Exospheric Potassium: Laboratory Measurements of Temperature-Dependent Depletion Cross-Sections for Potassium Adsorbed on Magnetite

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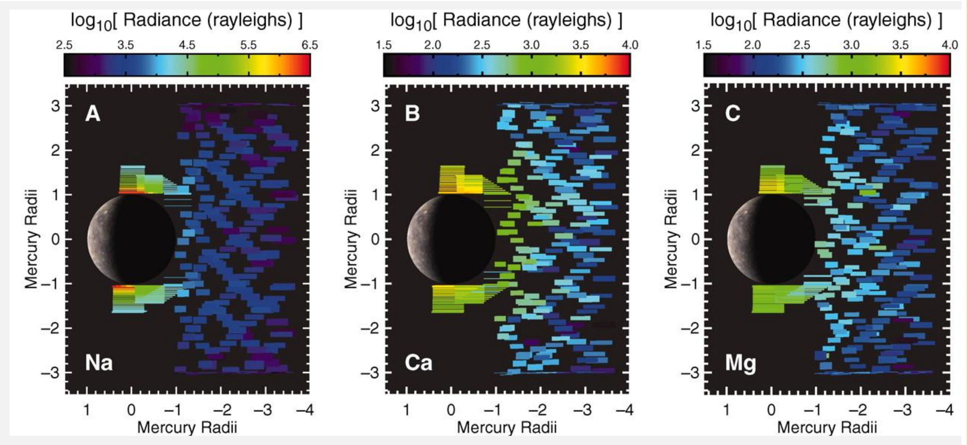
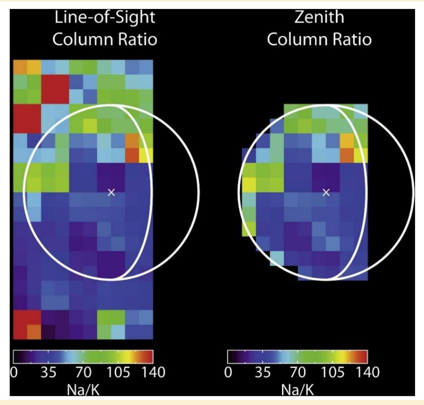
Abstract

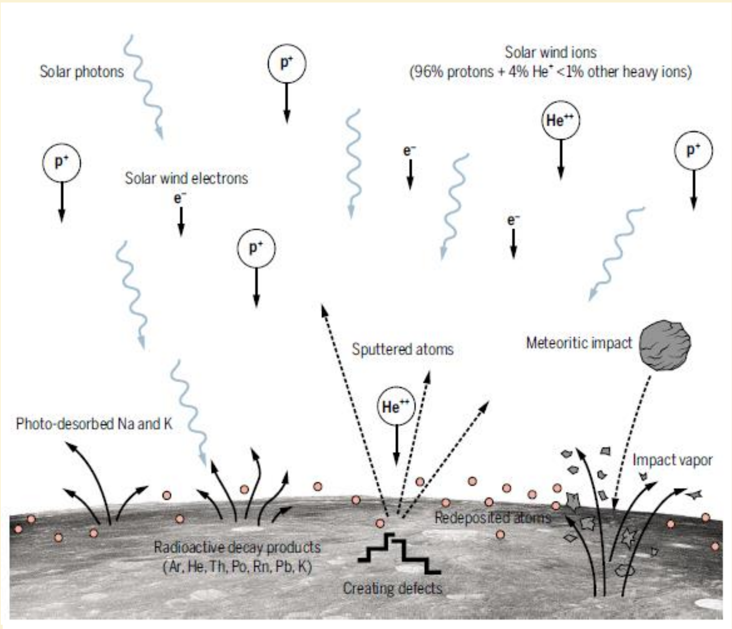
Mercury's exosphere shows a fascinating species-dependent variation in abundance and spatial distribution for Na, Mg, and Ca, identified by the Ultraviolet and Visible Spectrometer on the MErcury Surface, Space ENvironment, GEochemistry, and Ranging (MESSENGER) spacecraft, and for K from ground-based observations [1,2]. In particular, measurements of exospheric Na relative to K abundance vary hugely—from 22 to 400 depending on observation time and location with respect to Mercury's surface [2,3]—and differ significantly from the average lunar Na/K ratio of ~6 [4]. The source of this discrepancy is a mystery, but potentially due to differences in regolith composition, production processes and rates, transport mechanisms, and/or loss processes.



