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Chapter 16

Determination of Geochemistry on Mars Using an Array of Electrochemical Sensors

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Determining the geochemistry in the remote hostile Martian environment requires sensors specifically designed to meet such a unique challenge. We report here on the initial development, considerations, and a prototype array of electrochemical sensors for measuring in-situ a variety of ionic species in the Martian soil (regolith). The sensor array consists mainly of potentiometric ion selective electrodes but also includes conductivity, and voltammetric microelectrodes for determination of heavy metals. The array functions as an integral unit and is designed to take advantage of data processing systems such as neural networks.

After decades of intensive laboratory and on-site field investigations, we have only just begun to understand the complex chemistry and interactions of the active biogeochemical systems on Earth. Attempting to understand the past or present geochemistry, or any biogeochemistry if it exists, in a remote hostile extraterrestrial environment presents a truly daunting and unique challenge. To even consider such an undertaking, with the slightest hope of obtaining reasonably meaningful analytical data, requires sensors and instrumentation which must meet constraints and withstand rigors far beyond those encountered on Earth. In addition to limits of mass, volume, and power, the sensors and instrumentation have to withstand temperature fluctuations that may range from -120 to 60^{o}C, and attempt to anticipate any unexpected chemistry such an alien environment might present.

There are currently three bodies within our solar system which appear to have had, or still have, the potential to support aqueous biogeochemistry. These include the planet Mars and two of the moons of Jupiter, Europa and Ganymede. Recent data from the Galileo spacecraft confirmed earlier speculations that both Europa and Ganymede are not only covered by frozen water, but may also have thick layers of liquid water beneath their surface. However, it is unlikely that within the next two decades we will be able to land any type of robotic laboratory on their surface capable of taking subsurface samples or performing chemical analyses.

Mars, on the other hand, has been the target of ten successful missions since the early 1970s. Three of these missions included Landers which gave us the first close up look at the surface and chemistry of another world. During the coming decade numerous missions to Mars have been planned, at approximately 18-month intervals, by he National Aeronautics and Space Administration (NASA), the European Space Agency (ESA), and others. Several of these missions will include opportunities for landed exploration of the Martian surface and perhaps subsurface. Our current research efforts are aimed at developing analytical devices, for one or more of these missions, which will provide the maximum data return within the constraints of the transport craft and the planetary environment to be sampled.

The Martian Environment

After decades of astronomical observation and recent lander/orbiter missions, we know that Mars has a cold, desiccated, radiation bathed surface. A barren windswept landscape composed of rocks, soil, sand, and extremely fine adhesive dust. During the past billions of years the wind has swept the finer material into global dust storms, scattering a layer over the entire Martian surface. A detailed description of the geology, composition, mineralogy and structure of Mars can be found in the seminal 1992 compilation by Kieffer *(1)* and more recent findings of the Pathfinder mission in a special section of the Journal of Geophysical Research *(2)*.

A planet’s atmosphere also plays a crucial role in its geochemistry. Mars is currently blanketed by an atmosphere which is <1% of standard Earth pressure, and which varies between 6 to 10 torr depending on the season and altitude.

However, in stark contrast to Earth, it consists of 95% CO_2. This provides for a concentration of CO_2 that is about thirty times that found on Earth. Other gases include 2.7% N_2, 1.6% Ar, 0.15% O_2, and 0.03% H_2O. With only 40% of the gravitational attraction of Earth, Mars' atmosphere extends about three times as high as Earth's. Consequently, a 1 cm^2 column of air on Mars has a mass of about 15 g compared to 1000 g on Earth. This thin atmosphere allows the soil on Mars to be bombarded with both ultraviolet light and high-energy cosmic rays, probably resulting in both a highly ionized atmosphere and surface.

