Laboratory Measurements in Support of Present and Future Missions to Mars

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Abstract

The case is made that supporting laboratory measurements and facilities should be considered an integral element of the Nation's planetary exploration program. Laboratory measurements are important for the development of successful scientific instruments for space flight and, perhaps more importantly, to meaningfully interpret the data returned by the missions. They enable quantitative data to be obtained, hence interpretation of instrument results and insights into potential new planetary processes. There are ample examples of this in the history of the Mars program: The interpretation of data from the Viking surface measurements and biology experiments largely depended on post-mission laboratory studies. Provision of input data (rate constants for the adsorption and desorption of volatiles passing through regoliths, diffusion rates, etc.) is critical for global circulation and climate models. Many geologic features on Mars have been understood by the use of modeling of volcanic, lacustrine, fluvial and aeolian processes using flumes and wind tunnel experiments. Instruments can also be directly tested *in situ* and their results simulated with experiments. The potential of such experiments is boundless as new features are observed on the various surfaces of Mars and improvements in laboratory measurements allow more realistic simulation of the surface and subsurface conditions. Finally, as we enter a phase of sample return from the Moon, asteroids, and Mars, following the success of Apollo, Stardust and Genesis, we should focus resources on the establishment of laboratories for the analysis of extraterrestrial samples. The recommendations of this white paper are therefore as follows. (1) Support laboratories for fundamental research that is directly related to planetary science, missions, and programs of planetary exploration. (2) Support specialized facilities for community use such as large planetary environmental chambers, flumes, and wind tunnels. (3) Establish and support analytical laboratories in preparation for sample return from asteroids, the Moon, and Mars.

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Introduction

Since the Mariner missions, Mars has been the most studied planet in the Solar System. There is now a massive amount of data on Mars' atmosphere, surface and subsurface. The interpretation of these observations is based on sets of parameters or databases constructed on Earth. These include thermodynamic and kinetic data, spectral properties, and physical parameters. Mars has been a cold dry planet for most of its history. Modern processes occur there under environmental conditions that are extremely unusual for the Earth; hence terrestrial field data thus often have limited applicability to Mars. However, experiments conducted under controlled laboratory conditions yield reproducible datasets and describe fundamental chemical and physical processes that can be applied to a wide range of terrestrial and planetary environments.

Laboratory experiments under controlled conditions are absolutely necessary to establish fundamental parameters that accurately allow interpreting the data and calibrate the measurements and experiments conducted by future missions. Among the most important conclusions of several recent workshops (Phoenix chemistry, CO_2 polar caps energy balance, hydrous modeling workshop, ices in the Solar system etc.) was the need for more experimental data. In addition to the determination of parameters, simulation experiments shed light on complex processes modifying the surface and subsurface of Mars. Experiments are an indispensable part of scientific exploration because they connect observations to theoretical geochemical and/or physical models.

In this white paper, we attempt to bring the attention of the community to the necessity for a program of identification, measurements and application of laboratory datasets to the martian environment. In addition, we support the development of an experimental program aimed at simulating processes relevant to Mars. Such programs will benefit all fields of Mars exploration, from petrology, mineralogy and geochemistry to climate models, astrobiology and ultimately sample return and human exploration.

1. Background

Since the first *in situ* observations by the Viking landers, the study of the martian surface has been progressively dominated by work on mineralogy and geochemistry rather than biology, since we must first understand the environment before characterizing the potential for life. Although Mars' surface is largely dominated by volcanic deposits and igneous phases (olivine, pyroxene and plagioclase), abundant mineralogical, geochemical, and morphological evidence for past aqueous processes is observed in hydrated minerals and water-related geomorphologic features such as valley networks, gullies and lakes [*Malin and Edgett*, 2000]. By simulating the martian surface and subsurface, laboratory experiments were necessary for studying analogue materials and understanding the processes affecting the surface and the atmosphere. The puzzling results of the Viking landers' biology experiments [*Levin and Straat*, 1976], which showed extreme reactivity of the regolith but no sign of active life, were largely resolved by experiments in the laboratory [*Oyama et al.*, 1978]. Later, the Viking orbiter water vapor measurements were interpreted using Global Circulation Models, though the regolith contribution was demonstrated by diffusion and adsorption experiments [*Jakosky*, 1983].

