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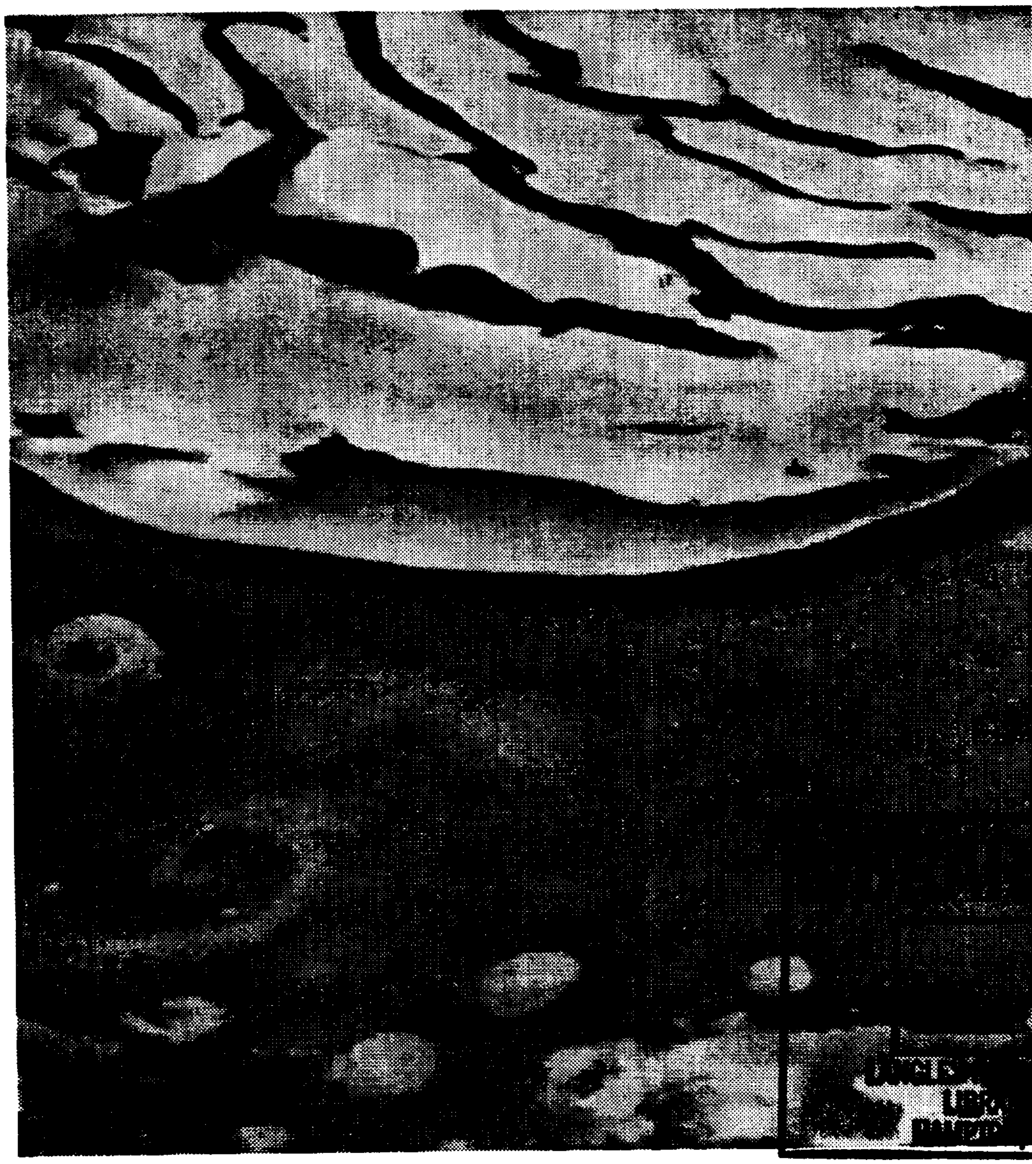
WORKSHOP ON EVOLUTION OF MARTIAN VOLATILES



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WORKSHOP ON

EVOLUTION OF MARTIAN VOLATILES

Edited by

B. Jakosky and A. Treiman

Held at
Houston, Texas

February 12–14, 1996

Sponsored by
Lunar and Planetary Institute

Lunar and Planetary Institute   3600 Bay Area Boulevard   Houston TX 77058-1113

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Cover: Volatiles on Mars: Water and carbon dioxide ices in the north polar icecap (top), and water vapor in cyclonic and convection clouds. *Viking Orbiter image 738A28.*

Introduction

With two spacecraft to be launched to Mars this year by the U.S., and possibly one by Russia, and two or more spacecraft to be launched to Mars during each opportunity for the next decade, Mars is clearly an important scientific focus for the planetary exploration program. The scientific focus for understanding Mars rests on its having been the most Earth-like planet at times during its history. During the early epochs in the solar system's history, Mars had abundant water at and/or near its surface. Where have the volatiles gone? What was the climate like during its early history? What triggered the apparent transition from an early, warm, wet environment to the colder, drier environment that we see today? Is it possible that life might have formed on early Mars? Is it possible that life might be present on Mars today? Obviously, these questions are fundamental to understanding not only Mars but the evolution of the solar system and the Earth as well.

The upcoming missions, and the ongoing scientific discussions regarding interpretation of existing data and the acquisition of new data from new instruments, provided the impetus for this workshop. A wealth of new results has been obtained during the past few years, from earlier spacecraft missions, from Earth-based telescopic data, and from detailed analysis of the SNC meteorites (which are from Mars).

Mars has continually shown us, however, that it is a complex planet. It is not possible to understand any one aspect of the Mars environment in isolation from the others. Thus, the geology is coupled to the interior, the atmosphere to the surface, and the upper atmosphere to the atmosphere. Our goal in bringing all aspects of Mars science together was to obtain an overall understanding of Mars as a system. In this regard, it is important that all aspects of martian science were represented at this workshop by researchers at the forefront of their fields, and, most importantly, that almost all attendees stayed for the entire workshop and contributed to the discussion in other areas of specialization as well as in their own.

