The Phoenix Mars Lander Mission:
Simple Findings - Global Implications on Mars, Earth & Venus?

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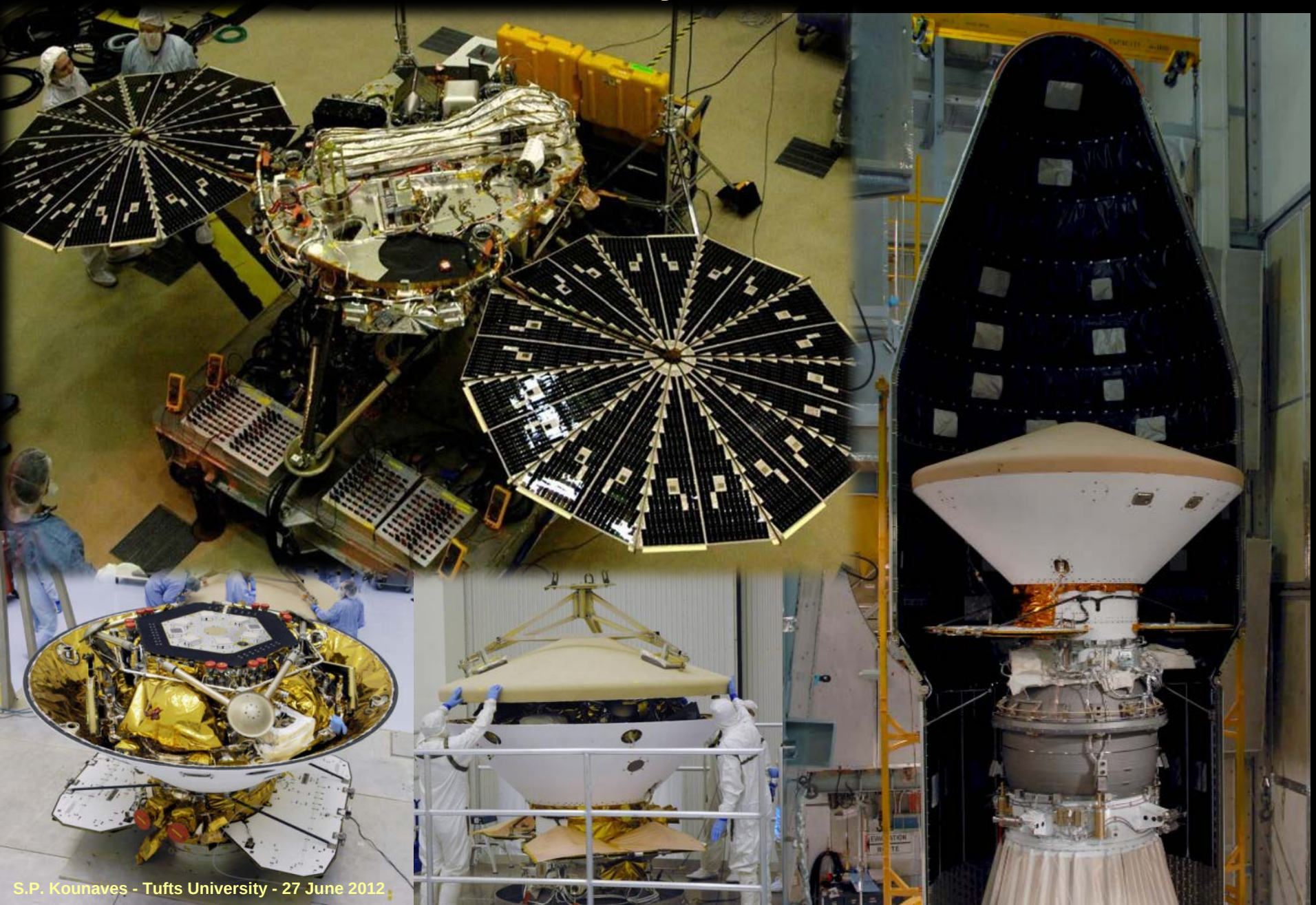
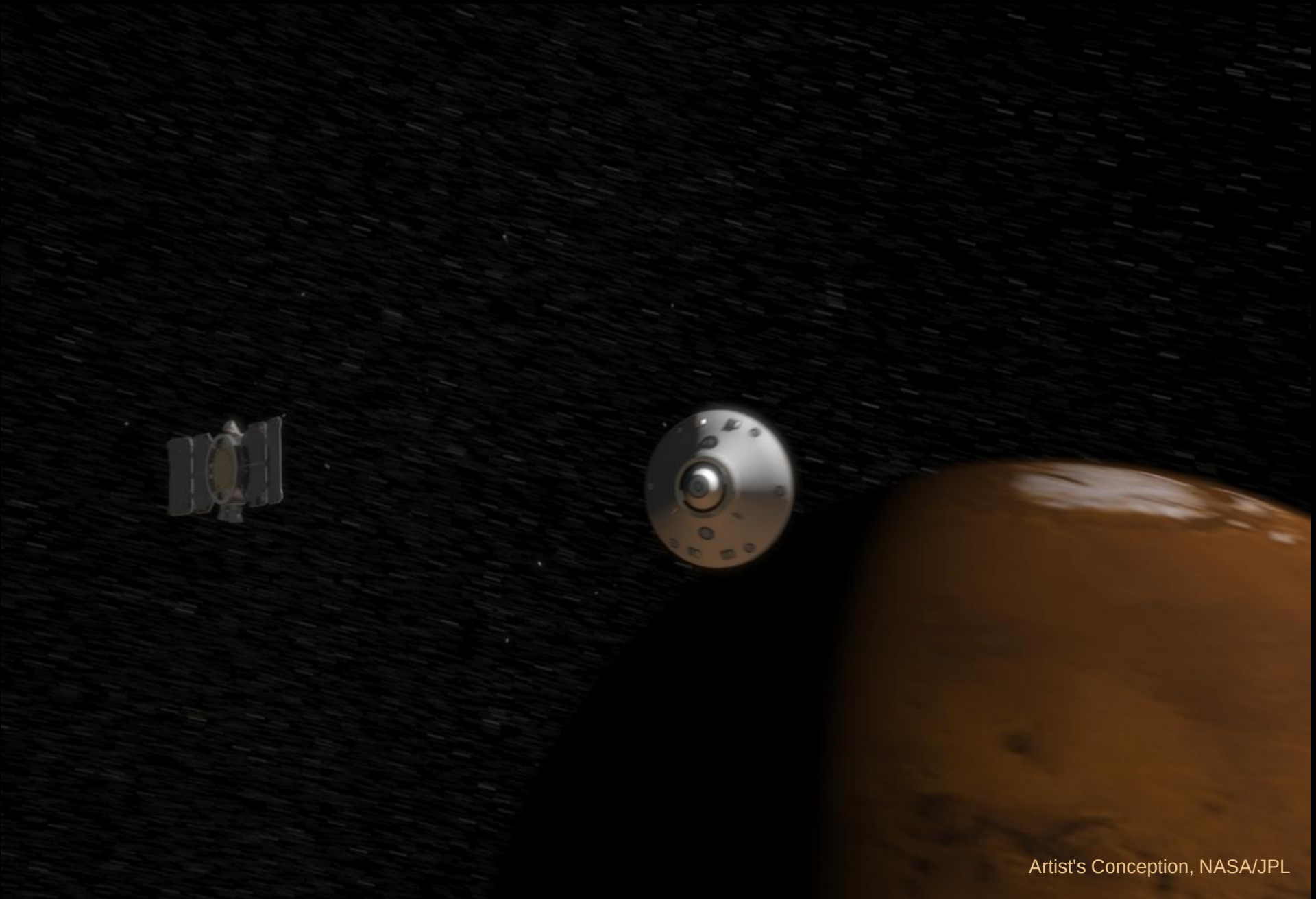
Phoenix Assembly at JPL and LMA

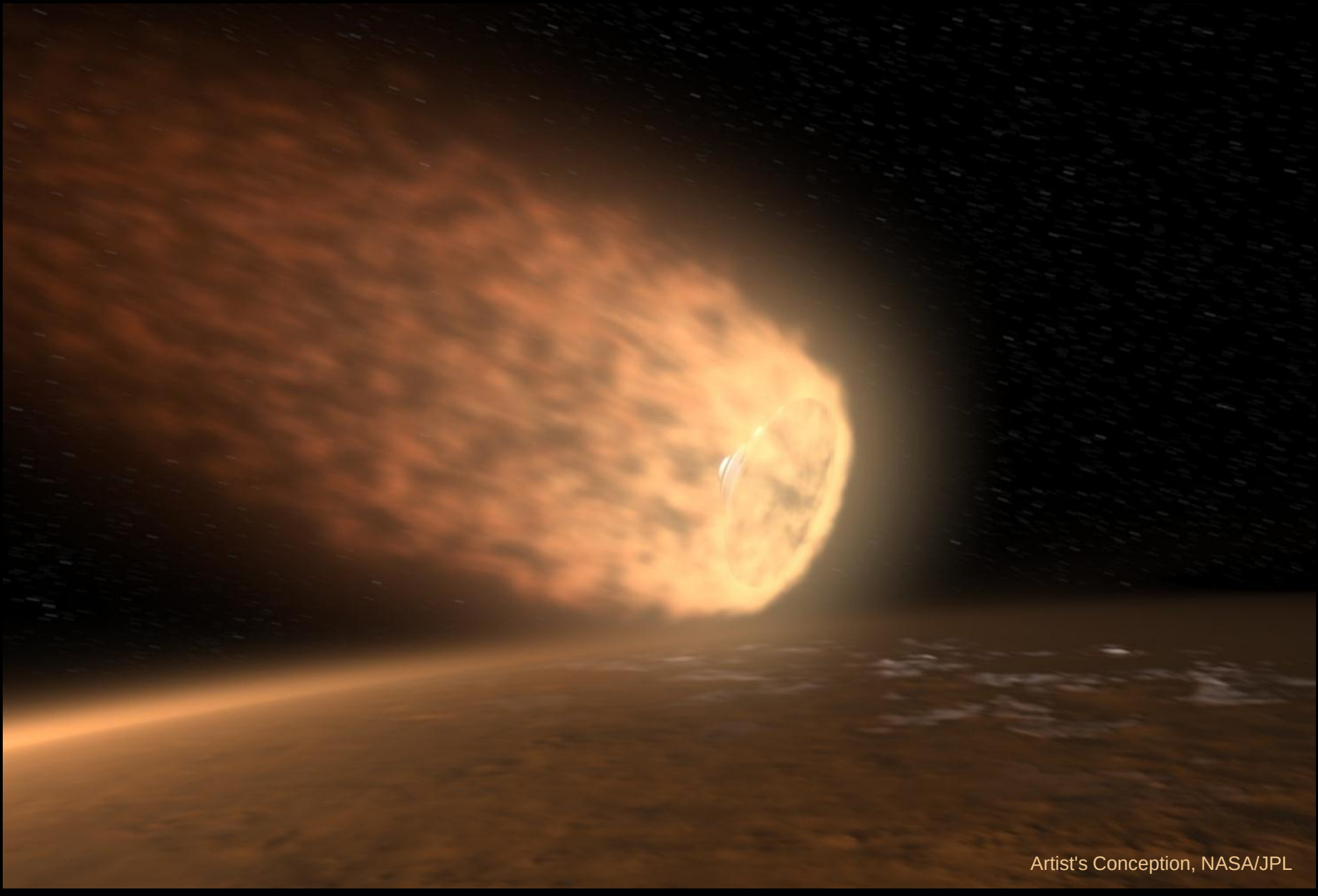


EDL - Entry Phase

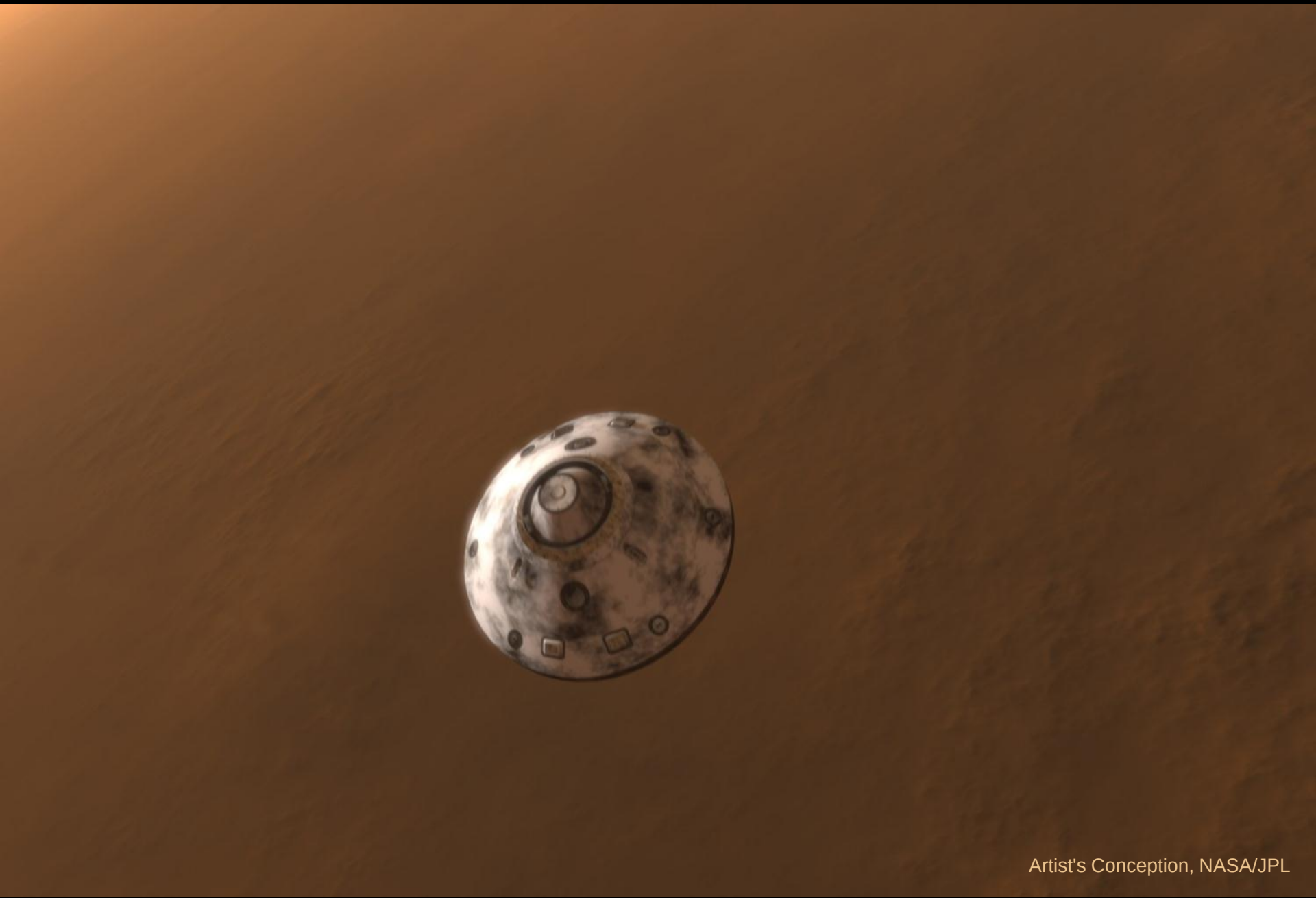


Artist's Conception, NASA/JPL

EDL Descent through Atmosphere



EDL Deceleration through Atmosphere



Artist's Conception, NASA/JPL

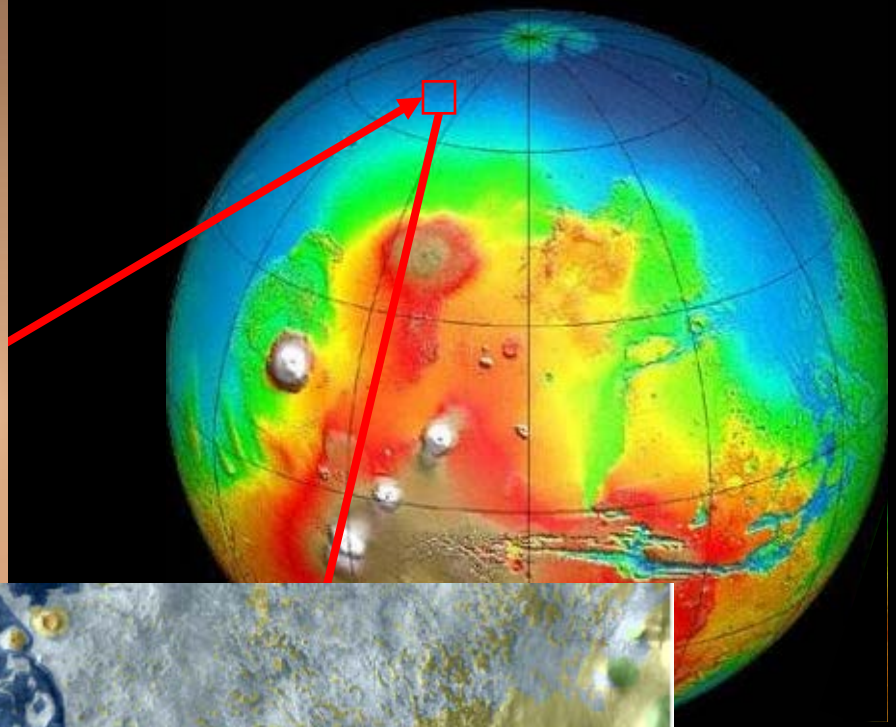
EDL Parachute Deployment

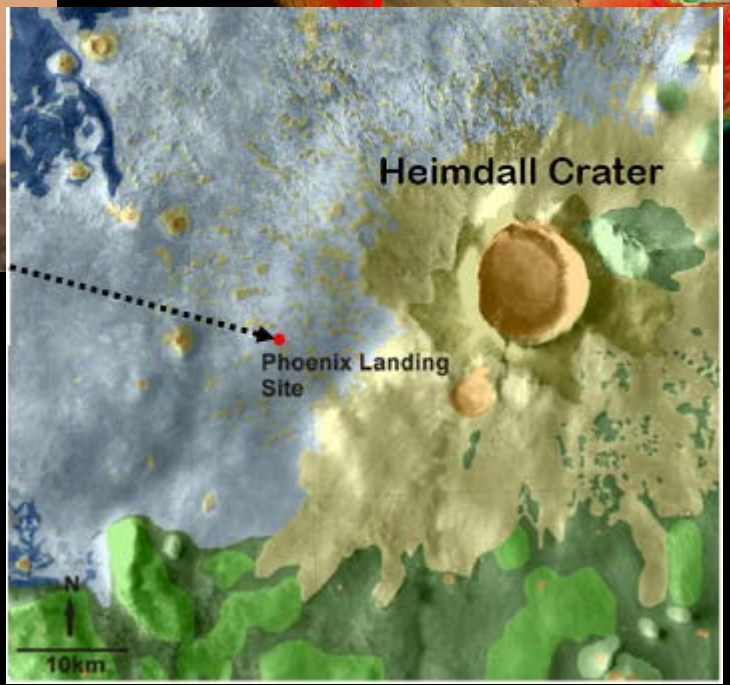
Artist's Conception, NASA/JPL

MRO EDL Image of Phoenix Over Heimdall

Phoenix is at about 13 km above the surface, just a few seconds after the parachute opened. MRO is 310 km above Mars, 760 km from Phoenix, and traveling at a ground velocity of 3.4 kilometers/second.

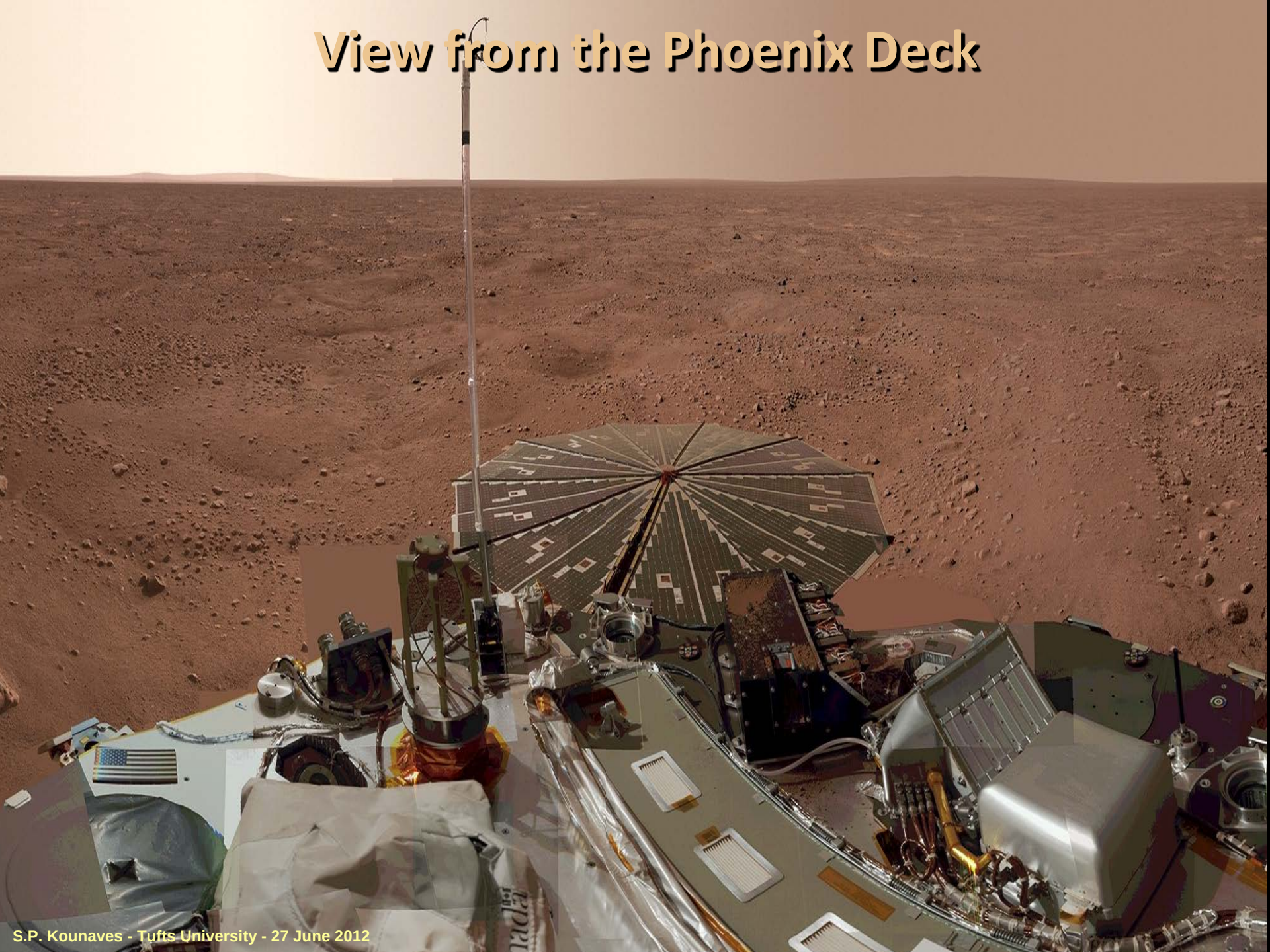
EDL Landing Phase



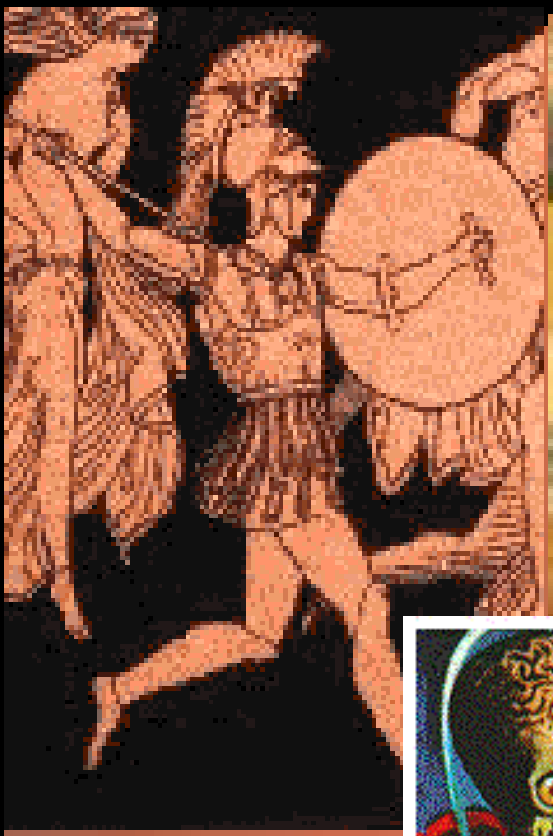


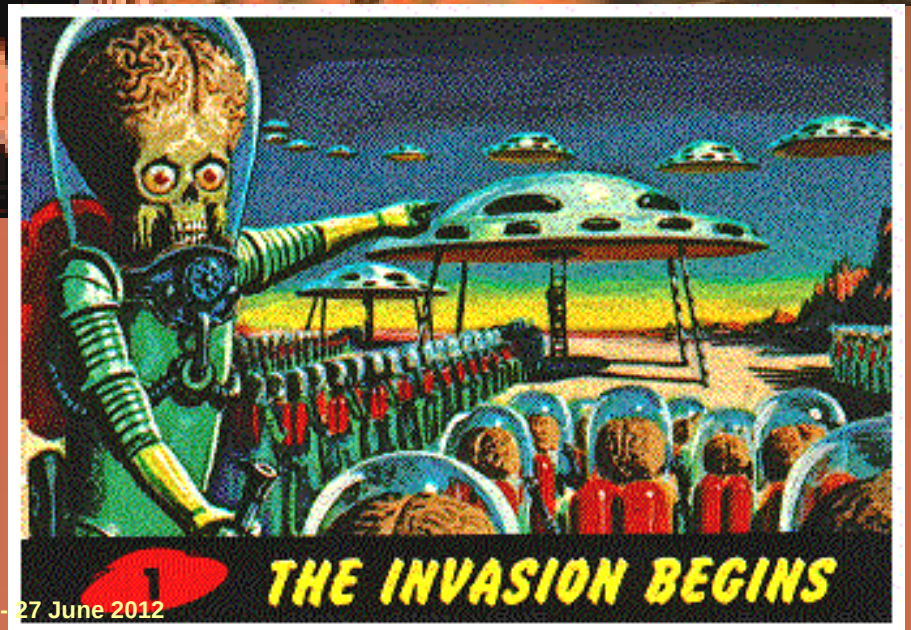
Landed at 68.2°N, 234.2°E
(≡ 230 mi north of Fairbanks AK!)
on May 25th 2008 & returned data until
October 28th 2008

View from the Phoenix Deck



Why Mars – Myths & Dreams

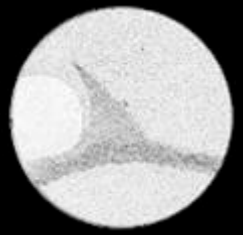




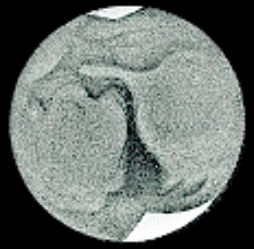
Its blood-red hue and disorderly conduct led the early Greeks to name it Ares and latter the Romans Mars.