The potential for important science return from the experimental approach to planetary processes is demonstrated by the Mars Exploration Rovers mineralogical and geochemical analyses. Just as experiments are necessary to understand the geological processes on the surface of the Earth, experiments simulating surface processes are necessary to understand the nature of the salt assemblages observed by Spirit and Opportunity [*Tosca et al.*, 2005].

Data returned by Orbiters are also successfully interpreted using a combination of modeling and experiments. The distribution of ice on Mars, as observed by Mars Odyssey is explained by a combination of modeling and experiments on the transfer of water vapor in the porous regolith [*Hudson et al.*, 2007]. The observation of gullies by Mars Global Surveyor and following missions (Mars Odyssey, Mars Express, Mars Reconnaissance Orbiters) generated the development of a large amount of experiments on the stability of liquid water on Mars [*Chevrier and Altheide*, 2008].

These are just a few significant examples on how the analysis of data returned by several previous missions benefit significantly from experiments in the laboratory. Overall, experimental work can be divided into two broad categories: determination of parameters and interpretation experiments. Most of the time they are linked. Complex experiments under carefully controlled conditions to simulate the surface and subsurface of Mars are very useful for validating of numerical models before they are applied to Mars.

2. Compelling scientific objectives

- ***Thermodynamic and Chemical Properties of Minerals and Compounds Relevant to Mars***

A complete understanding of the chemistry and mineralogy of the martian surface requires modeling of the geochemical evolution of liquid solutions, and thus the thermodynamic and eventually kinetic properties of compounds. These compounds include mostly oxides, sulfates, phyllosilicates, carbonates, chlorides and more exotic salts recently discovered such as perchlorates. The necessary thermodynamic properties are mostly the formation constants and their variation with temperature (or the Gibbs energy and enthalpy of formation). These parameters are known for various compounds relevant to the Earth (*i.e.* existing at ambient temperatures). This is the case for carbonates and some phyllosilicates. However, sulfates, chlorides and other soluble salts form hydrates at low temperatures and these hydrates are different from those found at typical terrestrial temperatures and thus must be determined along with their thermodynamic properties.

In addition to the thermodynamic constants, precise modeling of the soluble salts requires a knowledge of the Pitzer parameters [*Marion et al.*, 2008], which characterize the interactions between ions in aqueous solutions and allow the calculation of the behavior of complex solutions during evaporation or temperature changes. The Pitzer parameters only exist for common compounds on the Earth and then only close to ambient temperatures. Their determination for compounds related to the martian surface has been started [*Tosca et al.*, 2007], but the database remains largely incomplete, especially for martian temperatures.

Finally, chemical processes on Mars should be much slower than on the surface of the Earth because of the lower temperatures. The determination of the kinetics is thus of primary interest, especially for the potential formation of metastable phases, which include liquid brines, typical in cold environments [*Fairen et al.*, 2009]. This is relevant to Mars because understanding the reaction pathways requires the determination of the reaction kinetics and their dependence on temperature [*Elwood Madden et al.*, 2009].

- ***Physical Parameters Characterizing the Regolith and its Interactions with the Atmosphere***

Most of the surface mineralogy is determined using reflectance and emission spectrometry in the near to mid infrared. The usual identification process uses databases of terrestrial samples or synthetic samples measured under terrestrial conditions, which are not necessarily relevant to Mars. The spectral properties of many hydrates forming from soluble salts at low temperatures are largely unknown. A good example is the chlorides, which have been detected by THEMIS [*Osterloo et al.*, 2008] but not by OMEGA or CRISM, mostly because the databases contain only sodium and potassium chlorides at ambient temperatures. Most chlorides form hydrates, and therefore could be present but undetected due to the incompleteness of the databases.