The workshop was held at the Lunar and Planetary Institute in Houston on February 12–14, 1996. Conveners Bruce Jakosky (*University of Colorado*) and Allan Treiman (*Lunar and Planetary Institute*) put together a science advisory committee consisting of James Bell III (*Cornell University*), Steve Clifford (*Lunar and Planetary Institute*), Robert Haberle (*NASA Ames Research Center*), Jeffrey Kargel (*U.S. Geologic Survey*), James Kasting (*Pennsylvania State University*), John Jones (*NASA Johnson Space Center*), Laurie Leshin (*University of California, Los Angeles*), and Janet Luhmann (*University of California, Berkeley*). Announcements were sent out to as broad a spectrum of the community as possible, and the workshop was open to all interested scientists. There were 89 attendees, representing all the different aspects of Mars volatiles: early volatile inventory, evolution through time, geological influences, and present atmospheric properties, to name a few. Although the program was packed, we made an effort to encourage discussion through the use of designated discussion times, poster receptions, and breaks.

In the summary of technical sessions contained in this volume, the chairs of each session have made an attempt to summarize the results, context, and interpretations from their session. No effort has been made to provide a uniform format, allowing each summarizer to put together a summary in the format that they felt would provide the most useful integration of the results.

—Bruce Jakosky, University of Colorado
Allan Treiman, Lunar and Planetary Institute

Program

Monday, February 12, 1996

7:30–8:30 a.m. Registration

8:30–8:45 a.m. Introduction

INVITED REVIEWS
Chair: B. M. Jakosky

8:45–9:30 a.m. Invited Review Presentation by M. H. Carr

9:30–10:15 a.m. Invited Review Presentation by R. O. Pepin

10:15–10:30 a.m. Break

UPPER ATMOSPHERE AND ESCAPE
Chairs: J. Luhmann and J. F. Kasting

10:30 a.m.–12:00 p.m.

Evolution of the Solar EUV Radiation and Its Impact on Martian Exospheric Constituents Over Time
T. R. Ayres* (Invited Talk)

Role of the Martian Magnetic Field History in Loss of Volatiles to Space
J. G. Luhmann*

The Ancient Mars Thermosphere
S. W. Bougher* and J. L. Fox

The Ancient Mars Ionosphere
J. L. Fox* and S. W. Bougher

Sputtering of the Atmosphere of Mars
R. E. Johnson*, D. Schnellenberger, and M. Liu

12:00–1:45 p.m. Lunch

SURFACE-ATMOSPHERIC INTERACTIONS
Chairs: L. Leshin and J. H. Jones

1:45–5:00 p.m.

Isotopic Composition of Carbonates in Some SNC Meteorites
A. J. T. Jull*, S. Cloudt, and C. J. Eastoe

* Denotes speaker

Has Martian Atmospheric CO_2 Become Depleted in ^{13}C with Time?
I. P. Wright*, M. M. Grady, and C. T. Pillinger

Oxygen Isotopes in Martian SNC Meteorites
C. S. Romanek, E. K. Gibson Jr.*, R. A. Socki, and E. C. Perry

Hydrogen Isotope Geochemistry of SNC (Martian) Meteorites and the History of Water on Mars
L. A. Leshin*, S. Epstein, and E. M. Stolper

An Early Warm, Wet Mars? Little Support from the Martian Meteorite ALH84001
A. H. Treiman*

Trace Element Geochemistry of Martian Weathering Products in Lafayette
D. J. Lindstrom*, A. H. Treiman, and R. R. Martinez

Martian Volatiles: Insights from the SNC Meteorites
J. H. Jones*

Mars Volatile Evolution from Stable Isotope Abundances
B. M. Jakosky* and J. H. Jones

Evolution of Martian Atmospheric Argon and Neon
K. S. Hutchins* and B. M. Jakosky

A Geochemical Model for Volatile Storage Via Hydrothermal Systems on Mars
L. L. Griffith* and E. L. Shock

The Role of SO_2 for the Climate History of Mars
G. Dreibus* and H. Wänke

5:00–5:30 p.m. Discussion

RECEPTION AND POSTER PRESENTATIONS

5:30–7:00 p.m.

Thermal Evolution Models of Mars—Implications for Release of Volatiles
A. Weizman, D. Prialnik, and M. Podolak

Modeling the Martian Water Cycle
H. Houben, R. M. Haberle, R. E. Young, and A. Zent

Volatiles and Volcanoes: Very Late Amazonian Ash Deposits and Explosive Activity Along the Western Flanks of the Tharsis Montes, Mars
K. S. Edgett, B. J. Butler, J. R. Zimbelman, and V. E. Hamilton

Tuesday, February 13, 1996

MISSION/SCIENCE OPPORTUNITIES
Chairs: A. H. Treiman and B. M. Jakosky

8:30–11:15 a.m.

Mars Surveyor Program
D. J. McCleese* (Invited Talk)

Mars Volatiles and Climate Surveyor Integrated Payload
D. A. Paige* (Invited Talk)
W. V. Boynton, D. Crisp, A. M. Harris, C. J. Hansen, H. U. Keller, L. A. Leshin, R. D. May, P. H. Smith, and R. W. Zurek

SPICAM Solar Occultation Experiment
O. Korablev, M. Ackerman, E. Neefs, C. Muller, H. Deceuninck, D. Moreau, C. Hermans, W. Peertermans, P. C. Simon, S. Shadeck, E. Van Ransbeek, V. Moroz, A. Rodin*, A. Stepanov, D. Perepelkin, V. Jegoulev, A. Krysko, and V. Troshin

Mineralogy of the Martian Surface Analyzed In Situ by Mössbauer Spectroscopy, and Implications for Volatile Evolution on Mars
G. Klingelhöfer*, B. Fegley Jr., R. V. Morris, E. Kankeleit, E. Evlanov, O. Priloutskii, J. M. Knudsen, and M. B. Madsen

10:00–10:30 a.m. Break

What Will Returned Samples Tell Us About Martian Volatiles?
C. C. Allen*

Is Mars Water Rich?: Hydrologic, Topographic, and Latitudinal Considerations in the Search for Subpermafrost Groundwater
S. M. Clifford*

Lightweight SOS Solar Occultation Experiment
O. I. Korablev*, V. I. Moroz, M. Ackerman, E. Van Ransbeek, P. C. Simon, and J.-L. Bertaux

CLIMATE EVOLUTION
Chair: A. H. Treiman

11:15 a.m.–12:00 p.m.