Our Changing Views of Mars

Huygens 1659



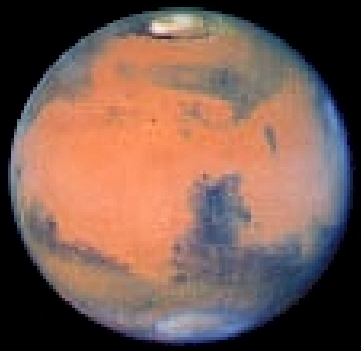
Schroeter 1783



DeLaReu 1856

Schiaparelli 1888

Mars Global Surveyor 2002

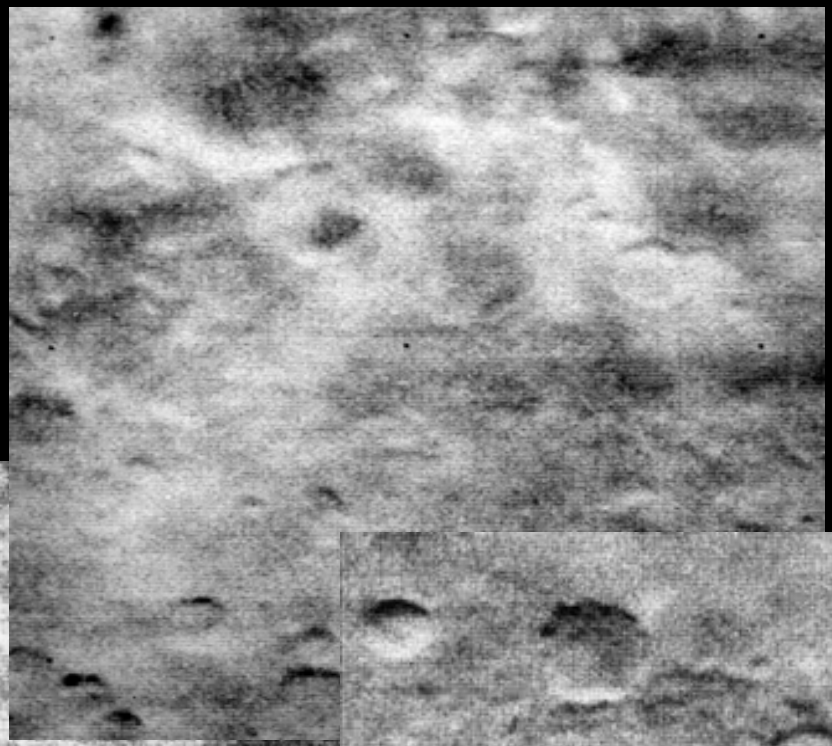


Hubble 1999

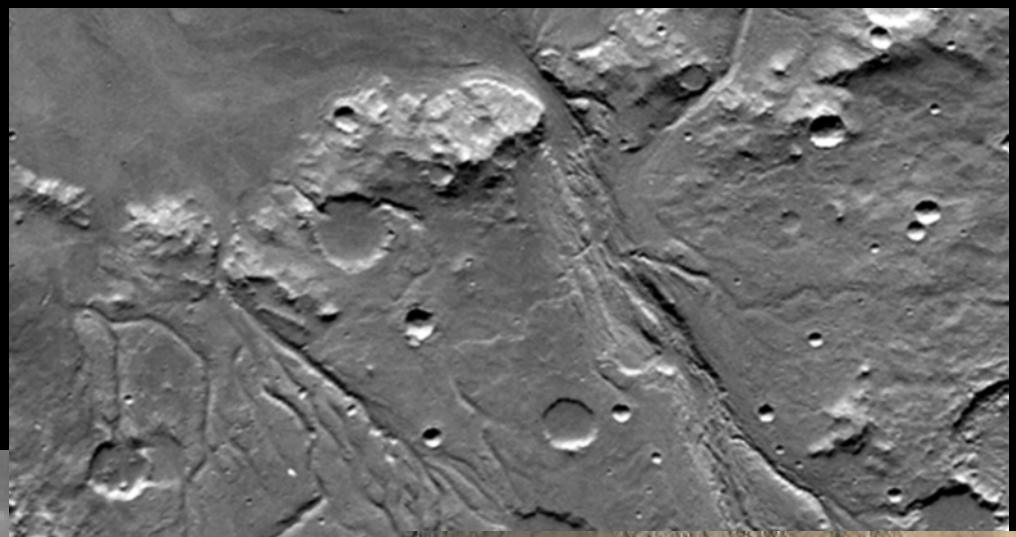
Lowell Observatory 1959

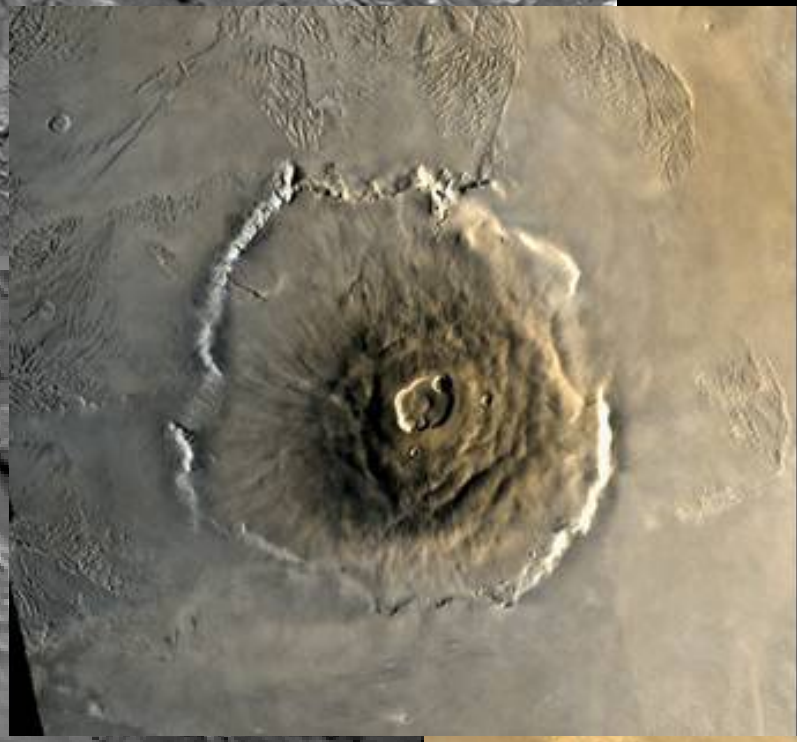
Lowell 1902

Mariner 4 Images – 1964 Technology

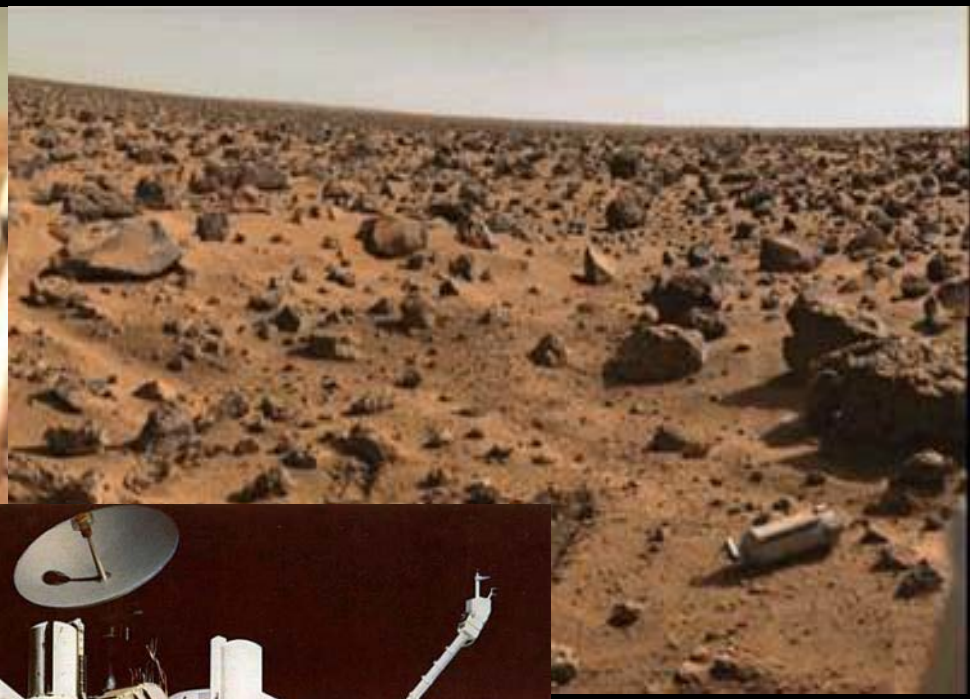


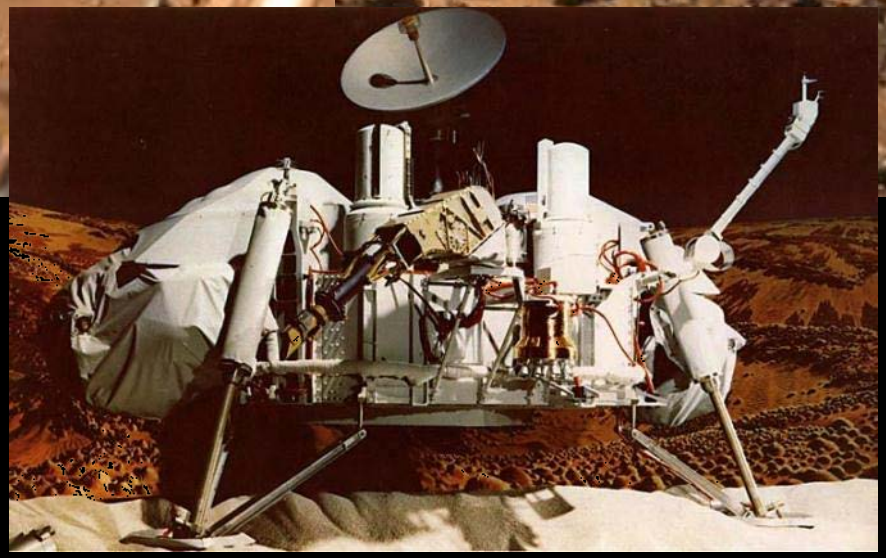
Viking Orbiter Images – 1976





Mars Viking Landers 1 & 2 (1976-82)





- Cameras (2)
- GC/MS
- XRF
- Biology experiments
  - Gas Exchange
  - Labelled Release
  - Pyrolytic Release
- Seismometer
- Physical and magnetic properties
- Meteorology (P & T)

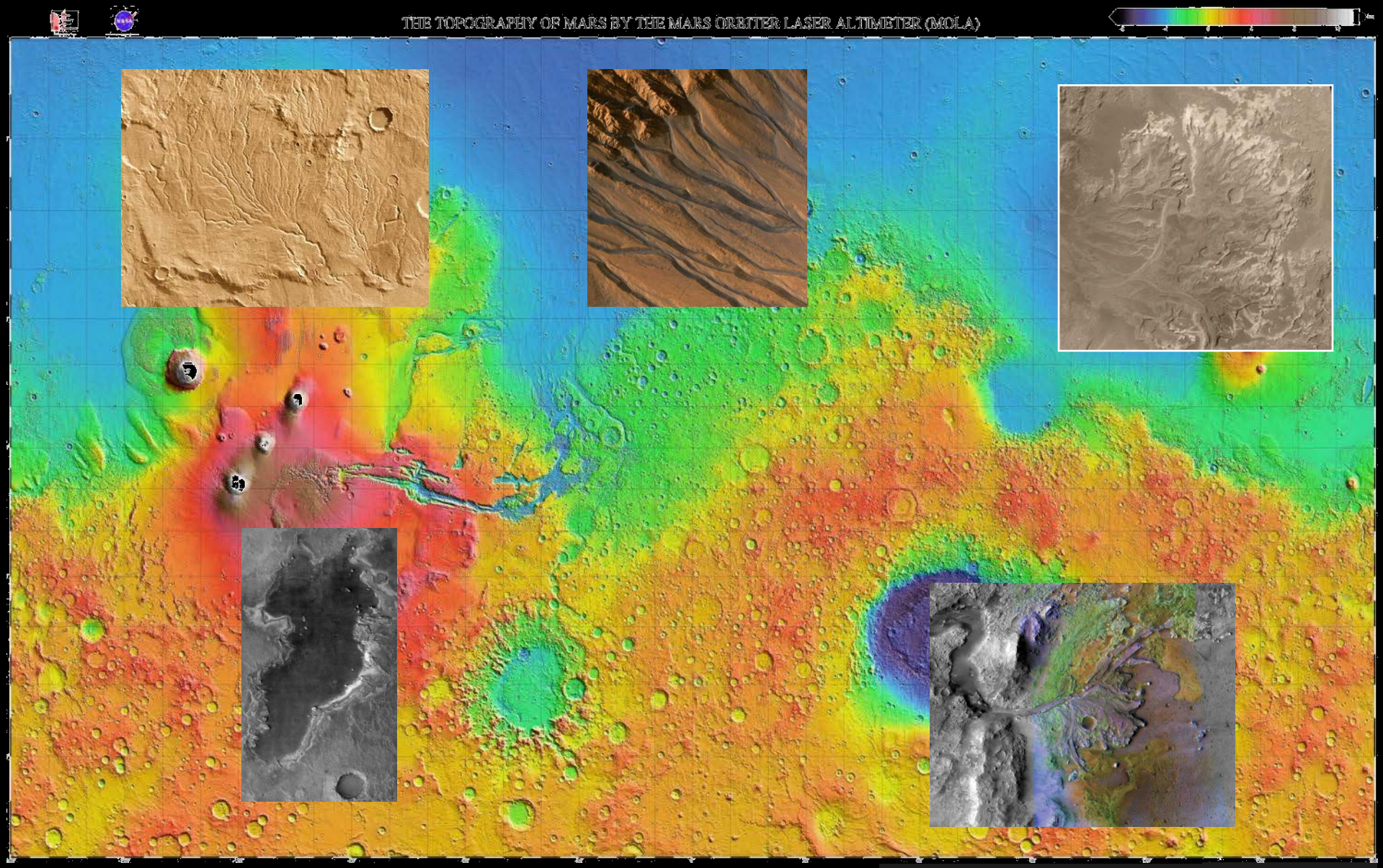
- Biology experiments (positive - confounded by geochemistry?)
- GC/MS (no organics – confounded by geochemistry?)

Was Mars Ever Warm & Wet?

WATER

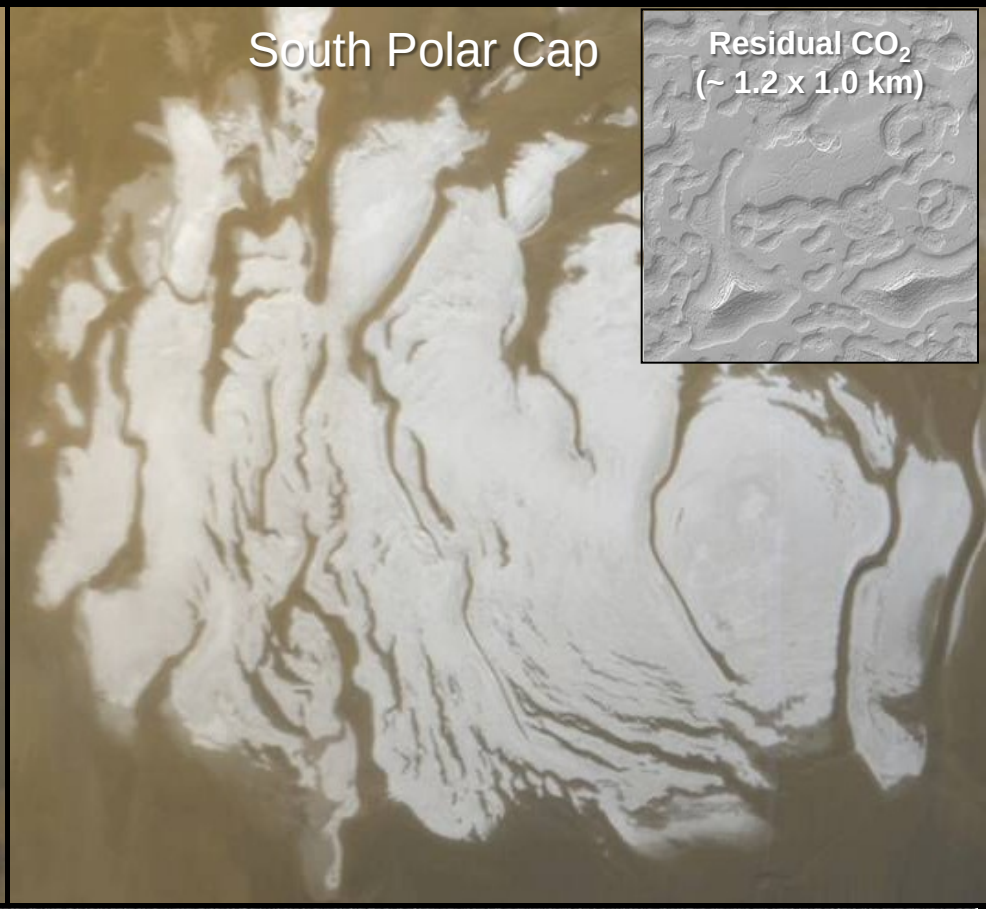
- Did Mars have an ocean?
- For how long?
- Where did the water go?
- What happened to the atmosphere?

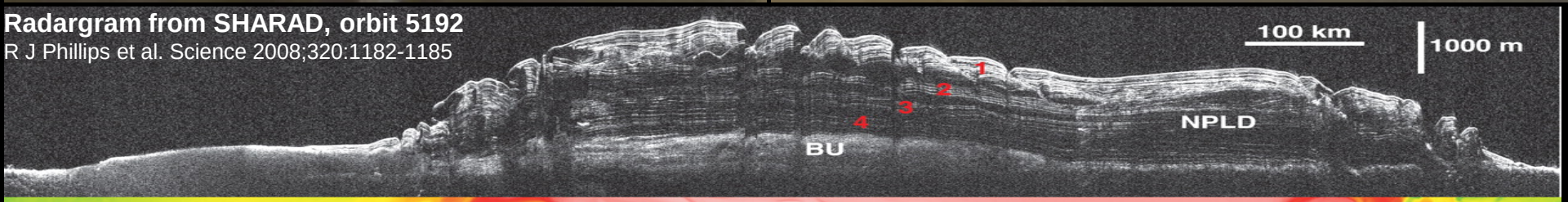
Liquid H_2O – Ancient & Recent? Modern?



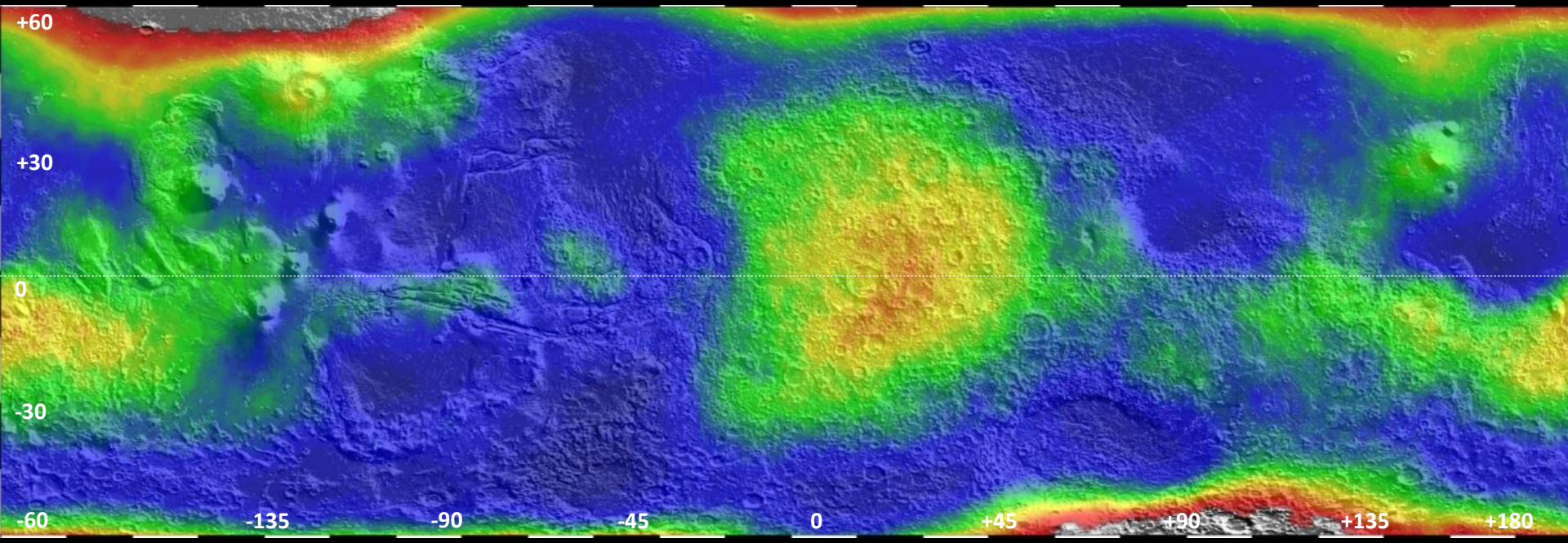
Highlands Coastal Lowlands

Mars' Polar Ice Caps

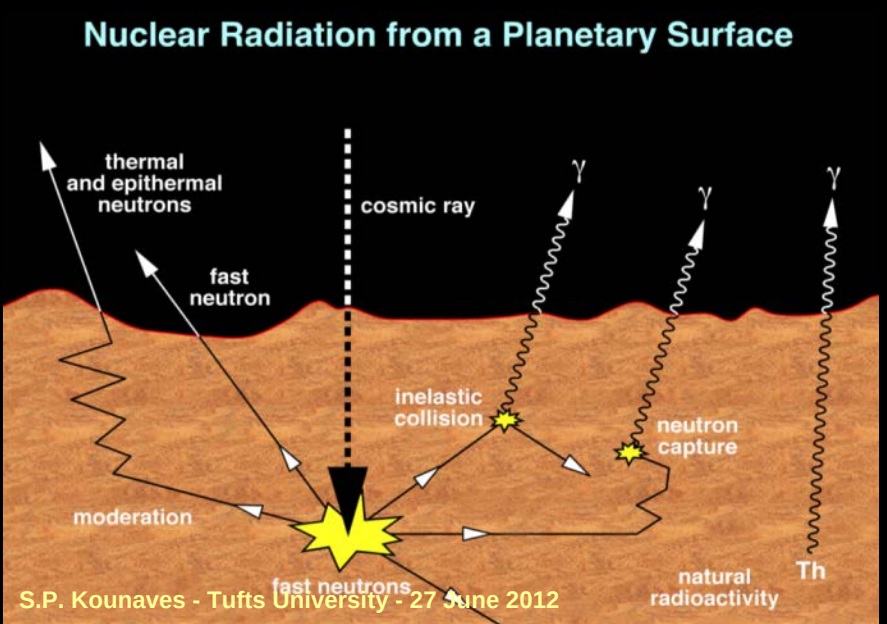


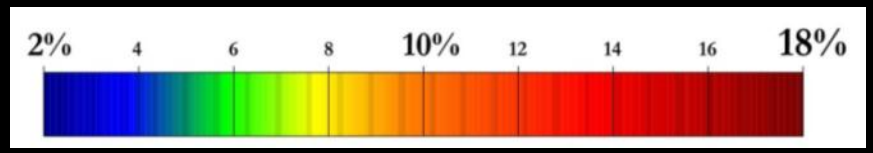


Mars Odyssey - Subsurface Water



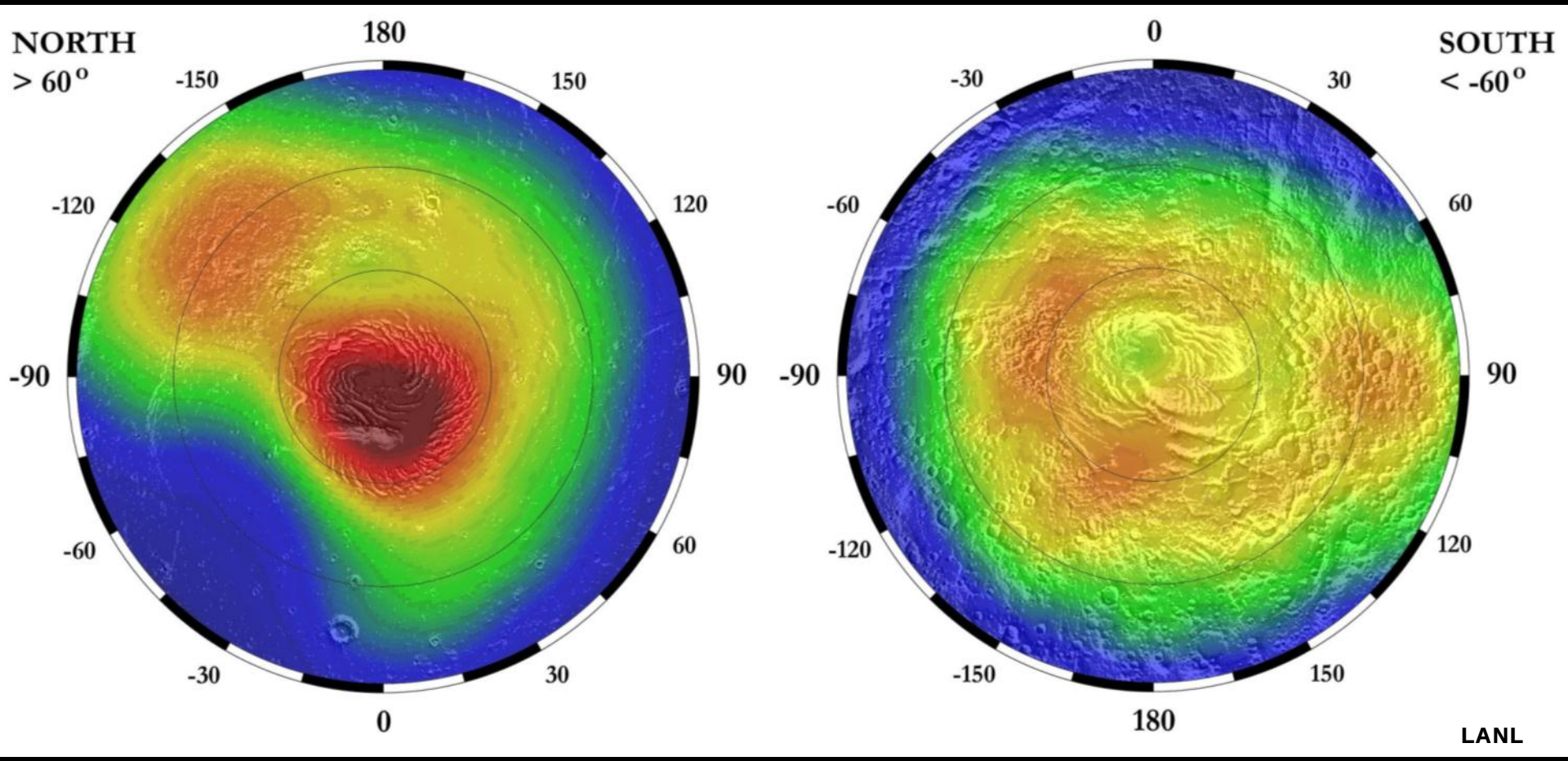
LANL

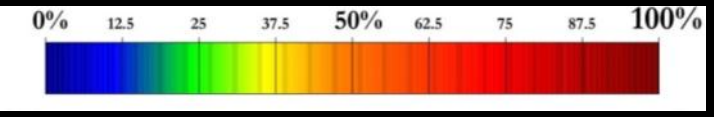




Hydrogen abundance as H_2O-equivalent mass % determined from epithermal neutron counting rates using the *Gamma Ray Spectrometer (GRS)* on the Mars Odyssey Orbiter (2002-03).