Phyllosilicates are present on heavily impacted terrains [*Poulet et al.*, 2005] and may have been significantly altered by meteoritic impacts. Experimental modeling of impacts using light gas guns will help interpret not only the nature of the phases present on the surface but also their geological history. Finally, the determination of the mineralogical and chemical composition of the primary basaltic silicates, that compose most of the martian surface has profound implications on its origin and evolution, magmatic and aqueous [*Hamilton et al.*, 2003].

Determining the interactions of the regolith with the atmosphere and its control on the climate at short and long timescales requires abundant laboratory work, starting with thermal modeling of the regolith, which requires the heat capacity and thermal conductivity of the surface for all relevant phases and mixtures. The regolith has also been hypothesized to stabilize ice deposits due to slow diffusion of water vapor through the porous medium. Although some preliminary work has been done on various regolith analogues, the diffusion coefficients of several gaseous species (CO_2, CH_4) remain undetermined for most mineralogies. Finally, the diurnal and seasonal cycles of CO_2, H_2O and CH_4 may also be controlled by adsorption on the regolith. Understanding adsorption on Mars, and implementing it in the presently existing models of water vapor transport (like the GCMs) requires the determination of thermodynamic and kinetic parameters. These parameters are then used by numerical models to extrapolate to the martian surface. Also complex experiments involving ice, regolith and the atmosphere can be used as a complement to the numerical models, helping their validation.

Radar sounding performed by the MARSIS instrument on Mars Express or SHARAD on MRO has become an important tool to study the 3D distribution and state of subsurface H_2O and other layered deposits [*Phillips et al.*, 2008]. Radar instruments are also part of the 2008 Lunar Reconnaissance Orbiter. The success of these investigations is strongly dependent on our understanding of how the radar wave propagation is affected by subsurface regolith as a function of the mineralogy, temperature, and porosity of the local environment. Much of the potential parametric space associated with the martian surface has still to be characterized by determining the electromagnetic properties of a broad range of analogues over various temperatures, porosities, and frequencies.

A last type of “physical” experiment is the simulation of geologic or geomorphologic processes on the surface. These experiments remain very limited since they require complex and voluminous apparatus. However, the formation of martian gullies and crater lake deltas has been undertaken by simulations in flumes [*Kraal et al.*, 2008; *Vedie et al.*, 2008] and important conclusions have been drawn on the nature, dynamics and stability of the fluids involved.

3. Relevance to Present and Future Missions

- ***Mars Exploration Rovers***

The MER rovers have returned a huge amount of data on the mineralogical and geochemical properties of the surface of Mars. These data point to the importance of salts as components of the regolith and as major components in geological outcrops [*Squyres et al.*, 2004]. The formations of such deposits and their interpretation in the evolution of the martian surface requires geochemical modeling and experiments in the lab not only to confirm the model results but also to identify potentially missing parameters [*Tosca et al.*, 2005]. For example, the abundant presence of iron sulfates required the determination from laboratory data of Pitzer parameters for the iron sulfate system [*Tosca et al.*, 2007]. Laboratory experiments investigating the kinetics of mineral dissolution and precipitation can also place temporal constrains on the duration of aqueous processes on Mars [*Elwood Madden et al.*, 2009].

- ***Phoenix***

Phoenix performed the first wet chemistry measurements and discovered perchlorates in the soil [*Hecht et al.*, 2009]. The interpretation of the results requires geochemical modeling of these exotic soluble salts, starting with the determination of thermodynamic properties and model parameters. Experiments must also be performed to reproduce the measurements from the lander, as well as investigate potential processes which may have produced the observed near-surface materials (freezing and evaporation of relevant solutions for example [*Fairen et al.*, 2009]). Interpretation of TEGA instrument results also requires a large amount of laboratory measurements, not only reproducing similar experiments (heating samples and measuring the gas produced), but also determining the thermodynamic properties of the potentially observed compounds (enthalpy of transformation).