Based on what is currently known about the evolution of the solar system and Earth, planetary scientists have hypothesized that about 3.5 billion years ago environmental conditions on both Earth and Mars were possibly very similar. Like Earth, Mars would have possessed a warm moist climate and perhaps conditions favorable to life and biogeochemical activity *(3, 4)*. The widespread presence of water on early Mars is clearly evident in photos from the Viking missions in the late 1970s and the Mars Orbital Camera (MOC) aboard the Mars Global Surveyor (MGS) spacecraft which has been orbiting Mars since late 1997 *(5-8)*.

Even though other processes such as volcanic, glacial, or eolian, may have contributed to some of the individual features, taken as a whole there is little doubt that a liquid (most likely water) flowed on the surface of Mars in its past. Photos from the Viking orbiters and the MOC show a variety of outflow channels, sapping, fluvial valley networks, drainage basins, and liquid erosion. Figure 1 shows two such areas on the edge of the northern lowland region of Chryse Planitia, a smooth 2000km wide depression that has the expected characteristics of a large ocean basin and that connects to the even larger basin of Acidalia Planatia. The Tiu Vallis (Fig.1A) and Ares Valles (Fig.1B) both clearly show the erosion of a massive flow into these lower basins *(9, 10)*. Figure 2 (A) shows what appears to be a valley network of tributaries draining into a smooth basin.

There is clear evidence that water still exists on the Martian surface in the form of the north polar ice cap *(11, 12)*, ice cover on many surface features, fogs, clouds in the atmosphere, and possibly in the colder south polar cap, below the crust of CO_2 ice *(12, 13)*. In the low atmospheric pressure of Mars, liquid water eventually phase-separates into vapor and ice, nonetheless a reservoir of water may exist under the surface and could contribute to an underground transport system. Images from the Mars Orbital Camera (MOC), as the one shown in Figure 2(B), suggest the possibility that sources of liquid water at shallow depth are responsible for the runoff features that apparently occurred in the geologically recent past *(14)*. Whether these hydrological features were the result of a few sudden floods or extended periods of moist climate, the presence of water will have had a significant impact on the geochemistry.