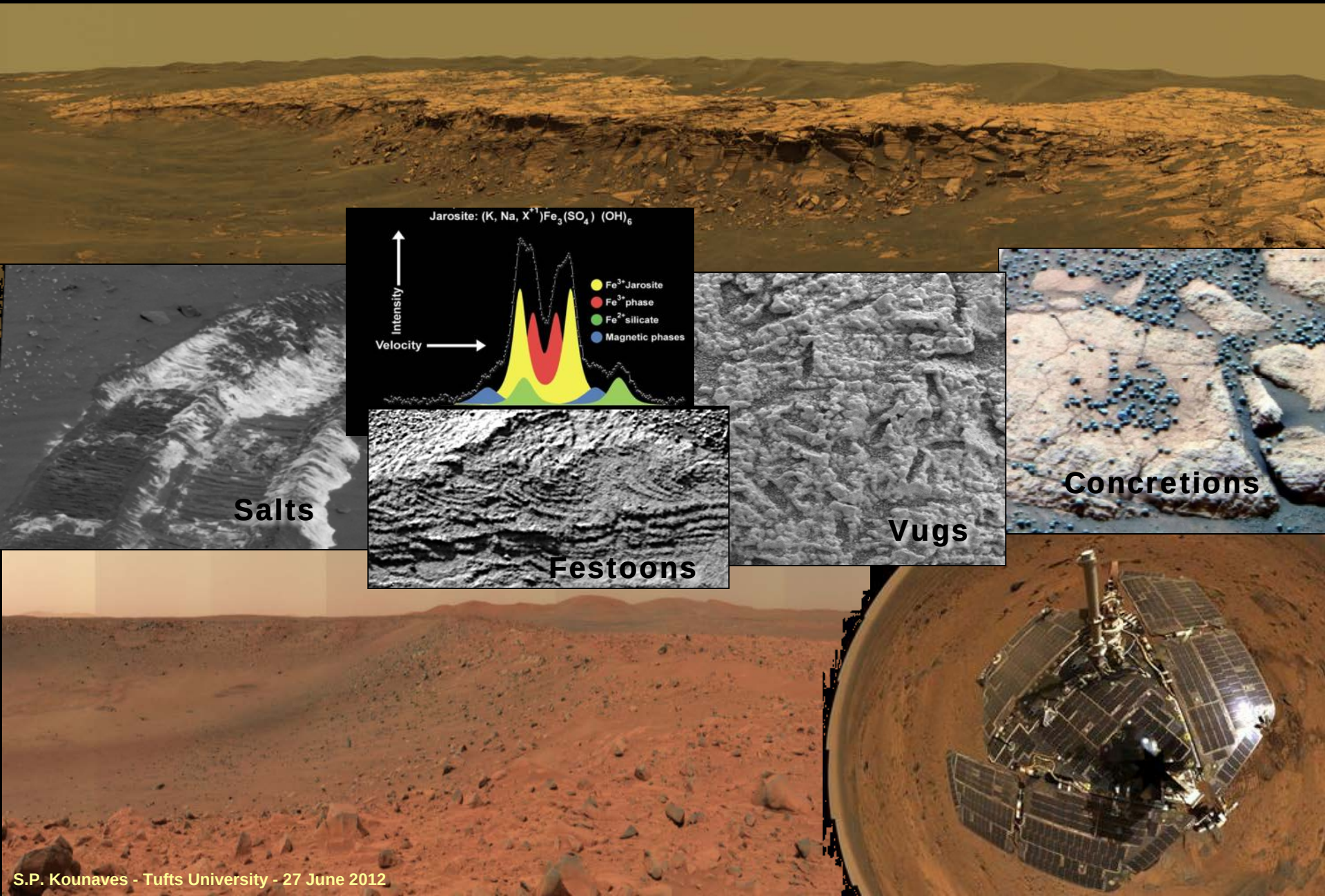
Mars Odyssey – Polar Subsurface Water





Hydrogen abundance as H_2O-equivalent mass % for the north & south polar regions. (February 2002 to April 2003).

MER - *Spirit* 2004-10 & *Opportunity* 2004 -?



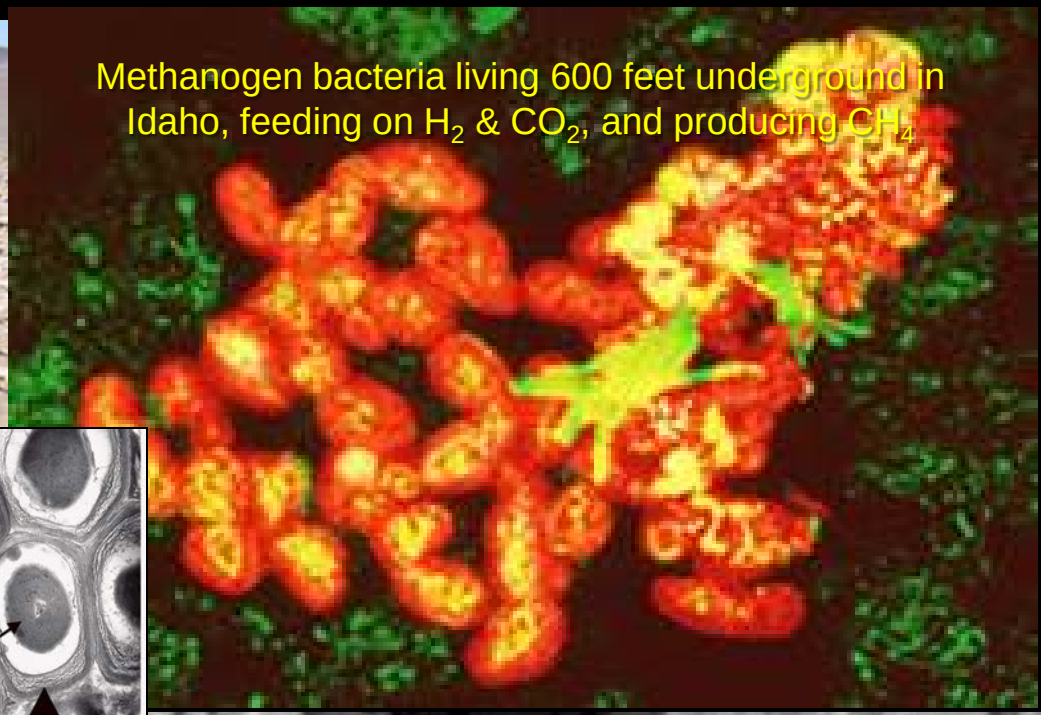
Was There Ever Life on Mars?

LIFE

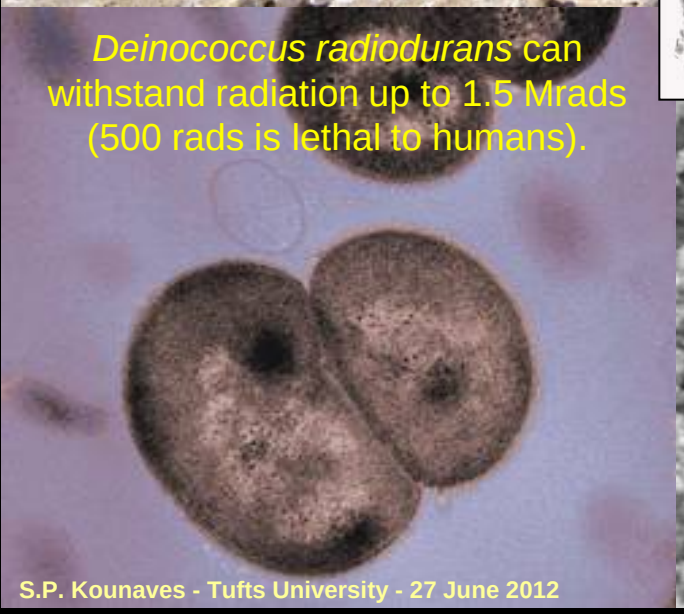
- Did life on Mars have a chance to develop and evolve?
- Why do we think it might have?
- Might its still be there?

Why Look for Life on Mars?

Salt rocks in the Atacama Desert (Chile) colonized just below the surface by the endoliths *chroococcidiopsis cyanobacteria*.



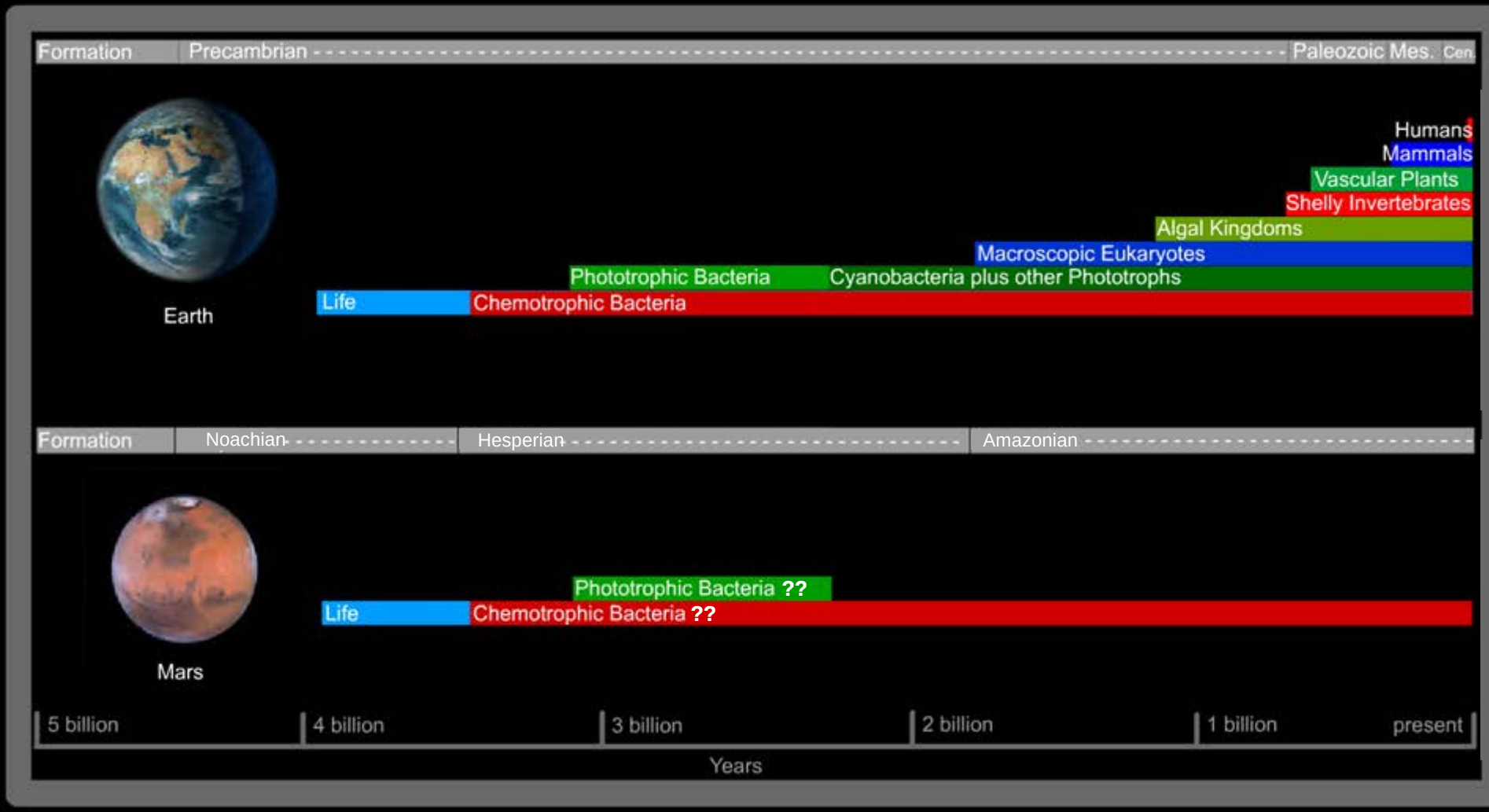
Methanogen bacteria living 600 feet underground in Idaho, feeding on H_2 & CO_2, and producing CH_4.

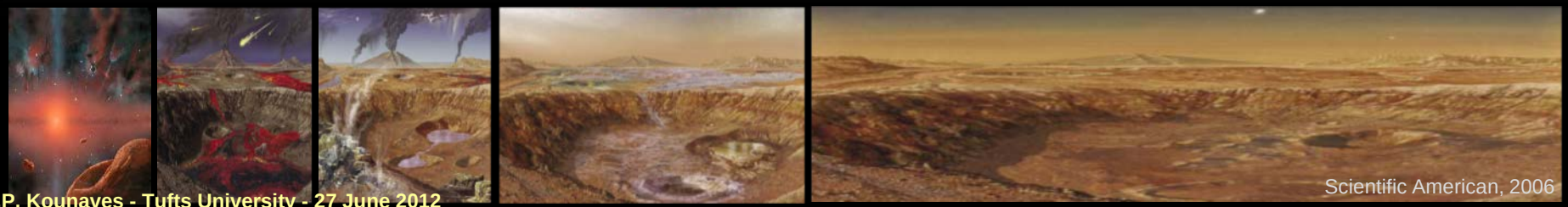


Deinococcus radiodurans can withstand radiation up to 1.5 Mrads (500 rads is lethal to humans).

Candidatus desulforudis bacteria living 3 km deep in South African gold mine @ T=60°C & pH = 9.3.

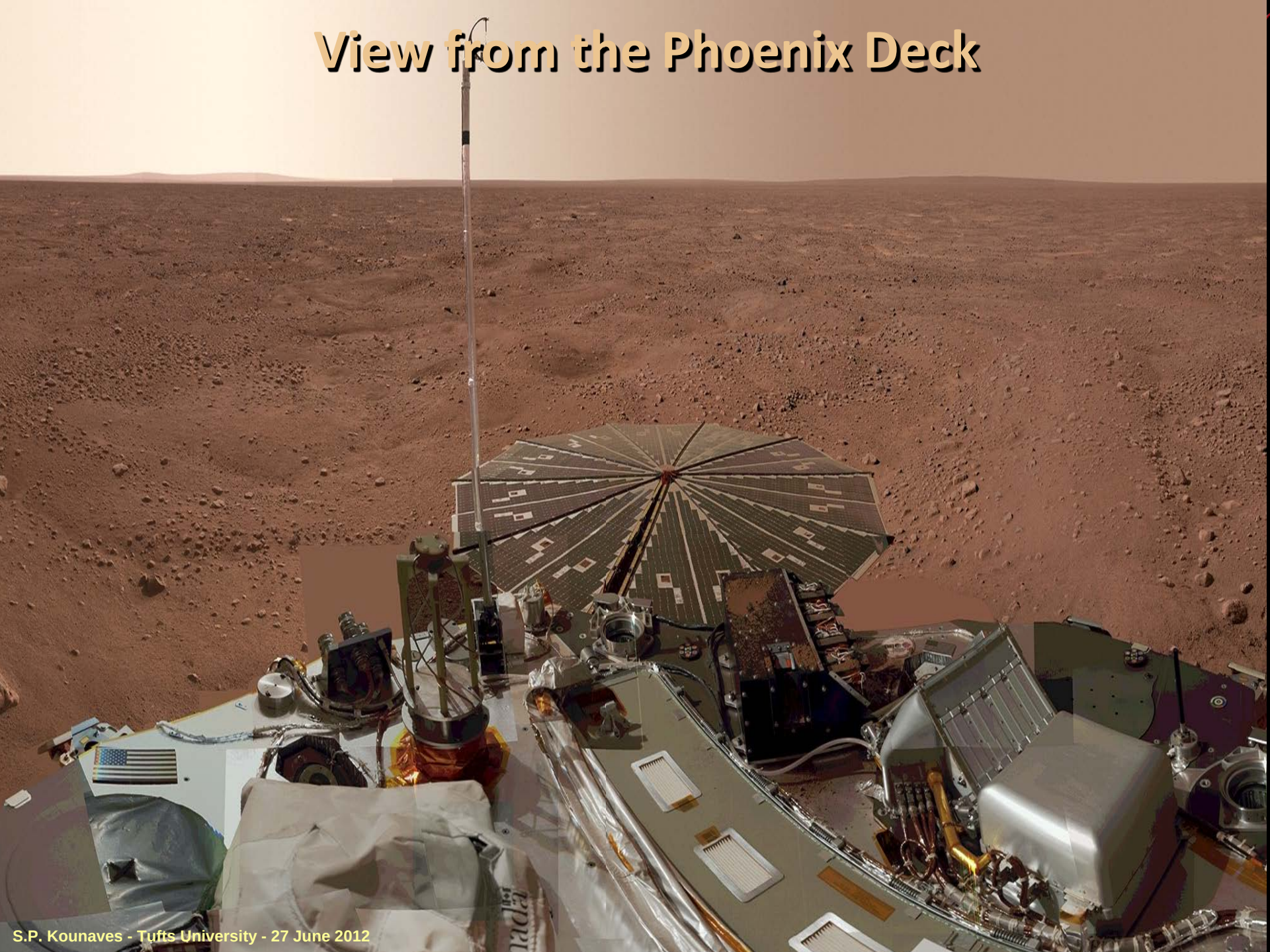
Evolution of Life on Earth & Mars?





