

August 4th 2007 5:26am EDT



S.P. Kounaves, Tufts University

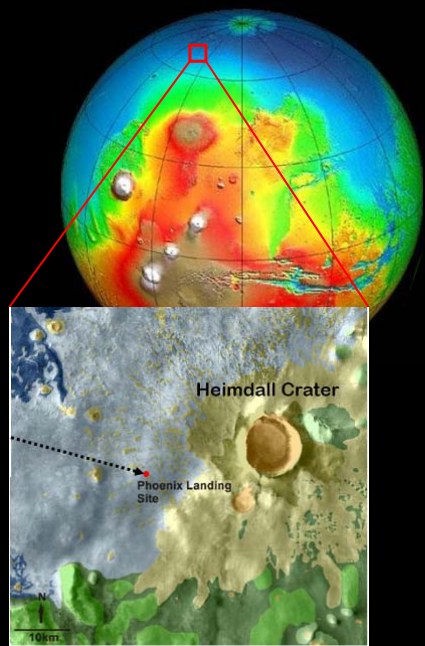
Phoenix Landing Site

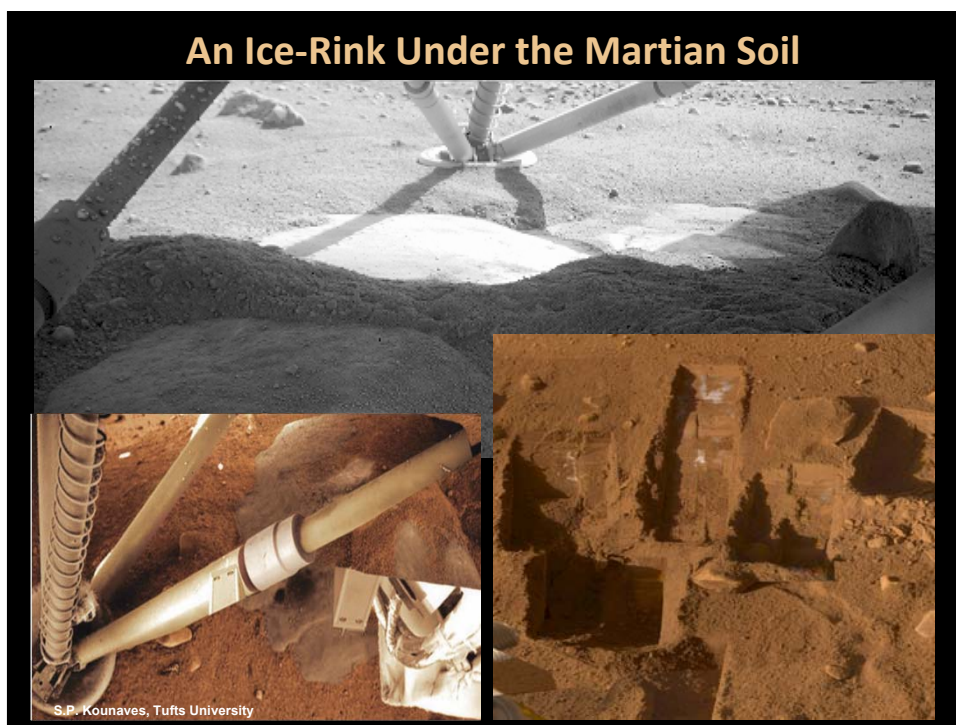
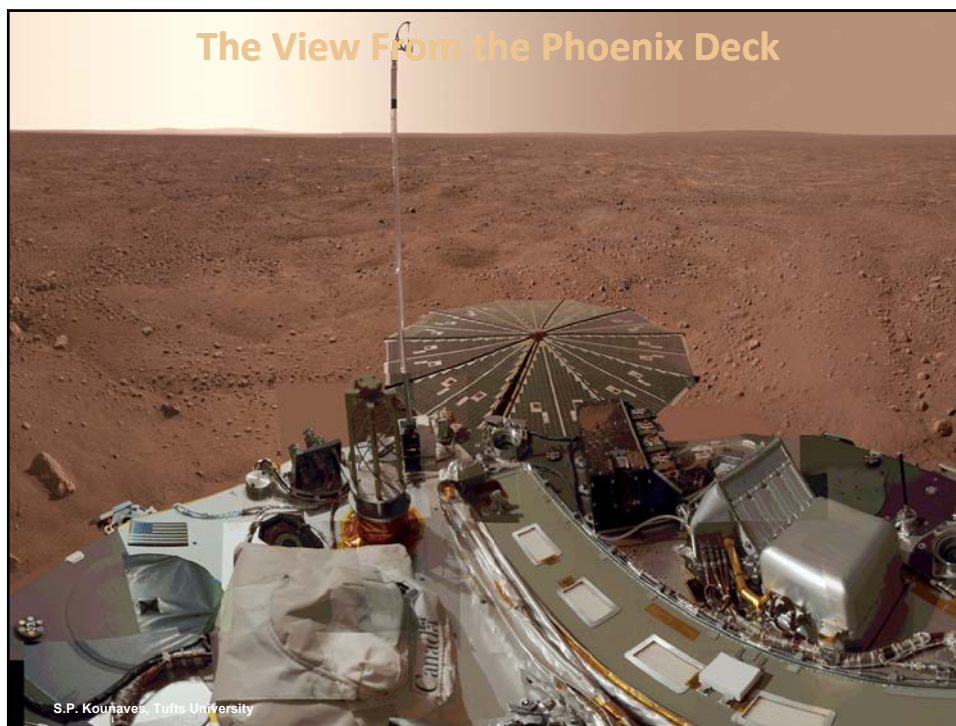


