WORKSHOP ON THE ISSUE

MARTIAN METEORITES: WHERE DO WE STAND AND WHERE ARE WE GOING?

November 2–4, 1998
Lunar and Planetary Institute, Houston, Texas

LPI

WORKSHOP ON THE ISSUE

MARTIAN METEORITES: WHERE DO WE STAND AND WHERE ARE WE GOING?

Held at
Houston, Texas

November 2–4, 1998

Sponsored by
National Aeronautics and Space Administration
Lunar and Planetary Institute

Abstracts in this volume may be cited as

Author A. B. (1998) Title of abstract. In *Workshop on the Issue Martian Meteorites: Where Do We Stand and Where
Are We Going?* LPI Contribution No. 956. Lunar and Planetary Institute, Houston. 64 pp.

Preface

This volume contains papers that were accepted for presentation at the Workshop on the Issue Martian Meteorites: Where Do We Stand and Where are We Going? The workshop was held November 2–4, 1998, at the Lunar and Planetary Institute in Houston, Texas.

Members of the Scientific Organizing Committee included D. C. Black, Co-Chair *(Lunar and Planetary Institute)*, C. Pilcher, Co-Chair *(NASA Headquarters)*, D. Des Marais *(NASA Ames Research Center)*, M. Drake *(University of Arizona)*, J. Ferris *(Rensselaer Polytechnic Institute)*, J. Longhi *(Lamont-Doherty Earth Observatory)*, D. McCleese *(Jet Propulsion Laboratory)*, D. McKay *(NASA Johnson Space Center)*, H. McSween *(University of Tennessee)*, M. Meyer *(NASA Headquarters)*, H. Newsom *(University of New Mexico)*, P. Rogers *(Smithsonian Institution)*, and A. Treiman *(Lunar and Planetary Institute)*.

Logistical, administrative, and publications support were provided by the Publications and Program Services Department of the Lunar and Planetary Institute.

Page intentionally left blank

Contents

Abstracts

GAMMA-RAY STERILIZATION OF MARS ANALOG ROCKS AND MINERALS.

C. C. Allen, Lockheed Martin, Houston TX 77258, USA (carlton.c.allen1@jsc.nasa.gov).

Samples of rock and soil, collected by robotic spacecraft on Mars, will be returned to terrestrial laboratories early in the next century. Plans call for the samples to be placed immediately in biological containment and tested for signs of present or past life and biological hazard. It is recommended that "controlled distribution of unsterilized materials from Mars should occur only if rigorous analyses determine that the materials do not constitute a biological hazard. If any portion of the sample is removed from containment prior to completion of these analyses it should first be sterilized" [1]. While sterilization of Mars samples may not be required, an acceptable method must be available before the samples are returned to Earth.

Various techniques are routinely used to sterilize biological samples. These include dry heating to temperatures of 150°C or higher, heating in the presence of steam, exposure to poisonous gases such as formaldehyde and propiolactone, exposure to H_2O_2 vapor or plasma, exposure to ultraviolet light, and exposure to γ radiation. The appropriate technique depends on the physical characteristics of the sample and the desired results.

Gamma radiation is routinely used to inactivate viruses and destroy bacteria in medical research. The most common commercial sterilizers utilize ^{60}Co, which emits γ photons with energies of 1.173 and 1.332 MeV. Absorbed doses of approximately 10^6 rad (10^4 γ ray = 10^4 ergs/gm) are sufficient to destroy most bacteria [2].

The current study is designed to investigate the effects of lethal doses of ^{60}Co γ radiation on geologic materials analogous to the first samples to be returned from Mars. The goals are (1) to determine the γ dose required to kill microorganisms within geologic samples, and (2) to determine the effects of lethal doses of γ radiation on the physical and chemical properties of the samples.

Samples and Methods: *Microorganisms in geologic samples.* Cores 8 mm in diameter and approximately 17 mm long were prepared from dense, fine-grained basalt taken from the Umtanum flow, Grande Ronde formation of the Columbia River basalts. A slot normal to the long axis was cut halfway through the center of each core. Half of the cores were sterilized by autoclaving in steam, and half were not sterilized.

Samples of two bacteria species, *Clostridium sporogenes* and *Bacillus subtilis*, were grown from pure cultures in gel media and inserted into the slots in the basalt cores. Both are spore-forming bacteria that are easily cultured. *C. sporogenes* requires incubation in a CO_2 environment while *B. subtilis* is incubated in air. The bacteria-loaded cores were placed in snap-top plastic vials and held at room temperature. Sets of samples were irradiated as described below.

After irradiation *C. sporogenes* was cultured in 90 ml of modified AC broth (without ascorbic acid) at a pH of 7.2, adjusted with sodium phosphate. The samples were incubated at 37°C, anaerobically in crimp top vials purged with CO_2. *B. subtilis* was grown in modified 90 ml of nutrient broth at a pH of 6. Samples were incubated in air at 30°C. After 116 hr of growth the samples were placed into liquid media and light absorbance through the media was measured at a wavelength of 600 nm.

Rocks and minerals. Fourteen types of materials were tested to assess the effects of γ radiation on the physical and chemical properties of rocks and minerals: basalt, halite, chert, Mars soil simulant (weathered volcanic ash), carbonaceous chondrite meteorite, plagioclase, olivine, pyroxene, $CaCO_3$, clay, quartz, gypsum, water, and Sn.

Triplicate splits of each sample were prepared for each radiation dose. The splits (~1 cm^3) were placed in snap-top plastic vials. Sets of samples were irradiated as described below.

Irradiation. The samples were irradiated in a Gammacell 220 High Dose Research Irradiator at the Centers for Disease Control and Prevention. Bacteria-loaded cores were exposed to total doses of 3×10^5, 3×10^6, and 3×10^7 rad at ambient temperatures, which did not exceed 100°C.

Gamma Dose Required to Kill Microorganisms in Geologic Samples: Both species of bacteria were successfully cultured from the unirradiated control samples. Bacteria viability decreased with increasing radiation at doses of 3×10^5 and 3×10^6 rad. No viability was detected in the samples irradiated at 3×10^7 rad. Estimates of viability, expressed in terms of light absorbance in liquid media, are listed in Table 1.

Effects of Radiation on Rocks and Minerals: *Induced radioactivity.* Samples were monitored for induced radioactivity at the Johnson Space Center (JSC) Radiation Counting Laboratory, one of the world's best low-background counting facilities. Entire sample sets (bacteria-loaded cores plus rocks and minerals) were placed in the counter together.

The sample set exposed to 3×10^5 rad produced 36 γ-ray peaks, all attributable to natural K, Th, and U in the samples or to ^{137}Cs produced by atmospheric nuclear tests. The net count rate attributable to these peaks across the energy range 0.05–2.0 MeV was 0.521 ± 0.003 counts/s. The sample set exposed to 3×10^7 rad produced the same 36-γ peaks and the identical net count rate.

Samples of Sn were irradiated to monitor the production of ^{117m}Sn, a γ emitter with a half-life of 13.6 days. After a radiation dose of 3×10^7 rad, a 3.64-g Sn sample showed no detectable counts above background, at a sensitivity of 0.004 counts/s (2s). This count rate sets an upper limit of <7000 atoms of ^{117m}Sn created, or $<5 \times 10^{-18}$ of the ^{117}Sn atoms present.

TABLE 1. Effects of γ radiation on bacteria.

Sample	Control	3×10^5	3×10^6	3×10^7
Clostridium (sterile cores)	0.63	0.53	ND	ND
Clostridium (nonsterile cores)	0.61	0.50	ND	ND
Bacillus (sterile cores)	0.99	0.50	0.01	ND
Bacillus (nonsterile cores)	> 0.60	0.22	0.00	ND

Light absorbance at 600 nm (sterile media = 0).

Elemental composition. Selected major-, minor-, and trace-element abundances in powdered basalt were measured by instrumental neutron activation analysis (INAA). The samples, standards, and control samples were encapsulated in pure SiO_2 glass tubes and irradiated at the Research Reactor Facility of the University of Missouri for 12 hr at a thermal neutron flux of 5.5×10^{13} n cm^{-2} s^{-1}. The samples were counted three times (roughly 0.5, 1, and 4 weeks after irradiation) in order to obtain data for nuclides of differing half-lives. Standards used, the data-reduction process, and correction procedures were the same as those previously employed in the Johnson Space Center laboratory [3].

Twenty-eight major-, minor-, and trace-element concentrations were determined. For all but one of these elements, the concentrations (within analytical error) were unchanged following irradiation at any of the three doses. The single exception was Ce, which showed a decrease in concentration from 53.9 ± 0.8 to 52.0 ± 0.8 ppm between the unirradiated control and the sample that received a dose of 3×10^7 rad.

Strontium isotopes. The ratios of $^{87}Sr/^{86}Sr$ were measured for unirradiated and irradiated basalt samples using standard procedures for radiometric age dating [4]. The values, 0.705542 ± 12 (control) and 0.705546 ± 12 (3×10^7 rad), were indistinguishable. Therefore, the effect of this dose of ^{60}Co irradiation on Sr-isotopic compositions of basalt was not detectable.

Future Analyses: The effects of γ radiation on a variety of microorganisms is currently under way. In addition, colleagues are measuring effects on the chemical composition, crystal structure, thermoluminescence, and reflectance spectra of the full range of rock and mineral samples.

Acknowledgments: Colleagues providing samples, experimental support, and analytical expertise for this study include F. Albert, J. Combie, D. Lindstrom, M. Lindstrom, D. Mittlefehldt, P. Morris, R. Morris, L. Nyquist, Y. Reese, P. Simpson, and H. Wiesmann.

References: [1] Space Studies Board (1997) *Mars Sample Return Issues and Recommendations,* National Research Council, Washington, DC. [2] Battista J. R. (1997) *Ann. Rev. Microbiol., 51,* 203–224. [3] Mittlefehldt D. W. and Lindstrom M. M. (1993) *Proc. NIPR Symp. Antarctic Meteorites, 6,* 268–292. [4] Nyquist L. E. et al. (1994) *Meteoritics, 29,* 872–885.

BIOMARKERS IN CARBONATE THERMAL SPRINGS: IMPLICATIONS FOR MARS.   C. C. Allen[1], S. J. Kivett[2], and D. S. McKay[3], [1]Lockheed Martin, Houston TX 77258, USA (carlton.c.allen1@jsc.nasa.gov), [2]University of Houston–Downtown, Houston TX 77002, USA, [3]NASA Johnson Space Center, Houston TX 77058, USA.

Evidence of possible relict biogenic activity has been reported in carbonate inclusions within martian meteorite ALH 84001 [1]. The initial evidence included ovoid and elongated forms 50–500 nm in length, morphologically similar to but significantly smaller than many terrestrial microbes. More recently, thin structures resembling the remains of organic biofilms have been reported in the same meteorite [2].

Carbonates have also been discussed in the context of Mars sample return missions. Thermal spring deposits have often been cited as prime locations for exobiological exploration [3]. By analogy to Earth, specialized microbes may have existed in the heated, mineralized waters, and precipitates of carbonate and/or silica from these waters may have trapped and preserved evidence of life. Since the geological interactions that produce thermal springs can be recognized in orbital imagery, directed searches for microfossils in such deposits are deemed possible [4].

We are engaged in a study of the signatures produced by contemporary biogenic activity (biomarkers) in carbonate thermal springs. We are examining the microbes that live in such environments and the preservation of microbial forms, biofilms, and petrographic fabrics indicative of life in thermal spring mineral deposits.

This work is part of a much more extensive study to refine the appropriate tools, techniques, and approaches to seek evidence of life in a range of planetary samples. A deeper understanding of biological signatures will prepare us for the detailed search for life on Mars and eventually on other planets. Overall, the study of biomarkers in rocks and soils will provide insight into the evolution of life because such signatures are a record of how life interacts with its environment, how it adapts to changing conditions, and how life can influence geology and climate.

Biomarkers in Carbonate Thermal Springs: We are currently studying samples from four active thermal springs: Le Zitelle in the Viterbo region of Italy [5], Narrow Gauge in the Mammoth complex of Yellowstone National Park, Wyoming [6], Hot Springs National Park, Arkansas [7], and springs at Jemez on the slopes of the Valles caldera, New Mexico [8]. In each case, water reaches the surface at 60°–72°C and near-neutral pH (6.3–7.5), rapidly precipitating large amounts of aragonite and calcite.

We are concentrating on samples from the hottest areas of each spring. The Italian, Yellowstone, and Jemez springs were sampled at the surface, while the Arkansas springs were sampled below ground. Various samples were fixed in glutaraldehyde, air dried or critical point dried, etched in 1% HCl, and examined in a high-resolution SEM.

Microbes. The near-vent environments of thermal springs support a variety of microorganisms. *Thermothrix thiopara,* a prolific S-oxidizing bacterium [8], is the highest-temperature species identified at our sites in Yellowstone and Jemez. Pentecost [9] identified a species of the photosynthetic, filamentous bacteria *Chloroflexus* as the dominant form immediately downstream from the vent of the Italian spring. Spherical microbes as large as 15 μm in diameter populate the waters at Hot Springs. Rod-shaped microbes several micrometers in length are found in samples from all four sites.

The thermal spring deposits also contain forms, many of which appear to be biological, significantly smaller than conventional bacteria. Large numbers of 100–200-nm spheres, the "nanobacteria" described by Folk [10], are common in portions of the Italian and Yellowstone carbonates. The spheres are composed of C, O, F, P, and Ca with detectable Si and S, and are often found enmeshed in organic mucus. Numerous 300–500-nm rods and spheres, some apparently dividing, populate the Arkansas samples.

Many of the microbes die and their remains are rapidly destroyed in carbonate thermal spring environments. Organic matter is generally rare in carbonate sinters deposited at >30°C, suggesting that decomposition rates in such thermal environments are very high [11]. Detailed SEM examination of samples from all four sites consistently reveal mineralized cell remains but only scattered intact cells.

While thermal spring microbes are apparently poorly preserved in carbonates, fossilization by silica can provide enduring evidence of life. At Jemez, amorphous silica spheres 50–300 nm in diameter preserve the forms of dissolved microbial cells. A wide variety of well-preserved thermophilic bacteria has been found in the silica sinter deposited by many Yellowstone thermal features [12]. Similar fossil assemblages have been described in siliceous thermal spring deposits as old as 400 Ma [13].

Biofilms. The three-dimensional network of polysaccharide mucus, living cells, and cell remains that constitutes a biofilm is a distinctive macroscopic biomarker. Carbonate samples from all four of our sites contain biofilms in various states of preservation.

Biofilms are stable in water as hot as 72°C and retain their three-dimensional nature as the water cools. Upon drying, however, the mucus shrinks and deforms but preserves its intercellular binding structure. Carbonate samples still display extensive biofilm remains after years of desiccation.

Morphologic evidence of biofilms can be preserved by mineralization. Biofilms in the Jemez samples are extensively coated with the 50–300-nm-diameter silica spheres. Cady and Farmer [12] have demonstrated that silica in thermal springs preferentially nucleates on and preserves organic mucus. Westall [14] provides evidence of silicified biofilm in deep-sea sediments at least 5.5 m.y. old.

Petrographic fabrics. The importance of microbes in promoting the deposition of $CaCO_3$, particularly aragonite, in thermal springs is a matter of ongoing debate. Pentecost [9] argues against significant microbial influence in the case of Yellowstone deposits. He accepts microbially induced precipitation only in cases where aragonite crystals clearly copy the structures of filamentary bacteria. Other investigators, however, provide evidence for a range of bacterially induced lithification styles [15].

Thermothrix thiopara, found near the vents of our Yellowstone sampling sites, forms filaments up to 10 cm long. Immediately downstream, the filaments become overgrown by aragonite. The result is a mass of parallel aragonite needles, each millimeters in diameter and centimeters long, which closely mimics the *Thermothrix* filaments. In this case bacterially induced precipitation yields a distinctive petrographic fabric in the carbonate rocks that is specifically attributable to life. This fabric has been recognized in deposits as old as ~360 Ma [11].

Biological action can also promote the selective dissolution of minerals. Partial dissolution and pitting in calcite crystals is a common feature of the Jemez samples. Pristine crystals show no evidence of associated microbes, while pitted areas are invariably associated with biofilms.

Implications for Mars: Extensive previous studies of life in carbonate thermal springs, coupled with our own results, have implications in the search for evidence of martian life:

1. Specialized microbes are common in carbonate-precipitating environments as hot as 72°C.

2. Several types of microorganisms in such environments have sizes significantly <1 μm.

3. Biofilms are characteristic of thermal spring microbial communities.

4. Microbes are poorly preserved in thermal spring carbonates.

5. Silicified microbes and biofilms can be well preserved over geologic time.

6. Some petrographic fabrics, recognizable in the geologic record, are specifically attributable to thermal spring microorganisms.

These observations support the interpretation of submicrometer features in ALH 84001 as possible relict life forms and biofilms. They also support the sample return strategy of searching for a variety of biomarkers in thermal spring deposits on Mars.

References: [1] McKay D. S. et al. (1996) *Science, 273,* 924. [2] McKay D. S. et al. (1997) *LPS XXVIII,* 919. [3] An Exobiological Strategy for Mars Exploration (1995) *NASA SP-530.* [4] Walter M. R. and Des Marais D. J. (1993) *Icarus, 101,* 129. [5] Folk R. L. (1994) *Geograph. Phys. et Quat., 48,* 233. [6] Chafetz H. S. and Lawrence J. R. (1994) *Geog. Phys. et Quat., 48,* 257. [7] Norsworthy S. F. (1970) Ph.D. dissertation, UCLA. [8] Caldwell D. E. et al. (1984) *Geomicrobiol. J., 3,* 181. [9] Pentecost A. (1995) *Microbios, 81,* 45. [10] Folk R. W. (1993) *J. Sediment. Petrol., 63,* 990. [11] Farmer J. D. and Des Marais D. J. (1994) in *Microbial Mats: Structure, Development and Environmental Significance,* p. 61, Springer Verlag. [12] Cady S. L. and Farmer J. D. (1996) in *Evolution of Hydrothermal Systems on Earth (and Mars?),* p. 150, Wiley. [13] Walter M. R. (1996) in *Evolution of Hydrothermal Systems on Earth (and Mars?),* p. 112, Wiley. [14] Westall F. (1994) *Darmstadter Beitrage zur Naturgeschichte, 4,* 29. [15] Chafetz H. S. and Buczynski C. (1992) *Palaios, 7,* 159.

FLUID INCLUSIONS IN ALLAN HILLS 84001 AND OTHER MARTIAN METEORITES: EVIDENCE FOR VOLATILES ON MARS.

R. J. Bodnar, Fluids Research Laboratory, Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg VA 24061-0420, USA (bubbles@vt.edu).

Introduction: The important role that volatiles play in planetary evolution is well known. On Earth, volatiles have and continue to play key roles in the development and properties of the crust, hydrosphere, and atmosphere. More recently, the recognition that the mantle contains small but ubiquitous quantities of volatile components has led to an improved understanding of mantle rheology and chemistry and the recycling of volatiles in the Earth system. And, of course, volatiles, especially water, are considered to be a prerequisite for the origin and evolution of life as we know it.

The recent announcement that evidence for life had been discovered in the ALH 84001 martian meteorite [1] combined with the highly successful Mars Pathfinder Mission has led to renewed interest in the geochemical evolution of Mars. Much of the scientific effort in this area has been devoted to characterizing the volatiles present in the SNC meteorites and, by inference, the volatiles present on Mars when the rocks formed. Here, the occurrence of "free" volatiles (i.e., volatiles occurring in the fluid state, and not as minor components of minerals and/or glasses) in the ALH 84001 and Nakhla meteorites is reported, along with possible implications.

Background: Fluid inclusions are microsamples of fluid (liquid or gas) trapped in rocks and minerals either at the time of their original formation or at some later time as fluids flow through rocks along fractures [2]. The presence of fluid inclusions in terrestrial rocks is the rule rather than the exception. Indeed, the rock sample that contains no inclusions that are visible at high magnification (>1000×) is rare, and many minerals such as milky quartz may contain up to 10^9 fluid inclusions per cubic centimeter.

The precursor of the martian meteorites is thought to be ultramafic igneous extrusive and/or intrusive rocks that were blasted from the surface of Mars during an impact event. Similar igneous rocks on Earth commonly contain fluid inclusions along with the more abundant silicate, sulfide, and carbonate melt inclusions. As such, it is reasonable to expect that the SNC meteorites should contain fluid inclusions that represent fluid trapped in the rocks while they were on the surface of Mars. A review of the recent literature failed to find any references to fluid inclusions in these well-studied samples, and a systematic search of available SNC meteorite samples was undertaken.

Observations: Fluid inclusions have been found in two thin sections of SNC meteorites: one in Nakhla (NSNM 5891-3) and one in ALH 84001,146.

Nakhla (NSNM 5891-3). The inclusion in the Nakhla sample is tubular and ~8 μm long. The inclusion is one of several dozen inclusions forming a healed fracture that cuts through an orthopyroxene crystal. Most of the inclusions along the fracture are dark with noticeable microfractures extending from the inclusion into the surrounding mineral, indicating that the inclusions have decrepitated (exploded) owing to pressure buildup within the inclusion. This behavior is common for high-density liquid fluid inclusions in terrestrial samples. A few other inclusions along the fracture were clear (transparent) but did not contain a visible bubble. This is because either the inclusions were empty, contained only liquid with no vapor bubble, or contained a bubble that was motionless and hidden in a corner of the inclusion. The bubble in the one unambiguous fluid inclusion in this fracture plane was in constant, slow motion, proving that the inclusion did indeed contain a liquid phase.

Although it was not possible to conduct the types of tests normally used to determine fluid inclusion compositions because of the manner in which the sample was prepared, the difference in index of refraction between the liquid and the vapor bubble is consistent with the inclusions containing liquid and vapor CO_2, although it is possible that the inclusion contained liquid water and water vapor.

ALH 84001,146. The second sample that contained liquid inclusions with moving bubbles was ALH 84001,146. The inclusions in this sample were spherical to negative-crystal shaped, about 1–2 μm in diameter, and not along an obvious fracture (Fig. 1). The fact that the inclusions are not along a fracture is important because it suggests that the inclusions are primary (i.e., trapped during growth of the enclosing pyroxene). The fluid in the inclusions thus represents the magmatic fluid that exsolved from the crystallizing melt as the igneous rock formed on Mars. As such, the inclusions can provide valuable information about degassing early in Mars history. As with the inclusion in Nakhla, no direct chemical tests could be conducted on these inclusions, but the optical behavior of the inclusions suggests that they contain liquid and vapor CO_2.

Implications: The occurrence of (presumably) CO_2 fluid inclusions in both the Nakhla and ALH 84001 meteorites suggests that CO_2 was migrating through these igneous rocks at some time duration or after their formation on Mars. If the CO_2 was present at or near magmatic temperatures, pyroxene (enstatite) would not be stable in the presence of CO_2, and would react to form a carbonate and a silica-rich phase [3]. This is consistent with a high-temperature origin for the carbonates in the SNC meteorites, as originally proposed by Harvey and McSween [4]. This interpreta-

Fig. 1. Series of photomicrographs captured from a videotape showing a fluid inclusion with a moving vapor bubble in the martian meteorite ALH 84001,146. The inclusion is about 1.8 μm in diameter. Note that the dark, rounded vapor bubble, indicated by the arrow in the third image from the top, is in a different position in each of the five images. When examined under the microscope at room temperature, the bubble is in continuous rapid Brownian motion from the small thermal gradients caused by the microscope light source.

tion also suggests that the carbonates were present in the rocks before they were ejected from the martian surface. However, by analogy with terrestrial samples, the carbonates did not necessarily have to form as a result of the impact event but, rather, may have formed as a result of natural high-temperature igneous metasomatic processes before the impact.

References: [1] McKay D. S. et al. (1996) *Science, 273,* 924–930. [2] Roedder E. (1984) *Mineralogy, 12,* 646. [3] Koziol A. M. and Newton R. C. (1995) *Am. Mineral., 80,* 1252–1260. [4] Harvey R. P. and McSween H. Y. Jr. (1996) *Nature, 382,* 49–51.

RUBIDIUM-STRONTIUM FORMATION AGE OF ALLAN HILLS 84001 CARBONATES.

L. E. Borg[1], L. E. Nyquist[1], C.-Y. Shih[2], H. Wiesmann[2], Y. Reese[2], and J. N. Connelly[3], [1]Mail Code SN2, NASA Johnson Space Center, Houston TX 77058, USA, [2]Mail Code C23, Lockheed Martin, 2400 NASA Road 1, Houston TX 77258, USA, [3]Department of Geological Sciences, University of Texas, Austin TX 78712, USA.

Synopsis: Our preferred age for the formation of carbonates in the martian meteorite ALH 84001 is 3.90 ± 0.04 Ga for $\lambda(^{87}Rb)$ = 0.01402 Ga^{-1}, or 3.85 ± 0.04 Ga for $\lambda(^{87}Rb)$ = 0.0142 Ga^{-1}. This age is determined by a three-point Rb-Sr isochron defined by leachates of high-graded carbonate-rich material. Major cation and especially phosphorous analyses of the leachates permit contributions from igneous whitlockite to be recognized for low-acidity leachates, and the corresponding data are omitted from the isochron. Data for the two highest acidity leachates plot close to the preferred isochron, but are omitted because we believe they contain contributions leached from the pyroxene substrate on which most of the carbonates are found. Nevertheless, the isochron age for all five highest-acidity leachates is 3.94 ± 0.04 Ga, and is within error of the age obtained for the more restricted data set. All leachates used to define the isochron have major cation compositions that are similar to those obtained by microprobe analyses of the carbonate rosettes and are consistent with progressive digestion of the carbonates according to their composition.

The age thus obtained for the carbonates is about 600 m.y. younger than the crystallization age of ALH 84001 determined by Sm-Nd analyses [1,2], but is within error limits of the age of impact metamorphism inferred from the Rb-Sr and Ar-Ar systematics of silicates, which yield ages of 3.85 ± 0.05 Ga [3] and 4.05–3.80 Ga [4] to 4.3–3.8 Ga [5], respectively. Similarities between the carbonate crystallization age and the age of impact metamorphism as determined by Ar-Ar and Rb-Sr suggest that the carbonate formation is impact-related. Nevertheless, both high and low-temperature scenarios for the origin of the carbonates are possible.

Introduction: The origin of carbonate minerals in ALH 84001 has received much attention since [6] reported that the carbonates possibly contain evidence for martian microbial life. Several models have been proposed for the origin of the carbonates in ALH 84001, including (1) impact metasomatism [7], (2) impact melting of preexisting carbonates [8], (3) evaporation of surficial fluids at low temperature [9–10], and (4) low-temperature alteration by hydrothermal fluids [11]. The time of carbonate formation has important implications for martian planetary evolution as well as its possible biological evolution. An old age would be consistent with a wetter, warmer early Mars and thus with models of carbonate formation involving aqueous activity. An intermediate age, combined with clear evidence of formation via aqueous processes, would gain special significance because it would extend the time period during which water might have been relatively abundant on the martian surface and available to support life. Carbonate formation via impact metasomatism or other high-temperature phenomena could be consistent with virtually any age, but also might be expected to be more prevalent at early times. We have approached the difficult problem of determining the age of ALH 84001 carbonates by isotopic analyses of a programmed sequence of carbonate-rich leachates.

Procedure: A 1-g sample of ALH 84001 was gently crushed and sieved at 100–200 and 200–300 mesh. Grains containing carbonates were hand-picked so that carbonate abundances in the high-graded sample approached 10%. A series of progressively more reactive reagents were used to leach this high-graded sample; these reagents were predetermined by experimentation with terrestrial carbonates. Small aliquots of each leachate were analyzed for Ca, Mg, Fe, K, P, Sr, Nd, and Pb by isotope dilution and atomic absorption. The remaining aliquots were spiked for Rb-Sr, Sm-Nd, and U-Pb and put through standard cation chromatography separation procedures. We report results of the Rb-Sr analyses of the leachates; the other isotopic analyses are in progress.

Results: The major-element analyses of the leachates are presented in Fig. 1. The first leachates have compositions that are unlike any of the carbonates analyzed in ALH 84001 [e.g., 12]. S1 and S2 (the first and second leachates) contain no Fe or P and lie on the magnesite-calcite join. The leaching agents used for S1 and S2 were extremely weak and are likely to have primarily removed surface coatings. The S3 leachate has significantly higher abundances of Ca and P. Assuming Sr contents in ALH 84001 whitlockite are similar to those estimated from whole rock leachates of the basaltic shergottite QUE 94201 from [13], mass balance cal-
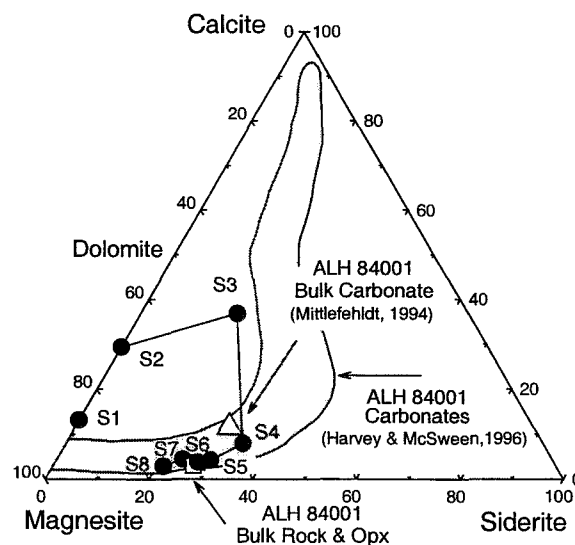

Fig. 1. Ternary diagram illustrating compositions of leachates from ALH 84001. Note compositional similarities between carbonate compositions (shaded area) from [7] and S4–S8 leachates. Also note compositional differences between the carbonate compositions and S1–S3 leachates.

culations based on P abundances suggest that ~5% of the Sr in this fraction is derived from whitlockite. The S4 leachate has a major-element composition that is similar to the bulk carbonate composition estimated by [13], but also has a significant amount of P. The maximum Sr contribution from whitlockite to the S4 leachate can be calculated assuming that 100% of the Sr in the S3 leachate is derived from whitlockite. In this case ~30% of the Sr in the S4 leachate would be of igneous origin. This is obviously an extreme upper limit; mass balance calculations similar to those made for S3 suggest that S4 contains ~1% whitlockite-derived Sr. The S5–S8 leachates have no measurable P. That the leachates would become progressively more Mg-rich with increasing acidity of the leaching reagent was expected from experiments with terrestrial carbonates in which dissolution of calcite, then siderite, and then magnesite was observed.

A Rb-Sr isochron diagram of our leachate data is presented in Fig. 2. The age of 3.90 ± 0.04 Ga is defined by our best leachates (S4–S6). Blank contributions to Sr in all of the leachates were <0.2%, with the exception of S8 (2.5%), which contained <1 ng of Sr. S4 lies on the isochron, suggesting that the whit-lockite contribution to its Rb-Sr systematics was indeed small. Those leachates having compositions unlike the carbonates (S1–S2), a high P/Sr ratio (S3), or a very low abundance of Sr (S8) lie off the best isochron. The S7 and S8 leachates appear to lie on a mixing line between the S6 leachate and our previous pyroxene analyses [1], suggesting that they contain a contribution from pyroxene leached by the strong reagents used. Furthermore, visual examination of a control suite of carbonates indicated that all were dissolved by the sixth step. The calculated age range for two (S4–S5; 3.89 Ga), three (S4–S6; 3.90 ± 0.04 Ga), four (S4–S7; 3.93 ± 0.04 Ga), or five (S4–S8; 3.94 ± 0.04 Ga) data points is ~3.9–4.0 Ga. Our preferred age of 3.90 ± 0.04 Ga is that determined by S4–S6.

Discussion: The age of carbonate formation in ALH 84001 is substantially younger than the crystallization age of 4.50 ± 0.13 Ga derived from Sm-Nd analyses of silicates and phosphates

[1,2], but is similar to the age of impact metamorphism determined by Ar-Ar and Rb-Sr analyses of silicate phases [3,4]. This suggests a relationship between the impact event and carbonate formation. Scenarios involving direct formation of the carbonates via impact metasomatism [6] or impact melting of preexisting carbonates [8] are clearly compatible with our data. However, another possibility is that ice buried beneath the martian surface was melted by heat from the impact to produce water that percolated into the newly formed basin and precipitated the carbonates, consistent with the models of [8,9]. Alternatively, if Mars were warmer and wetter at ~3.9 Ga, a crater lake may have persisted for a time interval that was short compared to the uncertainties of the radiometric ages. Thus, the carbonates could have been precipitated at relatively low temperatures and still have had crystallization ages indistinguishable from the age of impact metamorphism.

References: [1] Nyquist et al. (1995) *LPS XXVI*, 1065–1066. [2] Jagoutz et al. (1994) *Meteoritics, 29*, 479–479. [3] Wadhwa and Lugmair (1996) *Meteoritics & Planet. Sci., 31*, A145. [4] Turner et al. (1997) *GCA, 61*, 3835–3850. [5] Bogard and Garrison (1997) in *Papers Presented to the Conference on Early Mars*, pp. 10–12, LPI, Houston. [6] McKay et al. (1996) *Science, 273*, 924–930. [7] Harvey and McSween (1996) *Nature, 382*, 49–51. [8] Scott et al. (1997) *Nature, 387*, 377–379. [9] Warren (1998) *JGR, 103*, 16759–16773. [10] McSween and Harvey (1998) *Meteoritics & Planet. Sci., 33*, A103. [11] Romanek et al. (1994) *Nature, 382*, 655–657. [12] Mittlefehldt (1994) *Meteoritics, 29*, 214–221. [13] Borg et al. (1997) *GCA, 61*, 4915–4932.

RARE POTASSIUM-BEARING MICA IN ALLAN HILLS 84001: ADDITIONAL CONSTRAINTS ON CARBONATE FORMATION.

A. J. Brearley, Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque NM 87131, USA (brearley@unm.edu).

Introduction: McKay et al. [1] presented several intriguing observations suggesting evidence of fossil life in martian orthopyroxenite ALH 84001. These exciting and controversial observations have stimulated extensive debate over the origin and history of ALH 84001, but many issues still remain unresolved. Among the most important is the question of the temperature at which the carbonates, which host the putative microfossils, formed. Oxygen-isotopic data, while showing that the carbonates are generally out of isotopic equilibria with the host rock, cannot constrain their temperature of formation [2–4]. Both low- and high-temperature scenarios are plausible depending on whether carbonate growth occurred in an open or closed system [2–4]. Petrographic arguments have generally been used to support a high-temperature origin [5], but these appear to be suspect because they assume equilibrium between carbonate compositions that are not in contact. Some observations appear to be consistent with shock mobilization and growth from immiscible silicate-carbonate melts at high temperatures [6]. Proponents of a low-temperature origin for the carbonates are hampered by the fact that there is currently no evidence of hydrous phases that would indicate low temperatures and the presence of a hydrous fluid during the formation of the carbonates. However, the absence of hydrous phases does not rule out carbonate formation at low temperatures, because the carbonate forming fluids may

Fig. 2. Rubidium-strontium isochron plot of leachates from ALH 84001. Our preferred age of 3.90 ± 0.04 Ga is defined by S4–S6; leachates S4–S8 define an age of 3.94 ± 0.04 Ga. Leachates used to define the isochrons have major cation compositions similar to those of the carbonates (see Fig. 1).

have been extremely CO_2-rich, such that hydrous phases would not have been stabilized.

Although phyllosilicates are apparently not present at the scale observable by SEM, they may be present at the submicrometer scale. However, several detailed TEM studies of ALH 84001 have failed to find evidence of phyllosilicates [1,7]. In this study, I have carried out additional TEM studies of ALH 84001 and have found evidence of very rare phyllosilicates, which appear to be convincingly of preterrestrial origin. At present these observations are limited to one occurrence; further studies are in progress to determine if the phyllosilicates are more widespread.

Results: Transmission electron microscopy studies so far have concentrated on fragments of carbonate entrained within feldspathic glass throughout ALH 84001. The carbonate fragments have irregular shapes, but examination at high magnification using BSE and TEM imaging show that many grains are faceted and these facets are cleavage surfaces. This observation suggests that these grains are fragments of larger, continuous regions of carbonate that have been fractured, disrupted and entrained within the feldspathic melt during a post-carbonate formation impact and heating event. This is also consistent with the observation that adjacent fragments, separated by regions of glass, have zoning patterns consistent with their originally being part of a single grain. BSE images of the fragments show that they have a range of sizes from ~50 μm down to <10 μm. TEM observations [8] show that many of these carbonate fragments, despite having relatively Mg-rich compositions, contain myriad magnetite particles associated with voids. These magnetite grains have grain sizes and morphologies consistent with the magnetites observed by [1] and other workers [6].

A single carbonate fragment within the feldspathic glass contains the phyllosilicates. They occur as highly elongate, parallel to subparallel ribbonlike crystals, typically <10 nm thick and extending for several hundreds of nanometers through the carbonate grain. The abundance of phyllosilicates within the fragment is difficult to estimate, but is probably of the order of 10–20 vol%. It is notable that the phyllosilicate grains are always truncated at the edge of carbonate grains and never extend into the feldspathic glass. It also appears that close to the interface with the glass the phyllosilicates have curved morphologies, and some of the smallest grains appear to be amorphous. These observations are consistent with thermal decomposition during the postshock heating that followed fragmentation and entrainment of the carbonate fragments within the feldspathic glass [8,9]. Electron diffraction and high-resolution TEM studies of the phyllosilicates show that they have a basal spacing of 1 nm and appear to be well-ordered, with no evidence of stacking disorder or partial interlayers. The composition of the grains has not yet been obtained with any great certainty, because of their very limited thickness and the fact that they are closely intergrown with the carbonate. However, EDS spectra show the presence of Al, Si, and K, in addition to Mg, Ca, and Fe from the adjacent carbonate. The Al/Si ratio appears to be relatively low. These observations appear to be consistent with this phyllosilicate phase being a K-bearing mica, such as illite.

Implications: A preterrestrial origin for the mica is indicated by several lines of evidence. First, the mica occurs exclusively within the carbonate and does not extend into the surrounding feldspathic glass, clearly showing that it predated formation of the glass. If mica had formed after glass formation, it would most likely have formed by replacement of the feldspathic glass, rather than

Fig. 1. High-resolution TEM image of K-bearing mica from a carbonate fragment in ALH 84001.

intergrown with carbonate. Second, the mica appears to have been heated and partially decomposed where it is in contact with the glass, again showing that it must have predated glass formation. Third, terrestrial weathering products of meteorites are poorly crystalline clay minerals with an extremely fine-grain size, not well-ordered micas. Fourth, the carbonates appear to be completely entrained within the feldspathic glass and consequently would have been isolated from altering terrestrial fluids. The reasonable conclusion from these observations is that the mica formed prior to ejection of ALH 84001 from Mars.

Although phyllosilicates are not widespread in ALH 84001, the presence of mica clearly indicates that water-bearing fluids were present at some time during the history of ALH 84001. The very close intergrowth of carbonate with the mica suggests that the two phases grew simultaneously or that the mica may have preexisted before carbonate formation. Replacement of preexisting carbonate by long, thin ribbons of phyllosilicates does not seem probable. The very elongated morphology of the mica grains does not seem consistent with unimpeded growth from a solution; rather, it suggests growth constrained by adjacent growing carbonate grains (i.e., the

two phases grew contemporaneously). The presence of illite and its formation from smectite is widely used as a geothermometer in terrestrial pelitic rocks that have undergone diagenesis to low-grade metamorphism. However, this approach has been questioned, and it may be the case that both illite and smectite are metastable phases with respect to muscovite but form according to the predictions of Ostwald's step rule [9]. As a consequence, illite can occur under diagenetic conditions and up to temperatures in excess of 250°C. However, at temperatures >~300°C, muscovite would be expected to be the stable K-bearing mica and should form because temperatures are sufficiently high for equilibrium to be attained. This suggests that mica formation in ALH 84001 occurred at temperatures probably <250° ± 50°C. At low temperatures, such as occur during diagenesis, clay minerals are extremely fine-grained and are complex submicroscopic intergrowths of different layer lattice minerals such as smectite, illite, and chlorite, which are far from thermodynamic equilibrium. The mica grains in ALH 84001 show no evidence of this type of interlayering, and hence indicate that they most likely formed at temperatures >150° ± 50°C. If the mica formed contemporaneously with the carbonate as is indicated by the textural relations, then carbonate formation conditions between 100°–300°C are indicated. While this is a broad range in temperature, it rules out a high-temperature origin for the carbonates proposed by some workers.

Acknowledgments: This research was supported by NASA grant NAG5-4935 to A. J. Brearley, principal investigator.

References: [1] McKay D. S. et al. (1996) *Science, 273,* 924–929. [2] Romanek C. S. et al. (1994) *Nature, 372,* 655–656. [3] Valley J. W. et al. (1997) *Science, 275,* 1633–1638. [4] Leshin L. et al. (1997) *GCA, 62,* 3–13. [5] Harvey R. P and McSween H. Y. Jr. (1996) *Nature, 382,* 49–51 [6] Scott E. R. D. et al. (1997) *Nature, 387,* 377–379. [7] Bradley et al. (1996) *GCA, 60,* 5149–5155. [8] Brearley A. J. (1998) *LPS XXIX,* Abstract #1451. [9] Shearer C. K. and Brearley A. J., this volume. [10] Essene E. J. and Peacor D. R. (1995) *Clays Clay Minerals, 43,* 540.

WATER ON MARS: HOW MUCH WAS (IS) THERE, WHERE DID IT GO, AND WHEN? M. H. Carr, U.S. Geological Survey, 345 Middlefield Road, Menlo Park CA 94025, USA (carr@astmnl.wr.usgs.gov).

Optimism about the prospects for development of indigenous life on Mars has been fueled in large part by perceptions of the geologic evolution of Mars based mainly on remote-sensing data. The consensus view is that Mars is, or was, a water-rich planet and that it likely experienced warmer climates in the past. Yet this view has not been proved, and it is difficult to reconcile with most modeling studies of climate change and some characteristics of martian meteorites. Moreover, many variants have been proposed for the climate history of the planet and for the amounts and locations of water present at different times.

The evidence that water played a major role in the history of Mars, while circumstantial, is strong. A variety of fluids other than water have been suggested as the erosive agents that cut the large outflow channels, but water is by far the most compelling and is consistent with the presence of valley networks and numerous possible indicators of ground ice. Most outflow channels are Hesperian;

that is, they formed after the end of heavy bombardment, but still in the first half of Mars' history. Around the Chryse Basin, roughly 4×10^6 km^3 of rock was removed, which likely required at least 10^7 km^3 of water, or 70 m spread over the whole planet. Additional outflow channels around Elysium, Hellas, and Amazonis bring the total volumes of flood waters to over 100 m. This is only the water brought to the surface in floods. The most likely causes of the outflow channels are catastrophic eruption of groundwater or catastrophic release of groundwater-fed lakes, as, for example, in the canyons. This being so, then the 100 m probably represents only a fraction of the total near-surface inventory. Most of the water retained by the planet at the end of heavy bombardment probably remained in the ground as ice or water at greater depths.