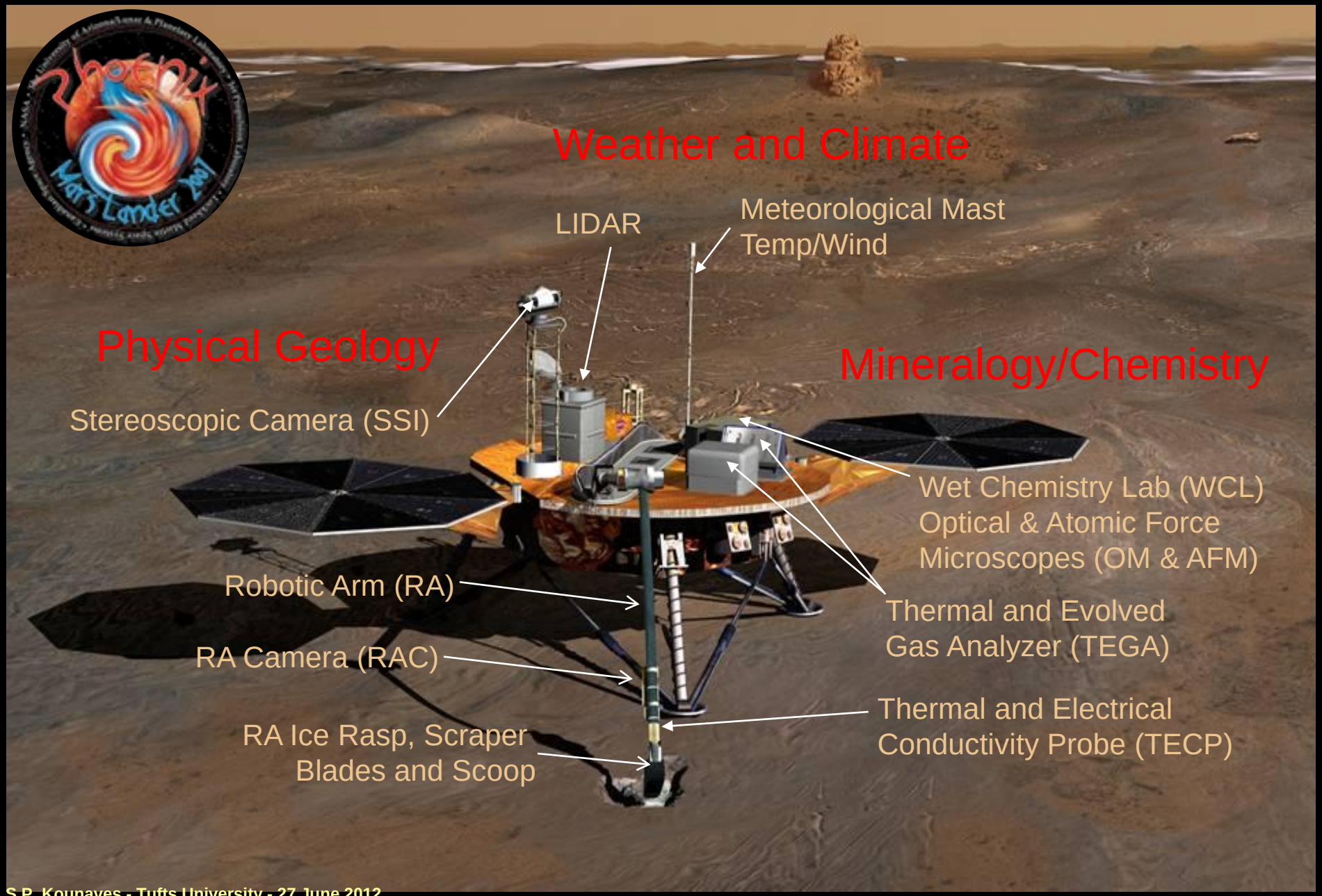
Scientific American, 2006

View from the Phoenix Deck

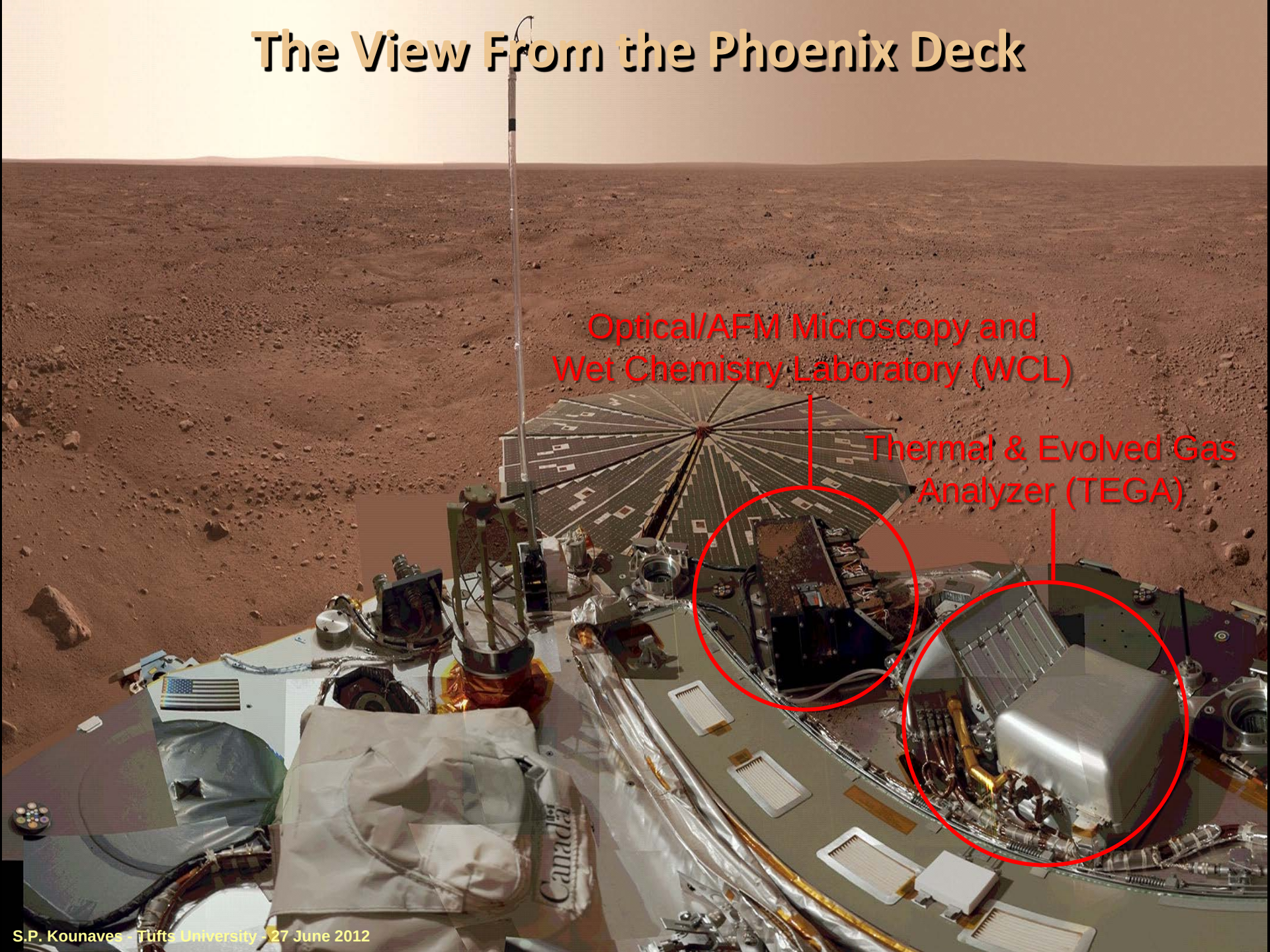


An Ice-Rink Under the Martian Soil

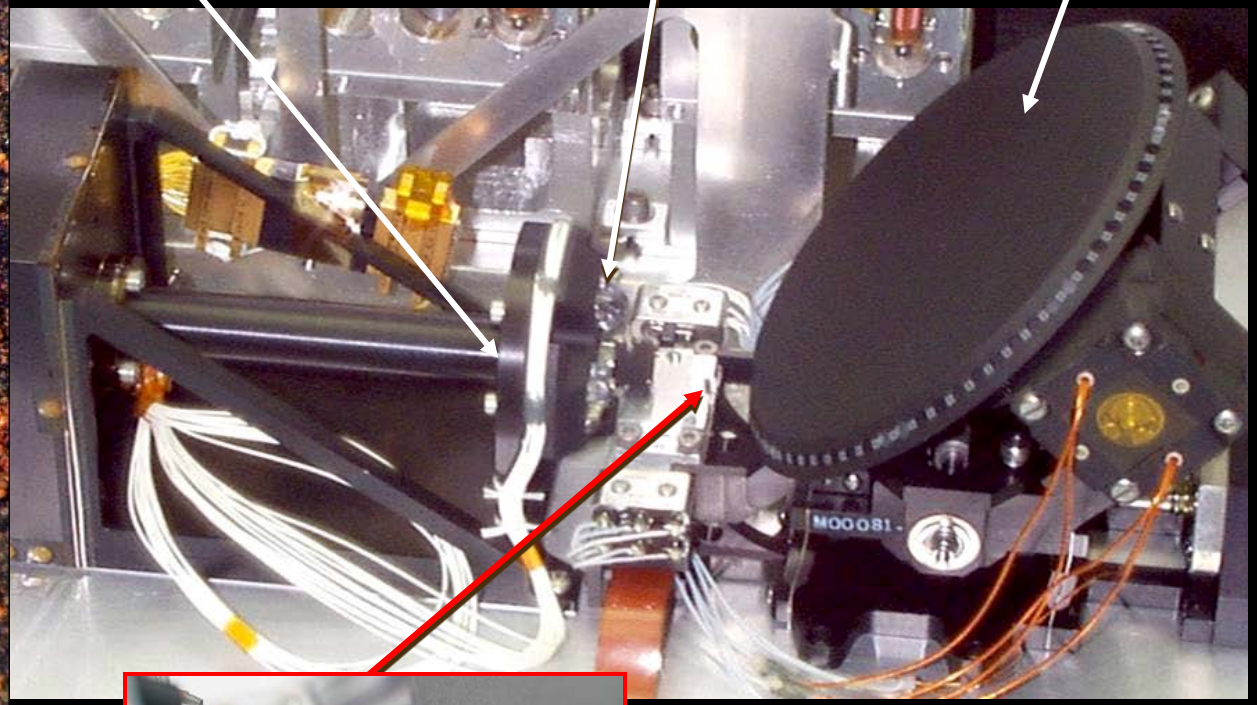
The 2007 Phoenix Mars Lander

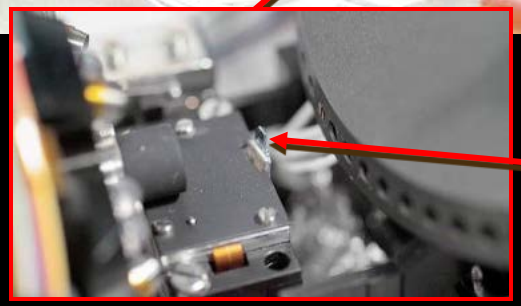


The View From the Phoenix Deck

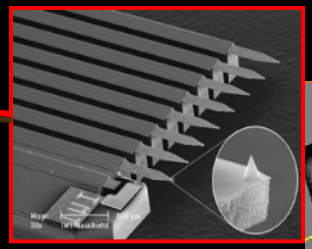


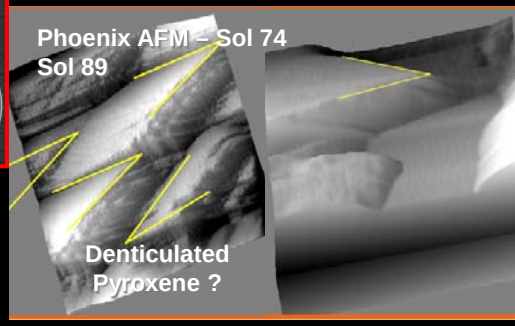
Optical (OM) & Atomic Force (AFM) Microscopes





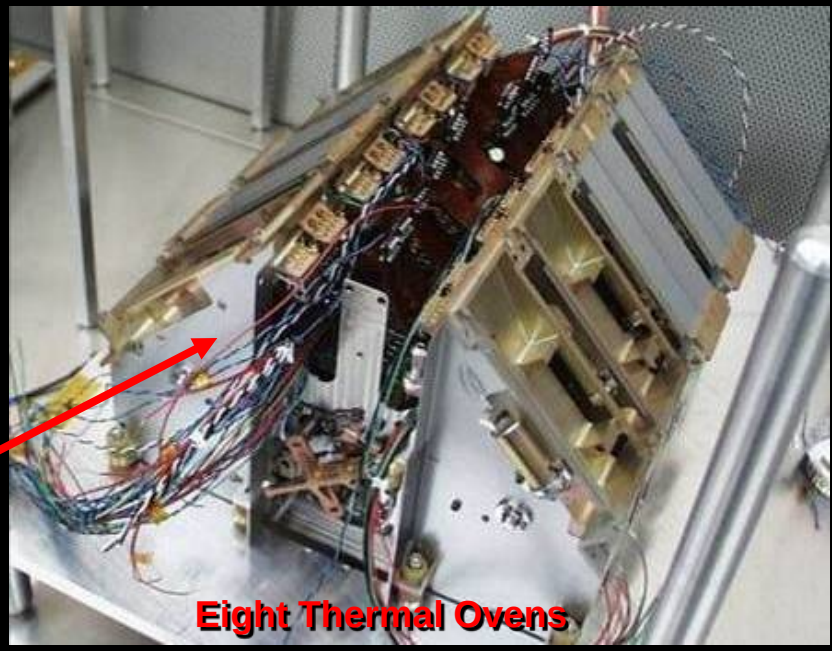
Atomic Force Microscope

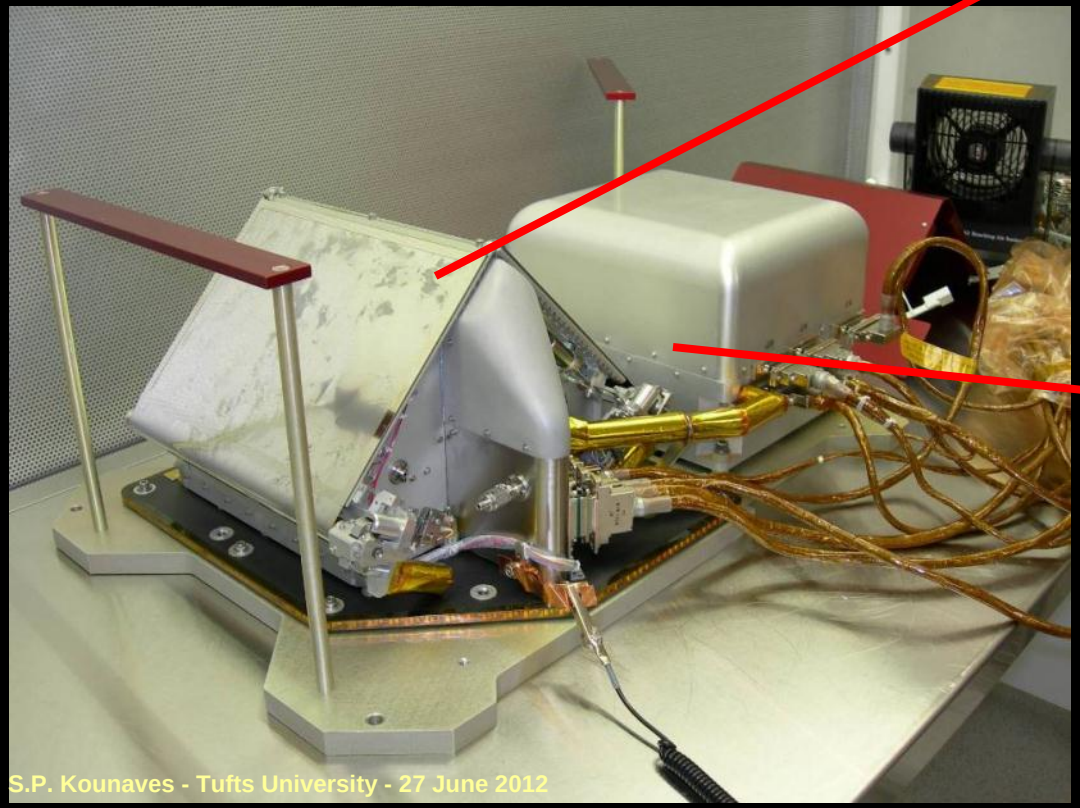


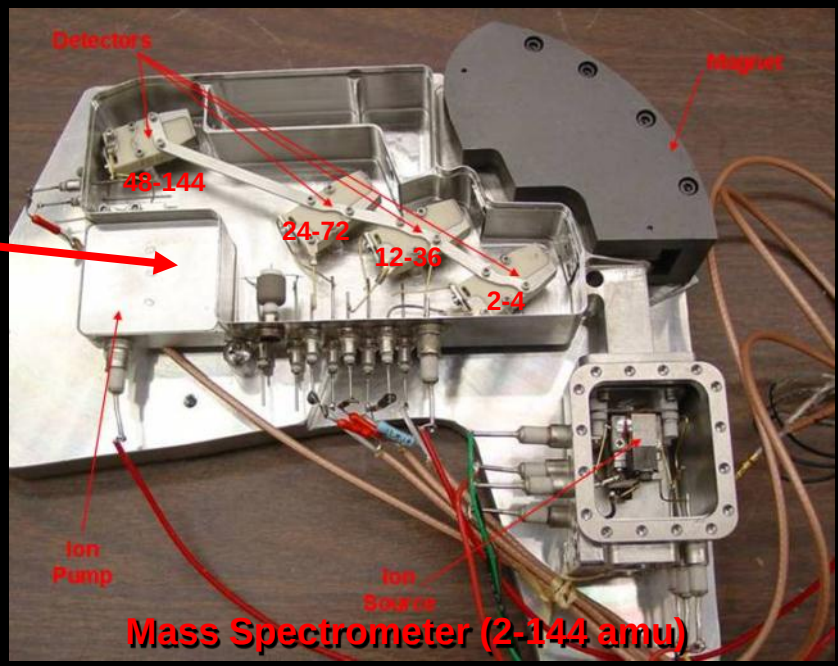


Thermal & Evolved Gas Analyzer (TEGA)

- Soil sample is sealed in 0.03 ml oven and heated slowly to 1000 °C to decompose.
- Heat is quantitatively monitored, looking for endothermic and exothermic phase transitions.
  - Temperature of phase transition identifies phase
  - Heat of reaction determines how much is present
- Generated gases are then carried to a magnetic sector mass spectrometer by 12 mbar N_2 carrier gas.

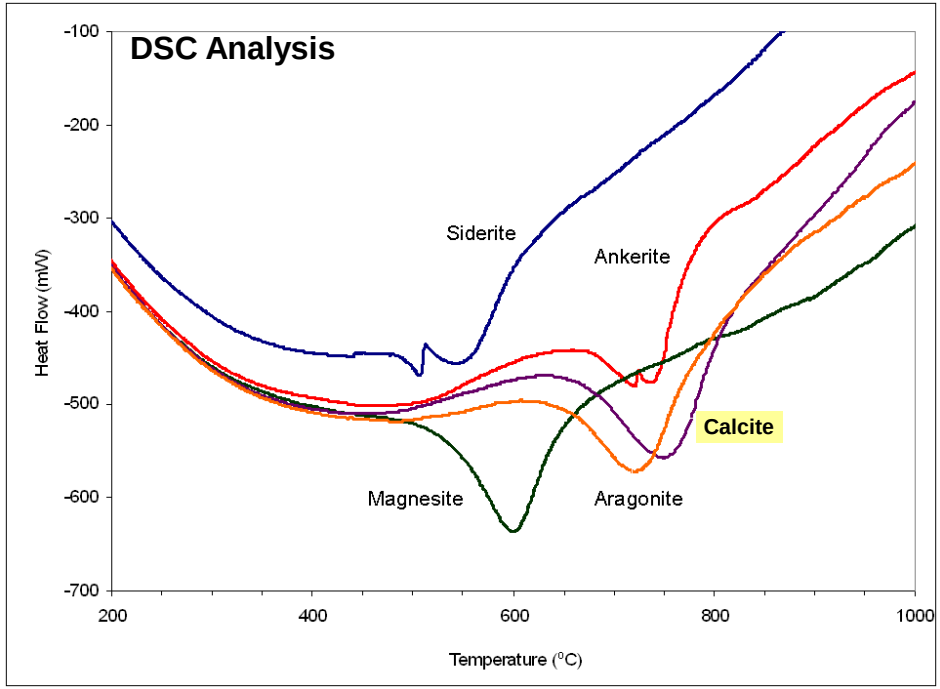


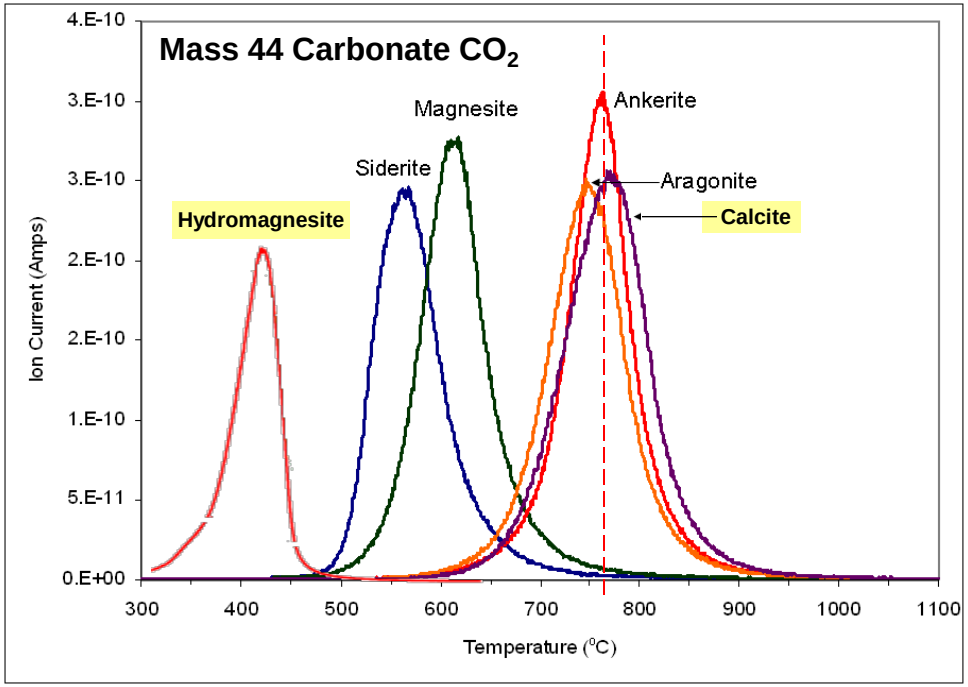




TEGA EQM Mineral Analysis (NASA-JSC)

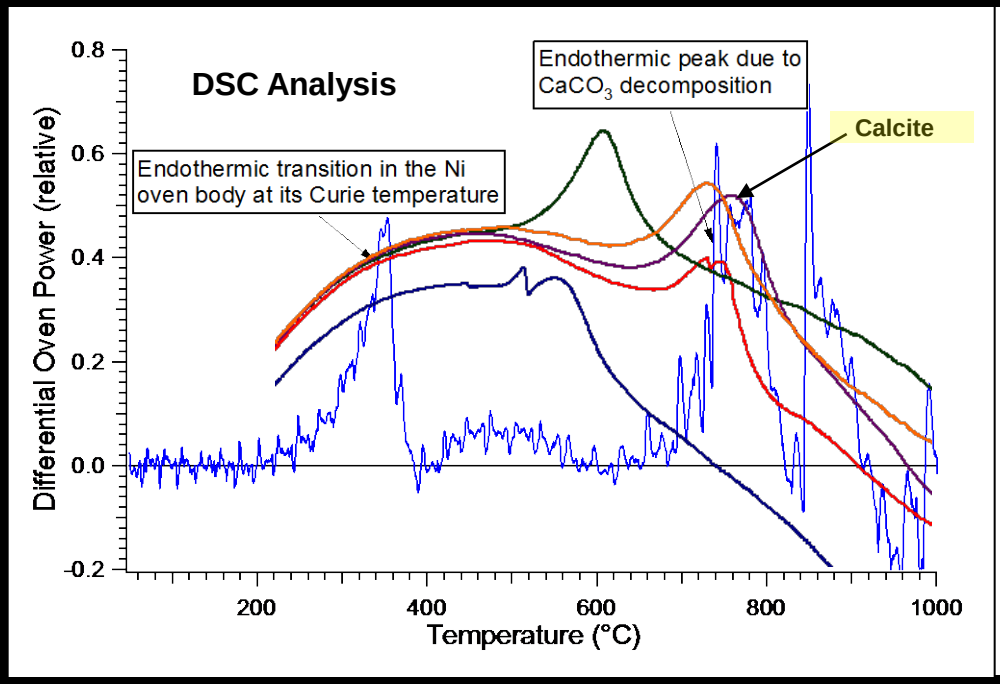
Carbonate	DSC Peaks	MS Peaks
Calcite ($CaCO_3$)	750°C	775°C
Magnesite ($MgCO_3$)	600°C	515°C
Hydromagnesite ($MgCO_3 \cdot H_2O$)	450°C	
Siderite ($Fe_{0.65}Mg_{0.35}CO_3$)	510 & 550°C	568°C
Ankerite ($Ca_{0.55}Mg_{0.40}Fe_{0.05}$)	730 & 740°C	760°C
Aragonite ($CaCO_3$)	720°C	750°C



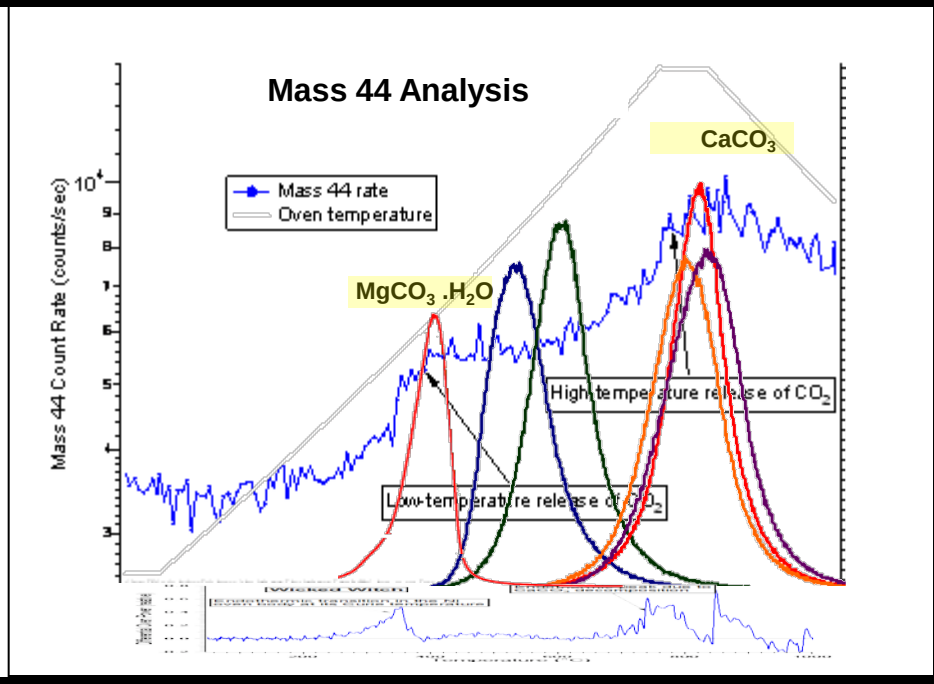


TEGA Analysis of Wicked Witch Sample

Endothermic power transition for Wicked Witch with an onset at about 680 °C due to $CaCO_3$

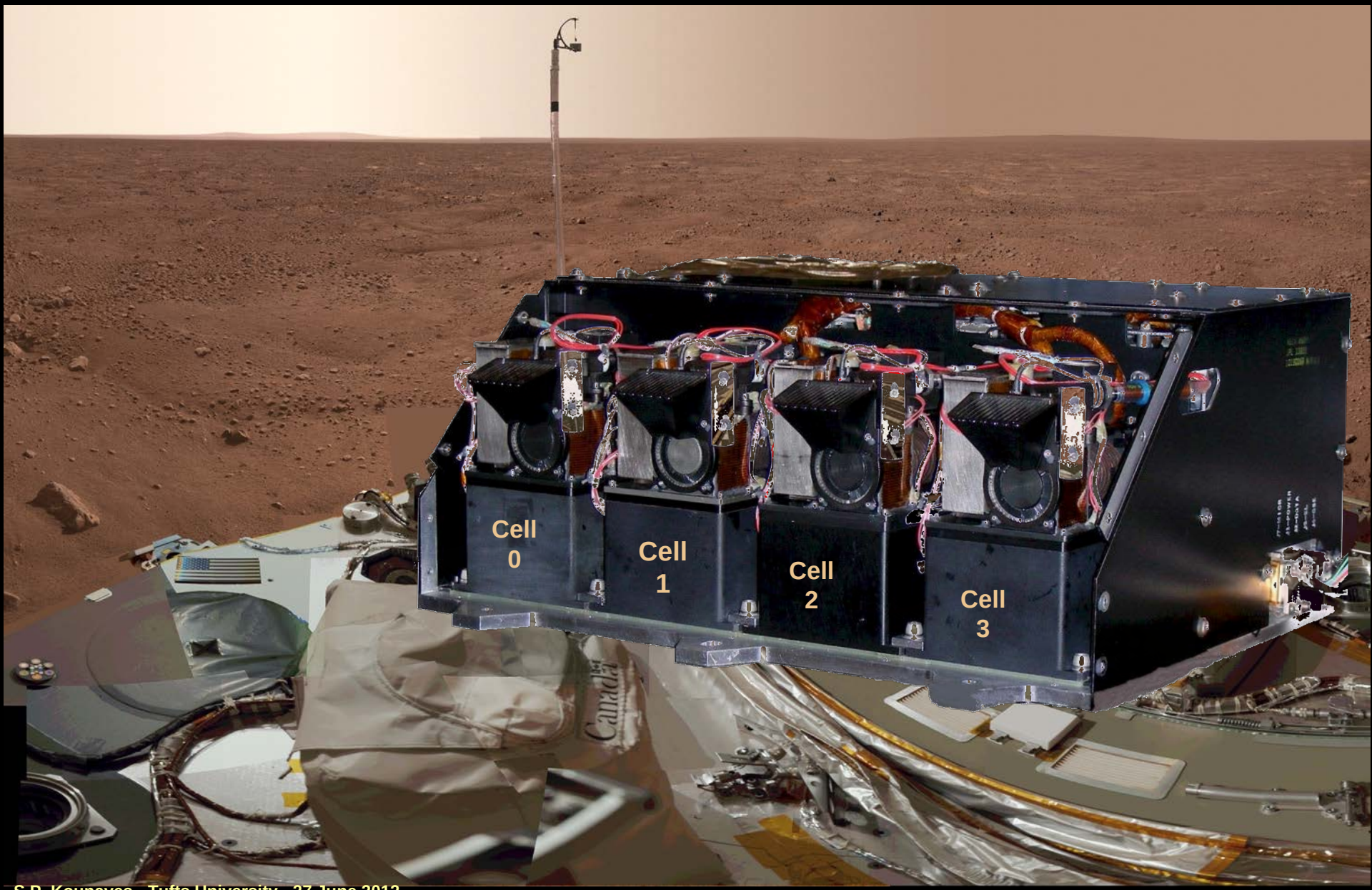


Mass 44 (CO_2) vs. temperature for Wicked Witch. Two distinct releases of CO_2 are observed.

