MCAL

A Wet Chemical Analysis Lab for In-Situ Planetary Analysis

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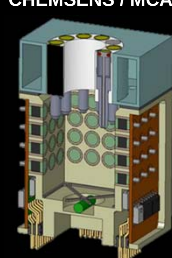
Next Generation Wet Chemistry Analyzers

The path forward for MSR and human exploration must be undertaken with sufficient understanding of the martian aqueous chemical environment, to maximize the science and minimize the risks to the Mars program and eventual human explorers.

To allow for operation on a rover over a wide area and for an extended time, the *Mars Chemical Analysis Lab* (MCAL) (CHEMSENS) can contain from a few to a 100+ mini-WCL type units. With improved & increased sensors can monitor instantaneous, real-time, and long term equilibrium.

The NERNST system is a lab-on-a-chip that can use the leachate from MCAL to manipulate and modify the solution to perform a large number follow-on detailed chemical analyses and reagent additions.

CHEMSENS / MCAL



Nernst

Up Front Summary

- Core of MCAL is highly successful & flight tested Phx WCL.
- Contains more types & redundant sensors than WCL.
- Has a true reference-electrode system.
- Requires 1/3 less resources, volume and mass.
- Modular configuration for flexible mission payload requirements.
- Addresses MSR, human exploration, & Jovian moons.
- Payload compatible with MER or larger class mission.
- Hardware will be ready for testing by end of 2012.
- TRL 5 by mid-2013, TRL 6 by mid-2014 and TRL 7 by mid-2015.

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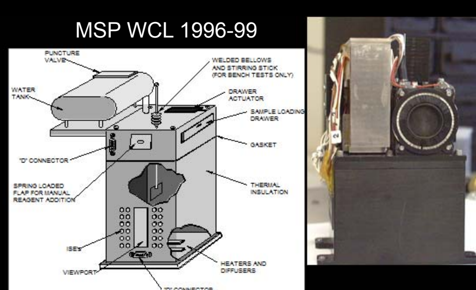
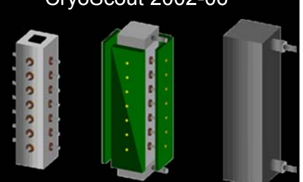
Wet Chemistry Heritage

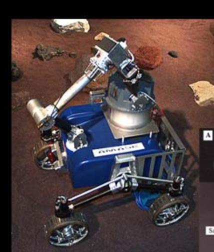
MSP WCL 1996-99



HEDS 2001-05

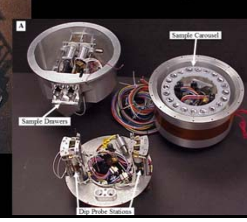
CryoScout 2002-06





PHX WCL 2005-09

RCAL 2002-10



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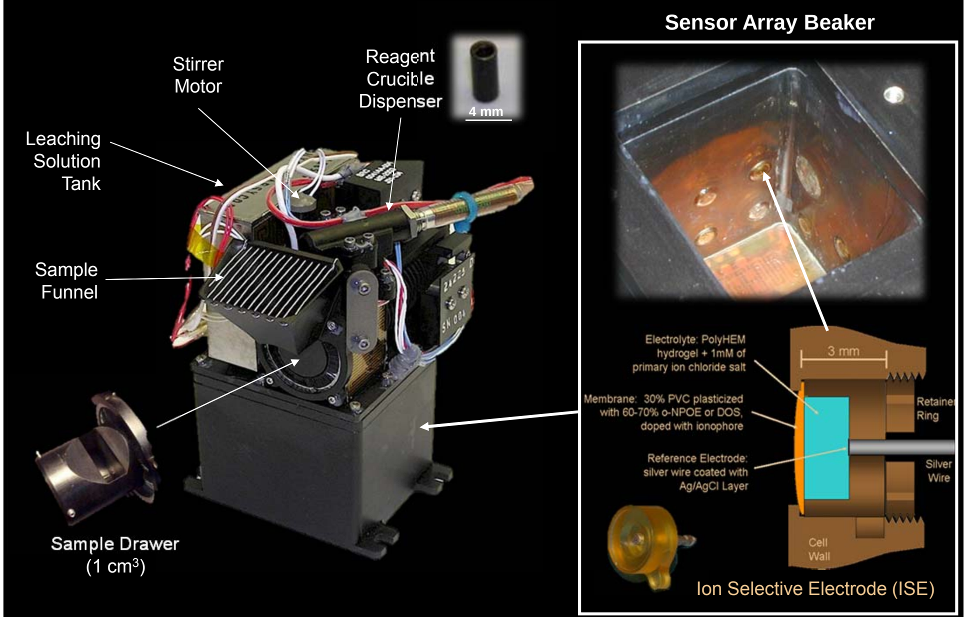
The Phoenix Wet Chemistry Laboratory (WCL)



