Solar Powered HYDROXYL & WATER on Mercury

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Origin and evolution of water on silicates

1. solar wind proton strikes surface (possibly neutralizes)

2. forms hydroxyl (preferably near defect like O vacancy)

$\Delta H$ or $e^-, p^+, h\nu$

3. when hydroxyl density is high enough, recombination occurs either thermally or radiation initiated (photon, electron or proton)

4. $H_2O$ forms, and may now migrate but is vulnerable to photo-desorption and photodissociation
Solar protons $\rightarrow$ hydroxyl

Steep cut-off in penetration depth

Bragg peak indicates clearly defined stopping depth.

A thin shell of hydrogen accumulates as OH.

Protons cause lattice disruption, chemical reduction.

Few hundred eV protons stop in top 10 nm.

Albite has $\sim$32 oxygen atoms per 0.29 nm$^3$ unit cell or $\sim 1.0 \times 10^{17}$ oxygen atoms per cm$^2$ with 10 nm depth.

Only about half of these are available for hydroxylation.
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Mercury’s Unique Space Environment

Energy: ~ few hundred eV

Most hydroxyl forms at high latitudes

Flux may be significantly non uniform, dominated by localized spots at high latitudes

from Benna et al., 2010
Most low latitude OH will immediately recombinatively desorb as water.

OH formed on cooler (late afternoon → nighttime) surfaces will accumulate until sunrise, and then recombinatively desorb.

Is this the true proton precipitation?

from Vasvada et al., 1999

from Benna et al., 2010
Any low latitude OH will immediately recombinatively desorb, if it’s formed at all.

OH formed on cooler (late afternoon → nighttime) surfaces will accumulate until sunrise, and then recombinatively desorb.

Mercury’s Unique Space Environment

from Vasvada et al., 1999

Or this?

from Trávníč et al., 2010

from Vasvada et al., 1999
Thermal Environment

A day in the life of….

Key Points:
[OH] formed where solar wind strongest, flux is highest
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\[\text{OH forms rapidly but desorption dominates,}\]
\[\text{OH production in possible balance with RD}\]
\[\text{OH forms and is stable; adsorbed water incr.}\]
\[\text{Adsorbed water is ‘stable’}\]
Thermal Environment

A day in the life of….

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@ 0° W

- OH forms and instantly desorbs
- OH forms rapidly but desorption dominates,
- OH production in possible balance with RD
- OH forms and is stable; adsorbed water accum.
- Adsorbed water is ‘stable’

Modified from Vasavada et al., 1999
Thermal Environment

Temperature inside a 40km crater

Max Ave

Location of high CPR

Adsorbed water possibly much more broadly stable than ice.
Simulating Mercury’s Surface Environment

• Temperature Programmed Desorption (TPD). The mass/no. density removed is measured as a function of temperature.

A unique system for (TPD) ensures no background.

Observed the thermal desorption of ice, adsorbed water, and OH from a Mercury analog.

Can derive binding energies.
Simulating Mercury’s Surface Environment

Laboratory Desorption Experiments

MINERALOGY!!

SILICATES

Adsorbed H and H₂O

(a) Basalt

(b) Na-Feldspar

Desorption Rate (arb)

Temperature (K)

0.00 0.05 0.10 0.15

0.2L 0.5L 1L 2L 4L

0.2 L 0.5 L 1 L 2 L 4 L
• TPD of TiO₂ shows distinct regimes of water release.

• Recombinative desorption for TiO₂ is low. Most oxides this is much higher ~400 K to ~600 K.

• Ilmenite (FeTiO₃) - proposed to exist on Mercury's surface, may have similarly low RD temperature.

Fig. 20. \(\text{H}_2\text{O}\) TPD spectra from various exposures of \(\text{H}_2\text{O}\) on the ideal TiO₂(110) surface at 135 K. The inset shows the TPD spectra for the lowest exposures, with the “bgld” spectrum corresponding to exposure to the background chamber pressure (2 x 10⁻⁹ Torr) for 40 min. Taken from Henderson [262].
Mercury’s Surface Environment

Water clusters on glass. No adsorption

Fe-rich Feldspar GLASS

Adsorbed H and H$_2$O

GLASS

Ice desorption (data and model)

Background contamination
Surface Area DETERMINES Abundance.