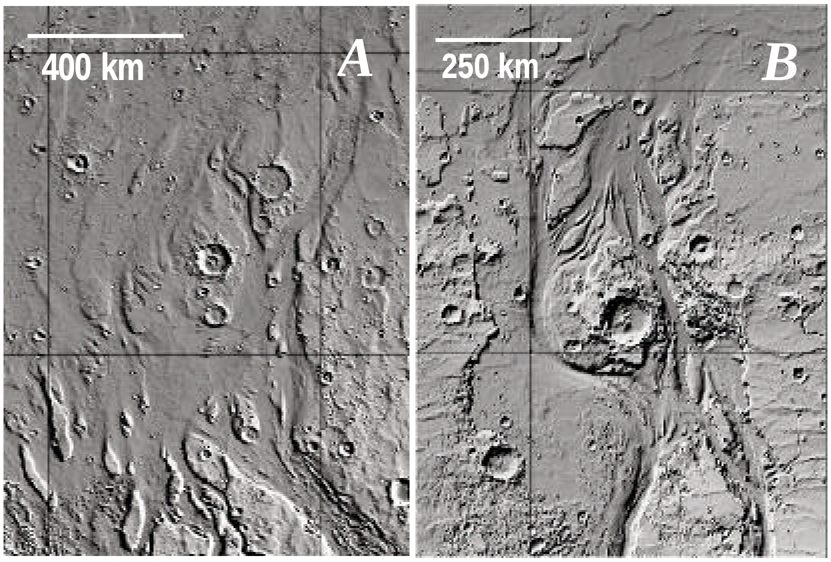

Figure 1.Water flows in the (A)Tiu Vallis and (B) Ares Valles. NASA/MOLA

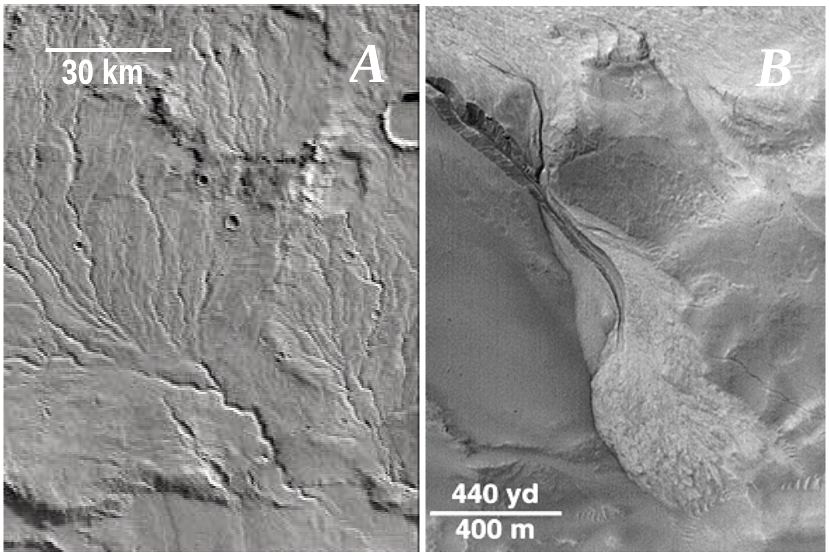

Figure 2.(A) Valley network in the Thaumasia Region 42^{o}S, 93^{o}W. NASA PIA00185. (B) Recent channels and aprons in East Gorgonum Crater. NASA/JPL/MSSS MOC2-241

Understanding The Geochemistry of Mars

The geology of Mars shows a clear demarcation of surface topography between the ancient cratered highlands in the south and younger, lower elevation basins in the north. This dichotomy has led to speculation that a significant portion of the planet was once covered by an ocean that was eventually desiccated by some catastrophic event *(9, 15)*. Geochemical indications of this aqueous period in Mars' past should be preserved in the form of salt-rich evaporites resulting from these standing bodies of water and in the geochemical alteration and transport of soluble ionic species. Any primitive biological activity would also have left an imprint on the geochemical differentiation and speciation of many trace metals and inorganic species.

The chemical composition reported by the two Viking and the Pathfinder Landers was very similar. Even though the elemental constituents have been assigned to an assumed set of oxides, it is important to recognize that the raw data from the Sojourner rover's x-ray spectrometer provided elemental composition only. Similar data from Viking has been interpreted as indicating a mix of iron-rich smectite clays, iron oxides, and magnesium sulfate. The iron content is around 15%, with ubiquitous sulfur that could either originate from precipitated salts or volcanic emissions. Although carbonates are expected to be abundant in the Martian soil *(16)*, they appear to be absent on the on the exposed surface *(17)*. However, carbonates can be easily destroyed by UV radiation *(18)* and volcanic sulfuric acid aerosols and sulfates *(19)*, both of which are prevalent on Mars. The Viking experiments also found the surface devoid of any organic molecules *(1)*. This has been attributed to the presence of one or more reactive oxidants in the surface material. Various inorganic oxidants have been proposed *(20, 21)*, most recently superoxide radical ion formation by UV on the soil has been suggested as a most likely mechanism *(22)*.

Data from the Viking and Pathfinder missions suggest that the Martian surface soil consists of approximately 10% salts (dominated by sulfur- and chlorine-containing salts, presumed to be sulfates and chlorides). Widespread salt evaporites can form and accumulate in small enclosed basins such as craters, or on a large scale associated with lakes *(5)* or a large northern ocean *(15)*. Salts can also accumulate wherever volcanic gases act upon the soil, and also in areas where microbial activity might have existed. Since characteristic salts are formed by each of the above processes, a chemical analysis of the salts present at a given location can provide information on the geochemical history of Mars, and in particular the history of liquid water on its surface.

Several models have been developed to theoretically determine likely salt and mineralogical compositions *(23, 24)*. Most recently Catling *(25)* has developed a sedimentation model and demonstrated its use in calculating the evaporite mineral sequence that would be expected in such closed basins.