Exospheric neutral Na, Ca, and Mg observed in the polar, night-side, and tail regions of Mercury during MESSENGER's third flyby. [*Vervack Jr. et al. 2010*]



Na/K in Mercury's exosphere taken at the McMath-Pierce solar telescope. "The values of Na/K > 70 are dominated by noise in K." "The sub-Earth point is marked with an X. North is at the top, and the terminator is to the right." [*Killen et al. 2010*]

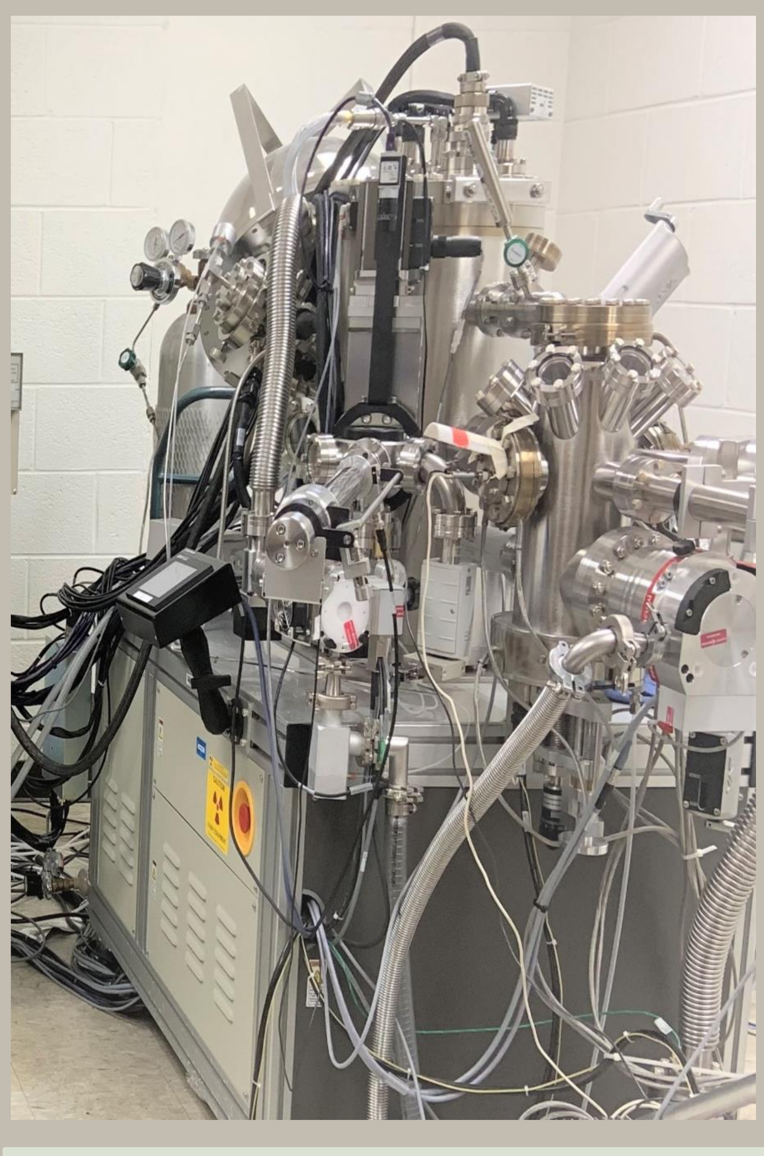


Dukes & Hurley [2016]

The production of exospheric constituents on airless bodies is derived from a number of factors, including: photon-stimulated desorption (PSD), thermal desorption, sputtering by solar wind ions, meteoritic impact, trapping of solar-wind constituents and radioactive decay. All of these factors are a function of planetary surface composition, and exosphere production is mitigated by recycling back to the regolith, magnetospheric/solar-wind removal of ionized species, or by Jeans' escape. The relative weights for each of these processes depends on local planetary conditions, and is generally species-dependent.