Primitive Methane Atmospheres on Earth and Mars
L. L. Brown* and J. F. Kasting

Photochemical Weathering of Martian Carbonates and Sulfates
A. P. Koscheev*, L. M. Mukhin, Yu. P. Dikov, J. Huth, and H. Wänke

The Contribution of Volatiles to the Surface and Atmosphere of Mars by the Accretion of Interplanetary Dust Particles
G. J. Flynn*

12:00–1:30 p.m. Lunch

GEOLOGICAL CONSTRAINTS AND EARLY HISTORY
Chairs: S. M. Clifford and A. H. Treiman

1:30–3:15 p.m.

Formation of the Martian Drainage System: Redistribution of Groundwater in Response to Global Topography and Cold Climates
M. H. Carr*

Hydraulic and Thermal Constraints on the Development of the Martian Valley Networks
S. M. Clifford*

Are the Martian Valley Networks Really Sapping Channels?
J. W. Rice Jr.*

Implications of Subsurface Volatile Distribution from Martian Impact Crater Morphology
N. G. Barlow*

Deposition and Badlands Erosion of Martian Chemical and Clastic Lacustrine Rocks
J. S. Kargel*

The Rich Geomorphic Legacy of the Argyre Basin: A Martian Hydrologic Saga
T. J. Parker*

Observational Tests for the Identification of Shore Morphology on Mars
T. J. Parker*

3:15–3:45 p.m. Break

SOILS AND VOLATILES
Chairs: A. P. Zent and R. V. Morris

3:45–5:00 p.m.

Acidic Volatiles and the Mars Soil
A. Banin*, F. X. Han, I. Kan, and A. Cicelsky

Iron, Sulfur, and Chlorine Phases on Mars
R. V. Morris*, D. C. Golden, D. W. Ming, and J. F. Bell III

Iron Formations on Mars?
M. W. Schaefer*

Quantitative Analysis of the 3-μm Water of Hydration Absorption Feature in the Eastern Valles Marineris
W. M. Calvin*

New Estimates of the Adsorption of H_2O on Martian Surface Materials
A. P. Zent*

5:00–5:30 p.m. Discussion

5:30–7:30 p.m. Dinner Break

MARS EXOBIOLOGY PANEL DISCUSSION
Chair: A. H. Treiman

8:00–10:00 p.m.

PANELISTS:
Geological Records of the Earth's Early Biosphere: Application to Mars
D. J. DesMarais

Life in Extreme Environments on Earth: Application to Mars
K. Nealson

Chemical Evolution in Hydrothermal Systems
E. L. Shock

Wednesday, February 14, 1996

POLAR VOLATILES
Chairs: R. M. Haberle and J. Kargel

8:30–10:00 a.m.

Geology of the Polar Layered Deposits on Mars
K. E. Herkenhoff* and J. J. Plaut

Limits on the CO_2 Content of the Martian Polar Deposits
M. T. Mellon*

Some Constraints on the Amount of CO_2 Stored in the Polar Regions of Mars
R. M. Haberle* and D. Tyler

CO_2 Ice: Rheological Properties and Impact Cratering
J. Leliwa-Kopystynski*

The Martian Climate System at High Obliquity: Simulations with the NASA/Ames Mars General Circulation Model
R. M. Haberle*

Atmospheric Dust-Water Ice Interactions: Do They Play Important Roles in the Current Mars Climate?
R. T. Clancy*

10:00–10:30 a.m. Break

SEASONAL AND DIURNAL CYCLES
Chairs: R. T. Clancy and A. L. Sprague

10:30 a.m.–12:00 p.m.

Water Ice in the Martian Atmosphere as Derived from PHOBOS/KRFM Data
W. J. Markiewicz*, H. U. Keller, E. Petrova, N. Thomas, and M. W. Wuttke

Spectroscopic Measurements of Martian Atmospheric Water Vapor
A. L. Sprague*, D. M. Hunten, and R. E. Hill

Diurnal Variability of the Atmospheric Water Content on Mars: Observations and Desorption Model
D. V. Titov*

Condensation-driven Vertical Profile of Water in Mars Troposphere: Phobos Revisited
A. V. Rodin*, O. I. Korablev, and V. I. Moroz

HST Observations of Time-Variable Regional Albedo Features on Mars
S. W. Lee*, M. J. Wolff, P. B. James, L. J. Martin, R. T. Clancy, and J. F. Bell

Martian Dust Storms: HST Observations
P. B. James*, J. Bell, R. T. Clancy, S. W. Lee, L. J. Martin, and M. Wolff

12:00–12:30 p.m. Discussion

12:30 p.m. Adjourn

PRINT ONLY ABSTRACTS

The Martian Noble Gas Isotopes Paradox
L. K. Levsky

Contents

Summary of Technical Sessions

UPPER ATMOSPHERE AND ESCAPE

Summarized by J. Luhmann

Since the end of the catastropic impact era, martian volatiles have continued to escape to space primarily by virtue of their thermal energy (in the case of H), their energy derived from photochemical reactions in the atmosphere in response to solar ultraviolet and extreme ultraviolet light (e.g., dissociative recombination of O^{2+} ionospheric ions, resulting in "hot O" escape), and the energy derived from the solar wind interacting with the ionized upper atmosphere (producing both direct atmospheric ion escape by solar wind "sweeping" and atmospheric sputtering by those pickup ions that instead impact the exobase). All these mechanisms thus depend on solar outputs and have changed in importance over time in accord with changes in the Sun.

