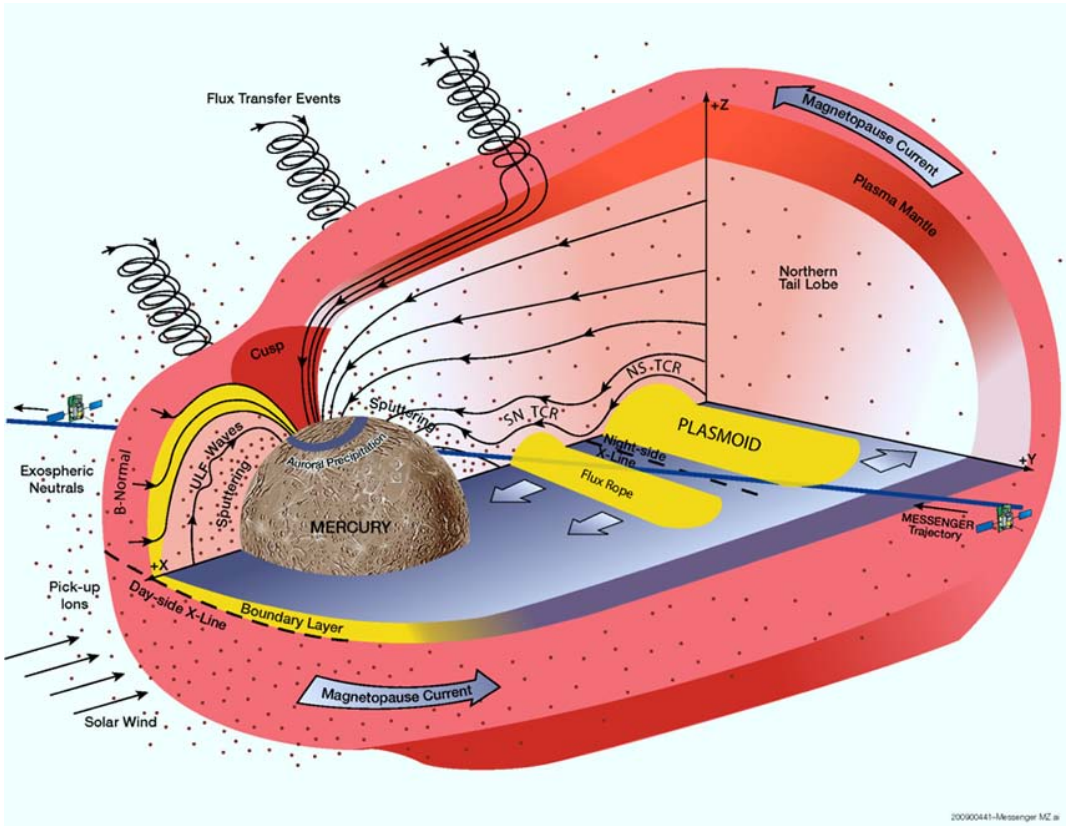
Valence level: 10^{-15} – 10^{-14} seconds

Kinetic Energies:

Neutrals: < 1 eV

Ions: 1-10 eV

Magetospheric interactions with Mercury's surface (Image from Slavin, et. al Science 85, 321 (2008)



The intensity and shape of the H^+ flux depends on the magnetospheric configurations and the opening of "leaks" via magnetospheric tornadoes and flux transfer events (FTE).

FTE's are produced by a localized magnetic reconnection between the internal magnetic field and the planetary magnetic field at the inbound magnetopause.

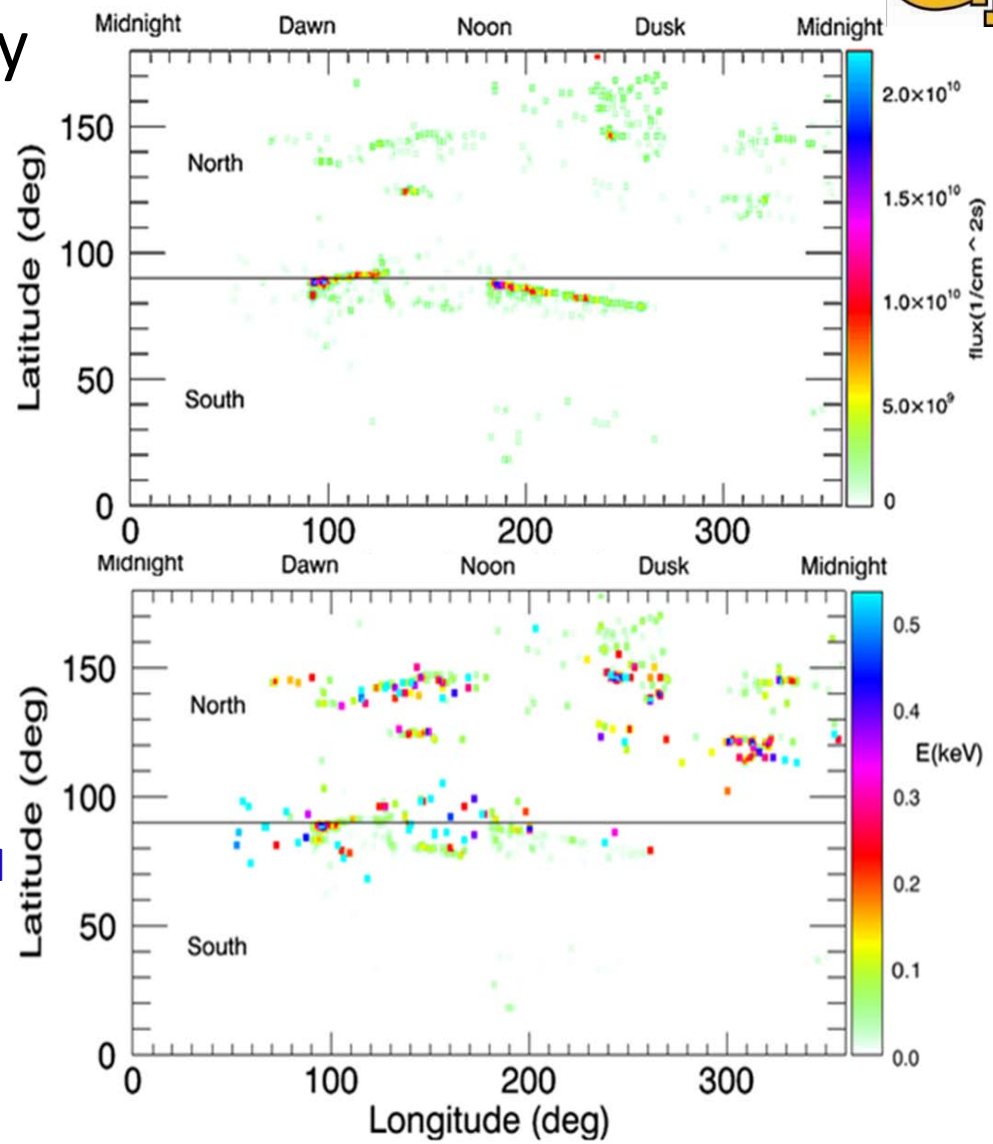
The H^+ flux onto Mercury may exceed values of 10^9 cm^{-2} s^{-1} and the total integrated flux can be as high as 10^{25} s^{-1}.

<u>Electron fluxes likely to be high.</u>

Simulation / Model of electron flux & energy Messenger 2nd Flyby

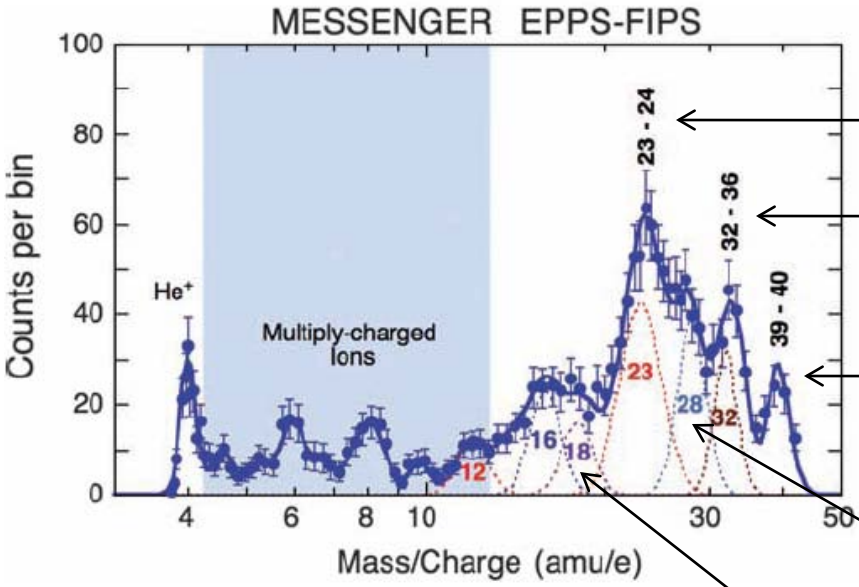
- **The electron fluxes;**
  Upper Plot: ~10^{10} $cm^{-2}s^{-1}$