In this laboratory simulation, we investigate the effect of regolith temperature on two of these physical parameters: 1) the thermal desorption of adsorbed potassium (K), as well as 2) the sputtering yield for adsorbed-K on mineral surfaces by solar-wind ions. Variation in sputtering yield as a function of temperature may be an important factor for exospheric production of volatile elements [5,6], which has not been previously investigated systematically. Temperature variation across the Hermean surface is significant—from 100K on Mercury's darkside and within permanently shadowed regions to 700K within the nearside equatorial regions. Thus, measurement of the thermal-dependence of ejection parameters is of high importance for understanding Mercury's exosphere kinetics, as data from Messenger continues to be processed and with BepiColumbo data expected in the future.

Experimental Details



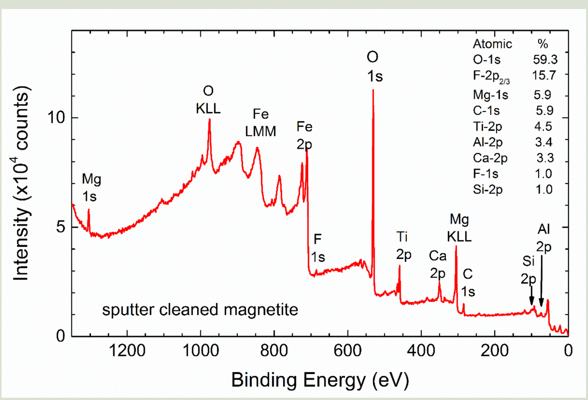
PHI Versaprobe III Scanning XPS Microprobe

1) ultra-high vacuum (~2 x 10^{-10} Torr)
2) In-situ preparation chamber (~ 3 x 10^{-9} Torr)
3) Hot-cold stage (110 K– 850 K)
4) XPS (spatial resolution < 10μm; sensitivity < 0.001; FWHM < 0.6 eV)
5) Ion gun for He irradiation and depth profiling (E = 0.05 – 5 keV)
6) Low-energy Ion and electron flood guns for charge compensation

X-ray photoelectron spectroscopy (XPS) provides quantitative compositional information within a surface layer of ~5 nm. XPS spectra presented were taken with a spot size of 200 μm and a pass energy of 140 eV.

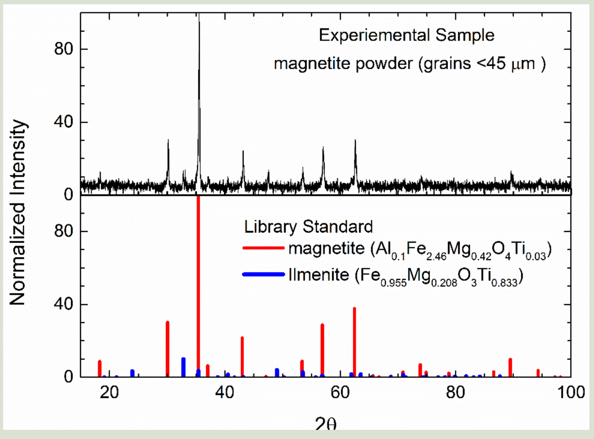
Ion irradiation: 4 keV He ions, which simulate the solar wind, were rastered uniformly over an area of 8 mm x 8 mm (much larger than the analysis area) at a flux of ~ 7 x 10^{12} He^+/cm^2 s. Samples were Zalar-rotated during irradiation, where the ion beam was 60° with respect to the surface normal.

Substrates: Sections of magnetite (Fe_3O_4) with ilmenite ($FeTiO_3$) inclusions, characterized by X-ray powder diffraction (XRD), were cut with a diamond saw, cleaned in an ultrasonic bath of methanol, purged with dry N_2 gas, and then admitted to the vacuum chamber. Prior to K-deposition samples were sputter cleaned with 4 keV He^+ to remove atmospheric contamination.



A representative XPS spectrum for sputter cleaned magnetite section shows O and Fe, and small amounts of Mg, Ti, Al, Ca, F, Si, and C.