The fate of the flood waters is controversial. One suggestion is that the floods formed under present climatic conditions and that each flood left a lake that immediately froze over and ultimately froze solid [1,2]. Successive floods would then have built thick, layered, permanent ice deposits in the low-lying northern plains where most of the floods terminated. This water was permanently removed from the global aquifer system so that flooding ultimately ceased. An alternative suggestion [3] is that ocean-sized (>10^7 km^3) bodies of water periodically accumulated in the low-lying northern plains, temporarily altering global climates. The oceans ultimately dissipated, leaving behind shorelines [4,5] as evidence of their former presence. Some support for the shoreline hypothesis is the similarity in elevations of some sections of the proposed shorelines, but the lack of detection of carbonates by Mars Global Surveyor [6] is difficult to reconcile with major climate excursions as late as late Hesperian.

Martian meteorites appear to contain water (and other volatiles) from two sources, a magmatic source and an atmospheric source that has experienced isotopic fractionation, probably as a consequence of losses from the upper atmosphere. This suggests that the atmospheric volatiles were mixed deep into the crust. Under present climatic conditions, CO_2 could diffuse from the atmosphere into the ground and be fixed as carbonate, but movement of water from the atmosphere into the ground is more difficult because of the thick cryosphere. One possibility is precipitation accompanying climate change, as suggested by the episodic ocean hypothesis, but this presents other problems and is inconsistent with the low post-heavy-bombardment erosion rates. Hydrothermal activity has been suggested, but this would be unlikely to be effective in introducing atmospheric water into the ground, given a thick cryosphere. Alternatives are polar basal melting and reintroduction of water (ice) into ground at low latitudes during periods of high obliquity.

The case for a major climate change early in Mars' history is much stronger than the case for changes after the end of heavy bombardment. Evidence for early climate change includes (1) the almost universal presence of valley networks in Noachian terrains, (2) the dramatic change in erosion rates near the end of heavy bombardment, and (3) the nonequilibrium distribution of water at the end of heavy bombardment (sources of valleys at high elevations). The lack of detection of extensive carbonate deposits is, however, troublesome. A possible way out of the dilemma is that early in the era of heavy bombardment Mars had a large inventory of CO_2 and a thick CO_2/H_2O atmosphere. Loss of CO_2 from the atmosphere by impact erosion [7] and volcanic burial was partly offset by recycling of CO_2 from carbonates into the atmosphere as a consequence of rapid burial and high heat flows [8]. However, as heat flow and the total inventory of CO_2 declined, recycling could not

keep pace with losses by impact. As a result the atmosphere was almost entirely lost through impact erosion in late Noachian, and no carbonates were left at the surface.

We can conclude that Mars emerged from heavy bombardment with at least a few hundred meters of near-surface water, of which at least 100 m flowed across the surface in the large floods. The fate of the flood waters is uncertain. Some was lost from the upper atmosphere, some may be in the polar layered terrain, and some may be in permanent ice deposits in the low-lying northern plains and elsewhere. This entire near-surface inventory may have been enriched in D as a consequence of massive losses during hydrodynamic escape and the earlier warm climates.

References: [1] Carr M. H. (1996) *Water on Mars,* Oxford. [2] Carr M. H. (1996) *Planet. Space Sci., 44,* 1411–1423. [3] Baker V. R. et al. (1991) *Nature, 353,* 589–594. [4] Parker T. J. et al. (1989) *Icarus, 82,* 111–145. [5] Parker T. J. et al. (1998) *JGR, 98,* 11061–11078. [6] Christensen P. R. et al. (1998) *Science, 279,* 1692–1698. [7] Melosh H. J. and Vickery A. M. (1989) *Nature, 338,* 487–489. [8] Pollack J. B. et al. (1987) *Icarus, 71,* 203–224.

ON INDEPENDENT PROOF OF A MARTIAN ORIGIN FOR THE SHERGOTTY METEORITE.

Yu. T. Chuburkov[1], V. P. Perelygin[1], and V. A. Alekseev[2], [1]Joint Institute for Nuclear Research, 141980 Dubna, Russia, [2]Troitsk Institute of Innovation and Thermonuclear Studies, 142092 Troitsk, Russia.

The Mendeleev's Periodic Law was used to obtain proof of the existense of the hypothetical process of element magnetic separation in protoplanetary nebula.

The share of free neutral atoms, N_o, for all elements in protoplanetary nebula has been determined with an account of their abundance and physical and chemical properties. The linear dependence for the ratio of nonvolatile and volatile element contents in igneous rocks of the Earth (R = 1 AU) up to the asteroid belt (R = 2.80 AU) on N_o was obtained.

To this end the concentration ratios of elements — analogs with different N_o in the matters of Venus, Earth, Mars, and chondrites — were compared. The data obtained are sufficient for the demonstration of the existence of the process of element magnetic separation in protoplanetary nebula. The concentration ratio Z_1/Z_2 for some pairs of chemically similar elements is presented in Table 1 for the Earth (IR), Mars (Ms), Shergotty meteorite (Sh), and chondrites (Ch).

TABLE 1. Data showing that Shergotty meteorite element composition is much closer to Mars than chondrite meteorites.

N/N	Z_1/Z_2	IR	Ms	Sh	Ch
1	Mg/Ca	0.6	1.3	0.9	10
2	Na/K	1	—	5	8
3	Ca/Sr	91	530	170	10^3
4	Ag/Rb	8×10^{-4}	—	2×10^{-3}	3×10^{-2}
5	Mg/Sr	62	7×10^2	2×10^3	3×10^5
6	Fe/U	2×10^4	—	10^6	2×10^7
7	Ir/K	5×10^{-8}	—	2×10^{-7}	6×10^{-4}
8	Mg/Ba	55	—	3×10^3	2×10^{-4}
9	Zn/Ba	0.2	—	0.4	10

THE SEARCH FOR EARLY LIFE ON MARS: A EUROPEAN SPACE AGENCY EXOBIOLOGY SCIENCE TEAM STUDY.

P. Clancy[1], A. Brack[2], B. Hofmann[3], G. Horneck[4], G. Kurat[5], J. Maxwell[6], G. G. Ori[7], C. Pillinger[8], F. Raulin[9], N. Thomas[10], F. Westall[11], and B. Fitton[12], [1]European Space Agency, Noordwijk, The Netherlands, [2]Centre de Biophysique Moleculaire, Centre National de la Recherche Scientifique, [3]Naturhistorisches Museum, Bern, Switzerland, [4]Institute of Aerospace Medicine, Deutsches Zentrum für Luft- und Raumfahrt, Porz-Wahn, Germany, [5]Naturhistorisches Museum, Wien, Austria, [6]Chemistry Department, Bristol University, Bristol, UK, [7]Dipartimento di Scienze, Universita d'Annunzio, Pescara, Italy, [8]Planetary Sciences Research Institute, The Open University, Milton Keynes, UK, [9]Centre National de la Recherche Scientifique, Universités de Paris 7 et 12, Créteil, France, [10]Max-Planck-Institut für Aeronomie, Lindau, Germany, [11]Dipartimento di Protezione Agrolimentare, Universita degli Studi di Bologna, Italy (currently at Planetary Sciences Branch, NASA Johnson Space Center, Houston TX, USA), [12]European Science Consultants, Sassenheim, The Netherlands.

Introduction: A recent initiative of the Manned Spaceflight and Microgravity Directorate of the European Space Agency was concerned with the identification of specific objectives in the search for life on Mars. The Exobiology Science Team, chaired by André Brack, consisted of experts in the fields of radiation biology, planetary geology, geochemistry, mineralogy, meteorology, and exobiology. The Science Team study emphasized present European capabilities in the areas of drilling, sample acquisition, and preparation, and *in situ* analysis.

Objectives: Objectives of the initiative were (1) to determine which surface and near-surface environments of Mars might provide the best evidence for past life and to establish a short list of preferred landing sites for a future exobiology mission; (2) to design an integrated set of analytical instruments with which to search for evidence of past or present microbial life in subsurface materials and rock samples on Mars; and (3) to develop a set of imaging and spectroscopic systems to facilitate a search for evidence of extinct microbial life at all scales down to 0.01 μm. These systems should also provide for the study of the mineralogy and petrography, as a function of depth, in the near subsurface region of Mars.

Landing Sites: Landing sites in areas that might have supported life should be chosen on the basis of (1) the inferred presence of sediments, especially in craters; (2) the partial excavation of sediments by younger impacts to allow access to buried sediments; (3) stratified canyon walls (possible sediments); (4) chaotic terrains indicating the presence of water and possibly hydrothermal activity; (5) high albedo features in craters (possible evaporites); (6) ground ice (cratered); (7) polygonal features (sediments/ ice?); and (8) terracing (water flow).

In the search for subsurface microfossils, the following rock types are suitable candidates for examination: (1) highly porous or diagenetically cemented sedimentary rocks, (2) voids in impact breccias and impact melts, (3) vesicles in volcanic rocks, and (4) fractured rocks of any type. Microfossils are most likely to be found in rocks that have been buried to a considerable depth and have resurfaced due to impact ejection or are exposed on canyon walls.

Drill and Sample Distribution System: This is an important feature of the Exobiology Package and will utilize various European technological developments in drills, moles, penetrations, and sample distribution systems.

Recommended Analytical Instrument Package

Microscope: for examination of samples
- 3-μm resolution
- mass, 250 g

Infrared spectroscopy: molecular analysis of minerals and organics (with Raman)
- wavelength range, 0.8–10 μm
- spectral resolution, >100 (1/D1)
- spatial resolution, 200 μm
- expected mass, <1 kg
- expected power, 3–4 W

Raman spectroscopy: molecular analysis of minerals and organics (with IR)
- must include near-IR excitation for biological and geochemical applications
- spectral range, 200–3500 cm^{-1}
- resolution, 8 cm^{-1}
- expected mass, 1 kg

APX-Spectrometer: elemental analysis, detection limit: a few 0.1%
- mass, 570 kg
- power, 340 Mw
- data output is 16 Kbytes per sample analysis

Mössbauer: quantitative analysis of Fe
- mass, 500 g
- power, 1.5 W
- radioactive source of about 300mCi

Pyr-GC-MS system: isotopic, elemental, organic, and inorganic molecular composition and chirality measurements
- Pyr: includes several ovens (for pyrolysis, combustion and chemical transformation of samples)
- GC: a minumum of 4 columns in parallel, likely to be capillary open columns for separation, respectively, of:
  - permanent gases and very low molecular weight organics
  - volatile, higher molecular weight organics of small polarity
  - volatile, higher molecular weight organics of high polarity
  - column for enantiomer separation (chiral or, if derivation with chiral reactant, nonchiral column)
  - additional detectors (nana-TCDs, chiral detectors) for each GC column
  - MS: ion trap or magnet or quadruple
In all cases a pumping device (e.g., miniaturized turbo molecular pump) will have to be developed.
  - total mass, 5.5 kg
  - power, 10–20 W (tbc)

H_2O_2 and other oxidant-dedicated sensors:
- expected mass, 100 g
- This has to be fully studied and developed.

Fig. 1.

Programmatic Plans for an ESA Exobiology Package: Following the recommendation of the Science Team, a nine-month Phase A study is about to start. This phase will cover a technical assessment at system and subsystem level of the required developments to produce miniaturized, space-qualified versions of drilling and sample acquisition systems, as well as miniaturized versions of existing analytical instruments or those in development stages. The study will also cover the elaboration of a system-integration approach and the means to clarify interface issues. Moreover, ESA will propose a program to member states of the European Community within the framework of the extension of its current Microgravity Programme (to start in 2000), which will include an element for the development of the Exobiology Package.

Human Missions to Mars: Manned missions will be necessary to do tasks that cannot readily be done by machines, i.e., those involved in the exercise of judgment, based upon extensive professional and personal experience, coupled with flexibility and ingenuity to adapt and improvise in real time. Such tasks include the selection of sample sites, sample acquisition and selection, *in situ* analysis and sample return, as well as the study of putative extant life under natural conditions.

STUDIES OF LIFE ON EARTH ARE IMPORTANT FOR MARS EXPLORATION. D. J. Des Marais, Space Science Division, NASA Ames Research Center, Moffett Field CA 94035-1000, USA.

The search for evidence of the early martian environment and a martian biosphere is benefitted by diverse studies of life on Earth. Most fundamentally, origin-of-life research highlights the challenge in formulating a rigorous definition of life. Because such definitions typically list several of life's most basic properties, they also help to define those observable features that distinguish life and thus might be sought through telescopes, spacecraft, and analyses of extraterrestrial samples. Studies of prebiotic chemistry also help by defining the range of environments and processes that sustain prebiotic organic synthesis. These studies might indicate if and where prebiotic processes occur today on Earth and elsewhere. Such studies should also help to identify which localities are good candidates for the origin of life. A better understanding of the most fundamental principles by which molecules are assembled into living systems will help us to appreciate possible alternatives to the path followed by life on Earth. These perspectives will sharpen our ability to recognize exotic life and/or those environments that can sustain it.

Life's environmental boundaries represent that locus of conditions that collectively push the flexibility of biomolecular machinery to its limits. It is extremely important to understand how this machinery adapts to environmental extremes, because, for terrestrial life at least, this helps to define life's constraints beyond Earth to a degree of understanding that can help to predict the environments that are the best candidates for a search. Exotic alternatives to Earth-like life, including those defined by Earth-based laboratory studies, might delineate different boundaries for survival. Thus, these alternative lifeforms enrich our understanding of the possibilities for life's distribution and diversity in the universe. The classic parameters by which life's limits have been measured are the

following: liquid water availability, temperature, source of metabolically useful energy, destructive energy levels, and temporal stability of conditions that support growth. How specifically do cell membranes, transport systems, enzymes, and the processes of information processing, storage, and reproduction cope mechanistically with extremes in these environmental parameters? How, if at all, do the dynamics of biological evolution differ between extreme and "moderate" environments? In the context of the original environment in which life arose, just exactly which environments are extreme — that is, which environments presented the greatest adaptive challenge for life?

Planetary science is centrally relevant to the study of life's origin and survival because biospheres must evolve to accommodate environmental changes driven by the normal evolution of silicate planets. Because silicate planets follow parallel paths of evolution that should produce more or less parallel consequences for their surface environments, studies of Earth's long-term habitability help us understand the prospects for life elsewhere. Key are those changes in relative areal extent of the particular environments that tend to support relatively high levels of biological activity (e.g., hydrothermal systems, shallow-water coastal environments, etc.). Long-term changes in relative rates of processes such as volcanism, weathering, and impacts have altered the chemical compositions of the oceans and atmospheres; thus, these compositional trends have been "emergent properties" of planetary evolution that directly affected the biosphere. Excellent examples of such effects are the roles played by planetary and biological changes in the evolution of the redox state of the oceans and atmospheres and how this evolution might have affected the development of multicellular life (plants, animals). Because silicate planets share many key long-term changes, parallel evolutionary phenomena certainly could occur elsewhere.

Earth-based research on the molecular and ecological mechanisms of evolution are relevant to planetary exploration, at least to the extent that they ultimately identify those particular planetary environments that were critical to our biosphere's earliest development. For example, the confirmation that thermal environments indeed were crucibles for our own biosphere's origin and/or early development could substantially influence our site selection strategy for Mars exploration.

Efforts to understand the extent and diversity of the fossil record of early life carry immediate and important benefits for planetary exploration. Our ability to detect fossils is directly enhanced by improved systematics for interpreting the multiple categories of fossil information, namely textures of cells and their excretion products, rock fabrics created by chemical activity and movements of biota, compositions of minerals and organic matter, and stable isotopic compositions of those elements affected by biological processes. Biological vs. nonbiological features must be distinguished, even after those features have suffered physical and chemical changes subsequent to their depositon (such studies are termed "taphonomy"). These changes are driven by mineral deposition and recrystallization as well as by alteration by thermal processes and/ or by fluids that invade rock fractures and pore space. Should sterilization be applied to returned samples, it would be yet another agent of alteration whose consequences must be understood. We need to understand the "taphonomy of planetary protection procedures!" Earth-based studies of life can also be made useful for plan-

etary exploration by examining the fossil records of key "extreme" ecosystems that inhabit hydrothermal and/or subsurface environments and by investigating evaporite and ice deposits.

Exploration efforts will benefit from remote-sensing studies of those sites and samples that represent meaningful analogs of extraterrestrial exploration targets (e.g., minerals deposited in hydrothermal systems or evaporating lakes). Indeed, the most significant rock types might be both relatively rare and hard to recognize. It will be important to cope effectively with mineral mixtures and spatial heterogeneities in the target. These imperatives create specific needs for the development of new technology, instrumentation and methods for data processing and interpretation. Space exploration will indeed benefit enormously from thoughtfully executed "missions," both to Earth's biosphere and rock record, as well as to our collections of astromaterials.

Relevant Literature:

Des Marais D. J. (1994) The Archean atmosphere: Its composition and fate. In *Archean Crustal Evolution* (K. Condie, ed.), pp. 505–523. Elsevier, Amsterdam.

Farmer J. D. et al. (1995) Site selection for Mars Exobiology. *Adv. Space Research, 15(3)*, (3)157–(3)162.

Jakosky B. M. (1998) *The Search for Life on Other Planets.* Cambridge Univ.

Meyer M. and Kerridge J., eds. *An Exobiological Strategy for Mars Exploration,* NASA SP-530.

Schopf J. W. and Klein C., eds. (1992) *The Proterozoic Biosphere: A Multidisciplinary Study.* Cambridge Univ., New York.

Walter M. R. and Des Marais D. J. (1993) Preservation of biological information in thermal spring deposits: Developing a strategy for the search for fossil life on Mars. *Icarus, 101,* 129–143.

Walter M. R., ed. (1996) *Evolution of Hydrothermal Ecosystems on Earth (and Mars?).* Wiley, Chichester (Ciba Foundation Symposium 202).

OPTIMIZING THE SEARCH FOR A FOSSIL RECORD OF ANCIENT MARTIAN LIFE.

J. D. Farmer, Department of Geology, Arizona State University, Tempe AZ 85287-1404, USA (jfarmer@asu.edu).

Introduction: An important focus of the decade-long Mars Surveyor Program is the search for evidence of past or present life and/ or prebiotic chemistry. Based on studies of terrestrial analogs, the highest-priority sites for a martian fossil record include such lithologies as fine-grained, clay-rich detrital sediments, water-lain pyroclastics and evaporite deposits of terminal paleolake basins, the deposits of mineralizing springs (including hydrothermal), and mineralized zones (hard-pans) within ancient soils. The systematic exploration for a martian fossil record critically depends on locating accessible surface outcrops of these and other aqueously deposited sediments. The following discussion identifies the steps needed to optimize a plan for implementing the present strategy for Mars exopaleontology.

Mineralogical Mapping from Orbit: Mineralogy is key for accurately assessing past geological environments and selecting and prioritizing landing sites. And from the standpoint of preservation, mineralogy provides the most logical basis for selecting samples for return to Earth. The simple fact is that fossil preservation is

strongly biased toward particular geological environments, and deposits indicate that site selection base on mineralogy is fundamental. In selecting the best sites on Mars for a sample return for exopaleontology, we logically begin with orbital data to enable us to narrow the vast number of potential sites. Given the premium placed on mineralogy in selecting targets, spectral mapping over a wavelength range useful for determinative mineralogy is requisite. The practical problem is to be able to isolate and identify key mineralogical signatures within complex mixtures and to specify the actual spatial location of outcrops within targeted terrains. The limitations presently imposed by landing errors and rover mobility underscore the importance of high-resolution mineral maps in the selection of landing sites. This is ostensibly the most crucial step leading to a targeted sample return for exopaleontology.

Improved Landing Precision and Rover Mobility: Once deposits of interest have been identified from orbit, accessibility on the ground will require improvements in landing precision and rover mobility. At a minimum, landing errors need to match the minimum traverse distances required for rovers to reach their intended targets within nominal mission times. The landing precision and mobility requirements will vary with each mission, depending on the size of the target deposits and terrain trafficability. Based on terrestrial standards, targets could be quite small, requiring landing errors and equivalent rover mobilities on the order of 5–10 km to allow rovers to reach deposits of interest. A practical example of the connection between the spatial resolution of orbital mapping data and rover mobility is provided by the TES data to be obtained by the Mars Surveyor orbiter. During subsequent surface missions, rover traverses will likely all be conducted within a single TES pixel. There is also an obvious synergy between improvements in the spatial resolution of orbital data and the need for enhanced rover mobility. Given that extensive improvements in rover mobility during MGS seem unlikely, it is all the more important that high spatial-resolution (outcrop-scale) spectral mapping data be obtained from orbit as early as possible in the MGS program.

Descent Imaging, Compositional Analysis at a Distance, and Rover Autonomy: Once on the ground, to optimize planning of rover traverses, it will be necessary to specify the highest priority targets within a site. In this context, descent imaging could be a great asset in mission planning. Analysis by rovers can be conducted at two levels. In planning traverses and defining optimal sampling strategies, spectral imaging from a distance can be used to survey rock fields, targeting the most interesting rocks for close-up mineralogical analysis using rover instruments. Given the distance and signal delay times between Earth and Mars, real-time telepresence will not be possible. But improvements in rover autonomy may enable multiple science objectives to be achieved during single command cycles. Actual traverse planning is likely to be accomplished by Earth-based scientists using virtual terrain models constructed from rover and lander imaging of the site.

Close-Up Imaging and *In Situ* Spectroscopic Analysis: As a first step in analyzing rocks in the field, geologists normally rely on microscopic (hand lens) imaging of rock surfaces to obtain microtextural information. This enables identification of rock type and qualitative mineralogical information. But for robotic missions, microscopic imaging can also provide important contextual information for more spatially targeted compositional analysis using rover instruments. Because of the minimal sample preparation, spectral reflectance methods (e.g., infrared and laser Raman spectros-

copy) have distinct advantages over more precise methods of identification (e.g., X-ray diffraction) that require a powdered sample. Spectral methods that combine mineralogical and organic analyses hold the greatest advantages in selecting samples for exopaleontology.

Sampling Rock Interiors: Viking and Pathfinder provided elemental abundance data (X-ray fluorescence and APXS respectively) for comparatively young sites on the northern plains. Viking analyses were obtained from wind-transported surface fines and probably had little to do with the local bedrock geology. Pathfinder advanced our understanding somewhat by providing elemental data for a variety of rocks that were transported to the site from a variety of highland sources during large outfloods and/or as ejecta from local impact craters. But in spite of the seemingly wide variety of source materials, the general uniformity of elemental analyses obtained from rocks and soils at the Viking and Pathfinder sites suggests surface weathering on Mars can mask true compositional differences. This underscores the importance of gaining access to unweathered rock interiors by breakage, abrasion, coring, or other means. Furthermore, because future sample return payloads will likely be very small (a few hundred grams), the ability to subsample larger rocks will be required if we are to return the most promising samples to Earth. This will necessitate a great deal of flexibility in rover sample acquisition and handling systems.

Compromises That Make Sense: In selecting potential sites for a sample return mission, it is important to realize that while science needs to drive missions, from a practical standpoint, the constraints imposed by budgets and politics ultimately determine the missions that actually fly. Sample return is one thing. But if the question of martian life is to remain the focus, then each opportunity must respond to these questions: How can we best adapt to budgetary challenges while optimizing our science goals? And what are the acceptable fall-back positions that will still make missions worth the cost and effort? I submit that compromise positions that settle for soils instead of rocks make no sense in the context of exploring for signatures of past life. And if we must rely on delivery systems with large landing errors and rovers of limited range, then we should optimize our understanding of surface geology and composition by using each orbital opportunity to progressively enhance the spectral range and spatial resolution of our orbital mapping efforts. Once we know where the most interesting targets are located, we can design the missions that will optimize our chances of sampling a broad range of compositions and ages relevant to the search for past life.

BACTERIAL MINERAL PRECIPITATION AND THE MAKING OF MICROFOSSILS. F. G. Ferris, Department of Geology, Earth Sciences Centre, University of Toronto, 22 Russell Street, Toronto, Ontario, M5S 3B1, Canada (ferris@quartz. geology.utoronto.ca).

An important prerequisite for the precipitation of minerals from aqueous solutions, even where bacteria are involved, is that a moderate degree of oversaturation must be achieved. This requirement is imposed thermodynamically by an activation energy barrier that constrains the spontaneous formation of insoluble precipitates from solution. Bacteria intervene in mineral precipitation reactions in two ways, either directly as catalysts of aqueous geochemical reactions

or indirectly as chemically reactive solids. In the first case, bacterial metabolic activity is often significant and can trigger changes in solution chemistry that lead to oversaturation (e.g., through the production of reactive ligands like sulfide). This alone can induce mineral formation by lowering the activation energy barrier for homogenous (precipitation in solution) and heterogeneous (surface precipitation on foreign solids) nucleation reactions. The second case relates to the presence of reactive amphoteric sites on bacterial cells that facilitate sorption of dissolved mineral-forming elements, and foster heterogeneous surface precipitation reactions. Thus, minerals precipitated directly from solution as a result of bacterial metabolic activity can form on the inside, outside, or even some distance away from cells. Indirect chemical precipitation as a consequence of changing geochemical conditions is also possible and is accompanied by passive epicellular nucleation and crystal growth on the outside of living or dead bacterial cells — this is the most likely pathway leading toward preservation of structurally intact microfossils. In natural systems, however, direct and indirect bacterial mineral precipitation reactions may occur at the same time and are difficult to recognize as entirely separate processes. When bacteria are metabolically involved in mineral formation, biogenecity can sometimes be inferred from chemical (e.g., stable isotope) or mineralogical (e.g., magnetite produced by magnetotactic bacteria) data. On the other hand, microscopic techniques are useful in the assessment of cell-surface-mediated mineral precipitation providing that diligence is exercised to unequivocally establish the composite nature (i.e., mineralogical and bacterial) of the specimen.

ORGANIC CARBON IN CARBONATE AND RIM FROM ALLAN HILLS 84001.

G. J. Flynn[1], L. P. Keller[2], C. Jacobsen[3], and S. Wirick[3], [1]Department of Physics, State University of New York, Plattsburgh NY 12901, USA, [2]MVA, Inc., 5500 Oakbrook Parkway, Norcross GA 30093, USA, [3]Department of Physics, State University of New York, Stony Brook NY 11794, USA.

Introduction: We previously reported scanning transmission X-ray microscope (STXM) C mapping, X-ray absorption near-edge structure (XANES) spectroscopy, and Fourier transform infrared (FTIR) spectroscopy on a carbonate globule and opaque "rim material" from the ALH 84001 meteorite [1]. The globule was consistent with the material described by McKay et al. [2]. However, the opaque "rim material" was dominated by feldspathic glass [1], appearing opaque mainly because of the presence of chromites, and containing only minor amounts of the carbonate, magnetite, and sulfide that are major components in the rims described by McKay et al. [2].

Percent-level organic C was associated with both the carbonate globule and the opaque material. The C-XANES spectrum of the organic compound in the globule was different from that in the opaque material [1]. FTIR spectroscopy indicated the presence of aliphatic hydrocarbons, having different ratios of $C-H_2$ to $C-H_3$ groups, in the two samples [1].

New Sample: To follow up on those measurements, a carbonate globule with attached rim material was extracted from a freshly broken surface of a chip of ALH 84001 (ALH 84001,255). This sample was embedded in elemental S, a series of ultramicro-

Fig. 1. STXM image of an ultramicrotome thin section of ALH 84001. The top consists of large carbonate in the interior of the globule. The lower ~2 µm is fine-grained rim. These two regions are separated by coarse-grained, porous carbonate.

tome thin sections were prepared and deposited on an SiO substrate. Several sections included a small (~2 × 2 µm) area of rim material attached to an ~8-µm globule fragment. These sections preserve the spatial associations between the rim and the globule.

Transmission electron microscope examination indicates the sections contain three distinct regions. Fine-grained rim material, consisting of carbonate, magnetite, and rare sulfides, and coarse-grained carbonate in the globule interior are separated by a region containing coarse-grained, porous carbonate and sparse, fine-grained magnetite. The rim is consistent in mineralogy with that described by McKay et al. [2].

The sample was examined using the STXM in a new stack imaging mode that eliminates problems previously experienced due to sample drift during the acquisition of C-XANES spectra. The stack-imaging mode allows us to take full advantage of the ~50-nm spatial resolution of the STXM for spectroscopy. In the stack-imaging mode, the absorption of focused, monochromatic X-rays is measured at each pixel on a thin section. Typically 150–200 absorption images are taken over the range 270–310 eV, with an energy spacing of ~0.1 eV in the pre-edge region. The images are aligned, correcting for sample drift during the sequence. The C-XANES spectrum is extracted either at a point by examining the image-stack along a single pixel or over a region of interest by adding the pixels corresponding to that region in each image. At each energy, the reference intensity (on the substrate) and sample intensity are measured on the same image, rather than in two successive spectra, which are sometimes offset slightly in energy due to nonreproducibilities in the monochrometer motion (a problem being addressed in a STXM redesign).

C-XANES Results: Figure 1 shows the STXM image of the entire sample. The highest-quality spectra are obtained by averaging over the largest number of pixels on the sample. Figures 2–4 show C-XANES spectra averaged over the rim material, the globule interior, and the region containing coarse-grained, porous carbonate and fine-grained magnetite that separates the globule interior from the rim.
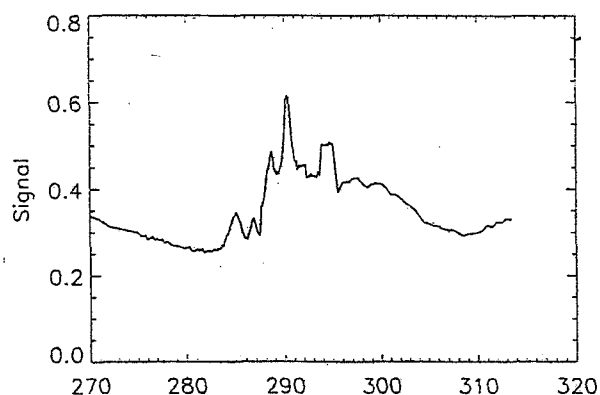
Fig. 2. C-XANES spectrum averaged over the rim of the ALH 84001 sample shows three π* peaks, at 285 eV, 286.2 eV, and 288 eV, indicative of organic C and a peak of 290 eV from carbonate.

Fig. 3. C-XANES spectrum averaged over the globule interior. The ratio of the intensity of the carbonate peak to the organic peaks is higher in the globule interior than in the rim (shown in Fig. 2).

Fig. 4. C-XANES spectrum averaged over the porous carbonate, located between the rim and interior. The spectrum is very similar to that of the carbonate in the interior (shown in Fig. 3).

Pre-edge (?*) absorptions occur at photon energies corresponding to induced electron transitions from the K-shell to unoccupied outer orbitals whose energies are very sensitive to the types and locations of neighboring atoms. The rim material showed four strong π* peaks (Fig. 2). Three peaks, at 285 eV, 286.2 eV, and 288 eV, are similar to the peaks at 284.8 eV, 286.5 eV, and 288.2 eV detected in the carbonate globule from ALH 84001 examined previously [1]. Those peaks were associated with organic C by FTIR spectroscopic examination of that globule [1]. The fourth peak, at 290 eV, is indicative of carbonate. The globule material (Fig. 3) and the porous carbonate (Fig. 4) separating the rim from the globule interior show the same four π* peaks.

In each C-XANES spectrum we can measure the ratio of the absorption at 290 eV to that at 288 eV to monitor the ratio of carbonate to organic C. Comparing the average C-XANES spectrum over the carbonate globule with the average over the rim indicates that the rim has a higher ratio of organic C to carbonate than does the globule. The porous carbonate appears to have approximately the same ratio of organic C to carbonate as the globule interior.

The highest ratio of organic C to carbonate was found in isolated spots within the rim. Thus far, however, we have been unable to locate regions in the rim that show only the organic or only the carbonate absorption feature(s), suggesting that organic C is intimately mixed with the carbonate on the scale of ~100 nm in the rim.

Conclusions: The same three organic absorption peaks occur with roughly the same peak height ratios in both the rim and the globule. This indicates that, in this sample, the rim and the globule contain the same type(s) of organic compound(s). Analyses of individual carbonates within the globule showed weak, but distinct, organic absorptions accompanying the strong carbonate absorption, indicating the presence of the organic component either within or associated with the large carbonates. The porous carbonate beneath the rim exhibits the same four C-XANES absorptions, and the average spectrum of the porous carbonate is indistinguishable from that of the core carbonate.

These new measurements confirm our earlier results indicating that relatively high concentrations (percent level) of organic C are spatially associated, at the 100-nm scale, with the carbonates in ALH 84001. They differ from the earlier results in that this sample of rim material, consisting of fine-grained carbonate, magnetite, and sulfides (i.e., the type of rim described by McKay et al. [2]), contains an organic component that is identical in its C-XANES spectrum to that of the carbonate globule to which it is attached. The opaque sample we analyzed previously, which was dominated by feldspathic glass and chromite, has a C-XANES spectrum that differs in absorption peak energies and height ratios from these rim and globule samples. Fourier transform infrared measurements, to identify specific C functional groups in this sample, are in progress.

References: [1] Flynn G. J. et al. (1998) *LPS XXIX*, Abstract #1156. [2] McKay D. S. et al. (1996) *Science, 273*, 924–927.

CHAINS OF MAGNETITE CRYSTALS IN ALLAN HILLS 84001: EVIDENCE OF BIOLOGICAL ORIGIN. E. I. Friedmann[1], J. Wierzchos[2], and C. Ascaso[3], [1]Department of Biological Science, Florida State University, Tallahassee FL 32306-1100, USA (friedm@bio.fsu.edu), [2]Servicio de Microscòpia Electrònica, Universitat de Lleida, 25198 Lleida, Spain (jacekw@suic-me.UdL.es),

3Centro de Ciencias Medioambientales, Serrano 115, bis, Madrid 28006, Spain (ascaso@fresno.csic.es).

Introduction: The presence of magnetite crystals in carbonate globules in ALH 84001 was one fact leading to the suggestion that this meteorite may contain relics of martian life [1]. These magnetite crystals are morphologically similar in shape and size to magnetosomes formed by magnetotactic bacteria, but less so to typical inorganically formed magnetite crystals [2,3]. The size range is significant, as within this range the magnetic moment of the crystals is maximal [4]. Terrestrial magnetobacteria produce magnetosomes, magnetite (Fe_3O_4), or greigite (Fe_3S_4) crystals assembled into chains, and the organisms use these chains for aligning themselves along the prevailing magnetic field [4]. No inorganic process is known to produce similar structures.

Methods and Results: We found numerous such chains composed of magnetite crystals in martian meteorite ALH 84001 (Fig. 1) by high-magnification scanning electron microscopy operating in the backscattered electron detection mode (SEM-BSE), a method that permits imaging of structures embedded in the rock substrate [5]. SEM-BSE images depict chemical compositions, not surface morphologies. Backscattered electrons originate not from the sample surface but from below it: Calculations show that in our material, features can be imaged to a depth of ~400–1000 nm. BSE images are fuzzy because of scattering of BS electrons. Atomic number is positively correlated with brightness, which is also affected by, e.g., the atomic number of the substances below and above, so single magnetite crystals may appear in different shades of grey. Only chains lying approximately parallel to the image plane will be clearly visible as such. Those oriented obliquely will appear foreshortened, and the individual crystals will not be resolved. Similarly, crystals lying below or above the chain will appear super-imposed, resulting in a stronger, blurred signal, as seen in Fig. 1b. We examined fine polished rock surfaces coated with 10 nm C. Elemental composition was identified by energy dispersive X-ray spectroscopy (EDS) microanalysis and auger electron spectroscopy (AES) with a 60-nm beam.

Figures 1a and 1b show chains from pancake carbonate globules. Figure 1c, from a small irregular carbonate globule embedded in orthopyroxene, shows on the left a cluster of magnetite crystals, probably a mixture of single crystals and chains, and a chain of seven or eight crystals on the right. Figures 1d and 1e show chains from a small, irregular carbonate globule embedded in plagioclase glass, from the area marked by the arrow in Fig. 1f. The chain in Fig. 1e appears to comprise about 15, perhaps more, larger magnetite crystals. The chains in Figs. 1c and 1e illustrate the approximate total size range of crystals. Their exact shape and size were studied by the method of [3]: cleaning with acetic acid and examination of the residue by TEM equipped with EDS microanalytical system. We confirmed the results [3] that the magnetite crys-
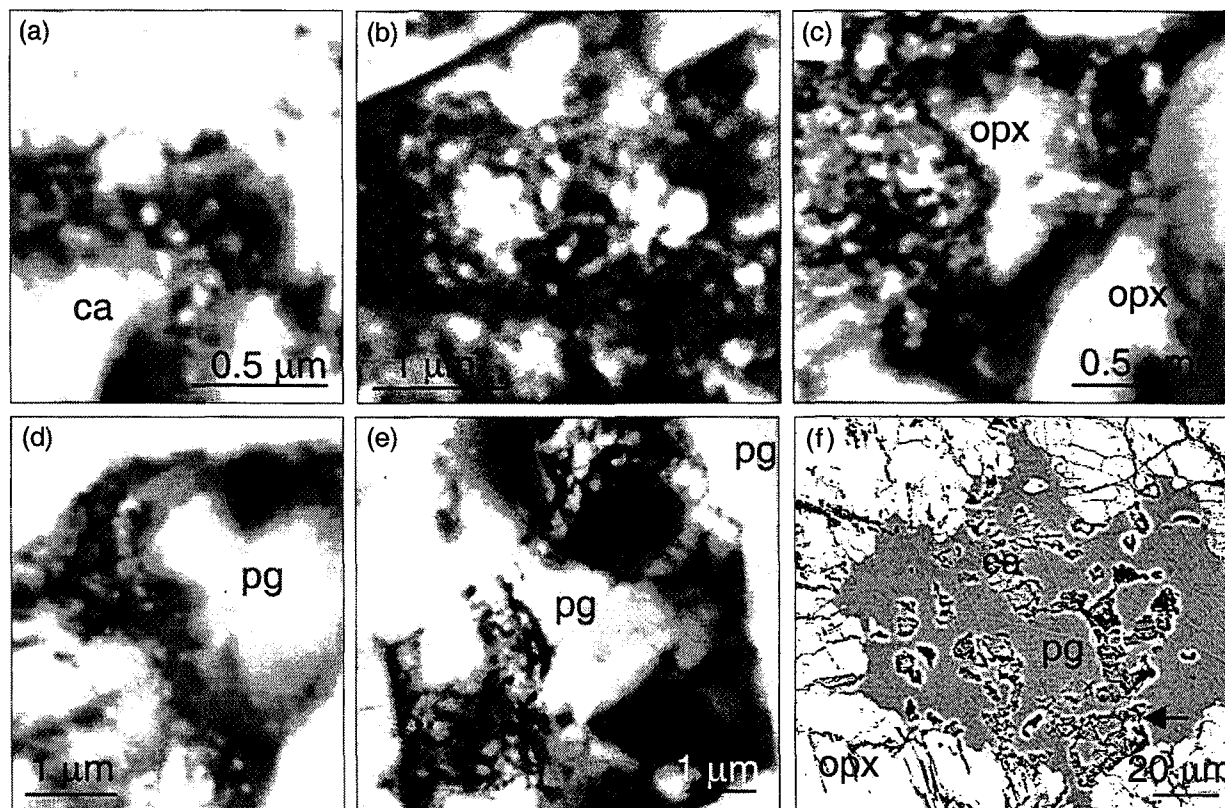

Fig. 1. Backscattered electron (BSE) images of magnetite crystal chains in ALH 84001. (a) and (b): Chains in pancake carbonate. (c)–(e): chains in small irregular carbonate globules. (d) and (e) are from the area indicated by arrow in (f). ca = carbonate, opx = orthopyroxene, pg = plagioclase glass. Further explanation in text.

tals are mostly paralellepipedal and, less frequently, bullet- or irregularly shaped, with a size range of 30–90 nm in length and 20–50 nm in width. This range of morphologies and sizes agrees well with those occurring in terrestrial magnetotactic bacteria. The magnetite crystals in the chain in Fig. 1e are larger (>200 nm). The frequency of magnetite crystal chains of different lengths (four crystals or more) in ALH 84001 shows a non-Gaussian distribution, and a negative exponential relationship between the number of chains and the number of magnetite crystals per chain. This pattern suggests that the chains are disrupted fragments of originally longer magnetosome chains of magnetotactic bacteria.

Our findings also help with the interpretation of the small microfossil-like structures in ALH 84001 [1]. Studies with atomic force microscopy [6] have shown that these structures are segmented and morphologically similar to the magnetite crystal chains described here. We suggest they are identical.

Although conditions favorable for microbial growth have been shown to exist in meteorites lying on the Antarctic ice sheet [7], contamination with terrestrial magnetobacteria in ALH 84001 can be ruled out: (1) The martian origin of the carbonate globules is not in doubt; (2) several carbonate grains containing magnetite crystal chains were enclosed in plagioclase glass (Fig. 1f); and (3) the insides of fragments of ALH 84001 kept in uranyl acetate solution under vacuum remained free of uranyl contamination.

Conclusion: We suggest the following scenario: Decomposed remains of dead martian magnetobacteria, possibly suspended in a carbonate-rich fluid, penetrated fissures of ALH 84001, already crushed by previous meteorite impact, perhaps after the second impact event (I2) postulated by [8]. Single magnetite crystals and chain fragments were deposited in carbonate globules. Finally, the rock suffered additional impacts [8] resulting in melting, geochemical and morphological transformations, and displacement of mineral components.

All known magnetobacteria are microaerophilic or at least facultative anaerobes, and it has been proposed [9] that they evolved on Earth at the time when partial pressure of atmospheric oxygen began to increase. It has also been suggested that, if Earth-like life ever appeared on the surface, then such conditions should have existed on early Mars [10]. Our findings seem to support this suggestion.

References: [1] McKay D. S. et al. (1996) *Science, 273,* 924. [2] Thomas-Keprta K. L. et al. (1997) *LPS XXVIII,* Abstract #1433. Golden D. C. et al. (1997) *LPS XXVIII,* Abstract #1675. [3] Thomas-Keprta K. L. et al. (1998) *LPS XXVIII,* Abstract #1494. [4] Bazylinski D. A. and Moskowitz B. M. (1997) *Rev. Mineral., 35,* 181. [5] Wierzchos J. and Ascaso C. (1994) *J. Microsc., 175,* 54. [6] Steele A. et al. (1998) *J. Microsc., 189,* 2. [7] Friedmann E. I. et al., personal communication. [8] Treiman A. H. (1998) *Meteoritics & Planet. Sci.,* in press. [9] Chang S. R. and Kirschvink J. S. (1989) *Annu. Rev. Earth Planet. Sci., 17,* 169. [10] Hartman H. and McKay C. P. (1995) *Planet. Space Sci., 43,* 123; McKay C. P. (1995) in *Chemical Evolution: Physics of the Origin and Evolution of Life* (J. Chela-Flores and F. Raulin, eds.), pp. 177–184, Kluwer.

BIOMIMETIC BUT ABIOTIC CARBONATES: NEW GEOCHEMICAL MARKERS FOR PRIMITIVE ENVIRONMENTS. J. M. García-Ruiz, Instituto Andaluz de Ciencias de la Tierra, CSIC-Universidad de Granada, Facultad de Ciencias, 18002-Granada, Spain (jmgruiz@goliat.ugr.es).