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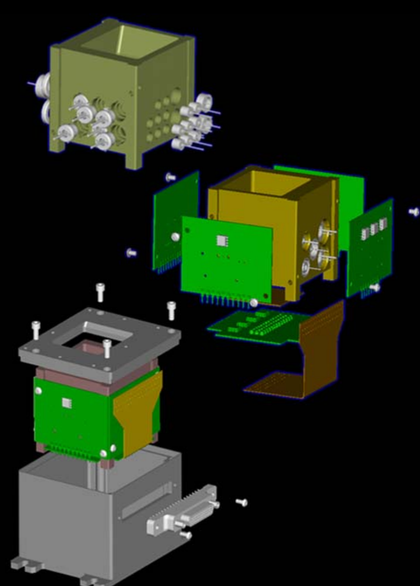
The WCL Beaker Assembly and Sensors



Sensor	Type
Ammonium (NH_4^+)	PVC, Nonactin
Barium ($Ba^{2+}/SO_4^{=}$)	PVC, Ba Iphor-I
Bromide (Br^-)	Solid Pellet Crystal
Calcium (Ca^{2+})	PVC, ETH-1001
Chloride (Cl^-)	Solid Pellet Crystal
Iodide (I^-)	Solid Pellet Crystal
Hydrogen (H^+) (2)	PVC, ETH-2418
Lithium REF (2)	PVC, Li Iphor-VI
Magnesium (Mg^{2+})	PVC, ETH-7025
Nitrate (NO_3^-/ClO_4^-)	PVC, Ion Exchanger
Potassium (K^+)	PVC, Valinomycin
Sodium (Na^+)	PVC, Na Iphor-VI
pH	Iridium-oxide disk
Conductivity	carbon disk/ring
CV (Redox)	0.25mm Au disk
CP (3) (Halides)	1-mm Ag disk