Magnetite section mounted on platen

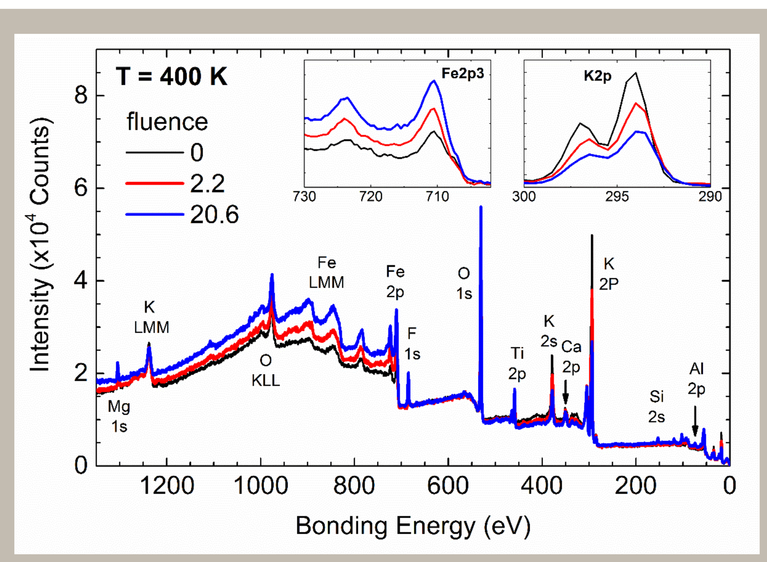


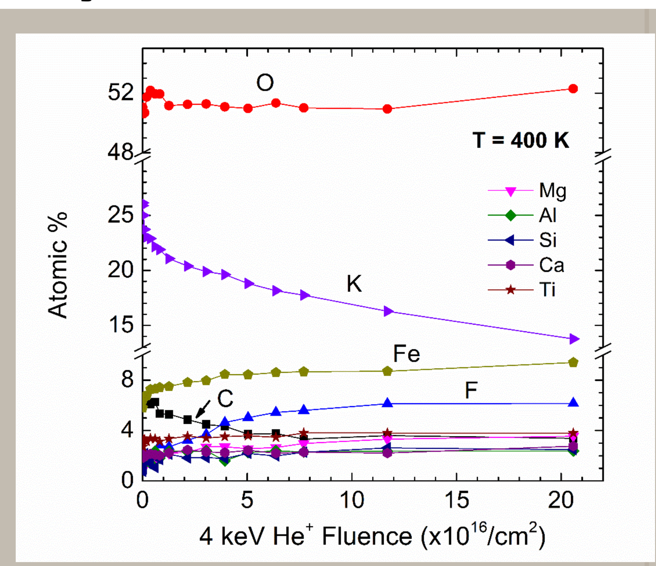
XRD pattern matches well with standard library spectrum for magnetite, with a small component of ilmenite .

Potassium (K) deposition: K was *in-situ* evaporated onto the sputter-cleaned magnetite using a alkali metal dispenser from SEAS Getters. Depositions were completed in 30 minutes with the dispenser temperature at ~750°C (6 A).

Sample temperatures: Substrates were at ~300 K during K deposition. The K-coated magnetite sections were then maintained at 110 K, 200 K, 300 K, and 400 K during He^+ irradiation (sputtering) and desorption.

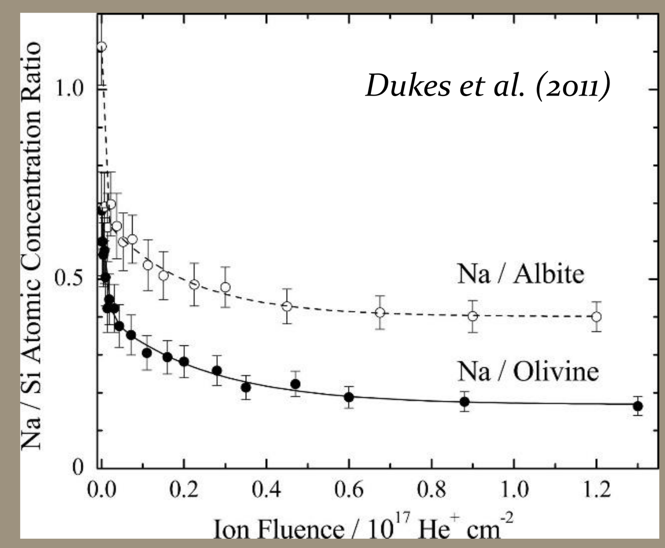
Removal of Adsorbed Potassium by 4 keV He+ Irradiation