The unambiguous detection of ancient life is a crucial necessity in assessing the timing of life on Earth. Today, the strategy to reveal features of past life forms is also of utmost importance in seeking out living beings on other planets.

Among other very few biomarkers used today (stromatolite structures, autigenic minerals, biological degradation compounds, and isotopic analysis), morphological recognition of living forms still plays a critical role in Precambrian micropaleontological studies. The underlying principle supporting life detection using morphological and textural tools derived from the old idea that inorganic precipitates are unable to produce neither shapes displaying certain symmetry groups nor certain bizarre textural arrangements. In this frame of mind, there is a substantial morphological difference between the inanimate and the animate worlds: it was thought that certain complex shapes with noncrystallographic symmetry were characteristic of life and would be impossible to obtain by inorganic precipitation. The most recent and conspicuous application of this "law" is the fossillike microstructures found in ALH 84001.

However, it is known that morphological patterns with symmetry properties characteristic of living forms may also be precipitated by purely inorganic mechanisms. Many of them are irrelevant to life detection, as they are unlikely to occur under geochemical conditions. In few cases, on the other hand, complex inorganic shapes form under laboratory conditions emulating a geological scenario, thus becoming of geological interest as they can be used as geochemical markers. This is the case with carbonate precipitation in silica-rich alkaline brines forming what I call induced morphology crystal aggregates [1]. The morphological emulation is particularly dramatic when Ba or Sr carbonate are precipitated (as shown in Fig. 1) while textural emulation is clear in the case of calcite [2].

These biomimetic carbonates (of Ba, Sr, or Ca) patterns are obtained in the laboratory into alkaline silica-rich brines. Extreme as these conditions can be (pH > 10; silica concentration > 500 ppm), there are today few lakes, particularly in the African Rift Valley,
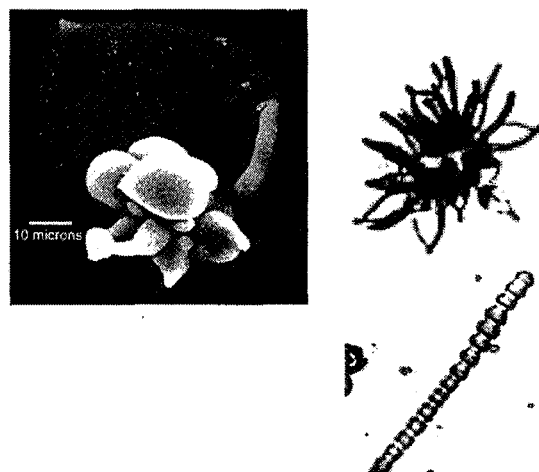

Fig. 1.

where these precipitation environments can be found. Therefore, beyond a chemical curiosity or materials-science innovation, this biomimetic carbonate precipitation is a plausible phenomenon under natural conditions [3].

Obviously, induced morphology crystal aggregation is an inorganic alternative to be considered when using morphology as a biomarker. I claim in this communication the importance of considering this bizarre precipitation phenomenon when detecting primitive life here on Earth or on other terrestrial planets. Silica biomorphs form into environments that are likely to be widely spread during earlier stages of the Earth and Mars, planets which are though to share a similar geological history during the Archean (Earth) and Noachian (Mars) periods [4]. In particular, some terrestrial Archean (baritic) cherts are thought to be the result of inorganic silica-precipitation under alkaline conditions. Silica leached from alkaline volcanic rocks increases the pH and, since there were no silica absorbing organisms during the Archean period, the pooling waters become enriched in silica. This draws an extremely favorable geochemical scenario for the precipitation of silica biomorphs. Similarly, the process leading to precipitate carbonate particles with properties of induced morphology crystal aggregates is likely to have been active in the geochemical scenario proposed for the carbonate formation in ALH 84001 [5,6].

References: [1] García-Ruiz J. M. (1985) *J. Crystal Growth, 85,* 251–262. [2] García-Ruiz J. M. (1994) *Origin of Life and Evolution of the Biosphere, 24,* 451–467. [3] García-Ruiz J. M. (1998) *Geology,* in press. [4] Chyba C. F. and McDonald G. D. (1995) *Annu. Rev. Earth Planet. Sci., 23,* 215–249. [5] McKay D. et al. (1996) *Science, 273,* 924–930. [6] Shearer C. K. et al. (1996) *GCA, 60,* 2921–2926.

HOW DO THE PROPERTIES OF ALLAN HILLS 84001 COMPARE WITH ACCEPTED CRITERIA FOR EVIDENCE OF ANCIENT LIFE?

E. K. Gibson Jr.[1], D. S. McKay[1], K. Thomas-Keprta[2], F. Westall[1], and C. A. Romanek[3], [1]Mail Code SN, Earth Sciences and Solar System Exploration Division, NASA Johnson Space Center, Houston TX 77058, USA, [2]Mail Code C23, Lockheed Martin, Houston TX 77058, USA, [3]Savannah River Ecology Laboratory, University of Georgia, Aiken SC 29802, USA.

Criteria for Past Life: To be confident that any sample contains evidence of past life or biogenic activity, one must determine beyond a shadow of a doubt that certain well-established features or biomarker signatures are present in the sample. In the case of martian samples, the criteria for past life have not been established because if life existed on the planet, we have no way of knowing its detailed characteristics. Lacking independent evidence about the nature of possible past life on Mars, the scientific community must use, for the time being, the criteria established for ancient samples from the Earth [1,2]:

1. Do we know the geologic context of the sample? Is it compatible with past life?

2. Do we know the age of the sample and its stratigraphic location? Are they understood enough to relate possible life to geologic history?

3. Does the sample contain evidence of cellular morphology?

4. What structural remains of colonies or communities exist within the samples?

5. Is there any evidence of biominerals showing chemical or mineral disequilibria?

6. Is there any evidence of stable isotope patterns unique to biology?

7. Are there any organic biomarkers present?

8. Are the features indigenous to the sample?

For acceptance of past life in a geologic sample, essentially all of these criteria must be met.

Allan Hills 84001 Data vs. the Established Criteria for Past Life: How do the data from the analysis and study of ALH 84001 compare to the established criteria?

Geologic context. A martian origin for ALH 84001 has been shown by both its O-isotopic compositions [3] and trapped martian atmospheric gases [4,5]. Although the exact martian provenance of this igneous rock is unknown, ALH 84001 does contains cracks and porosity that, based on textural microstratigraphy, clearly formed on Mars and could conceivably have harbored water-borne microbial cells and colonies introduced after the rock cooled (as known on Earth, [6]). The presence of secondary carbonate globules or pancakes in cracks has been interpreted by most workers as an indication of relatively low-temperature secondary mineralization by a fluid, possibly water. Thus, the most widely accepted broad geologic context of this rock is not incompatible with the presence of past life; if the secondary carbonates formed at low temperature from aqueous precipitation, their formation is completely compatible with past life, but would not require it.

Age and history. The isotopic age of ALH 84001 is 4.5 Ga and it is, therefore, a sample of the original martian crust. The sample underwent extensive shocking around 3.9–4.0 Ga [5,7]. Carbonate formation occurred around 3.9 Ga [8], shortly after the period of extensive bombardment and during a period when the planet had abundant water [9], greater concentrations of atmospheric gases, and higher temperatures. This corresponds to the time when life appeared and developed on Earth [10]. Evaporation of the fluids percolating through the impact-cracked surface could have resulted in the formation of carbonates [11,12]. The sample was ejected from the surface of Mars about 17 m.y. ago and spent 11,000 yr in or on the Antarctic ice sheets. We suggest that the geologic history of this rock is understood well enough to relate any possible life forms to the geologic history of Mars and to compare it to the history of life on Earth.

Cellular morphologies. Some bacterialike structures [13–15] occur in the rims of the carbonate globules that resemble in size and shape the mineralized casts of modern terrestrial bacteria and their appendages (fibrils) or byproducts (extracellular polymeric substances, EPS) [16]. Other bacteriomorphs are very small but within the size limit of known nanobacteria (i.e., 50–200 nm [17,18]). However, firm evidence that these bacterialike structures are truly the fossilized remains of martian bacteria has not been found. Although some of the originally identified features may have been coating artifacts or weathered mineral structure artifacts, some are definitely not [16]. Some of the features in ALH 84001 (e.g., filaments) are common biogenic markers on Earth. We conclude that the evidence for fossilized microbes and their products is not conclusive, but cannot be readily explained by nonbiologic processes and should not be ignored.

Microbial colonies. We have proposed that some of the features in ALH 84001 may be the remains of biofilms and their associated microbial communities [13,14]. Biofilms provide major evidence for bacterial colonies in ancient Earth rocks [19]. It is possible that

some of the clusters of microfossil-like features might be colonies, although that interpretation depends on whether the individual features are truly fossilized microbes.

Biominerals and disequilibria. The carbonates in ALH 84001 contain a population of magnetites having a highly peaked size distribution and unusual rectangular prism shapes that are indistinguishable from some known microbially produced terrestrial magnetite but match no known nonbiologic magnetite. Their formation can best be explained by biogenic activity and disequilibria of the Fe oxidation potential in the fluid that was the source of the Fe [15,20]. Other irregular magnetite grains could be either biogenic or nonbiogenic in origin. Whiskerlike magnetites (<5% total magnetites in carbonate) described by [21–23] are quite different in size distribution and shape, and may have had an origin unrelated to the rectangular prisms. Nanometer-sized iron sulfides described in our original paper are also suggestive of disequilibria related to microbial activity [24], as is the elemental composition of the carbonates. Overall, the mineral assemblages in the carbonates, as well as their extreme chemical variations, are compatible with known biominerals and known disequilibria related to microbial activity on Earth, although more work needs to be done to distinguish true biominerals and biogenically-related chemical disequilibria from totally nonbiologic minerals and disequilibria.

Biologic isotopic signatures. Stable isotope patterns have shown the presence of indigenous C components with isotopic signatures of −13 to −18‰ [25–27], which are in the direction of known biogenic C signatures. Additional detailed study of the C-isotopic signatures is needed to distinguish between indigenous C components within ALH 84001 and those introduced after its arrival on Earth. Overall, the C-isotopic signatures of the identifiable nonterrestrial, possibly organic C are compatible with biologic C-isotopic fractionation, when compared with the signatures of the martian carbonates, but they do not prove that it occurred.

Organic biomarkers. Possible organic biomarkers are present within ALH 84001 in the form of PAHs associated with the carbonate globules [28], some of which may be a unique product of bacterial decay [29]. The distribution of the reduced C compounds within the globules is irregular [28,30,31]. Clemett's data on PAHs [28], combined with recent amino acid data [i.e., 32], show that the detected PAHs are most likely indigenous to ALH 84001, whereas the detected amino acids are most likely Antarctic contamination. Exhaustive data must be collected before either component can be used as a biomarker for a specific sample [33].

Indigenous features. In our opinion, the recent studies of [28] have shown conclusively that the PAHs are indigenous to ALH 84001 and are not contaminants. Based on isotopic compositions [25,27,34,35] and textures, there is absolutely no question or disagreement that the carbonate globules and their included minerals formed on Mars and are indigenous to the meteorite. The possible microfossil structures and some regions of organic C that are embedded in the carbonates are therefore almost certainly indigenous, but other possible evidence for life (e.g., amino acids) may be Antarctic contamination.

Summary: Clearly, we have not completely satisfied all of the criteria needed for general acceptance of evidence for life in a sample. We argue that we are close on some (likely biominerals, possible organic biomarkers, and indigenous features) and not so close on others (well-documented geologic context, and evidence for cells and colonies). However, not one of the eight criteria has

been shown to be violated by any published data on ALH 84001 so as to preclude life, and some evidence exists supporting each criterion. Therefore, the jury is still out on early Mars life as revealed by this meteorite [36]. Evaluation against these criteria is still in progress and more data are needed.

References: [1] Schopf J. W. and Walker M. (1983) in *Earth's Earliest Biosphere: Its Origin and Evolution* (J. W. Schopf, ed.), pp. 214–239, Princeton Univ. [2] Cloud P. and Morrison K. (1979) *Precambrian Res., 9,* 81–91. [3] Romanek C. S. et al. (1998) *Meteoritics & Planet. Sci., 33,* in press. [4] Bogard D. and Johnson P. (1983) *Science, 221,* 651–655. [5] Bogard D. and Garrison D. (1998) *Meteoritics & Planet. Sci., 33,* A19. [6] Stevens T. O. and McKinley J. P. (1965) *Science, 270,* 450–455. [7] Ash R. D. et al. (1996) *Nature, 380,* 57–59. [8] Borg L. et al., in preparation. [9] Head J. et al. (1998) *Meteoritics & Planet. Sci., 33,* A66. [10] Mojzsis S. L. et al. (1996) *Nature, 384,* 55–59. [11] Warren P. (1998) *JGR,* in press. [12] McSween H. Y. and Harvey R. P. (1998) *Meteoritics & Planet. Sci., 33,* A103. [13] McKay D. S. et al. (1997) *LPS XXVIII,* 919–920. [14] McKay D. S. et al. (1998) *Nature.* [15] Thomas-Keprta K. et al. (1998) *LPS XXIX,* Abstract #1494. [16] Thomas-Keprta K. et al. (1998) *Geology,* in press. [17] Kajander E. O. et al. (1998) *Proc. SPIE 3441,* 86–94. [18] Vainshtein M. et al. (1998) *Proc. SPIE 3441,* 95–111. [19] Westall F. et al., *Precambrian Res.,* in press. [20] Devouard B. et al. (1998) *Am. Mineral.,* in press. [21] Bradley J. P. et al. (1996) *GCA, 60,* 5149–5155. [22] Bradley J. P. et al. (1997) *Meteoritics & Planet. Sci., 32,* A20. [23] Bradley J. et al. (1998) *Meteoritics & Planet. Sci., 33,* in press. [24] McKay D. S. et al. (1996) *Science, 273,* 924–930. [25] Grady M. et al. (1994) *Meteoritics, 29,* 469. [26] Grady M. et al. (1998) GEOSCIENCE 98 abstract. [27] Jull T. et al. (1998) *Science, 279,* 366–369. [28] Clemett S. et al. (1998) *Faraday Discussions* (Royal Chemical Society), *109,* in press. [29] Clemett S. et al., in preparation. [30] Flynn G. et al. (1997) *LPS XXVIII,* 367–368. [31] Flynn G. et al. (1998) *Meteoritics & Planet. Sci., 33,* A50–A51. [32] Bada G. et al. (1998) *Science, 279,* 362–365. [33] Gibson E. K. et al. (1998) *Astrobiology News,* in press. [34] Romanek C. S. et al. (1994) *Nature, 372,* 655–657. [35] Valley J. et al. (1997) *Science, 275,* 1633–1638. [36] Gibson E. K. et al. (1997) *Sci. Am., 277,* 58–65.

XENON AND ARGON ISOTOPES IN IRRADIATED, ETCHED NAKHLA: CHARACTERIZING THE HOST OF MARTIAN ATMOSPHERIC XENON. J. D. Gilmour, J. A. Whitby, R. Burgess, and G. Turner, Department of Earth Sciences, University of Manchester, Manchester, M13 9PL, UK (Jamie. Gilmour@man.ac.uk).

Introduction: A noble gas component with the elevated $^{129}Xe/^{132}Xe$ ratio characteristic of the martian atmosphere is found in Nakhla (and the other nakhlites) [1,2]. It is elementally fractionated with $^{84}Kr/^{132}Xe$ values depleted by factor of ~5 relative to the martian atmospheric value (as measured in EET 79001 lithology C). We believe this fractionation reflects the processes by which it was derived from the martian atmosphere and incorporated in the meteorite. If, as has been suggested, aqueous alteration is responsible for this fractionation, the Xe component should be associated with "iddingsite" [2]. Our aim is to locate the host phase(s) of the mar-

Fig. 1. The solution above the acid-treated sample (Nak3) is dominated by the dissolution products of olivine. Minor elements suggest additional dissolution of phases including aqueous alteration products. Olivine and rust compositions from [5].

Fig. 2. Water treatment (Nak2 = solid black bars) removes ~20% of the Cl content of (Nak1 = open bars). Acid treatment removes nearly all of the chlorine in these samples (Nak3 = gray bars).

tian atmospheric Xe component and so determine what led to its incorporation and whether the same process can account for the elemental fractionation.

We have previously reported analyses of mineral separates from Nakhla that showed that a component with elevated $^{129}Xe/^{132}Xe$ is associated with olivine and pyroxene but concentrated in mesostasis [3]. Combining our data with literature abundances of the major minerals [4] suggests that ~10% of the martian atmosphere derived component is found in olivine, with approximately half the remainder being associated with pyroxene and half with mesostasis. We have now supplemented these data with analyses of Nakhla samples crushed and etched in water and acid.

Experimental: Approximately 210 mg of Nakhla was lightly ground to <400 μm and divided into three subsamples: Nak1 (61.42 mg), Nak2 (97.99 mg), and Nak3 (57.96 mg). A finer grain size was not used because of the anticipated difficulty in handling and analyzing powders after irradiation. Samples Nak2 and Nak3 were derived from the untreated sample by 20 hr of dissolution in water and 0.3 molar HNO_3 respectively. The solutions above samples Nak2 and Nak3 were analyzed for a selection of cations using ICP-OES, while anions from the solution above Nak2 were analyzed by ion chromatography (the ionic strength of the acid solution above Nak3 prevented use of this technique).

Aliquots of each sample were prepared and subjected to neutron irradiation. After such irradiation, K, Cl, Ca, I, Ba, and U concentrations can be measured as enrichments in the daughter isotopes of Ar and Xe produced after neutron capture. Xenon-isotopic analysis using RELAX and conventional Ar-isotopic analysis of these samples are ongoing. Here we report results of laser step heating analyses of aliquots of Nak2 and Nak3.

Results: Chemical analysis of the solutions above Nak2 and Nak3 revealed that the major element removed during the water

Fig. 3. Laser step heating of Nak2 shows that ~50% of the excess ^{129}Xe correlates with I in a low-temperature release. The remaining, high-temperature Xe seems associated with a Ba-rich phase. Acid treatment removed ~50% of the I without removing Xe, and so destroyed the correlation.

etch was Cl (20% of the expected budget), with traces of Na and S also present. Acid-treatment removed ~6% of the sample mass, and the elemental concentrations were consistent with olivine dissolution and a contribution from iddingsite and phosphate (Fig. 1).

Argon. There is no variation among the $^{40}Ar/^{39}Ar$ age data from the three separates. The most dramatic difference is a reduction in the Cl content of Nak2 (as expected from analysis of the solution) and its near-complete removal from Nak3 (Fig. 2).

Xenon. There is no evidence for any depletion in the martian atmosphere-derived component (as measured by excess ^{129}Xe) between Nak2 and Nak3, and both are consistent with previously reported bulk values [2]. In Nak2, there is a good correlation between I and ^{129}Xe at low temperature (Fig. 3). The I concentration is reduced by a factor close to 2 by acid treatment. Somewhat surprisingly, this does not remove excess ^{129}Xe and so destroys the correlation. Around 50% of the martian atmospheric Xe is released at low temperature in this sample.

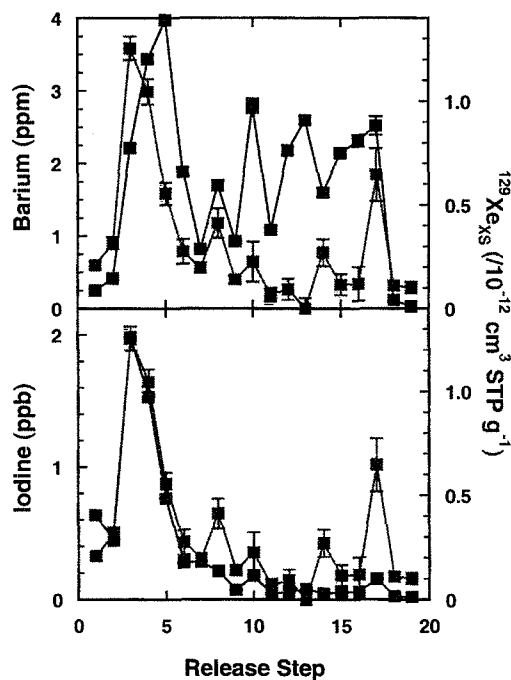**Discussion:** One martian atmosphere component is released at low temperature and is associated with I, and one is released during the high-temperature steps in which Ba-derived gas is evolved. In the light of our work on separates, it is reasonable to assign the first release to mesostasis and the second to pyroxene, although further work will be required to confirm this conclusion.

The partial removal of I during the acid etch stage of our analyses (along with near-total removal of Cl) and the associated destruction of the martian atmosphere Xe-I correlation is difficult to explain. We do not have accurate temperature data, but comparison of the release patterns suggests I and Cl may not be associated. The low temperature correlation between I and Xe is remarkably good and seems to require a common host phase. Leaching of I from this host phase may be capable of producing this effect; if so, it seems likely that it is fine grained and mesostasis is again implicated. The failure of acid etching to remove Xe in spite of its dissolution of olivine suggests that, although some excess ^{129}Xe is present [6], iddingsite is not a major carrier.

This work reveals differences between the Nakhlite component and the similarly elementally fractionated noble-gas component present in ALH 84001. In particular, the $^{129}Xe/^{132}Xe$ ratio of the trapped component in ALH 84001 is 2.0 ± 0.2 [7], while Nakhla yields 2.4. Furthermore, the dominant release of excess ^{129}Xe from ALH 84001 occurs at high temperature and is associated with orthopyroxene[7]. It seems that similar Kr/Xe fractionations in the Nakhlites and ALH 84001 do not indicate a common origin.

References: [1] Ott U. and Begemann F. (1985) *Nature, 317,* 509–512. [2] Drake M. J. et al. (1994) *Meteoritics, 26,* 854–859. [3] Gilmour J. D. et al. (1998) *EPSL,* submitted. [4] Treiman A. H. (1986) *GCA, 50,* 1061–1070. [5] Gooding J. L. et al. (1991) *Meteoritics, 26,* 135–143. [6] Swindle T D. at al. (1995) *LPS XXVI,* 1385–1386. [7] Gilmour J. D. et al. (1998) *GCA,* in press.

FORMATION OF CARBONATES IN ALLAN HILLS 84001 BY IMPACT METASOMATISM: COOKING WITH GAS.

R. P. Harvey, Department of Geological Sciences, Case Western Reserve University, Cleveland OH 44106-7216, USA (rph@po.cwru.edu).

Introduction: The possibility that the carbonates in ALH 84001 were formed by the process of impact metasomatism was first put forth in Harvey and McSween [1]. This short paper appeared roughly one month prior to that of McKay et al., in which specific features of ALH 84001 were suggested to be the result of biological activity on ancient Mars [2]. In the media frenzy following that announcement, and subsequent scientific research, the work of Harvey and McSween [1] was often cited as a counterpoint to the McKay groups hypothesis; often this was done as if it were the flag of a "resistance movement," rather than as a piece of the complex ALH 84001 puzzle. The purpose of this abstract is to explain the impact metasomatism hypothesis in greater detail and to offer an assessment of its validity in view of subsequent research.

Impact Metasomatism Hypothesis Restated: Harvey and McSween [1] suggested that the carbonates found in ALH 84001 formed when an anhydrous CO_2 fluid, heated and mobilized by impact, was flushed through impact-produced fractures of the original orthopyroxene cumulate lithology. This CO_2 fluid would initially be very hot and cool rapidly, with the whole event taking only a period of minutes or seconds. During the first moments, when temperatures and pressures were at a maximum, reactions would occur between the high-temperature fluid and the mafic components of the target lithology, enriching the fluid in Mg, Fe, and Ca. Immediate (a few seconds later) cooling of this fluid would induce precipitation of the carbonates as observed. Harvey and McSween used the term impact metasomatism to describe this scenario, based on its similarity to mechanisms suggested for scrubbing CO_2 out of the ancient martian atmosphere [3,4]. The plausibility of impact metasomatism as a mechanism producing ALH 84001 carbonates was based on many lines of evidence, as follows.

Mineralogical and Textural Considerations: Most researchers agree that carbonate is found exclusively within the fractured zones of ALH 84001. While some have suggested that several distinct types of carbonate exist, evidence for this is sketchy in that all are space-filling or coat-fracture surfaces and are compositionally indistinguishable. Indeed, the "type-specimen" carbonate has a circular or semicircular habit in thin section and on fracture surfaces, with a distinct pattern of compositional changes from core to rim, and all carbonates, regardless of setting, show a recognizable part of this pattern. This observation led Harvey and McSween to the common belief that all carbonate in ALH 84001 originated from a single event. This also implies that carbonates grew sequentially from core to rim, nucleating from point sources, suggesting kinetic control of crystallization and possible time-sequence information.

While most research on fracture-zone phases has centered on carbonate, the presence and absence of other phases is important to note. Chrome spinels form ubiquitous trains of crushed grains that characterize the maximum mechanical offset occurring during impact (on a scale of several millimeters in some cases). Maskelynite is also found preferentially associated with fracture zones and sometimes intimately intermixed with carbonate. While this has suggested to some that carbonate forms by replacement of maskelynite [5,6], it cannot be that simple; the Fe/Mg composition of the carbonates requires a source for these cations, and no aluminous byproducts have been identified. Olivine with distinctive amoeboid grain shapes is another phase found exclusively within crushed zones. Finally, the expected products of hydrous alteration of ultramafic rocks, such as chlorite, serpentine, or similar phases, are for all intents and purposes absent; only a few isolated submicrometer-sized grains have been identified, and it is not clear

that they are contemporaneous with carbonate formation [7]. These findings argue for carbonate formation during a single, anhydrous event associated with a fluid percolating through fracture zones in ALH 84001.

Harvey and McSween reported that the extreme "core" of carbonate growths was an Fe,Mg-rich calcite, intermixed with an ankeritic (50% Ca, 50% Mg,Fe) carbonate. This ankerite was in turn intermixed with the Fe-rich end member of the relatively Ca-rich magnesite-siderite carbonates most commonly observed. While some specific compositions had been observed in terrestrial rocks, the suite as a whole has no known counterparts. Unfortunately the initial description of this in [1] was termed a "three-carbonate assemblage," when it more accurately should have been considered a sequence of two component mixtures. That's how the assemblage was treated when carbonate geothermometry was applied, yielding temperatures of 685°C (calcite-ankerite) and 660°C (ankerite-siderite) [8]. These temperatures were in remarkable agreement with the previously observed correspondence between magnesite-siderite compositions and the Ca-rich border of the 700°C magnesite-siderite stability field [9].

Carbonate-producing Reactions: In the simplest possible scenario, ALH 84001 carbonates would be produced from components derived solely from the host ultramafic mineralogy. Unfortunately, reactions that produce carbonate and other nonhydrous products from ultramafic rocks are not well studied; most of the literature concerns reactions with a hydrous fluid. However, some reactions are known in both natural and experimental settings and provide insight into possible ALH 84001 carbonate formation mechanisms. Most notable are reactions that occur between ultramafic minerals and fluids with X_{CO_2} higher than 0.85. Two that are of direct importance are

$$2 \text{ forsterite} + 2 \text{ CO}_2 = 2 \text{ magnesite and 1 enstatite}$$

$$1 \text{ enstatite} + 2 \text{ CO}_2 = 2 \text{ magnesite} + 2 \text{ quartz}$$

Terrestrial studies predict these reactions will occur in sequence at about 660°C and 620°C respectively, at pressures between 3.5 and 5 kbar (or ~0.5 GPa) [10–12]. Several features of these reactions coincide well with what is observed in ALH 84001. The pressures are reasonable in the context of an impact event (mechanical twinning of pyroxene and conversion of plagioclase to maskelynite typically require 30 GPa or more), and the temperatures are suggestive. Furthermore, these reactions predict a mineralogical sequence that can be readily observed in ALH 84001. Olivine exhibiting reaction textures is surrounded by enstatite and associated with space-filling carbonate. In addition, spaces between carbonate growths are often filled with silica. One interesting point not noted in [1], however, is that while the interstitial silica requires that the reactions proceed toward production of that phase and carbonate, the olivine textures could be the product of decarbonation of preexisting carbonate.

Microphases and Microtextures: Harvey and McSween suggested that the typical grain size of ALH 84001 carbonate was somewhat smaller than 1 μm; while some carbonate areas showed crystal faces and compositional homogeneity on the 1–10-μm scale, plots of carbonate analyses showed linear mixing trends between calcite-ankerite and ankerite-siderite compositions. Following that lead, TEM and FE-SEM studies were conducted to explore carbon-

ate mineralogy at the submicrometer scale. These studies confirmed a complex texture at submicrometer scales and revealed evidence for the mechanical and thermal effects of shock. Several observations best made sense in terms of gas-phase reactions at temperatures above ambient. For example, the magnetite assemblage observed throughout the carbonate included a variety of morphologies, some with specific crystalline defects typically associated with high-temperature vapor-phase growth [13]. These same crystals often had a rigorous epitaxial relationship to the carbonate substrate, indicating sufficient free surface energy during magnetite crystallization to allow cation mobility (i.e., elevated temperatures) [14]. These and other observations suggest temperatures of at least a few hundred degrees Celsius either during carbonate crystallization or during alteration of preexisting carbonate [14,15]. These reactions could have occurred during the last moments of a metasomatic impact event, or during subsequent, lower-energy impact events.

Trace-Element and Isotopic Considerations: Trace-element studies strongly suggested metasomatic reactions between ALH 84001 and an invasive fluid [16]. The isotopic composition of ALH 84001 carbonates has been more extensively studied, with interesting if more controversial results. Early studies of ALH 84001 leachates showed enrichments in ^{13}C and ^{18}O that were consistent with either high or low temperatures of formation; in general, low-temperature, aqueous scenarios for carbonate formation were favored [17]. However, Harvey and McSween [1] argued that this interpretation was soft for several reasons. First, ^{13}C enrichments cannot unambiguously indicate a formation temperature without assuming a fluid composition, given the enriched nature of the martian atmosphere as a whole. Second, studies of natural impact-produced carbonates intermixed with mafic impact glasses show that isotopic disequilibrium between these phases is the norm, even though peak temperatures in excess of 1200°C must have been reached [4].

In situ studies of ALH 84001 carbonate using ion microprobe techniques produced equally polarized viewpoints. One study established that O isotopes within the observed sequential Mg,Fe compositional sequence were essentially homogenous, suggesting a disequilibrium commonly used to indicate formation temperatures below 300°C [18]. However, a much more complete study (including analyses of a wider range of carbonate compositions) found something distinctly different; that there was a distinct correlation between O-isotopic and major-element compositions [19]. While this correlation could not unambiguously distinguish between a high- or low-temperature formation for the carbonates, it did show that isotopic compositions could be consistent with the impact metasomatism scenario for a small volume system.

Other Observations and Conclusions: Many of the most vocal critics of the impact metasomatism hypothesis have focused on the notion that it required reaching equilibrium at high temperature, which would reset specific isotopic or physical systems to values other than those observed [e.g., 20]. Contrary to this assumption, Harvey and McSween envisioned a rapid, nearly instantaneous event; reactions at elevated temperatures provide Ca, Mg, and Fe to a CO₂ fluid, which on further cooling produces the observed carbonates and associated phases. Unfortunately, without knowing the exact temperature, pressure, fluid composition, and duration of the event, one can only explore the reactions supplying cations for the observed carbonates, rather than set strict limits on formation conditions. To use a common buzz word, the pro-

posed impact metasomatism is as much a "disequilibrium" process as any low-temperature precipitation mechanism, with one reaction supplying cations to a fluid that later deposits an oversaturated precipitate. Such reactions can be initiated either thermally or allochemically.

In summary, impact metasomatism still serves as a viable possible mechanism for carbonate formation in ALH 84001. Perhaps the biggest handicap of the impact metasomatism hypothesis has been its "alien" nature; i.e., it doesn't seem familiar to those favoring Earth-like conditions on early Mars, and, to paraphrase many, "it just doesn't feel right." But perhaps ALH 84001 carbonates should serve as a reminder that Mars is *not* Earth, and that processes such as impact metasomatism, which are almost certainly familiar to Mars, may require us to think "like a martian."

References: [1] Harvey and McSween (1996) *Nature, 382,* 49. [2] McKay D. et al. (1996) *Science, 273,* 924. [3] James P. et al. (1992) in *Mars,* p. 934, Univ. of Arizona, Tucson. [4] Martinez I. et al. (1994) *EPSL, 121,* 559. [5] Treiman A. (1995) *Meteoritics, 30,* 294. [6] Kring D. et al. (1998) *GCA, 62,* 2155. [7] Thomas-Keprta K. et al. (1997) *LPS XXVIII,* 1433. [8] Anovitz and Essene (1987) *J. Petrol., 28,* 389. [9] Mittlefehldt D. (1994) *Meteoritics, 29,* 214. [10] Trommsdorf and Connolly (1990) *Contrib. Mineral. Petrol., 104.* [11] Johannes W. (1969) *Am. J. Sci., 267,* 1083. [12] Ohnmacht W. (1974) *J. Petrol., 15,* 303. [13] Bradley J. et al. (1996) *GCA, 60,* 5149–5155. [14] Bradley J. et al. (1998) *Meteoritics & Planet. Sci., 33,* 765. [15] Wentworth and Gooding (1995) *LPS XXVI,* 1489. [16] Wadhwa and Crozaz (1995) *LPS XXVI,* 1451. [17] Romanek et al. (1994) *Nature, 372,* 655. [18] Valley J. et al. (1997) *Science, 275,* 1633. [19] Leshin L. et al. (1998) *GCA, 62,* 3. [20] Treiman and Romanek (1998) *Meteoritics & Planet. Sci., 33,* 737.

RECOVERING MORE ANTARCTIC MARTIAN METEORITES: ANSWERS TO COMMON QUESTIONS. R. P. Harvey[1] and W. A. Cassidy[2], [1]Case Western Reserve University, Cleveland OH 44106-7216, USA (rph@po.cwru.edu), [2]Department of Geology and Planetary Science, University of Pittsburgh, Pittsburgh PA 15260, USA (ansmet@vms.cis.pitt.edu).

Introduction: Of the 13 martian meteorites reported, almost half were collected in Antarctica. With the increased interest in martian meteorite studies accompanying the report of possible biogenic activity in ALH 84001, many have wondered whether recoveries of Antarctic martian meteorites could be enhanced or accelerated. Given that the recovery of Antarctic meteorites is a planned activity, (unlike the recovery of non-Antarctic martian meteorites via random finds and falls), such questions are worth considering. Listed below are several topical questions, followed by answers based on experience gathered during the 21 completed field seasons of ANSMET (the Antarctic Search for Meteorites program).

1. Can Antarctic meteorite collection activities be focused on recovery of martian samples?

The answer is no. Antarctic meteorite hunting is analogous to mining placer deposits — we visit areas where meteorites are concentrated by ice sheet processes, and only by collecting all the meteorites can we ensure recovery of a few of special interest. The reason is simple; martian meteorites are so physically and mineralogically similar to other meteorite types that they cannot be recognized as "martian" during observations possible in the field. Thin-section work would be the minimum needed to suggest that a specimen is martian, and positive confirmation would require much more detailed chemistry. Anecdotal evidence suggests that several of the martian meteorites were recognized as "different" in the field, but such designations have been notoriously inaccurate. Systematically collecting all the meteorites from a given stranding surface is the best possible way to increase the chances something rare will be recovered.

2. Could we recover more meteorites using technologically advanced techniques?

The answer is no, at least not with present-day technology. While technology makes available an amazing array of sensors, none can match the amazing capabilities of the human vision system. With just a few days' training, a meteorite hunter can visually acquire, recognize, and categorize dozens of rocks within view at rates surpassing any mechanical data acquisition system by several orders of magnitude. Humans store these data, learn as they go, and are mobile, easy to care for, abundant, and cheap (particularly graduate students). Proposals have been made to try magnetometers, spectral photometers, metal detectors, ground-penetrating radar, and brainy robots to help ANSMET find meteorites. Currently, humans outperform all of these by a huge margin in terms of speed, recognition, and cost.

One aspect of modern technology that has proved to be of enormous value is highly detailed satellite imagery. While satellites cannot "see" meteorites (or tell them from Earth rocks), they can help us find exposed blue ice, and help us discern the shape and topography of an icefield. These images speed up reconnaissance efforts and greatly facilitate systematic searches. They also serve as the only available basemap for precisely locating our finds, given that many Antarctic icefields lie off existing topographical maps.

3. If we sent an army of professional meteorite hunters, could we gather martian meteorites more quickly?

The answer to this one is "maybe." Success in finding Antarctic meteorites depends on a lot of factors, of which manpower is only one. Reconnaissance is perhaps the most important factor; you will recover more meteorites if you know where to go to find the densest concentration. Weather is another vitally important factor. Too much wind and you can't see because of blowing snow and freezing skin; too much snow and it buries the meteorites; too *little* wind and they stay buried. Given good weather and a meteorite stranding surface that is a known provider, adding more people to a field team means covering more territory more quickly. Experience among field party members also helps, and we typically aim for a 50:50 mix of novices and experts; however, the benefits of a fully "professional" field team are not as clear. While novices typically need a few extra days to learn to recognize meteorites, they are also more likely to be cautious and "over-identify" possible meteorites, helping ensure that nothing interesting gets left behind. Antarctic field work also demands a significant time commitment that many professionals would find difficult to commit.

It should also be recognized that, even if we did recover specimens at double or triple the average pace (~350/yr), there is a bottleneck at the initial characterization and curation end, where martian specimens would first be identified. Currently the Meteorite Processing Facility at Johnson Space Center can handle several hun-

dred recoveries per year very well; but recoveries of a thousand or more dramatically slow things down.

4. Do searches miss types of martian meteorites that resemble terrestrial rock?

It's possible, but past performance suggests such potential losses are minimal. Most of the areas of meteorite stranding surfaces are isolated from nearby sources of terrestrial rock. Areas like the Allan Hills Western Icefields (where ALH 84001 came from) are many kilometers from exposed bedrock and have no terrestrial rock on their ice surfaces; any rock we find is almost certainly a meteorite regardless of how "terrestrial" it looks. Regions of some icefields, however, lie close to exposed bedrock and can have a scattering of terrestrial rock on their surfaces. Only by careful observation of each and every rock can one find the meteorites included there; looking for fusion crust, a particular glossy patina, or perhaps just a rock that looks out of place by virtue of size or mineralogy. Luckily, we have just the instrument to allow such a search to succeed (see question 2 above). Proof that martian meteorites can be found mixed in with terrestrial rocks is that the last two discovered (LEW 88516 and QUE 94201) both came from regions with significant earth-rock; the latter from a moraine filled with millions of like-sized pebbles. In summary, while we might miss a fusion-crust-free martian sandstone mixed in with terrestrial sandstone, we wouldn't miss it lying on an isolated icefield or mixed in with dolerite; chances are such losses are minimal. It is also important to note that ANSMET field parties always err on the side of caution, routinely bringing back any rock that resembles a meteorite or simply doesn't fit within the observed range of local rock types and sizes.

5. What can be done to help gather more martian meteorites?

Scientists and others can take several steps to boost the recovery of martian meteorites.

First, support annual field parties. Going hunting every year minimizes the stochastic influence of the weather, maximizing the chance that ANSMET field parties will be in the right place at the right time. If you feel generous, support multiple field parties. This likewise minimizes the effect of weather, but also allows simultaneous reconnaissance and systematic searching. The annual rate of returns goes up because icefields for future searching can be more readily prioritized while recoveries take place, not in their stead.

Second, support survey-level characterization as fully as possible. In order to find the martians in the mix, all the specimens need to be characterized in a timely fashion. Yamato 793605 is a superb example of the importance of this early step. The 1979 Japanese Antarctic meteorite collection effort yielded nearly 4000 specimens, but because no infrastructure for rapid characterization was in place, many of the specimens were never carefully examined. Fifteen years after collection, Y 793605 was recognized as a "new" martian lherzolite. Similarly, support continued study of existing modern falls. By virtue of their masses, these specimens can include a more varied lithology within a single sample than is typically seen in Antarctic specimens and may contain new clues concerning the martian crust and its interaction with the martian environment. Witness the discovery of NaCl in Nakhla last year: who knows what lies in the many kilograms of Chassigny not yet studied?

Third, support recovery from dry deserts and searches in Greenland. Given that 1 of every 2000 meteorites found in Antarctica turns out to be martian, with even better odds for non-Antarctic recoveries, systematic recovery of more meteorites means finding more martian samples. However, such searches are meaningless if unbiased and rapid distribution of samples to interested scientists is not guaranteed. Commercial or private meteorite collection is antithetical to this goal.

Finally, minimize restrictions on the distribution of the martian samples. New martian samples can be most quickly studied if they are widely distributed; and the more complex and unique the sample, the wider and quicker this distribution should be. The hastily imposed moratorium on distribution of ALH 84001 samples is a case in point, since new researchers were effectively locked out of this research for almost a year.

ESTIMATES OF OXYGEN FUGACITY IN THE BASALTIC SHERGOTTITES FROM ELECTRON MICROPROBE OXYGEN ANALYSIS.

C. D. K. Herd[1] and J. J. Papike[2], [1]Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque NM 87131, USA (herdc@unm.edu), [2]Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque NM 87131, USA (jpapike@unm.edu).

The basaltic shergottites consist of four meteorites thought to have a martian origin: Shergotty, Zagami, EETA 79001, and QUE 94201. All are basaltic in composition, but only QUE 94201 contains no cumulus pyroxene and may therefore represent a martian liquid [1].

Previous estimates of f_{O_2} at the time of crystallization of the shergottites range from the quartz-fayalite-magnetite (QFM) buffer [2] to 4 log units below QFM [3], based on coexisting Fe-Ti oxides, for all but QUE 94201. Oxygen fugacity conditions for QUE 94201 are near the iron-wüstite (IW) buffer according to [1], about 4 log units below QFM.

The current research aims to refine the estimates of f_{O_2} for the basaltic shergottites, through electron microprobe techniques. The technique of quantitative analysis of O using the electron microprobe has been developed to the point where O can be analyzed with certainty comparable to the analysis of most cations. Practical application of the technique to naturally occurring spinels was demonstrated by [4]. A set of O standards now exists that can be readily obtained [5]. The technique also allows an assessment of stoichiometry, since the cation total, on the basis of four O atoms, does not rely on the assumption of stoichiometry. Instead, the amount of Fe^{3+} is determined by charge balance.

The method of analysis of the oxide minerals in the basaltic shergottites follows the technique of [4]. Initially, when analyses were carried out, O was not monitored for shift (constant machine error) or drift (gradual machine error), as outlined in [4]. Future analyses will include this aspect in the analytical routine. Raw data were corrected using the off-line CITZAF correction software [6]. A comparison of corrections on standard analyses revealed that the matrix correction of [7] corrected O the most accurately. However, cation amounts were unacceptable. Therefore, a custom correction was developed using the CITZAF software. The custom correction uses the absorption correction of [7], the stopping power correction of [8], and the backscatter correction of [9]. An O area-peak factor was also determined and used to adjust the O K-ratios before they were input into the customized correction.

The Fe-Ti oxide exchange model software of [10] was used to initially estimate temperature and f_{O_2} for the basaltic shergottites.