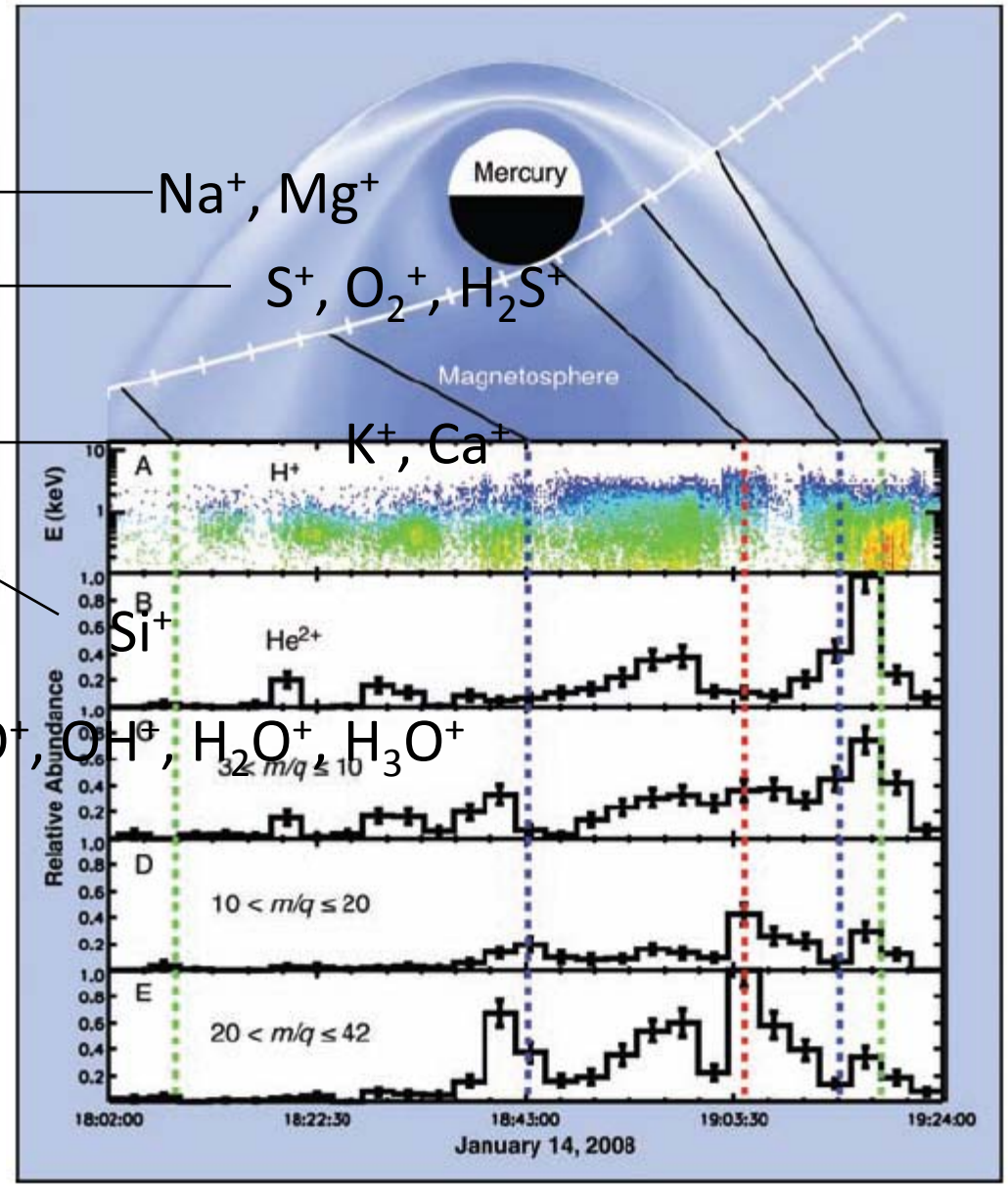
- **Average energies;**
  Lower plot: up to 500 eV.



Schriver et al. *PSS*, 2010. submitted

MESSENGER EPPS-FIPS Data





Na^+, Mg^+

S^+, O_2^+, H_2S^+

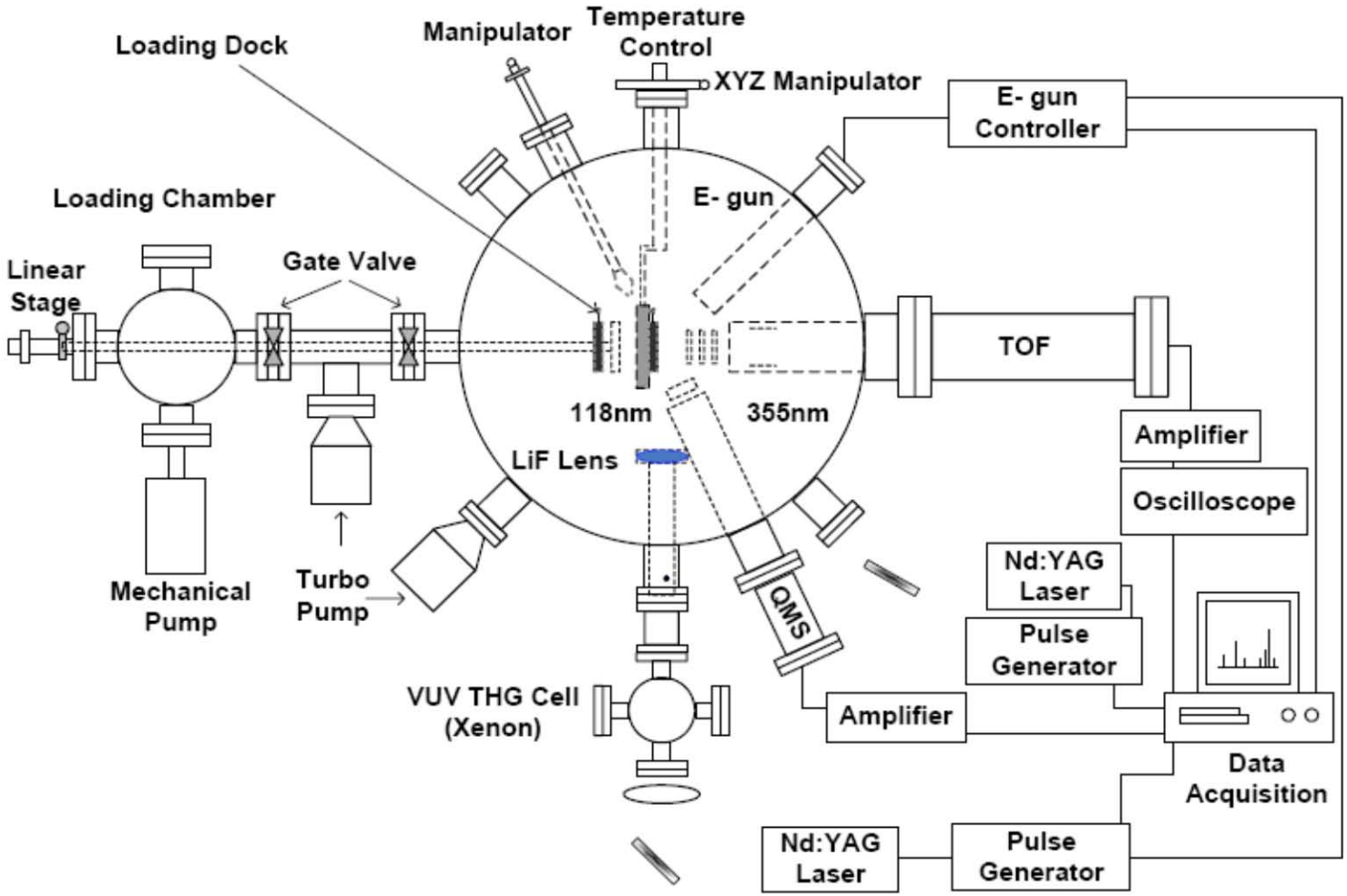
K^+, Ca^+

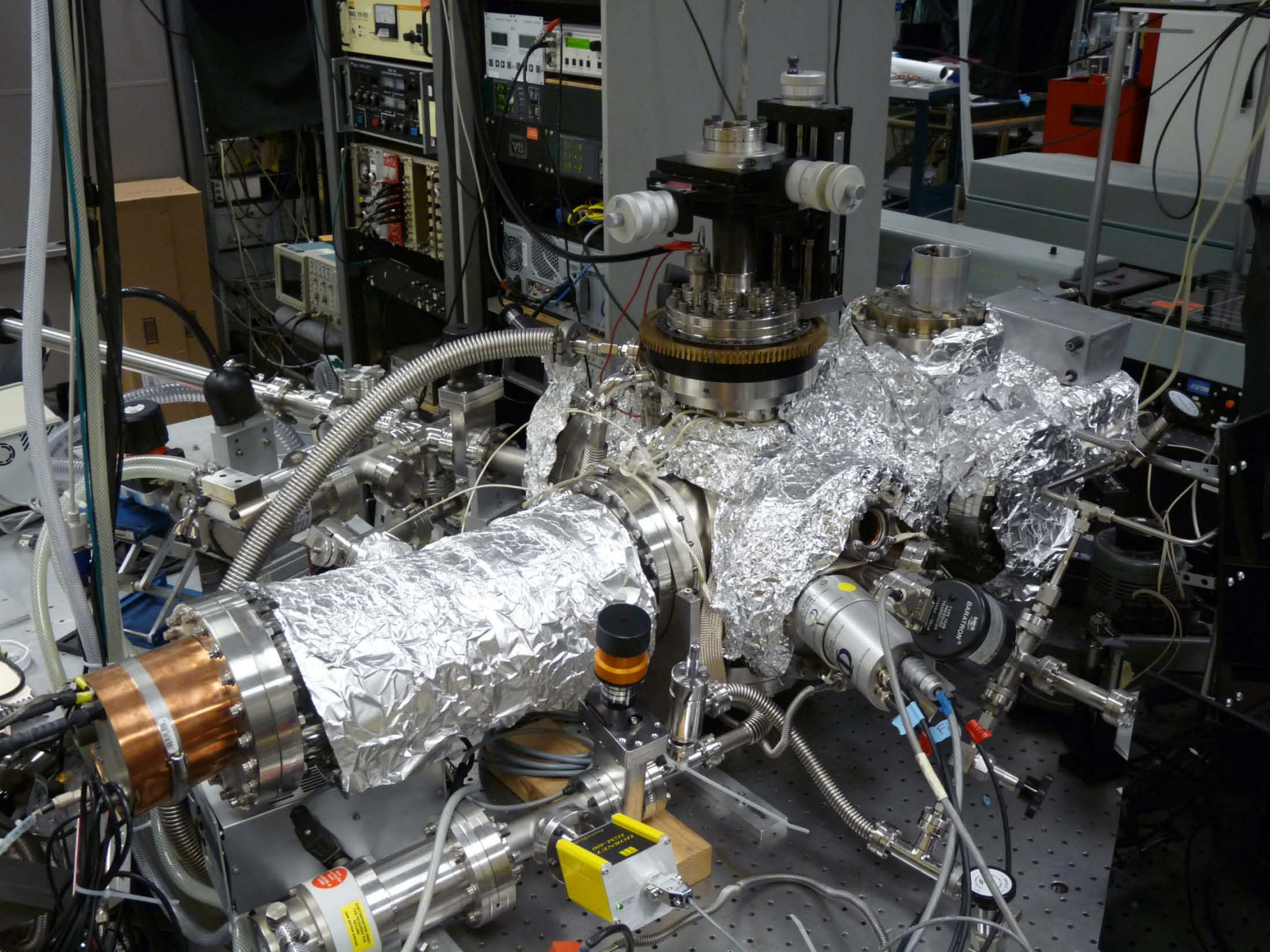
Si^+

O^+, OH^+, H_2O^+, H_3O^+

Ion data from FIPS sensor on MESSENGER – Zurbuchen, et. al. Science 321 90 (2008).