The session on Mars' upper atmosphere and escape was appropriately opened by T. Ayres, who provided an updated analysis of the evolution of the short-wavelength (<2000 Å) radiation from solar-type stars. These astronomical observations are uniquely capable of placing constraints on the early solar models used to estimate the changes in the photochemical and sputtering escape processes over time, but no specifically solar-system-oriented study of the subject had been made since that of Zahnle and Walker in 1982 [1]. New observations have become available from a variety of telescopes and spacecraft. Ayres described our present understanding of the origins of this energetic photon radiation, which lies outside the main continuum that makes up the bulk of solar luminosity. Various manifestations of solar activity, including flares and magnetically complex active regions, are the major sources, and as a result these radiations are highly variable compared to the solar constant. As a consequence of the known decay of stellar rotation with age of solar-type stars, and the connection between magnetic activity and rotation through the "dynamo" mechanism, their activity, and hence their energetic photon emissions, decreases with time. The most accurate picture of solar "EUV" flux evolution following the T-Tauri phase probably consists of an early period of ~0.5–1.0 G.y. duration when the EUV flux of interest for Mars' atmosphere escape processes was ~5–10× its present value, but lacking the cyclic reductions characteristic of solar cycle minima, followed by a nearly linear (in log luminosity vs. log time) decrease to present levels, during which cyclic variations of a factor of ~2 developed. On average, this picture turns out to be quite similar to the earlier estimates of Zahnle and Walker [1], thus supporting the assumptions of previous modeling studies that adopted their results. Future astronomical observations that improve stellar age determinations may lead to further refinement of these results, including better understanding of the types of activity contributing to the various parts of the EUV and X-ray spectrum of solar-type stars.

The impact of an early magnetic field of Mars on the sputtering loss of the atmosphere was considered by J. Luhmann, who examined what would happen to the sputtering rates if the accretionary dynamo model of Schubert and Spohn [2] were correct. Schubert and Spohn consider that the heat resulting from accretion would generate a significant martian field for the first few billion years of Mars' history, which is exactly when the maximum solar EUV fluxes and hence sputtering losses would occur. Using the same early solar wind model used in previous sputtering calculations, Luhmann estimates that a martian magnetopause would be located at subsolar radii of over 2 Rm at 2 G.y. age and over 3 Rm at 3 G.y. age. Since the region inside the magnetopause is largely shielded from the solar wind, this greatly diminishes both the losses from solar wind sweeping of upper atmosphere ions and diminishes the flux of potential sputterers (as well as their access to the exobase). To maintain the production rates outside the shielded region at their previously estimated levels requires unreasonably high EUV or solar wind fluxes (the latter to push the magnetopause to heights consistent with the low-obstacle altitudes used in the original sputtering calculations). The other possibility, if sputtering is the best way to explain the observed isotope ratios, is that Mars never had as strong an early internal field as the Schubert and Spohn [2] model suggests. Indeed, there is no observational evidence that supports the accretionary dynamo hypothesis, although there is geomorphological evidence of the planet interior cooling after formation. Paleomagnetic studies using dated Mars rocks can help to resolve this issue, as can further analyses of lunar and asteroid samples to determine long-term time variations in implanted solar-wind-particle concentrations.

S. Bougher and J. Fox presented improved and updated models for the early Mars upper atmosphere and ionosphere, which are at the heart of the evolutionary atmospheric escape calculations. Calculations of the loss of water from Mars over its history require that careful consideration be given to changes in atmospheric escape of neutral O (hot O and sputtering components) and O^+ (via ion pickup). These mechanisms are regulated by the changing solar EUV fluxes (all) and the solar wind parameters (O^+ pickup and sputtering). Fox and Bougher revisited the role of changing solar EUV fluxes upon the ancient Mars thermosphere and ionosphere. Upgraded neutral and ion models were exercised to evaluate the assumptions used earlier in the ancient Mars studies of Zhang et al. [3] and Luhmann et al. [4]. In particular, the neutral thermosphere calculations for 3.0× present EUV solar fluxes were redone using a three-dimensional global model. The resulting exobase O densities and temperatures are strongly influenced by the global dynamics in this model, suggesting that one-dimensional models are not adequate for estimating dayside mean conditions required for deriving hot O escape. However, corresponding ionospheric calculations can reasonably use a one-dimensional model approach, yielding improved O^{2+} densities and new estimates for hot O neutral escape. It is found that the ancient Mars exobase is substantially higher than its current altitude and, as a result, O^{2+} is more vibrationally excited than that in the present-day ionosphere. This change causes the estimated O escape from dissociative recombination of O^{2+} to be slightly more than triple the present-day values. This is only one component of O escape; nevertheless, it constitutes a necessary first step in reevaluating the total O escape (and water loss) over Mars' history. Further calculations using both the 3-EUV and 6-EUV cases will be done to provide the best possible models for both photochemical and sputtering losses over time based on our current knowledge.

Recently Kass and Yung (1994) had suggested that previous CO_2 sputtering loss calculations underestimated the effect by over an order of magnitude. They based their conclusion on new Monte Carlo calculations using the same assumptions about sputtering flux and target atmosphere used by Luhmann et al. [4]. R. Johnson pointed out that the difference between their calculations and those in Luhmann et al. is a result of their much higher sputtering yields. They assumed that all collisions with energies >16.5 eV resulted in complete dissociation of the CO_2 molecules present, and their total atomic loss for a mixed O + CO_2 atmosphere exceeded that from a fully dissociated atomic atmosphere. Johnson and collaborators carried out a detailed molecular dynamics calculation of the dissociation of CO_2 by energetic atoms in the energy range 20 eV–1 keV. They showed that, although CO_2 fragmented efficiently to CO + O, it did not efficiently dissociate to C + O_2. The calculated cross section for full dissociation was overestimated by more than an order of magnitude above 100 eV, and it becomes negligibly small below ~60 eV so that Kass and Yung [5] overestimated the net yield of C loss by a factor of ~50. While an increase in sputtering yield over that in Luhmann et al. [4] is expected if the dissociation of CO_2 is included throughout the full cascade of collisions, this effect cannot enhance the yield by more than a factor ~2. Therefore, the earlier, more conservative sputtering loss model still stands with some relatively small adjustments. Losses at about those rates do not appear to be out of line with what is necessary to produce some of the observed isotope ratios [6] (also described by R. Pepin and by K. Hutchins and B. Jakosky at this workshop).