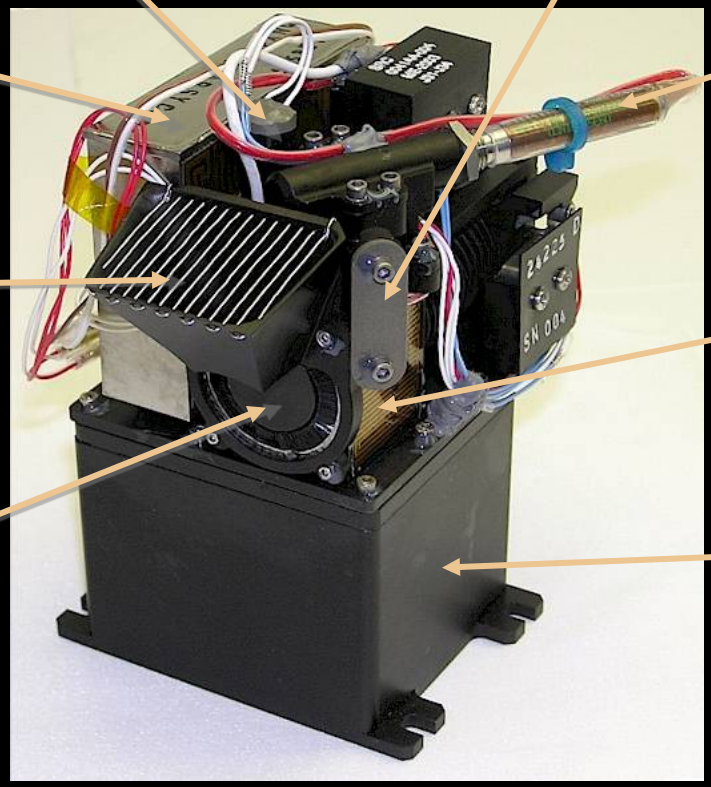


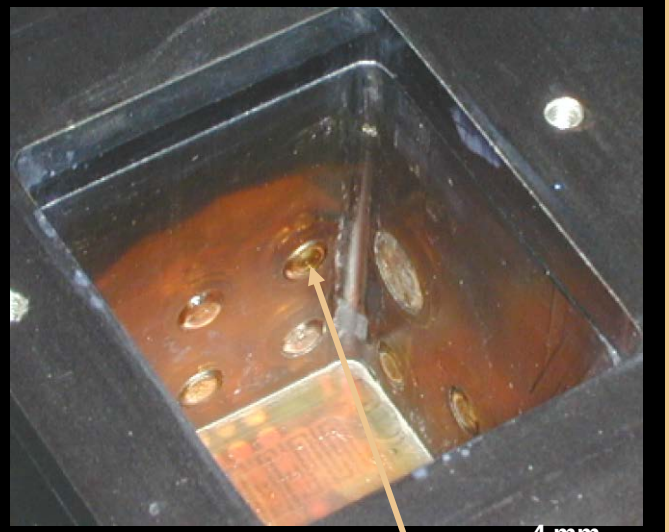
The DSC 700°C endotherm is most likely due to $CaCO_3$. The EGA peak at about 400°C is likely due to Fe, Mg, or organics while that at about 775°C is due to calcite. Enthalpy calculations indicate calcite in the soil at a level of 3 to 5% (wt).

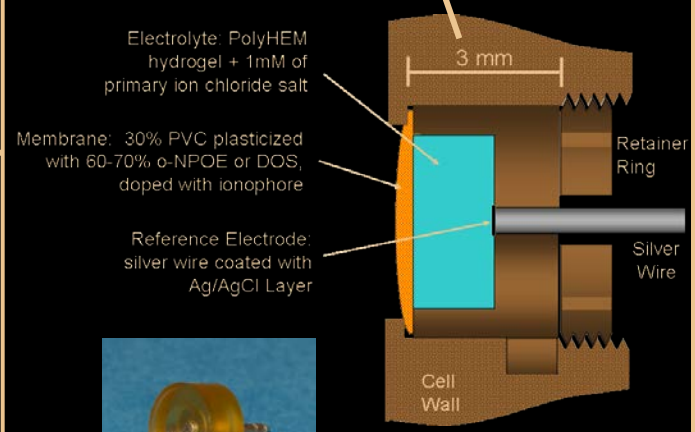
View of the WCL from the Phoenix Deck



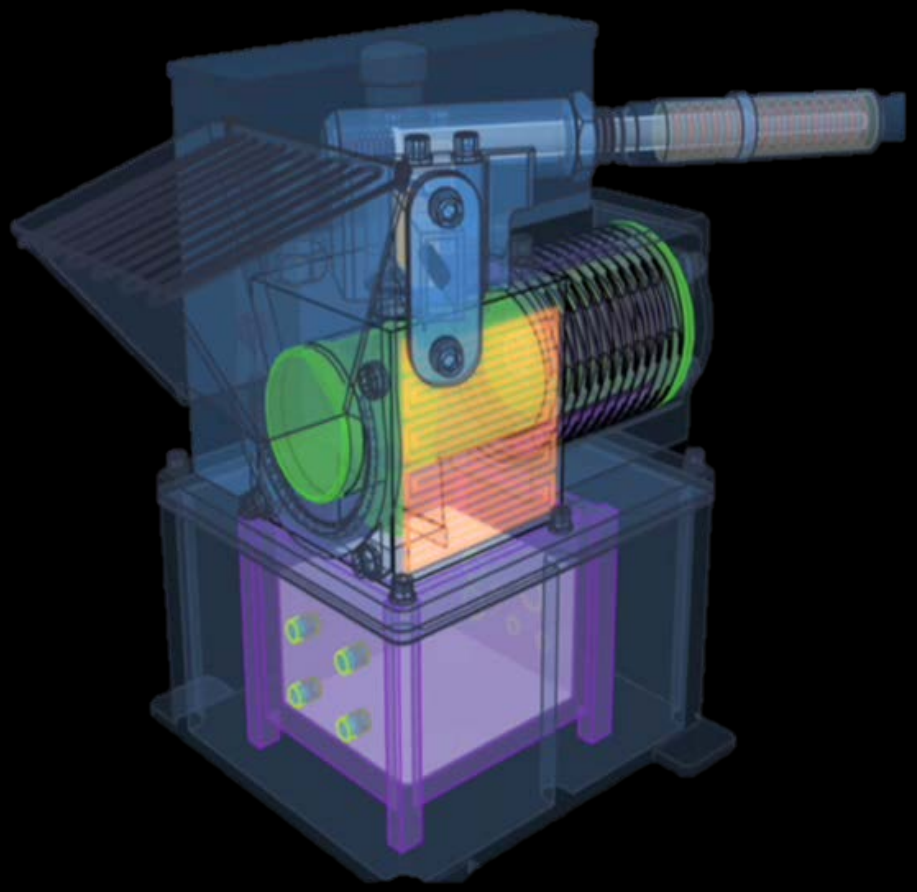
Wet Chemistry Lab (WCL) Components





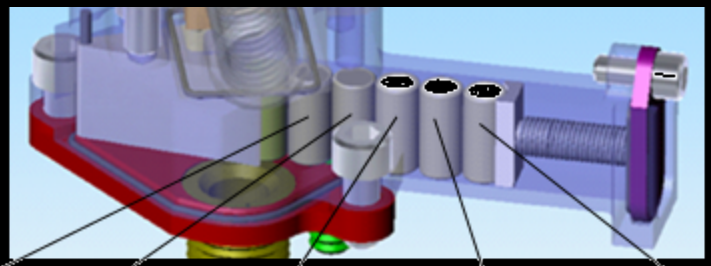


The WCL Beaker Assembly and Sensors



Sensor	Type/Composition
Ammonium (NH_4^+)	PVC, Nonactin, DOS, NaTPB
Barium (Ba^{2+})	PVC, Ba Iphor-I, o-NPOE, KTClPB
Bromide (Br^-)	Solid Pellet Crystal
Calcium (Ca^{2+})	PVC, ETH-1001, o-NPOE,NaTPB
Chloride (Cl^-)	Solid Pellet Crystal
Iodide (I^-)	Solid Pellet Crystal
Hydrogen(H^+)(2)	PVC, ETH-2418, o-NPOE, KTClPB
Lithium (2) REF	PVC, Li Iphor-VI, o-NPOE, KTClPB
Magnesium (Mg^{2+})	PVC, ETH-7025, o-NPOE, KTClPB
Nitrate (NO_3^-)	PVC, Ion Exchanger
Potassium (K^+)	PVC, Valinomycin, DOS, NaTPB
Sodium (Na^+)	PVC, Na Iphor-VI, o-NPOE, KTClPB
pH	Iridium disk coated with IrO_2
Conductivity	2-electrode (carbon disk/ring)
CV (Redox)	0.25mm Au disk electrode
CP (2) (Halides)	1-mm Ag disk electrode

The Wet Chemistry Experiment



≤1cc Soil

Leaching Solution (25mL)

D.I. water + 1.0×10^{-5} M NH_4^+, Na^+, K^+, Ba^{2+}, Ca^{2+}, Mg^{2+}, HCO_3^-, 5.0×10^{-5} M Cl^-, 1.03×10^{-3} M NO_3^-, 1.0×10^{-3} M Li^+

pH 5.0 @ 5°C

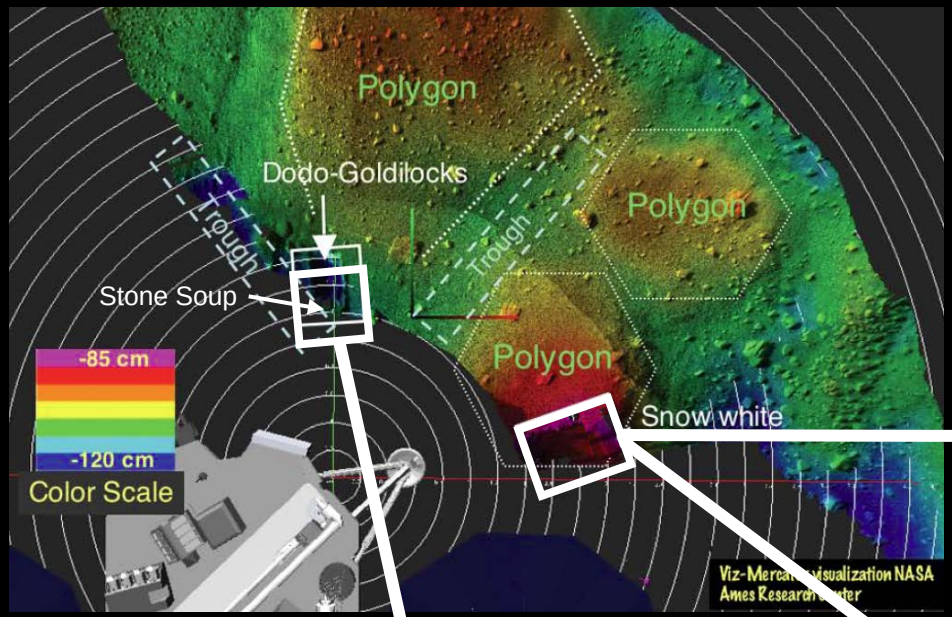
Reagent Additions

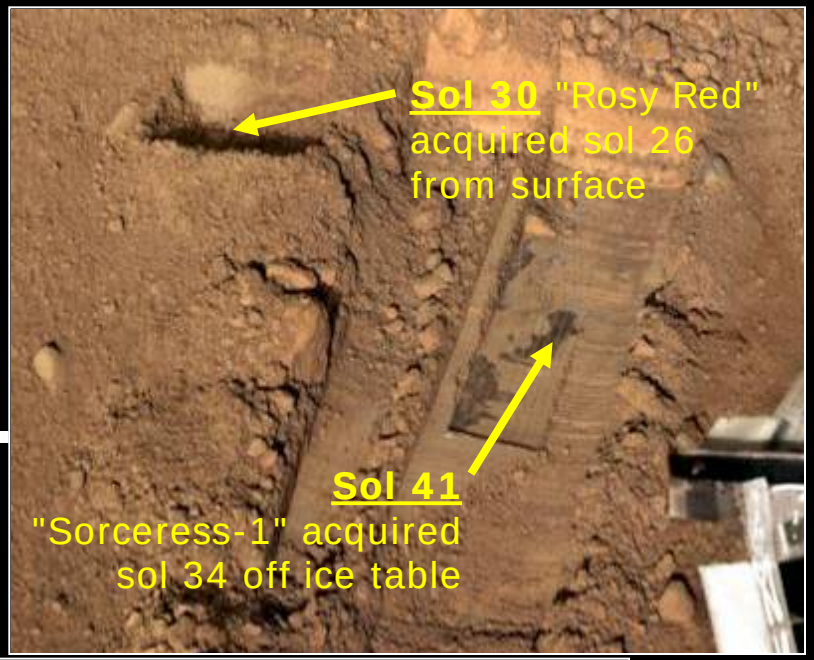
1st Crucible Calibrant	2nd Crucible Acid	3rd Crucible Barium	4th Crucible Barium	5th Crucible Barium
Addition to give: 3.0×10^{-5} M all cations + HCO_3^-, 1.5×10^{-4} M Cl^-, 1.09×10^{-3} M NO_3^-; pH ~ 6-7 @ 5°C	0.004g NBA (2-nitrobenzoic acid); pH → ?	0.1g $BaCl_2$ to give: 0.02 M Ba^{2+}; 1-5% $SO_4^=$ (1g sample)	0.1g $BaCl_2$ to give: 0.04 M Ba^{2+}; 5-10% $SO_4^=$ (1g sample)	0.1g $BaCl_2$ to give: 0.06 M Ba^{2+}; 10-15% $SO_4^=$ (1g sample)

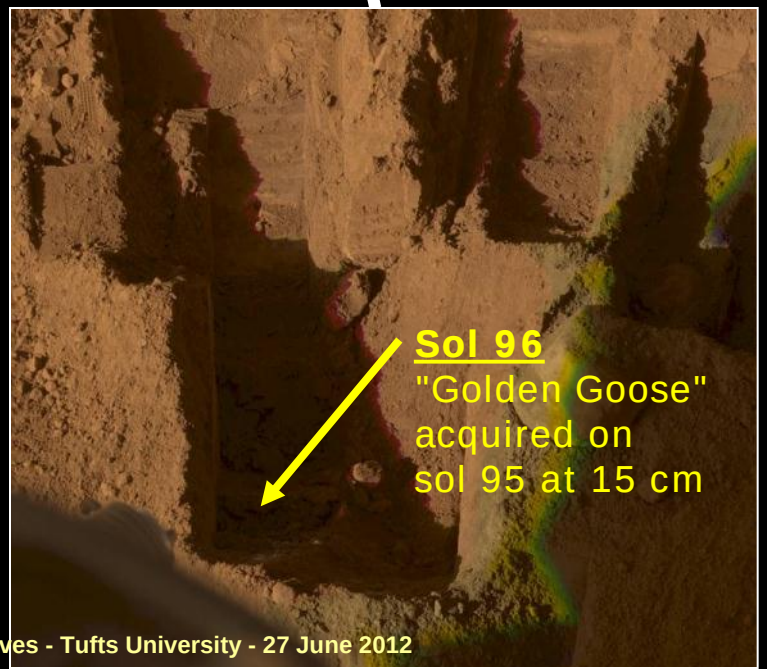
Sol A: Calibrate & measure dissolved salts

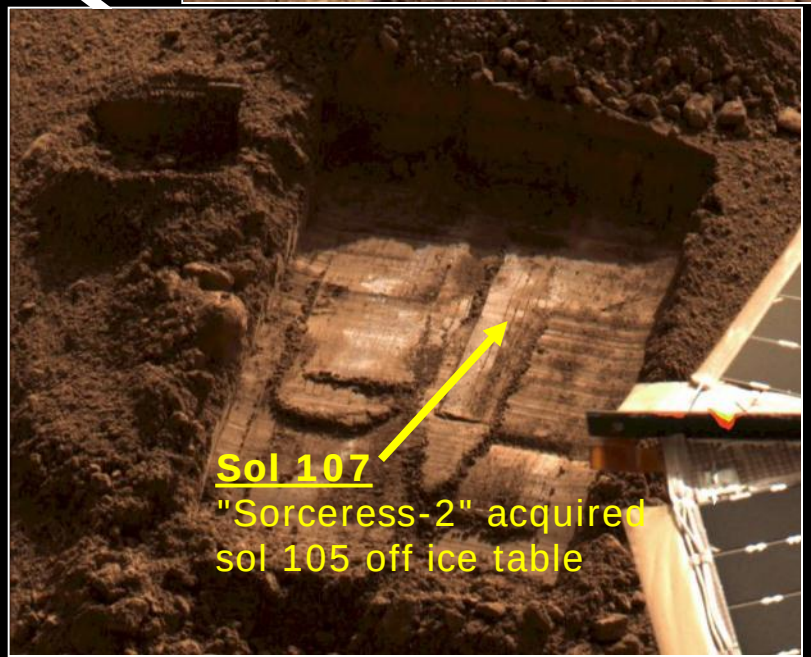
Sol B: ΔpH, continued solvation, and sulfate analysis via Ba^{2+} titration

Four WCL Sample Locations

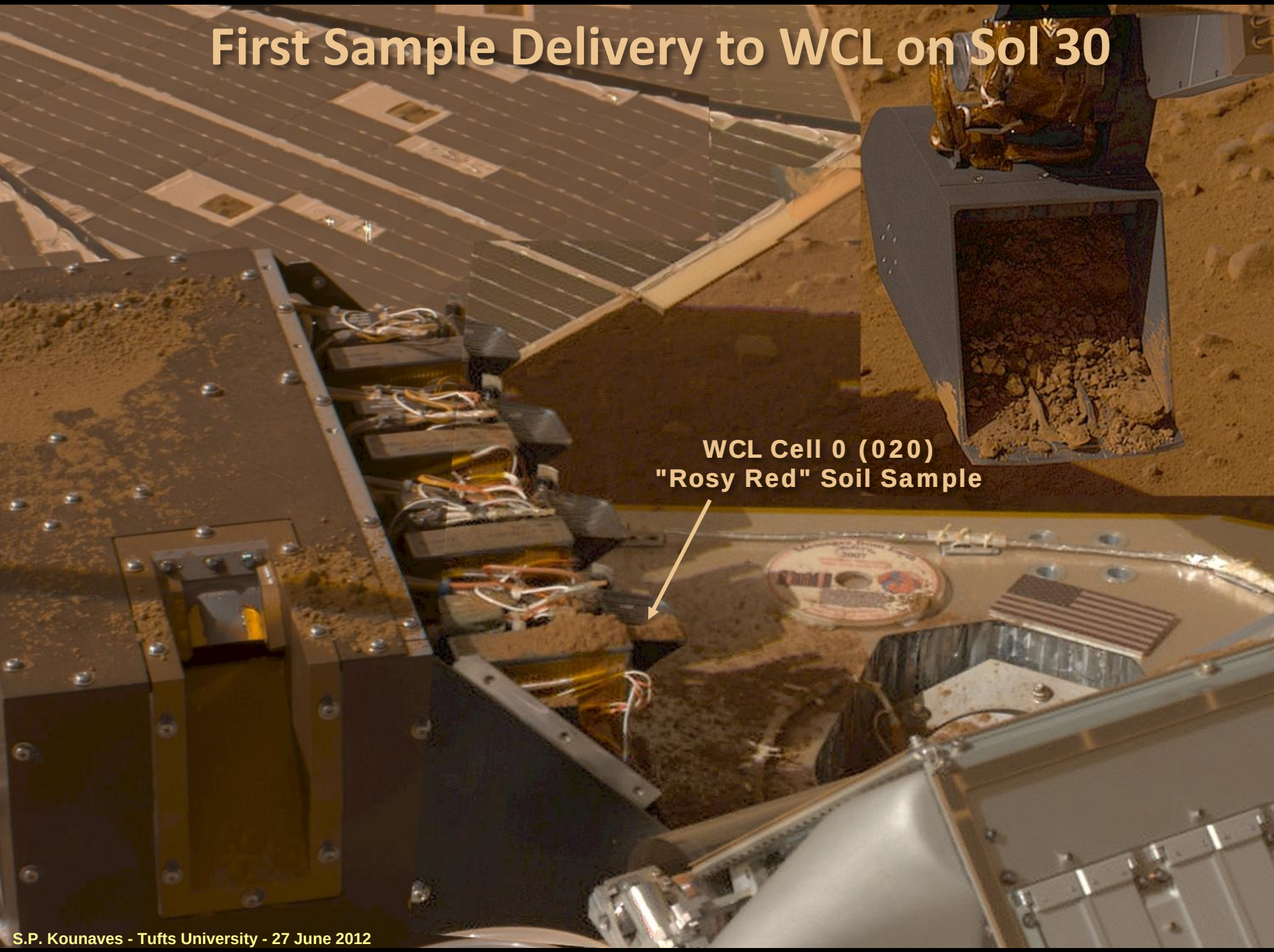






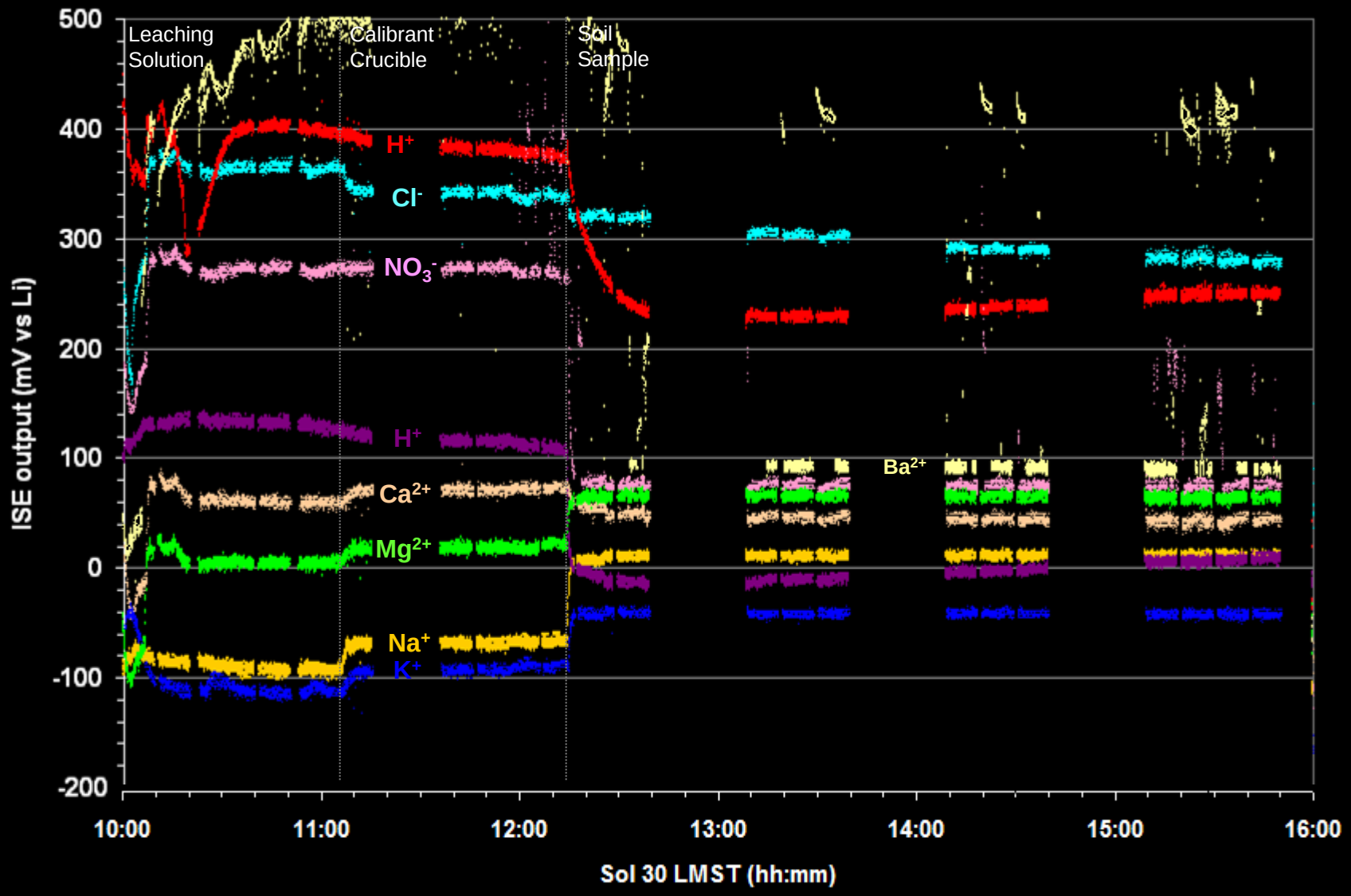


First Sample Delivery to WCL on Sol 30



WCL Analysis of Rosy Red, Sol 30

Increase = positive for cations, Increase = negative for anions



WCL Analysis of Rosy Red, Sol 30

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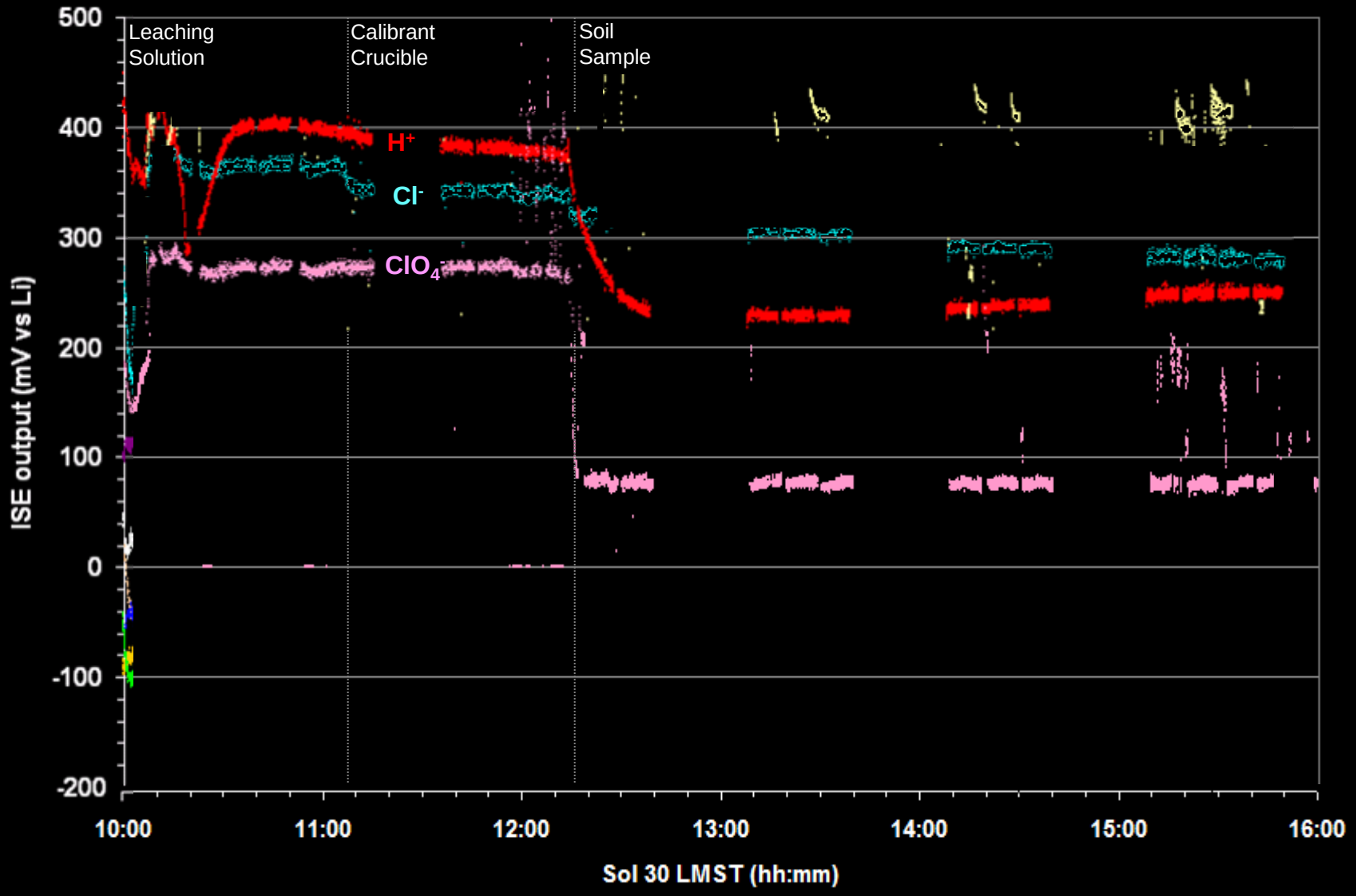
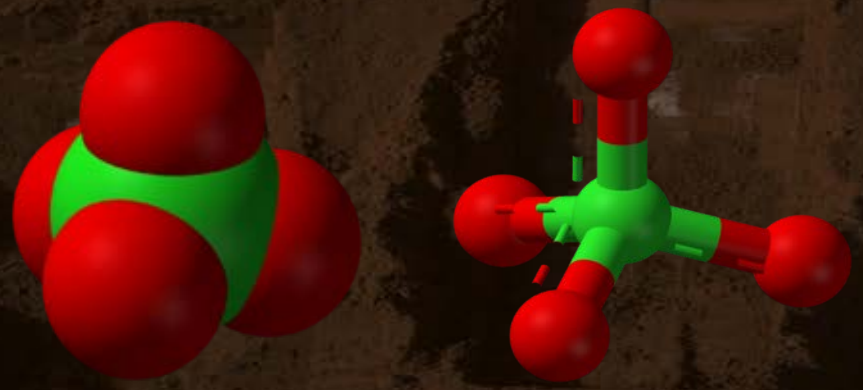


What is Perchlorate (ClO_4^-)?