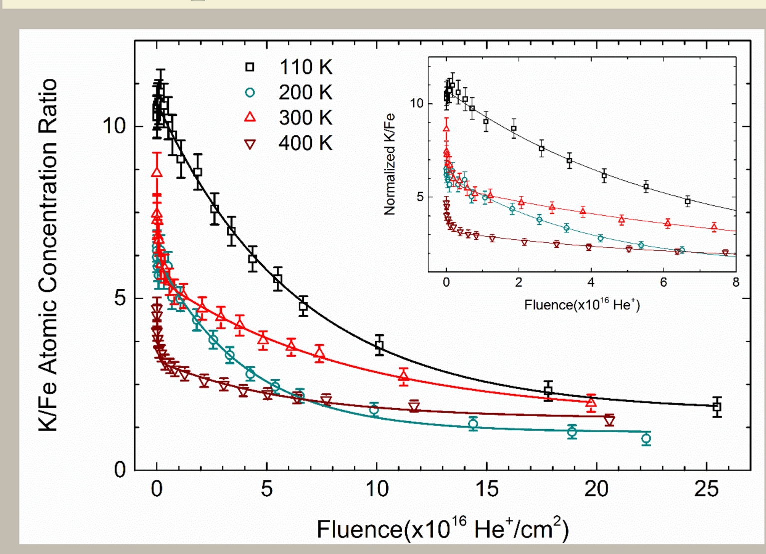
4 keV He^+ irradiation nominally results in changes to surface concentration by preferentially removing light atoms such as C and O, as well as K-atoms deposited on the mineral surface. We acquired XPS spectra vs. He-ion fluence and determined surface stoichiometry using the photoelectron peaks for K-2p, Fe-2p3, O-1s, C-1s, Al-2p, Si-2s, Ca-2p, and Mg-1s. To quantify the removal of K with respect to the underlying magnetite and to mitigate the effects of preferential sputtering, we measure and plot the K concentration relative to Fe (K/Fe).

Comparison with Measurements for Adsorbed Na



The decrease in sodium (Na) surface concentration for Na adsorbed on an ion-processed albite section and on olivine powder, measured with Na:Si ratios and as a function of 4 keV He^+ fluence at 300 K, are fit by a double exponential function, with decay constants of ~9 x 10^{-16} cm^2 /atom and ~4.5 x 10^{-17} cm^2/atom. These depletion cross sections are similar to those for K adsorbed on magnetite.

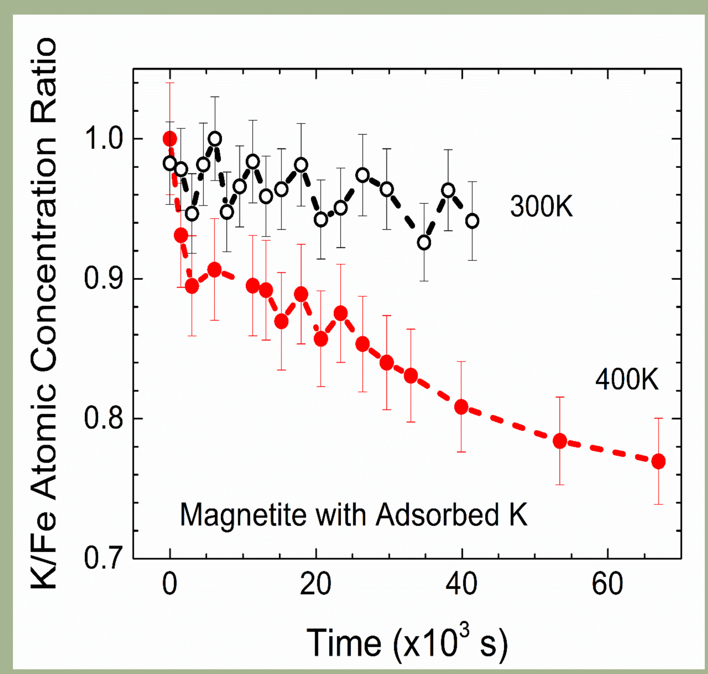
Temperature-Dependence of the Depletion Cross Sections