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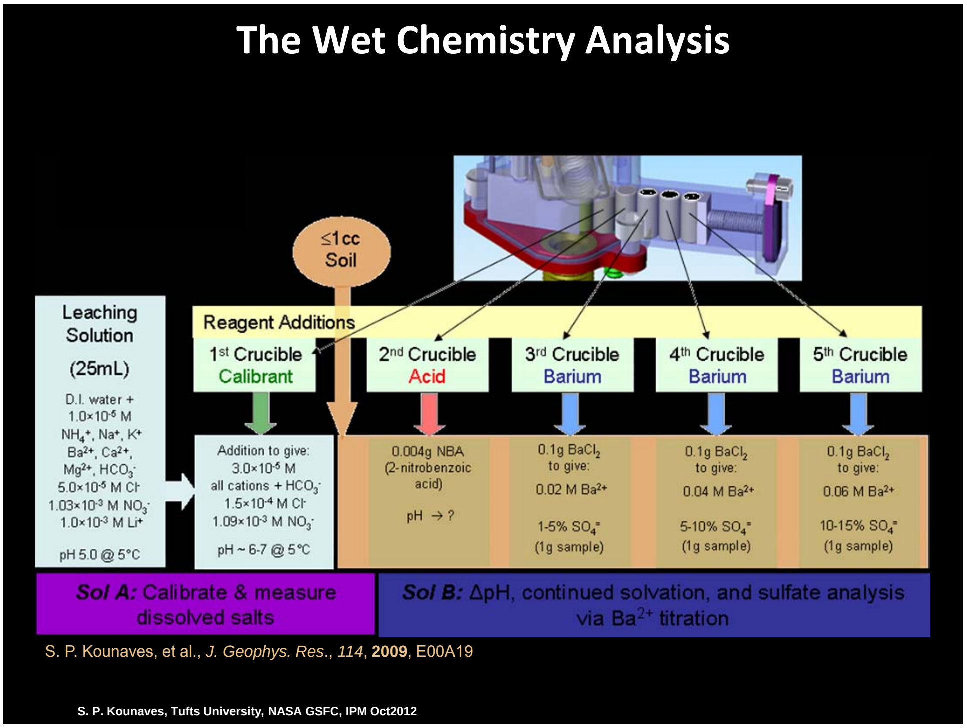
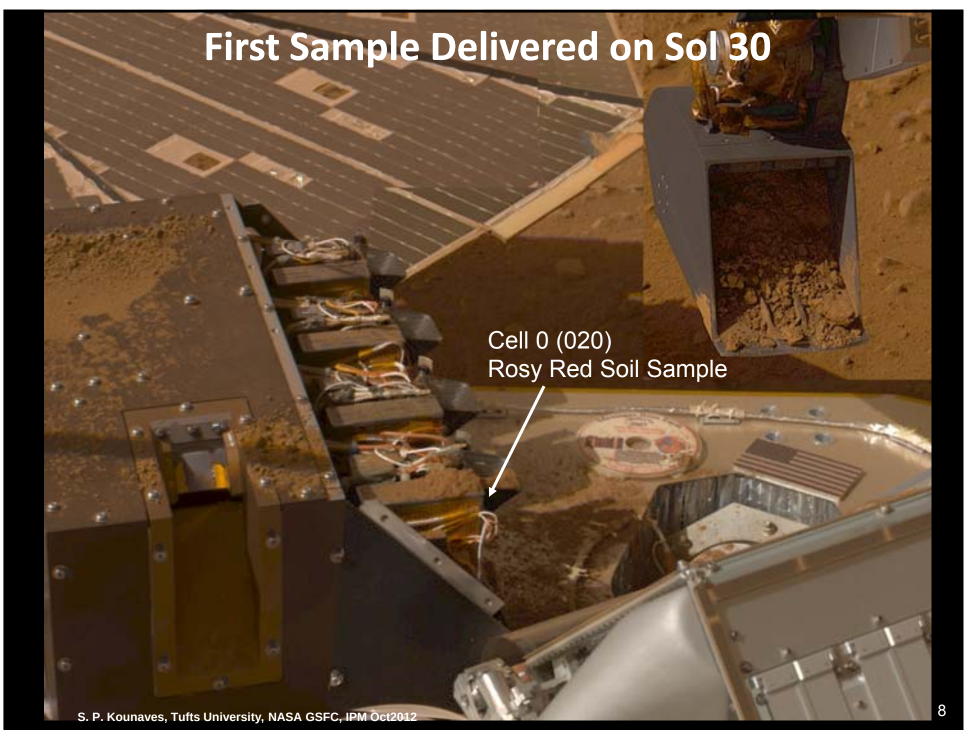


The Wet Chemistry Analysis
≤1cc Soil
Leaching Solution
(25mL)
D.I. water + 1.0×10-5 M NH4+, Na+, K+ Ba2+, Ca2+, Mg2+, HCO3- 5.0×10-5 M Cl- 1.03×10-3 M NO3- 1.0×10-3 M Li+
pH 5.0 @ 5°C
Reagent Additions
1st Crucible Calibrant
2nd Crucible Acid
3rd Crucible Barium
4th Crucible Barium
5th Crucible Barium
Addition to give: 3.0×10-5 M all cations + HCO3- 1.5×10-4 M Cl- 1.09×10-3 M NO3-
pH ~ 6-7 @ 5°C
0.004g NBA (2-nitrobenzoic acid)
pH → ?
0.1g BaCl2 to give: 0.02 M Ba2+
1-5% SO4= (1g sample)
0.1g BaCl2 to give: 0.04 M Ba2+
5-10% SO4= (1g sample)
0.1g BaCl2 to give: 0.06 M Ba2+
10-15% SO4= (1g sample)
Sol A: Calibrate & measure dissolved salts
Sol B: ΔpH, continued solvation, and sulfate analysis via Ba2+ titration
S. P. Kounaves, et al., J. Geophys. Res., 114, 2009, E00A19
S. P. Kounaves, Tufts University, NASA GSFC, IPM Oct2012



First Sample Delivered on Sol 30
Cell 0 (020)
Rosy Red Soil Sample
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Soluble Composition of the Phx 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