Figure 3 shows the expected layering using water soluble components derived from weathered igneous rock similar to Martian meteorite basalts, assuming an atmospheric P_{CO2} level of >0.75 torr, and that conditions are neither strongly reducing or oxidizing. The first major carbonate to precipitate would be siderite ($FeCO_3$), followed by magnesian calcites ($Ca_XMg_YCO_3$), hydromagnesite ($Mg_5(CO_3)_4(OH)_2$-$4(H_2O)$), gypsum ($CaSO_4 \cdot 2(H_2O)$), and finally by highly soluble salts such as NaCl.

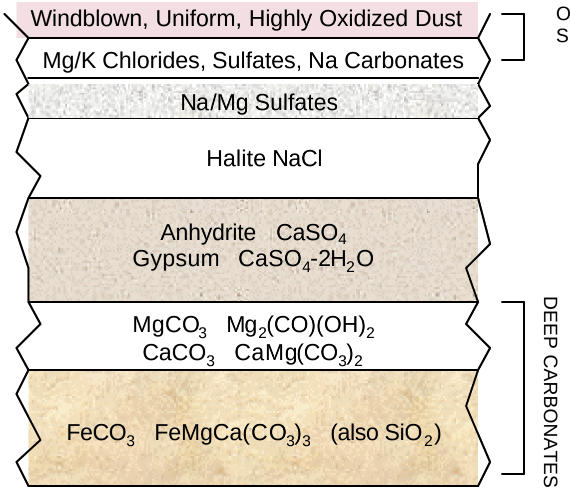

Figure 3. Theoretically derived layering in an evaporite basin.

The Legacy of the Mars Environmental Compatibility Assessment (MECA) Instrument Package

The MECA instrument package, shown in Figure 4, was originally designed and assembled for inclusion on NASA's Mars 2001 Lander Mission. The mission was cancelled in 2000 due to the loss of the Mars Polar Lander in December of 1999. MECA, which was completed and flight-qualified prior to being cancelled, was designed to evaluate potential geochemical and environmental hazards that might confront future Mars explorers, and to guide NASA scientists in the development of realistic Mars soil simulants. In addition to the NASA objectives, MECA had the potential to return data that would be directly relevant to basic geology, geochemistry, paleoclimate, and exobiology.