References: [1] Zahnle K. J. and Walker J. C. G. (1982) *Rev. Geophys. Space Phys., 20,* 280. [2] Schubert G. and Spohn T. (1990) *JGR, 95,* 14095. [3] Zhang M. H. G. et al. (1993) *JGR, 98,* 10915. [4] Luhmann J. G. et al. (1992) *GRL, 19,* 2151. [5] Kass D. and Yung Y. (1995) *Science, 268,* 697. [6] Jakosky B. M. et al. (1994) *Icarus, 111,* 271.

SURFACE-ATMOSPHERE INTERACTIONS

Summarized by J. Jones and L. Leshin

New $\delta^{13}C$ data on SNCs were presented both by T. Jull and co-workers and by I. Wright and co-worker. These talks highlighted the complexity of martian C systematics. Jull noted that C in most SNCs became heavier as stepwise heating proceeds, but Zagami analyses become lighter. Wright showed that $\delta^{13}C$ values ranged from –20% to +60%, a very large spread. This complexity may be due to mixing of heavy atmospheric C with light magmatic C.

E. Gibson and co-workers presented $\delta^{17}O$ vs. $\delta^{18}O$ data on SNCs from a new laser fluorination extraction system. Of particular interest were analyses of iddingsite from Lafayette that showed enrichments in $\delta^{18}O$ of up to +15%. These data, along with mineralogical observations, appear to indicate that Lafayette experienced aqueous alteration at low temperature (~0–100× C).

L. Leshin compared new δD data from SNC meteorites to the $\delta^{17}O$ data from Karlsson et al. [1] and saw little correlation between the O and H isotopic measurements. Surprisingly, Leshin et al. also saw no evidence of heavy H in whole-rock analyses of Chassigny that were so apparent in ion probe analyses of kaersutites from the same rock [2]. Possibly, terrestrial contamination makes "conventional" whole-rock analyses more difficult than the less-routine ion probe measurements.

A. Treiman noted that the relatively anhydrous nature of ALH 84001 lends little support for a warm, wet early Mars. ALH 84001 is a very old crustal rock (>~4.5 b.y.) and should have had ample opportunity to be weathered or altered. Although carbonates precipitated from aqueous fluids do exist in ALH 84001, this is a minor effect compared to what might be expected on a wet, geologically active body.

D. Lindstrom and co-workers and G. Flynn presented trace-element analyses of iddingsite from Lafayette. As might be expected, the iddingsite, which is a mixture of clays and Fe oxides, is greatly enriched in alkalis, with Cs enriched by 60× over bulk Lafayette. This observation, along with other mineralogical, chemical, and isotopic data, indicates that Lafayette was altered by low-temperature aqueous fluids.

J. Jones presented observations related to using Xe isotopes to trace the timing of the loss of an early martian atmosphere. Jones modeled the Xe isotopic composition of the martian atmosphere before hydrodynamic escape (thought to be similar to average carbonaceous chondrite, or AVCC) as resulting from ^{244}Pu decay combined with the approximately solar "juvenile" Xe as sampled by Chassigny. The success of this model implies that hydrodynamic escape occurred within a few half-lives of ^{244}Pu rather than ^{129}I, which extends the period of possible hydrodynamic escape.

Jakosky presented an overview of stable isotopic measurements relevant to the evolution of martian volatiles, including D/H, $^{13}C/^{12}C$, $^{18}O/^{17}O/^{16}O$, and $^{38}Ar/^{36}Ar$, and concluded that all isotope data support the conclusion that the present martian atmosphere has been substantially modified by escape of atmospheric species to space. Jakosky also stressed the probable role of hydrothermal systems for the exchange of atmospheric volatiles with the crust, and suggested that O in silicates in the crust could be buffering the O isotopic composition of atmospheric species, thereby explaining the lack of significant enrichment of the atmospheric $^{18}O/^{16}O$ value.

Hutchins discussed a model for the evolution of Ar and Ne in the martian atmosphere. The model included volcanic input of volatiles and loss to space. The calculations indicate that the source(s) of volatiles in addition to volcanic outgassing is required. Possible sources, such as release of noble gases mobilized by hydrothermal fluids, were discussed.

D. Bogard gave a short presentation focusing on the observation that the $^{36}Ar/^{38}Ar$ value in the martian atmosphere may not be as well known as is often assumed. He pointed out that analysis of data from SNC meteorites produces a range of values for this ratio of about 3.5–4.7, while the often-quoted ratio is 4.1. He suggested that the true atmospheric value may be as low as 3.5, with the observed variation arising from variable input to the SNC analyses from mantle-derived Ar also present in the samples.

Reaction-path models of hydrothermal alteration of a variety of igneous rock types were the subject of the presentation by L. Griffith. She concluded that a large amount of volatiles can be stored in the mineral products of hydrothermal systems on Mars.

G. Dreibus-Kapp presented the case for a significant role for SO_2 in martian climate history. She argued that data from the Viking landers and SNC meteorites support an important role for SO_2 in the martian volatile cycle, especially since SNC meteorites appear to be derived from a relatively water-poor mantle. Possible solid and liquid SO_2 reservoirs in the martian crust were discussed, as was the possibility that flowing liquid SO_2 could explain at least some of the erosional features on the martian surface.

References: [1] Karlsson et al. (1992) *Science, 255,* 1409–1411. [2] Watson et al. (1994) *Science, 265,* 86–90.