UltraHigh Vacuum (UHV, 10^{-10} Torr) Chamber Schematic for ESD Studies.




BARATRON
HORNET
IGM-400

ESD Techniques

- 100 -1us pulsed low-energy (5 eV – 1 keV) electron beams

  ~ 10^{10} electrons/pulse

- Electron-beam spot size of ~1 mm^2

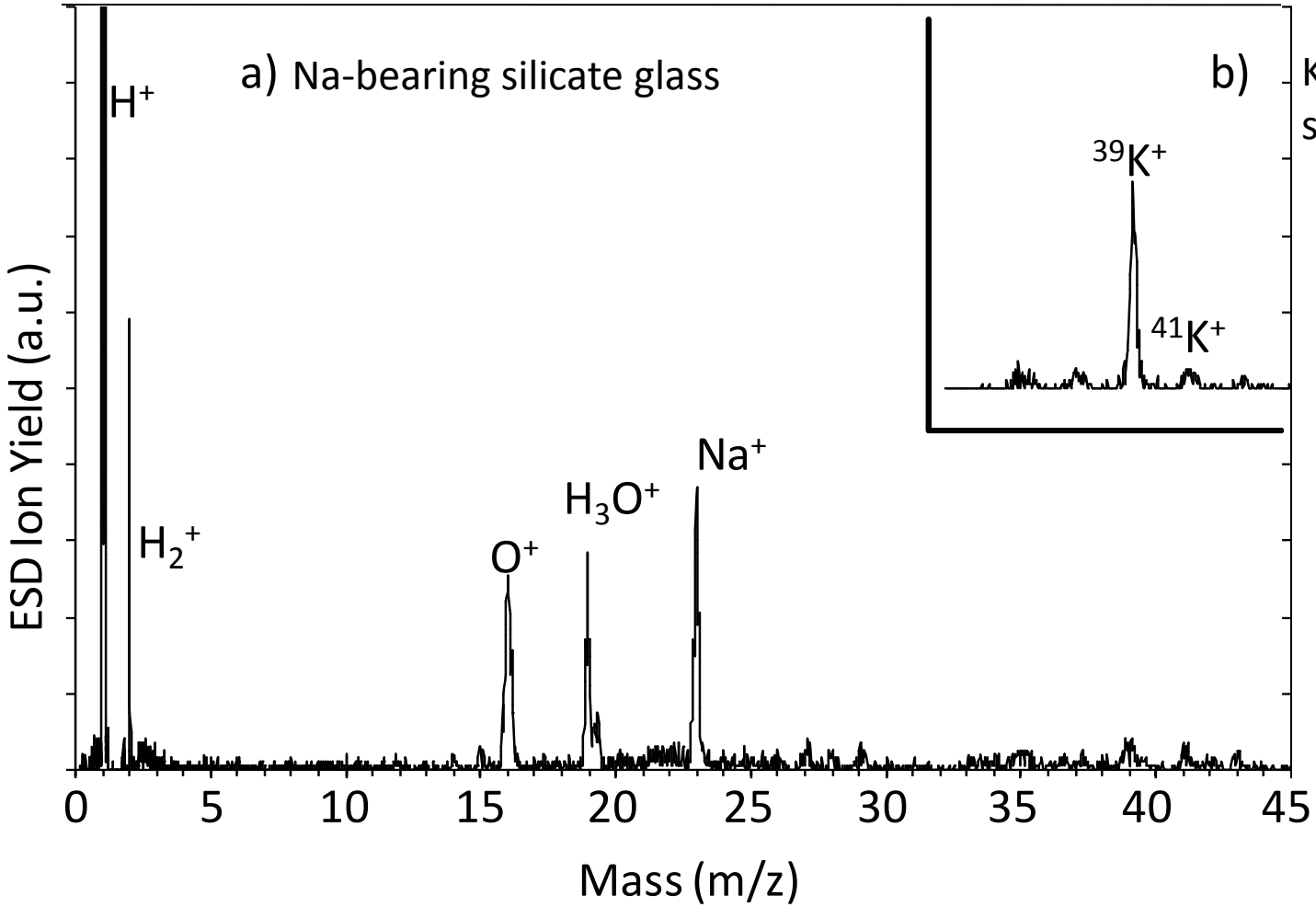
  Number density of surface sites is ~10^{15} cm^2

  Corresponding to 10^{-3} electrons per surface site.

- Departing ions and neutrals are detected as a function of electron energy and flux.

- Targets well-controlled under vacuum (10^{-10} Torr) and at variable temperatures (Controlled very accurately from 100-1000 K).

200 eV ESD ToF Spectra of Na and K containing silicates



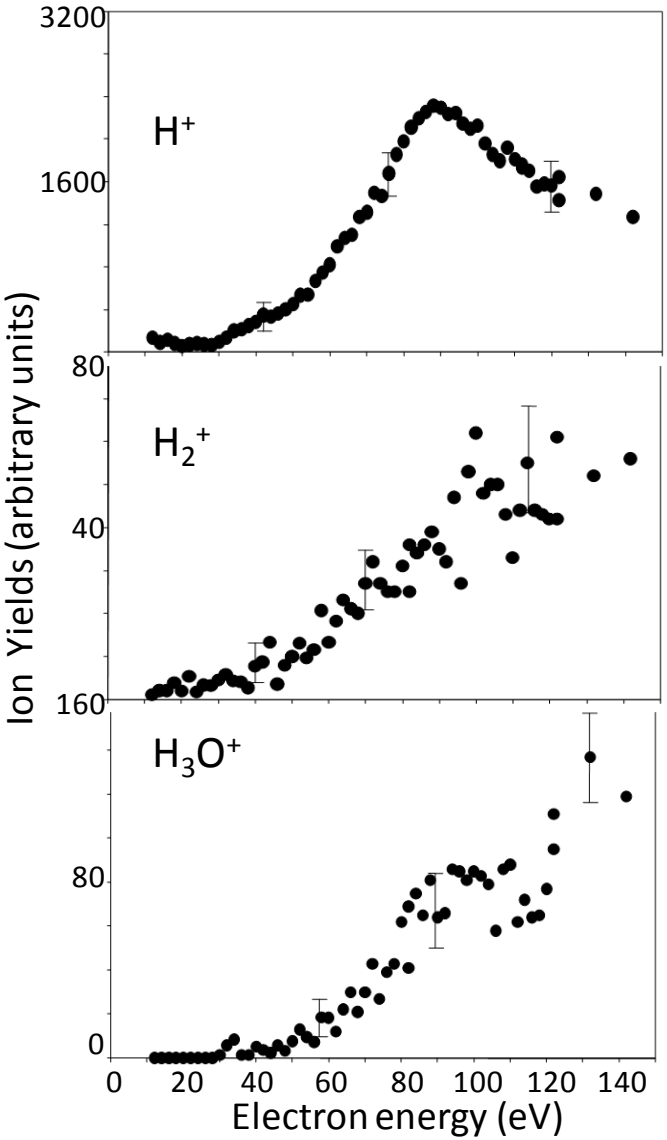
McLain et al., *JGR (Planets)* 2010, submitted

ESD Thresholds for Water Group Ions

- Threshold Energies H^+
  25 ± 2 eV

- Secondary Thresholds
  H_2^+ @ 40 ± 2 eV

- Additional Primary Threshold
  H_3O^+ 40 ± 2 eV



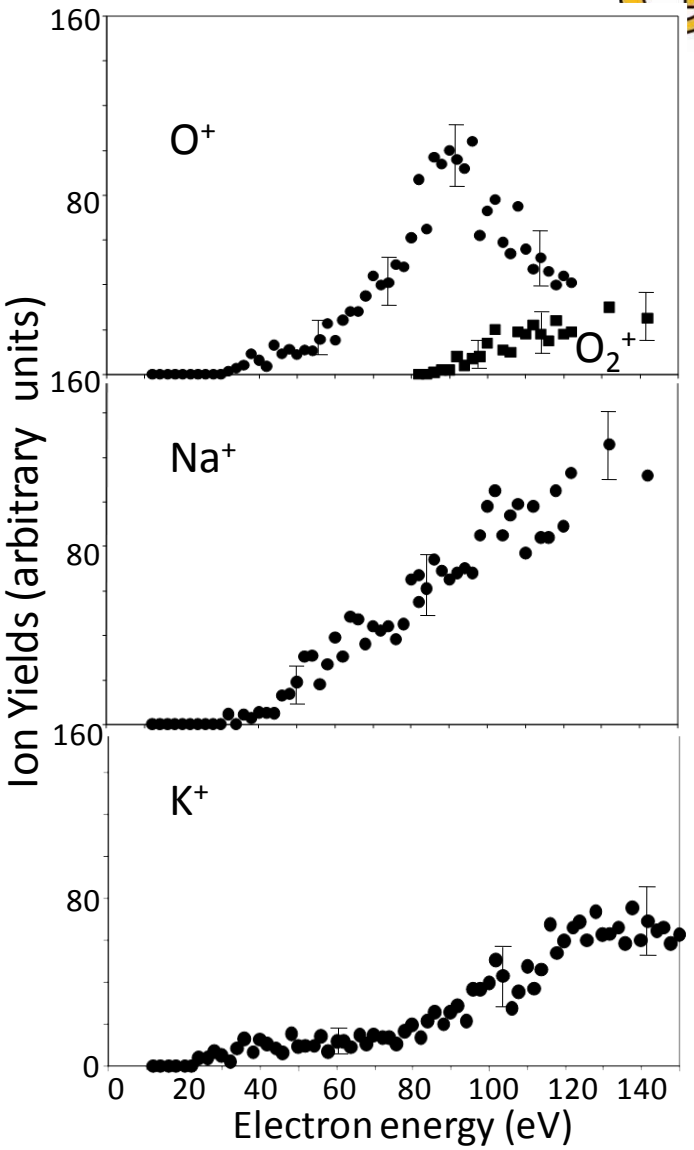
McLain et al., *JGR (Planets)* 2010, submitted