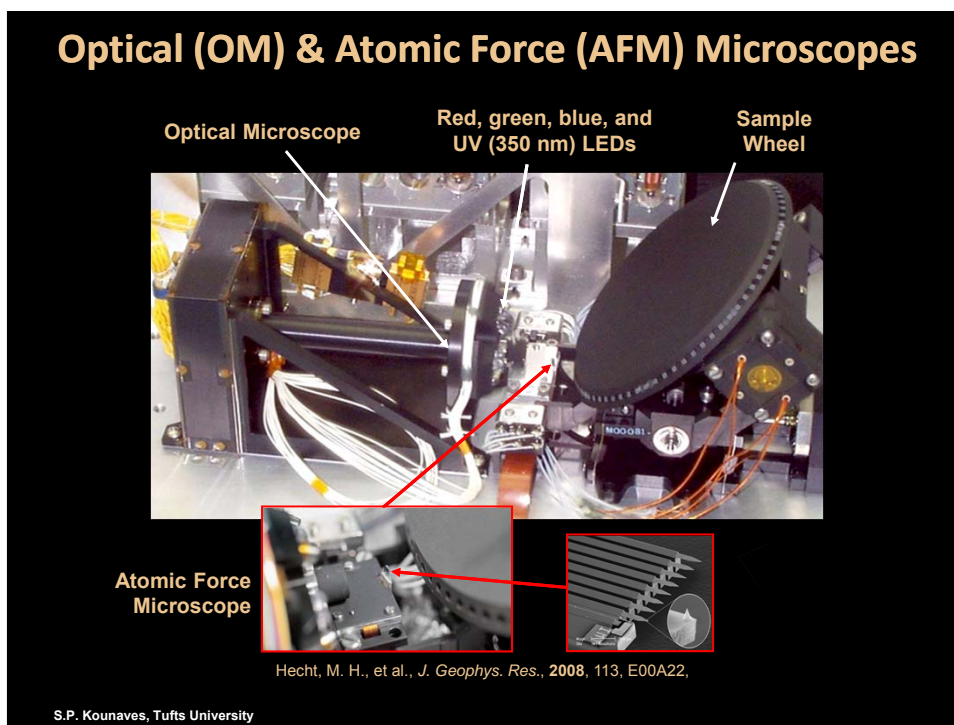
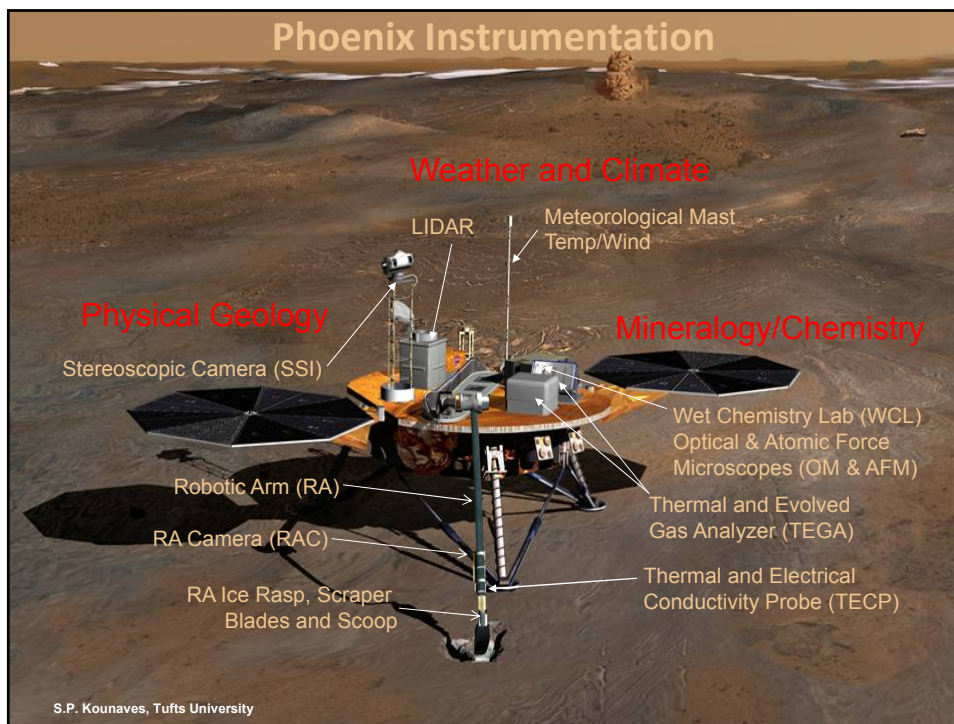
Artist's Conception, NASA/JPL