Finally, the results from the TECP instrument indicate a complex interaction between the subsurface ice, the regolith and the atmospheric humidity [*Chevrier et al.*, 2009]. Such interactions may be modeled through experiments in simulation chambers, allowing the determination of necessary parameters. Adsorption in particular appears to be a significant process affecting the diurnal cycle [*Zent et al.*, 2001], and has been often neglected.

- ***Mars Science Laboratory***

The Mars Science Laboratory will likely perform extensive measurements of phyllosilicate-bearing deposits potentially associated with salts (chlorides, sulfates etc). Thus, it is highly probable that a background of experiments will be necessary to interpret the data and place them in a more global geological context. For example a large dataset of samples measured in situ in the field has been acquired to interpret future results from the miniature XRD onboard MSL.

- ***ExoMars***

ExoMars will be an ESA rover, with NASA collaboration, both designed to perform mineralogical and geochemical studies of the surface, but with capabilities for astrobiology, which requires complete knowledge of the surface and subsurface. ExoMars will be equipped with a drill to study in details the subsurface structure down to about 1 meter. Interpretations of the behavior of ice, water vapor and potential liquids, pure water or brines (which have strong implications for potential life) will require abundant laboratory experiments and data. An ice-rich regolith could be the best chance to detect life forms. Running simulation experiments under Mars conditions could help refine analytical protocols for the detection and study of life on Mars.

4. Relevance to Global Circulation Models

Global Circulations Models have been extremely important tools for understanding the dynamics and evolution of the martian atmosphere and climate [*Forget et al.,* 1999], with a wide range of applications including main (CO_2) and trace (H_2O, CH_4) gas cycles, ice deposits distribution and liquid water presence and stability. However, a major limitation of these models is their lack of consideration of the regolith. For example, the regolith affects water vapor for example through diffusion and adsorption [*Chevrier et al.*, 2008]. Recent models have begun to include diffusion because diffusion coefficients have been measured for some analogues. However, the case of adsorption remains largely unexplored in these models. The implementation of these phenomena in the Global circulation models will require diffusion coefficients, adsorption thermodynamic and kinetic parameters and their dependency on temperature and pressure. Global maps of these parameters, analogous to those available for albedo or thermal inertia will be highly desirable and probably necessary in the future.

5. Relevance to Sample Return

Finally, the most relevant and important application for laboratory experiments and investigations is future sample return, which has been stated as a major research and exploration objective at the last MEPAG meeting. However, a full understanding of potential samples requires complete pre-analysis in the lab, for two major reasons: the first is the behavior of the sample on Mars with respect to the variation of environmental conditions and the behavior of the sample when put under terrestrial conditions. The behavior of salts with respect to temperature and humidity is a major issue, as has been shown for magnesium sulfates [*Vaniman et al.*, 2004]. Phase changes may affect interpretations related to water content (in particular with adsorption) but also isotopic ratios. Therefore, extensive preliminary tests in the lab on a large array of analogues must be carried out to further prevent or at least understand the effect of martian and terrestrial environments, and potential chemical and physical changes that can occur to samples in transit from Mars to Earth. This will optimize the science return on what will be a major technologic achievement.

6. Recommendations

- ***Support Laboratories for Fundamental Research***

We recommend increased support for the various aspects of experimental and theoretical studies of the martian surface and subsurface, which are presently underfunded in comparison with mission data analysis. However, these two branches are integral and necessary parts of any planetary science program. The evolution in complexity of the analytical systems on landers, rovers and orbiters requires a significant investment in laboratory tests and databases to provide the best scientific outcome. In addition, models that are used to interpret data need parameters and validation through experiments. Finally, most of these experiments can be applied to other planetary bodies through their scientific concepts or results.