ESD Thresholds for Ionic Species

- Threshold Energies O^+, Na^+, K^+
  25 ± 2 eV

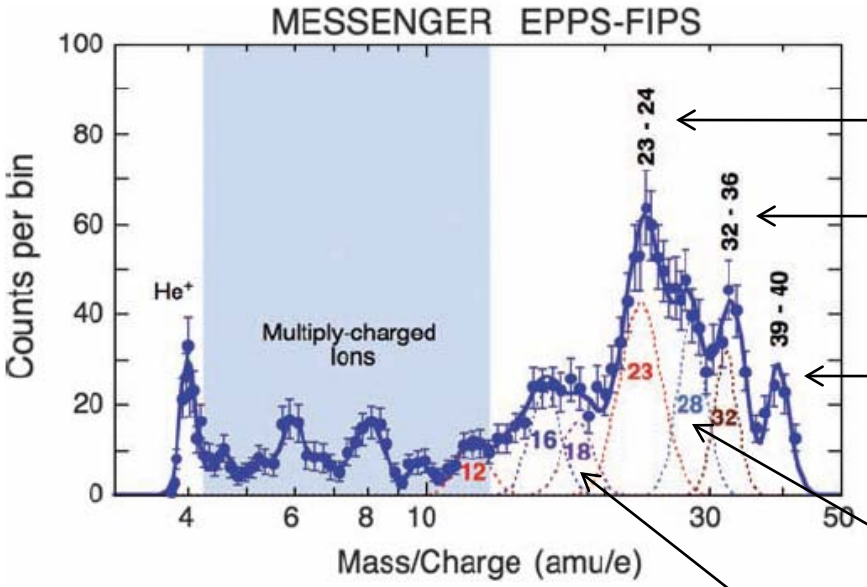
- Secondary Thresholds
  O_2^+ @ 90 ± 2 eV

- Additional Primary Threshold
  Si^+ (not shown)
  100 ± 2 eV



McLain et al., *JGR (Planets)* 2010, submitted

MESSENGER EPPS-FIPS Data



Na^+, Mg^+

S^+, O_2^+, H_2S^+

K^+, Ca^+

Si^+

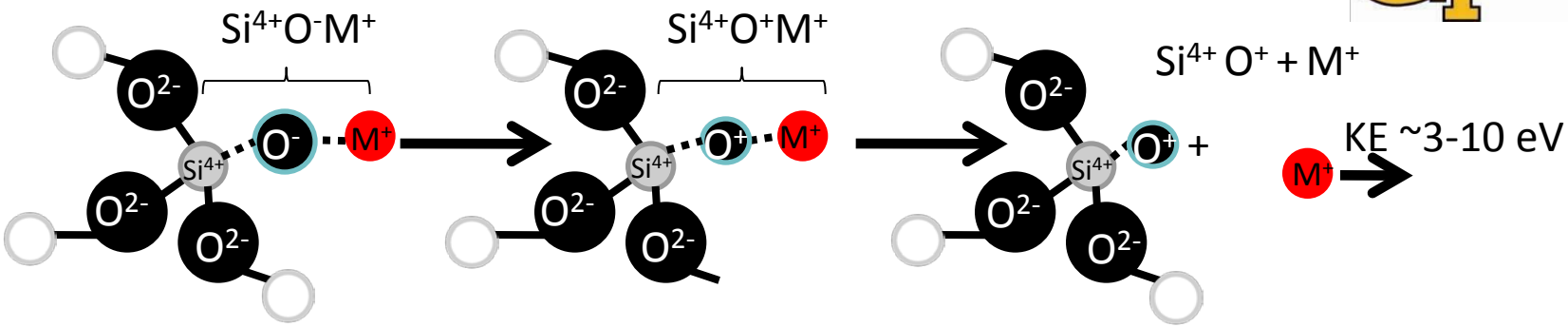
O^+, OH^+, H_2O^+, H_3O^+

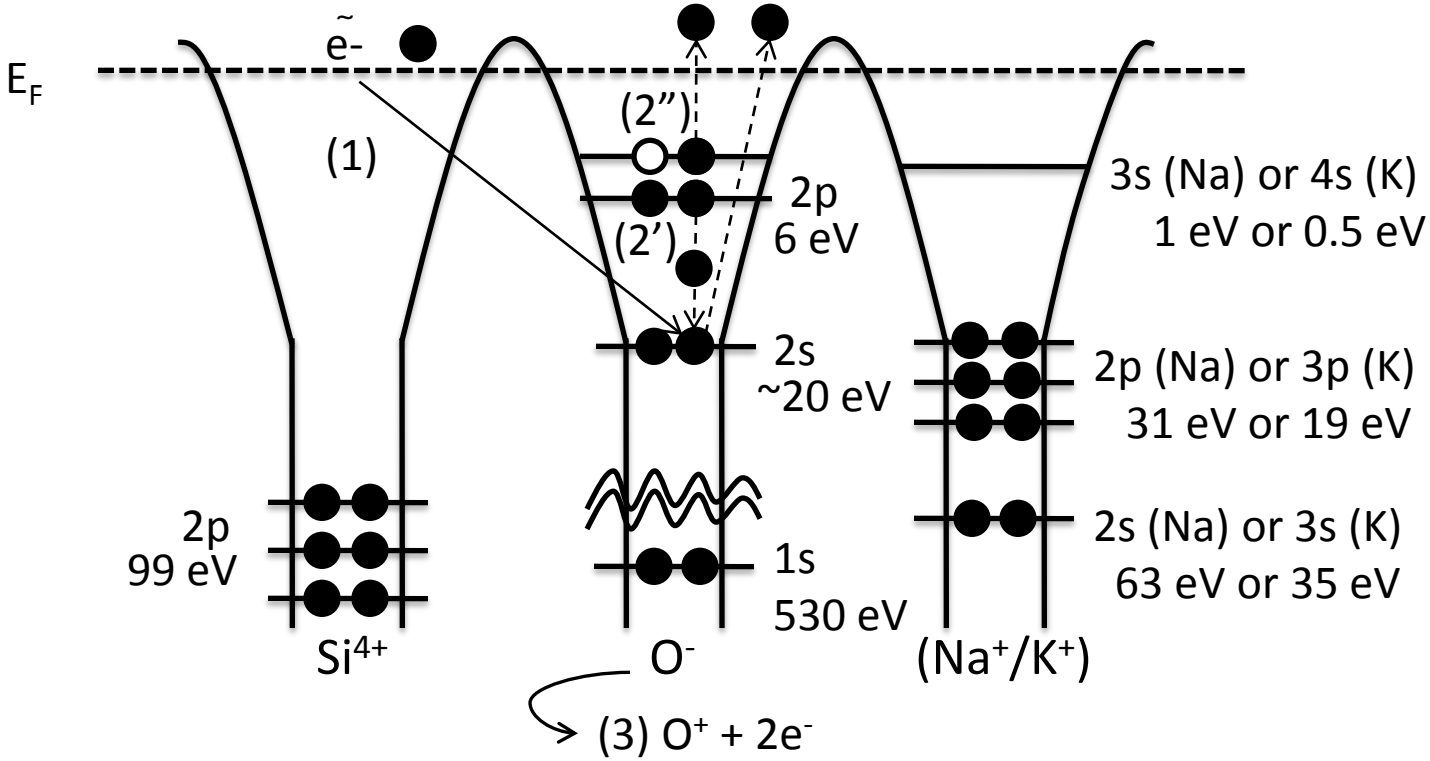
Ion data from FIPS sensor on MESSENGER – Zurbuchen, et. al. Science 321 90 (2008).

- **Many ions observed are the same as those assigned in the FIPS data.**
- **Si^+ and O_2^+ only observed from heavily damaged surface.**
- **Mg+ and Ca+ not seen.**
- **Neutrals also not examined but very important.**

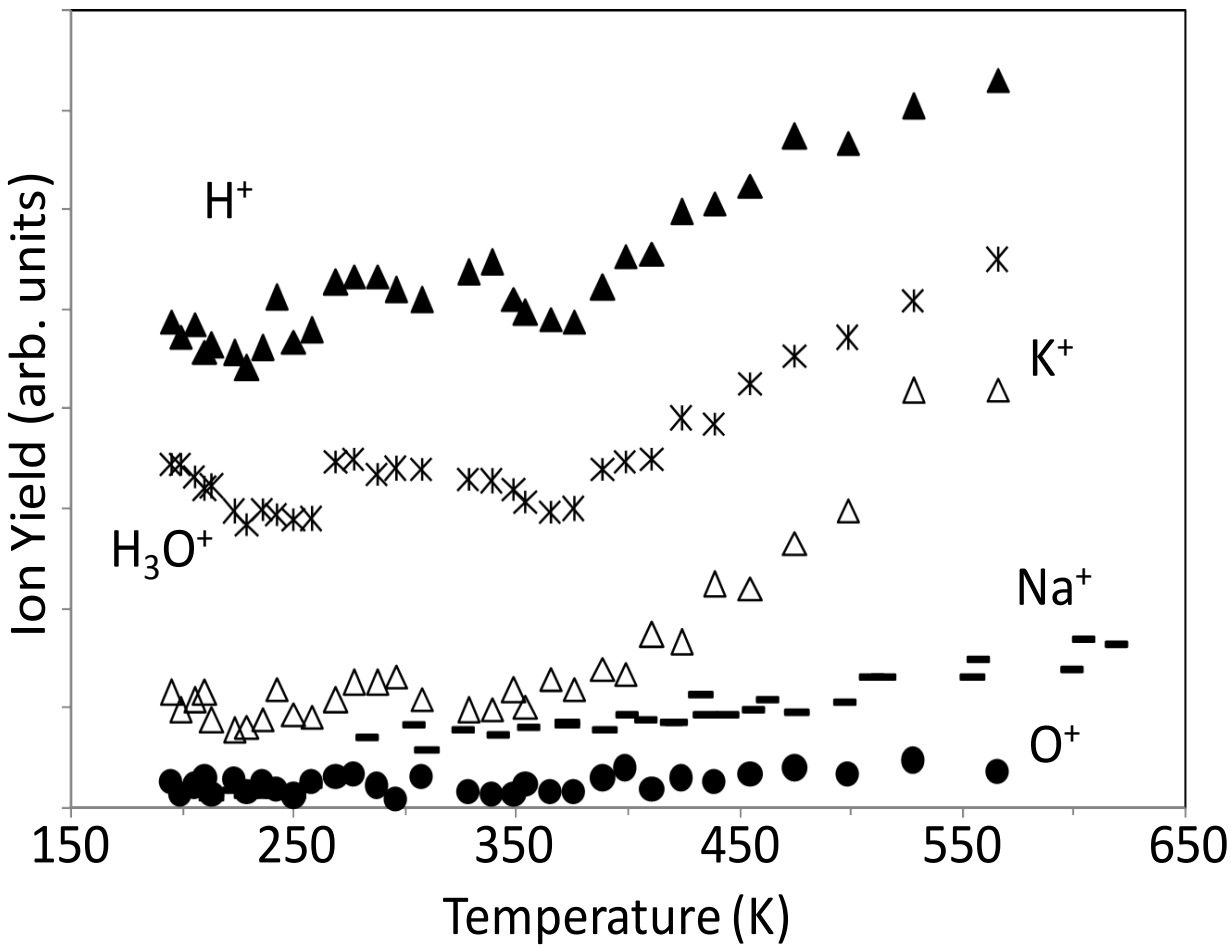
Knotek-Feibelman mechanism for ESD of Ions

Intra-atomic Decay





ESD Reversible Temperature Dependence for Ionic Species – Atypical result.