The program assumes stoichiometry, and thus provides an initial estimate with which data based on charge balance can be compared. The results for an individual shergottite apparently define a trajectory in T-f_{O_2} space that parallels the O buffer lines. According to this model, EETA 79001 (lithology A) records temperatures of 760°–900°C, and a trajectory ~1.75 log units below the QFM buffer, or 0.5 log units above the wüstite-magnetite (WM) buffer. Queen Alexandra Range 94201 records temperatures of 950°–990°C, and an f_{O_2} at or slightly below the WM buffer. Shergotty records relatively consistent temperatures of 840°–870°C, and f_{O_2} only 0.66 log units below QFM. Zagami records temperatures of 745°–860°C, and f_{O_2} from 0.75 to 1.3 log units below QFM.

Estimates based on charge balance were determined, in a rough manner, from a graph of coexisting spinel-rhombohedral oxide pair compositions (Fig. 4 of [10]). Elephant Moraine 79001 spinel and rhombohedral oxide (ilmenite) phases are stoichiometric, and temperatures range from 590° to 760°C, with f_{O_2} at or below the IW buffer. Queen Alexandra Range 94201 spinels are nonstoichiometric, with cation sums of 2.7–2.8. It should be noted that this degree of nonstoichiometry is uncommon and likely represents uncertainty in the O measurement. Ilmenites are stoichiometric. Approximate temperatures are 500°–700°C, and f_{O_2} is at or below the IW buffer. Shergotty spinels and ilmenites are stoichiometric, and the recorded temperatures are 600°–700°C, with f_{O_2} at or below the IW buffer. Zagami ilmenites are stoichiometric, but spinels display cation excess, reflecting uncertainties in the O measurements. Temperatures range from 650° to 900°C, again with f_{O_2} at or below the IW buffer. In general, the estimates from the graph of [10] indicate the need for software that does not assume stoichiometry, and reflect the uncertainty in measurement of O.

The rough estimates of f_{O_2}, based on charge balance instead of stoichiometry, are, on average, 3 log units below estimates from the Fe-Ti exchange software of [10]. Ilmenites are essentially stoichiometric, but nonstoichiometry in the spinel phases is common, in accordance with the study of terrestrial spinels by [4]. Future analyses using a refined analytical procedure for O will allow the impact of the stoichiometry assumption on the estimation of f_{O_2} in the basaltic shergottites to be assessed.

References: [1] McSween H. Y. Jr. et al. (1996) *GCA, 60,* 4563–4569. [2] Stolper E. and McSween H. Y. Jr. (1979) *GCA, 43,* 1475–1498. [3] Ghosal S. et al. (1998) *Contrib. Mineral. Petrol., 130,* 346–357. [4] Kamperman M. et al. (1996) *Am. Mineral., 81,* 1186–1194. [5] McGuire A.V. et al. (1992) *Am. Mineral., 77,* 1087–1091. [6] Armstrong J.T. (1995) *Microbeam Analysis, 4,* 177–200. [7] Love G. and Scott V. D. (1978) *J. Phys. D., 11,* 1369–1376. [8] Pouchou J.-L. and Pichoir F. (1991) in *Electron Probe Quantitation,* pp. 31–75, Plenum Press, New York. [9] Duncumb P. and Reed S. J. B. (1968) in *Quantitative Electron Probe Microanalysis,* pp. 133–154, U.S. Government Printing Office, Washington, DC. [10] Ghiorso M. and Sack R. O. (1991) *Contrib. Mineral. Petrol., 108,* 485–510.

IMPLICATION OF HYDROUS WEATHERING PRODUCT ON MARS FOR FUTURE EXPLORATION.

L. E. Kirkland[1] and K. C. Herr[2], [1]Lunar and Planetary Institute and Rice University, Houston TX 77058, USA (kirkland@lpi.jsc.nasa.gov), [2]The Aerospace Corporation, El Segundo CA, USA.

Introduction: Analysis of the newly recovered and recalibrated 1969 Mariner 7 Infrared Spectrometer (IRS) spectra (1.8–14.4 μm) provide evidence for the presence of a hydrous weathering product on the martian surface, interpreted to be goethite. A hydrous weathering product such as goethite may mark areas with a higher abundance of water vapor or areas where water was more abundant in the past. Such areas may contain interesting geologic structures, and an increased abundance of water vapor would have implications in the search for areas most conducive to life. These areas may thus warrant more in-depth examination, and may also make prime targets for future landers.

One point the goethite interpretation illustrates that has relevance for future spectral instruments is the importance of obtaining a full spectrum to search for unexpected constituents. A multi-band radiometer, such as the Viking IRTM or the proposed Mars Surveyor 2001 THEMIS, has the advantage of lower data rate requirements, and it does provide information on the surface. However, it cannot be used to uniquely identify unexpected constituents, such as goethite.

Data: The IRS returned high-quality spectra covering 1.8–14.4 μm (5550–690 cm⁻¹), and the spectral range covered remains unique. However, much of the dataset and calibration information was lost by the late 1970s, so the spectra have not been fully utilized. To reconstruct the dataset, we located the original IRS data tapes, recovered the missing data, and collected information from the original IRS team [1]. Thus, for the first time since the 1970s, we have IRS spectra calibrated in wavelength and intensity using the original dataset and calibration information and expertise provided by the IRS team.

Infrared Spectrometer at Thermal Wavelengths: Goethite measured in transmission has bands at approximately 11.25, 12.5, and 20 μm (890, 800, and 500 cm⁻¹) [2]. Many Fe-bearing minerals exhibit a 20-μm band; however, an 11.25- and 12.5-μm doublet seems to be rare. For example, other common ferric oxides, such as hematite, magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), akaganeite (β-FeO•OH), and lepidocrocite (γ-FeO•OH), do not have the doublet at 11.25 and 12.5 μm [3].

Bands centered near 11.25 and 12.5 μm that are a close match to transmission bands in goethite appear in many of the IRS spectra, although atmospheric CO_2 features partially obscure the 12.5-μm band. The intensities of the 11.25- and 12.5-μm bands are approximately equal and correlated, which indicate the same constituent causes both bands. Neither band depth correlates with atmospheric path length; therefore, both are assigned to the surface spectrum.

Comparison of the IRS bands to spectra measured in emission do not match the sharpness of the features in IRS spectra, indicating the goethite is seen in transmission. This is the expected result if the goethite is present as a very thin layer or coating (less than ≈100 μm thick). Such coatings occur on Earth as a desert varnish or as a coating of very fine (clay-sized) particles on sand-sized grains. Alternatively, a thermal gradient at the surface layer would have the same effect.

The 11.25-μm band does not correlate with the 9-μm band, indicating it is not from the aerosol dust. It does not correlate with topography or 2.2-μm albedo, and it shows a weak, positive correlation with the 3-μm band depth. We see no correlation with geologic units.

Infrared Spectrometer at Reflected Wavelengths: Goethite has a 2.4-μm band and a very strong 3-μm band. A detailed examination of the 2.4-μm region in IRS spectra must await the full

calibration of this region, which is not yet complete. However, preliminary analysis indicates the presence of a 2.4-μm band, along with a stronger 3-μm band.

Water Vapor: The stability of goethite depends in part on the amount of water vapor present, and IRS spectra provide a measurement of the water vapor band at 6.45 μm. However, background variations in this region make water vapor amounts difficult to determine from this band. Nonetheless, it may be significant that the strongest 11.25-μm band, recorded along the western side of the Hellas basin, also contains the strongest 6.45-μm water vapor band. Other work [4] also indicates this region exhibits unusual variations in water vapor.

Thermal Emission Spectrometer: The Mars Global Surveyor Thermal Emission Spectrometer (TES) recently returned spectra from Mars covering ~6–50 μm (1700–200 cm⁻¹), and the spectra are in the early stages of calibration and interpretation. Both TES and IRS have a spectral resolution of ~10 cm⁻¹ at 10 μm. However, TES has a lower spectral sampling rate than IRS, which decreases its effective spectral resolution relative to IRS. Both measure this spectral region with similar signal-to-noise ratios (~400 for TES and ~600 for IRS).

We examined four TES spectra taken from the same region as the spectra published in (see Fig. 3 in [5]). The main cause of variations of features in these spectra had been attributed to the presence of pyroxene [5]. The lower spectral sampling of TES, combined with interference from the overlapping CO_2 bands, precludes a detailed examination of the 12.5-μm region in TES spectra. However, the TES spectra exhibit a feature that matches the 11.25-μm band seen in IRS spectra.

To further examine the 11-μm region, we calculated ratios to enhance the spectral differences between the published TES spectra. The close match of the residual spectrum to water ice shows that variations in water ice amounts rather than variations in surface mineralogy likely cause most of the difference in spectral shape from 10 to 13 μm for these TES spectra. The shape of the residual spectra indicates the TES spectra measured a water ice cloud rather than ice on the surface. The weakness of the band indicates the cloud is probably optically thin at visible wavelengths. Both TES and the 1971 Mariner 9 Infrared Interferometer Spectrometer (IRIS) reported measurements of water ice clouds on Mars using this spectral region [5,6].

Pyroxene or Goethite? An early interpretation of the 9- and 11-μm bands measured by TES attributed them to pyroxene [5], but our work indicates the most likely cause of these features is water ice [7].

The shape and depth of the TES 9-μm band in these spectra is consistent with a spectrum of dust, with the 9.4-μm CO_2 band causing the sharp feature at the base of the band. TES spectra also show a weak 20-μm band, and goethite has a 20-μm band. Therefore, these TES spectra appear to be consistent with the goethite interpretation, with spectral features attributed to the following: 9-μm band = dust as an aerosol and on the surface; 10–13-μm region band depth variations = water ice clouds; 11.25-μm band = goethite; and 20-μm band = possibly goethite.

Advantage of Full Spectrum: One lesson to be learned from these measurements is the importance of obtaining the full spectrum in order to search for unexpected constituents. A multiband radiometer has the advantage of lower data rate requirements, and this is an important consideration for a spacecraft instrument. However, a multiband radiometer cannot be used to uniquely identify unexpected constituents, and in the search for areas most conducive to life, it may be the unexpected that proves the most informative.

Determining the presence of a doublet at 11.25 and 12.5 μm caused by goethite requires spectra with sufficient spectral resolution and spectral sampling rate to measure the shape of the bands and thus determine the band centers. Although a multichannel instrument may be used to determine the presence of spectral variations in the 11.25/12.5-μm region, it cannot return enough information to determine the cause. Finally, in the near-IR to thermal-IR region, a goethite interpretation is strengthened by coverage from ~2 to 25 μm, where goethite has spectral features.

References: [1] Kirkland and Herr (1998) *LPS XXIX,* Abstract #1518. [2] Hunt et al. (1973) *Icarus, 18,* 459. [3] Bell et al. (1995) *JGR, 100,* 5297; Estep-Barnes (1977) in *Infrared Spectroscopy* (Farmer, ed.), Ch. 11. [4] McAfee et al. (1998) *LPS XXIX,* Abstract #1315. [5] Christensen et al. (1998) *Science, 279,* 1692. [6] Curran et al. (1973) *Science, 182,* 381. [7] Christensen P. (1998) personal communication.

THE SIGNATURE OF LIFE: IS IT LEGIBLE? A. H. Knoll, Botanical Museum, Harvard University, 26 Oxford Street, Cambridge MA 02138, USA (aknoll@oeb.harvard.edu).

Everyday experience suggests that the gulf between biology and the physical world is conspicuous. This impression arises, however, because the biology most familiar to us is largely that of organisms found on distal branches of the tree of life. The difficulty in distinguishing biogenic from abiogenic forms lies at the other end of the tree; life arose as the self-perpetuating product of physical processes, and it is likely that the characteristics of Earth's earliest organisms — their size, shape, molecular composition, and catalytic properties — bore a close resemblance to products of the physical processes that gave rise to life.

Organisms have structure, they have a chemical composition, and they affect their environment; thus, paleontological evidence of ancient life can be morphological, geochemical, or sedimentological. Experience with terrestrial samples makes it clear that features found in ancient sedimentary rocks can be accepted as evidence of former life only if they meet two distinct criteria. First, the features must be compatible with formation by known biological processes. Second, they must be incompatible with formation by physical processes. This is straightforward in principle, but it requires that we understand the limits of pattern generation by both biological and physical processes. There remains a good deal of ignorance about the range of features that can be generated by biological and physical processes. We know, for example, that microbial mats can facilitate episodic carbonate precipitation to form the layered sedimentary structures known as stromatolites, but we also know that layered carbonate precipitates can form in the absence of a templating mat community and did so in Archean oceans. What we don't yet know is the dimensions of the gray zone within which the products of biology and physical processes are difficult or impossible to distinguish. As the ALH 84100 debate illustrates, similar problems attend the interpretation of microscopic morphologies, organic molecules, and isotopic signals found in rock samples. Taphonomic processes, the processes by which a dead organism becomes a fossil, exacerbate the problem. Organisms decompose

in characteristic ways, but degradation can strip them of their diagnostic characters.

Environment is a key aspect of any discussion of potentially biological features in ancient terrestrial or martian rocks. The patterns formed by biological and physical processes are environment specific, so nuanced debates about the interpretation of ancient features require some estimate of the conditions under which encompassing rocks were deposited and diagenetically modified. To give a single example, biologists have recently reported the presence of extremely small bacteria in the human blood stream, but this places few limits on the interpretation of objects formed in dilute aqueous environments.

It is hard to overstate the importance of understanding the limits of physics and chemistry in pattern formation, because at present we have little way of knowing which features of contemporary terrestrial biology are likely to prove universal and which may be the peculiar products of Earth's specific evolutionary history. The bottom line is that we need to learn a great deal more about morphological, geochemical, and sedimentological pattern formation by physical processes. We need to know more about the limits of biological pattern formation, especially in environments likely to approximate those on Mars. And at the end of the day, we must admit that when we have learned much more than we know now, the gray zone will be better defined, but it won't disappear. Certainty about martian life will only become possible if and when we find evidence that lies outside of the gray zone.

MARTIAN BIOGENIC ACTIVITY: LOOKING FOR VIRUSES AND DNA TRACES INSTEAD OF EXTANT BACTERIA TRACES. L. V. Ksanfomality, Space Research Institute, Moscow, Russia.

A current program of investigations of organic components in ALH 84001 meteorite findings includes a study of the polyaromatic hydrocarbons traces [e.g., 1,2], C-isotopic analysis [e.g., 3], a search for amino-acid traces [4], O-isotopic analysis [5], etc. All of these studies are based on a hypothesis about a presence of martian prehistoric primitive life traces in the SNC meteorite from Mars. The hypothesis is based on the contemporary existing notions of the origin of life that originated in natural fashion, through numberless chemical reactions, which were highly probable under the conditions of young Earth [6]. There are a number of proofs that these same conditions occured early in martian history, which means life could have originated on Mars as well.

The only known terrestrial life form is amino-nucleic-acid life that uses nucleic acids as an information system. Primitive life forms include both microbes and viruses. It is known that viruses are able to withstand much more severe conditions than bacteria [7]. Their inactive forms may survive for a long time until favorable conditions occur again. Thus, it could make sense to look for viruses or even DNA traces both in the body of the ALH 84001 meteorite and on Mars in future space missions.

References: [1] McKay D. S. et al. (1996) *Science, 273,* 924–930. [2] Clemett S. and Zare R. (1997) *Planetary Systems — The Long View,* 9èmes Rencontres de Blois, pp. 22–28. [3] Jull A. J. T. et al. (1998) *Science, 279,* 366–369. [4] Bada J. L. et al. (1998) *Science, 279,* 362–365. [5] Galimov E. M. (1997) *Solar System Res., 31(3),*183–190. [6] de Duve C. (1997) in *Astronomical and*

Biochemical Origins and the Search for Life in the Universe (C. Cosmovichi et al., eds.), pp. 391–399, Editrice Compositori, Bologna, Italy. [7] Yushkin (1996).

THE STRUCTURE OF FINDINGS IN ALLAN HILLS 84001 MAY HINT AT THEIR INORGANIC ORIGIN. L. V. Ksanfomality, Space Research Institute, Moscow, Russia.

The ALH 84001 lessons showed that science at the end of the 20th century is ready for discovery of the simplest organisms on celestial bodies, where minimum conditions for life exist. These conditions, as well as the ways of the origin of primitive microorganisms, are already understood and described in the scientific literature. McKay et al. [1] reported that the SNC meteorite ALH 84001 possibly contains traces and fossils of ancient primitive life from Mars. Nevertheless, the authors of this very first study believed that a highly comprehensive verification and more careful further investigation were needed. In this paper, a few remarks on the origin of the structures in the ALH 84001 meteorite are proposed. They may be of interest as a possible proof of their abiogenic nature.

One of the most intriguing electron-microscopic photos is the peculiar morphology observed in the globule, shown in Gibbs and Powell [2] and in McKay et al. [1]. The features are microscopic elongated formations and resemble the fossils of a colony of an-
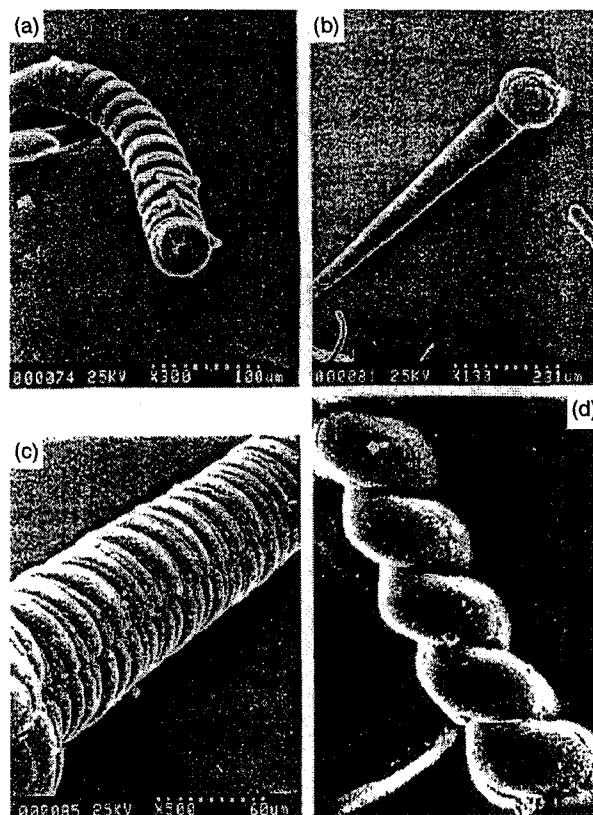

Fig. 1.

cient terrestrial bacteria from travertines and limestone. Besides the fact that these ovoids are approximately the same size, which is not the case for terrestrial bacteria [3], there is an another interesting detail. All the elongated ovoids are apparently separated from the solid top layer and the lower layer. If so, it can be presumed that all the bacteria constituted a continious layer before the separation. It seems more likely that one can see in this photo the process of fragmentation of some inorganic film. Such processes are known to exist and have nothing in common with bacteria [4].

Another photo of a very small structure resembling a worm fossil by its shape was published by Kerr [5] and McKay et al. [1], as possible evidence of ancient primitive life on Mars. For comparison, a set of electron-microscopic photos of four microstructures found in kerite from pegmatites in granites (Volin' area in Russia) can be examined (Fig. 1). The images were obtained and published by Yushkin [6] and reproduced by Galimov [7]. One can see how unusual and strange the shapes of inorganic structures of some minerals are. Their structures mimic some bacteria and may be misleading as to their real nature.

References: [1] McKay D. S. et al. (1996) *Science, 273,* 924–930. [2] Gibbs W. W. and Powell C. S. (1996) *Sci. Am., 275,* 12–13. [3] Schopf W. (1997) *Planetary Systems — The Long View,* 9èmes Rencontres de Blois, pp. 22–28. [4] Ksanfomality L. V. (1997) *Solar System Res., 31(3),* 175–182. [5] Kerr R. A. (1996) *Science, 273,* 864–865. [6] Yushkin N. P. (1996) *J. Cryst. Growth, 167,* 237–247. [7] Galimov E. M. (1997) *Solar System Res., 31(3),* 183–190.

CONSTRAINTS ON MARTIAN VOLATILE HISTORY FROM STUDIES OF MARTIAN METEORITES: LESSONS LEARNED AND OPEN QUESTIONS.

L. A. Leshin, Department of Geology, P.O. Box 871404, Arizona State University, Tempe AZ 85287-1404, USA (laurie.leshin@asu.edu).

Studies of the shergottites, nakhlites, Chassigny, and ALH 84001 have provided valuable information on the origin, evolution, and interaction of martian volatile reservoirs. Understanding these reservoirs provides the broadest possible context within which to consider the possibility of life on Mars, and thus such studies are an important component of the quest for addressing issues related to a martian biosphere. The purpose of this work is to outline some of the important insights into martian volatiles provided by studies of martian meteorites, and to highlight inconsistencies and gaps in our knowledge that could be addressed by further research on the meteorites themselves, or by future missions, including sample returns. This is by no means meant to be an exhaustive review of all that has been learned from studies of volatiles in martian meteorites. Rather, it is intended to highlight major conclusions and to stimulate discussion about "what we really know."

In terms of the number of different samples (currently 13, of which 12 have been extensively studied), the amount of material available, and, perhaps most importantly, the diversity in rock types (or relative lack thereof), our current collection of martian meteorites represents an extremely limited sample base. Considering this, the influence of martian meteorites on our current thinking about "global" volatile issues on Mars is impressive. This is especially true when consideration is given to the overall paucity of volatile-bearing phases in these samples. Initial studies of volatiles in mar-

tian meteorites were the key to establishing the connection between the samples and the planet Mars [1,2]. More recent studies have explored the volatile history of Mars as recorded in the samples in increasing detail.

Working Hypothesis #1: Martian magmas are relatively dry, indicating a dry martian mantle.

Observational evidence. Hydrous primary (magmatic) minerals are rare in all of the martian meteorites. They contain two main types of primary hydrous minerals: apatite (a Ca-phosphate) and kaersutite (a Ti-rich amphibole). A single 15-μm biotite has also been found in Chassigny [3]. However, the dominant phosphate mineralogy in the samples is merrillite (also referred to as whitlockite, although merrillite is probably a more proper designation), an anhydrous Ca-phosphate. On Earth, merrillite is essentially absent, probably attesting to a significant difference between the volatile contents of magmas on the two bodies. Even in the most evolved rock compositions, such as shergottite QUE 94201, which should have the highest concentrations of volatiles, merrillite is the dominant phosphate, constituting ~4% of the sample, with apatite present at the <1% level [4].

The kaersutites in the martian meteorites are found only inside partially crystallized magmatic inclusions within pyroxene and olivine [e.g., 3,5]. Their presence was initially used to indicate rather substantial water content for primary magmas of ~1.5 wt% [3,6]. However, the low water content of the amphiboles (<0.2 wt% [7]) probably indicates a significantly lower magmatic water content.

Implications. A low martian mantle water content has been used to support a homogeneous accretion model for Mars [8,9] in which volatile-rich and metal-rich planetesimals accreted together on Mars, the metal was oxidized and the water reduced to H, which escaped. Preservation of this low water content supports the suggestion that plate-tectonic-style recycling of surface materials (which appear to be more volatile rich — see below) has been unimportant in martian history.

Open questions. Although the mineralogical observations support low magmatic water content, questions remain about exactly what conditions are necessary for the production of the phases present in martian meteorites. For example, kaersutites such as those in the meteorites, which contain up to 11 wt% TiO_2 [3,5], have not been successfully synthesized in the laboratory. By understanding the parameters under which these types of minerals form, we will be able to better constrain the volatile contents of the martian magmas that produced the meteorite samples.

The two-component homogeneous accretion model of [8] may not be capable of producing a Mars with the proper moment of inertia [10]. In addition, the efficiency of the accretion-H reduction-loss process for eliminating much of Mars' primordial water is unknown. Thus, many open questions remain about the mechanism for accreting Mars with a dry interior.

Working Hypothesis #2: There is a substantial reservoir of water (and other volatiles) in the martian crust that interacts with crustal rocks.

Observational evidence. The evidence for the interaction of martian crustal volatiles with crustal rocks comes in two main forms: mineralogical and isotopic. Secondary minerals, from sulfates to carbonates to clays, have been found in all types of martian meteorites [e.g., 11]. These minerals, which in most cases can be convincingly shown to be preterrestrial, attest to the ubiquitous presence of fluids in the martian crust. However, it should be re-

membered that in all the samples, these secondary minerals represent minor components of the rocks, suggesting rather low fluid-rock ratios in the alteration environment. Isotopic studies point to exchange of H in some magmatic minerals after crystallization [7], and to the postmagmatic origin of many of the carbonate minerals in the samples [e.g., 12–16].

Implications. The interaction of fluids and rocks appear to be an important crustal process on Mars, as it is on the Earth. This conclusion is especially important because it suggests that "environments" on Mars that could be suitable for life (e.g., "hydrothermal" environments) are plentiful, since some evidence for such environments is found in all the martian samples we have.

Open questions. There are many open questions about the fluid-rock interaction in the martian crust. What is the source of the fluids in the crust and what is their abundance? Has this reservoir of volatiles changed with time due either to magmatic influx or atmospheric loss? What are the conditions under which the martian samples have experienced fluid-rock interaction? What are the temperatures, durations, and timing of these events relative to the igneous crystallization ages of the samples? More detailed analyses of the alteration products, an active area of current research, should shed light on at least some of these questions.

Working Hypothesis #3: Crustal and atmospheric volatiles have interacted over time.

Observational evidence. From groundbased and Viking observations, we know that the current martian atmosphere has a unique isotopic signature in H, C, N, Ar, and Xe, among others [e.g., 17,18]. In many cases this unique signature can be traced to loss of atmospheric constituents accompanied by isotopic fractionation. This "atmospheric" signature can be found in the volatiles introduced into the martian meteorites by the fluid-rock interactions discussed above [e.g., 12,13,15,19,20]. In terms of O-isotopic signatures, three isotope analyses of water and carbonates from the meteorites have shown that the crustal volatile reservoir is not in isotopic equilibrium with the silicate crust [19,20].

Implications. All isotopic data point to interaction of the atomosphere and crustal reservoirs of volatiles. The O-isotopic data that indicate a lack of equilibration between the crustal fluid and rock O reservoirs would seem to require that fluid-rock exchange took place for short periods and/or at relatively low temperatures to preserve the observed disequilibrium.

Open questions. The mechanism by which the interaction between crustal and atmospheric volatiles takes place is very unconstrained. The proposal that atmosphere-crust exchange took place through "hydrothermal systems" [18] fails to explain physically how this exchange would take place. Clearly, the fluid-rock exchange can happen in this way, but the atmosphere-crustal fluid exchange remains unconstrained.

The origin and time history of some of the atmospheric isotopic anomalies remains unknown. Of particular interest is the O anomaly, which could be an indicator of photochemical processes in the martian atmosphere, of atmospheric loss processes, or of a crustal reservoir that has been out of equilibrium with the crust since its formation [19–21]. This latter possibility would suggest the crustal and atmospheric volatiles were supplied from some exotic source such as a late cometary input.

References: [1] Bogard D. D. and Johnson P. (1983) *Science, 221,* 651. [2] Becker R. H. and Pepin R. O. (1984) *EPSL, 69,* 225. [3] Johnson M. C. et al. (1991) *GCA, 55,* 349. [4] McSween H. Y. Jr. et al. (1996) *GCA, 60,* 4563. [5] Treiman A. H. (1985) *Meteoritics, 20,* 229. [6] McSween H. Y. Jr. and Harvey R. P. (1993) *Science, 259,* 1890. [7] Watson L. L. et al. (1994) *Science, 265,* 86. [8] Dreibus G. and Wänke H. (1985) *Meteoritics, 20,* 367. [9] Carr M. H. and Wänke H. (1992) *Icarus, 98,* 61. [10] Bertka C. M. and Fei Y. (1998) *LPS XXIX,* Abstract #1252. [11] Gooding J. L. (1992) *Icarus, 99,* 28. [12] Carr R. H. et al. (1985) *Nature, 314,* 248. [13] Leshin L. A. et al. (1996) *GCA, 60,* 2635. [14] Leshin L. A. et al. (1998) *GCA, 62,* 3. [15] Romanek C. S. et al. (1994) *Nature, 372,* 655. [16] Valley J. W. et al. (1997) *Science, 275,* 1633. [17] Pepin R. O. and Carr M. H. (1992) in *Mars,* p. 120, Univ. of Arizona, Tucson. [18] Jakosky B. M. and Jones J. H. (1997) *Rev. Geophys., 35,* 1. [19] Farquhar J. et al. (1998) *Science, 280,* 1580. [20] Karlsson H. R. et al. (1992) *Science, 255,* 1409. [21] Jakosky B. M. (1993) *GRL, 20,* 1591.

THE FUTURE SEARCH FOR LIFE ON MARS: AN UNAMBIGUOUS MARTIAN LIFE DETECTION EXPERIMENT. G. V. Levin, Biospherics Incorporated, 12051 Indian Creek Court, Beltsville MD 20705, USA.

A simple, robotic method to provide an *unambiguous* determination of extant life in the martian surface or subsurface material is presented. It cannot render a false positive, nor can it mistake a chemical response for a biological one.

Not since the landing of Viking has interest in life on Mars been so high. The finding [1] of possible biochemicals and microbial fossils in meteorites attributed to Mars has provided incentive for many new scientific investigations. Similar inclusions have recently been found [2] in nonmartian meteorites. The latter have rekindled interest in earlier reports [3,4] of meteorites containing "organized elements." Exquisite techniques are being developed [5] to examine and analyze these minute inclusions, and to distinguish them from possible terrestrial contaminants.

Intensive efforts are under way in a number of laboratories to develop reliable biomarkers for use in examining meteorites in laboratories, return Mars samples, and samples obtained on robotic missions to Mars and other celestial bodies. Chemical, biochemical, genetic mapping, physical, optical, computer recognition of morphological attributes, and laser ablation and sniffing techniques, along with their appropriate instrumentation, are under development. These techniques are focused on the detection and study of fossilized cellular remains. Other efforts are aimed at drilling to depths where lenses of liquid water with live microorganisms may exist. However, none of these biomarker recognition methods can distinguish living organisms from dead ones.

Recent developments have resuscitated the possibility that live microorganisms might be indigenous on the surface of Mars. Living microorganisms recovered [6] from permanent ice in which minute quantities of liquid water are extracted have provided a good model for Mars, since evidence of frozen water deposits was often seen on the surface by Viking. An analysis [7] of the dynamics of the martian atmosphere made possible by Pathfinder data shows that liquid water is most likely present diurnally on the martian surface. The calculated amounts are sufficient to sustain soil microorganisms on Earth.

The new life detection method is based on the legacy of the Mars Viking Labeled Release (LR) experiment [8], which is gaining re-

newed attention in view of the recent discoveries on Earth and Mars cited above. In addition, the salient arguments against the LR findings have been answered: (1) Theories that H_2O_2 caused the LR results have been negated by recently reported [9] direct observations that established an upper limit of 2×10^{-3} precipitable μm of H_2O_2 for Mars (this miniscule amount, were it present, could not have produced the LR results); and (2) the failure of the Viking GCMS [10] to detect organic matter on Mars, often cited as proof against the presence of microorganisms, has been contravened by the finding [11] of fully metabolizing microorganisms in permafrost in which no organic C was detected by GCMS.

The enhanced LR experiment exploits the fact that all known life forms make and utilize L-amino acids and D-carbohydrates preferentially over the respective stereoisomers. On the other hand, no natural chemical reactions can distinguish between stereoisomers. Therefore, any strong response by an unknown agent to one isomer of an administered compound over its stereoisomer constitutes indisputable proof that the agent producing the reaction is biological. A modified, miniaturized LR instrument can administer L and D isomers of amino acids and carbohydrates individually to discrete portions of the same soil sample. A stereospecific response would be proof of life. Should stereospecificity be found, and should it be the same as that of terrestrial life, a possible relationship between the two life forms would be indicated. Should the stereospecificity differ from that of Earth life, an independent origin of life forms would have been established. A variety of thermal controls on replicate samples could determine the thermal sensitivity of any life forms found and would also serve as a redundant verification of the biological result.

Using new technology, the LR instrument can be simplified and miniaturized. It can be deployed on the planetary surface, or, placed in penetrators, it can sample at depth. The instrument can be lodged in a cocoon and the entire assembly heat-sterilized before being mated to the spacecraft. Upon landing, the cocoon door would pop open, and, in the same motion, the instrument would be ejected beyond the contamination zone of the lander, thereby eliminating the high cost of spacecraft sterilization. Two-way radio communication between the instrument and the lander would provide for instructions and data exchange.

It is recommended that this simple, small, easily and cheaply developed instrument be flown on the next Mars mission and on missions to other candidate life-bearing bodies.

References: [1] McKay D. S. et al. (1996) *Science, 273*, 924–930. [2] Hoover R. B. et al. (1998) *Proc. SPIE, 3441*, 203–216. [3] Nagy B. et al. (1962) *Nature, 193*, 1129–1133. [4] Rossignol-Strick M. and Barghorn E. S. (1971) *Space Life Sci., 3*, 89–107. [5] Westfall F. et al. (1998) *Proc. SPIE, 3441*, 225–233. [6] Priscu J. C. et al. (1998) *Science, 280*, 2095–2098. [7] Levin G. V. and Levin R. L. (1998) *Proc. SPIE, 3441*, 30–41. [8] Levin G. V. (1997) *Proc. SPIE, 3111*, 146–161. [9] Krasnopolsky V. et al. (1997) *JGR, 102*, 6525–6534. [10] Biemann K. et al. (1977) *JGR, 82*, 4641–4658. [11] Gilichinsky D. (1998) Russian Acad. Sci., personal communication.

CURATION OF U.S. MARTIAN METEORITES COLLECTED IN ANTARCTICA.

M. Lindstrom[1], C. Satterwhite[2], J. Allton[2], and E. Stansbery[1], [1]Mail Code SN2, NASA Johnson Space Center, Houston TX 77058, USA (marilyn.m.lindstrom1@jsc.nasa.gov), [2]Mail Code C23, Lockheed Martin, Houston TX 77058, USA.

Meteorites: To date the ANSMET field team has collected five martian meteorites (see below) in Antarctica and returned them for curation at the Johnson Space Center (JSC) Meteorite Processing Laboratory (MPL). The meteorites were collected with the clean procedures used by ANSMET in collecting all meteorites: They were handled with JSC-cleaned tools, packaged in clean bags, and shipped frozen to JSC. The five martian meteorites vary significantly in size (12–7942 g) and rock type (basalts, lherzolites, and orthopyroxenite). Detailed descriptions are provided in the Mars Meteorite Compendium [1], which describes classification, curation, and research results. Table 1 gives the names, classifications, and original and curatorial masses of the martian meteorites.

Meteorite Processing Laboratory: The MPL is a class-10,000 clean lab containing N atmosphere glove-box cabinets and laminar flow benches for meteorite processing and additional N cabinets and stainless-steel open-air shelves for sample storage. All tools and sample containers are made of restricted materials and are carefully cleaned using the same procedures used for lunar sample tools. All sample handling follows strict published procedures, and all staff are trained in those procedures. All sample handling is also documented by weighing and photographing samples and kept permanently in computer and hard-copy records.

Although the meteorites were handled using procedures standard for achondrites, those procedures depend on sample size and have varied over time. Thus, the processing histories of the martian meteorites differ slightly. Because most of the meteorites were identified as achondrites by the field team, they were processed early in the classification queue (LEW 88516 is an exception), and all samples were stored only in N cabinets. The medium and large samples (ALHA 77005, EETA 79001, and ALH 84001) were initially processed and sawed in N cabinets. Slabs and small splits of these meteorites were processed on flow benches. The small

TABLE 1.   U.S. Antarctic martian meteorites.

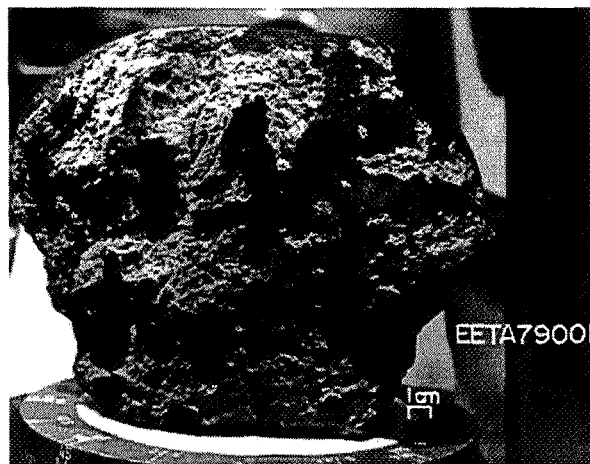| Name	Class	Original Mass (g)	MWG Mass (g)	Curator Mass (g)	Thin Sections TS	Thin Sections PB	Allocated Chips No. of Chips	Allocated Chips Mass (g)
EETA 79001	S-basalt	7942	6694	798 S/J	74	20	141	263
QUE 94201	S-basalt	12.0	6.4	0	12	1	19	3.5
ALHA 77005	S-lherzolite	482.5	185	212 N	32	14	47	45.8
LEW 88516	S-lherzolite	13.2	8.3	0	11	1	23	3.0
ALH 84001	Opxite	1931	1470	213 S	52	14	160	217

Fig. 1. Martian meteorite EETA 79001.

samples (LEW 88516 and QUE 94201) were always processed on a flow bench, but sample containers were later sealed in a N atmosphere. All samples had some exposure to air in the clean room, as they did for much longer times in Antarctica.

The most intense allocation of a given sample to researchers is just after its recovery and classification. The exception is ALH 84001, which was originally classified as a diogenite and reclassified as martian nine years later. The reclassification and the announcement of possible fossil life triggered major allocations in 1994 and 1997. For the small samples, little allocation is done at a later date. For the largest sample, EETA 79001, there has been a steady demand for samples. For the three largest samples, some of the material has been transferred permanently to various meteorite curatorial partner institutions. Allan Hills 77005 was collected jointly with Japan and the sample split with NIPR in Tokyo. Both the Smithsonian and JSC have display samples of EETA 79001, while only the Smithsonian has a ALH 84001 display sample. The remaining meteorites remain the property of NSF and are allocated by the Meteorite Working Group.
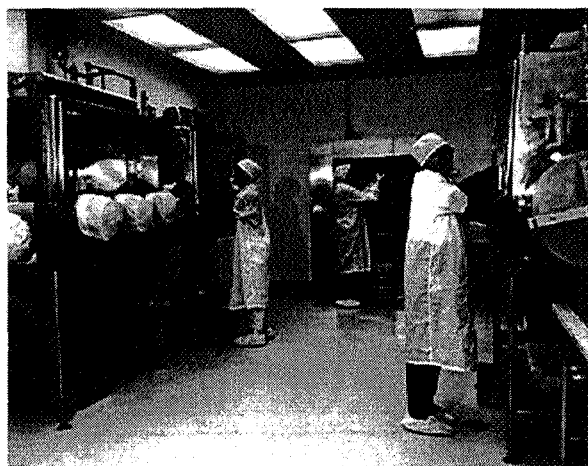
Contamination Control: The MPL has always had strict measures for controlling inorganic contamination. These measures were patterned after those developed for lunar samples, but were less rigorous due to the residence time of the meteorites in Antarctica. With the announcement of possible fossil life in one of our martian meteorites, the requirements for contamination control suddenly included organic and biological contaminants as well as inorganic ones. The MPL staff did a simple self-assessment of possible sources of organic contamination. The top of the list was human staff working in the lab, followed by plastics in bags and containers, organic soaps, and solvents. We requested review by an outside committee of specialists in organic chemistry and biology, and NASA Headquarters appointed Dr. Jeff Bada to head the Organic Contamination Review Committee. The group met at JSC in December 1996 and submitted a report to NASA Headquarters in March 1997 [2]. Their basic conclusion was that the MPL did not have obvious organic contamination (except as noted above), but that we had not monitored or documented the levels of minor contamination. JSC set out in 1997 to eliminate as many of the noted contaminants as possible and to document those that remained.

The first steps were taken to process ALH 84001 samples for both organic and inorganic analyses in 1997. First the meteorites were isolated from other achondrites in processing to avoid any cross-contamination. Next, all plastics were removed from the Mars Meteorite Processing Cabinet. The major change was the development of new procedures for cleaning the cabinet. Instead of using soap and organic solvents, we now use hot (140°C) ultrapure water (UPW) and monitor the three rinses. The UPW does an excellent job of removing particulates and leaves low levels of total organic C (TOC).

The second phase of organic contamination control is in the process of being implemented with FY98 funds from NASA Headquarters and the JSC Center Director's Discretionary Fund (CDDF). The UPW system is being upgraded and more monitoring and documentation of contamination is being done [3]. The plans for martian meteorite curation can be used as a starting point for curation of returned martian samples.

References: [1] Meyer C. (1998) *Mars Meteorite Compendium,* JSC curator. [2] Bada J. et al. (1997) *Rept of Org. Contam. Rev. Comm.* [3] Schilling E. and Schneider M., this volume.

Fig. 2. The JSC Meteorite Processing Laboratory.

PRINCIPAL COMPONENT ANALYSIS FOR BIOSIGNATURE DETECTION IN EXTRATERRESTRIAL SAMPLES.
G. D. McDonald and M. C. Storrie-Lombardi, Mail Stop 183-301, Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena CA 91109, USA (Gene.D.McDonald@jpl.nasa.gov).

Analysis of extraterrestrial samples for organic signatures of past or present life presents several problems. Chief among these is distinguishing bona fide extraterrestrial organic material from terrestrial contamination, either carried on a spacecraft or present in the terrestrial environment to which the sample is exposed. A related problem is separating biologically derived molecules from those produced by abiotic syntheses in the interstellar medium, on meteorite parent bodies, or in planetary atmospheres and oceans.

We have begun to address these problems using a technique, principal component analysis (PCA), borrowed from classical multivariate analysis. Also known as the Karhunen-Loéve or Hotelling

transform, PCA identifies linear combinations of raw parameters accounting for maximum variance in the dataset. Denoting input spectra as $S_{i,l}$, where i represents n input parameters for each spectra and l indexes the m training spectra, PCA first finds the mean spectrum, $\Delta S_{i,l}$, such that $\Delta S_{i,l} = \Delta S_{i,l} - <\Delta S_{i,l} > l$, calculates the difference between this mean and each individual spectra, then estimates the parameter covariance matrix, $C_{j,k}$, where

$$C_{j,k} = < \Delta S_{i,l} \times \Delta S_{i,k} > l$$

and decomposes this into constituent eigenvalues and normalized eigenvectors. If we restrict the decomposition to the first p terms, the method yields the optimum (in a least-squares sense) linear reconstruction of the input signal using the fewest p parameters. Since the covariance matrix is an average over many spectra, and since noise is uncorrelated between spectra, the method is quite robust to modest amounts of noise. The key advantage of this algorithm is its ability to shift the measurement output of disparate sensors to a common statistical metric. Specifically, datasets shift to zero mean and unit variance. This transformation is a central prerequisite for scientifically testing a null hypothesis and addressing queries about the existence of biomarkers in a specific unknown sample.