Landed at 68.2°N, 234.2°E
(= 230 mi north of Fairbanks AK!)
on May 25th 2008 & returned data until
October 28th 2008

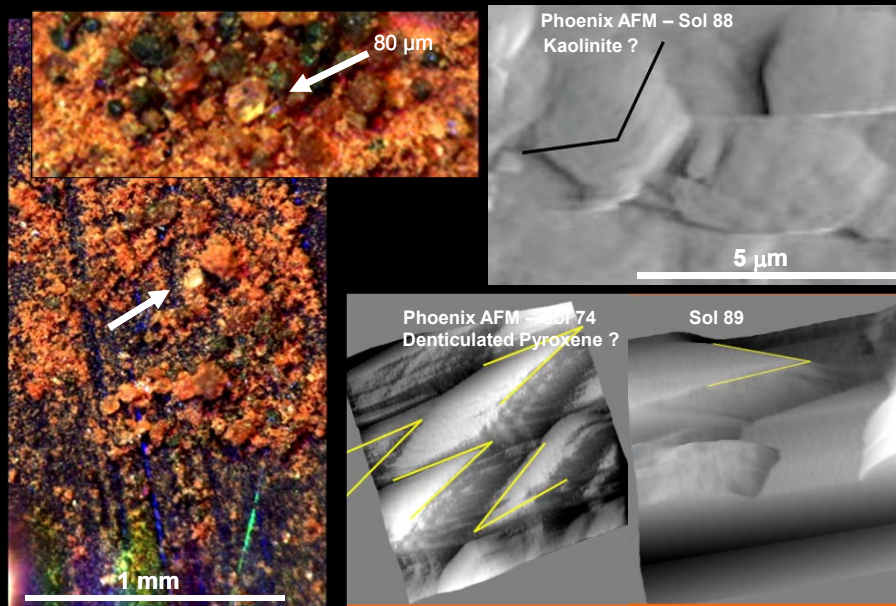
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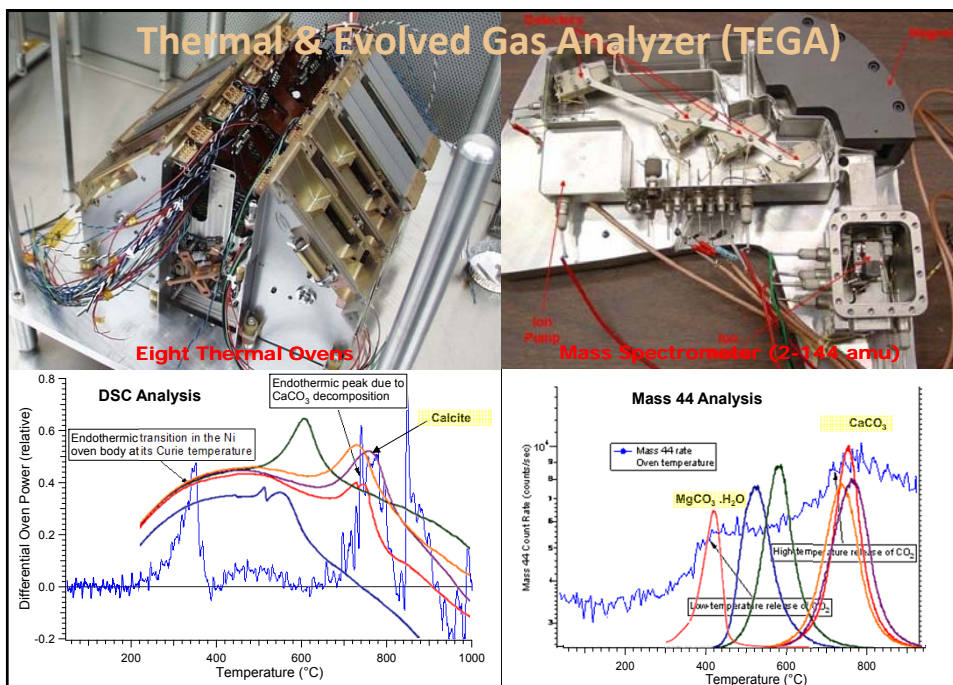
Optical (OM) & Atomic Force (AFM) Microscopes



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Hecht, M. H., et al., *J. Geophys. Res.*, 2008, 113, E00A22,