Relative temp dependence greatest for K^+, H^+ and H_3O^+. Likely associated with diffusion of holes or interstitials.

Yields are high at Mercury surface temperatures

McLain et al., *JGR (Planets)* 2010, submitted

Mercury Regolith Desorption Processes

•Thermal desorption
Neutrals - rate depends on coverage, temperature and binding sites.

•Photon Stimulated Desorption (PSD)
Neutral cross-sections (σ) = 10^{-21} cm^2 for Na

•Ion sputtering mainly H^+, "cosmic rays", **multiply charged ions**
Releases ions and neutrals

•Micro-meteoritic impacts
Releases mostly neutrals

•**Electron-stimulated desorption**
Releases **ions** and neutrals

For ions from PSD

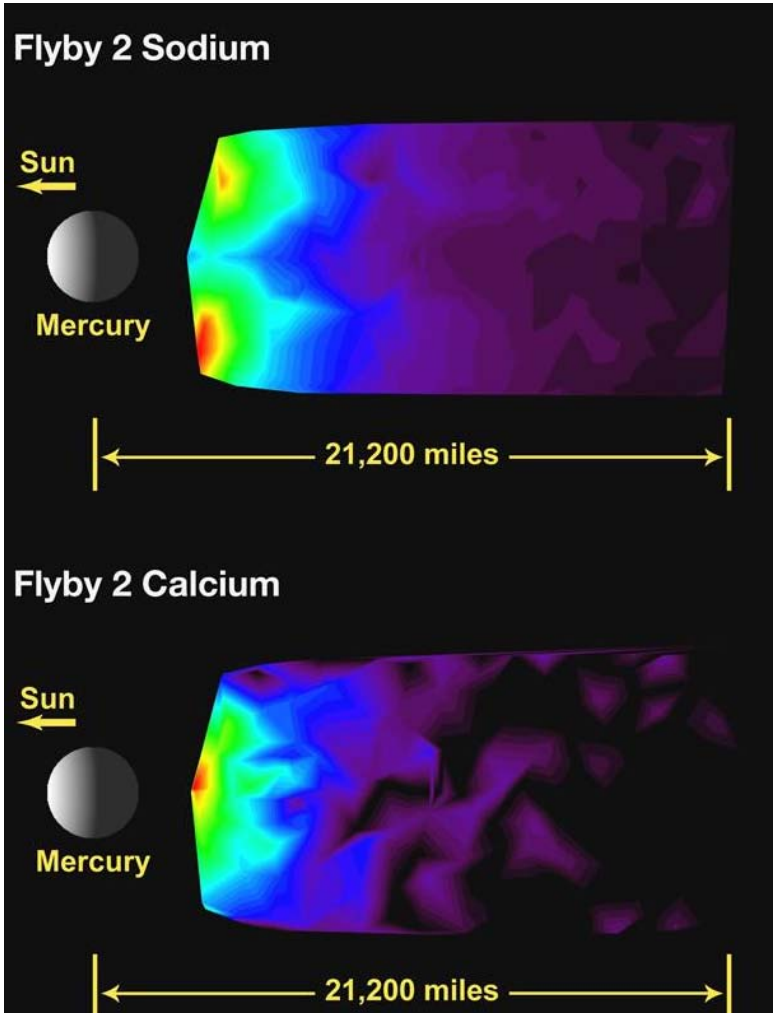
$$\sigma_{(eff)} = \sigma(1) * \sigma(2) * \sigma(3)$$

$\sigma(1)$ is desorption = 10^{-20}
$\sigma(2)$ is photodissociation = 10^{-15}
$\sigma(3)$ is ionization = 10^{-15}
$\sigma_{(eff)}$ is > 10^{-50} cm^{-6}

•Electron Stimulated Desorption (ESD)
•Direct Desorption of Ions from ESD cross-sections (s) = 10^{-19} cm^2

Killen et al., *Icarus*, 2004
Mura et al., *PSS,* 2007

Recent results from the MESSENGER Mission flyby: McClintock - Science 321, 92 (2008)

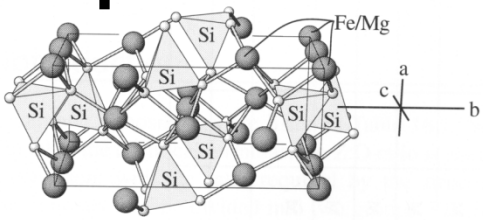


Recent MESSENGER results for exospheric sodium and calcium show that Na is concentrated near the polar regions while Ca is localized equatorially. These spatial differences in source terms strongly suggests different mechanisms for desorption, assuming uniform distribution of source minerals on the surface. Image credit: NASA, Johns Hopkins Applied Physics Lab, Carnegie Institution.

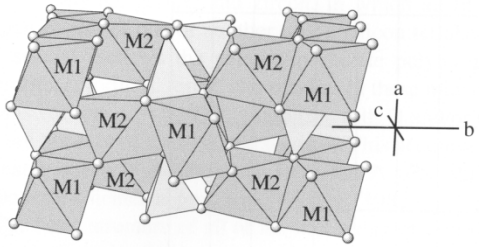
Ca and Mg seen….where are they from???

Probably from surface minerals.

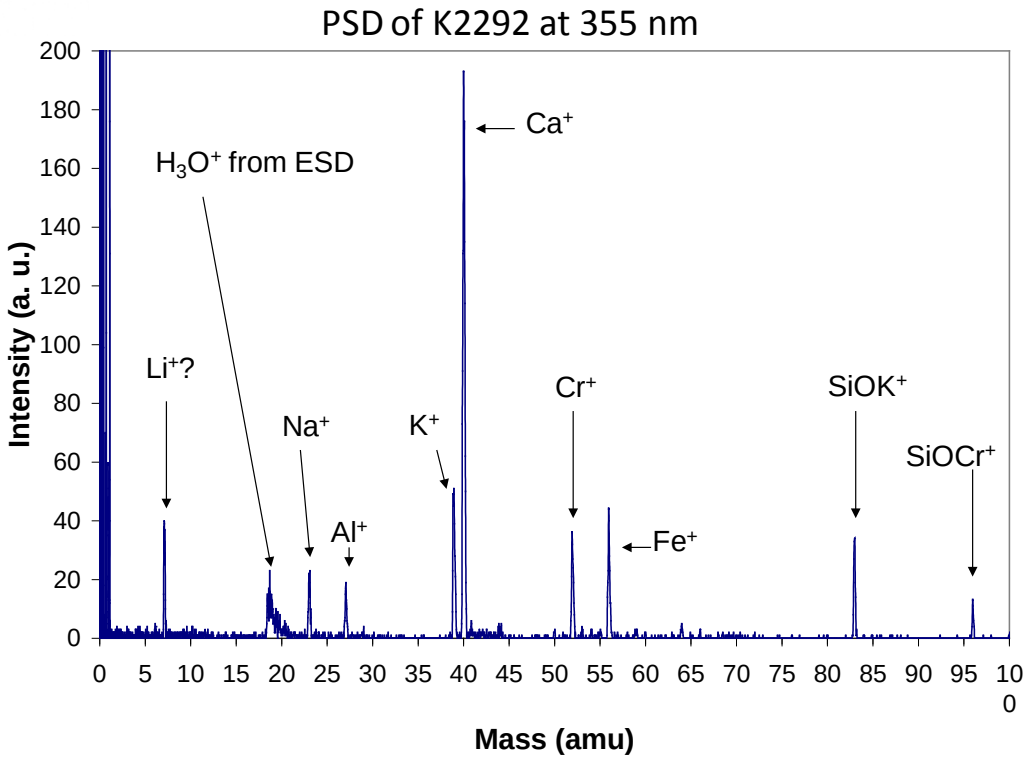
Laser ablation (355 nm) simulation of dust grain impact. We can see Ca^+ , Al^+ and Fe^+, etc.