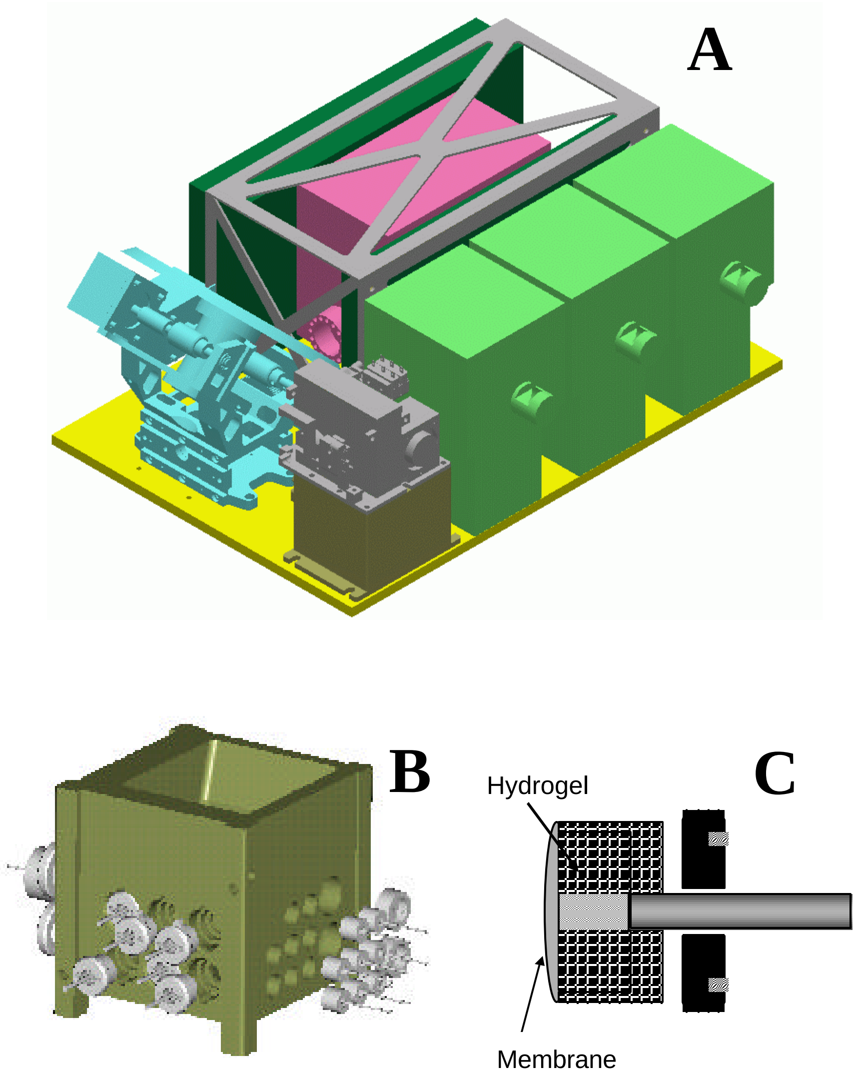

Figure 4. (A) The MECA instrument box showing the four wet chemistry cells and the microscopy station. (B) Exploded view of a wet chemistry cell showing lateral placement of ISE sensors. (C) Diagram of typical ion selective electrode.

The MECA instrument package contained a wet chemistry laboratory, an optical and atomic force microscope, an electrometer to characterize the electrostatics of the soil and its environment, and an array of material patches to study the abrasive and adhesive properties of soil grains. Due to launch vehicle limits, the MECA package was limited to; a mass of 10 kg, peak power of 15 W, and a 35×25×15cm volume. In addition to these flight constraints, MECA had to withstand temperatures ranging from -120 to 60°C, a near vacuum atmosphere, and any unexpected chemistries such an alien environment might present.

The development of MECA, and its use to analyze the surface material in a remote hostile environment, posed a unique set of challenges for remote chemical analysis and more specifically for electrochemical analysis. MECA served as a rigorous test bed for next-generation electrochemical sensors for in-situ planetary chemical analysis.

The MECA Wet Chemistry Laboratory (WCL)

The WCL consisted of four thermally insulated, single-use, independent analysis cells. Each cell was capped with a water reservoir/actuator assembly. The actuator assembly consisted of a sealed water tank with a puncture valve, a sample loading drawer, a stirrer motor with impeller, and a solid pellet dispenser. The pressurized tank contained 30 mL of a "leaching" solution. The solution, which contained several ions at 0.01 millimolar concentrations corresponding to the ISE, served both to extract the soluble components from the soil and as a calibration standard for the reference and ion selective electrodes. The sample loading “drawer” would receive the soil from the lander robotic arm, remove excess soil, deposit it in the chamber, and effect a crude chamber seal. The sample drawer sealed with enough force to maintain a chamber overpressure sufficient to prevent boiling at 27°C (less than 25 torr). The drawer loading compartment held approximately 1.0 cm^3 of soil, and the base was a spring-loaded flap, which would retract to allow the soil to fall into the cell as the drawer was closed. A sieve or screen prevented particles >0.5 mm from falling into the receptacle, while a gap between the receptacle and the seal allowed excess soil to fall off. A scraper or leveling tool removed excess soil as the drawer closed.

Each rectangular cell, fabricated from an epoxy resin and designed to be inert in a range of environments, was 4×4 cm wide and 5 cm deep, with an internal volume of about 35 mL. The cells were designed to lose < 0.5 thermal watts of power against a 40°C temperature gradient. A Viton sealing surface insured a leak rate of < 0.1 cm^3/minute of water vapor at 30 torr (corresponding to 4 micrograms per minute) against an outside pressure of 5 torr, over the operating temperature range, despite contamination with dirt and dust. This leak rate corresponds to a partial pressure of water ten times lower than that of the Mars ambient contribution at 1 cm from the leak.