CLIMATE EVOLUTION

Summarized by A. Treiman

The short session on martian climate evolution focused on processes and conditions that may have affected the long-term evolution of the martian atmosphere and volatile budget.

First, L. Brown argued that methane could have been a significant greenhouse gas in the early martian atmosphere. Inclusions in terrestrial diamonds suggest that the Earth's early atmosphere could have contained more methane than previously thought. In addition, radiative transport models suggest that methane is much more effective at warming the troposphere than previously thought. For Mars, a methane mixing ratio 0.05–0.1 in a thick CO_2 atmosphere could maintain global surface temperatures above 273 K even under an early, dimmer Sun. In questioning, there was some concern expressed about the relevance of terrestrial diamond data to the bulk Earth.

Next, A. Koscheev presented results of experiments on the dissociation of carbonates and sulfates under the influence of ultraviolet radiation. The results suggest that such photochemical reactions may "weather" chemically signficant quantities of CO_2 from surface carbonates. In the discussion that followed, it was noted that the weathering products would likely recombine with atmospheric volatiles on short timescales.

Finally, Flynn reminded the audience of the continual flux of interplanetary dust onto Mars and its contribution to Mars' volatiles inventory. Integrated over time, the dust carries small but significant quantities of H_2O and C to the martian surface. The dust's contribution of noble gases is much larger (compared to the indigenous reservoirs), and could be a major contributor to the noble gas inventory of the martian atmosphere.

GEOLOGICAL CONSTRAINTS AND EARLY HISTORY

Summarized by S. Clifford and A. Treiman

M. Carr opened the afternoon session with a discussion of how the martian drainage system may have evolved in response to the planet's early climate, global topography, and declining heat flow. He argued that the enormous difference in relative preservation of lower Hesperian- over Noachian-aged craters provides considerable evidence that a dramatic change in surface conditions occurred near the end of heavy bombardment. An initially high global water table was then progressively lowered over the next several hundred million to one billion years by episodic failures of the confining layer of frozen ground, permitting the discharge of groundwater to the surface, but with decreasing frequency as the planet's declining heat flow increased the thickness of frozen ground.

Hydraulic and thermal constraints on the development of the early martian drainage system were discussed in additional detail by S. Clifford. Clifford noted that with the development of a freezing front in the early near-surface crust, the local water table would have been cut off from any possibility of atmospheric resupply, resulting in the subsequent decay of the global water table until it reached hydrostatic equilibrium in ~10^5–10^7 yr (a duration dependent on the large-scale permeability of the crust). In light of this fact, and in light of the association of many valley networks with the outside rims of craters in the southern highlands, Clifford noted that some mechanism for the dynamic support of high water tables was required. Given the expected volume of impact melt produced in the formation of craters >10 km in diameter, Clifford argued that a logical candidate for this mechanism was impact-generated hydrothermal systems.

J. Rice suggested that an alternative mechanism for maintaining the high water tables necessary to account for the development of the valley networks was atmospheric precipitation, and he cited two primary lines of reasoning in support of this conclusion. First, Rice noted that, contrary to popular belief, the dominant morphologic influence on the development of terrestrial "sapping" channels has been precipitation and surface runoff, an argument he then extended to Mars by the strong similarities he identified between selected terrestrial and martian examples. Second, Rice argued that the water-to-rock ratios required to erode the networks ($\sim 10^2$–10^5) were simply too high to satisfy by a sapping process alone, necessitating some efficient mechanism for recycling or resupply. Rice concluded that the most reasonable mechanism to provide this volume of water was atmospheric precipitation and runoff.

N. Barlow presented the results of her study of the ejecta morphology of 3819 craters with diameters ≥8 km, discussing its implications for the distribution of subsurface volatiles. Barlow's observations indicate a relationship between crater size, latitude, and the degree of ejecta fluidization, results she believes are most consistent with theoretical predictions of the vertical and areal distribution of water and ice within the crust. Barlow noted that the greatest obstacle to using ejecta fluidization onset diameters to quantify the depth to ground ice is the uncertainty regarding how much volatile-rich material must be incorporated into the ejecta to initiate fluidization. Barlow is currently extending her study to craters with diameters <8 km in the hopes of better understanding some of these outstanding questions.

J. Kargel reviewed the arguments and evidence for the development of lakes and possible seas on Mars, discussing the sedimentary and chemical implications that this concentration of drainage waters might have had on the development of the martian landscape. Kargel identified terrestrial badlands as the closest morphologic analog to the catchment areas he has identified in the martian highlands.

The geomorphic development of the Argyre impact basin and its implications for the planet's local hydrologic development were the main focus of T. Parker's first presentation. He presented a summary of his recent investigations, which indicate that Argyre is an ancient structure that has undergone considerable modification by a combination of mass-wasting, fluvial, lacustrine, and eolian processes.

Parker concluded the session with a separate presentation on the observational tests he has developed for the identification of shoreline morphologies on Mars. Noting the enormous volume of water and sediment that the northern plains must have received from the discharge of the outflow channels, Parker argued that vast lakes, and perhaps even an ocean, must have resulted, if only temporarily. Because the water level resulting from such flooding would have defined an equipotential surface, Parker believes the mor-phologic signature of such large bodies of water are readily distinguishable from the erosional effects of other agents in high-resolution Viking images. Parker supported his identification of shoreline forms by comparisons with numerous terrestrial examples imaged at moderate and high resolution by satellites and aerial surveys.

SOILS AND VOLATILES

Summarized by R. V. Morris and A. Zent

Three presentations dealt with studies of martian analog materials. New results for palagonitic soils from Mauna Kea volcano (a martian process analog region) that relate to the nature and formation process of weathering products on Mars were presented by both A. Banin and R. Morris. Banin discussed laboratory experiments in which palagonitic soil was artificially weathered by addition of acidic solutions. He suggested that martian soil consists of a salt-rich mixture containing the salts of the anionic sulfate and chloride ligands resulting from volcanic emanations. Morris and co-workers found direct evidence for acid sulfate weathering on Mauna Kea by an occurrence of the ferric sulfate mineral jarosite. They attributed the source of sulfate to volcanic fluids. M. Schaefer discussed processes leading to banded Fe formations, which are some of the oldest surviving sedimentary features on Earth, as analogs for martian weathering processes. The processes involve formation of waters rich in soluble ferrous and subsequent oxidation and precipitation of ferric-bearing minerals.