	400 K	300 K	200 K	110 K
σ_1 (10^{-16}cm²/atom)	(10±2)	(8 ± 2)	N/A	N/A
σ_2 (10^{-17} cm²/atom)	(1.5 ± 0.1)	(1.2 ± 0.1)	(2.5 ± 0.2)	(1.6 ± 0.1)

At 300 K and 400 K, the K/Fe as a function of He-ion fluence can be fit to a *double* exponential decay, while following a *single* exponential decay at 110 K and 200 K. The fitting depletion cross sections (decay constant, shown in the table) increases as the irradiation temperature increases.

At What Temperature can Adsorbed K be Desorbed?

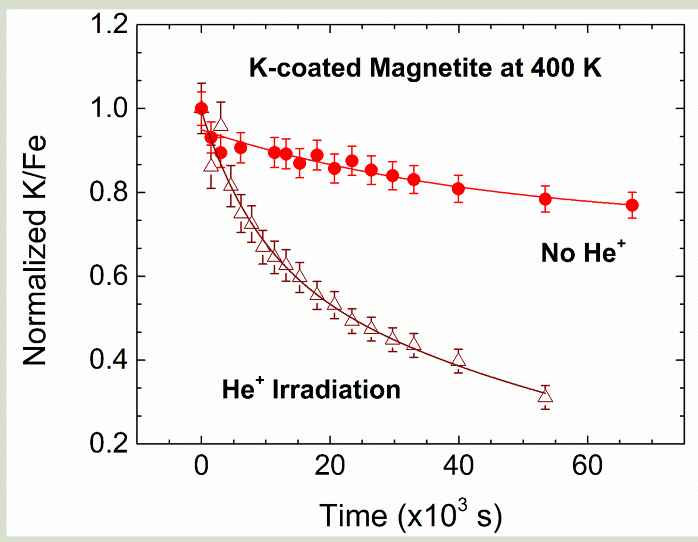


K/Fe thermal desorption was also measured as function of time for K-coated magnetite, sitting at different temperatures in vacuum and without ion irradiation.

At 110 K and 200 K, changes in surface composition or to the K/Fe ratio are within experimental error, suggesting no significant condensation of vacuum residual gases (~10^{-10} Torr) or loss/diffusion of the adsorbed K. The decrease in K/Fe is still minimal at 300 K but becomes more significant at 400 K, implying thermal desorption of the surface K at temperatures above 300 K.

However, the thermal-induced preferentially removal of surface K is not sufficient to explain the faster initial decrease in K/Fe observed during 4 keV He^+ irradiation at temperatures of 300 and 400 K.

	no He^+	He^+
σ_1 (x 10^{-4} s^{-1})	N/A	(1.2 ± 0.5)
σ_2 (x 10^{-5} s^{-1})	(2 ± 1)	(1.3 ± 0.5)