Ten terrestrial amino acids (alanine, aspartic acid, glutamic acid, glycine, isoleucine, leucine, proline, serine, threonine, and valine) found in the Murchison carbonaceous chondrite, Mars meteorite ALH 84001, and/or an Allan Hills ice sample were characterized using 13 physiochemical features including hydrophobicity, pKa, tendency to form alpha helices, residual mass, and preferred Ramachandran angles. PCA feature extraction provided five factors accounting for more than 85% of the variance. These five factors were multiplied by the amino-acid relative frequencies for 108 terrestrial protein families [1,2], seven Murchison meteorite amino-acid determinations [3–6], four Allan Hills meteorite assays [7], and one Allan Hills ice sample [7]. Ten factors extracted by PCA from the resulting matrix accounted for >99% of the variance in the test samples. Since PCA transposes the data to zero mean and unit variance, two-dimensional plots of orthogonal factors represent the dispersion of the amino-acid distributions in units of σ. This means that in a graphic representation such as that shown in Fig. 1, if the weighted centers of two clusters appear, for example, >2 units apart, then the clusters differ by more than two standard deviations. Analysis of the features comprising the factors provides insight into the portions of the amino-acid distribution contributing to the clustering. In Fig. 1 we have chosen to plot factors 3 and 10. Serine, and to a lesser extent proline, isoleucine, and glutamic acid, contribute to factor 3, while glycine, and once again proline and serine, contribute to factor 10.

The presumably abiotic Murchison amino acids form a cluster distinct from the terrestrial protein families, although partial terrestrial biological contamination in some of the Murchison analyses is indicated. The profiles from various extracts of ALH 84001 are also distinct from proteins, but less tightly clustered. The Allan Hills ice sample also does not cluster tightly with the protein families, suggesting that geochemical fractionation of the biogenic amino acids deposited in the ice has taken place at some point.

The PCA method is particularly suited for sample analyses involving datasets from a variety of disparate instruments designed to detect and quantify different classes of organic compounds. Such data can be reduced to common compositional or physiochemical factors and combined to generate a profile of the overall organic composition of a sample. This profile can then be compared with profiles of known biological and nonbiological systems to assess the probability that the extraterrestrial sample contains evidence of past or present life.

References: [1] Dayhoff M. O. (1972) *Atlas of Protein Sequence and Structure, vol. 5,* Natl. Biomed. Res. Found. [2] Dayhoff M. O. (1978) *Atlas of Protein Sequence and Structure, vol. 5, supl. 3,* Natl. Biomed. Res. Found. [3] Cronin J. R. and Pizzarello S. (1983) *Adv. Space Res., 3,* 5–18. [4] Engel M. H. and Nagy B. (1982) *Nature, 296,* 837–840. [5] Engel M. H. et al. (1990) *Nature, 348,* 47–49. [6] Engel M. H. and Macko S. A. (1997) *Nature, 389,* 265–268. [7] Bada J. L. et al. (1998) *Science, 279,* 362–365.

Fig. 1. The interaction of principal component factors 3 and 10 distinguish both ALH 84001 (A) and Murchison (M) amino-acid distributions from that of terrestrial protein families (o) by as much as 1–4 σ along both dimensions. Six of the seven Murchison samples form a cluster in the lower left quadrant distinct from both the protein and the Allan Hills meteorite and ice samples.

EVIDENCE FOR ANCIENT LIFE IN MARS METEORITES: LESSONS LEARNED. D. S. McKay, Mail Code SN, NASA Johnson Space Center, Houston TX 77058, USA (david.mckay@jsc.nasa.gov).

The lines of evidence we first proposed [1] as supporting a hypothesis of early life on Mars are discussed by Treiman [2], who presents pros and cons of our hypothesis in the light of subsequent research by many groups. Our assessment of the current status of the many controversies over our hypothesis is given in Gibson et al. [3]. Rather that repeat or elaborate on that information, I prefer to take an overview and present what I think are some of the "lessons learned" by our team in particular, and by the science community in general, as a result of the martian meteorite studies.
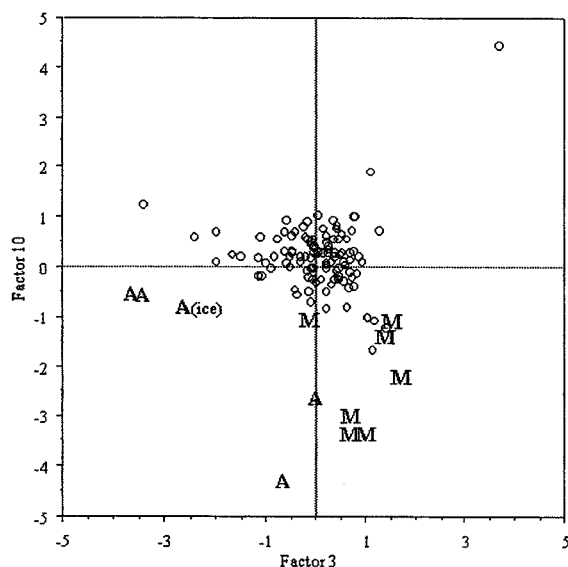
1. Mars meteorites are more complicated than we thought. Returned Mars samples are likely to be more complicated than we can imagine.

First, we have learned that ALH 84001 is an exceedingly complex rock that has withstood multiple shock and heating events (Treiman — meteoritics). It is an igneous rock with an overprint of impact features and secondary alteration, some of which is high temperature and some of which is low temperature (Gooding, Wentworth). The time and place of the low-temperature alterations are not well understood. Some may have occurred on Mars, and some may have occurred in Antarctica. One of the first lessons is that, at least for Antarctic meteorites, it is very difficult (but not impossible) to separate indigenous features from features acquired in Antarctica or the laboratory. However, it adds enormously to the task of reconstructing the histories of these meteorites. For returned Mars rocks, we will be dealing with samples from a planet whose geologic history is only poorly understood, whose impact, volcanic, sedimentary, metamorphic, and weathering processes are major mysteries. The returned samples are likely to show the effects of any one of these processes and may show the effects of all of them. And that's before we consider the possible effects of living systems. Unless we are extremely careful, we may also have alteration and contamination acquired during sampling, return, unloading, and initial processing. Then we are faced with a situation analogous to the Antarctic contamination problem.

2. We need better and more reliable biomarkers.

The problem with ALH 84001 is not the lack of potential biomarkers. It clearly has *potential* biomarkers, including organic compounds (PAHs, amino acids, and kerogenlike forms), carbonates, magnetites, sulfides, and fossillike forms. The problem is that we do not understand any of these biomarkers well enough to be confident that the properties of these features in ALH 84001 truly indicate life-related processes as opposed to strictly nonbiologic processes. Are the minerals precipitated by strictly inorganic chemistry, or are they precipitated with the aid of living organisms or organic compounds derived from living organisms? Are the PAHs and amino acids all derived from living systems, or were they generated by inorganic processes? (This is a separate question from possible Antarctic contamination.) Are the fossillike morphologies truly formed from microbes and their products, or are they formed by nonbiologic precipitation? Is the extreme C-isotopic fractionation a result of biologic processing? All these features are present in ALH 84001. But do we understand their properties and occurrences well enough to be confident which are true biomarkers and which are impostors? I think the answer is no. Before we bring samples back from Mars, we must have in a database, a set of tested, reliable, and certified biomarkers with well-documented distinguishing properties so that we can search for and describe these biomarkers in the returned samples and use them to answer unequivocally the question of whether or not there is evidence for life in these Mars samples. We need to be confident that the biomarkers we use cannot be formed by any conceivable nonbiologic process. We also need to decide whether a single biomarker is sufficient or whether we need several. Conversely, we need to decide whether the absence of known biomarkers is sufficient to eliminate the possibility of Mars life.

3. We need ways to date secondary processes.

It has been extraordinarily difficult to date the age of the carbonate pancakes in ALH 84001. No one has attempted to date the multiple shock and heating events recorded in this sample. The formation age of the magnetites, Fe sulfides, gypsum, and other secondary minerals is simply not known. If we could date their formation ages, we would have a better understanding of the rock history, the possibility that some are biomarkers, and even where they were formed. Returned Mars rocks (as well as samples from Europa, Titan, Io, etc.) are likely to also have both primary features and secondary features, and telling them apart and determining their formation and alteration timetables becomes very important to understanding their history. Primary crystallization age dating, while important, is not the only game in town.

4. A robotic mission analyzing ALH 84001 would have totally missed the data, the hypothesis, and the whole controversy.

If we had sent a mission to Mars and that mission encountered ALH 84001 on the surface and analyzed it with the Pathfinder/Sojourner instruments or the instruments proposed for subsequent lander missions, it is likely that the data and observations would not have included any of the major lines of evidence we and others have described in this rock: PAHs and their location and profile, submicrometer minerals of several types, carbonate pancakes of widely ranging mineral, elemental, and isotopic compositions, and small microfossil-like features. Furthermore, without the ALH 84001 experience, it is unlikely that a rock with a basaltic composition and obvious igneous texture would even be considered as a possible site for microbial life forms. None of the data that has caused the controversy about ALH 84001 comes from the bulk major-element composition or the major mineralogy. If we only had that data, however accurate, we would likely have missed what we consider to be the most interesting features of this rock.

This is not to criticize the flight instrument packages, but to point out how subtle and small the features are, how important their spatial locations are within the rock, and how difficult it is to analyze for them. Clearly, the entire ALH 84001 controversy could only come from analysis of returned rocks with complex state-of-the-art laboratory equipment.

5. It is sometimes difficult to either prove or disprove a hypothesis.

Our original hypothesis was that several observed features in ALH 84001 could all be reasonably explained by the presence of early life on Mars. This was a hypothesis, and the original paper was filled with qualifiers. The hypothesis, was based on circumstantial evidence or scientific observations of several different types, and the hypothesis seemed to explain all of the evidence with a single kind of event, namely the presence in the rock of microbial activity. Many other investigators have been able to reproduce our original data, although others have added a number of new kinds of data to our original observations. Only in one or two cases have completely contradictory data been reported.

Refuting one line of circumstantial evidence supporting a hypothesis (by either showing that the data were wrong or that the proposed explanation can be replaced by a clearly better one) does not mean that the hypothesis is wrong; it simply means that that line of circumstantial evidence is incorrect. While it may weaken the hypothesis, it does not invalidate it. Only when all proposed lines of evidence supporting a hypothesis are refuted can that hypotheses be considered wrong (and wrong hypotheses may benefit scientific progress as much as right ones). A hypothesis can be also be considered wrong if none if its predictions are correct.

Conversely, the hypothesis can only be proved to be correct when either multiple kinds of circumstantial evidence become overwhelming, or a single line of evidence is so strong that it cannot

be explained by any alternate hypothesis — in other words, a smoking gun. A hypothesis can be greatly strengthened if its predictions are subsequently shown to be true. In our view, the ALH 84001 hypothesis of early life on Mars is still valid and has neither been adequately refuted nor adequately proved. The people who propose a hypothesis are not necessarily responsible for proving it because they may not have the correct tools, technical specialties, or samples, although they may have a moral obligation to either try to prove it or to refute it themselves. For ALH 84001 and the other martian meteorites, the question is still open and may not be answered until martian samples are returned by a space mission.

When we do get samples back, we should expect that a number of different hypotheses will be advanced by various investigators, because, as discussed above, the rocks (and soils) may be very complex and may record many overlapping processes. The hypotheses advanced to explain their features may even be mutually exclusive and contradictory. But we should concentrate on the data, give all the hypotheses a fair hearing, and attack the problems, not the people.

References: [1] McKay et al. (1996) *Science, 273,* 924. [2] Treiman, this volume. [3] Gibson et al., this volume.

KEY RESEARCH: MARTIAN METEORITES AND THEIR RELATIONSHIPS TO PLANETARY GEOLOGY AND PERHAPS BIOLOGY.

H. Y. McSween Jr., Department of Geological Sciences, University of Tennessee, Knoxville TN 37996-1410, USA (mcsween@utk.edu).

Introduction: Allan Hills 84001 and other SNC meteorites are bewilderingly complex rocks that have generated as many questions as answers. Here are some remaining questions with profound implications for the geological and perhaps biological evolution of Mars.

Whence Carbonates? The paleoenvironment of carbonate formation in ALH 84001 remains disputed. Various authors have advocated reactions between the rock and aqueous hydrothermal fluids [1] or hot metasomatic CO_2-rich fluids [2], precipitation by martian organisms [3], recrystallization during shock [4], or precipitation from evaporating brines percolating through subsurface fractures [5]. Definition of the full alteration mineral assemblage might provide a crucial constraint on formation mechanisms. Formation temperature and the temperature range remain critical parameters in assessing the plausibility of biologic arguments. Definitive radiometric ages of the carbonates have not yet been determined, and there remains some controversy about how many carbonate depositional events occurred [6]. The existence of significant carbonate deposits formed by collapse of a CO_2-rich atmosphere has implications for the planet's climate history. This may be addressed by TES orbital data and soil mineralogy determined by landers. The discovery of evaporites (e.g., carbonates, sulfates, and halides) on Mars, as well as mineralogic, chemical, isotopic, and fluid inclusion studies of salts in other SNC meteorites [7], might also bear on this question. Identification and characterization of terrestrial analogs for ALH 84001 carbonates are sorely needed.

How Well Can We Recognize Biochemicals, Biominerals, and Microfossils? Is it possible to unambiguously distinguish extraterrestrial biomarkers from terrestrial contaminants and artifacts? Most of the ALH 84001 organic matter appears to be contamina-

tion in the Antarctic, although this remains disputed [8], and an experiment is needed to determine if a small preterrestrial C component is organic or merely undigested magnesite. Continued studies of other SNC meteorites or martian rocks may reveal indigenous organics, and future work should focus on biologically relevant organics rather than PAHs. Microanalytical techniques for separating and identifying compounds and measuring their isotopic composition and optical activity are needed. The nature of a proposed martian surface oxidant and its ability to destroy organic materials must be understood from *in situ* measurements of martian soil. Some progress in recognizing biogenic minerals similar to putative biominerals in ALH 84001 has been made, and the interrelationships between morphologies, internal structures, and mechanisms of growth in biominerals and inorganic minerals that resemble them must be pursued [9]. The biology of nanoscale bacteria remains contentious [10], as does the possibility of their fossilization. Are there stable isotope biomarkers, such as S [11], or perhaps combinations of isotope biomarkers that might be analyzed in martian rocks? What is the mineralogy of the purported nanofossils, and what features are artifacts of sample preparation [12]? The search for biomarkers on the surface of Mars will require the location of promising sites (clastic sediments, evaporites, and hot springs deposits) by orbiters, surface mobility, the identification of rocks most likely to preserve biomaterials (phosphates, silica?), and significant technical advances for *in situ* analysis. Most of these studies will probably necessitate returned, uncontaminated samples.

How Much Water? The existence of liquid water on the ancient surface of Mars is unquestioned, but its amount and timing are disputed. Estimates of the amount of water outgassed from the martian interior vary over many orders of magnitude, with geochemical estimates [13] being systematically smaller than geological estimates [14]. Geochemical estimates might be improved by more quantitative understanding of initial atmospheric gas abundances and their behavior during hydrodynamic escape and impact erosion, estimation of the water contribution made by comet accretion, and experimental determination of magmatic conditions required to stabilize OH-deficient kaersutite. The global inventory of water on Mars is based on an accretion model using SNC meteorites [15], which does not appear to be consistent with new estimates of the planet's moment of inertia [16]. Although considerable water can potentially be stored within pore spaces in the martian crust [17], the amount actually present and its geographic and vertical distributions are unknown. Because of a lack of information on soil mineralogy, the amount of water stored in the regolith is also unknown. A refined geochemical model for Mars, as well as high-resolution orbital images for studies of terrain softening, direct orbital measurements of H distributions, and determination of soil mineralogy are needed. An accepted crater stratigraphy, perhaps anchored to absolute time by the identification of SNC launch sites, might allow determination of when water was abundant. Also, the relation of surface water to past climate needs to be resolved.

What Is the History of Biogenic Elements and Compounds on Mars? The histories of H, C, O, N, and S are probably best revealed by their isotopic compositions. Measurements of SNC O isotopes reveal the existence of two reservoirs (the atmosphere and lithosphere), but there is disagreement about the cause of atmospheric fractionation [18]. However, concentration of heavy H, C, and N isotopes [19] not affected by photodecomposition of ozone may favor an escape mechanism. Incorporation of isotopically heavy H and O into SNC minerals suggests the existence of cycles that

allow communication between the atmosphere, hydrosphere, and lithosphere, but the way such cycles work is unclear. Fractionation of S isotopes has also been documented in ALH 84001 and nakhlites [11], and recycling of surface S into the interior, perhaps by hydrothermal fluids, has been suggested. Mars Pathfinder data confirm earlier results suggesting sulfate is enriched in soils, and redox state may play a critical role in S fractionation. Isotopic fractionations due to inorganic processes must be understood before these systems can be used as biomarkers. The nature of any martian organic compounds, as well as the mineralogy of volatile elements, is virtually unknown. Understanding prebiotic chemistry must await detailed analyses by landers or sample return. Determining the redox states of Fe and Mn in surface materials is important because reduced forms may serve as a source of energy for organisms.

What Is the Geologic History of the Ancient Crust?   The ancient terrain of Mars, sampled only by one probably nonrepresentative meteorite, provides the geologic context for any potential life. The petrology of the ancient crust is likely to be complex, and it is not clear to what degree Mars Pathfinder rocks of andesitic composition might represent the composition of this crust. The ages of this crust are unknown because of uncertainty in cratering stratigraphy, but the 4.5-Ga age of ALH 84001 [20] was not expected. Mapping magnetic anomalies by Mars Global Surveyor might eventually provide a correlation tool. The impact history of ALH 84001 is complex and the number of impacts it has experienced is disputed [21]. However, a 4-Ga shock age for ALH 84001 suggests that Mars also experienced the late heavy bombardment [22]. The study of sedimentary and igneous strata is particularly important for reconstructing the geologic record. Crustal recycling has been discounted [23], but more geologic information is required to understand lithospheric origin and evolution, including inputs from materials cycled through the atmosphere. Some progress has been made in deciphering the composition and evolution of the crust, mantle, and core through studying SNCs [24] and by Mars Pathfinder [16,25], but much more needs to be done.

References: [1] Romanek C. S. et al. (1994) *Nature, 372,* 655–657; Valley J. W. et al. (1997) *Science, 275,* 1633–1638; Leshin L. A. et al. (1998) *GCA, 62,* 3–13. [2] Mittlefehldt D. W. (1994) *Meteoritics, 29,* 214–221; Harvey R. P. and McSween H. Y. (1996) *Nature, 382,* 49–51. [3] McKay D. S. et al. (1996) *Science, 273,* 924–930. [4] Scott E. R. D. et al. (1997) *Nature, 387,* 377–379. [5] McSween H. Y. and Harvey R. P. (1998) *Intern. Geol. Rev.,* in press; Warren P. H. (1998) *JGR, 103,* 16759–16774. [6] Treiman A. H. (1995) *Meteoritics & Planet. Sci., 30,* 294–302. [7] Gooding J. L. (1992) *Icarus, 99,* 28–41; Treiman A. H. et al. (1993) *Meteoritics, 28,* 86–97. [8] Bada J. L. et al. (1998) *Science, 279,* 362–365; Jull A. J. T. et al. (1998) *Science, 279,* 366–369; Clemett S. J. et al. (1998) *Faraday Disc.,* in press. [9] Bradley J. T. et al. (1996) *GCA, 60,* 5149–5155; Steele A. et al. (1997) *J. Micros., 189,* 2–7; Posfai M. et al. (1998) *Science, 280,* 880–883; Bradley J. T. et al. (1998) *Meteoritics & Planet. Sci.,* in press. [10] Nealson K. H. (1997) *Science, 276,* 1776. [11] Shearer C. K. et al. (1996) *GCA, 60,* 2921–2926; Greenwood J. P. et al. (1997) *GCA, 61,* 4449–4453. [12] Bradley J. T. et al. (1998) *Nature, 390,* 454; Barrat J. A. et al. (1998) *Science, 280,* 412–414. [13] Yung Y. L. et al. (1988) *Icarus, 68,* 462–480; Dreibus G. and Wänke H. (1987) *Icarus, 71,* 225–240; Scambos T. A. and Jakosky B. M. (1990) *JGR, 95,* 14779–14787; McSween H. Y. and Harvey R. P. (1993) *Science, 259,* 1890–1892. [14] Carr M. H. (1986) *Icarus, 68,* 187–216; Baker V. R. et al. (1991) *Nature, 352,* 589–594. [15] Wänke H. and Dreibus G. (1988) *Philos. Trans. R. Soc. London, A325,* 545–557. [16] Folkner W. M. et al. (1997) *Science, 278,* 1749–1752. [17] Clifford S. M. (1993) *JGR, 98,* 10973–11016. [18] Karlsson H. R. et al. (1992) *Science, 255,* 1409–1411; Farquhar J. et al. (1998) *Science, 280,* 1580–1582. [19] Wright I. P. et al. (1990) *JGR, 95,* 14789–14794; Watson L. L. et al. (1994) *Science, 265,* 86–90. [20] Nyquist L. E. et al. (1995) *LPS XXVI,* 106–107. [21] Treiman A. H. (1998) *Meteoritics & Planet. Sci.,* in press. [22] Ash R. D. et al. (1996) *Nature, 380,* 57–59. [23] Carr M. H. and Wänke H. (1992) *Icarus, 98,* 61–71. [24] Longhi J. (1991) *Proc. LPSC 19th, 19,* 451–464; Longhi J. et al. (1992) *Mars,* 184–208; McSween H. Y. (1994) *Meteoritics, 29,* 757–779; Lee D. and Halliday A. N. (1997) *Nature, 388,* 854–857. [25] Rieder R. et al. (1997) *Science, 278,* 1771–1774.

WHAT WERE THE MAJOR FACTORS THAT CONTROLLED MINERALOGICAL SIMILARITIES AND DIFFERENCES OF BASALTIC, LHERZOLITIC, AND CLINOPYROXENITIC MARTIAN METEORITES WITHIN EACH GROUP?   T. Mikouchi[1], M. Miyamoto[1], and G. A. McKay[2], [1]Mineralogical Institute, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan (mikouchi@min.s.u-tokyo.ac.jp), [2]Mail Code SN2, NASA Johnson Space Center, Houston TX 77058, USA.

Introduction: Twelve martian meteorites that have been recovered so far are classified into five groups (basalt, lherzolite, clinopyroxenite, dunite, and orthopyroxenite) mainly from petrology and chemistry [e.g., 1]. Among them, the dunite and orthopyroxenite groups consist of only one meteorite each (dunite: Chassigny, orthopyroxenite: ALH 84001). The basalt group is the largest group and consists of four meteorites (Shergotty, Zagami, EETA 79001, and QUE 94201). The lherzolitic and clinopyroxenitic groups include three meteorites each (lherzolite: ALH 77005, LEW 88516, and Y 793605; clinopyroxenite: Nakhla, Governador Valadares, and Lafayette). These meteorites within each group are generally similar to the others, but none of them is paired with the others. In this abstract, we discuss the major factors that controlled mineralogical similarities and differences of basaltic, lherzolitic, and clinopyroxenitic meteorites within each group. This may help in understanding their petrogenesis and original locations on Mars in general.

Basalt: Pyroxene and maskelynite (shocked plagioclase glass) are major minerals in the basaltic martian meteorites. Pigeonite and augite show two distinct textural occurrences of chemical zoning patterns. In Shergotty and Zagami, pigeonite and augite are usually present as separate grains that are zoned from a Mg-rich core to an Fe-rich rim, respectively. Both pigeonite and augite usually have homogeneous cores, considered to be cumulus phases. Zagami pyroxenes are not zoned as extensively as those in Shergotty, but their mineralogy is quite similar. On the other hand, pigeonite and augite in EETA 79001 and QUE 94201 are both present in individual composite grains. These pyroxenes are complexly zoned; typically the cores are Mg-rich pigeonites, mantled by Mg-rich augite, and the rims are Fe-rich pigeonite. Maskelynite compositions also correspond to differences in pyroxene zoning. Maskelynites in Shergotty and Zagami are more alkali-rich than those in EETA 79001 and QUE 94201, suggesting later crystallization.

Shergotty and Zagami maskelynites indicate growth from the surrounding pyroxene walls in interstitial melts, whereas EETA~79001 and QUE 94201 normally grew from core to rim. FeO in the maskelynite cores is different between Shergotty and Zagami (0.5–0.6 wt%) and EETA 79001 and QUE 94201 (0.3–0.4 wt%). The lower Fe content of EETA 79001 and QUE 94201 maskelynite cores reflects earlier crystallization of plagioclase. Aluminum zoning in pyroxenes also marks the beginning of plagioclase crystallization. Decrease of the Al/Ti of pyroxenes further suggests plagioclase crystallization, and the Al-Ti distribution shows a clear difference between Shergotty and Zagami on the one hand and EETA 79001 and QUE 94201 on the other. Such mineralogical differences of EETA 79001 and QUE 94201 from Shergotty and Zagami can be understood by undercooling of the magmas from which they have crystallized [e.g., 2]. We believe that Shergotty and Zagami experienced only slight undercooling, resulting initially in cotectic growth of pigeonite and augite, later joined by plagioclase. On the other hand, EETA 79001 and QUE 94201 experienced significant undercooling of their melts, and their crystallization sequence was pigeonite, augite, plagioclase, and then Fe-rich pigeonite, with each phase crystallizing metastably alone, because the melt compositions did not follow the equilibrium phase boundaries.

Lherzolite: Pigeonite, olivine, augite, maskelynite, and chromite are major phases in the three lherzolitic martian meteorites. Texturally, the three lherzolites are very similar and are characterized by the presence of two distinctive textural patterns: poikilitic and nonpoikilitic. In the poikilitic area, a large pigeonite oikocryst encloses smaller rounded olivine and euhedral chromite grains. The pigeonite oikocryst has augite bands, usually along its rim. The pigeonite oikocryst is weakly zoned from core to rim ($En_{77}Fs_{19}Wo_4 \sim En_{65}Fs_{20}Wo_{15}$). Pyroxene in the non-poikilitic area is mainly pigeonite that is more Ca-Fe-rich ($En_{65}Fs_{28}Wo_7 \sim En_{58}Fs_{26}Wo_{16}$) than that in the poikilitic area. Olivine is brown to yellowish in both textures. Yamato 793605 olivines in the nonpoikilitic area are more Fe-rich (average: Fa_{34}) than those in the poikilitic area (average: Fa_{31}), and the Fa content shows bimodal distribution, which is also observed in the LEW 88516 olivines (Fa_{25-36}). Allan Hills 77005 olivines (Fa_{23-30}) are clearly more Mg-rich than those of LEW 88516 and Y 793605, and mineral compositions are almost identical between the two different textures. Olivine usually contains magmatic inclusions (up to a few micrometers in size) consisting of Al-Ti-rich pyroxene, Si-rich glass, and chromite. Maskelynites are rare in the poikilitic area but are abundant in the nonpoikilitic area. Maskelynites in both textures have nearly identical compositions ($An_{55}Ab_{44}Or_1 \sim An_{45}Ab_{52}Or_3$). Minor element chemical zoning of maskelynite is unique. Iron oxide in the core is about 0.5 wt%. It first drops down to 0.2 wt% and again slightly increases to 0.4 wt% at the edge, with some decrease and increase. Chromites show chemical zoning toward the ulvöspinel-rich rim. Thus, the mineralogy of all three lherzolitic martian meteorites is very similar in contrast to the basaltic martian meteorites, which show a variety of mineralogical differences. This suggests that all three lherzolitic meteorites generally followed similar crystallization and thermal histories, although the degree of late-stage annealing or cooling rates was different and changed olivine compositions in different degrees [e.g., 3].

Clinopyroxenite: Nakhla, Governador Valadares, and Lafayette mainly consist of 80–90% cumulus augite and 5–10% olivine in plagioclase-rich mesostases, and their texture is remarkably similar to one another. Mineral compositions are also similar, suggesting similar history in general. Augite is fairly homogeneous in composition, and the core compositions of augite are identical ($En_{39}Fs_{23}Wo_{38}$) among the three meteorites. They are chemically zoned from the Mg-rich cores to the Fe-rich rims and overgrowth of low-Ca pyroxene is observed at some edges. Chemical zoning of augite in Nakhla and Governador Valadares shows more Fe-rich compositions than that of Lafayette. The bulk composition of overgrowth in Lafayette pyroxene is also more Mg-rich and Ca-poor than the other two meteorites. Olivines in Nakhla and Governador Valadares exhibit chemical zoning in both major and minor elements, whereas that in Lafayette is almost homogeneous. Lafayette olivine also differs from those of Nakhla and Governador Valadares because symplectic inclusion composed of complex intergrowth of augite and magnetite is absent in Lafayette olivine. Thus, overall mineralogy of the three meteorites is similar, but microstructures in pyroxenes and olivines are slightly distinct. These differences can be explained by different degrees of late-magmatic and subsolidus diffusion [e.g., 4]. That is, Nakhla and Governador Valadares experienced fairly fast subsolidus and late-magmatic cooling. As a result, they preserved both chemical zoning and symplectite in olivine, and pyroxene became more Fe-rich. On the other hand, Lafayette experienced slightly slower late magmatic cooling, which erased symplectites and rehomogenized olivine.

Discussion and Summary: It is clear that each group has generally similar mineralogy within each group, but is distinct from the other groups. Such a similarity within the same group is especially remarkable for lherzolitic and clinopyroxenitic groups. This is also supported by both crystallization and exposure age data [e.g., 5,6]. Unlike them, the basaltic group shows fairly diverse mineralogy within the group, although they generally share similar crystallization and exposure ages [e.g., 6,7]. Such a diversity can be understood by different degrees of undercooling of the magma, as explained above. Although it is unlikely that all four basaltic rocks share a common parent magma, their compositions were probably similar. We believe that these basaltic rocks formed near the surface of Mars, and this might have caused large differences in temperature gradient during cooling even though the burial depths were not so different. That is why the basaltic group shows fairly diverse mineralogy. The lherzolitic and clinopyroxenitic group would be deeper in origin than basaltic rocks, at least in the early stages of their crystallization, and thus undercooling effects of magmas were probably minor. The slight mineralogical difference within each group is most evident in olivine compositions. This is probably because atomic diffusion rates in olivine are much faster than those in pyroxene and plagioclase. Because most olivines in these groups still preserve chemical zoning, they originated from near the surface, at least in the late stages of their crystallization history. Pyroxene preserves the initial composition at the core. Although the parent-magma compositions of these groups were distinct from each other, the sequence of crystallization location — that is, from deep to shallow — would be similar. The basaltic group started crystallization in shallow locations from the beginning, and undercooling of magma was a major factor that controlled their overall crystallization history. In contrast, lherzolitic and clinopyroxenitic meteorites originally started crystallization at deep positions (and thus nearly free from the undercooling effects of early-stage magmas). However, after they moved to near-surface locations at their last stages, late-stage cooling rates or thermal annealing affected them a lot. Although such effects would also occur in the basaltic

meteorites, the influence was not so major in the present phases because they do not contain olivine.

Acknowledgments: This study was partly supported by Moritani Science Foundation.

References: [1] McSween H. Y. Jr. (1994) *Meteoritics, 29,* 757–779. [2] Mikouchi T. et al. (1998) *Meteoritics & Planet. Sci., 33,* 181–189. [3] Harvey R. P. et al. (1993) *GCA, 57,* 4769–4783. [4] Harvey R. P. and McSween H. Y. Jr. (1992) *GCA, 56,* 1655–1663. [5] Nakamura N. et al. (1982) *GCA, 46,* 1555–1573. [6] Eugster O. et al. (1997) *GCA, 61,* 2749–2757. [7] Nyquist L. E. et al. (1995) *LPS XXVI,* 1065–1066.

GENESIS OF THE MARS PATHFINDER "SULFUR-FREE" ROCK FROM SNC PARENTAL LIQUIDS. M. E. Minitti and M. J. Rutherford, Department of Geological Sciences, Brown University, Providence RI 02912, USA.

Introduction: In July 1997, the Mars Pathfinder mission touched down in the Ares Valles region of Mars to begin its scientific study of the Red Planet. The Sojourner rover used its onboard cameras and α-proton X-ray spectrometer (APXS) to study the soils and rocks of the landing site. Currently, preliminary analyses of five rock samples and six soil samples have been completed. They are based only on the spectra obtained from the X-ray portion of the APXS [1]. When plotted on oxide vs. S diagrams, the Pathfinder soil and rock data fall on a line extending between the soil data, which fall at high S contents, and the rock data, which fall at lower S contents. Because the solubility of S in basaltic melts is ≤ 0.2 wt% [2], the range of S contents in the rocks implies that each rock analysis has a differing amount of soil component. The rock compositions, therefore, fall along a mixing line between the soils and a hypothetical "S-free" rock obtained by extrapolating the regression line through the soil and rock data back to 0 wt% S [1]. The composition of the S-free rock is contained in Table 1. Accepting the argument that the Pathfinder rocks are igneous, as done by [3],

the S-free rock may be classified by its SiO_2 and alkali content as an andesite. The S-free rock has the characteristic low Al_2O_3 and high FeO content expected from martian igneous rocks [3].

According to [3], the compositions of the Pathfinder rocks and the S-free rock fall along a tholeiitic trend of andesite formation, which is characterized by strong FeO enrichment without SiO_2 enrichment until late in the crystallization sequence. Eventual Fe-Ti oxide crystallization pushes tholeiitic liquids to higher SiO_2 and lower FeO contents, thus creating andesitic and rhyolitic liquids [4]. Terrestrial andesites formed via the tholeiitic differentiation trend are associated with the low-pressure crystallization of basaltic parent liquids, as occurs in Iceland [5] or the Galapagos Spreading Center [6]. Thus, it could be argued that the Pathfinder rocks developed through low-pressure fractional crystallization of a tholeiitic basaltic parent.

To determine the nature of the basaltic parent liquid and the evolutionary path it followed to produce the S-free rock, McSween et al. [3] attempted to reproduce the composition of the S-free rock via two separate pathways. First, they [3] calculated a liquid line of descent for a basaltic SNC intercumulus melt in Shergotty [7] (Table 1), using the MELTS program [8]. The liquid line of descent produced by the MELTS calculation illustrates that the Shergotty starting composition does not lead to the S-free rock composition. Therefore, it was concluded that SNC liquids like the Shergotty intercumulus melt could not produce the analyzed rocks of the Pathfinder landing site under dry, low-pressure conditions. Second, McSween et al. [3] applied the liquid line of descent relevant to development of the Galapagos Spreading Center andesitic liquids [6] to the S-free rock composition. According to [3], the experimentally determined Galapagos liquid line of descent, which traces the evolution of a dry, basaltic parent liquid during fractional crystallization, successfully reproduces many of the compositional characteristics of S-free rock. Therefore, it was concluded that the conditions associated with the development of the Galapagos liquid line of descent are relevant to the formation of the S-free rock, most notably the dry nature of the basaltic starting material.

TABLE 1. Relevant melt and rock compositions.

Oxide	Shergotty[1]	A*[2]	POO.82N2[3]	MS-1[4]	S-free Rock[5]
SiO_2	50.8	50.33	51.35	60.78	62.0 ± 2.7
Al_2O_3	8.0	8.16	13.21	12.27	10.6 ± 0.7
FeO*	19.8	19.87	13.43	10.82	12.0 ± 1.3
MgO	7.7	7.39	6.12	2.74	2.0 ± 0.7
CaO	9.7	8.95	10.74	6.82	7.3 ± 1.1
Na_2O	1.5	1.71	2.30	3.15	2.6 ± 1.5
K_2O	0.2	0.43	0.10	0.91	0.7 ± 0.2
TiO_2	1.0	1.75	2.14	1.31	0.7 ± 0.1
P_2O_5	0.9	0.50	0.18	0.73	na
MnO	0.5	0.52	na	0.43	na

na = analysis not available.

[1] Shergotty intercumulus melt composition [7].

[2] Experimental starting material based on calculated Chassigny parent magma [10]; composition of fused glass was determined via electron microprobe analyses (see text).

[3] Composition of experimental starting material used by [6].

[4] Preliminary experimental glass composition from run at P = 200 bar, $P_{total} = P_{H_2O}$, T = 1050°C; composition normalized to 100%.

[5] Sulfur-free rock composition of [1], normalized to 98%.

This initial work raises two interesting questions. The parent basalt for the Galapagos liquid line of descent is a high-Al_2O_3, low-FeO basalt unlike that expected from a low-Al_2O_3, high-FeO martian mantle proposed by [9]. Thus, while the Galapagos liquid line of descent leads to liquids resembling the S-free rock composition, the composition of the starting basalt is not in keeping with the basaltic liquids calculated for known martian basalts [e.g., 10]. Second, the liquid line of descent of the tested SNC melt was calculated with MELTS and, by nature of the program, was thereby a dry liquid line of descent. Water, though, has played a prominent role in the development of surface features on Mars [11], including the Mars Pathfinder landing site. The presence of water in martian magmas is indicated by kaersutitic hornblende found within melt inclusions in four SNC meteorites and a biotite found in a Chassigny melt inclusion [10]. Thus, a dry martian parent magma may not be appropriate to the development of the S-free rock composition. Water has a known and significant effect on phase equilibria of crystallizing melts, as illustrated by the differences in the liquid lines of descent of hydrous and anhydrous experiments on a Galapagos Spreading Center basalt [12]. Thus, its presence in a SNC melt may make it possible to derive the S-free rock from a martian basaltic parent melt.

Experimental: To investigate if the addition of water to a basaltic SNC melt could produce a liquid line of descent leading to the S-free rock composition, we conducted experiments on a SNC basaltic parent magma, A*, whose composition was determined for Chassigny [10]. This starting composition has the characteristic high-FeO and low-Al_2O_3 concentrations associated with martian igneous rocks (Table 1). A* closely resembles other experimentally and theoretically determined SNC parent-magma compositions, including the starting SNC magma composition used by [3] in their MELTS calculations (Table 1). For each experimental run, an oxide mix with the A* composition was placed, with sufficient water to saturate the melt, in a sealed AgPd tube. This sample tube was then sealed in a larger AgPd tube with water and a QFM buffer assembly. All experiments were buffered at QFM, as this is the f_{O_2} believed to be most representative of the conditions on Mars under which the SNC meteorite magmas crystallized [10]. Experiments were run at 200 bars in TZM pressure vessels using a mixture of Ar and CH_4 gases to provide the pressure. Run temperatures were between 1089°C and 975°C. Experiments were water quenched at pressure, and before thin sections were made of the experimental products, a grain mount of the buffer was made to ensure that the experiment maintained QFM. In addition to the hydrous, 200-bar experiments, 1-atm experiments buffered at QFM were also conducted on A* in order to experimentally investigate the evolution of the * magma under dry conditions. The 1-atm experiments were run in Fe_3O_4-saturated $Au_{90}Pd_{10}$ tubes in evacuated SiO_2-glass tubes.

Major-oxide analyses of the experimental products were conducted on the Brown University Cameca Camebax electron microprobe. Analysis conditions included a 15-kV accelerating voltage, a 10-nA defocused beam for glasses, and a 15-nA focused beam for oxide and silicate analyses. During glass analyses, the electron beam was blanked between analyses and a Na loss program [13] was utilized to obtain Na_2O concentrations.

Preliminary Results: In the hydrous, 200-bar experiments, crystallized phases include pigeonite and an intermediate-Ca pyroxene. Magnetite is also found in experiments run below 1075°C.

The compositions of the residual liquids from the suite of water-saturated, 200-bar experiments define a liquid line of descent that approaches the S-free rock composition. A sample composition of one of the experimental residual liquids is contained in Table 1. Thus, the hydrous experiments demonstrate that the addition of small amounts of water (1.0–1.5 wt%) to a crystallizing SNC magma yields residual liquids that resemble the S-free rock composition. While the exact composition of the S-free rock has not been experimentally obtained, we expect that variations in P_{H_2O}, P_{total}, f_{O_2}, and bulk composition will lead to a residual liquid with the S-free rock composition. Thus, reproduction of the S-free rock from a SNC parent magma does appear possible via near-surface crystal-fractionation processes.

References: [1] Rieder R. et al. (1997) *Science, 278,* 1771. [2] Carroll M. R. and Webster J. D. (1994) *Rev. Mineral., 30,* 232. [3] McSween H. Y. Jr. et al. (1998) *LPS XXIX,* Abstract #1054. [4] Hess P. C. (1989) *Origin of Igneous Rocks,* Harvard Univ., Cambridge, 336 pp. [5] Carmichael I. S. E. (1964) *J. Petrol., 5,* 435. [6] Juster T. C. (1989) *JGR, 94,* 9251. [7] Hale V. P. S. (1997) *LPS XXVIII,* 405. [8] Ghiorso M. S. and Kelemen P. B. (1987) *Geochem. Soc. Spec. Pub., 1,* 319. [9] Wänke H. and Dreibus G. (1988) *Philos. Trans. R. Soc. London, A545.* [10] Johnson M. C. et al. (1991) *GCA, 55,* 349. [11] Carr M. H. (1981) *The Surface of Mars,* Yale Univ., New Haven, 226 pp. [12] Spulber S. D. and Rutherford M. J. (1983) *J. Petrol., 24,* 1. [13] Nielsen C. H. and Sigurdsson H. (1974) *Am. Mineral., 66,* 547.

RECOGNIZING LIFE AND ITS EVOLUTION THROUGH BIOMARKERS.

J. M. Moldowan, Department of Geological and Environmental Sciences, Stanford University, Stanford CA 94305-2115, USA (moldowan@pangea.stanford.edu).

Biomarkers are molecular fossils found in sedimentary rocks and petroleum. Like fossils, they are recognized as remnants of enzyme-mediated biosynthesis dictated by genetic code. They cannot be confused with abiogenic molecules, because they are produced in abundances that far exceed their relative chemical stabilities.

On a broad scale, evolution can be followed in the biomarker record as chemically more complex molecules are biosynthesized by more advanced taxa. Numerous correlations have been established between various taxa and biomarkers. Kingdoms of organisms can be differentiated by hopanes for prokaryotes, extended head-to-head isoprenoids for archea, steranes for protista, and various terpanes for plantae. At lower taxonomic levels, relationships include dinoflagellates with dinosteroids, porifera (sponges) with 24-isopropylcholestane, and angiosperms (flowering plants) with oleanane. At the species level, examples include *Botryococcus braunii* and *botryococcane* and *Gloeocapsomorpha prisca* and a specific assemblage on odd C-numbered n-alkanes below C_{19}. Such taxon specific biomarkers can be used to trace the origins of life and its evolutionary lineages.

This molecular information supports fossil records and provides important evidence for life forms where anatomical remains are ambiguous or absent. Recent examples include (1) the prediction of an extended record of Vendian porifera before Vendian sponge spicules were discovered, and (2) identification of ancestral dinoflagellates among Lower Cambrian acritarchs having partial dino-

flagellate morphology and dinoflagellate biomarkers, extending the widely accepted fossil record (Middle Triassic) by ~280 m.y.

Biomarker assemblages, like microfossils, provide a window into the depositional environment of sedimentary rocks. Factors such as redox potential, acidity, salinity, and thermal maturity influence biomarker fingerprints; therefore, biomarkers can be used to determine these specific characteristics of the depositional environment.