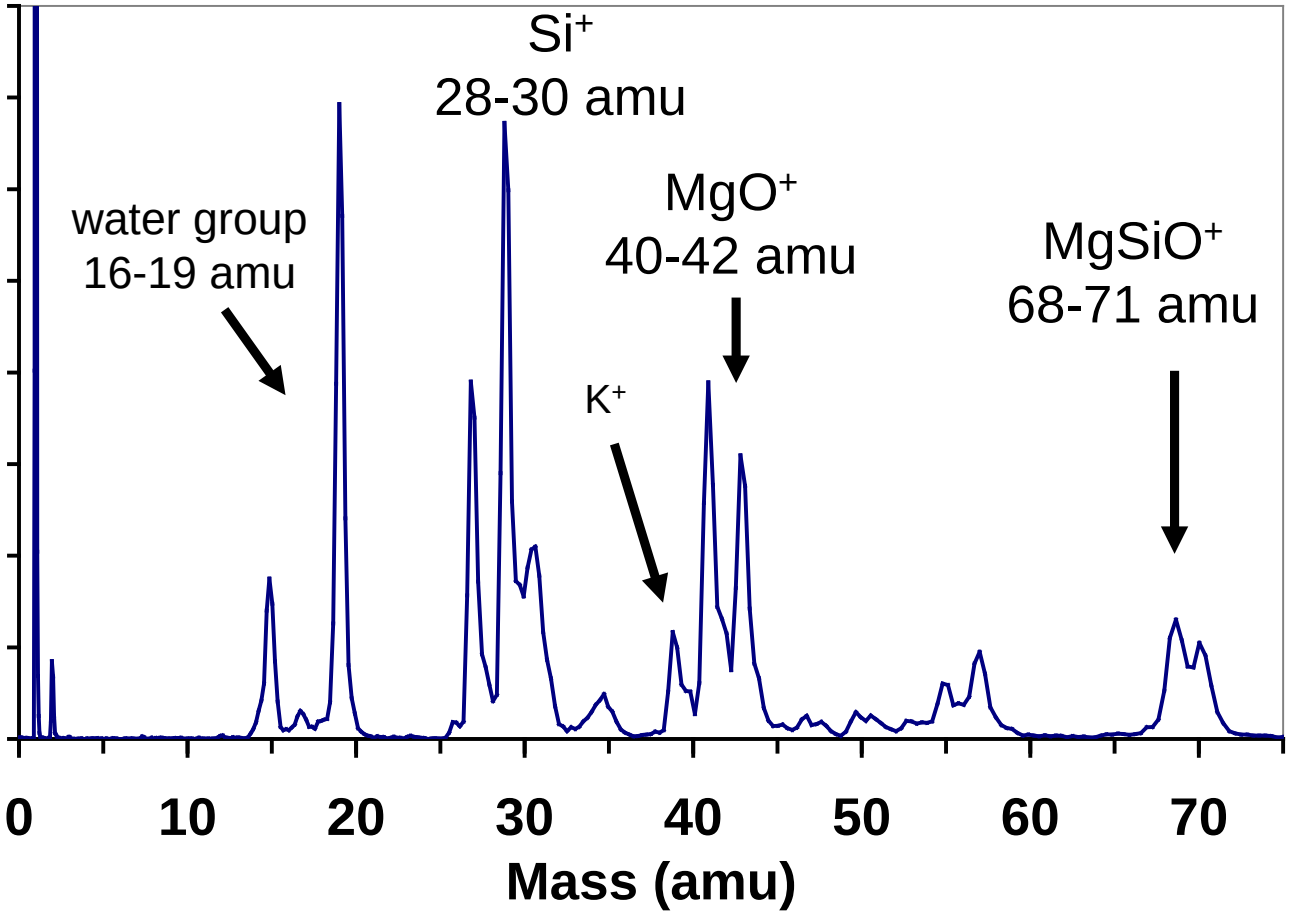
Surface atomic structure of Fe-Ca/Mg silicate such as anorthositic glass.



We do NOT observe Mg^+ or Ca^+ from ESD. However, preliminary results from laser-beam irradiated minerals and simulants due release Si^+, Ca+, etc. Laser field is strong so multiple photon processes are occurring.



Laser ablation of dust grain simulants. We can see MgO^+, Si^+, etc. (Preliminary)



Can the material left by grain impact be the source of some of these ions?
This would involve dust grain impact followed by ESD or sputtering.

Conclusions:

- ESD should be considered as a possible source term for direct ejection of ions into the exosphere.
- The inelastic scattering of secondary electrons is very important . (They float like butterflies but sting like bees.)

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Hannah Barks
Michele Dawley
Michael Poston
Alice Johnson
Josh Symonds
Kristin Shepperd

Issues addressed (see Karl Hibbitts talk):

•What is the binding energy of water on regoliths?

•Range is from 0.5 – 1.2 eV

•A what temperature does chemisorbed water exist/persist?

Water is likely made in the warm regions but transported to the poles and permanently shadowed regions

•What is the source of molecular water ?

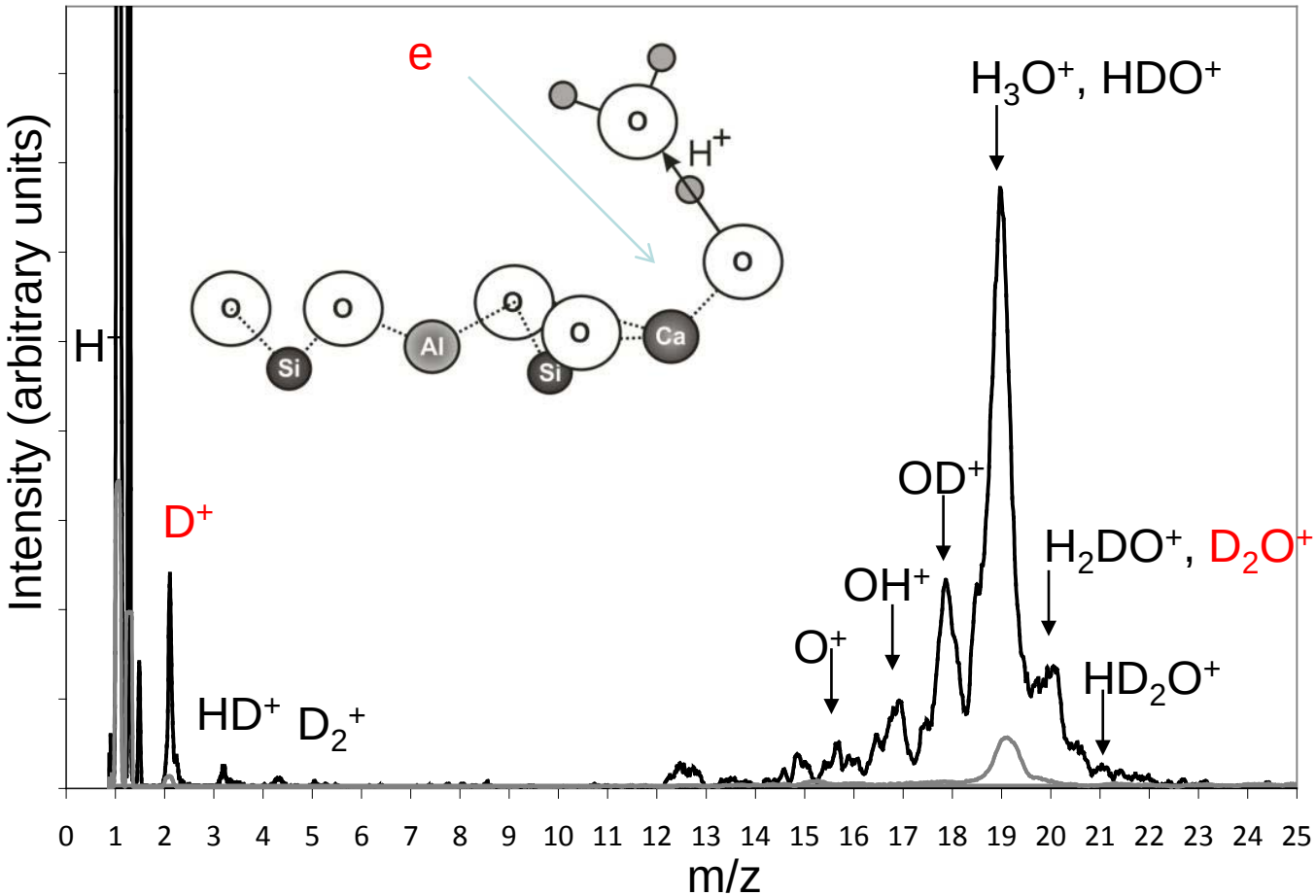
Does the solar wind produce it?

The solar wind makes hydroxyl groups.

Recombinative desorption is probably required

•What governs the spatial distribution?

Proton induced formation of water? 5 keV proton (D^+ and D_2^+ bombardment) of very clean JSC-1A FOLLOWED by 200 eV ESD.

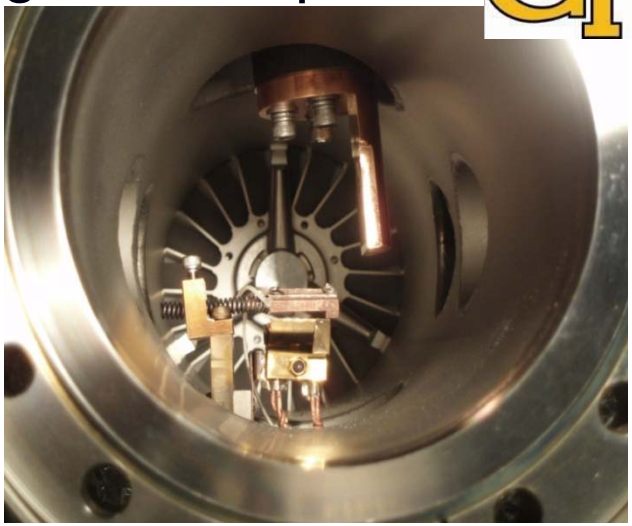


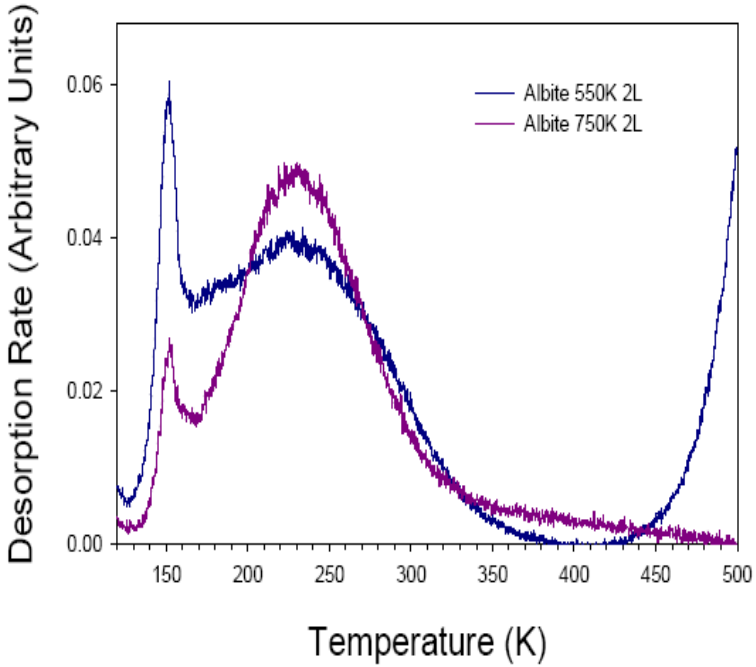
- Preliminary data indicates that proton induced hydroxylation occurs.
- Isotope ratio indicates D^+ induces isotope exchange.
- NO evidence for water production.

We built a “novel” system for Temperature Programmed Desorption (TPD) of mineral powders/regolith samples.

- The mass/no. density removed is measured as a function of temperature – temperature programmed desorption (TPD).