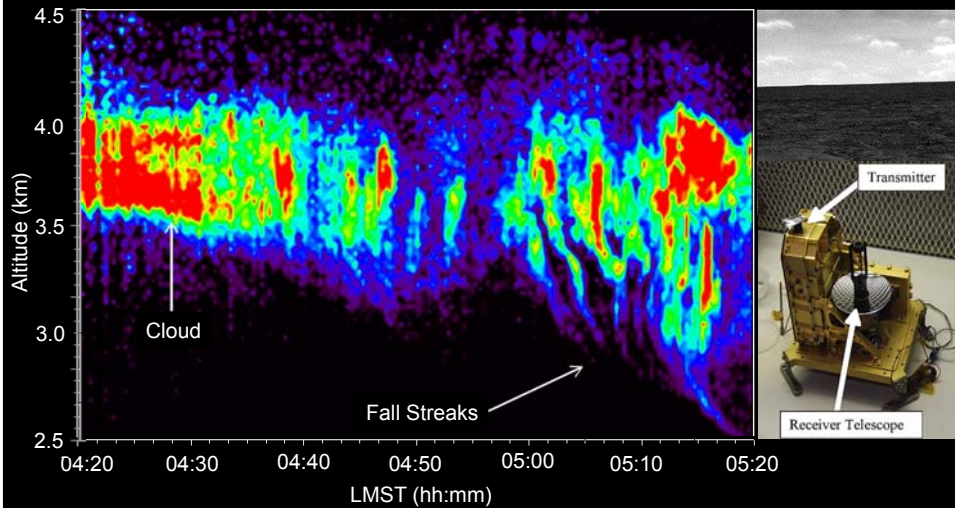
Thermal & Evolved Gas Analyzer (TEGA)



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W. V. Boynton, D. W. Ming, S. P. Kounaves, et al., *Science*, 2009, 325, 61-64.

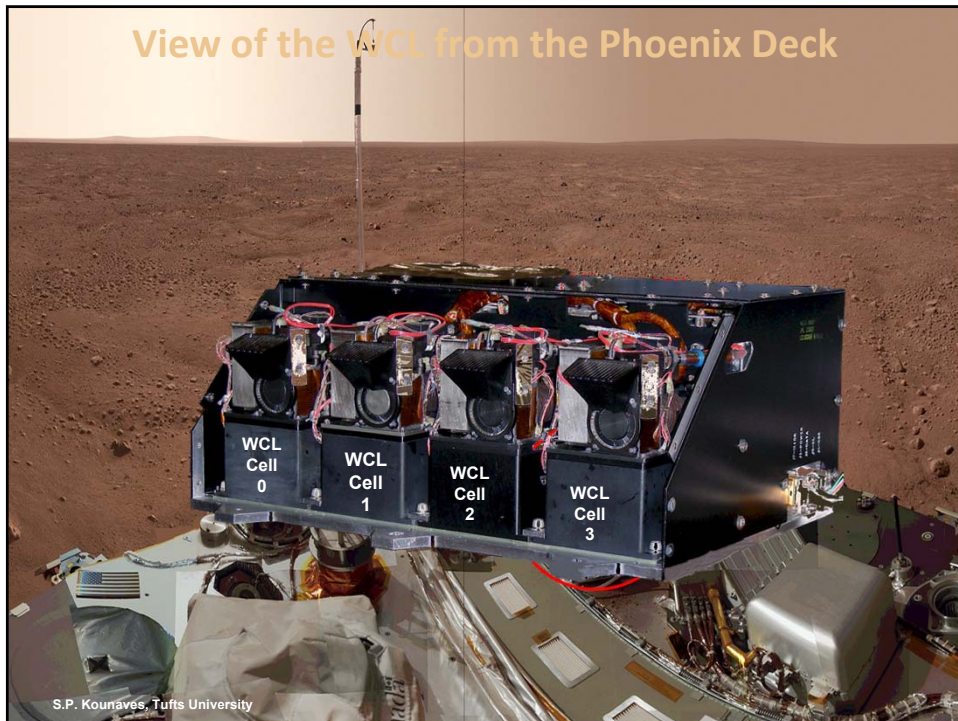
LIDAR Observations of Martian Clouds (Sol 99)



The vertical streaks at the base of the cloud on the right show falling water ice crystals, similar to snow. Streaks are curved by higher winds at 3 km.

Whiteway, J., M. et al., "Lidar on the Phoenix mission to Mars, *J. Geophys. Res.*, 2008, 113, E00A08, S.P. Kounaves, Tufts University