The WCL Electroanalytical Sensor Array

Arrayed around the perimeter at two levels were 26 sensors. A description of the sensors included in the MECA WCL can be found in Table 1 and shown in Figure 4B-C. The array included both voltammetric and potentiometric based sensors. The *ion selective electrodes* (ISEs) were based on commercially available polymer membrane and solid pellet technology (ThermoOrion Research, Inc.). The *anodic stripping voltammetry* (ASV) for measuring concentrations of heavy metals such as lead, copper, mercury, and cadmium at part-per-billion levels was performed at an array of 10μm microfabricated ultramicroelectrodes *(26-28)*. Specially designed and configured metal electrodes were used to measure conductivity and redox potential.

Table 1. Species and Parameters Measured by the MECA Wet Chemistry Cell Sensor Array.

Parameter/Species	*Sensor Configuration &Method*
Total Ionic Content.	Conductivity cell, 4-electrode planar chip
H^+	pH, polymer membrane, potentiometric
H^+	pH, iridium dioxide, potentiometric
Dissolved O_2	Au electrode 0.25-mm, membrane-covered, 3-electrode, Au cathode, using CV.
Dissolved CO_2	ISE gas permeable membrane, potentiometric
Redox Potential.	Pt electrode, 1.0-mm disc, potentiometric
Oxidants and Reductants	Au electrode, 0.25-mm disc, using CV
Cu^{2+}, Cd^{2+}, Hg^{2+}, & Pb^{2+}	Au MEA, chip, 512 10-μm elements, ASV
Ag^+, Cd^{2+}, Cl^-, Br^-, I^-,	ISE, solid-state pellet, potentiometric
Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, NO_3^-, ClO_4^-, HCO_3^-	ISE, polymer membrane, potentiometric

CV: Cyclic Voltammetry, ISE: Ion Selective Electrode, ASV: Anodic Stripping Voltammetry, MEA: Microelectrode Array

In some cases the sensors and/or the sensing function of the WCL were duplicated. This was necessitated by; (a) the relative importance of the measured parameter; and (b) the expected reliability of the individual sensor. After being subjected to a series of freeze/thaw cycles during the equipment qualification stage, the solid-state sensors proved to be very reliable. Thus, only one sensor each for ORP, conductivity, CV, ASV, silver, and cadmium were included. There are also several redundant measurements. For example, oxygen and other oxidants or reductants are determined not only by the bare and membrane-covered CV electrodes but also by the ORP sensor; heavy metals are determined by ASV as well as by silver and cadmium ISEs. Because the pH and reference electrodes are inherently less reliable than solid-state sensors and these parameters are so important, three pH sensors and three reference electrodes were included. The reference electrodes were critical for all measurements except CV, CO_2 and conductivity. Since the chloride ISE could have also served as a reference if all the others had failed, a second chloride ISE was also included.

The most critical electrochemical sensors were designed to suffer minimal effects from exposure to a dry evacuated environment. Several of these, the solid-state ISEs, ORP, and conductivity sensors, contain no fluid and could tolerate a vacuum environment well. The gel-backed polymer ISEs were tested in simulated flight environments and were shown to be sufficiently robust and even tolerant of complete dehydration. Ion-selective electrodes (ISEs) were chosen as the predominate sensor because they possess several desirable characteristics. These include, a wide dynamic detection range, availability for a substantial number of ions, and intrinsic simplicity compared to most other analytical tools. Many ISEs can be made compact, rugged, capable of surviving harsh chemical and physical environments, and resistant to radiation damage. In the WCL they were used for determining soluble ions such as sodium, potassium, magnesium, calcium, the halides, pH, dissolved CO_2, and O_2 levels.