Two presentations related to the abundance and state of water in martian soil. W. Calvin discussed work related to determining the hydration state of martian surface materials from quantitative analysis of the water of hydration spectral feature near 3 µm. The analysis is being done by comparison to corresponding spectra for a variety of terrestrial materials. A. Zent discussed important new experimental data relating to the adsorption of H_2O on martian surface materials. Zent reported data showing that extrapolations based on the previous adsorption isotherm for H_2O adsorption on basalt were unrealistic. The revised version of the basalt isotherm is consistent with the stability of ice in the uppermost millimeters of martian regolith at night.

MARTIAN EXOBIOLOGY

Summarized by A. Treiman

On Tuesday evening, workshop participants met to hear invited talks about exobiology in relation to martian volatiles and to participate in an open discussion. The three invited speakers were D. DesMarais, K. Nealson, and E. Schock.

DesMarais began the program with a summary of the current search for life on Mars. The search does not focus on extant life, but on how to find evidence of past life. The earliest fossil record on Earth provides an example of what kinds of creatures might have lived on Mars and how they might have been preserved. For instance, stromatolites and similar structures on Earth preserve inorganic laminae produced by ancient algal mats, and rarely preserve traces of the algal filaments. These layered rocks apparently formed in quiet ocean or lake environments. Hot mineral springs are also a promising environment for the preservation of fossil traces of martian life. Many types of organism live in and around hot springs on Earth, and are readily and rapidly preserved in the springs' mineral deposits. Nealson followed with a discussion of energy production strategies used by terrestrial organisms. A living creature must gain enough energy from its environments to force H ions across its biological membranes. Once across, that H can be used to convert ADP to ATP, a universal (among Earth organisms) energy storage chemical. Organisms gain the energy for H transport from an amazing variety of chemical reaction couples. Most familiar life on Earth uses a redox couple between gaseous O and organic C for its energy. But many bacteria use other couples, for instance, including various oxidation states of C, S, H, I, and/or Mn. So, the usual view of life on Earth is quite restricted, and Nealson pleaded for an open mind in considering possible energy sources (and thus environments) for martian life.

Schock concluded the invited talks with a summary of his group's work on prebiotic evolution. First, he showed that most primitive and presumably ancient organisms on Earth tend to be thermophilic, i.e., requiring very high temperatures to survive. Some bacteria are known to thrive at temperatures up to 115°C, and others are incapable of active metabolism at temperatures below (for instance) 80°C. Thus, his group has explored chemical reactions in the environments surrounding undersea hot springs on the early Earth. Enormous energy is available for biological organisms near hot springs where the hot, reducing, sulfurous spring water mixes with cold, relatively oxidixing, carbonic ocean water. Sulfur redox couples alone can provide bacteria with a "free lunch." In these mixed zones, reduction of carbonate in ocean water can readily produce long-chain organic molecules, at least as long and complex as octanoic acid. This C redox reaction is also energetically favorable in mixed water near hot springs, so an organism can be "paid to eat its free lunch," in the speaker's words.

POLAR VOLATILES

Summarized by R. Haberle

K. Herkenoff led off this short session with a discussion of some of the more puzzling aspects of the polar layered terrains. High-resolution images of the north polar layered terrains reveal a lack of craters >100 m in diameter. This is in contrast to the southern polar layered terrains, which therefore appear to be much older. Yet erosional processes are believed active in the north at the present time. Furthermore, the inferred age of the southern deposits is much older than an obliquity variation timescale, suggesting that at least some of the southern terrains have not been modified for quite some time. M. Mellon and R. Haberle followed with papers dealing with the amount of CO_2 that can be stored in the polar regions. Their work was motivated by the recent suggestion that as much as 800 mbar could be buried in the polar regions at the present time [1]. Mellon noted that basal melting would limit the thickness of the caps and presented calculations for both clathrate and pure CO_2. He pointed out that the thermal conductivity of CO_2 ice is 5–6× lower than that of water ice; this leads to an increase in the geothermal gradient that, in turn, puts the depth to melting closer to the surface. Accordingly, he found that only 100–250 mbar of CO_2 could be stored in the polar regions, an amount much less than Jakosky et al.'s upper estimate. Haberle's approach was less direct. He reasoned that if too much CO_2 was released into the atmosphere at times of high obliquity, it would provide enough heating of the polar regions through the greenhouse effect and atmospheric heat transport that it might not be able to return when the obliquity reached its minimum in the cycle. Using a simplified energy balance model, he estimated that the present-day poles could store no more than 370 mbar, a higher upper limit than that found by Mellon, but one still lower than Jakosky et al.'s.