View of the WCL from the Phoenix Deck



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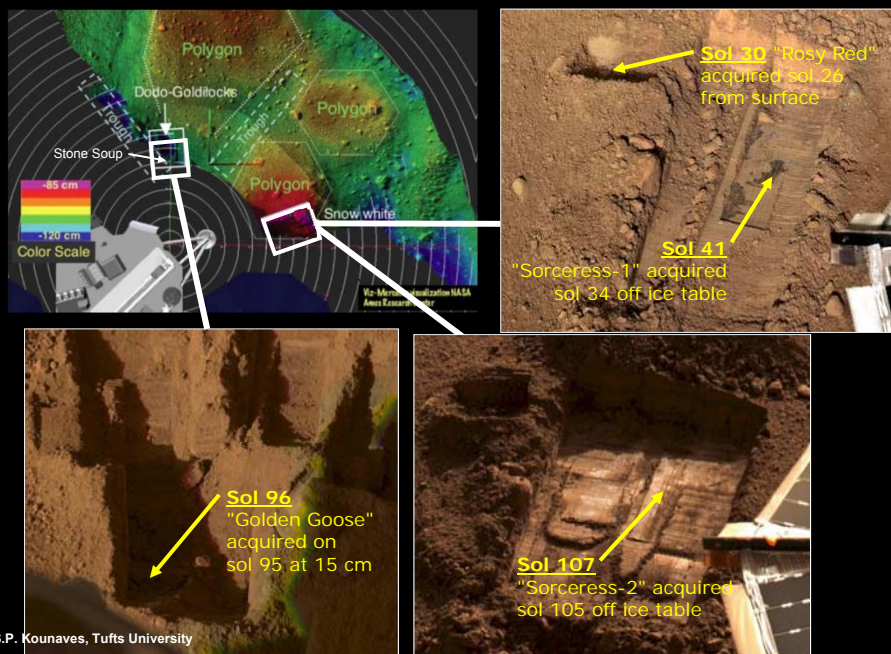
Wet Chemistry Lab (WCL) Components

S. P. Kounaves, et al., *J. Geophys. Res.*, 114, 2009, E00A19
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The Wet Chemistry Experiment

S. P. Kounaves, et al., *J. Geophys. Res.*, 114, 2009, E00A19
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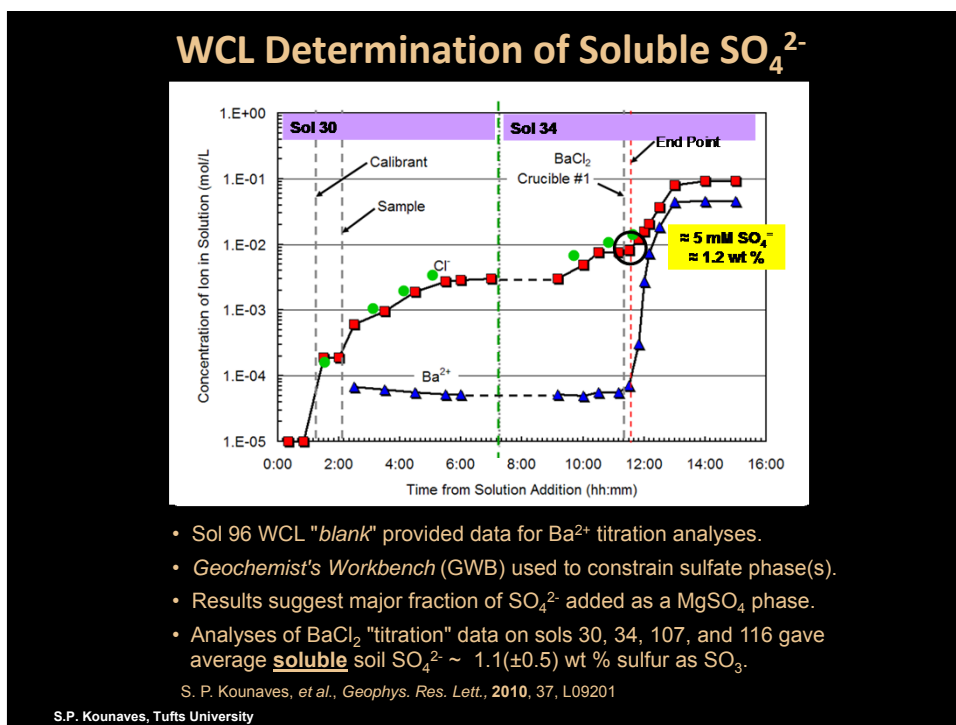
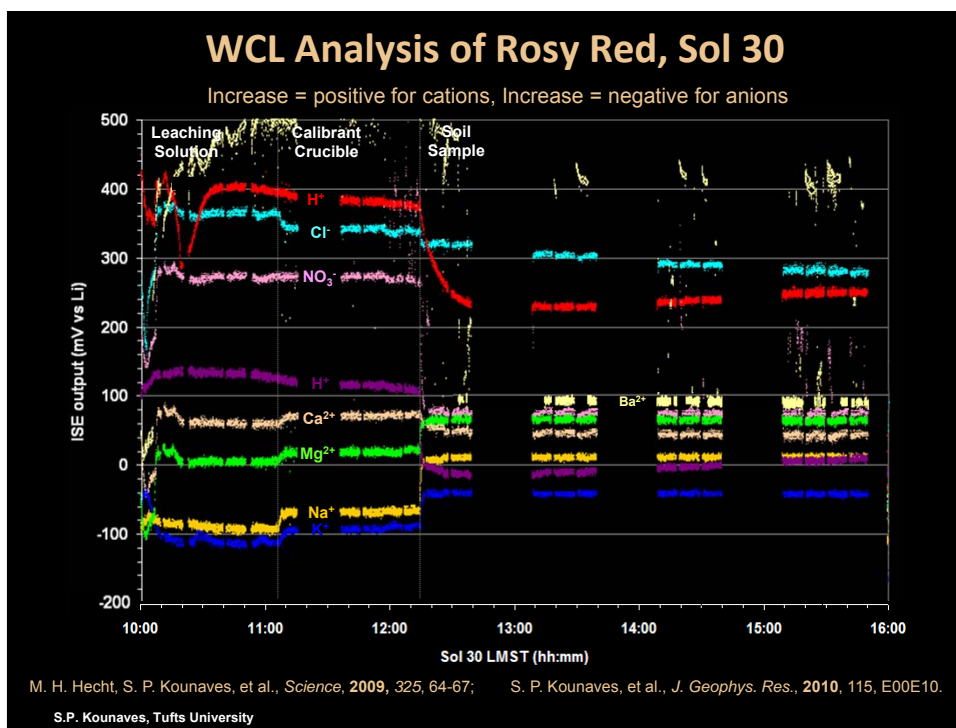
Four WCL Sample Locations