From Lane et al., 2007, Fig 1

Mare Soil
Frame size: 660 μm
IM: ilmenite
PX: pyroxene
GL: glass
PL: plagioclase

Lunar Dust Grain
Frame size: 100 μm

JSC-1A Lunar Simulant
Frame size: 520 μm
OL: olivine
GL: glass
PL: plagioclase

Surface Area / Volume Ratios for Spheres of Varying Diameter

Diameter = 1 μm

Surface Area / Volume (S A / V) = 6

Diameter = 10 μm

Surface Area / Volume (S A / V) = 0.6

Diameter = 0.1 mm

Surface Area / Volume (S A / V) = 0.06

Diameter = 1 mm

Surface Area / Volume (S A / V) = 0.006

Surface dominates

Interior dominates
Water diffusion simulations

- Here we consider the interface boundary condition to be “soft”.
- Thermal conductivity of surface is assumed very poor ($10^{-4}$ to $10^{-8}$)
- Solar radiation heating produces steep temperature gradients in the top several cm (Vasavada et al., 1999)
- Temperature varies nonlinearly with depth, residence time varies nonlinear with temperature, therefore residence time varies super-nonlinear with depth.
Diffusion vs. Desorption at poles

Diffusion: movement along a grain’s surface. Does not require complete desorption. \( E_{\text{diff}} \sim \frac{1}{2} E_{\text{desorb}} \), so is faster than desorption. However, diffusion is rate limited by needing to “bridge” contact surface between grains. SLOW

Desorption: one stop shopping. FAST

Assume polar temperature \( \sim 250 \text{ K} \)

diffusion “lifetime” \( \sim 10^{-7} \text{ s} \)
path goes as particle radius\(^2\)
100 um particle \( \sim 10^{12} \text{ Angstrom} \)
Site to site distance \( \sim 3 \text{ Angstroms} \)

assuming non-infinitesimal contact area between grains, can take \( \sim 3 \times 10^{18} \) hops or \( 10^4 \) seconds.

at 250 K
desorption lifetime \( \sim 0.3 \text{ s} \)
Solar wind implantation forming hydroxyl as an intermediate

Modeling the reactions:
\[ p^+ + [*] \rightarrow [OH] \]
\[ [OH] + [OH] \rightarrow [H_2O] \]

Gives the equations:
\[ [OH]' = k\Phi (N_0-[OH]) - k_r[OH]^2 \]
\[ [H_2O]' = \sqrt{\Phi} / [OH] \]

[OH] surface bound hydroxyl

[*] surface defect (implicit, assume unlimited abundance)

[H_2O] is released into gas phase or allowed to diffuse

N_0 = 3\times10^{16} the maximum estimated oxygen depletion from silicate
Hopping lifetimes

- Polanyi-Wigner theory of desorption-adsorption kinetics

\[ I(T) \propto \frac{\mathrm{d}M}{\mathrm{d}t} = -\frac{\mathrm{d}\theta M}{\mathrm{d}t} = \nu(\theta_M) \cdot \theta_M^n \cdot \exp\left(-\frac{E_{\text{des}}(\theta_M)}{R \cdot T}\right) \]

- Residence time on a particle (activation energy \( E_{\text{des}} = 60 \, \text{kJ/mol} \))

- First approximation, take as zero order kinetics.

- Temp depends \(~\text{exponentially}~\) on depth

\[ T(z) = A \exp(-z/z_0) + T_0 \]
3D Random Walk

- Mean deviation from origin

\[ \sigma^2 = \frac{t}{\delta t} \epsilon^2 \]

- Time of walk \( t \), step interval \( \delta t \) and step size \( \epsilon \)

- Equate \( \sigma \) with depth \( z \)

- Equate \( \delta t \) with Residence time \( R(z) \) then can make estimates based on certain percentile of walkers.

- \( \epsilon \) taken to be a grain diameter
Thermal only evolution of hydroxyl

Time to:
1. Desorb from a grain
2. Diffuse around at 1 $\mu$m grain
3. Travel 100 $\mu$m in any one direction
Solar powered hydroxyl/OH models

Modeled [OH] surface concentration (log intensity scale)

WITH NO MERCURIAN DIPOLE

[H$_2$O] production rate is inverse: [H$_2$O] generated strongest under subsolar point because [OH] is reacting away to form it.

[OH] density is high where [H$_2$O] production is slow.
Conversely, where [OH] is low, [H$_2$O] production rate is high.

p$^+$ + [*] $\rightarrow$ [OH]
[OH] + [OH] $\rightarrow$ [H$_2$O]
Mercury’s Unique Space Environment

WITH DIPOLE
and due to high temperatures

OH only sufficiently stable for recombinative desorption at high latitudes.
Mercury’s Unique Space Environment

WITH DIPOLE
And assuming Travnic model

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Temperature

100K
570K

Latitude (deg.)

Longitude (deg.)

OH recombinatively desorbes at sunrise.

0.8 eV $E_a$

Temperature

Water Production

Latitude (deg.)

Longitude (deg.)
Polar day (outside of PSR)

Water will migrate into the surface

Surface temp @ 80° lat ~ 4000 K

Loss rate over time
SUMMARY

1. Precipitation of solar wind protons controls production of OH.

2. Composition and crystallinity are important for water adsorption.

3. Most/all OH formed in polar regions.

4. OH will recombinatively desorb to produce water to accumulate in cold traps.

5. Adsorbed water is stable outside of PSRs at very high latitudes, probably > 85° though possibly lower if sequestered in craters.

6. Less stable polar water will tend migrate into the subsurface.