Figure 5 shows the typical response of an array of ISEs to a calibration solution containing 10^{-5}M of $KHCO_3$, NH_4NO_3, NaCl, $CaCl_2$, and $MgCl_2$, and $2.5x10^{-3}$M of Li_2SO_4. Each ion was calibrated minus its own ion. For example, the Li^+ ISE was calibrated in the presence of all the above ions except Li^+. Only the perchlorate ISE was calibrated by itself in de-ionized water. All ISEs were calibrated with a primary ion concentration ranging from 1M to 10^{-6}M. Serial dilutions were performed using a 1M stock of each solution to the desired concentration. The calibration was performed using several beakers containing the range of primary ion to be monitored. Stock solutions of the other leaching solution components were added to each solution so the proper background of 10^{-5}M or $2.5x10^{-3}$M would be maintained in relation to the primary ion.

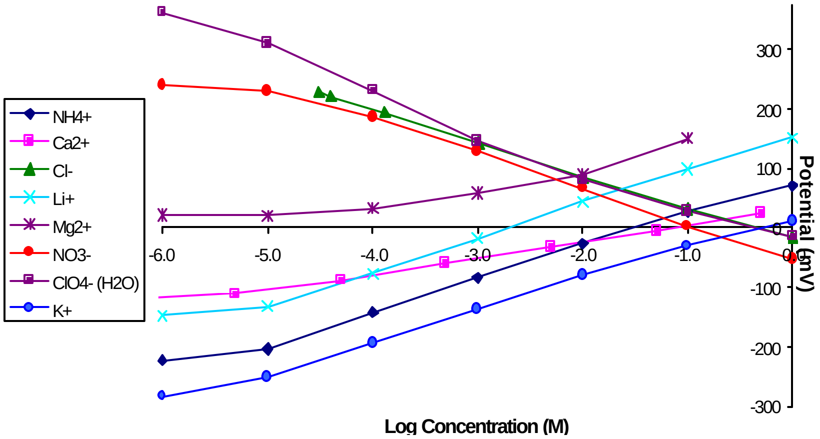

Figure 5. Typical ISE response to nine ions dissolved in multi-analyte solution

The Electronic Tongue – An Integrated Electrochemical Sensor Array

The MECA WCL demonstrated both the untapped potential of electrochemical sensing, and the challenges that still need to be met. Rarely have electrochemical sensors been required to operate and survive under the conditions imposed by an in-situ planetary analysis, including the heat and humidity of the Cape Canaveral launch pad, the desiccating vacuum of space, and the extreme temperatures found on the surface of Mars. During the MECA evaluations the sensors were subjected to a full regimen of shock, vibration, and environmental cycling tests. Even though some sensors such as the glass pH electrode have been used in laboratories for decades, they were eliminated early in the program because of cracking when subjected to temperatures ranging from –100 to 60 °C. But even more troublesome was the degradation of the insulation caused by the repeated expansion and contraction, and the resulting electrical leakage paths between the test solution and the wire lead.

One important finding of the MECA project was that polymer-based ISEs proved to be more resilient under such harsh conditions than originally expected. The MECA ISEs survived despite fears that temperature cycling might cause the membranes to undergo glass transition at low temperature and become brittle. Dehydration of the hydrogel also proved to be of minor concern.

As a next generation of MECA-type WCL sensors, we have been developing an integrated, rugged, low mass/power, electroanalytical sensor composed of an array of *ion selective electrodes (ISE)* and *microelectrodes* (MEA). This *ion sensor array* (ISA) (also referred to as electronic-tongue or e-tongue), builds on the MECA legacy but also extends it based on several new transduction and fabrication concepts. Figures 6 through 8 show the general configuration of the sensor assembly on the ceramic substrate and the analysis chamber with the controller electronics board. The microfabrication, integration, and multiplexing of a large number of individual ISEs and MEAs on a single substrate had not been previously attempted. The key to fabrication is the customization of each sensor by incorporating within it a species selective carrier (ionophore) using several special electrochemical processes to immobilize the ionophore within the sensing membrane.