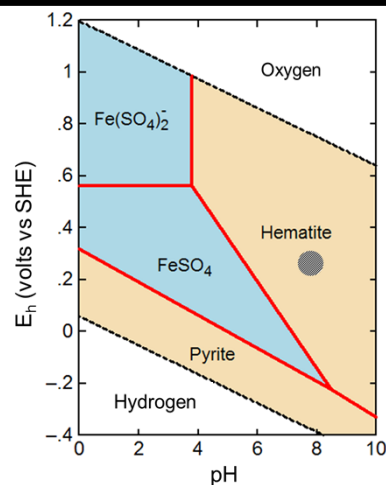
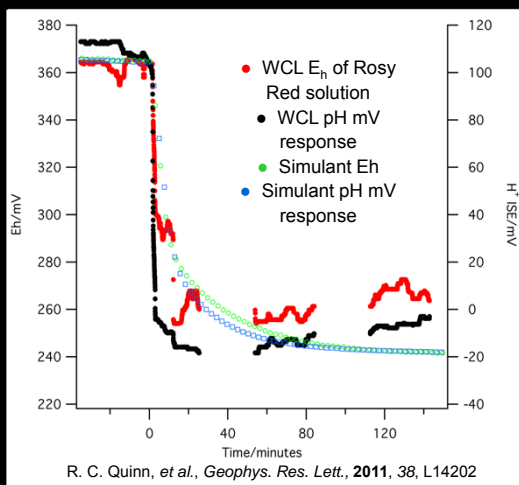
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WCL Determination of Redox Potential (E_h)



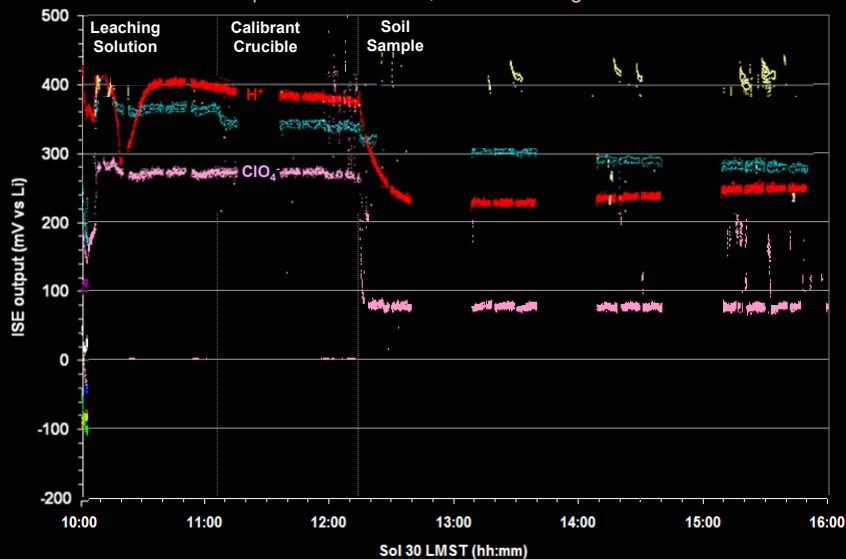
$E_h = 253 \pm 6$ mV for Rosy Red in WCL at pH of 7.7 ± 0.1 ($E_h \propto a_{H^+} \propto P_{CO_2}$, $[CO_3^{2-}]$, $[HCO_3^-]$ & CO_2)
 Simulant results compatible with ppm-level oxidants & indicate soluble Fe(II) is ≤ 1 ppm.