- ***Support Facilities for Community Use***

Many research groups around the country have built, for example, planetary environmental chambers to simulate present and past conditions on Mars. Usually these chambers are small (desk top) and suitable for a specific experiment. Large, multipurpose chambers are expensive and challenging to construct and operate, yet are needed to provide space and pathlengths for many experiments. In addition large chambers are ideal tools to test space flight instruments under a wide range of conditions. Some needed research is neglected because of the lack of such equipment for groups without this special focus. We therefore recommend NASA and NSF establish a community facility devoted to the study of martian surface and subsurface environments in the laboratory. We also recommend that the federal agencies continue to support existing facilities for the simulation of fluvial and aeolian processes on Mars and other planets.

- ***Prepare Laboratories for Mars Sample Return***

During the years leading up to the return of samples from the Moon, NASA invested relatively large amounts of funding to the establishment of laboratories for the analysis of Apollo samples. Most of these facilities are still operating, as shown by the steady stream of Apollo sample papers. We propose continued support for these laboratory facilities. We recommend that NSF cooperate with NASA to implement a program of research to support existing and new laboratories whose primary focus is, based on previous experience under simulated planetary conditions, to analyze the wealth of planetary samples expected to be returned from the asteroids, the Moon, and Mars over the next decade and beyond.

7. References

Chevrier, V., and T. S. Altheide (2008), Low Temperature Aqueous Ferric Sulfate Solutions on the Surface of Mars, *Geophys. Res. Lett.*, *35*(L22101), doi: 10.1029/2008GL035489.

Chevrier, V., D. R. Ostrowski, and D. W. G. Sears (2008), Experimental study of the sublimation of ice through an unconsolidated clay layer: Implications for the stability of ice on Mars and the possible diurnal variations in atmospheric water, *Icarus*, *196*(2), 459-476.

Chevrier, V., J. Hanley, and T. S. Altheide (2009), Stability of perchlorate hydrates and their liquid solutions at the Phoenix Landing site, Mars, *Geophys. Res. Lett.*, *36*(L10202), doi: 10.1029/2009GL037497.

Elwood Madden, M. E., A. S. Madden, and J. D. Rimstidt (2009), How long was Meridiani Planum wet? Applying a jarosite stopwatch to determine the duration of aqueous diagenesis, *Geology*, *37*(7), 635-638.

Fairen, A. G., A. F. Davila, L. Gago-Duport, R. Amils, and C. P. McKay (2009), Stability against freezing of aqueous solutions on early Mars, *Nature*, *459*, 401-404.

Forget, F., F. Hourdin, R. Fournier, C. Hourdin, O. Talagrand, M. Collins, S. R. Lewis, P. L. Read, and J. P. Huot (1999), Improved general circulation models of the Martian atmosphere from the surface to above 80 km, *J. Geophys. Res.*, *104*(E10), 24,155-124,175.

Hamilton, V. E., P. R. Christensen, and J. L. Bandfield (2003), Volcanism or aqueous alteration on Mars ?, *Nature*, *421*, 711-712.

Hecht, M. H., S. P. Kounaves, R. C. Quinn, S. J. West, S. M. M. Young, D. W. Ming, D. C. Catling, B. C. Clark, W. V. Boynton, J. Hoffman, L. P. DeFlores, K. Gospodinova, J. Kapit, and P. H. Smith (2009), Detection of Perchlorate and the Soluble Chemistry of Martian Soil at the Phoenix Lander Site, *Science*, *325*, 64-67.

Hudson, T. L., O. Aharonson, N. Schorghofer, C. B. Farmer, M. H. Hecht, and N. T. Bridges (2007), Water vapor diffusion in Mars subsurface environments, *J. Geophys. Res.*, *112*(E5, E05016), doi: 10.1029/2006JE002815.

Jakosky, B. M. (1983), The role of seasonal reservoirs in the Mars water cycle: I. Seasonal exchange of water with the regolith, *Icarus*, *55*, 1-18.

Kraal, E. R., M. van Dijk, G. Postma, and M. G. Kleinhans (2008), Martian stepped-delta formation be rapid water release, *Nature*, *451*, 973-976.

Levin, G. V., and P. A. Straat (1976), Viking labeled release biology experiment: interim results, *Science*, *194*(4271), 1322-1329.