Recent developments have made it practical to decrease the size of the ISE sensor to a point were a large number of them can be fabricated within a small area, thus, allowing a broad spectrum of analytes to be detected and measured. To fabricate such a device requires the efficient and reproducible deposition of the desired ions or ionophores onto small 50-200μm diameter areas. The novel concept in this work is the electrochemical modification of an individual element in an array of ISE sensor substrates, by electronically addressing it. By applying a voltage to the desired element, the appropriate ionophore or counter-ion is immobilized via an electropolymerization process. The cell allows a rapid flow-through exchange of reagents such so that every electrode pad can be customized in rapid succession. In additon to polymers, other materials may also be deposited on any electrode pad.

Unlike pattern-dependent sensor array devices, this electrochemical sensor will provide both identification and reliable quantitative chemical data. The use of an integrated set of species-semispecific, ionophore-based ISEs, has required that we simultaneously address several fundamental scientific questions, including the scaling of the transduction mechanisms, the doping process, the selection and deposition mechanisms of the appropriate ionophore matrices and polymer substrates, the processing of the array of electroanalytical signals, and the chemometric analysis for interpreting and generating the chemical speciation of the sampled environment.

Such integrated sensor array would have a dramatic impact by enabling a small, low-power, cubic-centimeter-sized device that could be used in-situ on remote planets. This sensor could determine the inorganic constituents of the soil, elucidate the speciation of trace metals, and identify possible chemical biosignatures. The successful implementation of this new ISE fabrication technique will also allow the development of other microsensor arrays that can be used for the in situ determination of the chemical composition of water and water-solvated soil samples in terrestrial oceans, waters, and other aqueous systems.

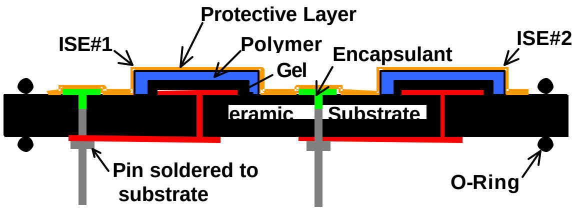

Figure 6. Schematic diagram of two ISE sensor array elements fabricated on a ceramic substrate.

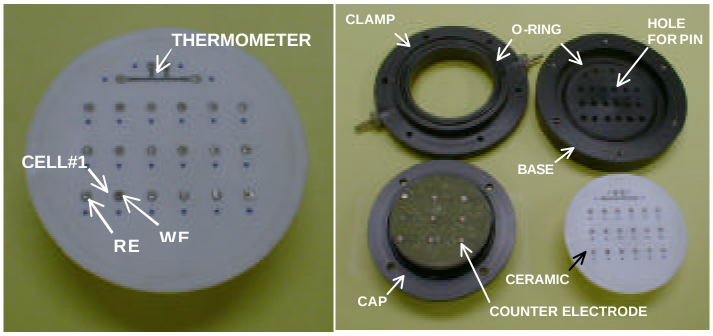

Figure 7. Left: The 4.5-cm diameter ceramic substrate showing the working (WE) and reference (RE) electrodes and a four-terminal thermometer. Right: Chamber parts including ceramic substrate (lower right) and three chamber units: Base (upper right), Clamp (upper left), and Cap (lower left).

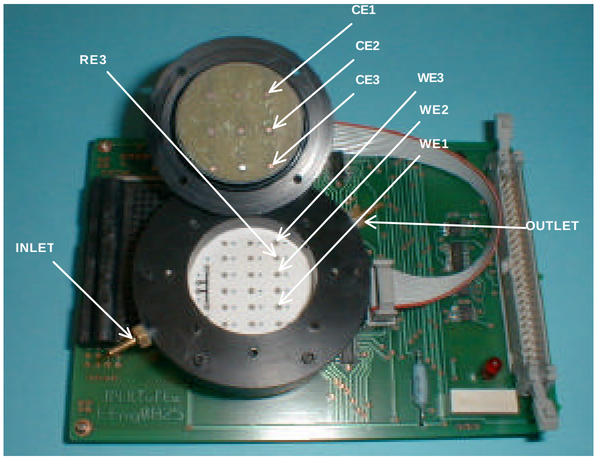

Figure 8. Deposition/Sensor chamber mounted on electronics board.

Acknowledgments

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