(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

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)	-

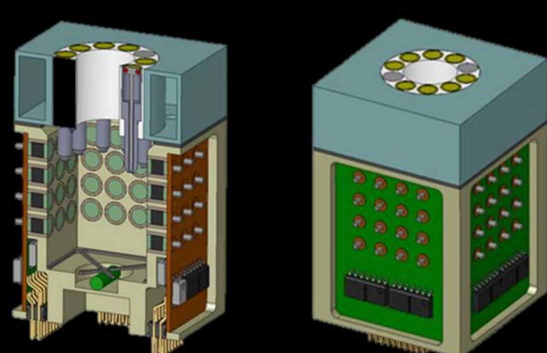
M. H. Hecht, S. P. Kounaves, R. C. Quinn, S. J. West, et al., *Science*, **2009**, *325*, 64-67
S. P. Kounaves, J. Kapit, K. Gospodinova, L. DeFlores, R. C. Quinn, et al., *J. Geophys. Res.*, **2010**, 115, E00E10.
S. P. Kounaves, M. H. Hecht, J. Kapit, R. C. Quinn, D. C. Catling, B. C. Clark, et al., *Geophys. Res. Lett.*, **2010**, 37, L09201
R. C. Quinn, J. D. Chittenden, S. P. Kounaves, and M. H. Hecht, *Geophys. Res. Lett.*, **2011**, 38, L14202

CHEMSENSE/MCAL - Mini-WCL

Each "mini-WCL" consists of a lower "beaker" where the sensors are housed, and holds 1 cc of soil and 7 mL of a leaching solution.

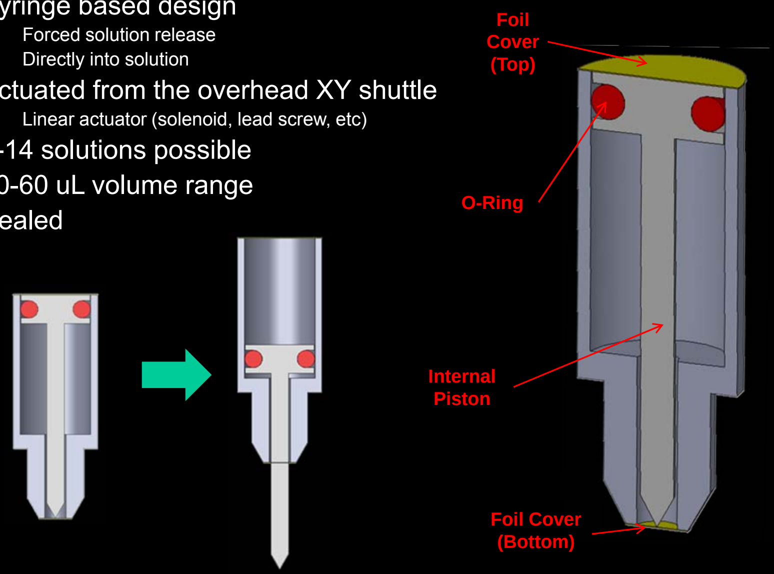
An upper "actuator assembly" incorporates the leaching solution tank, sample and liquid calibration delivery mechanisms.

Instead of using calibration pellets composed of pressed salts as the Phoenix WCL did, the mini-WCL allows for addition of **liquid** reagents to ensure rapid dissolution and equilibration of any added reagent.



Overhead Syringe Design

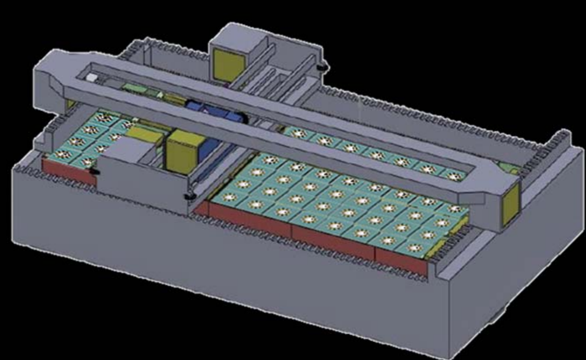
- Syringe based design
  - Forced solution release
  - Directly into solution
- Actuated from the overhead XY shuttle
  - Linear actuator (solenoid, lead screw, etc)
- 8-14 solutions possible
- 20-60 uL volume range
- Sealed



MCAL Modular Concept

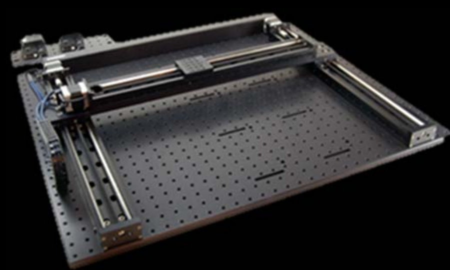
MCAL is built on a "modular" concept so that it can be adjusted to facilitate the specifications set by any future mission payload limits.