POSSIBLE MICROFOSSILS (WARRAWOONA GROUP, TOWERS FORMATION, AUSTRALIA, ~3.3–3.5 Ga).   P. A. Morris[1], S. J. Wentworth[2], C. C. Allen[2], and D. S. McKay[3], [1]University of Houston–Downtown, 1 Main Street, Houston TX 77002, USA (smithp@dt.uh.edu), [2]Lockheed Martin, Houston TX 77258, USA, [3]NASA Johnson Space Center, Houston TX 77058, USA.

Introduction: Early in the twentieth century there were reports of Archean stromatolite-like structures that were similar to organic rich stromatolites from the base of the Cambrian (600 m.y.) [1,2]. It was not until the latter half of this century that fossilized Archean-age (3.9–2.5 Ga) life forms were found in the Fig Tree Formation of South Africa and the Towers Formation of Australia [3–7]. Some of the ancient stromatolites contained streaks and clots of kerogen, pyrite grains, remnants of microbial cells, and filaments that represented various stages of preservation, while others appeared to lack fossils [8,9]. A set of physical criteria was established for evaluating the biogenicity of these Archean discoveries [10]: (1) rocks of unquestionable Archean age; (2) microfossils indigenous to Archean sediments; and (3) microfossils occurring in clasts that are syngenetic with deposition of the sedimentary unit. In the case of bedded cherts, the fossils should predate the cherts; (4) the microfossils are biogenic; and (5) replicate sampling of the fossiliferous outcrop firmly demonstrates the provenance of these microfossils.

Sample 002 from the Precambrian Paleobiology Research Group (PPRG) was examined. This stromatolitic carbonaceous chert contains microbial remains that meet the established criteria [10]. Using a scanning electron microscope (SEM), we have analyzed the morphologies and chemistry of these possible microbial remains [7,10].

Methods: Freshly fractured chips and petrographic thin sections were analyzed with an Oxford ISIS energy-dispersive spectrometer (EDS) and a Phillips SEM XL 40 FEG (SEM).

Discussion: Scanning-electron microscope and EDS analysis of sample 002 indicates the presence of hematite, quartz, barite, carbonate minerals, including Fe carbonate (siderite), and kerogen [11,12]. The kerogens are organic derivatives.

Sample 002 includes several morphologic features clearly indigenous to the sample that may have been produced by biologic activity. These features include several sizes of spheres, rods the size of bacteria, ellipsoids, filaments, and smooth blanketing material resembling present-day biofilms. Each of these features are rich in both Fe and C compared to the surrounding quartz matrix. X-ray element maps of two of the largest spheres (16–27 μm, 5–12 μm) indicate that the Fe and C are localized within the spheres, but are nearly absent from the surrounding quartz matrix (Figs. 1–3). Iron is known to be important in microbial preservation [13].

The spheres are intimately intergrown with the quartz matrix and are clearly indigenous to the sample (Fig. 1). They display a rough,
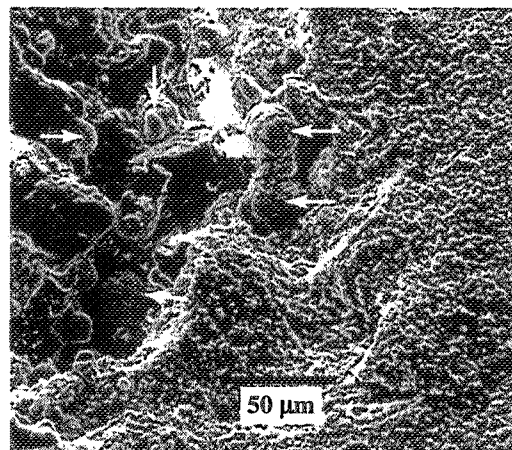

Fig. 1.   Scanning-electron microscope image of X-ray element maps for Fe and silica. Arrows indicate some of the biogenic spheres.

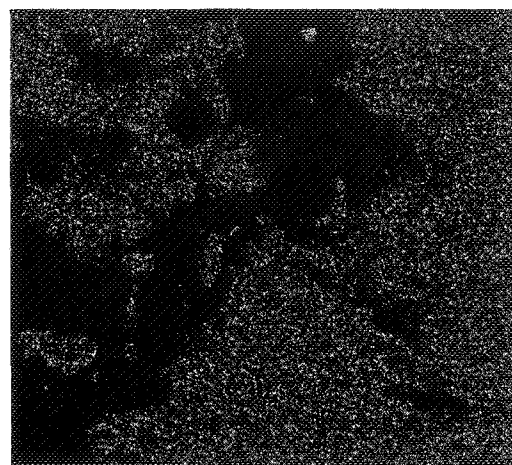Fig. 2.   X-ray element map for Fe. Iron is found in association with biogenic spheres indicated in Fig. 1.

Fig. 3.   X-ray element map of Si. The areas occupied by the biogenic spheres lack this element.
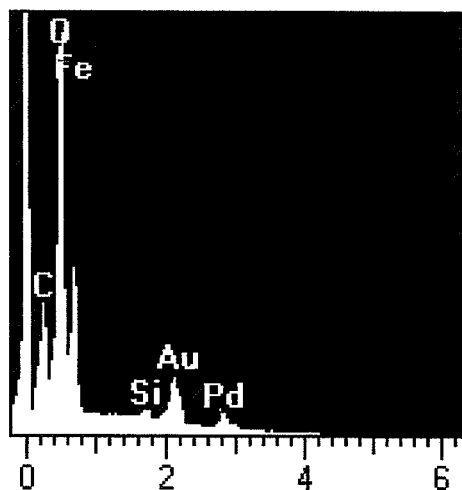
Fig. 4. Energy-dispersive spectrometer analysis of biogenic spheres at low kV. Notice the relative abundance of C, O, and Fe (Fe/L) in relation to Si. The specimen was coated with Au and Pd for 30 s.

uneven texture. The chemical composition of these spheres is compatible with that of siderite. Siderite can be an indicator of microbially induced precipitation [14]. These spheres are within the size range and appear to be identical to those accepted as biogenic by Schopf [6,7,10].

Energy-dispersive spectrometer analysis of smaller spheres that are within the size range of bacterial cocci, as well as filaments and the smooth, blanketing morphology reveal a similar composition — that is, the presence of significant levels of C and Fe and the absence of significant levels of Si. Comparison with the surrounding matrix indicates that although C may occasionally be present in the form of relict Ca carbonate minerals, and Fe may occur as irregular hematite grains, the matrix itself is low in both Fe and C. We interpret all of the C and Fe-rich features shown in Figs. 1–3 as biogenic remains of bacterial colonies, individual cells, and biofilms that have been mineralized by replacement with Fe carbonate and possibly other Fe-bearing minerals. An understanding of the complex processes by which microbes and their products are mineralized and preserved will be important in analyzing additional Mars meteorites and returned samples from Mars. This provides one example showing that likely fossilized microbial features may retain their distinctive morphologic and chemical identity over several billion years of geologic history.

Acknowledgments: We wish to thank L. Hulse for many hours of help on the SEM and E. K. Gibson for obtaining the sample from the PPRG. This investigation was supported by NASA Grants NAG9-980 and NAG9-867.

References: [1] Rothplez A. (1916) *Abh. Bayer. Akad. Wiss., 28(4),* 1–91. [2] Walcott D. (1912) *Geol. Surv. Canada Mem, 28,* 16–23. [3] Barghoorn E. S. et al. (1966) *Science, 152,* 758–763. [4] Barghoorn E. S. (1971) *Sci. Amer., 224,* 30–42. [5] Prashnowsky A. A. et al. (1972) in *Advances in Organic Geochemistry,* pp. 683–698, Pergamon, NewYork. [6] Awramik S. M. et al. (1983) *Precambrian Res., 20,* 357–374. [7] Schopf et al. (1987) *Science, 237,* 70–72. [8] Schopf J. W. (1977) *Precambrian Res., 5,* 143–173. [9] Gutstadt A. A. et al. (1969) *Nature, 233,* 165–167. [10] Schopf et al. (1992) *Proterozoic Biosphere,*

Cambridge Univ., 1348 pp. [11] Schopf J. W. (1983) *Earth's Earliest Biosphere,* Princeton Univ., 543 pp. [12] Morris et. al. (1998) *LPS XXIX.* [13] Ferris G. et. al. (1988) *Geology, 16,* 149–152. [14] Liebig K. et. al. (1996) *N. Jb. Geol. Palaeont. Abh, 199,* 269–293.

PERSPECTIVES ON THE FUTURE SEARCH FOR LIFE ON MARS AND BEYOND.

K. H. Nealson, Mail Stop 183-301, Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena CA 91109, USA (nealson@scn1.jpl.nasa.gov).

One can view the search for life on Mars in two ways: first, as the initial step in the search for life elsewhere, and second, as the one place where *in situ* methods for life detection can be tested and proved via sample return. After Mars, most of the life detection will be done via *in situ* studies with data return. Mars offers us the opportunity to fine tune our methods — perhaps for a long time to come. Our group is involved in the development of methods for life detection that are independent of specific signals used for detection of life on Earth. These approaches include general indicators of metabolic activity and organismal structure and composition. Using such approaches, we hope to detect the signals of life (biosignatures) that are independent of preconceived notions and yet are convincing and unambiguous. The approaches we are focusing on include stable isotopic analyses of metals, mineral formation and disolution, and elemental analysis. These methods allow us to examine samples at a variety of scales, looking for nonequilibrium distribution of elements that serve as biosignatures. For futures studies of Mars and beyond, they, or some variation of them, should allow inference or proof of life in non-Earth locations.

OXYGEN-ISOTOPIC COMPOSITION OF NAKHLA SIDERITE: IMPLICATIONS FOR MARTIAN VOLATILES.

J. M. Saxton, I. C. Lyon, and G. Turner, Department of Earth Sciences, University of Manchester, Manchester M13 9PL, UK (jsaxton@fs1.ge.man.ac.uk).

We have previously [1] reported the O-isotopic measurements of two grains (C1 and C3) of Mn-rich siderite in Nakhla. Four O-isotopic measures were identical within error, yielding mean $\delta^{18}O = 34 \pm 1‰$ SMOW. This is the heaviest carbonate yet reported from a martian meteorite. We now explore the implications of these data for martian volatiles. More recently, we have measured more carbonate grains (C8, C9, C10) that differ chemically from C1 and C3, being richer in Mg and lower in Mn. These new grains still have $\delta^{18}O$ near 34‰ (the accuracy of each measurement is 1–2‰). The carbonate grains are orange-brown in transmitted light, suggesting some staining by ferric oxides; C8 was particularly badly stained, and its lower $\delta^{18}O$ probably reflects contamination by oxides and/or silicates.

Various authors have considered the isotopic composition of martian volatiles. Clayton and Mayeda [2] considered production of a hydrosphere and atmosphere by high-temperature outgassing of CO_2 and H_2O, followed by cooling to low temperature. This process can also be considered on a local scale [e.g., 3,4]. An alternative view of martian volatiles was taken by Hutchins and Jakosky [5], who suggested the hydrosphere/atmosphere might have been enriched in heavy isotopes; this would render models with high-

TABLE 1.

	Mg	Ca	Sd	Rh	$\delta^{18}O$ ‰ SMOW
C1	3	1	70	26	+32.4
C1	3	1	70	26	+34.8
C1	3	1	70	26	+33.9
C3	10	1	81	8	+34.9
C8	27	5	66	2	+28.0
C9	38	5	55	1	+31.6
C10	33	3	62	2	+35.6

temperature fluid-silicate equilibrium inappropriate. It is also possible that, by the time the Nakhla carbonate formed, the $\delta^{18}O$ of the hydropsphere could have been reduced through fixation of CO_2 as carbonate. Assuming fixation as $CaCO_3$ at 0°C, we estimate $\delta^{18}O$ may be reduced ~4–6‰ by this process.

In Fig. 1 we relate the siderite $\delta^{18}O$ and formation temperature to potential martian H_2O/CO_2 reservoirs. In the left-hand panel, we show $\delta^{18}O$ of H_2O/CO_2 produced by inital outgassing [after 2]; X is the mole fraction of O as water in the degassed reservoir. Clayton and Mayeda [2] suggested X ~ 0.8 since it could account for their measurements of the carbonate in EET 79001. In the right- hand panel, we calculate the isotopic composition of martian surface reservoirs capable of generating the Nakhla carbonate. We assume that a hydrosphere/atmosphere exists at 0°C, from which is taken a sample of fluid having mole fraction X_{local} O as water. This sample of fluid is then heated to temperature T, at which temperature siderite forms in equilibrium with it. No isotope exchange takes place between the fluid and the silicate minerals. The figure shows the values of H and C required to obtain siderite having $\delta^{18}O$ = +34‰.

Comparing the two panels of the figure, we see that at low temperatures, H and C lie within the range of values that may be produced in initial outgassing, provided X_0 is sufficiently high. Water-siderite equilibration at $0 < T < 60°C$ requires $X_0 > 0.74$. Therefore, our data do not require a hydrosphere/atmosphere highly enriched in ^{18}O, which might have been expected by analogy with atmospheric H, C, and N. If the siderite formed from a water rich fluid ($X_{local} \to 1$) at temperatures >60°C, the inferred values of H and C are too high to be consistent with fluids produced by initial

outgassing and subsequently unmodified. Formation at higher temperatures would require heavy isotope enrichment of the hydrosphere/atmosphere such as that implicit in the model of Hutchins and Jakosky [5]. We note also that isotopic exchange with the silicate would imply higher values of H and C.

Bridges and Grady [6] have suggested that the Nakhla siderite formed from a melt, derived by melting of an evaporite. A problem with this model is that the present siderite is not in isotopic equilibrium with the igneous assemblage. In principle, the carbonate textures could be igneous, and the high $\delta^{18}O$ value reflects subsequent (low-T) equilibration with an aqueous fluid. This would raise the possibility of isotopic exchange between the fluid and other phases, such as the feldspar. Since, in fact, the feldspar does not appear to have undergone isotopic exchange (L. A. Leshin, personal communication) it may be more appropriate (and also simpler) to consider the carbonate as secondary and fluid-rock isotopic exchange as unimportant in Nakhla. We note also that Bridges et al. [8] also found no evidence for isotopic alteration of Lafayette feldspar.

The siderite $\delta^{18}O$ also places a lower limit on $\delta^{18}O$ of present-day CO_2 of about 40‰ (or about 36‰ if the siderite equilibrated with water (brine) at −20°C). After making a simple allowance for low-temperature H_2O $_{vapor}$-CO_2 fractionation, this is consistent with terrestrial infrared spectroscopy [8].

References: [1] Saxton J. M. et al. (1997) *Meteoritics & Planet. Sci., 32,* A113. [2] Clayton R. N. and Mayeda T. K. (1988) *GCA, 52,* 925. [3] Saxton J. M. et al. (1998) *EPSL,* in press. [4] Leshin L. et al. (1998) *GCA, 62,* 3. [5] Hutchins K. S. and Jakosky B. M. (1997) *GRL, 24,* 819. [6] Bridges J. C. and Grady M. M. (1998) *LPS XXIX.* [7] Bridges et al. (1997) *Meteoritics & Planet. Sci., 32,* A21. [8] Bjoraker G.L. et al. (1998) *Bull. AAS, 21,* 990.

RECONNAISSANCE SAMPLING OF AIRBORNE MO-LECULAR ORGANIC CONTAMINATION IN THE METEORITE CURATION FACILITY OF JOHNSON SPACE CENTER. E. A. Schilling[1] and M. N. Schneider[2], [1]Lockheed Martin, Houston TX 77058, USA, current address: St. Olaf College, Northfield MN 55057, USA (schillie@stolaf.edu), [2]Lockheed Martin, Houston TX 77058, USA, current address: Stanford University, Palo Alto CA 94305, USA (schneimn@stanford.edu).
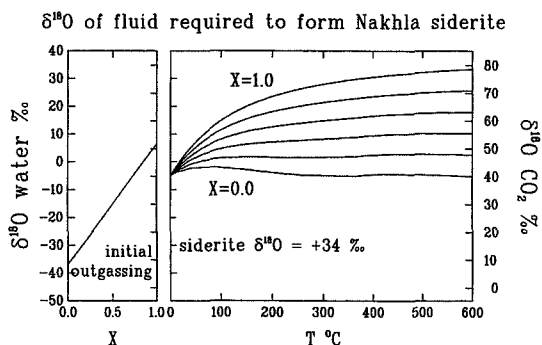
Introduction: Determining the extent of contamination of meteorites by terrestrial organic compounds has become a question of critical importance in the last several years. Contamination issues have been considered in the past and recognized as important, resulting in a good deal of study [1]. However, more thoroughly understanding organic contamination issues is especially pressing when considering possible evidence of previous life on Mars and in future Mars sample-return missions.

"Organic contamination," often vague terminology, can be defined in the following way, adapted from the NASA-appointed Organic Contamination Review Committee [1]. Type 1 organics are the building-block materials of life. These are compounds that have an essential role in terrestrial biochemistry, such as amino acids and metabolic byproducts. Type 2 organics are cosmochemical and biogeochemical environmental compounds, those compounds that do

$\delta^{18}O$ of fluid required to form Nakhla siderite

Fig. 1.

Fig. 1. Airborne Molecular Contamination sampling device attached to outlet port of Mars meteorite cabinet in JSC's Meteorite Processing Lab.

not have an essential role in biochemistry, such as hydrocarbons, polycyclic aromatic hydrocarbons (PAHs) and nonbiogenic amino acids. Type 3 organics, macromolecular biomolecules, are polymers of type 1 compounds such as DNA, proteins, and lipids. Finally, Type 4 organics are viable microorganisms such as bacteria and fungi. Type 1 and type 2 organic contaminants are often considered together and called molecular contamination.

While many particulate and inorganic contamination issues have been addressed in the past, curators at Johnson Space Center have initiated efforts to determine the baseline levels of organic contamination in curation facilities. Described here is a portion of the preliminary work done on developing and utilizing techniques for

detecting levels of molecular organic contamination (types 1 and 2) in the Meteorite Processing Laboratory (MPL) at Johnson Space Center.

Sampling Technique: The general room atmosphere of the MPL and the positive pressure, high-purity N atmosphere of the Mars meteorite cabinet were sampled for trace amounts of airborne molecular contaminants (types 1 and 2). A stainless-steel tube filled with activated charcoal and other proprietary sorbents (Balazs Analytical Laboratories [2]) was attached to an air pump, which drew air through the tube at a rate of 100 ml/min. The device was placed in the center of the MPL and air was sampled for 6 hr while typical activities took place in the room. Another sampling device was attached to an outlet port of the Mars meteorite cabinet, home of ALH 84001, and allowed to run for 6 hr at a rate of 130 ml/min (Fig. 1). Because meteorites are stored and processed in high-purity N cabinets, and often handled outside cabinets on a laminar flow bench, these two measurements are representative of the types and amounts of organic contaminants to which meteorites are often exposed. The two sample tubes, along with an unopened shipping blank, were returned to Balazs Analytical Laboratories, where they were analyzed by Thermal Desorption-Gas Chromatography-Mass Spectrometry. The estimated sensitivity of this method was 0.1 ng/L, but most compounds were not quantified below 1 ng/L.

Results: Measurable levels of airborne molecular organic contamination were detected both in the MPL room center and in the Mars meteorite cabinet. The compounds detected in highest concentrations were silicones [cyclic siloxanes: $cyclo(Me_2SiO)_n$] and low- to medium-boiling hydrocarbons (Table 1). MPL airborne contaminants included butanol, benzene, toluene, ethylbenzene, xylenes, siloxanes, texanol isobutyrate, fluorocarbons, isopropanol, propoxypropanol, 2-butoxyethanol, butoxypropanol, dipropylene glycol, methoxypropoxypropanol, 2-ethylhexanol, nonanal, diethyl phthalate, dibutyl phthalate, and dioctyl phthalate. Mars meteorite cabinet contaminants included toluene, siloxanes, isopropanol, 2-ethylhexanol, and caprolactam. The shipping blank contained measurable levels of certain organic compounds but at levels below those measured in the MPL and Mars meteorite cabinet. Although cabinet levels were generally lower than those of the MPL room

TABLE 1.   Selected organic compounds measured in an unopened shipping blank,
MPL room center, and Mars meteorite cabinet.

Contaminant	Shipping Blank (ng/L)	Meteorite Lab Room Center (ng/L)	Mars Cabinet Outlet (ng/L)
Hydrocarbons (C6-C10)	8	32	10
Hydrocarbons (C11-C18)	1	43	3
Toluene	2	4	3
Isopropanol	<1	1	2
$cyclo(Me_2SiO)_3$	<0.1	2.9	5.8
$cyclo(Me_2SiO)_4$	<0.1	2.6	3.0
$cyclo(Me_2SiO)_5$	<0.1	26	1.0
$cyclo(Me_2SiO)_6$	<1	2	(0.3)
$cyclo(Me_2SiO)_7$	<1	<1	(0.5)
Caprolactam	<1	<1	(0.2)

The detection limit for most compounds was 1 ng/L, but this was lower for select compounds. Compounds detected at less than 1 ng/L are reported in parentheses.

center, several siloxanes, isopropanol, and caprolactam were detected at higher levels in the Mars meteorite cabinet than in the MPL room center.

Discussion: The detection of measurable amounts of molecular organic contamination in the MPL and in the Mars meteorite cabinet raises a number of concerns, such as the potential sources of the contaminants and the effect of the contaminants on the integrity of meteorite samples. The potential sources for contamination, as with most indoor air, are numerous. Hydrocarbons, benzene, toluene, and xylenes are commonly found as industrial air pollutants and usually enter through air-handling systems. However, measured levels of these compounds are several times lower than external Houston air, which contains benzene, toluene, and xylenes at levels between 5 and 10 ng/L [3]. Compounds such as butanol may also be produced as human metabolic byproducts. Fluorocarbons within the room air probably result from residual Freon 113 once used to clean processing tools or from refrigerants used in laboratory freezers. Compounds such as isopropanol, butanol, propoxypropanol, 2-butoxyethanol, butoxypropanol, dipropylene glycol, and methoxypropoxypropanol are commonly found in solvents and may be the result of outgassing of room materials such as flooring, paints, markers, and wet wipes. Plasticizers such as texanol isobutyrate, diethyl phthalate, dibutyl phthalate, and dioctyl phthalate probably come from the outgassing of sample bags, vinyl gloves, gasket materials, or other room plastics. The variety of detected siloxanes have probable sources in silicone rubber sealant materials, silicone adhesives, and elastomers in ceiling-light gaskets.

Contamination in the Mars meteorite cabinet may be from airlock transfer of tools and bags with adsorbed or electrostatically attached contaminants, from previous samples, from contaminants due to the attachment technique, or from impurities in the N supply. Measurements of the molecular organics in the incoming N supply line need to be made to verify which contaminants come from the N and which come from processing materials and the sample itself. The source of isopropanol is likely residual material from the cleaning of heat sealers. Caprolactam is a common breakdown product of Nylon-6, often used as sample storage bags, and is likely released during heat sealing of these bags. The siloxanes present in the cabinet may be due to a heat-sealer malfunction the day prior to measurement in which the silicone rubber upper plate was overheated.

The organic contamination measured in the MPL and in the Mars meteorite cabinet may or may not have significant effects on processed samples. Though present in the air, it is possible that certain compounds may become selectively concentrated on meteorite surfaces, potentially resulting in misleading geological and geochemical analyses. Experimentation has not yet taken place exploring such selective concentration. It is notable that caprolactam is used in a variety of biotechnological processes producing the amino acid lysine [4]. Though the process appears to be highly catalyzed, the similarity in structure of caprolactam and lysine argues for further consideration of this contaminant in terms of assessing the possibility of lysine formation on meteorite surfaces.

Through the acknowledgment of these, and perhaps other, contamination sources and the further development of continuous detection protocols, the uncertainties associated with organic contamination on martian samples can be reduced. Sample curators at JSC continue to explore these issues.

References: [1] Bada J. L. et al. (1997) Letter from Organic Contamination Review Committee to Dr. Joseph M. Boyce, NASA HQ, 2/5/97. [2] Camenzind M. J. et al. (1995) *Micro*. [3] Texas Natural Resource Conservation Commission (1997) AS-134. [4] Ahmed S. A. et al. (1982) *Agric. Biol. Chem., 47,* 1149–1150.

BIOGENIC OR ABIOGENIC ORIGIN OF CARBONATE-MAGNETITE-SULFIDE ASSEMBLAGES IN MARTIAN METEORITE ALLAN HILLS 84001.

E. R. D. Scott, Hawai'i Institute of Geophysics and Planetology, School of Ocean and Earth Science and Technology, University of Hawai'i at Manoa, Honolulu HI 96822, USA (escott@pgd.hawaii.edu).

Introduction: McKay et al. [1,2] suggested that the carbonates and submicrometer grains of magnetite, pyrrhotite, and an Fe-S phase identified as "probably griegite" were all biogenic in origin. Their arguments were based on similarities in the compositions, structures, shapes, and sizes of these minerals with terrestrial biominerals and the apparent absence of plausible abiogenic origins. Here we compare the carbonate assemblages to possible martian, terrestrial, and meteoritic analogs and discuss new and published arguments for and against abiogenic and biogenic origins for these minerals.

Magnetite: McKay et al. [1,2] argued on the basis of structure, size, morphology, and chemical composition that the submicrometer-sized magnetites (Fe_3O_4) were largely formed intracellularly by magnetotactic microorganisms. Magnetites in ALH 84001 are mostly cuboid, cubo-octahedral, teardrop and irregular in shape [1–3]. A small fraction are elongated rods or ribbons [4] and some are parallelepipedal or hexagonal prisms [5]. Cubo-octahedra and hexagonal prisms elongated along [111] and bullet-shaped crystals formed by asymmetric growth on cubo-octahedra are most characteristic of magnetotactic bacteria [6], and some of these shapes are observed in ALH 84001. However, with the exception of the bullet shapes, they can also be formed inorganically [7]. Thus although the shapes and sizes of many martian grains are highly suggestive of magnetosomes, except possibly for the teardrop shapes, they cannot definitely be identified as crystals from magnetotactic microorganisms. Teardrop-shaped magnetite crystals were originally reported in magnetotactic bacteria; this term was used for oblate spheroids and "teardrop-shaped cones" [8,9]. However, it is not clear whether the martian teardrops resemble these shapes. Contrary to [4], rod-shaped and twinned magnetites are formed biogenically. However, elongated, ribbon-shaped magnetites and rods with central screw dislocations are very unlikely to be biogenic [4].

Most martian magnetites are single magnetic domains, as observed for magnetotactic bacteria; however, the proportion that is superparamagnetic [5] is larger than observed for magnetotactic bacteria [10]. Parallelepipedal particles <30 nm in length and cuboids <50 nm in size, which are present in ALH 84001 [1–5], would not have been classified as biogenic if they had been found in a terrestrial sediment. McKay et al. [1] suggested that the smaller, superparamagnetic magnetites resembled those formed extracellu-

larly by the bacterium *Geobacter metallireducens*. However, this organism is not motile and forms magnetites that are irregularly shaped and poorly ordered [10]. There are no reports suggesting that superparamagnetic martian magnetites are more irregular in shape and less well ordered than single domain magnetites.

Some clusters of elongated magnetites are crystallographically oriented with respect to one another and to the carbonate substrate [11–13]. Epitaxial growth is inconsistent with intracellular growth [12], and extracellular biogenic deposition is also very unlikely as such magnetites are poorly crystalline and irregular in shape. Although biogenic magnetites can be crystallographically oriented on organic substrates with great precision [14], no organism is known to deposit carbonate and magnetite on the same organic substrate. Thus there is no reason to expect epitaxial, biogenic deposition of magnetite on carbonate on any planet.

It is very difficult to understand how magnetites from magnetotactic organisms could have been introduced into a plutonic rock like ALH 84001. It is unlikely that magnetotactic organisms would navigate and swim through a maze of cracks in an igneous rock. It is also very unlikely that any biogenic magnetites from sediments or aqueous environments could be washed into fractures in ALH 84001 by percolating fluids and preferentially trapped during the final stages of carbonate crystallization, forming uniformly thin, double shells around carbonates. These factors and the abundance of abiogenic magnetites make it very unlikely that any biogenic magnetites are present in the ALH 84001 carbonates.

Iron Sulfides, Pyrrhotite, and Griegite: Griegite (Fe_3S_4), pyrrhotite ($Fe_{0.9}S$), and other Fe sulfides can be formed extracellularly by sulfate-reducing bacteria, but these sulfides cannot be distinguished morphologically or chemically from abiogenic sulfides [6]. The absence of isotopically light S indicates that the martian sulfides did not form by this process [15].

Pyrrhotite is not known to form intracellularly in magnetotactic bacteria [16]. In addition, some martian pyrrhotites are rounded and polycrystalline and thus could not be magnetic single domains like magnetosomes. Griegite magnetosomes are known, but it is very unlikely that griegite from magnetotactic microorganisms is present in ALH 84001. The particles identified by McKay et al. [1] as griegite are more irregular than known griegite magnetosomes, and the identification of griegite is questionable as it was based on the similarity in shape (irregular and approximately rectangular) of a polycrystalline griegite particle formed in soil by nonmagnetotactic bacteria. The martian "griegite" particles had pyrrhotite compositions and were unstable in the electron beam, whereas griegite can be studied in the TEM without decomposing [16]. Thus, no evidence suggests that the martian sulfides formed biogenically, either intra- or extracellularly.

Carbonate: McKay et al. [1,2] concluded that the carbonate disks in ALH 84001 were similar in size and shape to some marine, bacterially induced calcite aggregates of submicrometer crystallites [17]. However, martian carbonate crystals appear to be much larger [1]. The unique dumbbell-shaped and brush-shaped aggregates formed by bacteria have not been reported in the martian carbonates.

McKay et al. [2] also compared the martian carbonates to chemically zoned concretions of siderite or ankerite in sedimentary rocks. These compositions are closer to those of the martian carbonates, but terrestrial examples lack the extensive Ca zoning found in small portions of the martian grains. Valley et al. [18] also compared the

martian carbonates to concretions but noted that disequilibrium in the terrestrial carbonates may be due to biogenic or abiogenic processes.

Barrat et al. [19] compared the martian carbonates to terrestrial calcite aggregates that may have formed biogenically in the Tatahouine meteorite when it lay in the Saharan desert for 63 yr. However, these carbonates are not chemically zoned and lack magnetite rims. Direct evidence favoring a biogenic origin of the martian carbonates is lacking.

Abiogenic Origins: Anders [20] suggested that the ALH carbonate assemblages were similar to those in carbonaceous chondrites and had formed abiogenically at low temperatures. However, McKay et al. [2] noted numerous differences in grain size, composition, and texture between martian and chondritic occurrences. Although CI and CM chondrites contain calcite, dolomite, and magnesite [21,22], there are no chemically zoned grains like those in ALH 84001. Magnetites in CI chondrites are larger than those in ALH 84001, and those in CM chondrites are rare and not associated with peripheral magnesite. Carbonates in carbonaceous chondrites are also not found embedded in pyroxene and plagioclase glass, as in 84001.

McKay et al. [1] rejected a high-temperature origin for the carbonate assemblages in ALH 84001 on the basis of C- and O-isotopic data. However, other authors have found that calculated formation temperatures could be 40°–250°C [23] or any temperature in the range of 0° to >500°C [24]. The presence of shock-formed glass that solidified *in situ* in fracture zones in ALH 84001 is not consistent with the conclusions of Kirschvink et al. [25], who argued against high temperatures after formation of the fracture zones.

Brearley [3] found evidence for high temperatures in the microstructures at carbonate-glass boundaries and suggested that shock-melted plagioclase had heated carbonate. The presence of pores in carbonate around magnetites [1] favors decomposition of Fe-rich carbonate during shock heating, melting, or vaporization [3,26]. Such a process also appears consistent with Bradley et al. [4], who concluded that magnetite had condensed above 500°C from a fluid. Rapid heating and cooling in seconds of shock-formed fluids formed above 35 GPa [26] would be consistent with the constraints of Valley et al. [18], who argued against high temperatures over periods of minutes to hours.

Conclusions: Arguments for a biogenic origin for the carbonate, magnetite, and Fe sulfides in ALH 84001 are absent or very weak: An origin from shock-formed fluids appears much more plausible. Nevertheless, martian sediments and sedimentary rocks should be searched for single-domain magnetites with the unique characteristics of crystals in magnetotactic bacteria. Further searches of carbonates in heavily shocked martian meteorites for grains of biogenic minerals cannot be recommended.

References: [1] McKay D. S. et al. (1996) *Science, 273,* 924. [2] McKay D. S. et al. (1996) *Science, 274,* 2123. [3] Brearley A. J. (1998) *LPS XXIX,* Abstracts #1451, #1452. [4] Bradley J. P. et al. (1996) *GCA, 60,* 5149. [5] Thomas-Keprta K. L. et al. (1998) *LPS XXIX,* Abstract #1494. [6] Bazylinski D. A. and Moskowitz B. M. (1997) in *Geomicrobiology* (J. F. Banfield and K. H. Nealson, eds.), p. 181. [7] Maher B. A. (1990) in *Iron Biominerals,* p. 179, Plenum. [8] McNeill D. F. et al. (1988) *Geology, 16,* 8. [9] Petersen N. et al. (1986) *Nature, 320,* 611. [10] Sparks N. H. C. et al. (1990) *EPSL, 98,* 14. [11] Bradley J. P. et al. (1998) *LPS XXIX,* Abstract

#1757. [12] Bradley J. P. et al. (1998) *Meteoritics & Planet. Sci.*, *33*, in press. [13] Blake D. et al. (1998) *LPS XXIX*, Abstract #1347. [14] Mann S. et al. (1993) *Science, 261*, 1286. [15] Greenwood J. P. et al. (1997) *GCA, 61*, 4449. [16] Postfai M. et al. (1998) *Science, 280*, 880. [17] Buczynski C. (1991) *J. Sed. Petrol., 61*, 226. [18] Valley J. W. et al. (1997) *Science, 275*, 1633. [19] Barrat J. A. et al. (1998) *Science, 280*, 412. [20] Anders A. (1996) *Science, 274*, 2119. [21] Johnson C. A. and Prinz M. (1993) *GCA, 57*, 2843. [22] Endress M. and Bischoff A. (1996) *GCA, 60*, 489. [23] Hutchins K. S. and Jakosky B. M. (1997) *GRL, 24*, 819. [24] Leshin L. A. et al. (1998) *GCA, 62*, 3. [25] Kirschvink J. L. et al. (1997) *Science, 275*, 1629. [26] Scott E. R. D. et al. (1996) *Nature, 387*, 377.

ORIGIN OF CARBONATE IN MARTIAN METEORITE ALLAN HILLS 84001.

E. R. D. Scott and A. N. Krot, Hawai'i Institute of Geophysics and Planetology, School of Ocean and Earth Science and Technology, University of Hawai'i at Manoa, Honolulu HI 96822, USA (escott@pgd.hawaii.edu).

Introduction: A significant argument advanced by McKay et al. [1,2] in favor of a biogenic origin of the carbonates in ALH 84001 was that abiogenic origins — both low and high temperature — appeared to be less plausible. However, subsequent shock studies have suggested that impact heating may have modified carbonates [3–7]. We inferred that plagioclase glass and rare silica grains formed from impact melts, and Raman spectroscopy [8] confirmed that plagioclase had been melted at >1200°C, suggesting shock pressures exceeded 35–45 GPa. Morphological similarities between grains of plagioclase glass and irregularly shaped carbonates in fractures and the occurrence of intermixed grains in fractures suggested that carbonates may also have been shock heated so that a CO_2-rich fluid was injected into cooler-fractured pyroxene during shock decompression causing crystallization in seconds.

Types of Carbonate: Carbonates in ALH 84001 occur in three locations: (1) disks, veins, and irregularly shaped grains in healed fractures in pyroxene; (2) massive grains and globules and smaller grains associated with plagioclase glass on pyroxene grain boundaries; and (3) generally equant grains that appear to poikilitically enclose pyroxene fragments in fracture zones (also called granular bands and crushed zones [9,10]). McKay et al [1,2] studied disk-shaped carbonates, which are abundant on freshly broken surfaces; we studied all kinds of carbonates in polished thin sections. The close association of the three carbonate types and the uniformity of their chemical zoning trends on $MgCO_3$-$FeCO_3$-$CaCO_3$ plots show that all carbonates in ALH 84001 formed by the same process [4,11].

Origins of Carbonate: Three different origins have been proposed for carbonates in ALH 84001: (1) biogenic or abiogenic precipitation from CO_2-rich fluids that percolated through fractures at low temperatures [1,12]; (2) reaction between CO_2-rich fluids and pyroxene, plagioclase, or plagioclase glass at low or high temperatures [13,14]; and (3) shock heating and mobilization of preexisting carbonates [3–5]. Because voids are absent next to carbonates (except for fractures that postdate carbonate crystallization), grains in pyroxene crystals and plagioclase glass appear to have replaced the adjacent phase. However, replacement mechanisms are not plausible because phases rich in Si, Al, Na, etc. that form during such replacement reactions are totally absent [14]. In addition, there should be compositional differences between carbonates in pyroxene and those in plagioclase, but none are observed. Carbonate grains in pyroxene could not have formed by replacement of plagioclase glass because carbonates are more abundant than glass in pyroxene, composite grains are rare, and glass grains are surrounded by radiating cracks whereas carbonates are not.

Carbonates in Fractures: Studies of disks and veins in thin sections show that carbonate-bearing fractures were closed after carbonates had started to form so that unfilled portions of fractures were resealed around the carbonates. The concentration of planar defects around carbonate and plagioclase glass inclusions on fractures suggests that these fractures were closed by impact. If carbonates formed from externally derived fluids, chemical variations across carbonate grains would reflect external changes in fluid composition over time and fractures would have been closed after carbonate growth. However, if carbonates formed rapidly from impact-derived fluids, the chemical variations must reflect internal fractionation in trapped fluids, and fractures would have been closed during carbonate growth.

Several features favor crack closure during growth and internal control of chemical fractionation. The tapered edges of some carbonate disks and veins, the absence of deformation in the tapered rims of carbonate grains, and the presence of well-faceted magnesite rims favor crack closure during carbonate growth. Occurrences of magnesite at the enclosed end of carbonate-filled cracks are difficult to reconcile with late deposition from an externally derived fluid, as the cracks would have been effectively sealed with early-formed Ca-rich carbonate. In addition, magnesite microdisks are found around some disks and veins, but not elsewhere, implying that chemical fractionation of the fluid was caused by carbonate crystallization. We infer that the magnesite microdisks formed from residual trapped fluid that was squeezed a short distance along the fractures as they closed. Carbonates in pyroxene fractures are heterogeneously distributed: Heavily deformed pyroxene crystals around interstitial plagioclase glass can contain up to 5–10 vol% carbonate, consistent with limited transport of carbonate-rich fluids along fractures.

Studies of plagioclase glass and metal-troilite in heavily shocked L and E chondrites [15] show that monomineralic melts of readily deformed minerals such as troilite and plagioclase are injected into fractures that were formed by shear stresses and then resealed during shock decompression. Grains of plagioclase glass and metal-troilite are heterogeneously distributed in healed fractures in pyroxenes as spheroids, sheets, and irregularly shaped grains, like the carbonates in ALH 84001. Metal grains are chemically zoned and form crystals >100 μm because of rapid diffusion in metallic melts.

Carbonates in Fracture Zones: Fracture zones contain broken pyroxene crystals 5–100 μm in size that were formed from millimeter-to-centimeter-sized crystals by localized shear stresses, rotated >20° and squeezed together to remove voids. Fracture, rotation, and compression occurred during impact(s). We and others [e.g., 11,14] found no evidence for metamorphic equilibration of minerals after fracture zones were formed [9,16]. Localized, brief frictional heating probably aided void removal. Fracture zones contain grains of carbonate and plagioclase glass that are sparsely distributed among the pyroxene fragments and are not fractured and deformed like the pyroxene, showing that they formed after the py-

roxene crystals were fragmented. Carbonates fill only a tiny fraction of the spaces that once existed between pyroxene fragments and could not have formed after the pyroxene fragments were squeezed together to remove voids. Carbonates must therefore have formed from fluids that were present between the pyroxene fragments when the fracture zones formed. Occurrences of aligned trails of plagioclase glass and chromite grains within fracture zones that lead to larger peripheral grains show that plagioclase was molten and chromite solid when the fracture zones formed by shear stresses. One large carbonate-plagioclase grain was also found with emanating parallel trails of carbonate and plagioclase glass grains [5]. Carbonate-pyroxene boundaries within large carbonate grains may be subhedral [3,6], inconsistent with low-temperature precipitation of carbonate in fractures. Carbonates and plagioclase glass in fracture zones both appear to have formed at high temperatures from impact-mobilized fluids that solidified as voids closed.

Carbonates Mixed with Plagioclase Glass on Pyroxene Grain Boundaries: Textures in these occurrences are highly varied and complex. However, the concentration of carbonate grains in fractured pyroxene around grain-boundary carbonate-plagioclase glass intergrowths implies that prior to impact heating, carbonates in ALH 84001 were concentrated at interstitial sites together with plagioclase. Small amounts may also have been distributed in fractures. The first carbonates could not have formed at high temperatures, as burial depths of >120 km at 900°C would have been needed to prevent carbonate and pyroxene from reacting to form CO_2. The first carbonates probably crystallized instead from fluids at low temperatures in voids formed by gas bubbles during the final stages of igneous crystallization. Carbonates in other martian meteorites probably formed this way, possibly as evaporite deposits. The presence of partly filled voids and adjacent plagioclase shock melts would have enhanced the shock heating of carbonates. Partial decomposition of carbonates by shock heating [6] without mobilization of shock-formed fluids appears less plausible, as there is no correlation of chemical zoning with proximity to plagioclase melt.

Arguments Against Shock Formation of Carbonates: In some shock experiments [17], calcite appears to have been unaffected by shock pressures of 50 GPa. However, shock heating of minerals is heterogeneous and probably controlled by shear stresses. Thus, shear stresses and matrix effects will be critical. Shock pressures in ALH 84001 may also have exceeded 50–60 GPa. Chemical zoning in carbonates is not explained by this model. However, given our poor understanding of phase relations and kinetics at high T and P in the ternary carbonate system, it is not implausible that zoning resulted from fractionation between solid, melt, and vapor. Impact melt pockets in heavily shocked rocks cool at diverse rates according to local conditions so that a unique crystallization sequence cannot be specified. Numerous generations of crosscutting melt veins and brecciation are observed in the floors of terrestrial craters so that many impacts [16] are not required to account for deformation features in ALH 84001.