- TPD of powders can be obtained WITHOUTbackground subtraction





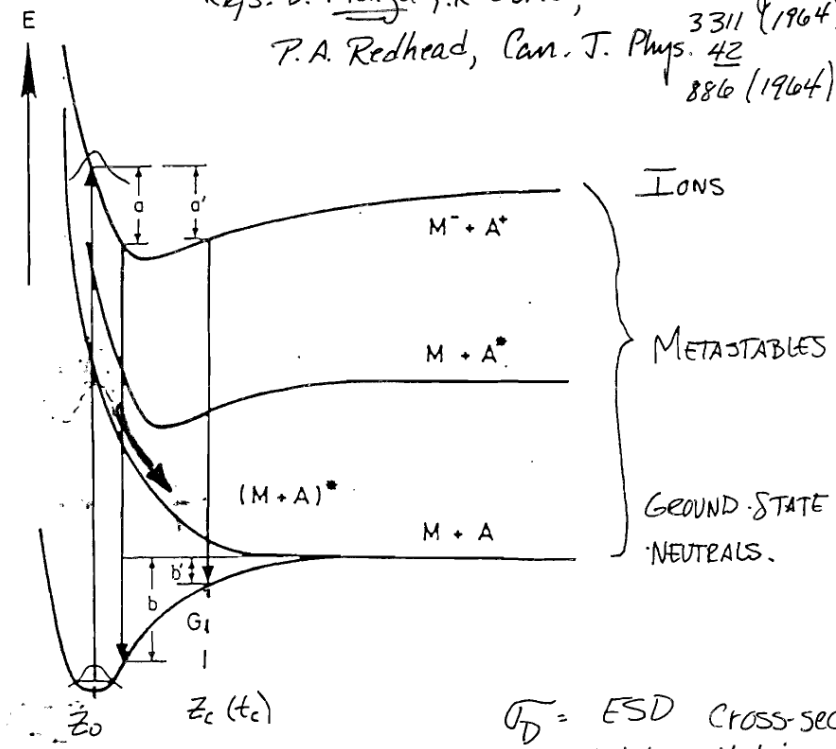
Sharp peak is ice. Broad peak is chemisorbed water.

Obvious difference between the two pretreatment temps at 550K and 750K.

The peak above 400K could be due to recombinative desorption?

GENERAL MGR MODEL

Refs. D. Menzel & R. Gomer, J. Chem. Phys. 41 3311 (1964)
P. A. Redhead, Can. J. Phys. 42 886 (1964)



$$\sigma_D = \sigma_e P_E |FC|^2$$

$$P_E = \exp\left(-\int_0^{t_c} dt/\tau\right)$$

σ_D = ESD cross-section
σ_e = total excitation cross sec.
P_E = 'escape' probability
FC = Franck-Condon factor

τ = Excited State Lifetime
t_c = critical recapture time

∴ MGR model describes bonding-to-antibonding transitions well.

Photon stimulated desorption of cations from yttria-stabilized cubic $ZrO_2(100)$

D.P. Taylor [1, 2], W.C. Simpson [2], K. Knutsen [2], M.A. Henderson, T.M. Orlando *

Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, M / S K8-88, Richland, WA 99352, USA

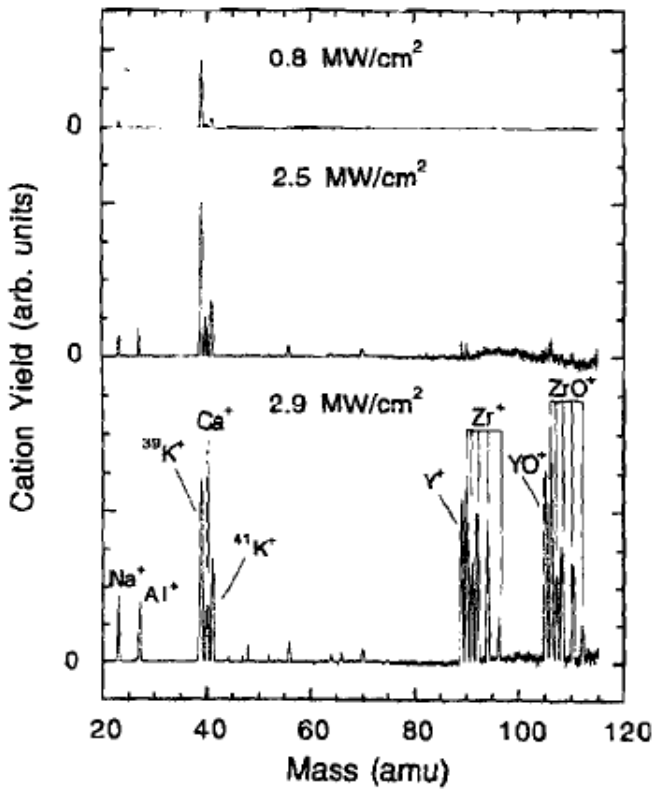


Fig. 2. Photon-stimulated desorption cation mass spectra obtained using 266-nm photons. The three frames represent three different laser fluences. Only desorption of K^+ and other impurity ions is observed in the low fluence regime (0.8 MW/cm^2). A small yield of yttrium and zirconium ions and their oxides are observable near 2.0 MW/cm^2. The yield of these species becomes appreciable above 2.5 MW/cm^2.

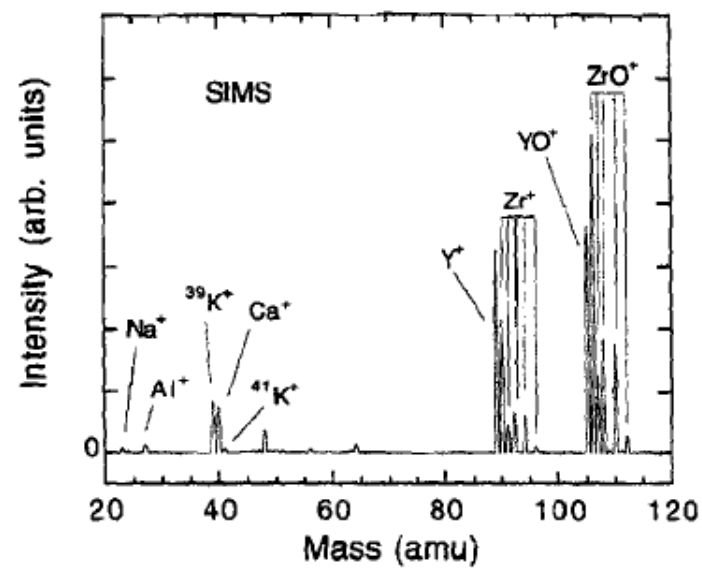
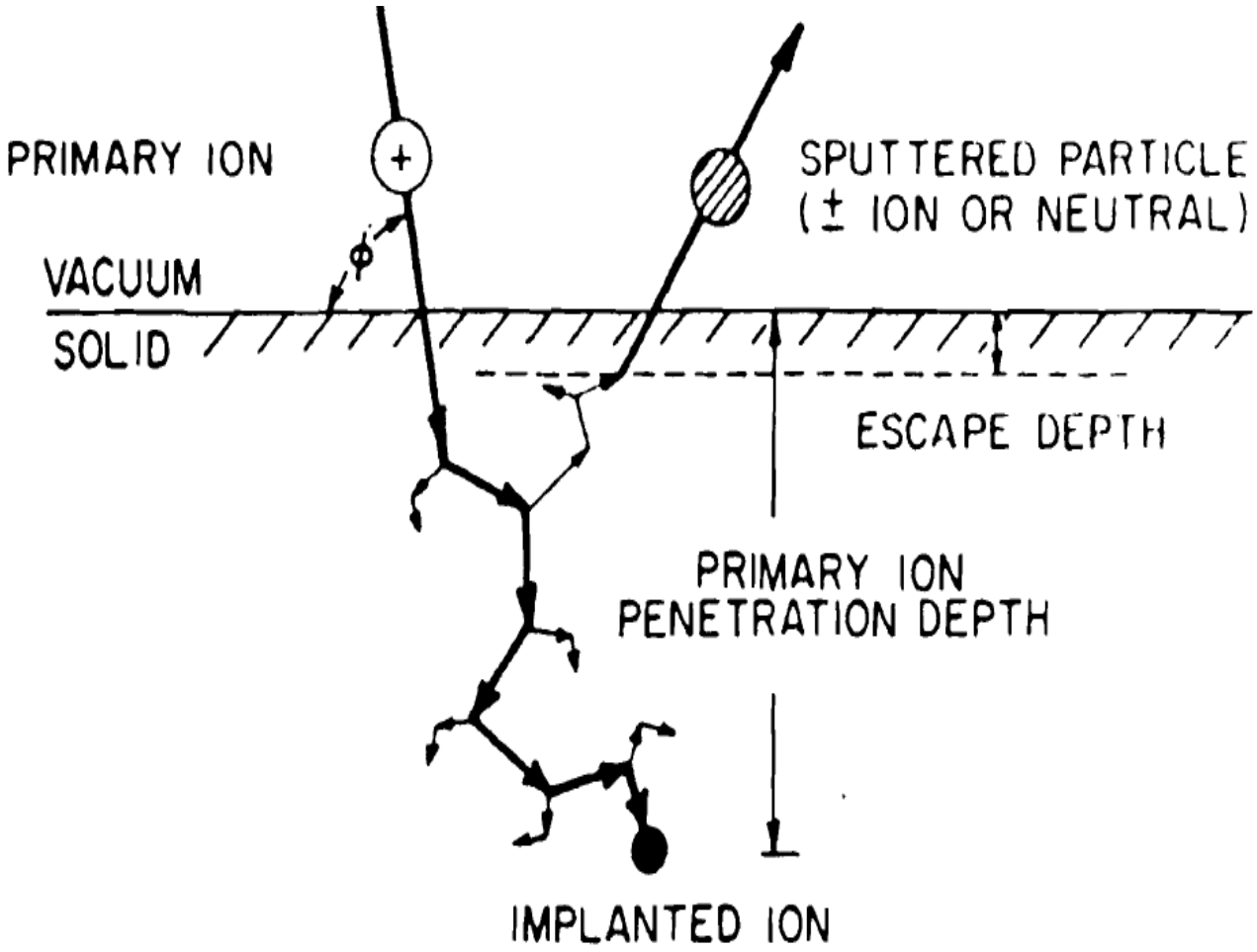
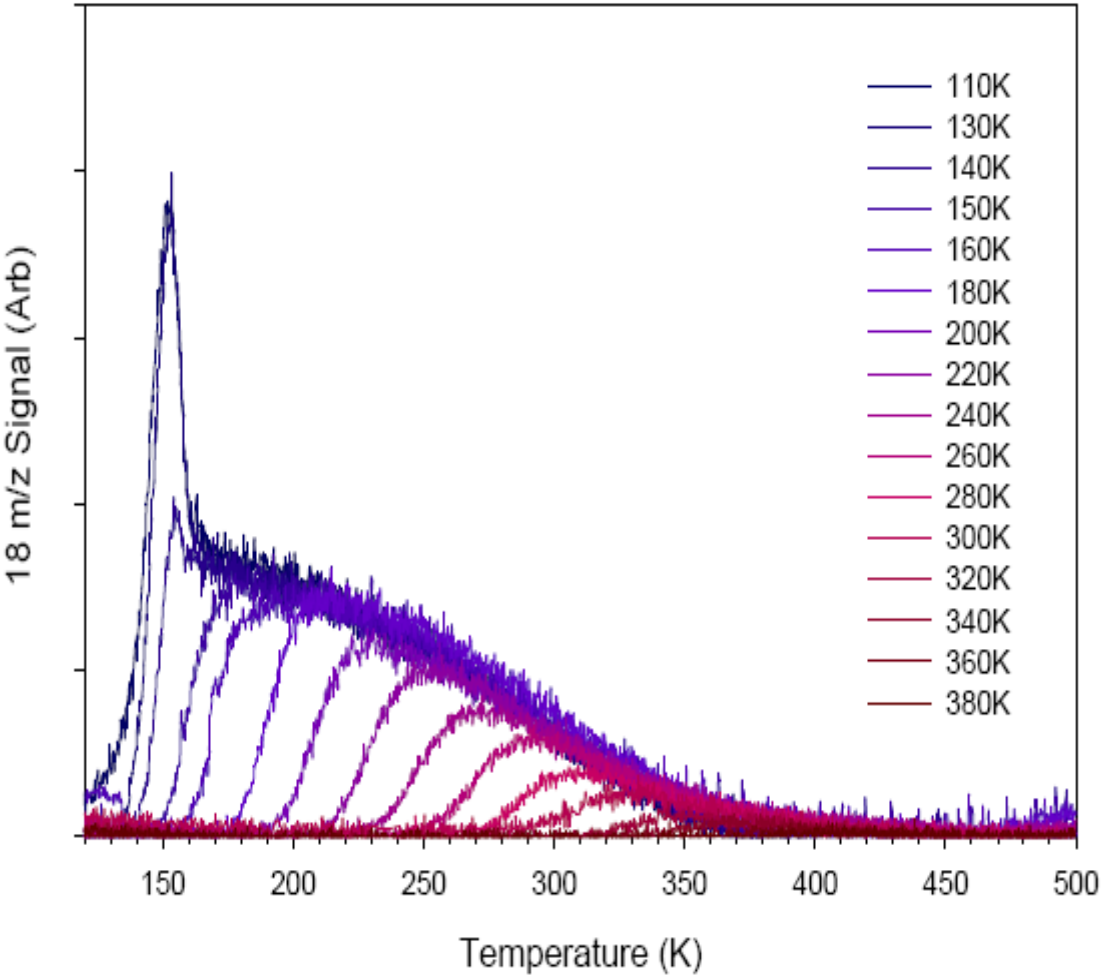