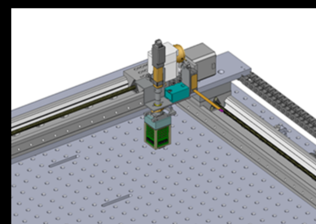
MCAL is configured on a grid system that can accommodate any number of individual mini-WCL units, from a 1×4 grid as in the Phoenix MECA package, or for example a 5×20 grid with 100 units as shown below. An even larger number of units could conceivably be accommodated if payload limits allow.

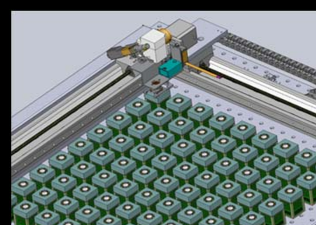


MCAL Movable Gantry

Above the grid of beakers is a movable gantry system to ferry a shuttle to the selected unit for sample acquisition, delivery, and analysis.



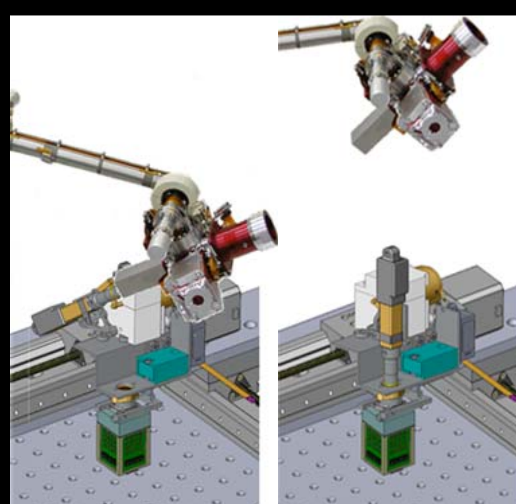




MCAL Sample Delivery

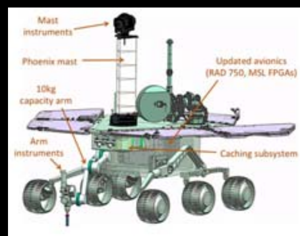
At right is shown a single unit accepting a sample from a MER class robotic arm, similar to one recently proposed for a MSR caching mission[1].

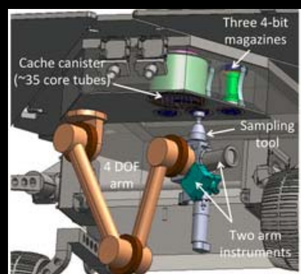
The shuttle houses a linear actuator for positive displacement of the soil sample from the shuttle container into the beaker. This actuator, shown on the left, rotated to accept a soil sample and the subsequent loading (right) of the sample into the beaker.



[1] Ehlmann, B. L. et al., (2012) Concepts and Approaches for Mars Exploration LPI Workshop, Abstract 4228

MCAL Integration on a MER-Class Rover





P. Backes, et al., Concepts and Approaches for Mars Exploration, LPI 2012, Abstract 4143

Ehlmann, B. L. et al., Concepts and Approaches for Mars Exploration LPI 2012, Abstract 4228

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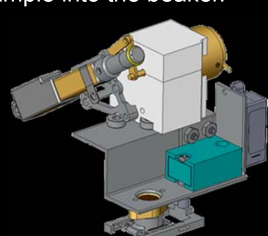
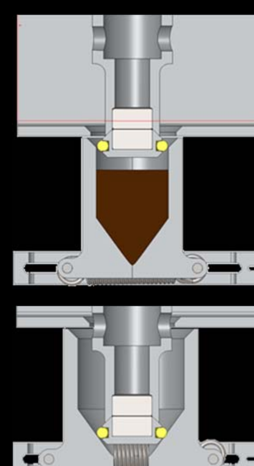
MCAL Sample Weighing & Delivery

Each mini-WCL includes a load-cell integrated directly into the soil transfer mechanism (blue). The design minimizes component volume and allows for a lower profile shuttle.