References: [1] McKay D. S. et al. (1996) *Science, 273,* 924. [2]] McKay D. S. et al. (1996) *Science, 274,* 2123. [3] Scott E. R. D. et al. (1997) *Nature, 387,* 377. [4] Scott E. R. D. et al. (1998) *Meteoritics & Planet. Sci., 33,* 709. [5] Scott E. R. D. et al. (1998) *LPS XXIX,* Abstract #1786. [6] Brearley A. J. (1998) *LPS XXIX,* Abstract #1451. [7] Bradley J. P. (1996) *GCA, 60,* 5149. [8] Cooney T. F. et al. (1998) *LPS XXIX,* Abstract #1332. [9] Trei-man A. H. (1995) *Meteoritics, 30,* 294. [10] Mittlefehldt D. W. (1994) *Meteoritics, 29,* 214. [11] McKay G. et al. (1998) *Meteoritics & Planet. Sci., 33,* A102. [12] Valley J. W. et al. (1997) *Science, 275,* 1633. [13] Harvey R. P. and McSween H. Y. (1996) *Nature, 382,* 49. [14] Gleason J. D. et al. (1997) *GCA, 61,* 3503. [15] Fagan T. J. et al. (1998) *Meteoritics & Planet. Sci., 33,* A46. [16] Treiman A. H. (1998) *Meteoritics & Planet. Sci.,* in press. [17] Schwandt C. S. et al. (1998*) Meteoritics & Planet. Sci., 33,* A139.

A COMPARISON BETWEEN SULFIDE ASSEMBLAGES IN MARTIAN METEORITES ALLAN HILLS 84001 AND GOVERNADOR VALADARES.

C. K. Shearer and C. Adcock, Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque NM 87131, USA.

Introduction: Understanding the development, timing, and setting of sulfide and sulfate deposition is critical to interpreting S-isotopic systematics in martian meteorites and future mission samples. For example, to properly interpret S isotopes as a marker for biogenic activity in low-temperature hydrothermal mineral assemblages, it is important to understand the relative sequence of sulfide and/or sulfate precipitation, the temperature of precipitation [1], the openness of the system [2], and the postdepositional thermal history of the sulfide-sulfate assemblages [3]. To interpret S isotopes in magmatic assemblages, it is critical to decipher the effect of subsolidus processes.

Approach: In this study, the sulfide assemblages in ALH 84001 (orthopyroxenite) and Governador Valadares (nakhlite) were documented using optical microscopy, EMP, and SEM. The orthopyroxenite assemblage of ALH 84001 represents crystallization and crystal accumulation in a larger intrusive body, whereas the clinopyroxenite assemblage of Governador Valadares reflects the crystallization and crystal accumulation in either a ultramafic basalt flow or a shallow intrusion. Identification of individual sulfide grains were made using reflectance characteristics and EMP analyses. Individual sulfide grains were analyzed for $\delta^{34}S$ using the Cameca ims 4f at the University of New Mexico using the approach of Shearer et al. [1].
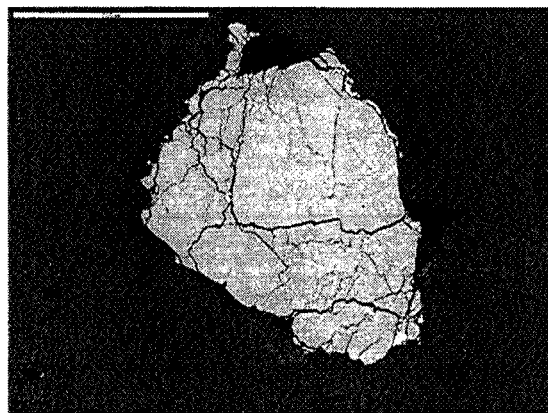

Fig. 1. Chromite with minute sulfide inclusions. Scale bar = 200 μm.

Results: ALH 84001 and Governador Valadares contain both pyrite and pyrrhotite. Pyrite is the dominant sulfide in ALH 84001, whereas pyrrhotite is dominant in Governador Valadares. Other S-bearing phases that were identified include chalcopyrite in
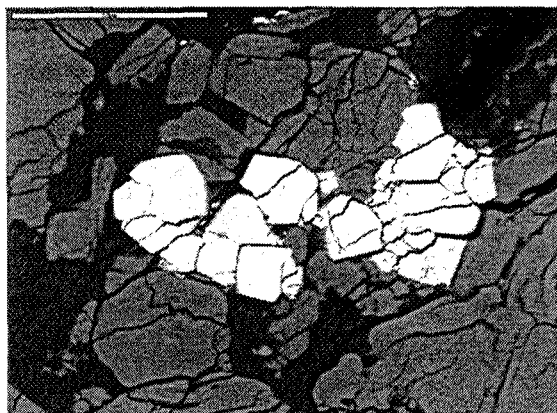

Fig. 2.   Large pyrite aggregate within brecciated zone. Chromite grains are commonly associated with aggregates. Scale bar = 50 μm.
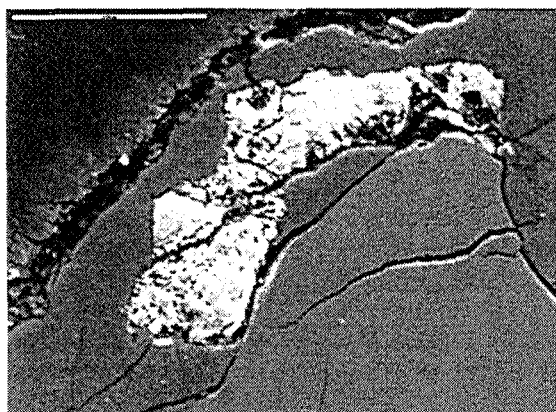

Fig. 3.   Sulfide grain entrained within shock glass. Irregular surfaces on grain appear to be sulfates. Scale bar = 10 μm.

Governador Valadares and a sulfate associated with pyrite in ALH 84001. The sulfides in ALH 84001 occur in several different textural settings that imply different origins and thermal histories.

Sulfide type 1.   Small pyrite and pyrrhotite inclusions (1–10 μm) are associated with large, relatively unbrecciated chromite grains (Fig. 1). Small pyrite grains also occur near the grain boundary between the chromite and orthopyroxene.

Sulfide type 2.   Large pyrite aggregates (10–80 μm) occur within brecciated zones (Fig. 2). Ubiquitous chromite and rare pyrrhotite are phases that may be spatially associated with the pyrite aggregates. The interface between the pyrite and silicate phases are sharp. There is a transition between textural type 1 and 2 that is associated with highly deformed chromate.

Sulfide type 3.   Small, irregular grains of pyrite are associated spatially with the base of the carbonate globules.

Sulfide type 4.   Very irregular-shaped sulfides occur in the shock glass. The sulfide is probably pyrite. EDS compositional maps indicate that the sulfide is not homogeneous and may contain abundant sulfate (Fig. 3).

Sulfide type 5.   Submicrometer-sized sulfides have been identified in the carbonate. These sulfides have not been well characterized. In EDS maps of the carbonates, the sulfide abundance as reflected by S concentration appears to be highest in the two Fe-rich zones in the carbonate globules and lowest in the Mg-rich zones (Fig. 4). The sulfide mineralogy in Governador Valadares is not as complex. Pyrrhotite and minor pyrite predominantly occur as minute grains (2–25 μm) that are immersed in the mesostasis that is interstitial to the cumulate augite (Fig. 5). Pyrrhotite also occurs infrequently as inclusions in the subhedral augite.

Discussion: The wide variability in the $\delta^{34}S$ of sulfides in ALH 84001 compared to that in other martian samples [1,4,5] reflects the multigenerational nature of sulfide formation and the effect of postmagmatic heating-impact events. The sequence of events that affected the $\delta^{34}S$ in the sulfides is as follows: (1) magmatic crystallization and accumulation of sulfides; (2) precipitation of pyrite following the formation of the impact-induced cataclastic texture; the S source was both internal and external to the orthopyroxenite; (3) fine-grained, submicrometer sulfides coprecipitated with the carbonate; the Fe-rich carbonates contained a high proportion of sulfides; and (4) a postcarbonate heating event undoubtedly affected the sulfides and may have perturbed the $\delta^{34}S$. Small
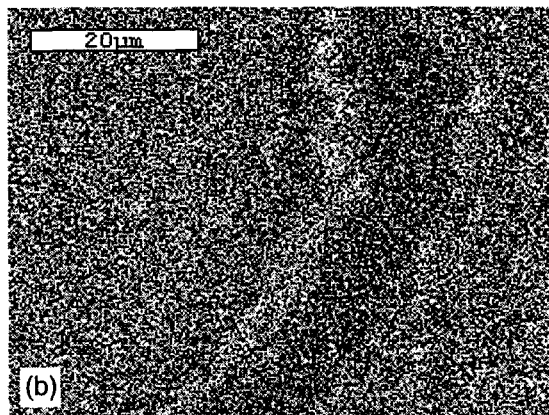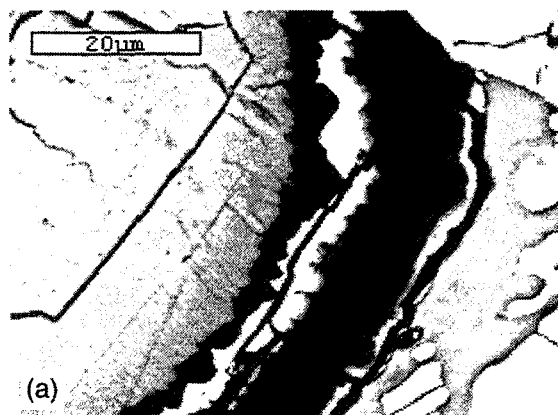

Fig. 4.   (a) Back-scattered electron image of outer zones in carbonate globule. The two high-Fe zones are bright. The two high-Mg zones are black. (b) X-ray map of the distribution of S in the carbonate globule. High-S concentrations are associated with high-Fe zones.
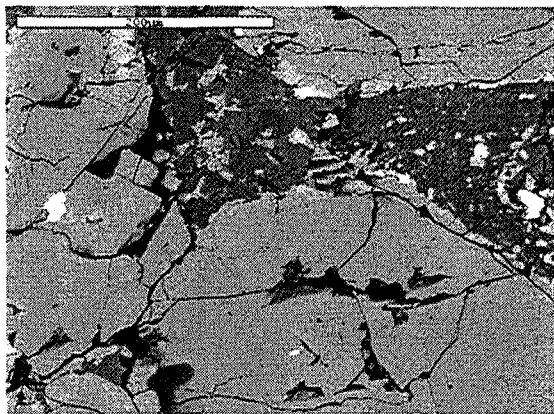
Fig. 5. Sulfides in Governador Valadares. Pyrrhotite inclusion occurs in the augite. Pyrrhotite and minor amounts of pyrite are immersed in the mesostasis and closely associated with the Fe-Ti oxides. Scale bar = 200 μm.

Evidence for a Postcarbonate, High-Temperature Event: There are at least three lines of evidence that suggest that these low-temperature carbonates [1–3] were exposed to a rapid, high-temperature event: disruption of the carbonate globules during the formation and mobilization of the shock glass, the formation of olivine inclusions in the orthopyroxene, and the amorphous character of sheet silicates near the carbonate-glass boundary.

The degree of disruption of the carbonate globules by the mobilization of shock glass is illustrated in Figs. 1–3. Figure 1 shows relatively undisturbed, zoned carbonate. The zoning is particularly complex as the carbonates precipitated within small cracks in the orthopyroxene, dissolution voids and adjacent to crushed fragments of orthopyroxene. Figure 2 shows a similarly zoned carbonate globule, its base crushed and injected with shock glass. Within the crushed zone, carbonate cleavage fragments provide evidence that this texture does not represent carbonate growth within shock-glass voids. Also, the complex zoning observed in the individual fragments was not a product of carbonate melt interaction or growth in glass voids, but rather reflects complex carbonate growth as il-
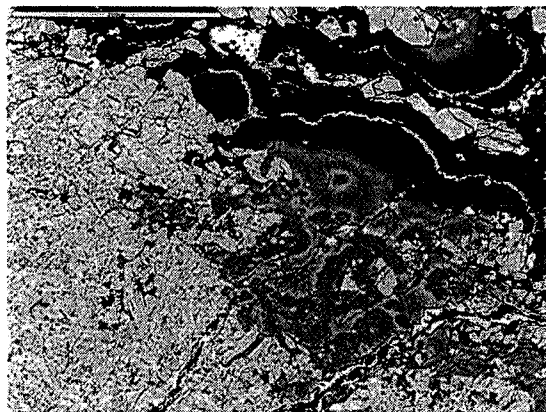
sulfides were entrained in and reacted with the shock glass during this heating event (Fig. 3). In addition, it is possible that the submicrometer sulfides in the carbonates were formed during a high-temperature heating event that resulted in preferential volatilization of the Fe-,S-enriched carbonate zones.

Conclusions: Although ALH 84001 and Governador Valadares have similar sulfide assemblages (pyrrhotite and pyrite), they differ in their complexity. The sulfide assemblage in Governador Valadares is dominated by pyrrhotite and appears to be magmatic in origin with some subsolidus reequilibration. On the other hand, the sulfide assemblages in ALH 84001 reflect magmatic and multiple low- and high-temperature subsolidus processes. The more complex genetic history of the sulfides in ALH 84001 is reflected in the relatively large variability of $\delta^{34}S$ (1–9‰) compared to other martian meteorites. This range reflects both high-temperature and low-temperature reservoirs and *in situ* mixing of these components.

References: [1] Shearer et al. (1996) *GCA, 60,* 2921. [2] Shearer (1997) *LPS XXVIII,* 1289. [3] Shearer and Adcock (1998) *LPS XXIX.* [4] Greenwood et al. (1997) *GCA, 61,* 4449. [5] Greenwood et al. (1998) *LPS XXIX.*

Fig. 1. Complex zoning in carbonate globule. Orthopyroxene wall is highly crushed and partially included in carbonate.

EVIDENCE FOR A LATE-STAGE THERMAL OVERPRINT IN ALLAN HILLS 84001 AND IMPLICATIONS FOR BIOMARKERS.

C. K. Shearer[1] and A. Brearley[2], [1]Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque NM 87131, USA, [2]Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque NM 87131, USA.

Introduction: Deciphering the thermal history of ALH 84001 is essential in evaluating the evidence for possible fossil life in that martian meteorite. The focus of this debate has primarily involved the temperature of carbonate formation and has virtually ignored the postdepositional history of the carbonates [1–7]. Here, we provide evidence for a transient, high-temperature thermal pulse following carbonate deposition and describe possible effects on the carbonates that previously have been attributed to low-temperature processes and biogenic activity.
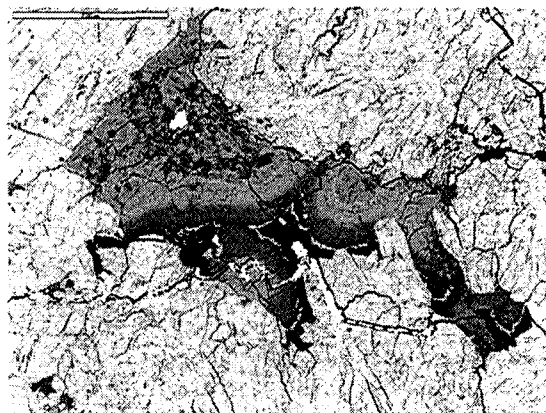

Fig. 2. Carbonates with complex zoning as shown above. The base of these carbonates is highly fractured and injected with shock glass. Carbonate fragments are broken along cleavage planes. Olivine (irregular, small white masses) occurs in the opx adjacent to the carbonate base.
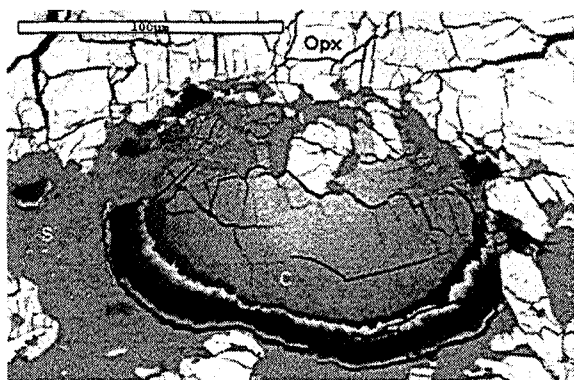
Fig. 3. Carbonate globule displaced from opx wall. Carbonate cleavage fragments and crushed opx are entrapped in shock glass.

lustrated in Fig. 1. Figure 3 also illustrates the disruption and transport of carbonate globules by the shock melt. Clearly, in Fig. 3, the carbonate has been pulled from the orthopyroxene wall on which it had initially crystallized. The crushed zone between the carbonate and the orthopyroxene consists of carbonate cleavage and orthopyroxene fragments immersed in shock glass. Displacement is on the order of 10–30 μm. Even greater displacement of carbonate globules (200–300 μm) has been observed. Evidence for a late-stage shock event has been recognized by Treiman [8].

A second line of evidence for the carbonate experiencing a high-temperature event is the olivine "inclusions" in the orthopyroxene adjacent to the carbonate. The olivine occurs only near fractures that contain disrupted carbonate. Note the absence of olivine in Fig. 1 and the abundance of olivine in Fig. 2. The inclusions are irregular and range in size from ~40 μm to submicrometer. The inclusions are in sharp contact with the enclosing orthopyroxene and often contain small inclusions of chromite. The $\delta^{18}O$ values of the olivine and orthopyroxene that were analyzed range from +4.3 to +5.3‰ and are indistinguishable from each other within analytical uncertainty. The $\delta^{18}O$ values of the olivine provide strong evidence that the olivine was not in isotopic equilibrium with the carbonate. In addition, the specific location of the olivine adjacent to fractures containing disrupted carbonates is highly suggestive of a non-magmatic origin. The olivine may have been formed by a reduction of magmatic orthopyroxene and spinel during this late, high-temperature event.

A third line of evidence for postdepositional heating of the carbonates has been described by Brearley [9]. Minute sheet silicates within the carbonate are not observed in the shock glass and appear to be amorphous near the carbonate-glass interface. This implies that the glass and the carbonate interface were involved in a late-heating event.

Conditions of High-Temperature Event: Mineral geothermometers using olivine and associated phases (orthopyroxene, spinel) record a high-temperature, subsolidus environment. Iron-magnesium exchange between olivine and chromite inclusions in the olivine gives equilibrium temperatures of 850°–900°C. The olivine-orthopyroxene geothermometer yields temperatures of 800°–900°C.

The textures implying mobilization of the carbonates indicate flow of the shock melt. The viscosity of the shock glass at various temperatures can be calculated from its chemical composition [10]. Melts with viscosities of 10^8 p (log 10 viscosity = 8) have the consistency of cool asphalt or very thick paste. To reproduce the textural relationships between the carbonate and shock glass, the viscosity of the shock glass must have been $<10^6$ p, indicating that it was injected at temperatures exceeding 1000°C. This agrees with previous qualitative estimates for the flow of plagioclase glass [11,12].

In such a scenario, would a high-temperature thermal event destroy the delicate, low-temperature chemical zoning observed in the carbonate? The destruction of the chemical zoning by chemical diffusion processes is not necessarily a final outcome to this thermal event. The chemical effects the thermal event has on the carbonates is dictated by the length of the event and the thermal diffusion profile across the carbonates. In a simple thermal model, assuming a single 200-μm vein of shock melt at a temperature of 1100°C intruded into an infinite carbonate layer at a temperature of 0°C, the carbonate adjacent to the shock glass will be heated to 400°–500°C and will fall to <50°C within seconds of the event. Under more complex scenarios, it is conceivable that the carbonate was exposed to slightly higher temperatures (500°–600°C). The thermal event, however, is very short lived. If the diffusion coefficients of Mg and Fe in carbonate are similar to other rock-forming minerals at these temperatures (10^{-18} to 10^{-21} cm^2 s^{-1}), this thermal event would have heated the carbonates to temperatures of 400°–600°C without destroying the intricate, low-temperature chemical zoning.

Implications for Biomarkers in ALH 84001: This late-stage heating event has a number of important implications for the origin of "biomarkers" in ALH 84001. First, this model explains the occurrence of magnetite in carbonate [13]. The concentration of magnetite in Fe-rich carbonate bands is produced because this carbonate composition is the least thermally stable and will produce the most magnetite on decomposition. At temperatures as low as 385°C, siderite decomposition can be detected [14,15], whereas magnesite and calcite are stable to temperatures of at least 650°C and 985°C respectively [16]. The voids in the carbonates commonly associated with magnetite are produced by the loss of CO_2 resulting from the decomposition of the siderite component in solid solution.

Second, the wide variability in $\delta^{18}O$ observed in the carbonates may be attributed to this late thermal pulse. The Mg-rich carbonates have $\delta^{18}O$ values of 18–22‰, whereas the $\delta^{18}O$ of the Fe-rich carbonates is much more variable and lower (6–18‰) [3,17]. The effect of decarbonation is to decrease the $\delta^{18}O$ value of the carbonate [18]. This could explain the lower and variable $\delta^{18}O$ for the Fe carbonates, assuming the O-isotopic composition of the carbonates was similar prior to heating.

References: [1] McKay et al. (1996) *Science, 273,* 924. [2] Shearer et al. (1996) *GCA, 60,* 2921. [3] Valley et al. (1997) *Science, 275,* 1633. [4] Bradley et al. (1996) *GCA, 60,* 5149. [5] Harvey and McSween (1994) *Meteoritics, 29,* 472. [6] Mittlefehldt (1994) *Meteoritics, 29,* 214. [7] Scott et al. (1997) *Nature, 387,* 377. [8] Treiman (1998) *LPS XXIX.* [9] Brearley, this volume. [10] Shaw (1972) *Am. J. Sci., 272,* 870. [11] Stöffler et al. (1986) *GCA, 50,* 889. [12] Stöffler et al. (1988) in *Meteoritics and the Early Solar System,* p. 165. [13] Brearley (1998) *LPS XXIX.* [14] Gallagher et al. (1981) *Thermochim. Acta, 50,* 41. [15] Gallagher and Warne (1981) *Thermochim. Acta, 50,* 253.

[16] Harker and Tuttle (1955) *Am. J. Sci., 253*, 209. [17] Leshin et al. (1998) *GCA, 62*, 3. [18] Valley (1986) *RIMS, 16*, 445.

OVERVIEW: THE SEARCH FOR LIFE ON MARS. S. W. Squyres, 428 Space Sciences Building, Cornell University, Ithaca NY 14853, USA.

The search for evidence of life has become the driving force behind NASA's Mars exploration program. At present, however, the evidence that Mars once harbored life is controversial, and our understanding of how to search for better evidence is rudimentary. A search might be based on the following assumptions:

At a minimum, life requires biogenic elements, liquid water, and a biologically useful source of energy. Other requirements are possible as well, but just these simple ones can help to narrow the search significantly.

The goals of the search should include both ancient and extant life. Because liquid water is now absent near Mars' surface, it may be a reasonable strategy to search for evidence of ancient life first and evidence of extant life subsequently.

Ancient life forms, if they existed at all, are most likely to have been simple, microbial forms. The same is probably true for extant life.

The best approach to searching for evidence of ancient life is probably to look for organic materials. Organics of biological origin may be less open to ambiguous interpretations than putative microfossils, and they have the added virtue of potentially containing important information about prebiotic processes if life never arose.

Working from these initial assumptions, several important problems must be addressed:

1. In what materials are organics most likely to be preserved? The Viking biology experiments failed to detect organic materials in the near-surface martian regolith at the parts-per-billion level. The reasons for this are not certain, but it is generally attributed to the action of some powerful oxidizing agent produced photochemically in the martian atmosphere. This putative substance diffuses into martian surface materials, destroying organic materials that may exist there. Whether or not organics will be found in a given martian material depends both on whether they would plausibly be there in the first place and whether or not they can be preserved subsequently against oxidation. Organics are not expected in primary igneous rocks. However, they might be found in sedimentary rocks, in the regolith, or in aqueous mineral inclusions within rocks of all types. Preservation depends on their distance from the martian atmosphere and the diffusive permeability of the intervening medium. These considerations suggest two possible approaches to the search for organics. One is to look within the martian regolith, although the distance beneath the surface that one must look is poorly known and may be considerable. Another is to look within sedimentary rocks or within rocks containing aqueous mineral deposits. This strategy could involve penetrating only very short distances, but such rocks may be difficult to find. One potentially attractive strategy might be to look in portions of the regolith cemented by ice, which can dramatically reduce diffusive permeability. Our knowledge of the distribution of ground ice on Mars is poor, however, and ice-rich sites may tend to lie at high latitudes where the past presence of liquid water is questionable.

Overall, better knowledge is needed of the nature of the oxidant, the diffusive permeability of the martian regolith, and anything that can be learned about the vertical profile of the regolith oxidation state.

2. Where/when has liquid water been available? This question can be partially answered morphologically, since a variety of landforms on Mars provide clear evidence for the flow of liquid water in the past. However, flowing surface water environments are not the most promising target for the search for evidence of life, since high-energy stream bed environments generally do not favor formation of the fine-grained sedimentary deposits or aqueous minerals that tend to best preserve organics. More attractive targets are the remains of standing water bodies and subsurface hydrothermal systems. These are more difficult to identify, however, and are poorly recognized on the basis of present data. Sites of former standing water bodies may be identified by subtle morphologic clues like ancient shorelines, by topographic data (e.g., closed depressions into which water-carved valleys debouch), and, potentially, by the mineralogical signatures of evaporites. Sites of past hydrothermal systems might be found based on morphologic clues, but probably will be best identified on the basis of the mineralogical signature of hydrothermal minerals. Exhumation by impacts may help in exposing formerly subsurface hydrothermal environments. Subsurface liquid water might be present today, but we have no real knowledge of its distribution. Techniques like long-wavelength radar sounding could be useful in this regard.

3. Where/when have biologically useful energy sources been available? Two plausible energy sources have been available in martian history: sunlight and hydrothermal interactions. Sunlight would be available primarily in shallow regions of surface water bodies. Although cold early climates could cause such bodies to be ice covered, light levels beneath meters of ice could still be sufficient to support life. Because of the absence of surface water, sunlight is unlikely to be a biologically significant energy source on Mars today. Hydrothermal activity was probably common in the ancient crust of Mars. The ancient highlands contain widespread probable volcanic plains and some discrete volcanic features. Abundant crustal water is indicated by the many fluvial features in the old terrains, and interactions between water and hot volcanic rocks were inevitable. Hydrothermal activity also would have been triggered by impacts, since an impact leaves a major thermal anomaly beneath it. Both volcanism and impacts have decreased with time on Mars, so hydrothermal interactions probably have decreased and moved to deeper levels in the crust.

4. What is the appropriate strategy for the search for evidence of martian life? The answer to this question depends on both the scientific considerations discussed above and the practical constraints imposed by availability of technology and funding. As noted above, the depth to which oxidants can diffuse is a function of the diffusive permeability of the medium it is diffusing through. The permeability of a porous regolith may be high enough that plausible estimates of oxidant diffusion depths are many meters. The permeability of solid rock, however, is typically many orders of magnitude lower, so that plausible diffusion lengthscales are centimeters or millimeters. The technology to drill remotely through many meters of regolith is not available at present, but several techniques exist for breaking or drilling short distances into surface rocks. This fact, then, suggests a strategy that focuses in the near term on use of instruments that locate rocks containing aqueous

mineral precipitates, and on a sampling technique that can obtain materials from within such rocks and return them to Earth. At the same time, it will be important to explore the vertical oxidation profile in the regolith via penetrators or drills, and the subsurface distribution of liquid water via radar sounding. The information gained would then be used to choose locations and techniques for deep sampling activities on subsequent missions.

THE LATERAL DISTRIBUTION OF POLYCYCLIC ARO-MATIC HYDROCARBONS IN ALLAN HILLS 84001: IM-PLICATIONS FOR THEIR ORIGIN.

T. Stephan[1], D. Rost[1], C. H. Heiss[1], E. K. Jessberger[1], and A. Greshake[2], [1]Institut für Planetologie/Interdisciplinary Center for Electron Microscopy and Microanalysis, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Strasse 10, D-48149 Münster, Germany (stephan@uni-muenster.de), [2]Museum für Naturkunde, Institut für Mineralogie, Humboldt-Universität zu Berlin, Invalidenstrasse 43, D-10115 Berlin, Germany.

Introduction: Polycyclic aromatic hydrocarbons (PAHs) in ALH 84001 were considered to be evidence for relic biogenic activity on Mars [1]. Crucial for their proposed connection to early life forms is a suggested spatial association with carbonates that contain internal structures resembling terrestrial microfossils. Although each observation can be explained individually [2,3], a lateral correlation would suggest a genetic link between PAHs and the microstructures.

A preliminary study of ALH 84001 by Thomas et al. revealed no clear correlation of PAHs and the so-called carbonate globules [4]. Three regions on a freshly fractured surface with a total size of 1×0.5 mm^2 were found to be enriched in PAHs. Although a relationship seems to exist between the region with the highest PAH concentration and a carbonate spheroid, the two other regions with enhanced concentrations of PAHs did not correlate with carbonates. On the other hand, not all carbonate globules in the analyzed sample contain PAH excesses or even PAH concentrations above background.

Nevertheless, in a later work by the same authors, a spatial association of PAHs and carbonates was proposed and interpreted as a major clue to relic biogenic activity without presenting convincing new results [1]. Even in a recent paper, some of the authors used the first study to claim that such a correlation exists [5].

Crucial for the investigation of spatial associations is the lateral resolution of the applied analytical methods. In the mentioned studies, microprobe two-step laser mass spectrometry (μL^{2}MS) was used for the analysis of PAHs. With this technique, an unambiguous determination of a spatial association is limited by its lateral resolution, about 50 μm, a size that is comparable with the typical dimension of the carbonate globules.

Scanning transmission X-ray microscope (STXM) C mapping and X-ray absorption near-edge structure (XANES) spectroscopic measurements on carbonates from ALH 84001 indicated the presence of organic C (π-bounded C) within or associated with carbonate globules on the scale of ~100 nm [6]. A definite identification of the nature of this organic C, which seems to be locally present at percent levels, is not possible with these techniques. Only a small fraction, <1 wt%, of the organic material in this meteorite may actually be represented by PAHs, and there is isotopic evidence fa-

voring a terrestrial origin for the majority of organic matter in ALH 84001 [7].

Analytical Technique: To investigate the actual distribution of PAHs in ALH 84001 on a submicrometer scale, we used time-of-flight secondary ion mass spectrometry (TOF-SIMS) with a lateral resolution of about 0.2 μm to analyze areas on three different thin sections of ALH 84001 [8,9]. This technique uses a time-of-flight mass spectrometer for the analysis of positive or negative secondary ions sputtered from the uppermost monolayers during primary ion bombardment. Besides atomic ions, large molecules also survive the sputtering process, at least as characteristic fragments. Using a fine-focused Ga liquid metal primary ion source, a simultaneous measurement of the lateral distribution for all secondary ion species with one polarity is possible. High mass resolution allows for the separation of atomic ions from hydrocarbons at the same nominal masses.

Results: Our TOF-SIMS studies revealed PAHs on all three sections of ALH 84001, but in no case was a correlation of PAHs with carbonates observed. On the contrary, a general trend of a lower PAH concentration in carbonates compared to orthopyroxene or feldspatic glass seems to exist [8,9].

Since the information depth in a typical measurement is on the order of a few atomic monolayers, surface contamination is a major concern in TOF-SIMS. The three investigated thin sections were prepared from three different pieces of ALH 84001 in two different laboratories, minimizing the probability of a common contamination with external PAHs during sample preparation. A section of Chassigny [10] that was treated exactly like one of our ALH 84001 sections and measured directly before and after ALH 84001 contained no detectable PAHs. Therefore, contamination with PAHs not indigenous to the sample is unlikely.

On the other hand, redistribution of indigenous PAHs may have occured during sample preparation, e.g., polishing. This indeed was observed in one of our samples. For this section we observed first a rather uniform distribution of PAHs on the very surface. After extensive sputtering with an Ar ion beam that removed several atomic monolayers, the indigenous PAH distribution was revealed, showing the previously observed "anticorrelation" of PAHs and carbonates [9].

To understand the relative intensities of characteristic PAH mass peaks in the TOF-SIMS spectra [8], which vary significantly from those observed by μL^{2}MS [1], we investigated with TOF-SIMS pure PAH substances, pentacene and coronene (Fig. 1), on Ag substrates. Both substances showed fractionation during primary ion bombardment. Pentacene, being more susceptible to fractionation, revealed similar relative maxima, although in different proportions,
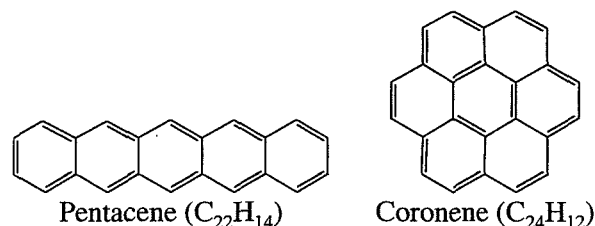

Pentacene ($C_{22}H_{14}$)   Coronene ($C_{24}H_{12}$)

Fig. 1. Pure pentacene and coronene samples were investigated on Ag substrates using TOF-SIMS.

in the mass spectrum as observed for ALH 84001. Differences from μL^2MS spectra, especially the high abundance of low-mass PAHs observed by TOF-SIMS, can be explained by differences in ionization processes, e.g., stronger fractionation during ion bombardment. It is therefore plausible that spectra obtained by μL^2MS and TOF-SIMS result from the same mixture of PAHs.

Discussion: A major question is where these PAHs, unambiguously present in ALH 84001, come from. Are they indigenous [1,5] to this meteorite or were they acquired during residence in the Antarctic ice [3]? An important argument against their terrestrial origin is believed to be the reported decrease by a factor of 5–10 of the PAH signal toward the fusion crust of the meteorite [1,5]. This decrease can at least in part be explained by different morphological properties of the fusion crust, which has an inherently smaller surface area. If the PAHs observed in ALH 84001 result from terrestrial contamination and now reside along submicrometer-sized fractions or grain boundaries, a correlation of PAH concentration with internal surface area would be expected. From the TOF-SIMS measurements, such a concentration along grain boundaries or submicrometer fractions can neither be confirmed nor ruled out.

Conclusions: Irrespective of their origin, a genetic link between PAHs and carbonate globules, the carrier of the so-called nanofossils, can be excluded based on the lack of spatial association. Consequently, these observations have to be taken individually and should not be considered collectively.

References: [1] McKay D. S. et al. (1996) *Science, 273,* 491–504. [2] Bradley J. P. et al. (1997) *Science, 390,* 454. [3] Becker L. et al. (1997) *GCA, 61,* 475–481. [4] Thomas K. L. et al. (1995) *LPS XXVI,* 1409–1410. [5] Clemett S. J. et al (1998) *Faraday Discussions (Royal Soc. Chem.), 109,* 417–436. [6] Flynn. G. J. (1998) *Meteoritics & Planet. Sci., 33,* A50–A51. [7] Jull. A. J. T. (1998) *Science, 179,* 366–369. [8] Stephan T. et al. (1998) *LPS XXIX,* Abstract #1263. [9] Stephan T. et al. (1998) *Meteoritics & Planet. Sci., 33,* A149–A150. [10] Greshake A. et al. (1998) *LPS XXIX,* Abstract #1069.

MINERAL BIOMARKERS IN MARTIAN METEORITE ALLAN HILLS 84001?
K. L. Thomas-Keprta[1], D. A. Bazylinski[2], S. J. Wentworth[1], D. S. McKay[3], D. C. Golden[1], E. K. Gibson Jr.[3], and C. S. Romanek[4], [1]Mail Code C23, Lockheed Martin, NASA Johnson Space Center, Houston TX 77058, USA (kthomas@ems.jsc.nasa.gov), [2]Department of Microbiology, Immunology, and Preventive Medicine, Iowa State University, Ames IA 50011, USA, [3]Mail Code SN, NASA Johnson Space Center, Houston TX 77058, USA, [4]Drawer E, Savannah River Ecology Laboratory, University of Georgia, Aiken SC 29802, USA.

Introduction: The occurrence of fine-grained magnetite in the Fe-rich rims surrounding carbonate globules in the martian meteorite ALH 84001, originally described in [1], have been proposed as fossil remains of primitive martian organisms. Here we report observations on size and shape distributions of magnetites from ALH 84001 and compare them to biogenic and inorganic magnetite crystals of terrestrial origin. While some magnetite morphology is not unequivocally diagnostic for its biogenicity, such as cubodial forms of magnetite [3], which are common in inorganically formed magnetites, other morpholgies of magnetite (parallelepiped or elongated prismatic [4] and arrowhead forms [5]) are more likely signatures of biogenic activity [2]. Some ALH 84001 magnetite particles described below have unique morphology and length-to-width ratios that are indistinguishable from a variety of terrestrial biogenic magnetite and distinct from all known inorganic forms of magnetite.

Methods: Two ALH 84001 chips containing carbonate globules were immersed in ~20 ml of 20% acetic acid at ~50°C for 72 and 96 hr. Controls show that magnetite is not affected by this acid treatment. The residual chips were removed from the acid; the acid containing the magnetite was placed on C-coated TEM (transmission electron microscope) grids and allowed to evaporate. These grids were examined at 160 and 200 kV using a JEOL 2000 FX TEM equipped with a Link System IV energy-dispersive X-ray spectrometer.

Results and Discussion: Thousands of magnetite grains in clumps or groups were found on the TEM grids. The magnetite ranges from ~10 to 200 nm in size (in the longest dimension) and
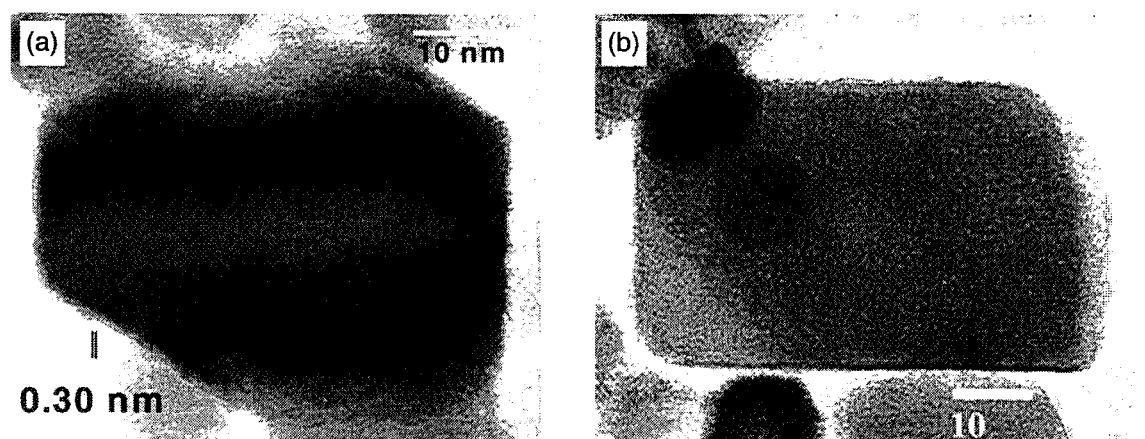

Fig. 1. Two views of a magnetite crystal from ALH 84001. **(a)** displays a hexagonal cross section at +17°; **(b)** shows a hexagonal outline at –22°. Compare with Fig. 4a,b.

are composed only of Fe and O. Of the 526 magnetites documented, we have identified three distinct populations: elongated prisms, whisker, and irregular. Elongated prismatic magnetites constitute 27% of the population and are defined as moderately elongated (length/width <2.6) magnetites with rectangular projections hav-
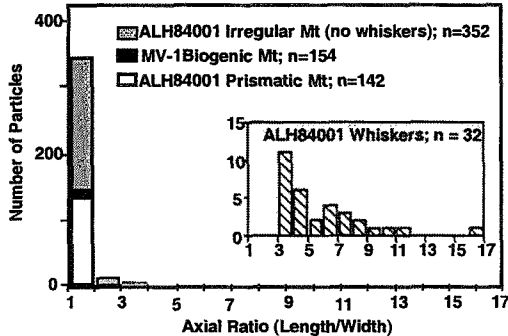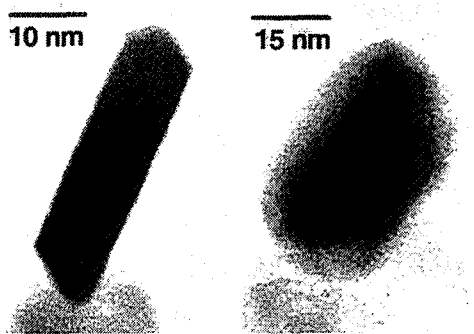
ing hexagonal cross sections when viewed along the (111) axis (see Figs. 1a,b on previous page). More than 99% of these magnetites have length/width or axial ratios between 1 and 2 (Fig. 2). Whisker magnetites, defined as having length/width ratios >3, constitute 6% of the total (Figs. 2 and 3). We found two types of whisker magnetites (rounded ends with rounded cross sections and whiskers that turn platy when viewed form another angle of rotation (see Fig. 3). Irregular magnetites (including cuboidal, teardrop, and generally irregular forms) made up 67% of the population. For comparison, we performed similar analyses of magnetite crystals isolated from bacteria strain MV-1 and specific abiotic magnetite; we also compared these results to those described in the literature for abiotic magnetite [6,7]. The elongated prismatic magnetite particles in ALH 84001 have high chemical purity, a restricted range of axial ratios, and distinct size distributions. Additionally, they have a unique morphology characterized by elongated growth along the (111) axis, a hexagonal cross section when viewed along that axis, and a rectangular outline when viewed normal to the (111) axis (Figs. 1a,b). These specific properties make them identical to magnetite crystals produced by specific extant terrestrial magnetotactic bacteria (Figs. 4a,b; [8]). These unique properties are not observed in any known natural, inorganically produced magnetite crystals. Inorganic magnetite particles we observed and those from the literature are nearly equidimensional (axial ratios ~1), and none observed or described from the literature have the elongated prismatic shapes and axial ratios of the elongated prismatic magnetites in ALH 84001 and specific biogenic magnetite crystals (e.g., MV-1). Unless an inorganic analog for these crystals is found, the presence of elongated prismatic magnetite crystals in martian meteorite ALH 84001 must be considered as likely evidence for primitive life on early Mars.

References: [1] McKay et al. (1996) *Science, 273,* 924. [2] Bazylinski and Moskowitz (1997) in *Geomicrobiology: Interactions between Microbes and Minerals* (Banfield and Nealson, eds.), p. 181. [3] Balkwill et al. (1980) *J. Bacteriol.,141,* 1399. [4] Bazylinski et al. (1988) *Nature, 334,* 518. [5] Thornhill et al.
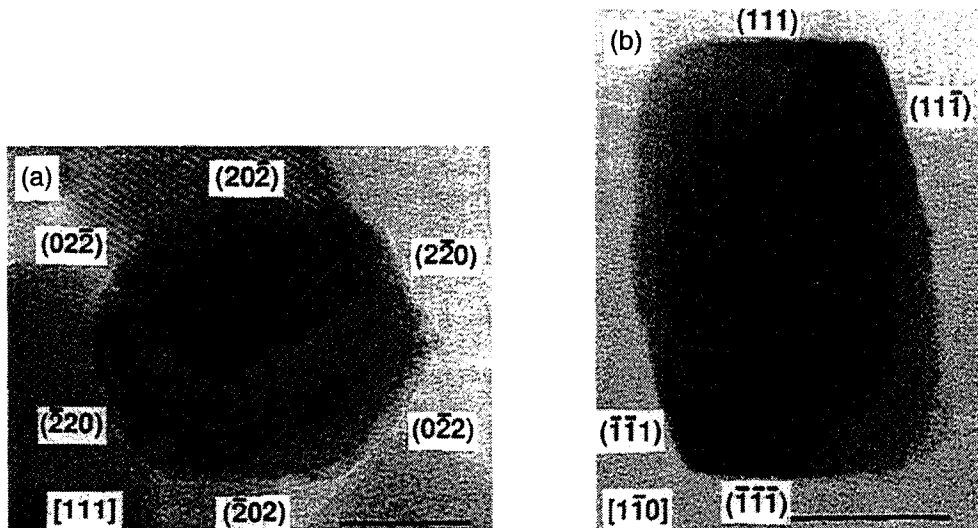

Fig. 2.