Quinn, R. C., J. D. Chittenden, S. P. Kounaves, and M. H. Hecht, *Geophys. Res. Lett.*, **2011**, 38, L14202

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WCL Analysis of Rosy Red, Sol 30

Increase = positive for cations, Increase = negative for anions

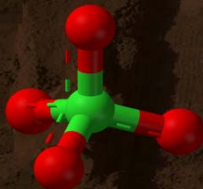


M. H. Hecht, S. P. Kounaves, et al., *Science*, **2009**, 325, 64-67; S. P. Kounaves, et al., *J. Geophys. Res.*, **2010**, 115, E00E10.

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What is Perchlorate (ClO_4^-)?

Stable tetrahedral anion; most oxidized form of chlorine: ClO_4^-



Anions:

ClO_4^-	perchlorate
ClO_3^-	chlorate
ClO_2^-	chlorite
ClO^-	hypochlorite
Cl^-	chloride

Implications of 0.6% ClO_4^- in the Soil

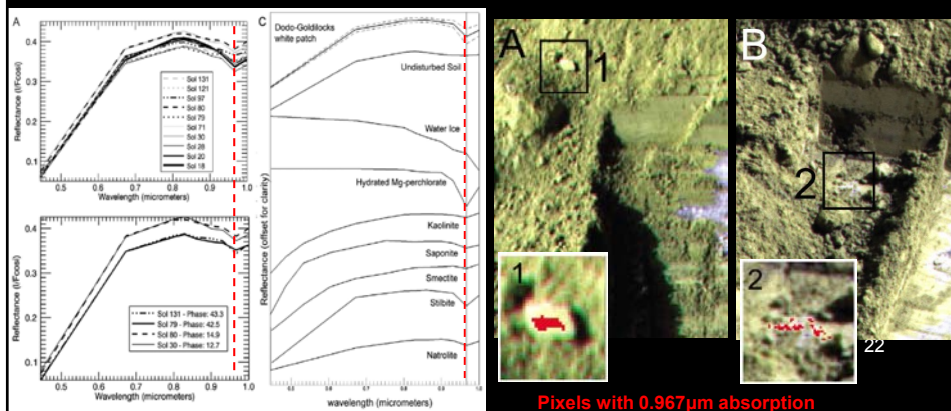
- Viking 1/2 GC-MS and Phoenix TEGA detected no organics.
- Stable at ambient but for $>200^\circ\text{C}$ becomes strong oxidant - thus ClO_4^- in the soil could have prevented detection of organics?
- Even if shown that ClO_4^- can prevent detection by GCMS, does not mean that organics are present !
- UV photolysis and oxidation of organics still possible !
- Thus, the question of organics on Mars is still open.

M. H. Hecht, S. P. Kounaves, et al., *Science*, **2009**, 325, 64-67; S. P. Kounaves, et al., *J. Geophys. Res.*, **2010**, 115, E00E10.

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Identification of the ClO_4^- Parent Salt

- Phoenix *Surface Stereo Imager* (SSI) was used to map distribution of perchlorate in soil. (S. Cull, et al., *GRL*, **2010**, 37, L22203)
 - if absorption at $0.967\mu\text{m}$ is due to perchlorate, it **constrains parent phases to hydrated Mg and Ca salts**, while K, Na, and Fe perchlorates are ruled out.



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Soluble Composition of Martian Soil

A "habitable" soil?

- H₂O ice at 5-10cm depth.
- EC ≈ 1.5 mS/cm (1g/25mL).
- Moderately alkaline pH 8.
- E_h ≈ 253 ± 6 mV

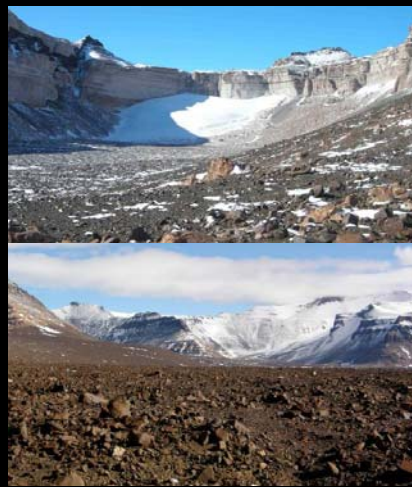
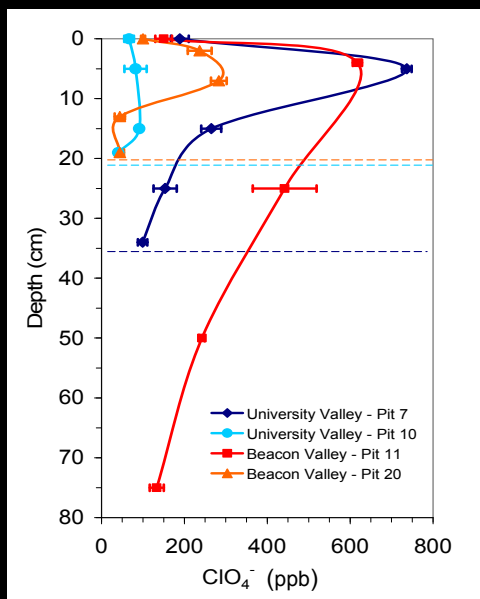
- (1) As determined by TEGA & WCL
- (2) Minimum required to give saturated Mg²⁺
- (3) Equivalent to 5.3 mM total SO₄²⁻ in solution.
- (4) Equilibrium in solution calculated using *GWB* React at 7°C and a 4 mbar CO₂ headspace