In contrast to the Phoenix WCL, soil delivery is accomplished using positive displacement to insure delivery.

Once the sample is loaded into the shuttle weighing container, a linear actuator pushes the sample into the beaker.





Scale closed (top) for sample weighing and opened (bottom) via soil plunger actuation to release soil.

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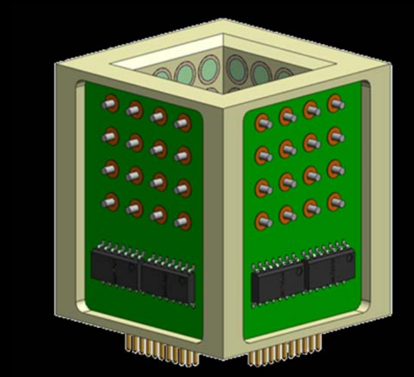
Mini-WCL Sensors

Each beaker contains three walls of ISE type sensors in a 4×4 grid, in addition to the Phx-WCL sensors, included are sensors for ions such as **Cr^{6+}, Cd^{2+}, and Pb^{2+}.**

The remaining beaker wall is reserved for other type of sensors (e.g., EC, pH, Eh, CP, CV, ASV, etc.).

These sensors are similar to the Phoenix WCL with the exception that the hydrogel was replaced with nanoporous carbon (NPC).

The mini-WCL sensors provide increased lifetime, stability, and able to better withstand the drastic changes in temperatures and thaw/freeze cycling.



"Carbon Nanofiber-Based Nanocomposite Membrane as a Highly Stable Solid-State Junction for Reference Electrodes", G. D. O'Neil, R. Buiculescu, S. P. Kounaves, and N. Chaniotakis *Anal. Chem.*, 2011, 83, 5749-5753

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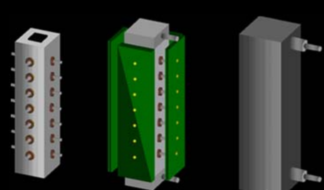
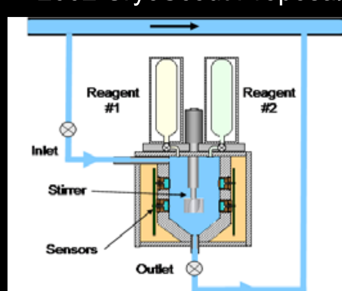
Mars/Europa Inorganic Chemistry Analyzer
Analysis of Ions in Liquid Water



2002 CryoScout Proposal

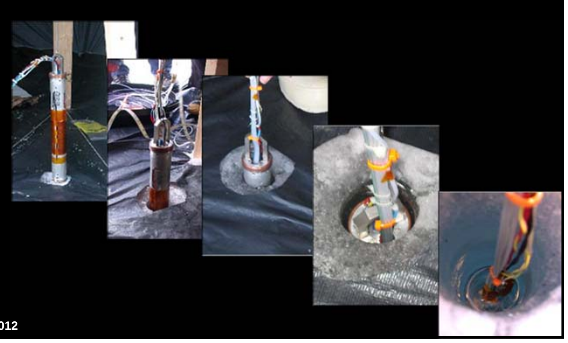


2006 Chronos Proposal

Basically a Flow Through Version of the Phoenix WCL .

Tested to 30m in Norway glacier.

Could be used on Mars' northern ice cap or on jovian moons such as Europa.



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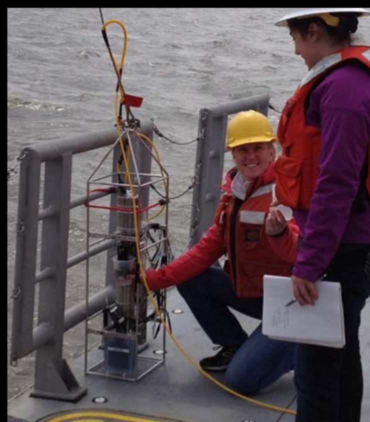
A WCL Sensor Array for Deep-Sea HT Vents

A compact array of real-time sensors using WCL ISEs has been funded by NSF and is being developed to measure in real time *in-situ* the unique characteristics and chemistry found around deep-sea hydrothermal vents.



The Phoenix WCL ISE sensors on steroids!!

HTVs are over 4000 m in depth with temperatures ranging from 2 to 450°C, and pressures near 400 bar.

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