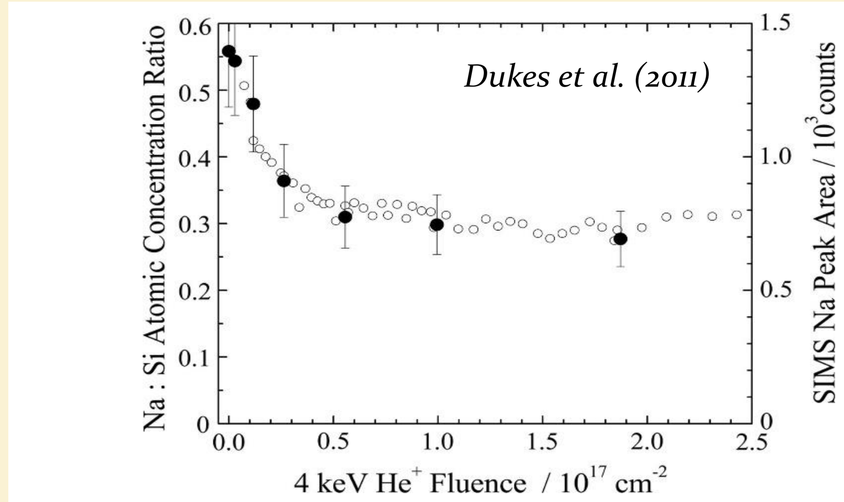


Conclusions

- The depletion cross sections by 4 keV He^+ for potassium adsorbed on magnetite show a dependency on irradiation temperatures at 110 K – 400 K.
- The depletion cross sections by 4 keV He^+ irradiation at ~300 K for potassium adsorbed on magnetite is similar to that for sodium adsorbed on albite or olivine.
- Thermal desorption was observed for potassium adsorbed on magnetite at temperatures above 300 K.
- Ion irradiation of a substrate enhances the inward diffusion of the adsorbed potassium, rapidly distributing K deeper into the surface.

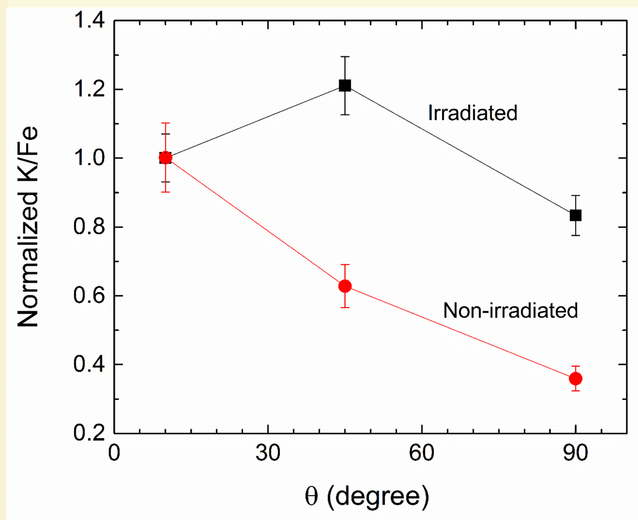
Where is the K Going?

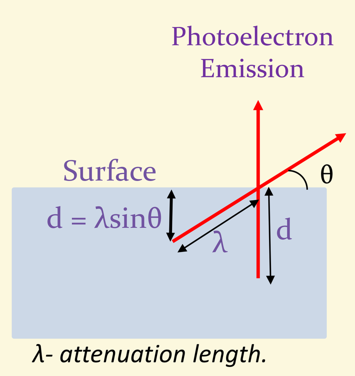
Based on XPS measurements alone, we can not exclude the possibility that the depletion of surface K is attributable in part or wholly to thermal diffusion into the bulk magnetite; however, analogous measurements with Na imply ejection.



For clean albite samples under 4 keV He^+ irradiation, the ejected Na intensity measured by secondary ion mass spectrometry (SIMS) falls with ion fluence, at an identical decay constant as Na:Si measured by XPS. This implies that the decrease in Na observed by XPS describes Na-leaving the sample and not in-diffusion. Similarly, we expect that the measured deceases in K/Fe by XPS is due to sputtering removal of surface K.

Distribution of Adsorbed K in the Surface





To understand how K behaves when deposited onto a planetary regolith, we compare the abundance of K with depth for pristine vs. irradiated minerals. With the same evaporation conditions, the K/Fe ratio for magnetite pre-irradiated with 4 keV He^+ is distributed more deeply and uniformly within the top ~ 5nm of the mineral, compared to that for magnetite with no pre-irradiation. For unirradiated material, the K remains on the surface and composition with depth is consistent with a single overlayer.

Relevant Publications:
[1] R. J. Vervack, Jr, et al. (2010), Science 329(5992), 672-675; [2] A. Doressoundiram et al. (2010), Icarus 207(1), 1-8; [3] R. M. Killen et al. (2010), Icarus 209(1), 75-87; [4] A. E. Potter and T. H. Morgan (1988), Science 241 (4866), 675-680; [5] R. E. Johnson and R. Evatt (1980), Radiation Effects 52, 187-190; [6] B. V. Yakshinskiy & T. E. Madey (2005), Surface Science 593, 202-209; [7] R. J. Vervack Jr. et al. (2010), Science 329 (5992), 672-675; [8] C. A. Dukes & D. Hurley, Science (2016), 351 (6270), 230-231; [9] C. Dukes, et al. (2011), Icarus 212(2) 463-469.

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