Species	Equil. Conc. (mM)	Conc. in Soil (wt %)
CaCO ₃ (calcite)	Saturated	3 - 5 ⁽¹⁾
MgCO ₃ (magnesite)	Saturated	≥ 1.8 ⁽²⁾
MgSO ₄ (epsomite)	Dissociated	3.3 ⁽³⁾
ClO ₄ ⁻	2.5	0.6
Na ⁺	1.4	0.08
Cl ⁻	0.40	0.04
K ⁺	0.40	0.04
Mg ²⁺	6.4 ⁽⁴⁾	-
SO ₄ ²⁻	3.9 ⁽⁴⁾	-
HCO ₃ ⁻	5.4 ⁽⁴⁾	-
MgSO ₄ (aq)	1.2 ⁽⁴⁾	-
Ca ²⁺	0.75 ⁽⁴⁾	-
CaSO ₄ (aq)	0.17 ⁽⁴⁾	-

Kounaves et al., *Geophys. Res. Lett.*, 2010, 37, L09201

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Back on Earth: ClO₄⁻ in Beacon & University Valleys!



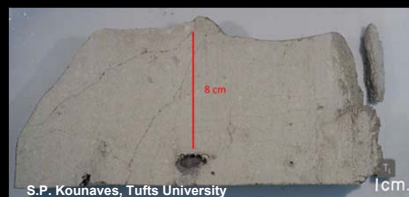
Analysis of University & Beacon Valley soils revealed ClO₄⁻ in all samples and horizons. Continuous ClO₄⁻ profile is the result of hyper-aridity preventing aqueous migration of ClO₄⁻.

Kounaves et al., *Environ. Sci. Technol.*, 2010, 44, 2360-64.

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How Widespread is Perchlorate on Mars

The Mars meteorite EETA79001 was recovered from Elephant Moraine in 1979, 200 km north of Beacon Valley in the Antarctic Dry Valleys.



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1cm.

Stroble & Kounaves, *Icarus*, 2012, doi:10.1016/j.icarus.2012.08.040

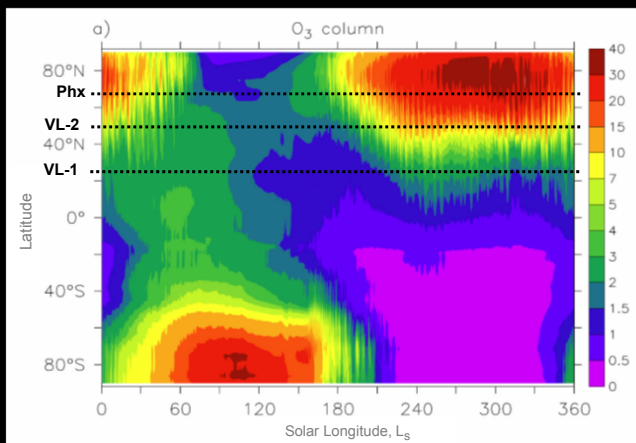
- ❖ Sample analyzed: 35.3 g sawdust from cross-section cut.
- ❖ Cut exposed ~ 1-2 cm dia. vug and glass inclusion at center containing granular “white druse”.
- ❖ Druse consists of CaCO_3 , $\text{Mg}_3(\text{PO}_4)_2$, with lesser amounts of CaSO_4 and MgCO_3 .
- ❖ Isotopic analysis has shown material to most likely be extraterrestrial.

How Widespread is Perchlorate on Mars

- ❖ Multiple IC analyses found 400-600 ppb ClO_4^- in EETA79001.
- ❖ Ion concentrations and conductivity were ~ 4% of those measured on Mars, except Ca^{2+} which was ~ 16%.
- ❖ Terrestrial age of EETA79001 from cosmogenic ^{14}C content is 12 ± 2 k years, with residence time probably less.
- ❖ The ~ 500 ppb of ClO_4^- in ADV soil has accumulated over 130k to 1.2m years (Lacelle et al., 2011).
- ❖ Plausible that ClO_4^- is from Mars with differences due to:
 - Pre-ejection processes resulting in leaching and/or destruction of a portion of the ClO_4^- originally present.
 - Launch from location where levels of ClO_4^- were lower than Phoenix site.
- ❖ Results suggest ClO_4^- may be present at other locations on Mars?

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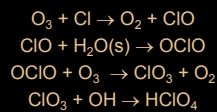
Ozone → Perchlorate on Mars



Zonally averaged ozone column density ($\mu\text{-atm}$) on Mars from SPICAM/MEX UV measurements.

Perrier, S., et al., *J. Geophys. Res.*, 2006, 111, E09S06

Atmospheric chemistry on Mars & Earth ?



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