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



Anions:

ClO_4^-	per<u>chlor</u>ate
ClO_3^-	<u>chlor</u>ate
ClO_2^-	<u>chlor</u>ite
ClO^-	hypo<u>chlor</u>ite
Cl^-	<u>chlor</u>ide

Implications of 0.6% ClO_4^- in the Soil

- Viking 1/2 GC-MS and Phoenix TEGA detected no organics.
- Could ClO_4^- in the soil have prevented detection of organics?
- Even if shown that ClO_4^- <u>can</u> 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.

Soluble Composition of Martian Soil

A "habitable" soil?

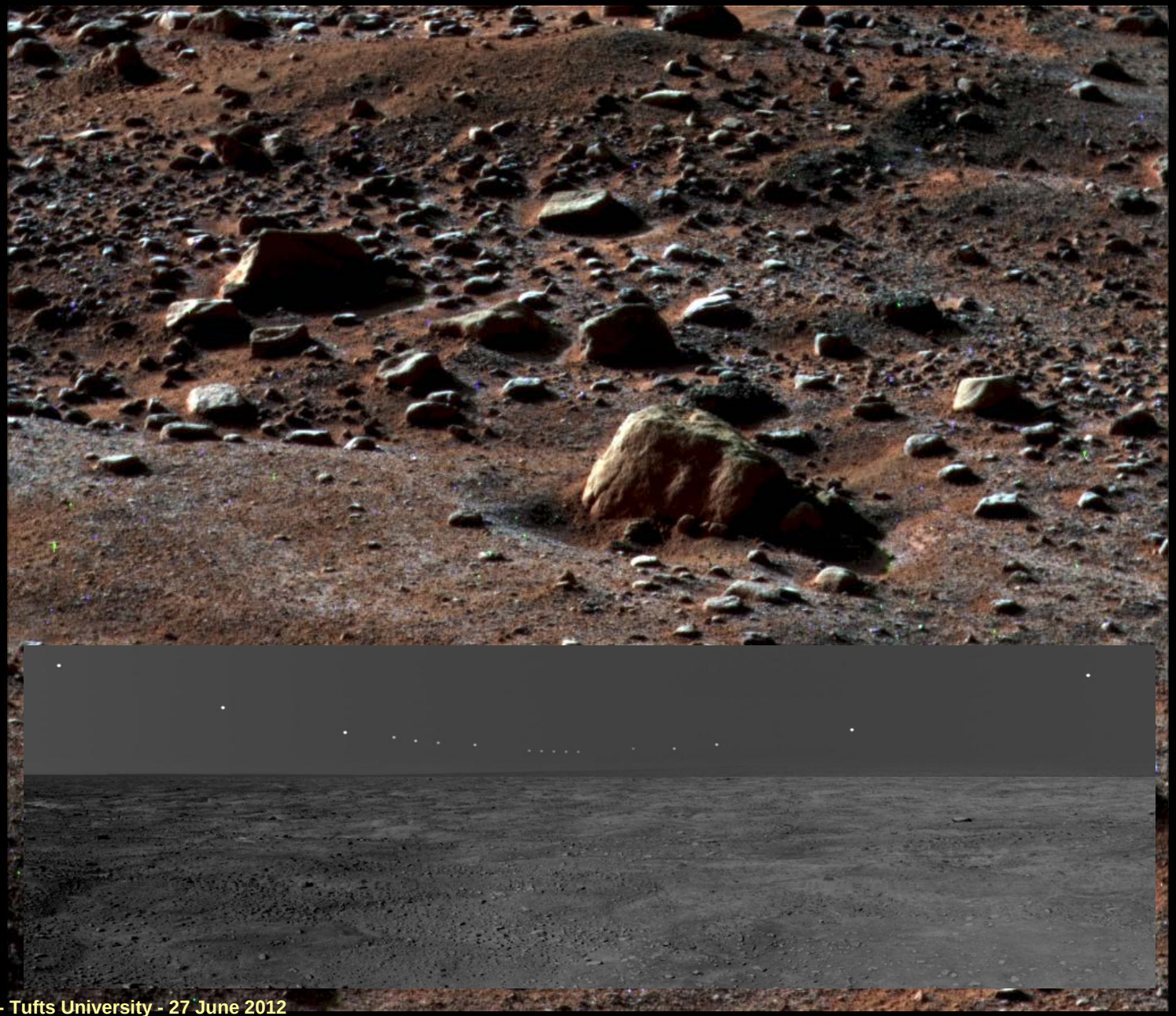
- H_2O ice at 5-10cm depth.
- EC ≈ 1.5 mS/cm (1g/25mL).
- Moderately alkaline pH 8.
- E_h ≈ 253 ± 6 mV

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

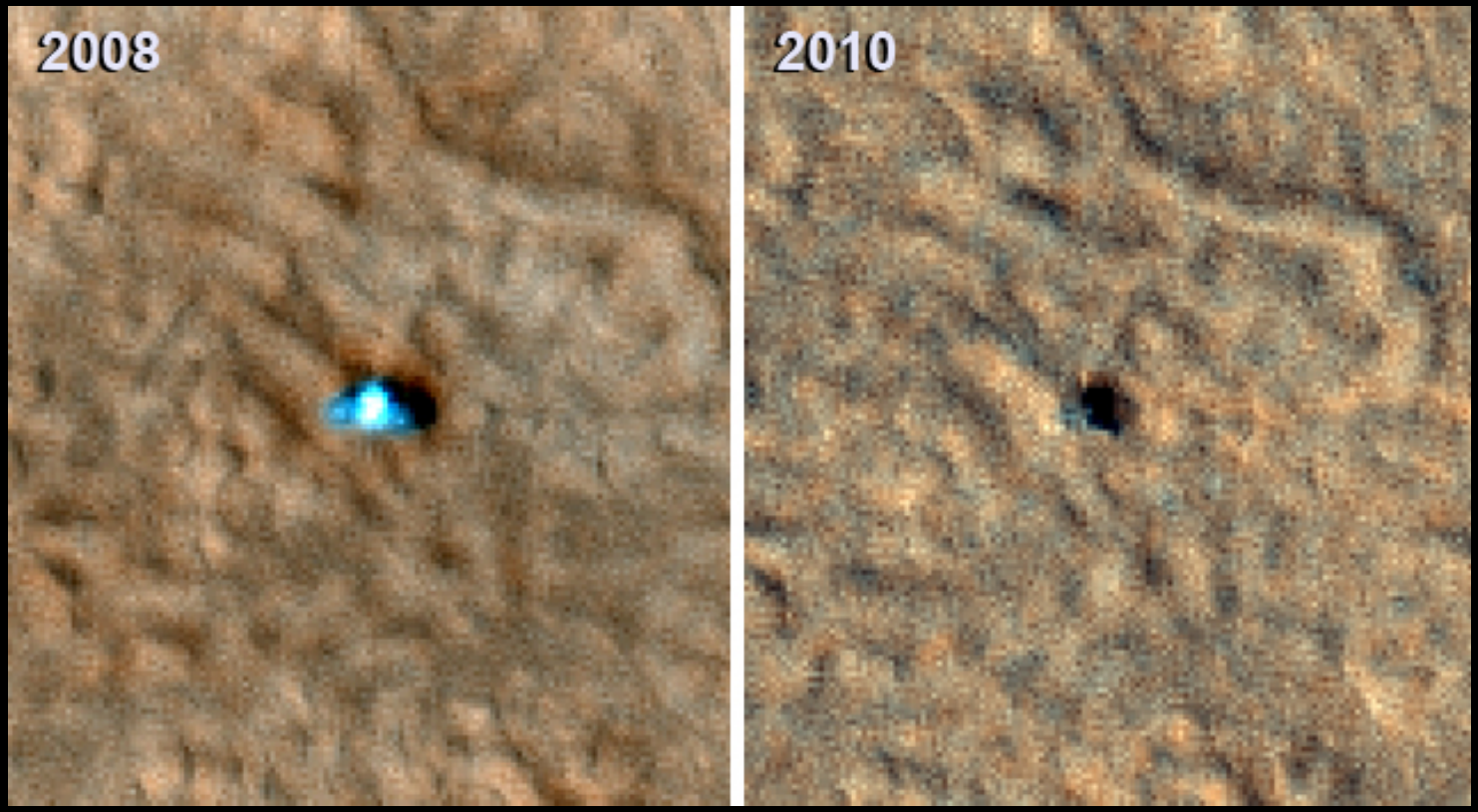
Species	Equil. Conc. (mM)	Conc. in Soil (wt %)
$CaCO_3$ (calcite)	Saturated	3 - 5 (1)
$MgCO_3$ (magnesite)	Saturated	≥ 1.8 (2)
$MgSO_4$ (epsomite)	Dissociated	3.3 (3)
ClO_4^-	2.5	0.6
Na^+	1.4	0.08
Cl^-	0.40	0.04
K^+	0.40	0.04
Mg^{2+}	6.4 (4)	-
SO_4^{2-}	3.9 (4)	-
HCO_3^-	5.4 (4)	-
$MgSO_4(aq)$	1.2 (4)	-
Ca^{2+}	0.75 (4)	-
$CaSO_4(aq)$	0.17 (4)	-

(1) As determined by TEGA & WCL
(2) Minimum required to give saturated Mg^{2+}
(3) Equivalent to 5.3 mM total SO_4^{2-} in solution.
(4) Equilibrium in solution calculated using *GWB React* at 7°C and a 4 mbar CO_2 headspace

Summer Ends - Sun Almost Sets!

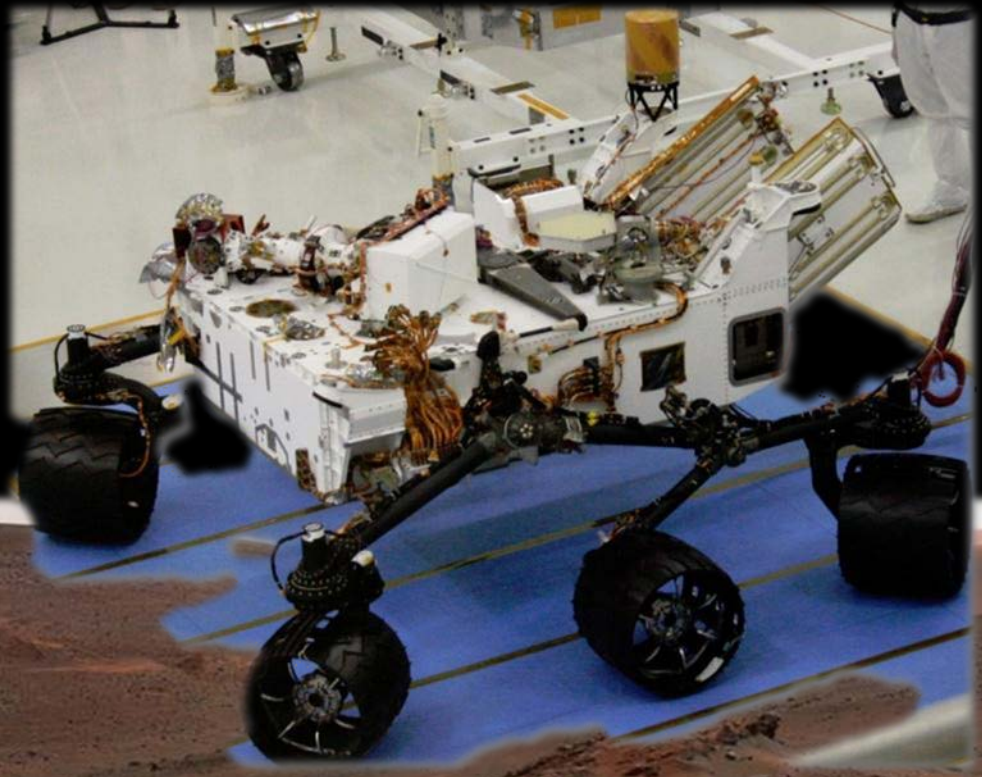


Last Transmission - November 2, 2008



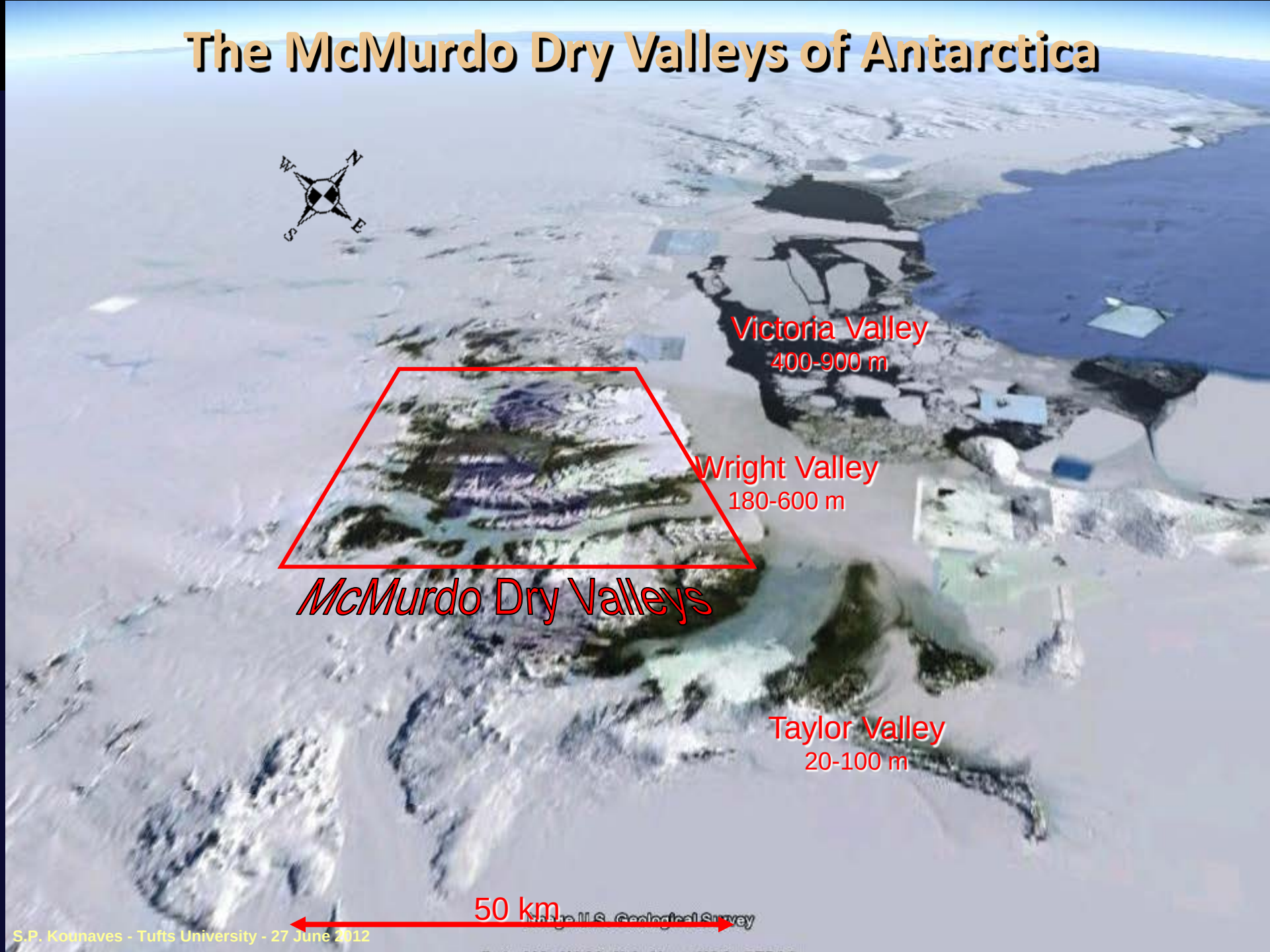
Mars Science Laboratory (MSL) "Curiosity"

Launched 11/25/2011 – EDL 9/6/2012



Meanwhile back on Earth

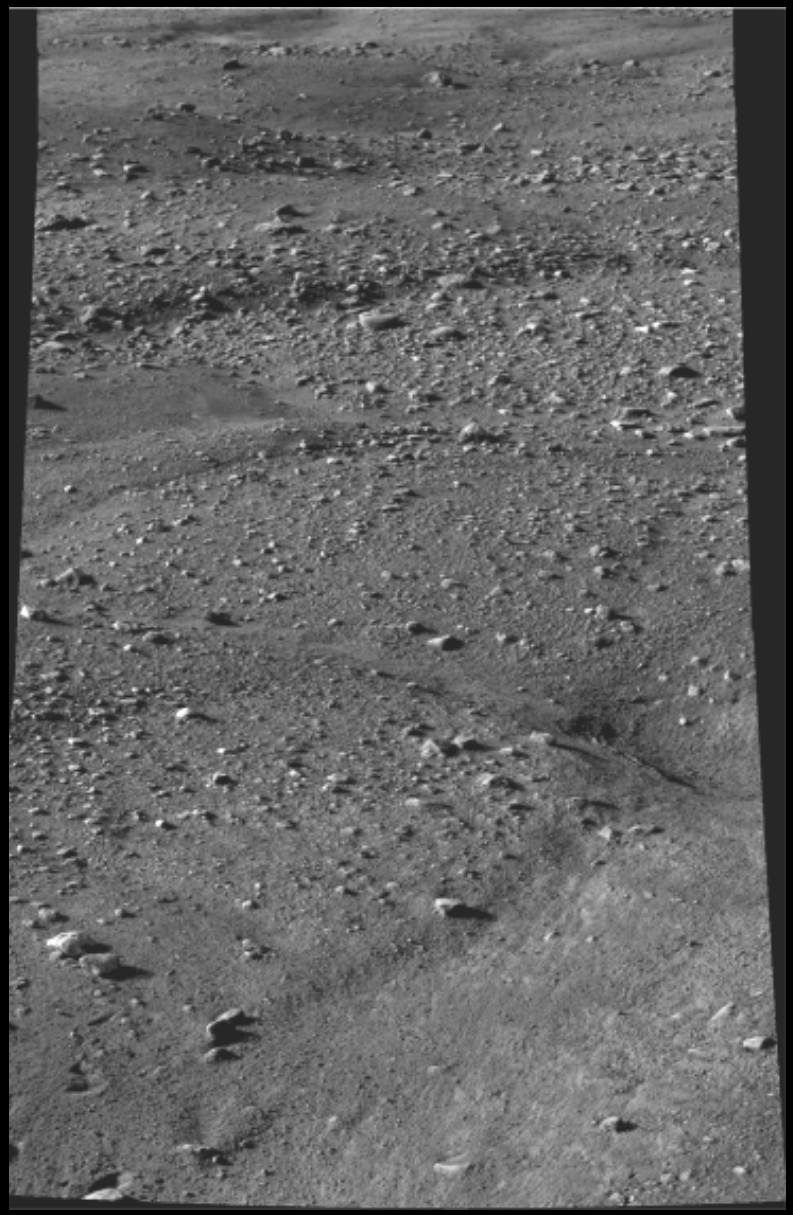
The McMurdo Dry Valleys of Antarctica



The MDV as Mars Analogs

Taylor Valley

Phoenix Landing Site

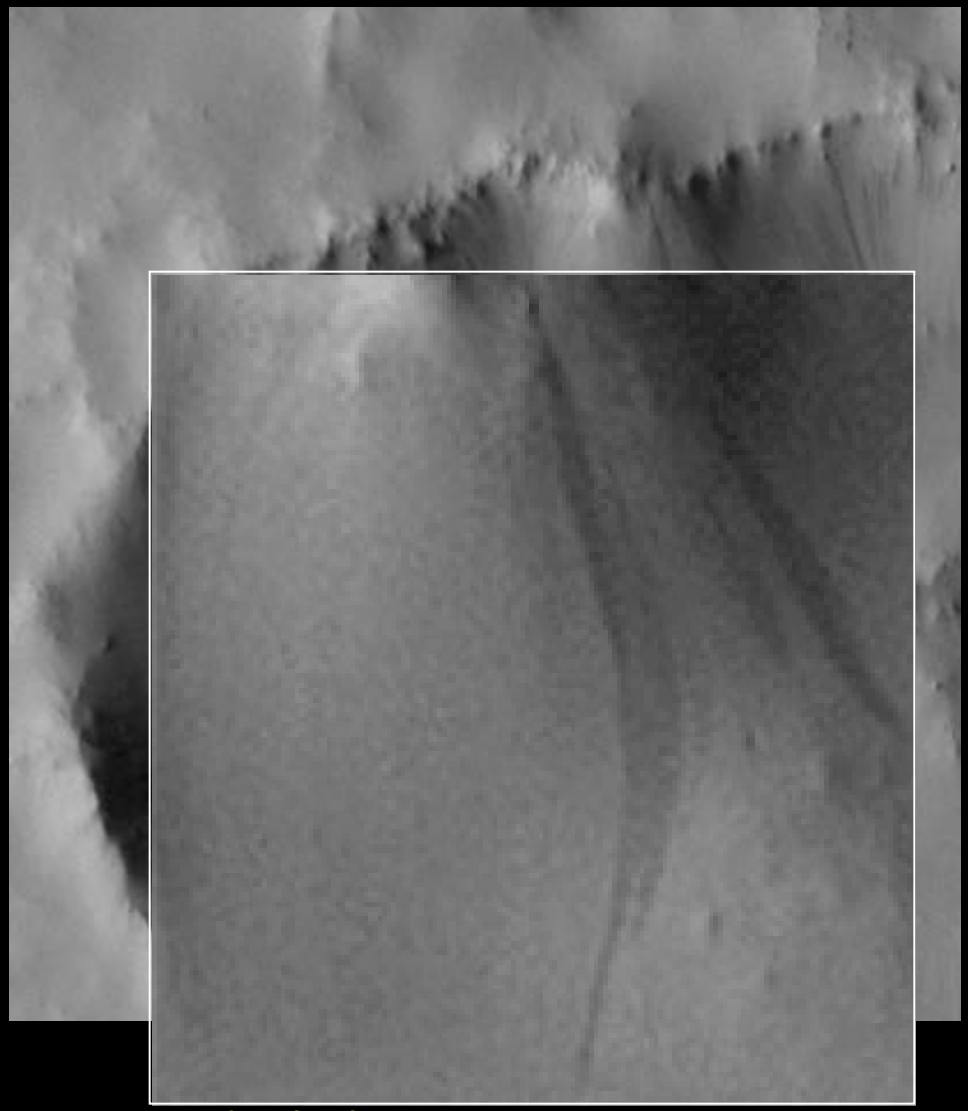


The MDV as Mars Analogs

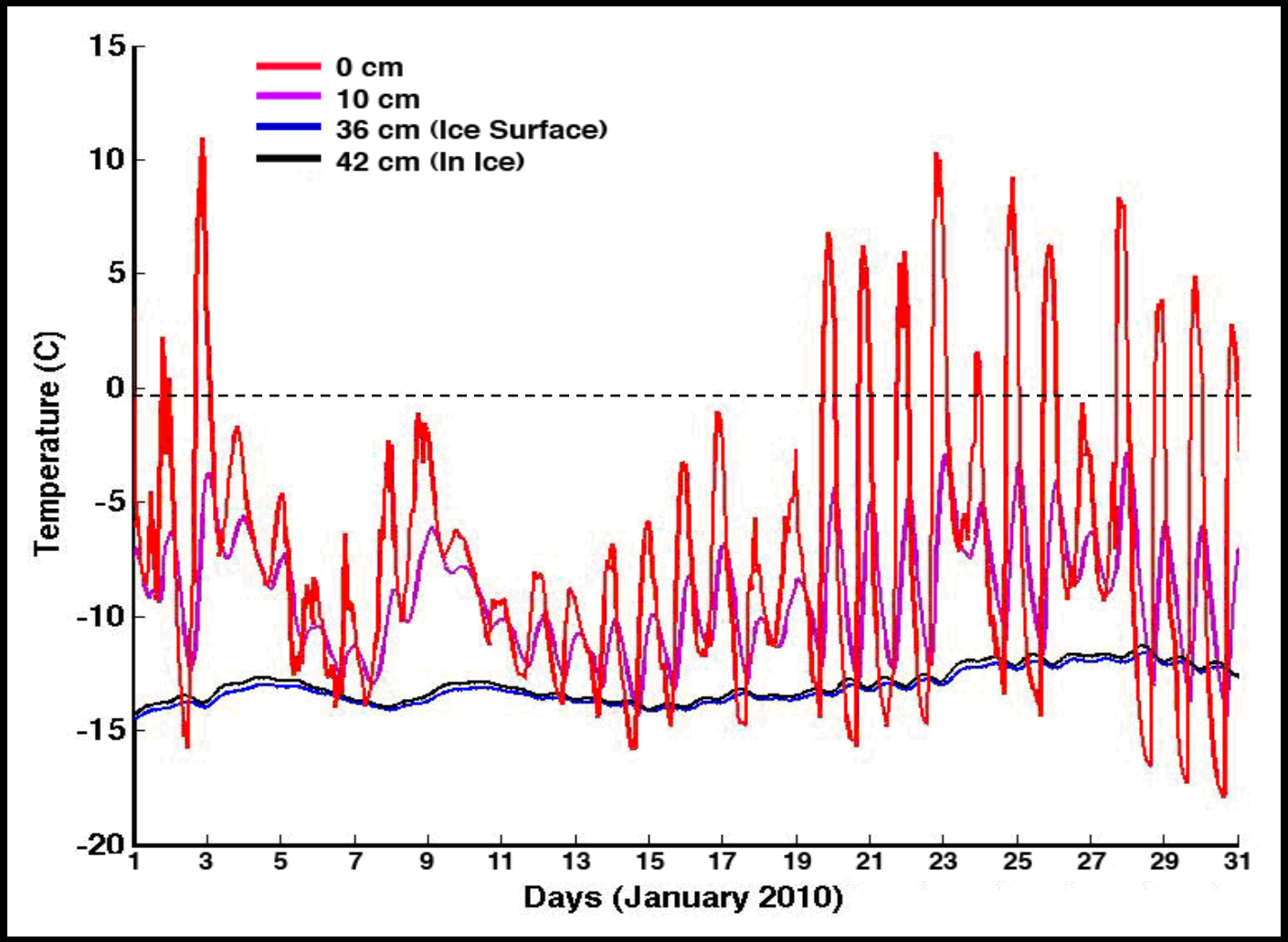
Mars & Beacon Valley - Polygons !