Fig. 3. Cation mass spectra obtained using secondary ion mass spectrometry. The incident Ar^+ ion energy was 3 keV and the incidence angle was 45° from the surface normal.

Proton and rare gas ion sputtering involves electronic excitations and re-neutralization



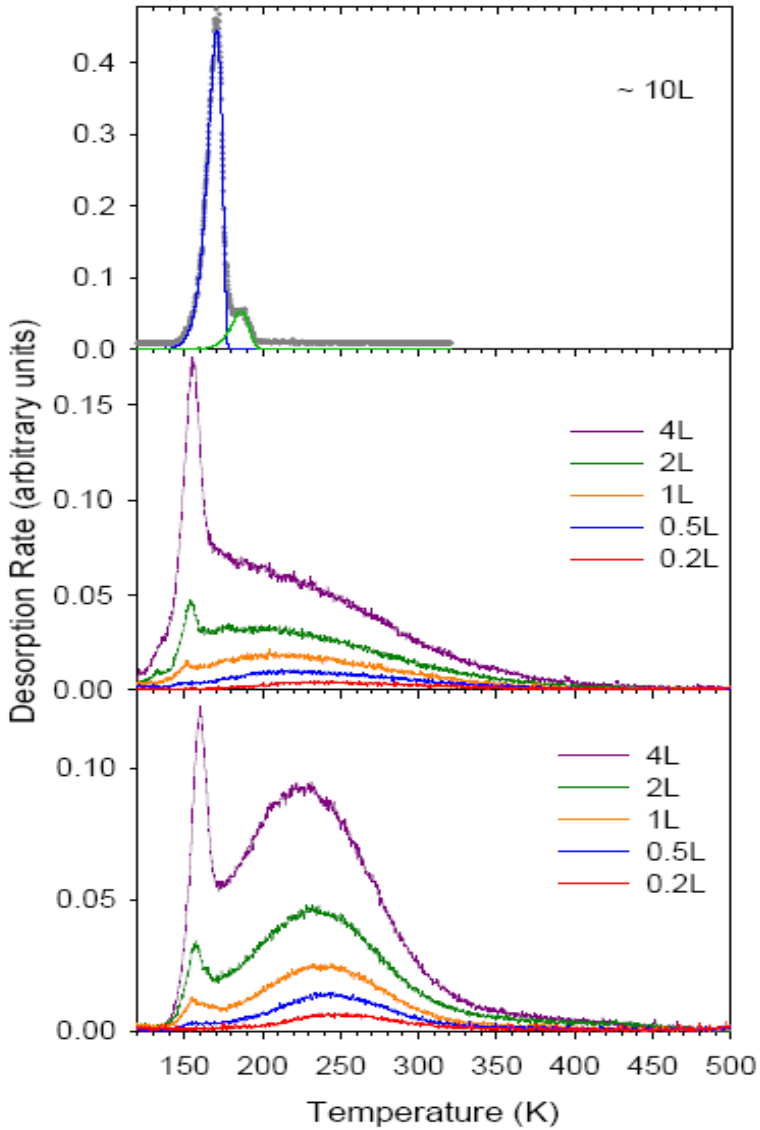
TPD from JSC-1A at various dosing temperatures



- TPD features shift to lower energy as a function of dosing temperature. This can be modeled assuming a distribution of chemisorption states (and not diffusion effects).
- Chemisorbed bond energies range from 0.5 eV to 1.0 eV.
- 0.6 eV is used in Greg's model

Comparison of water TPD from three samples,

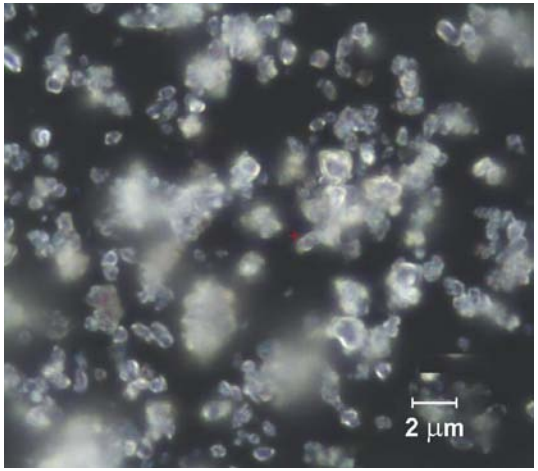
Hibbitts, Dyar, Grieves, Poston and Orlando, Submitted, Icarus.



K2294 glass, high iron, so more like the maria

JSC-1A, maria

surrogate



Albite, highlands surrogate

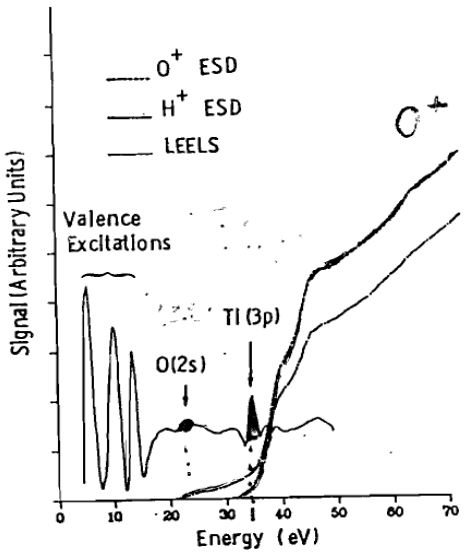
It is probably the surface defect/ grain boundary densities that matter with respect to binding water..

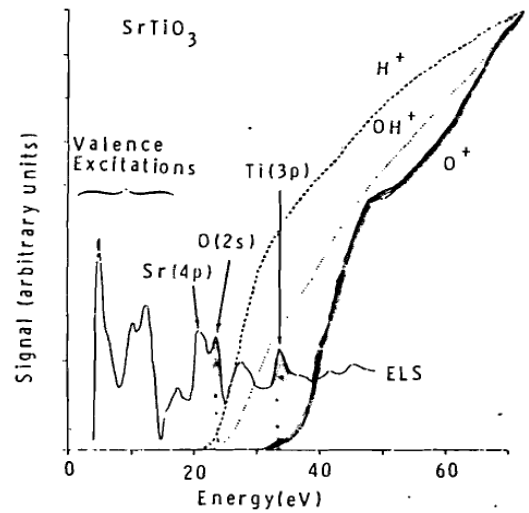
MGR Model works well for "covalent" systems and is a "1" electron model.

--Can NOT explain "ion" thresholds as observed from oxidized surfaces. (Maximal valency compounds such as TiO_2, V_2O_5, etc.) **Minerals, regolith material**

OBSERVATIONS:
1.)O^+ ions even though O is $O^{(1+x)-}$

2.)Dominant thresholds ~25-35 eV. (In the MGR model the desorption threshold is the FC transition energy ~10-15 eV).





P. Feibelman and M. Knotek, Surf. Sci. Phys. Rev. Lett. 40 (1978) 964, M. Knotek, Surf. Sci. 101, (1980) 334

CORE-HOLE AUGER DECAY MODEL
--Knotek-Feibelman (KF) Mechanism