J. Leliwa-Kopystynski's scheduled talk on the results of compaction and impact experiments with CO_2 ice was canceled. Workshop participants then heard from Haberle about what kind of climate changes might be expected when Mars is at its maximum obliquity (60°). The presentation was based on simulations with the NASA Ames Mars general circulation model and the assumption that 7.6 mbar of CO_2 was available to the atmosphere + cap system. One of the most striking changes seen in the model was the intensification of the solstice circulation. Dust lifting appears inevitable at both solstices according to the model. This is interesting, since surface pressures are actually less than they are for the contemporary obliquity experiment. Evidently, regolith desorption is not required for dust lifting at times of high obliquity. Another result of the model is that daily mean temperatures in the northern plains remain above freezing during the weeks around summer solstice; winters are correspondingly harsher than for present obliquity. Haberle then speculated about the fate of polar water ice deposits, which he believed will be rapidly exchanged between poles during the year, rather than deposited in tropical regions where the annual mean insolation at the top of the atmosphere is less than it is at the poles for this obliquity. There was some discussion about this, especially about feedbacks related to cloud formation, and it was agreed that hard calculations need to be performed before the issue can be resolved. The session concluded with a presentation from T. Clancy on his microwave and HST observations. Todd reviewed the long time series of microwave data and pointed out how it seemed to indicate that Mars was unusually warm during the Viking mission. He focused on the observations taken around the aphelion season and emphasized his 1995 observations, which showed a warm, nearly adiabatic lower atmosphere that he attributed to dust heating. Above 10–15 km, however, the temperature profile stabilized considerably. He interpreted these measurements in terms of water ice/dust interactions. HST observations showed both clouds and dust to be present at this season. Evidently, the clouds confine the dust to lower levels by scavenging. Support for this idea comes from the coincidence of an estimated "freezing level" and the altitude at which the lapse rate changes from nearly adiabatic to more nearly isothermal.

References: [1] Jakosky et al. (1995) *JGR, 100,* 1579–1584.

SEASONAL AND DIURNAL CYCLES

Summarized by T. Clancy and A. Sprague

Two talks documented the coexistence of water ice and dust aerosols in the low-latitude Mars atmosphere during the northern spring and summer season of 1989, based on Phobos spacecraft observations. Two talks presented recent HST observations that indicate substantial changes of surface albedos over the Cerberus region, as well as significant atmospheric dust and cloud aerosol loading during the northern summer season of 1995. Groundbased observations of Mars atmospheric water vapor over the 1991–1995 period indicate general consistency as well as significant temporal deviations from the Viking climatology of Mars water vapor.

A. Rodin presented the results of a reanalysis of the Phobos-2 solar occultation infrared spectroscopy experiment, which focused on the nature of the aerosols leading to the observed near-IR limb extinction. This reanalysis is the first to incorporate recalibrated channels, which are sensitive to water vapor absorption (at 1.87 μm). These measurements indicate water mixing ratios that decrease dramatically above ~25 km altitude over the low latitudes observed by Phobos in 1989. Rodin argued that the observed water vapor vertical distribution implies the presence of water ice clouds at 20–25 km, which helps to resolve some of the previous inconsistencies in the dust aerosol profiles derived from earlier Phobos occultation analyses. These results suggest low-latitude water vapor saturation conditions occurred around 25 km altitude during the early northern spring season of these measurements. Microphysical modeling implies cloud particle radii of ~2 μm and cloud formation timescales on the order of one week.

J. Markiewicz presented new interpretations for photometric profiles of atmospheric dust obtained in the 1989 Phobos mission. Profiles were obtained with the KRFM instrument between 315 and 550 nm. The model includes a time-evolving, near-surface layer of silicate particles covered with water ice that provided a good fit to the data. An estimate of overnight condensate on dust particles was given of about 0.5×10^{-5} g cm^{-2}. In addition, an estimate of the sublimation rate was found: 10^{-15} g μm^{-2} s^{-1}. The model indicates that the ice haze contribution to the total optical depth decreases from about 0.05 at dawn to zero within about an hour.

A brightness increase of another type, observed in the afternoon UV profiles of the Valles Marineris, is shown to be consistent with the presence of water ice clouds and was discussed. Ice crystal shape seems to be an important factor in matching the data.

P. James presented the newest HST images of Mars obtained during the northern summer season in 1995. The appearance of significant dust loading is apparent in the late-August images ($L_s \sim 145$), as is the presence of water ice clouds over much of the disk of Mars. This global-scale dust storm activity correlates with the lower atmospheric heating measured by microwave temperature sounding of the Mars atmosphere over this same time period (as presented by Clancy in the previous session). Radiative transfer analysis of the ultraviolet and violet images suggests dust and cloud opacities of 0.5–1.0 over Hellas Basin, and dust and cloud opacities of 0.2–0.4 over the 20°S to 20°N latitude region. The dust loading shows peak loading over distinct regions (such as Hellas, Isidis, and the northern polar ice cap), as well as substantial temporal variations over the L_s = 65–145 seasonal range in 1995. It was pointed out that the L_s = 145 period is the same season during which the Pathfinder lander will arrive at the Mars surface in 1997.

James presented the talk of Lee et al., regarding HST monitoring of surface albedo variations over the 1990–1995 period of Mars HST observations. The Syrtis Major region, which was regarded as one of the most time-variable albedo regions on the basis on Viking studies, has not displayed substantial albedo variations during this period. However, the dark Cerberus region is nearly unrecognizable as a dark albedo feature in January 1993 HST imaging. Only a few separated dark spots appear to remain from the large extended dark-albedo feature observed by Viking and Mariner 9. This fading of Cerberus as a dark-albedo region may have occurred in the 1980s, according to long-term, groundbased monitoring by D. Parker. However, near-IR imaging of Mars in the 1990s still shows Cerberus as an extended dark-albedo region, which suggests that only a very small amount of dust (on the order of several micrometers) has covered the Cerberus region to brighten its albedo at the 673-nm wavelength of the HST imaging.

A. Sprague presented the results of measurements of martian atmospheric water vapor for the period 1991–1995. Overall abundances are similar to those of the Viking MAWD experiment and other groundbased measurement programs, but large daily fluctuations are apparent and indicate weather (cloud formation and dissipation) on Mars. Strong latitudinal variations were observed for all L_s (seasons), with late spring and summers wet in both hemispheres, but northern latitudes up to 5× wetter than southern. Equatorial regions (+30° to –30°) show a rather stable abundance of atmospheric water varying between 2 and 20 pr μm, while much larger variations are observed at high latitudes. Our high northern measurements show as much as 80 pr μm in northern summer. Southern atmospheric water rapidly drops below 10 pr μm in early autumn and is below our measurement threshold by late autumn. Diurnal variations are strong, with lowest abundance near the morning terminator. Abundances at the subsolar longitude are up to 8× higher than along the terminator.

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