The MDV as Mars Analogs

Mars & Beacon Valley - Streaks !

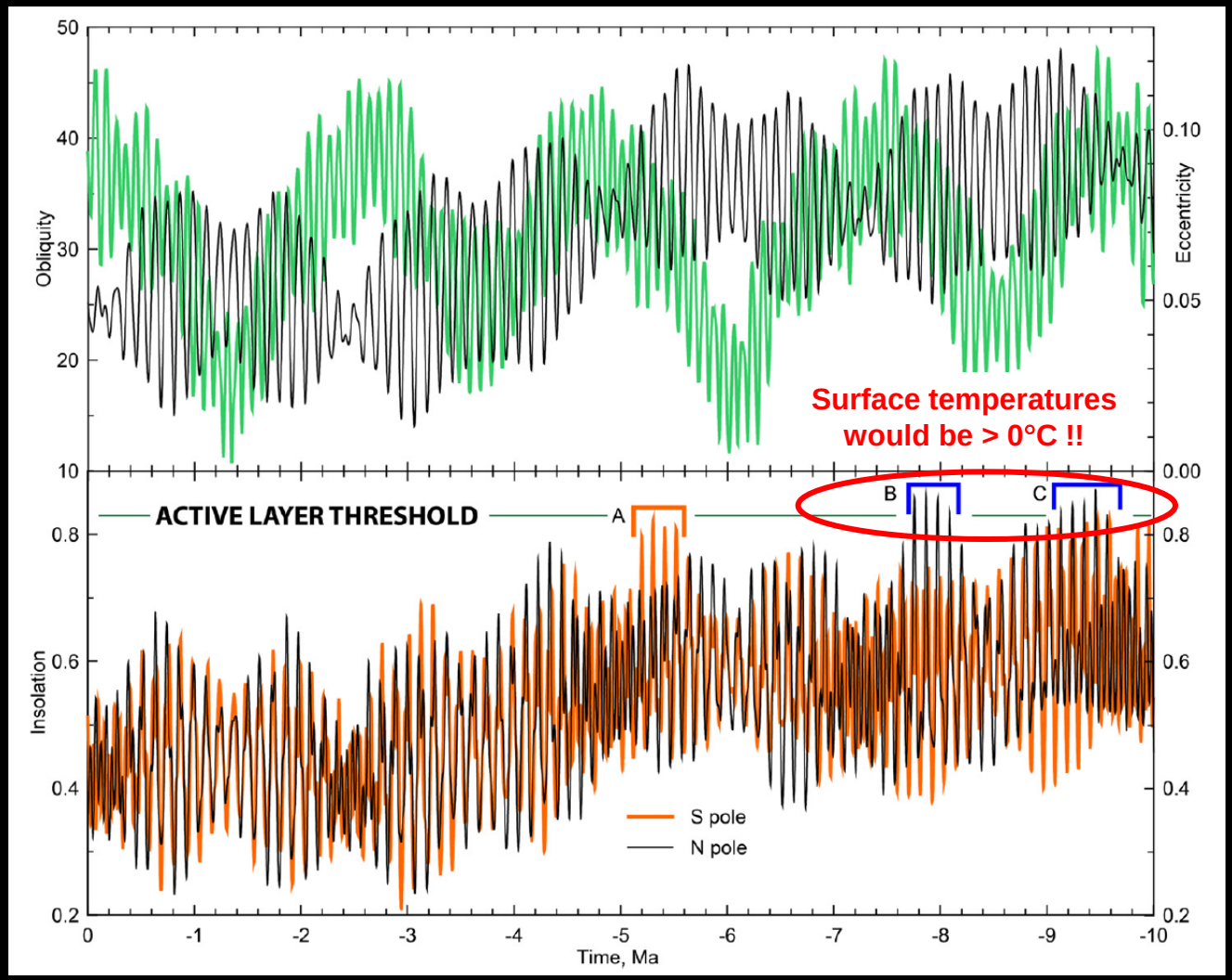


Temperature Profiles for UV



For UV soil, the 0°C isotherm does not reach beyond ~10 cm. At the ice table (36 cm), temperatures ≤ -12°C. (L. K. Tamppari - S. Kounaves, et al., *Antarctic Science*, **2011**, *24*, 211-228

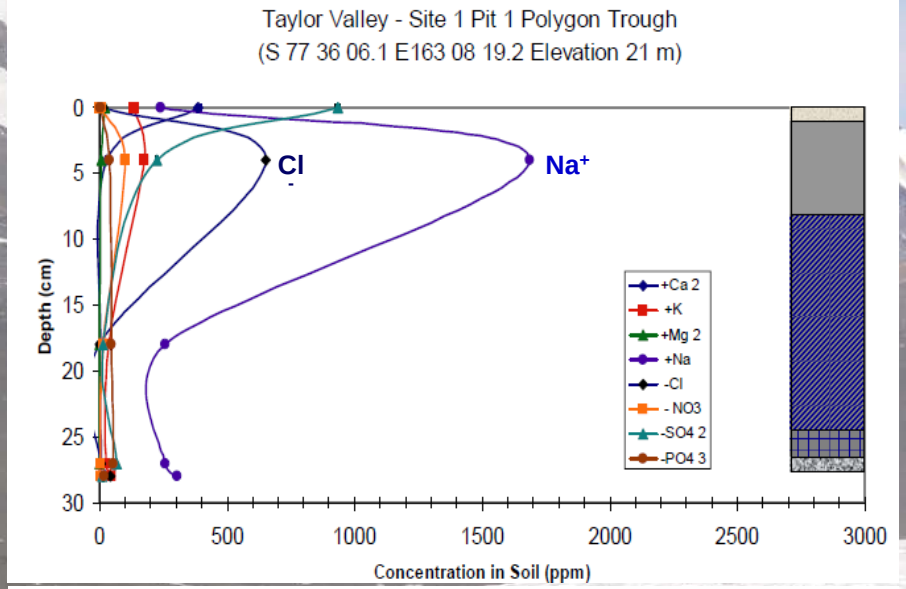
Mars' Obliquity Change With Time

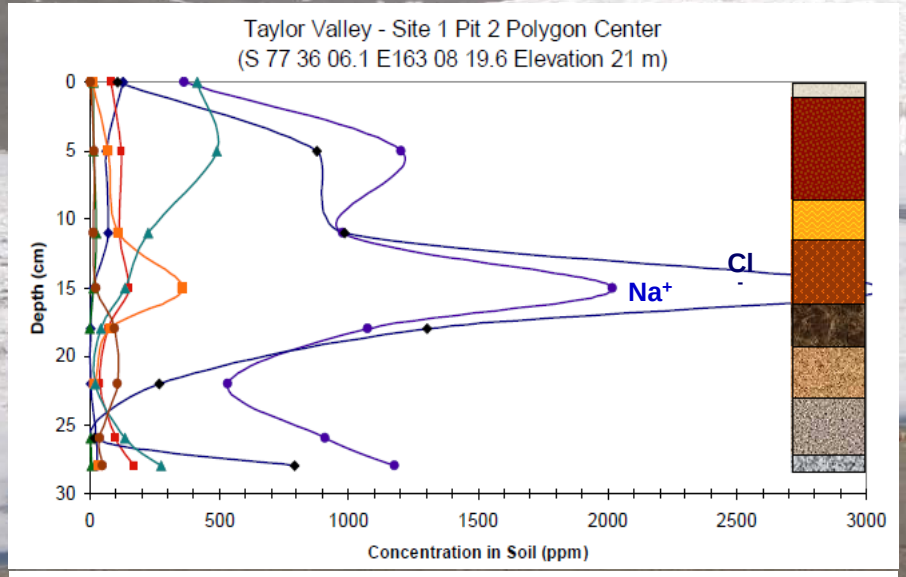


D. R. Marchant and J. W. Head, *Icarus*, 2007, *192*, 187-222

Models predict that at high obliquity, surface temperatures at PHX latitude would be similar to present-day UV with soil temperatures -13 to 17°C *(Zent Icarus, 196, 2008).*

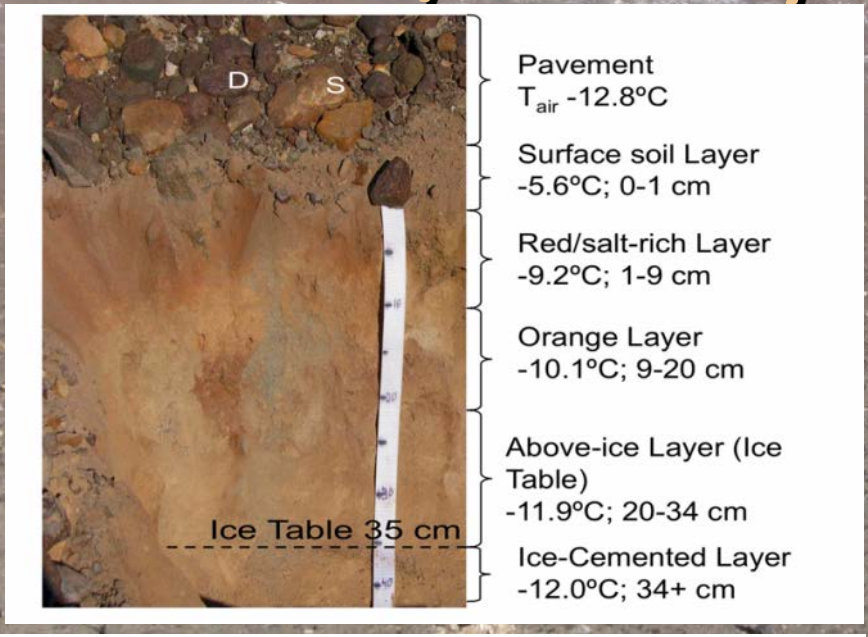
Taylor Valley (20-110m)

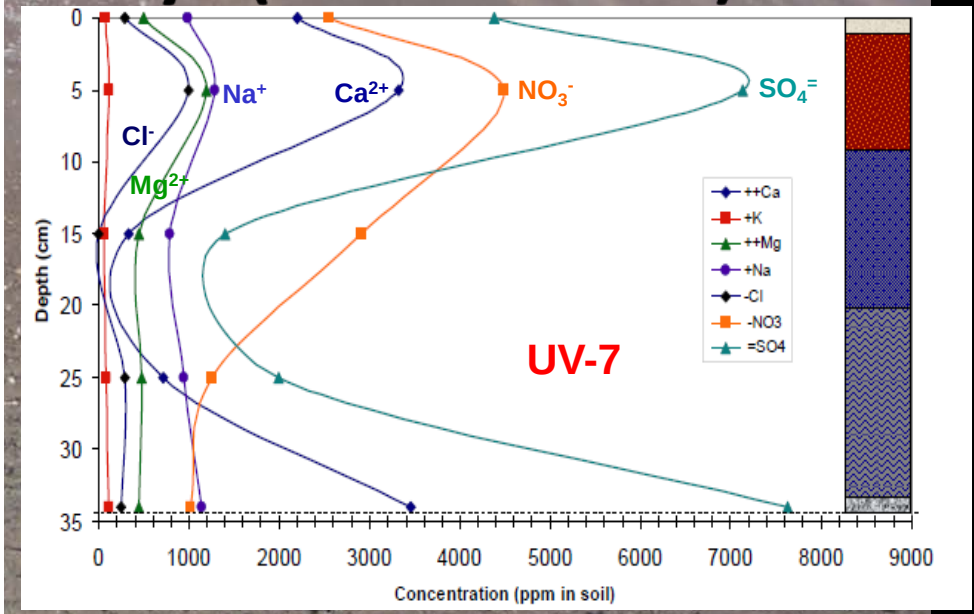


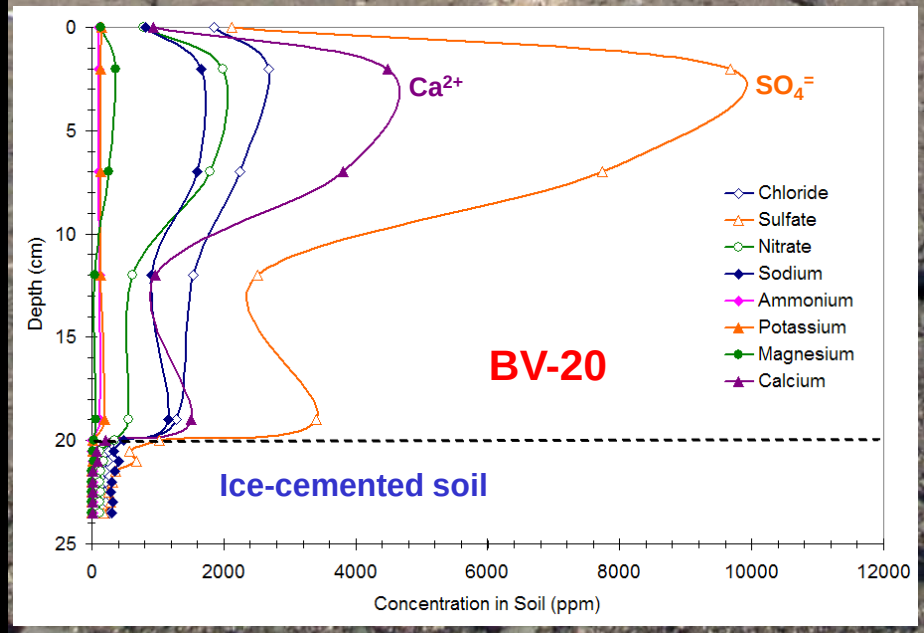


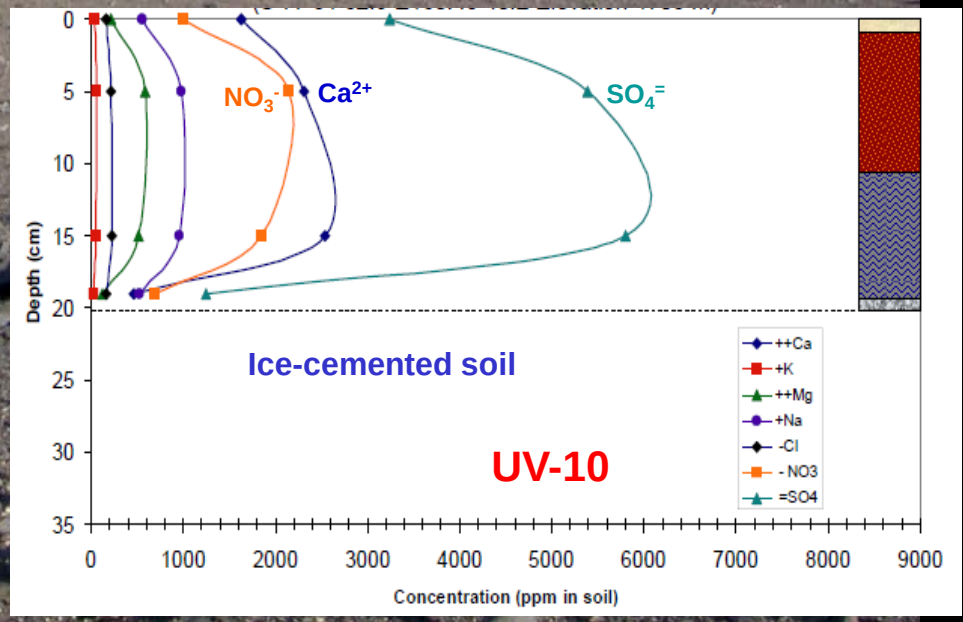
L. K. Tamppari - S. Kounaves, et al., *Antarctic Science*, 2011 (In Press)

Beacon/University Valleys (1200-1700m)

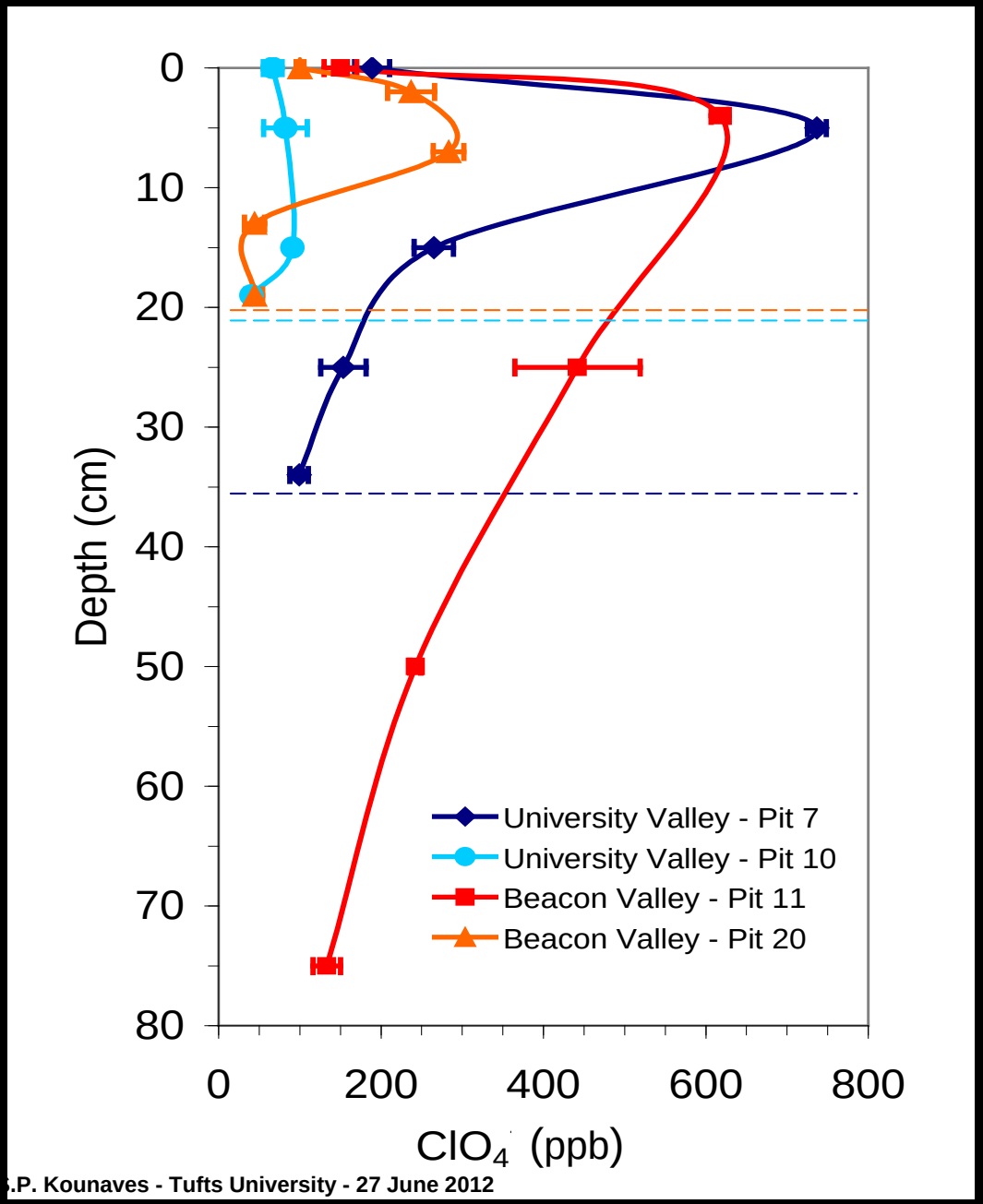








Perchlorate in Beacon & University Valleys



Analysis of University & Beacon Valley soils revealed ClO_4^- in all samples and horizons.
The continuous ClO_4^- profile is the result of hyper-aridity preventing aqueous migration of ClO_4^-.

Perchlorate in EETA79001

Analysis of Mars meteorite EETA79001, recovered from Elephant Moraine in 1979, ~ 200 km north of BV, contains ~ 400 ppb of ClO_4^-

Perchlorate in EETA79001 may originate from:

1. Mars - suggesting that ClO_4^- may be widespread on Mars?

2. Earth - suggesting that ClO_4^-, adsorbed from melted ice/snow, is widespread on Antarctica and globally.

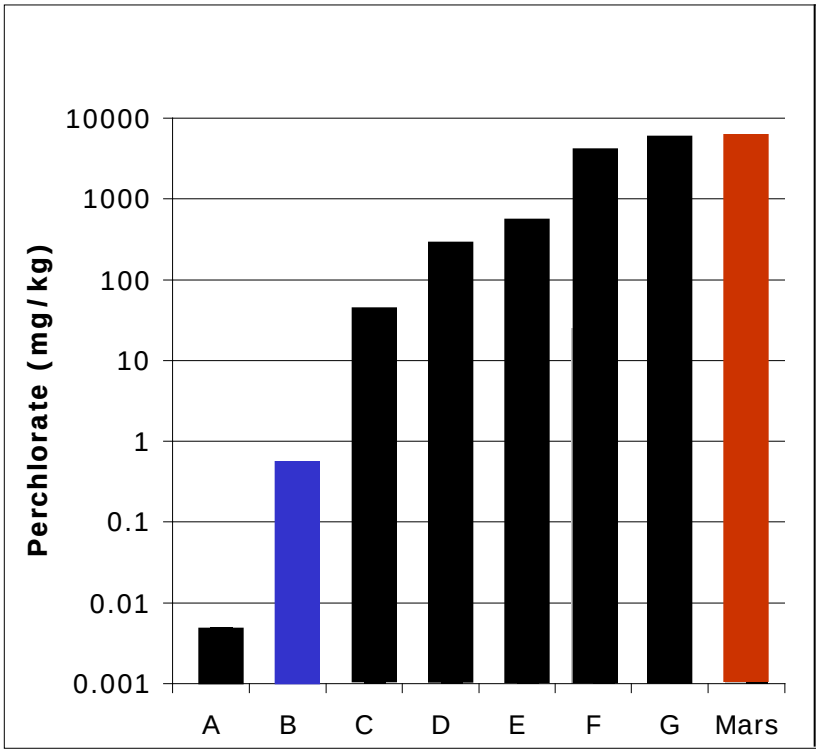
Proposed ClO_4^- Formation Mechanisms

Although exact mechanism is not known, isotopic analysis demonstrates stratospheric origin of ClO_4^- in the Atacama Desert and most locations on Earth.

Mechanism	**Chlorine source**
Atmospheric photochemical reactions with oxidants such as O_3 or H_2O_2	(i) Volcanic HCl (or CH_3Cl for the Atacama) (ii) HCl liberated from acid displacement reactions (iii) Cl atoms liberated from aerosol chloride
Electrostatic discharge (?)	(i) Aerosol or surface soil chlorides (ii) Volatile species as above
Photochemistry of precursors on mineral surfaces (?)	Chlorides on mineral surfaces and precursors such as ClO^-, ClO_2^-, and ClO_3^-

D. C. Catling, M. W. Claire, K. J. Zahnle, R. C. Quinn, B. C. Clark, M. H. Hecht, and S. P. Kounaves, *J. Geophys. Res.*, **2010**, *115*, E00E11

Levels of Perchlorate on Earth & Mars



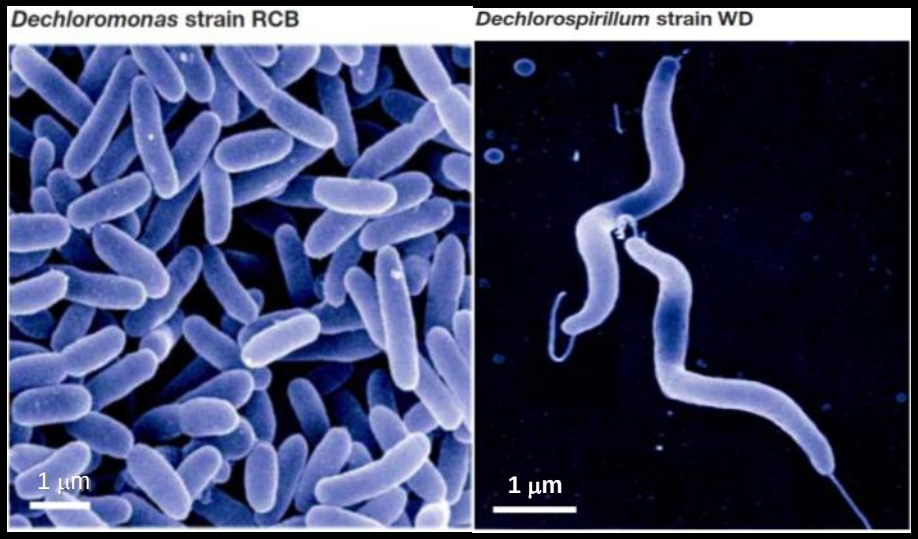
Modified from: D. C. Catling et al., *J. Geophys. Res.*, **2010**, *115*, E00E11

Perchlorate levels at the **Phoenix landing site** compared to Earth in:

A - sulfate aerosols in stratosphere [Murphy and Thomson, 2000];
B - Antarctica (University Valley) soil [Kounaves et al., 2010]
C - potash sylviniterich ore, Saskatchewan [Orris et al., 2003]
D - Searles Lake evaporites, California [Orris et al., 2003]
E - Bolivian playa evaporite crusts in the Andean Altiplano [Orris et al., 2003]
F - Permo-Triassic sylvinite potash ore, Carlsbad, New Mexico [Orris et al., 2003]
G - Atacama caliche blanco veins (best nitrate ore) [Ericksen, 1981].