Malin, M. C., and K. S. Edgett (2000), Evidence for recent groundwater seepage and surface runoff on Mars, *Science*, *288*(5475), 2330-2335.

Marion, G. M., J. S. Kargel, and D. C. Catling (2008), Modeling ferrous–ferric iron chemistry with application to martian surface geochemistry, *Geochim. Cosmochim. Acta*, *72*, 242-266.

Osterloo, M. M., V. E. Hamilton, J. L. Bandfield, T. D. Glotch, A. M. Baldridge, P. R. Christensen, L. L. Tornabene, and F. S. Anderson (2008), Chloride-Bearing Materials in the Southern Highlands of Mars, *Science*, *319*, 1651-1654.

Oyama, V. I., B. J. Berdahl, F. Woeller, and M. Lehwalt (1978), The chemical activities of the Viking biology experiments and the arguments for the presence of superoxides, peroxides, gamma-Fe2O3 and carbon suboxide polymer in the Martian soil, *Life Science and Space Research*, *16*, 3-8.

Phillips, R. J., M. T. Zuber, S. E. Smrekar, M. T. Mellon, J. W. Head, K. L. Tanaka, N. E. Putzig, S. M. Milkovich, B. A. Campbell, J. J. Plaut, A. Safaeinili, R. Seu, D. Biccari, L. M. Carter, G. Picardi, R. Orosei, P. Surdas Mohit, E. Heggy, R. W. Zurek, A. F. Egan, E. Giacomoni, F. Russo, M. Cutigni, E. Pettinelli, J. W. Holt, C. J. Leuschen, and L. Marinangeli (2008), Mars North Polar Deposits: Stratigraphy, Age, and Geodynamical Response, *Science*, *320*, 1182-1185.

Poulet, F., J.-P. Bibring, J. F. Mustard, A. Gendrin, N. Mangold, Y. Langevin, R. E. Arvidson, B. Gondet, C. Gomez, and the OMEGA Team (2005), Phyllosilicates on Mars and Implications for the Early Mars History, *Nature*, *481*, 623-627.

Squyres, S. W., J. P. Gotzinger, R. E. Arvidson, J. F. Bell III, W. Calvin, P. R. Christensen, B. C. Clark, J. A. Crisp, W. H. Farrand, K. E. Herkenhoff, J. R. Johnson, G. Klingelhöfer, A. H. Knoll, S. M. McLennan, H. Y. McSween Jr., R. V. Morris, J. W. Rice Jr., R. Rieder, and L. A. Soderblom (2004), In situ evidence for an ancient aqueous environment at Meridiani Planum, Mars, *Science*, *306*, 1709-1714.

Tosca, N. J., S. M. McLennan, B. C. Clark, J. P. Grotzinger, J. A. Hurowitz, A. H. Knoll, C. Schröder, and S. W. Squyres (2005), Geochemical modeling of evaporation processes on Mars: insight from the sedimentary record at Meridiani Planum, *Earth Planet. Sci. Lett.*, *240*, 122-148.

Tosca, N. J., A. Smirnov, and S. M. McLennan (2007), Application of the Pitzer ion interaction model to isopiestic data for the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system at 298.15 and 323.15 K, *Geochim. Cosmochim. Acta*, *71*, 2680-2698.

Vaniman, D. T., D. L. Bish, S. J. Chipera, C. I. Fialips, J. W. Carey, and W. C. Feldman (2004), Magnesium sulphate salts and the history of water on Mars, *Nature*, *431*, 663-665.

Vedie, E., F. Costard, M. Font, and J. L. Lagarde (2008), Laboratory simulations of Martian gullies on sand dunes, *Geophys. Res. Lett.*, *35*(L21501), doi: 10.1029/2008GL035638.

Zent, A. P., D. J. Howard, and R. C. Quinn (2001), H_2O adsorption on smectites: Application to the diurnal variation of H_2O in the Martian atmosphere, *J. Geophys. Res.*, *106*(7), 14667-14674.