Where is all the ClO_4^- on Earth?

- Dissimilatory (per)chlorate-reducing bacteria (DPRB) and their ability to reduce ClO_3^- and ClO_4^- were discovered in 1952.
- Microbial ClO_4^- reduction is inhibited by O_2 and, for some species, by NO_3^-.
- Redox potential of ClO_3^- ($E°$ = 1.03 V) and ClO_4^- ($E°$ = 1.287 V) makes them ideal electron acceptors for microbial metabolism
- Metabolic capability of ClO_4^- reduction is widespread throughout the *Proteobacteria*, which has interesting evolutionary implications in light of apparent widespread distribution of natural ClO_4^-.

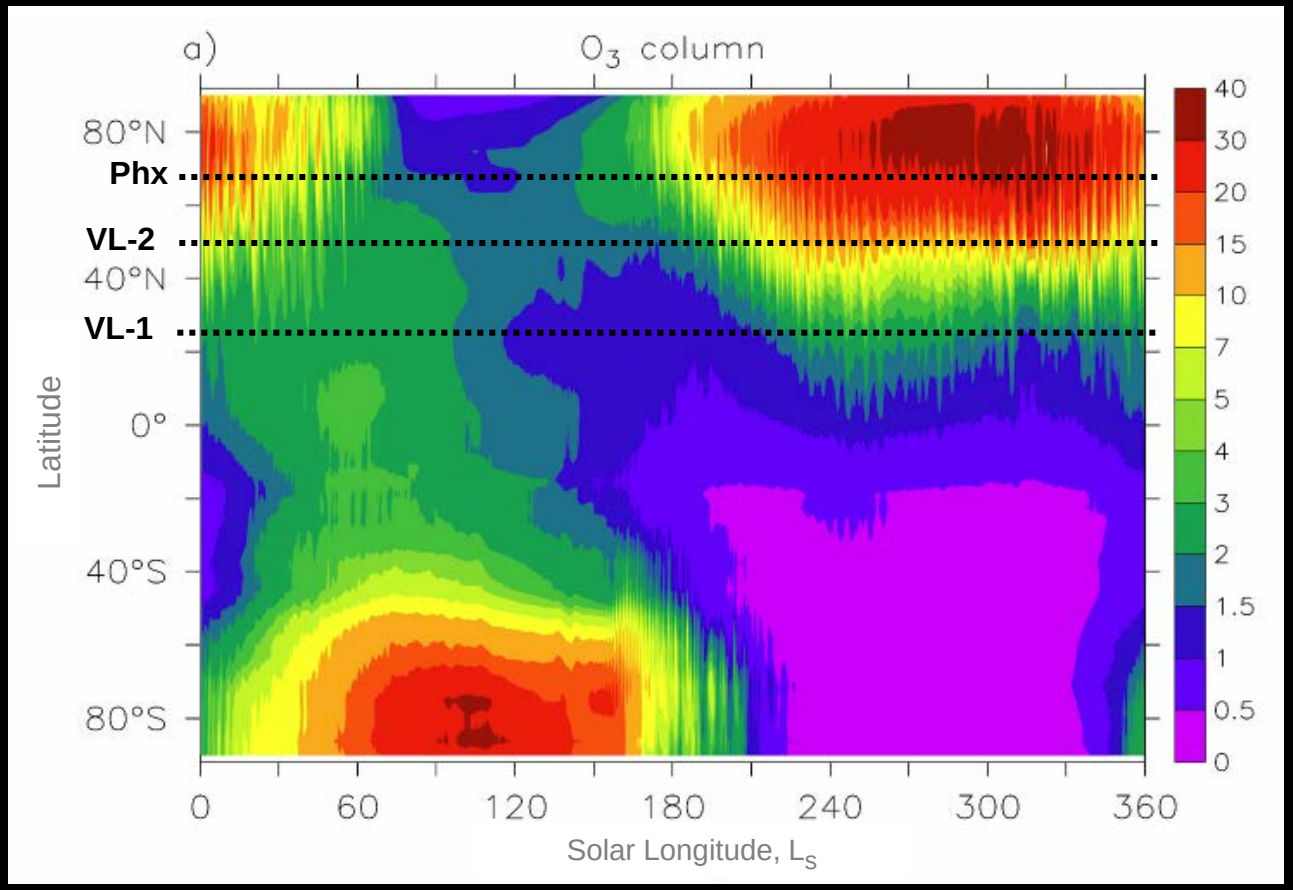


DPRB grow by oxidation of organics or inorganic electron donors (H_2, H_2S or Fe^{2+}) coupled to the reduction of ClO_4^- in anoxic environments.

DPRB are phylogenetically, physiologically, and as can be seen on the left morphologically diverse.

Coates, J. D.; Achenbach L. A., *Nature Reviews*, 2004, *2*, 569-573.

Ozone → Perchlorate on Mars



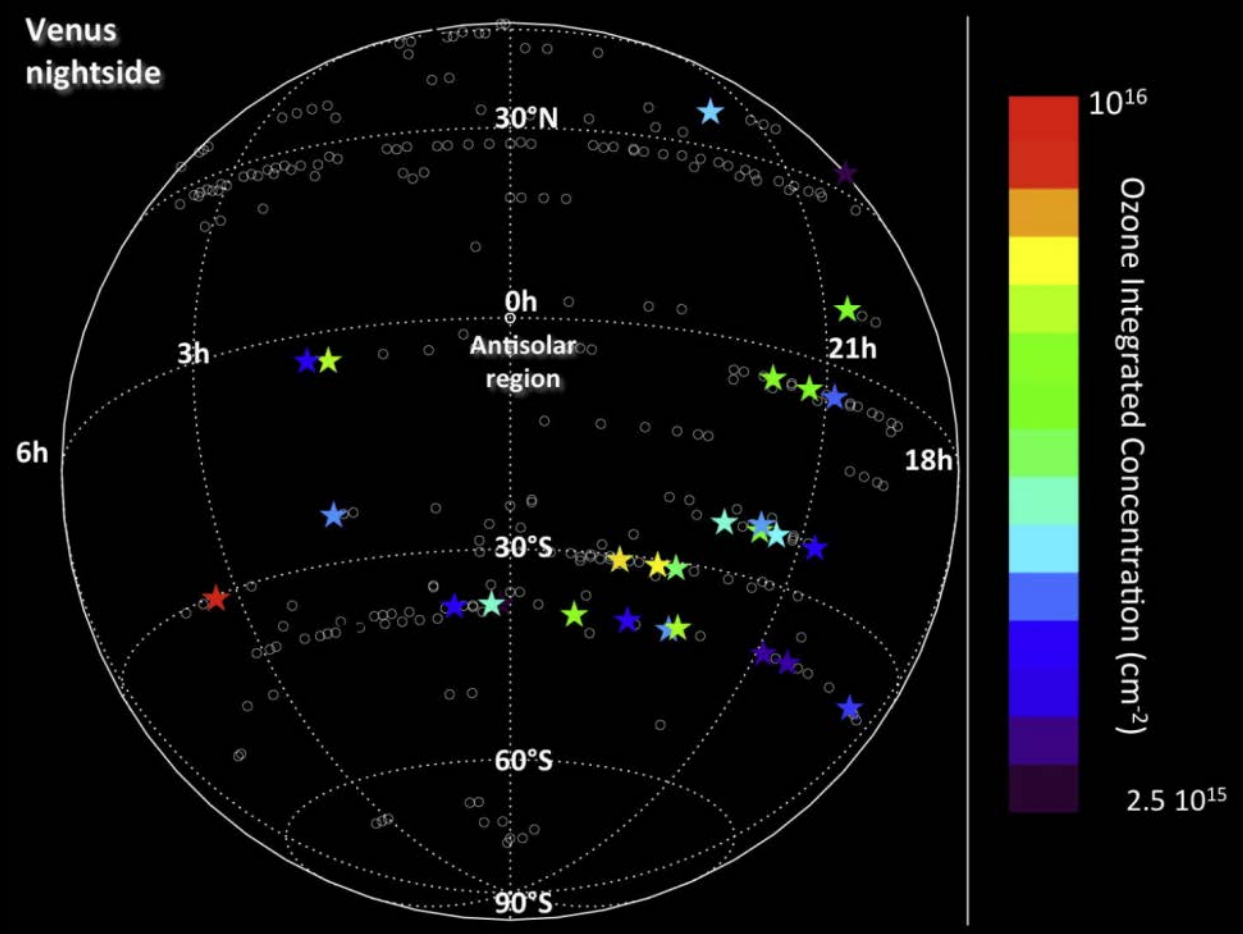
Zonally averaged ozone column density (μm-atm) on Mars from SPICAM/MEX UV measurements.

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

Atmospheric chemistry on Mars & Earth ?

$$O_3 + Cl \rightarrow O_2 + ClO$$
$$ClO + H_2O(s) \rightarrow OClO$$
$$OClO + O_3 \rightarrow ClO_3 + O_2$$
$$ClO_3 + OH \rightarrow HClO_4$$

Speculation: Ozone → Perchlorate on Venus ???



Night-side view of Venus showing ozone detection by SPICAV.

Montmessin, F., *et al*., *Icarus*, **2011**, 216, 82-85

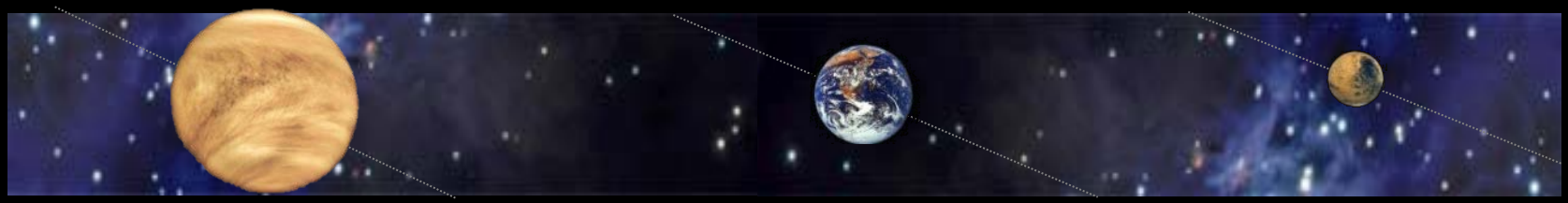
Conclusions

Combining the results for the MDV with recent reports for the Arctic and the continental United States, provides an emerging picture of global atmospheric perchlorate deposition.

Additionally, the discovery of ClO_4^- on Mars and a wide area of Antarctica, provides evidence that natural ClO_4^- may be ubiquitous on both planets. If ozone is a prerequisite, Venus may also harbor perchlorate!

The results support emerging hypotheses that ClO_4^-

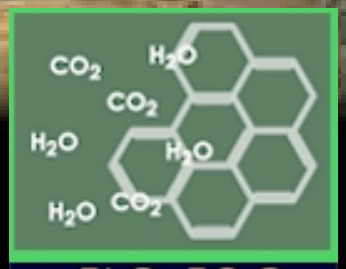
- is produced globally and continuously in the atmosphere of Earth (Mars & Venus?) but *accumulates only in arid areas with long-term evaporation and/or sublimation.*
- on Earth, a global microbial ecology, on land and in the oceans, prevents its accumulation by reduction to chloride.

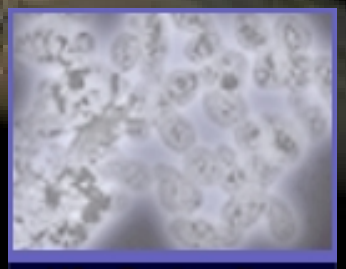


In-Situ Biogeochemical Analysis

We are interested in these extreme environments on Mars, Earth, and other planets, because they often contain within them chemical and biological records that can provide unique evidence to help us better understand:

- the interaction of geochemistry with biology
- clues to the local and global climactic history
- their potential to have supported and preserved evidence of past life
- and their present and future biohabitability.



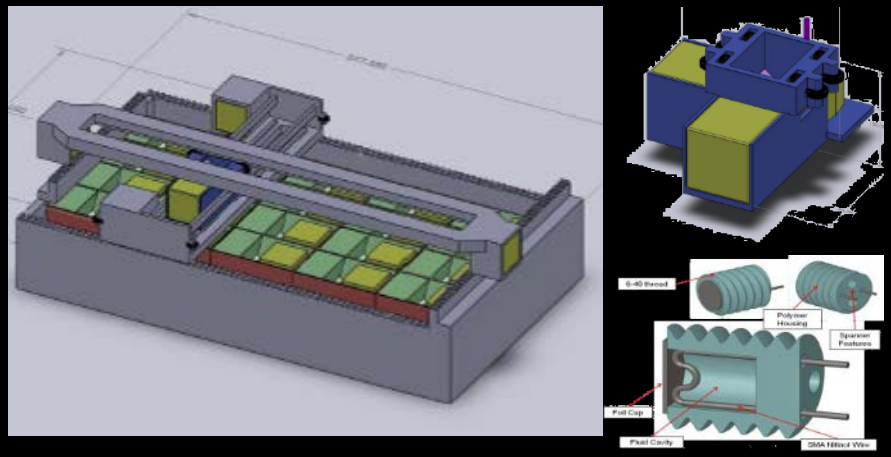


Next Generation Chemical Analysis on Mars

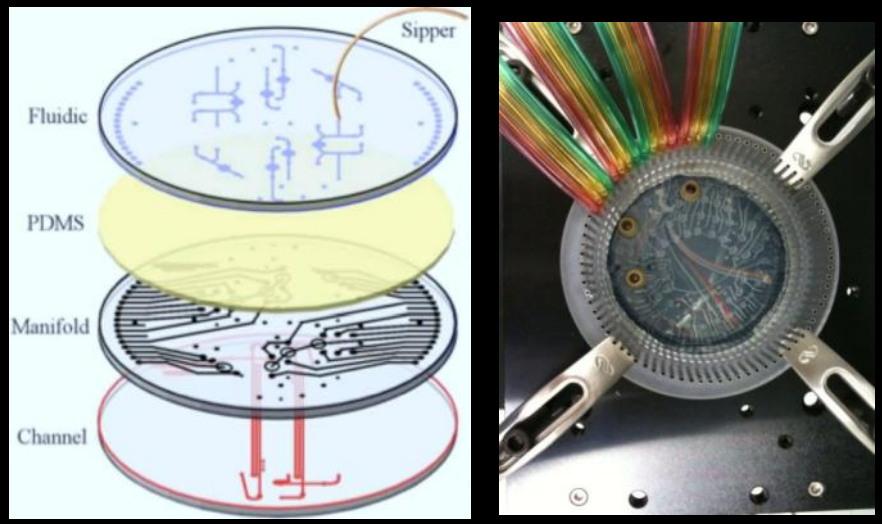
Two complimentary analytical systems are currently being developed to allow for a larger number of analyses:

CHEMSENS (top) consists of 40-60 mini-WCL type units similar to those used on the 2007 Phoenix mission.

NERNST (bottom) is a lab-on-a-chip that can use the leachate from CHEMSENS to manipulate and modify the solution to perform a large number detailed chemical analyses.



CHEMSENS

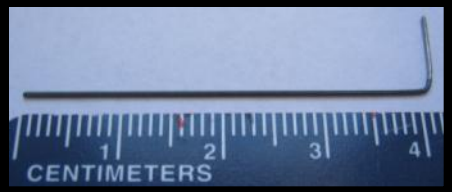


NERNST

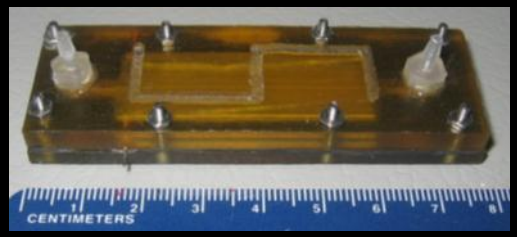
Mars Organic Carbon Analyzer (MOCA)

A small, compact and light weight electrochemically-based total organic carbon (TOC) analyzer is being developed to determine the presence and evolution of organic molecules on Mars & other planets.

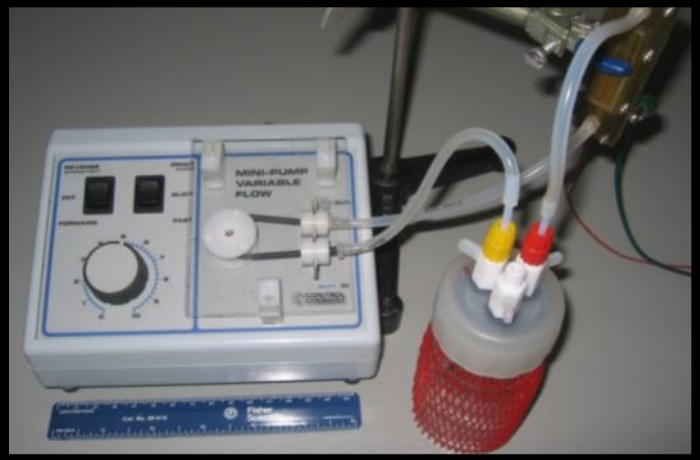
The uses a boron-doped diamond (BDD) electrode to oxidize water soluble organics to carbon dioxide. The carbon dioxide is equal to the total organic carbon in the sample.



Boron-Doped Diamond Electrode



Electrochemical Cell

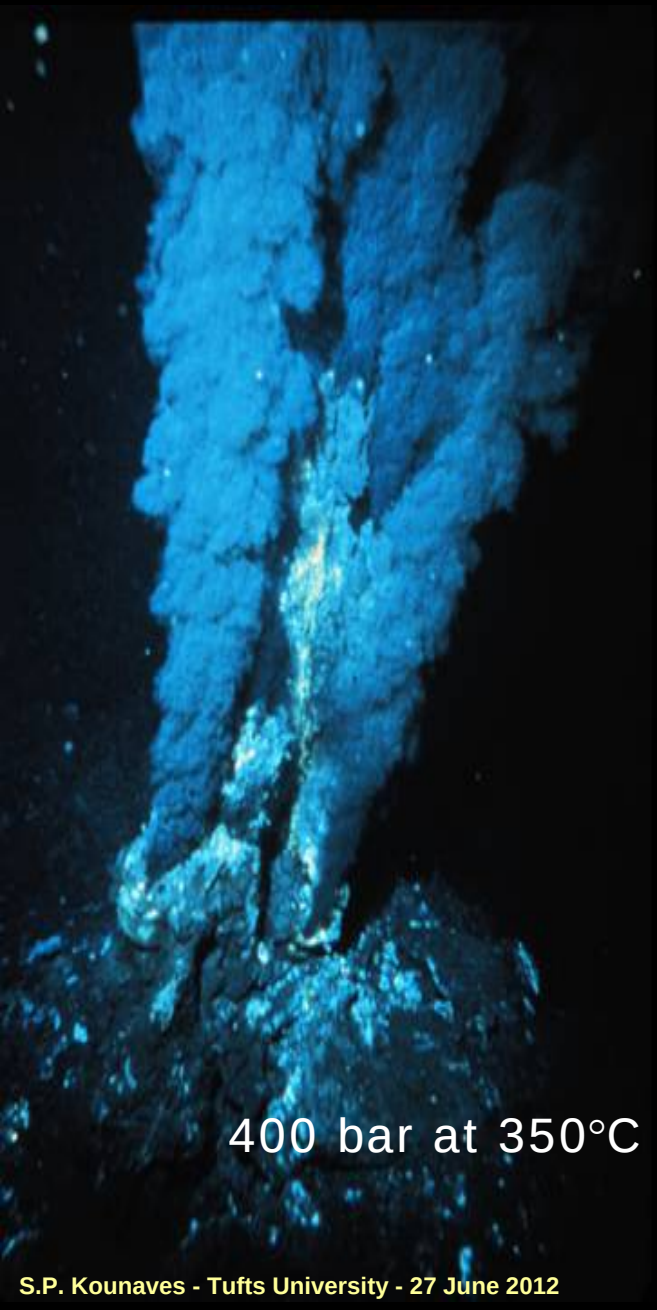


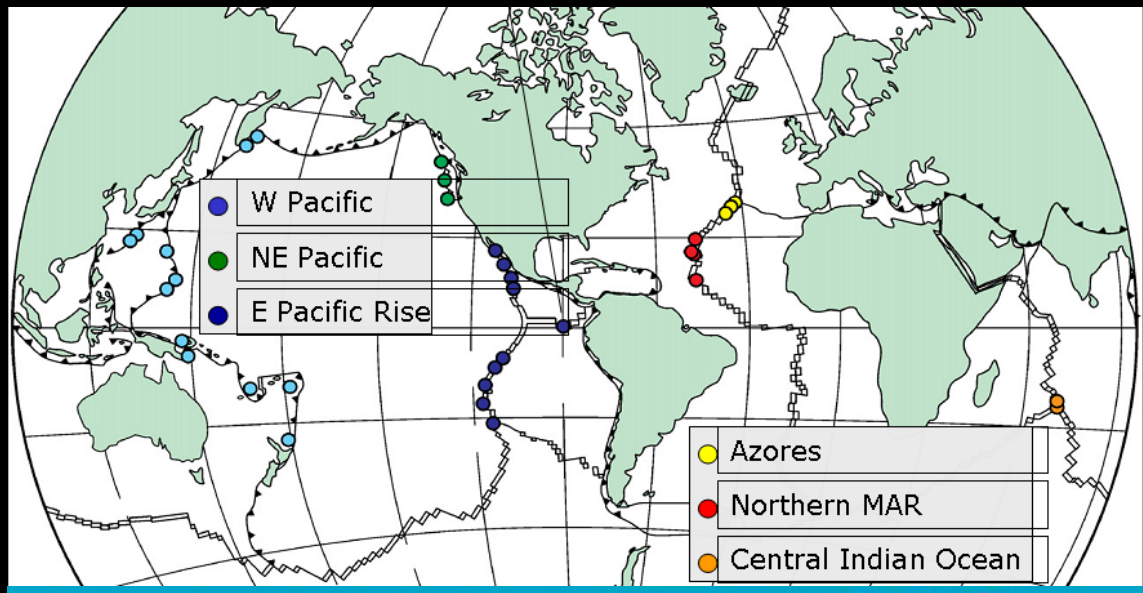
Electrochemical Flow-Through System

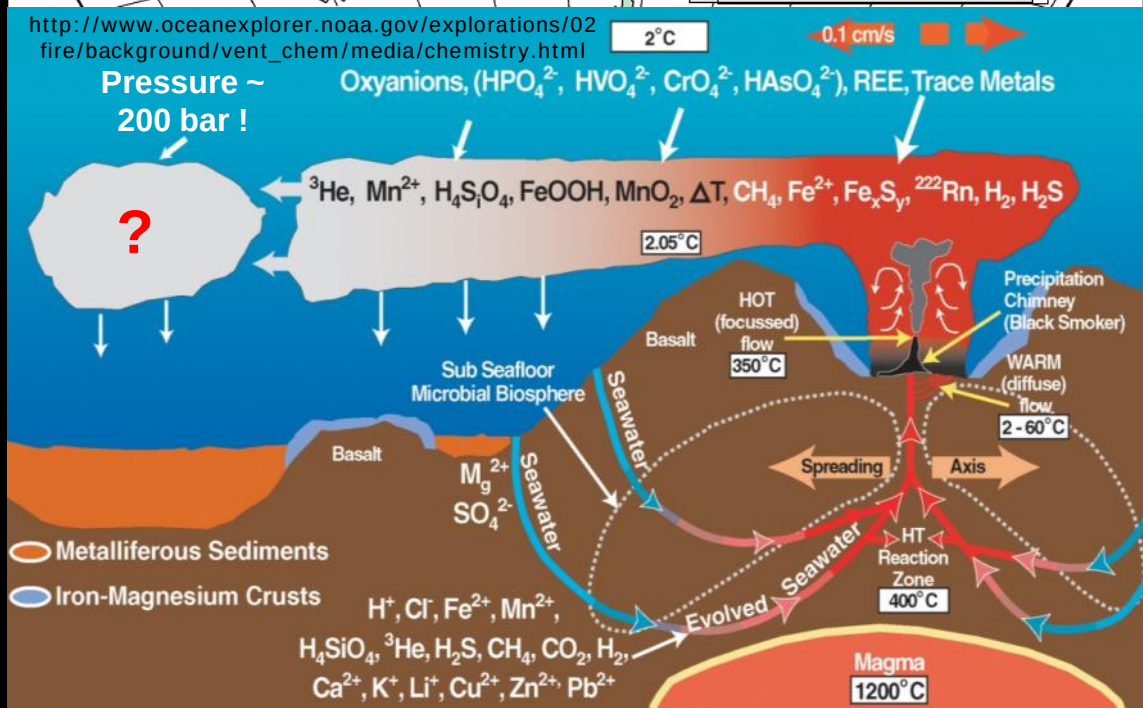
Mars Simulation Measurements

- Determine ability of selected organics adsorbed on or below surface in simulated martian soil to resist oxidation as a function of:
  - UV dose
  - Depth
  - atrix

Chemistry & Life at Deep Sea HT Vents







High Pressure & Temperature Test Chamber

The Phoenix WCL ISE sensors on steroids!!

Collecting Data at Sea with the Deep-Sea Probe

Thank You