Fig. 3.

Fig. 4. Two views of an elongated prismatic biogenic magnetite [from 8]; scale bar = 20 nm.

(1994) *FEMS Microbiol. Lett., 115,* 169. [6] Schwertmann and Cornell (1991) in *Iron Oxides in the Laboratory: Preparation and Characterization,* p. 111. [7] Nanophase magnetite produced by Nanophase Technology at www.nanophase.com/TEXT/PROD-UCTS/IronOxide.html. [8] Sparks et al. (1990) *EPSL, 98,* 14.

MINERALIZATION OF BACTERIA IN TERRESTRIAL BASALTIC ROCKS: COMPARISON WITH POSSIBLE BIOGENIC FEATURES IN MARTIAN METEORITE ALLAN HILLS 84001. K. L. Thomas-Keprta[1], D. S. McKay[2], S. J. Wentworth[1], T. O. Stevens[3], A. E. Taunton[4], C. C. Allen[1], E. K. Gibson Jr.[5], and C. S. Romanek[6], [1]Mail Code C23, Lockheed Martin, NASA Johnson Space Center, Houston TX 77058, USA (kthomas@ems.jsc.nasa.gov), [2]Mail Code SN, NASA Johnson Space Center, Houston TX 77058, USA, [3]Battelle, Pacific Northwest Laboratory, P.O. Box 999, Richland WA 99352, USA, [4]Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville AR 72701, USA, [5]Mail Code SN4, NASA Johnson Space Center, Houston TX 77058, USA, [6]Drawer E, Savannah River Ecology Laboratory, University of Georgia, Aiken SC 29802, USA.

The identification of biogenic features altered by diagenesis or mineralization is important in determining whether specific features in terrestrial rocks [e.g., 1,2] and in meteorites may have a biogenic origin [3]. Unfortunately, few studies have addressed the formation of biogenic features in igneous rocks, which may be important to these phenomena, including the controversy over possible biogenic features in basaltic martian meteorite ALH 84001 [3]. To
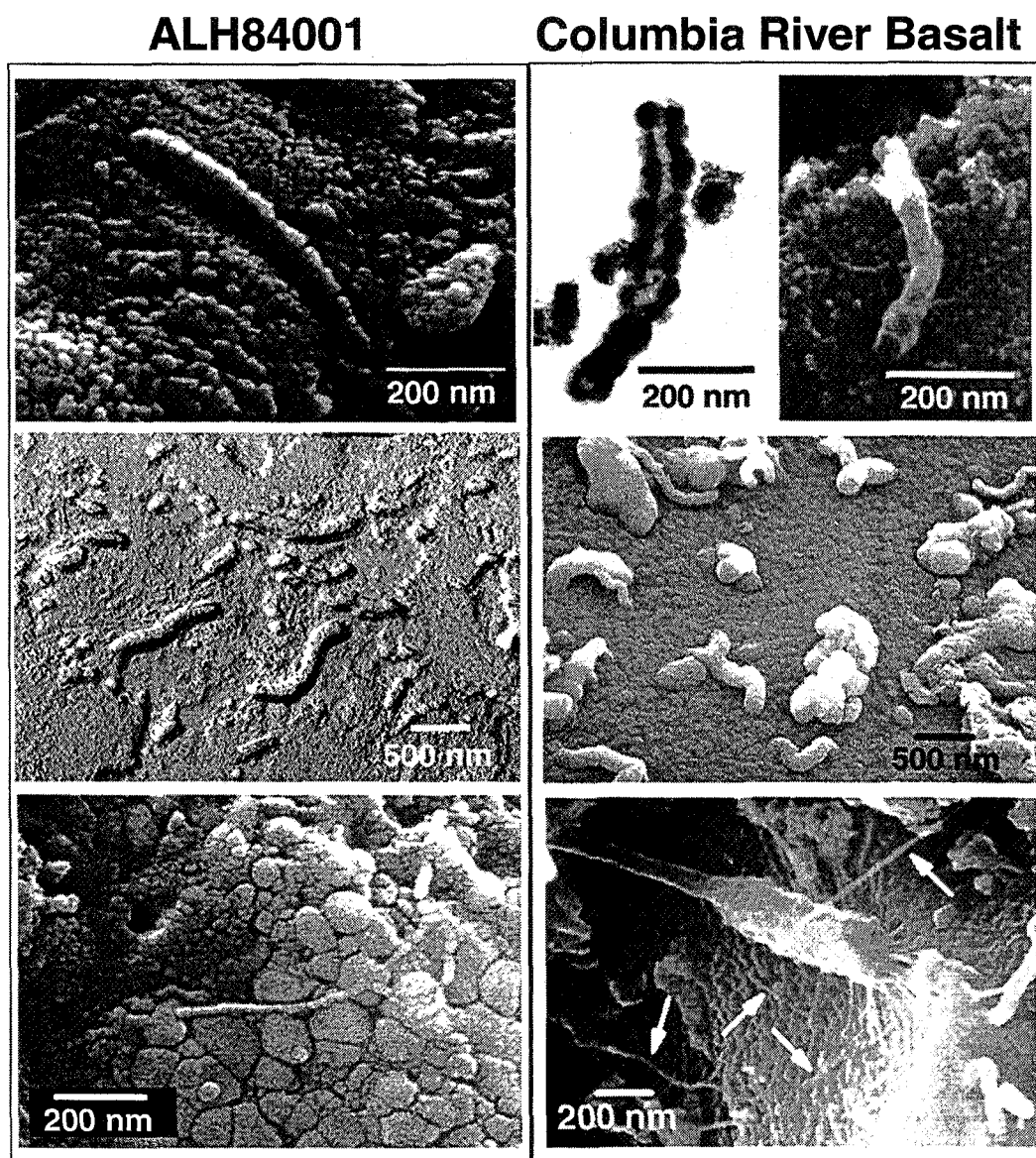

Fig. 1.

explore the presence of biogenic features in igneous rocks, we examined microcosms growing in basaltic small-scale experimental growth chambers or microcosms. Microbial communities were harvested from aquifers of the Columbia River Basalt (CRB) group and grown in a microcosm containing unweathered basalt chips and groundwater (technique described in [4]). These microcosms simulated natural growth conditions in the deep subsurface of the CRB, which should be a good terrestrial analog for any putative martian subsurface ecosystem that may have once included ALH 84001 [9].

Inoculated, fresh (control), and sterile-solution rock chips were examined with a high-resolution Philips XL 40 field emission gun scanning electron microscope (FEGSEM) and a JEOL 2000 FX transmission electron microscope (TEM). FEGSEM samples were coated with ~2–5 nm of Au-Pd conductive coating. Uncoated microorganisms were also examined in the TEM at 160 kV.

We examined more than 30 surfaces of rock chips from the inoculated basaltic microcosms. A detailed study of five chips of uninoculated basalt chips revealed no cell-like forms or appendages. The inoculated chips displayed three dominant morphological types of forms that we interpret as microorganisms: Type 1 is an oval-shaped (coccobacillus) form with a smooth surface texture that ranged from ~1 to 2.5 μm in length and slightly less in width. These organisms are composed chiefly of Fe, Mn, and O with minor elements including P. Type 2 is a similarly shaped coccobacillus form in the same size range but with a textured surface composed of thousands of thin (~2–5 nm diameter) interwoven filaments composed mainly of Fe and O as ferrihydrite, an Fe^{+3} hydroxide with minor elements including P. Type 1 and 2 organisms are significantly mineralized; both types display organisms that appear hollow. It is not clear if the formation of a mineralized shell was a replacement for the original cell wall or a coating that developed external to the cell. Nevertheless, there was no evidence for the preservation of any ultrastructure, such as the cell wall. Type 3 is a tubular (bacillus or rod) form to which a single appendage may be attached at one end. Type 3 forms range from ~0.30 to 2.4 μm in the longest direction without appendage. Microcolonies of bacillus forms are frequently observed embedded in biofilm. Type 3 organisms are composed mainly of C, O, and Na with minor P, S, and Cl; they are unmineralized cells. All three types of organisms contain minor P whether they are mineralized or not. In addition to the organisms, we observed attached and unattached filaments. Filaments are generally longer and thinner than organisms; they have distinctive tubular morphologies. Attached filaments are similar in composition to the type 3 unmineralized cells. Unattached filaments are composed of ferrihydrite and other minor elements inlcuding P; their composition is similar to the type 2 organisms. Some unattached filaments are hollow (Fig. 1). We believe that these unattached filaments are mineralized cellular appendages because they are not present in the uninoculated control microcosms; we conclude that they were likely produced by biological mechanisms. In addition, the presence of P indicates that these filaments are most likely biogenic. If so, it is clear that the mineralization of bacteria is not necessarily restricted to the main body of the organisms; much smaller appendages can also be preserved. The present observations suggest that microfossils in basaltic rocks may contain little C, lack evidence of cellular ultrastructure, and include mineralized subcellular appendages. The presence of abundant biofilm may also serve as a substrate upon which minerals may be deposited. If so, it is likely that mineral-

ized weblike biofilms may also be preserved and suggest previous biogenic activity.

Here we present new size measurements and photomicrographs comparing the putative martian fossils to biogenic material in the CRB microcosms (Fig. 1). The range of size and shapes of the biogenic features on the CRB microcosm chips overlaps with and is similar to those on ALH 84001 chips. Although this present work does not provide evidence for the biogenicity of ALH 84001 features, we believe that, based on criteria of size, shape, and general morphology, a biogenic interpretation for the ALH 84001 features remains plausible.

References: [1] Hoffman H. J. and Schopf J. W. (1983) in *Earth's Earliest Biosphere: Its Origin and Evolution* (J. W. Schopf, ed.), Princeton Univ. [2] Ferris F. G. et al. (1986) *Nature, 320,* 609. [3] McKay D. S. et al. (1996) *Science, 273,* 924. [4] Stevens T. O. and McKinley J. P. (1995) *Science, 270,* 450.

ANCIENT MARTIAN LIFE IN ALLAN HILLS 84001? STATUS OF SOME CURRENT CONTROVERSIES. A. H. Treiman, Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston TX 77058, USA (treiman@lpi.jsc.nasa.gov).

Four lines of evidence were taken to suggest that ALH 84001 contained traces of ancient martian life preserved in its carbonate mineral masses [1]: abundance of organic compounds (PAHs), disequilibrium mineral assemblages, morphology of submicrometer magnetite crystals, and presence of objects comparable in size and shape to bacteria. This evidence is predicated on the carbonate globules having formed at temperatures conducive to life. Here, I review evidence on carbonate formation temperature, martian origin of organic compounds, and bacteria-shaped objects.

Formation Temperature: A precondition for signs of life associated with the carbonate masses [1] is that the masses formed at a temperature amenable to life as we know it [2], <~150°C. The formation temperature of the carbonates is poorly constrained [3,4]; most current hypotheses suggest either formation at T < ~200°C from water-rich fluid (possibly saline) or formation at T > ~250°C from CO_2-rich fluid. Relevant evidence cannot be interpreted unambiguously, in part because the geologic context of ALH 84001 is unknown, and in part because of its complex history [5].

The range of elemental compositions of the carbonates has been taken as indicating quasi-equilibrium at T ~700°C [4,6]. The fine-scale chemical zoning of the carbonates requires that this high temperature must have lasted only a short time, as might be expected in an impact event [4,7]. On the other hand, the elemental compositions could have formed at chemical disequilibria at low temperature [8,9]. The absence of hydrous minerals in ALH 84001 can be explained in either model. At higher temperature, the absence of hydrous minerals may reflect the presence of CO_2-rich fluid [4,7,10,11]. At low temperature, one can invoke slow reactions or very saline aqueous fluids [12–14].

The O-isotopic compositions of the carbonates may suggest equilibrium at low temperature from hydrous fluids [3], although the inferred temperatures depend on what O-isotopic composition is taken for the depositing fluids [15]. On the other hand, the O isotopes also appear consistent with carbonate growth either from aqueous solutions at variable low temperature or from carbonic fluids at T > ~500°C [11].

The carbonates in ALH 84001 occur as fracture fillings, lacy patches, and rounded volumes among and within pyroxene and plagioclase glass. These textures have been interpreted as void fillings (low temperature) [1,16], products of solution/precipitation (indeterminate T) [10,14], or solidified carbonate melt (high temperature) [7].

Considerable work has gone to the temperature significance of submicrometer magnetites in the carbonates. Equant magnetites have been interpreted as biogenic magnetosomes from magneto-tactic bacteria [1,17], although these shapes might equally well form without life. Elongate magnetite grains, some epitaxial on carbonates and some with axial screw dislocations, have been suggested as products of vapor deposition at high temperature [18,19], although similar magnetite shapes occur in bacteria [20]. Also, it is possible that the elongate magnetites formed at high temperature, but after the carbonates formed [5]. Magnetites are also present in void spaces in the carbonate, either as the product of decarbonation at high temperature [21] or as entrapped from the aqueous fluid that deposited the carbonates [22].

Summary. There is no consensus on the formation temperature or mechanism of carbonate masses. The bulk of evidence, in my opinion, is not consistent with T > 400°C [4,6,7]. At present, there seems no way to tell whether the carbonates formed at moderate or low temperature (hotter or colder than ~150°C).

Organic Matter: McKay et al. [1] presented evidence that the carbonate pancakes in ALH 84001 are enriched in polycyclic aromatic hydrocarbons, PAHs, which are organic compounds commonly formed from (or by) biological organisms. Absence of PAHs near the meteorite's fusion crust implied that the PAHs are martian. Confirming evidence included the high abundance of organics in ALH 84001 [23]. Work here has followed many interconnected threads.

Are PAHs associated with the carbonate globules? The association was amplified by [24] and confirmed by XANES analyses [25]. An early abstract from the McKay group states that some carbonate globules have low PAH content [26]. Recent TOFSIMS analyses on polished surfaces found PAHs evenly distributed through the silicate and oxide minerals, but less abundant in the carbonates [27]; this result seems improbable.

Are the PAHs martian? The absence of PAHs near ALH 84001's fusion crust suggests that they are preterrestrial [1,24]. It has been claimed that the PAHs are similar to those of Antarctic ice, and hence contaminants, and this is supported by experiments on solubility, transport, and adsorption behavior of PAHs [28]. These results have been strongly criticized [24].

Are the PAHs biogenic? The PAHs in ALH 84001 are claimed to be like those produced by degradation of bacteria [1,24] (possibly not martian [28]). But the variety and abundances also show similarities to PAHs in CM chondrite meteorites and common interplanetary dust particles [29]. The PAHs could also have formed inorganically (Fischer-Tropsch reaction), possibly catalyzed by magnetite grains [30]. But it may be impossible to determine the origin of the PAHs, because Antarctic weathering can degrade most distinguishing characters of biogenic PAHs [31].

Are other organics martian? Probably not. Nearly all the organic C in ALH 84001 has live ^{14}C, meaning that it formed fairly recently on Earth [32]. Similarly, amino acids extracted in bulk from ALH 84001 have abundances and chirality typical of Earth biological matter [33].

Summary. It seems likely that the PAHs in ALH 84001 are (at least in part) martian, but that other organic matter is terrestrial. It is not known whether the PAHs are biogenic or not, nor whether this issue can be resolved.

Possible Biogenic Objects: The most publicly compelling line of evidence is the presence of bacteria-shaped objects (BSO) in carbonate masses [1,34]. However, their identification as biogenic is ambiguous in the absence of internal structures (contrary to early hints [35]), undisputed martian biochemicals (see above), and biologic community structures [e.g., 36]. Morphology alone is problematic; BSOs can arise in many ways [e.g., 37].

Too Small? At the 1996 press conference on ALH 84001, the BSOs were claimed to be too small for life: 20–100 nm [1] vs. >200 nm diameter for free-living bacteria [38]. The BSOs enclose too little volume to contain the requisite molecules for Earth life [2,38], a point contested by some [39]. The BSO size range has been extended to 750 nm, and there is some evidence of Earth bacteria as small as 80 nm [40]. The smaller objects in ALH 84001 could also be bacterial appendages, not whole organisms [41].

Inorganic? The 100-nm elongate BSOs may be magnetite crystals that formed at high temperature [14,19]. Aligned "swarms" of ~100-nm BSOs [1] may be magnetite crystals epitaxially oriented on carbonate mineral substrates [19,42,43] or irregularities on mineral surfaces [14]; McKay et al. may no longer consider the swarms biogenic [40].

Terrestrial? In the absence of (bio)chemical characterizations, it remains possible that the BSOs are terrestrial. Endolithic organisms are well known [44]; fungi and bacteria can live in Antarctic meteorites [45]. Spores of these organisms, and larger biologic objects like diatom tests [46], are distributed worldwide by wind. BSOs have been found in lunar meteorites from Antarctica, which presumably never experienced clement conditions before landing in Antarctica [34]. This last result suggests that BSOs in ALH 84001 are terrestrial, although McKay [47] reports never having found BSOs in lunar rocks or other meteorites.

Artificial? It has been suggested that some BSOs figured in [1] are artifacts of sample preparation [18]. This claim is disputed [40], and scanning force microscopy measurements appear to suggest the BSOs are not artificial [48]. Yet, the morphology of some images, especially the popular "worm," is suggestive of coating artifact.

Summary. The bacteria-shaped objects in ALH 84001 are visually appealing, but their actual identity remains uncertain.

Conclusions: The hypothesis that ALH 84001 contains traces of ancient martian life [1] has not been proved nor disproved, and all parts of the hypothesis remain controversial. So far, it has not been shown that the carbonate masses formed at a high temperature inimical to life. This failure is not proof of the hypothesis; it is merely not a disproof. It seems likely that the PAHs in ALH 84001 formed on Mars, but this is not proof of martian biology. The missing link is the correlation between observed PAHs and those of degraded bacteria, and that link may have been permanently severed [31]. The "Mars Bugs" are under siege, attacked from all sides and so far with few reinforcements.

Whether or not it is proved correct, the hypothesis of [1] has stimulated interest and research on ALH 84001, other martian meteorites, and Mars itself. Renewed interest in science is good for the nation, and renewed funding is beneficial to the research community. But this debate has stirred some difficult questions: (1) Are

the standards for publication less stringent for "hot-topic" papers than for "routine" papers? (2) Why has it been so difficult to reach a consensus about ALH 84001? Are the carbonates so intractable that our best scientists cannot agree on their formation temperature within 700°C? Or are we not nearly as clever as we thought? (3) How will NASA fare if the "life in ALH 84001" hypothesis is conclusively refuted?

References: [1] McKay et al. (1996) *Science, 273*, 924. [2] Nealson K. H. (1997) *JGR, 102*, 23675. [3] Romanek et al. (1994) *Nature, 372*, 655. [4] Harvey and McSween (1996) *Nature, 382*, 49. [5] Treiman A. (1998) *Meteoritics & Planet. Sci., 33*, in press. [6] Mittlefehldt D. (1994) *Meteoritics, 29*, 214. [7] Scott E. et al. (1997) *Nature, 387*, 377. [8] Valley J. et al. (1997) *Science, 275*, 1633. [9] Treiman and Romanek (1998) *Meteoritics & Planet. Sci., 33*, in press. [10] Kring D. et al. (1998) *GCA, 62*, 2155. [11] Leshin L. et al. (1998) *GCA, 62*, 3. [12] Warren P. (1998) *JGR, 103*, 16759. [13] McSween and Harvey (1998) *Meteoritics & Planet. Sci., 33*, A103. [14] Treiman A. (1995) *Meteoritics, 30*, 294. [15] Hutchins K. and Jakosky B. (1997) *GRL, 24*, 819. [16] McKay G. and Lofgren G. (1977) *LPS XXVIII*, 921. [17] Thomas-Keprta K. et al. (1998) *LPS XXIX*, Abstract #1495. [18] Bradley J. et al. (1997) *Nature, 390*, 454. [19] Bradley J. et al. (1996) *GCA, 60*, 5149–5155. [20] Thomas-Keprta K. et al. (1997) *LPS XXVIII*, 1433. [21] Brearley A. J. (1998) *LPS XXIX*, Abstract #1757. [22] Blake D. et al. (1998) *LPS XXIX*, Abstract #1347. [23] Grady M. M. et al. (1994) *Meteoritics, 29*, 469. [24] Clemett S. et al. (1998) *Faraday Disc., 109*, in press. [25] Flynn G. et al. (1998) *Meteoritics & Planet. Sci., 33*, A50. [26] Thomas K. et al. (1995) *LPS XXVI*, 1409. [27] Stephan T. et al. (1988) *Meteoritics & Planet. Sci., 33*, A149. [28] Becker L. et al. (1997) *GCA, 61*, 454. [29] Bell J. (1996) *Science, 274*, 2121. [30] Anders E. (1996) *Science, 274*, 2119. [31] Sephton M. and Gilmour I. (1988) *Meteoritics & Planet. Sci., 33*, A142. [32] Jull A. et al. (1998) *Science, 279*, 366. [33] Bada J. et al. (1998) *Science, 279*, 362. [34] Sears D. and Kral T. (1998) *Meteoritics & Planet. Sci., 33*, in press. [35] Swartz M. (1996) *Texas Monthly, November*. [36] Schopf J. (1993) *Science, 260*, 640. [37] Peiming W. and Odler I. (1990) *Proc. 12th. Intl. Conf. Cement Micros.*, pp. 382–402. [38] Maniloff J. et al. (1997) *Science, 276*, 1775–1776. [39] Folk R. L. (1997) *Science, 274*, 1287; *Science, 276*, 1776. [40] McKay D. S. et al. (1997) *Nature, 390*, 455. [41] Thomas-Keprta K. et al. (1998) *LPS XXIX*, Abstract #1495. [42] Bradley J. et al. (1998) *Meteoritics & Planet. Sci., 33*, in press. [43] Bradley J. et al. (1997) *Meteoritics & Planet. Sci., 32*, A20. [44] Friedmann E. and Weed R. (1987) *Science, 236*, 703. [45] Steele I. et al. (1998) *Meteoritics & Planet. Sci., 33*, A149. [46] Burckle L. and Delaney J. (1998) *Meteoritics & Planet. Sci., 33*, A26. [47] McKay D. et al. (1996) *Science, 274*, 2123. [48] Steele A. et al. (1998) *J. Microsc., 189*, 2.

HIGH STRAIN-RATE DEFORMATION AND FRICTION MELTING AS A POSSIBLE ORIGIN FOR "SHOCK" FEATURES IN ALLAN HILLS 84001. C. H. van der Bogert and P. H. Schultz, Department of Geological Sciences, Brown University, Box 1846, Providence RI 02912, USA.

Summary: Many of the debates surrounding martian meteorite ALH 84001 address the questions of the temperature and age of carbonate deposition [e.g., 1–3] and its ultimate effect on the gen-eration and preservation of evidence for life [4]. To fully answer these questions, we must determine the processes that formed the textures in the meteorite and what implications these have for the environment of carbonate deposition. Discussions of the history and origins of the textures in ALH 84001 have been synthesized by [1,3,5,6], among others. All such histories propose the occurrence of shock melting and metamorphism for ALH 84001 despite nonunique evidence for shock. Here we present an alternative mechanism for the formation of crush zones in ALH 84001, which may also explain the occurrence of feldspar, silica, and carbonate melts.

Introduction: One of the puzzling aspects of ALH84001 is its shock state. Treiman [5], in his interpretation of the shock history of ALH 84001, describes the orthopyroxene clasts within the granular bands ("crush zones" of [1]) as having irregular or undulose extinction, pervasive microfracturing, and polygonization. These observations, coupled with the presence of maskelynite and a glassy matrix, lead Treiman [5] to propose that ALH 84001 underwent shock levels equivalent to S5 or S6 of Stöffler et al. [7]. Their classification scheme, however, requires the analysis of olivine grains rather than orthopyroxene grains, due to the wide-ranging nature of shock deformation in orthopyroxene [7]. The presence of melt veins, pockets, and dikes must occur, with high-shock indicators in olivine and maskelynite to warrant a classification of S5 and S6 materials [7]. As further illustrated by friction melting experiments in meteorites, the presence of veins of melted materials alone cannot be used as a unique indicator of a high-shock process [8]. Unfortunately, the presence of olivine in ALH 84001 is limited and its origin unconstrained [e.g., 9,10]. Consequently, the classification scheme of [7] is not directly applicable.

Minerals show even less evidence for shock outside the crush zones. Scott et al. [3] observe only minimal mosaicism of the pyroxenes outside the zones. As a result, they interpret shock pressures outside the crush zones to be small, whereas shock pressures of greater than ~50 GPa are thought to be required for the melting and mobilization of silica and plagioclase melts [11] within the crush zones [3]. It is suggested that these shock pressures would be lower if the target rock were warmer [e.g., 3,11,12]. However, this scenario still requires extreme pressure gradients across only millimeters of section from the pyroxenes outside of the crush zones to those within it. Besides the presence of plagioclase and silica melts, there is no other evidence for high shock levels within the crush zones [3].

In addition, no high-pressure polymorphs have been identified in ALH 84001; all evidence for high shock pressures is textural. In Shergotty, the presence of glasses with radiating fractures may indicate rapid quenching from high-pressure melts and expansion upon decompression [13]. Maskelynite in ALH 84001 and is also normal rather than diaplectic glass [e.g., 14,15]. Shock levels exceeding 80 GPa are inferred for these types of glasses [13]. Raman spectra of martian "maskelynites" in ALH 84001 are similar to those that have been experimentally subjected to only 31 GPa [15]. These observations require either that the glass was totally melted at a higher shock level than that for the formation of diaplectic glass, or the melting event included temperatures high enough to melt the plagioclase grains *in situ*.

An Alternative: The presence of glass and deformation textures, yet ambiguous evidence for shock, may indicate that an alternate process controlled the petrologic evolution of ALH 84001.

Treiman [5] suggested that the crush zones could be generated during high strain-rate deformation or shock associated with either a tectonic or impact event on Mars. Here we suggest that the crush zones and even melts can develop from high strain-rate deformation without high shock levels. Our scenario is based on the evidence for pervasive shear in ALH 84001, while evidence for shock is minimal. For example, Treiman [5] describes "augen or ribbon" structures of orthopyroxene within the crush zone, with chromite stringers, which are "wavy or swirled." Small (<10 μm) Fe sulfides are also present in elongated bands within the crush zone [16]. Olivine inclusions are elongate and "boudinage-like" [10]. Such textures are indicators of shear deformation [e.g., 17,18]. In addition, the crush zones themselves have been described as cataclastic, with larger clasts having rounded edges and smaller clasts having sharper edges [3]. These observations, along with evidence for recrystallization suggest that these crush zones are pseudotachylites or friction melts, a type of high strain-rate rock typically associated with ultracataclasites [e.g., 19]. In fact, Treiman [5] notes that the crush zones could texturally "be called recrystallized mylonite or pseudotachylite." Further, "the structures of the granular bands are typical of dynamic recrystallization (high strain rates), which can occur during rapid tectonic motions or during shock" [5]. Scott et al. [3] note that the "crush zones were probably heated and welded by friction during crushing, as in pseudotachylites." Such comments, coupled with the absence of shock features, support a high strain rate rather than shock origin.

The best terrestrial analog for ALH 84001 is a terrestrial ultramafic pseudotachylite, which occurs in the Balmuccia peridotite, Ivrea-Verbano zone, northern Italy. Textures in the pseudotachylites of the Ivrea-Verbano zone closely resemble the textures observed in ALH 84001. These pseudotachylites contain several distinctive features: dynamic recrystallization; chaotic cataclastic to mylonitic textures; olivine and pyroxene with undulose extinction and densely spaced laminar kink bands; and hornblende locally replacing pyroxene, which shows undulatory extinction [20]. The pseudotachylite zones occur in two types: (1) fault vein type, which is parallel to the deformation plane, and (2) injection vein type, which is anastomosing and can form networks of veins [20]. The wall rocks show a high degree of recrystallization, which drops off sharply away from the pseudotachylite vein [20]. These observations, along with small amounts of interstitial glass [20], closely resemble the petrography of ALH 84001. Additionally, the temperature during pseudotachylite formation exceeded 1300 K due to frictional heating. This was adequate to almost completely melt the minerals within the shear zone [20]. Such petrographic features are quite similar to those selected criteria used to define a shock state for ALH 84001, and further suggest that ALH 84001 underwent high strain-rate deformation and friction melting, rather than severe shock.

Treiman [5] proposes that the textures in ALH 84001 are likely the result of a shock event rather than a tectonic event on Mars, because the random orientations of the crush zones are not typical of tectonic fabrics and there are more impact than tectonic features on Mars. Large-scale friction melt bodies, however, are associated with large craters on Earth such as the Sudbury structure, Ontario, and the Vredefort structure, South Africa [e.g., 21]. These pseudotachylite bodies, although impact related, do not necessarily show evidence for shock. They have anastomosing zones and veinlets similar to those described in the Balmuccia peridotite,

which could explain the random orientation of crush zones in ALH 84001 while allowing for an origin other than shock. Furthermore, high strain-rate experiments on meteorites suggest that non-shock-related melting can occur during impacts [8]. High-strain-rate processes with potentially low shock levels that occur during impact include superfault formation during the modification stage of crater formation [22] and impact-directed material flow during oblique impacts [23,24].

Conclusions: The pervasive high strain-rate metamorphic textures similar to those in a terrestrial ultramafic pseudotachylite, lack of conclusive shock classification, and the absence of high-pressure polymorphs lead us to propose that the "shock" features in ALH 84001 may instead reflect high strain-rate deformation and friction melting with minimal shock. High temperatures created during deformation can account for recrystallization textures, melting plagioclase grains *in situ*, and generating plagioclase, silica, and carbonate melts. The friction melting process is also an effective mechanism for dispersing melts and blebs of metals and metal compounds along shear zones [8]. This process could take place in a tectonic setting similar to the Balmuccia peridotite, northern Italy, or during the formation of pseudotachylite bodies like the Sudbury and Vredefort pseudotachylites. The deformation and melting also may have occurred during the event that ejected the meteorite from Mars. This scenario does not exclude the presence of shock features within the pseudotachylites; rather, it does not necessitate their presence.

The absence of high-pressure shock features requires that ejection occurred at low shock levels. Also, if the plagioclase glass formed prior to ejection, temperatures during ejection could not have exceeded those that allow the recrystallization of plagioclase glass (e.g., 900°C for 1 hr [25]).

In agreement with previous studies [3,5], the crush zones are likely impact related. Here, we consider the possibility that the textures preserve a high strain-rate process that allows both localized high temperatures and low shock levels. For example, the crush zones and melt veins may be related to the launch process or pre-existing pseudotachylite bodies sampled by the event.

References: [1] Mittlefehldt D. W. (1994) *Meteoritics, 29,* 214–221. [2] Harvey R. P. and McSween H. Y. Jr. (1996) *Nature, 382,* 49–51. [3] Scott E. R. D. et al. (1997) *Nature, 387,* 377–379. [4] McKay D. S. et al. (1996) *Nature, 273,* 924–930. [5] Treiman A. H. (1995) *Meteoritics, 30,* 294–302. [6] Treiman A. H. (1998) *LPS XXIX,* Abstract #1195. [7] Stöffler D. et al. (1991) *GCA, 55,* 3845–3867. [8] van der Bogert C. H. et al. (1998) *LPS XXIX,* Abstract #1693. [9] Harvey R. P. and McSween H. Y. Jr. (1994) *Meteoritics, 29,* 472. [10] Shearer C. K. and Adcock C. T. (1998) *LPS XXIX,* Abstract #1281. [11] Stöffler D. et al. (1988) in *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Matthews, eds.), pp. 165–202, Univ. of Arizona, Tucson. [12] Schmitt R. T. et al. (1994) *Meteoritics, 29,* 529–530. [13] El Goresy A. et al. (1997) *Meteoritics & Planet Sci., 32,* A38–A39. [14] Treiman A. H. and Treado P. (1998) *LPS XXIX,* Abstract #1196. [15] Cooney T. F. et al. (1998) *LPS XXIX,* Abstract #1332. [16] Foley C. N. et al. (1998) *LPS XXIX,* Abstract #1928. [17] Spry A. (1969) *Metamorphic Textures,* 350 pp. [18] Borradaile G. J. et al. (1982) *Atlas of Deformational and Metamorphic Rock Fabrics,* 551 pp. [19] Sibson R. H. (1977) *J. Geol. Soc. London, 133,* 191–213. [20] Obata M. and Karato S.-I. (1995) *Tectonophysics, 242,* 313–328. [21] Spray J. G. and Thompson L. M. (1995) *Nature, 373,* 130–132.

[22] Spray J. G. (1997) *Geology, 25,* 579–582. [23] Schultz P. H. (1996) *GSA Abstr. with Progr.,* A384. [24] Schultz P. H. (1996) *JGR, 101,* 21117–21136. [25] Mikouchi T. et al. (1998) *Antarct. Meteorites XXIII,* 77–79.

THE COMMON ION EFFECT IN DEPOSITION OF MARTIAN (e.g., ALLAN HILLS 84001) CARBONATES.

P. H. Warren, Institute of Geophysics and Planetary Physics, University of California, Los Angeles CA 90095-1567, USA (pwarren@ucla.edu).

The most plausible model for origin of the carbonates in the ALH 84001 meteorite involves deposition from a playa lake or zone of groundwater that underwent evaporative concentration at or near the surface of Mars [1,2]. A key constraint for such a model is the virtual absence of sulfate in ALH 84001. In a simple closed-system evaporation sequence, abundant sulfate would be expected to form from any plausible martian lake or shallow groundwater. However, several factors would potentially alter the course of the evaporation-deposition sequence enough to engender extremes of sulfate/carbonate fractionation, including the extremely low sulfate/carbonate ratio of ALH 84001. Assuming the evaporating water body was transient in nature (i.e., the product of a flood), the water level could easily have been receding during the evaporation-deposition process, and we need only assume that carbonate deposition, but not sulfate deposition, occurred before the water level receded below the level where ALH 84001 was perched [1]. Occlusion of pores by incipient sulfate precipitation, in the outer fringes of the rock that ultimately became ALH 8001 and/or in overlying solid materials, might also have reduced the yield of sulfate deposition in ALH 84001 [1,2]. Another factor that probably played a key role is the common ion effect.

When two salts sharing a common ion are present in an aqueous solution, the dissolved ions of the more soluble salt act to substantially decrease the solubility of the less soluble salt. For application to Mars and ALH 84001, relevant sulfates have much greater solubilities than relevant carbonates. Assuming, for example,

Fig. 1. Common ion effect on solubility of $MgCO_3$ in presence of dissolved sulfate.

that the main ions in the solution are Mg^{2+}, CO_3^{2-}, and SO_4^{2-}, then by the time the solution could be evaporatively concentrated to the point of $MgSO_4 \times 7H_2O$ saturation, the solubility of $MgCO_3$ would be diminished by a factor of 400, compared to its solubility in the absence of SO_4^{2-} (Fig. 1).

The actual solution chemistry would not be so simple, but given the magnitude of the common ion effect, potentially operating in conjunction with the water-level drawdown and pore occlusion effects, it hardly seems surprising that the evaporitic carbonates in ALH 84001 are unaccompanied by significant sulfates.

In general, evaporitic martian sulfates probably formed only from extremely concentrated waters, whereas evaporitic carbonates probably formed as more diffuse deposits, filling pores in rocks (e.g., ALH 84001) and the megaregolith. Extremely concentrated waters, and thus sulfates, probably developed mainly in places where floods (surface and groundwater) terminated in playas. In contrast, carbonates developed as diffuse deposits in the mega-regolith along the routes followed by the waters on their way to the playas. Evaporitic sulfates are notoriously fragile and tend to easily disintegrate upon exposure to eolian erosion. This model helps explain the extremely high abundance of SO_3 (~6 wt%) in the surface global regolith [3] and the virtual absence of carbonate signals among spectral measurements of the martian surface.

References: [1] Warren P. H. (1998) *JGR, 103,* 16759–16773. [2] McSween H. Y. Jr. and Harvey R. P. (1998) *Meteoritics & Planet. Sci., 33,* A103. [3] Rieder R. et al. (1997) *Science, 278,* 1771–1774.

PLANETARY CORE FORMATION: EVIDENCE FROM HIGHLY SIDEROPHILE ELEMENTS IN MARTIAN METEORITES.

P. H. Warren, G. W. Kallemeyn, and F. T. Kyte, Institute of Geophysics and Planetary Physics, University of California, Los Angeles CA 90095-1567, USA (pwarren@ucla.edu).

We present new bulk compositional data for six martian meteorites, including the highly siderophile elements Ni, Re, Os, Ir, and Au. These and literature data are compared with the siderophile systematics of igneous rocks from Earth, the Moon, and the HED asteroid. The composition of ALH 84001 is anomalously siderophile-poor. Whether this reflects a more reducing environment on primordial Mars when this ancient rock first crystallized or secondary alteration is unclear. Queen Alexandra Range 94201 shows remarkable similarity with EET 79001-B for siderophile as well as lithophile elements; both are extraordinarily depleted in the "noblest" siderophiles (Os and Ir), to roughly 0.00001× CI chondrites. As in terrestrial igneous rocks, martian rocks display strong correlations of Ni, Os, and Ir vs. MgO. In the case of MgO vs. Ni, the martian trend is displaced toward lower Ni by a large factor (5), but the Os and Ir trends are not significantly displaced from their terrestrial counterparts. For Mars, Re shows a rough correlation with MgO, indicating compatible behavior, in contrast to its mildly incompatible behavior on Earth. Among martian MgO-rich rocks, Au shows a weak anticorrelation vs. MgO, resembling the terrestrial distribution except for a displacement toward 2–3× lower Au. The same elements (Ni, Re, Os, Ir, and Au) show similar correlations with Cr substituted for MgO. Data for lunar and HED rocks generally show less clear-cut trends (relatively few MgO-rich
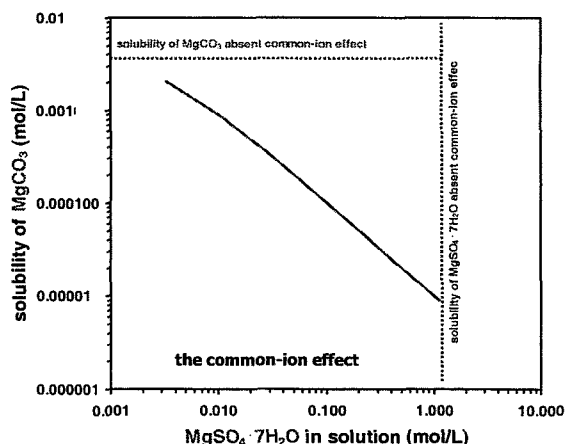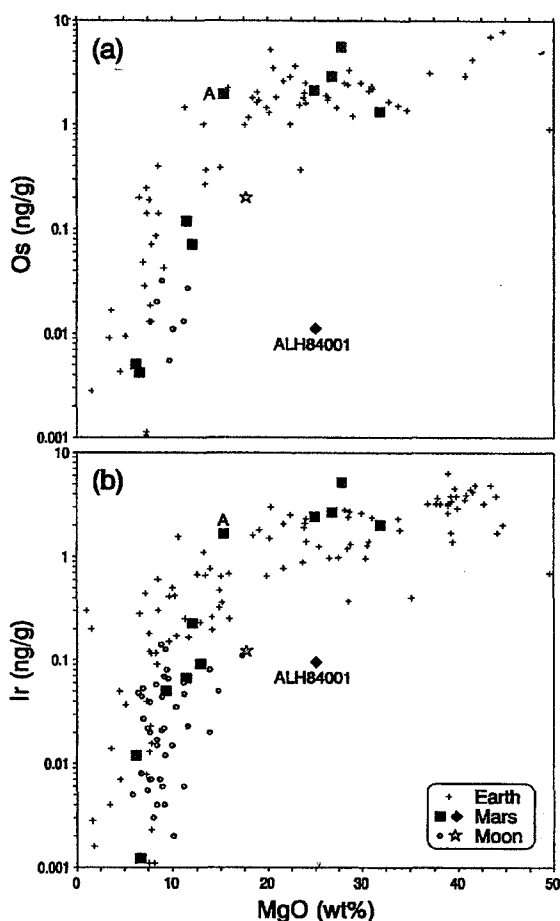
Fig. 1. MgO vs. Os and Ir for igneous rocks from Mars, Earth, and the Moon (mare basalts). "A" is main lithology of EET 79001, possibly meteorite contaminated. Lunar star point is 15426 VLT green glass (literature data).

samples are available). These trends are exploited to infer the compositions of the primitive Earth, Mars, Moon, and HED mantles, by assuming that the trend intercepts the bulk MgO or Cr content of the primitive mantle at the approximate primitive mantle concentration of the siderophile element. Results for Earth show good agreement with earlier estimates. For Mars, the implied primitive mantle composition is remarkably similar to the Earth's, except for 5× lower Ni. The best constrained of the extremely siderophile elements, Os and Ir, are present in the martian mantle at 0.5× CI, in comparison to 0.7× CI in Earth's mantle. This similarity constitutes a key constraint on the style of core-mantle differentiation in both Mars and Earth. Successful models should predict similarly high concentrations of noble siderophile elements in both the martian and terrestrial mantles ("high" compared to the lunar and HED mantles and to models of simple partitioning at typical low-pressure magmatic temperatures), but only predict high Ni for the Earth's mantle. Models that engender the noble siderophile excess in Earth's mantle through a uniquely terrestrial process, such as a Moon-forming giant impact, have difficulty explaining the similarity of outcome (except for Ni) on Mars. The high Ni content of the

terrestrial mantle is probably an effect traceable to Earth's size. For the more highly siderophile elements like Os and Ir, the simplest model consistent with available constraints is the veneer hypothesis. Core-mantle differentiation was inefficient on the largest terrestrial planets, because during the later stages of accretion these bodies acquired sufficient H_2O to oxidize most of the later-accreting Fe metal, thus eliminating the carrier phase for segregation of siderophile elements into the core.

References: Warren and Kallemeyn (1998) *GCA,* submitted.

ALTERATION PRODUCTS AND SECONDARY MINERALS IN MARTIAN METEORITE ALLAN HILLS 84001.

S. J. Wentworth[1], K. L. Thomas-Keprta[1], and D. S. McKay[2], [1]Mail Code C23, Lockheed Martin, 2400 NASA Road 1, Houston TX 77058, USA (susan.j.wentworth@jsc.nasa.gov), [2]Mail Code SN2, NASA Johnson Space Center, Houston TX 77058, USA.

The martian meteorites contain alteration products and secondary minerals that are a critical part of understanding their near-surface histories on both Mars and Earth. In some martian meteorites, suspected martian (preterrestrial) alteration products can be distinguished from terrestrial weathering effects [e.g., 1–5]. Using scanning electron microscopy (SEM), field emission SEM (FE-SEM), transmission electron microscopy (TEM), and energy-dispersive X-ray analysis (EDS), we are studying natural fracture surfaces of ALH 84001 chips, including samples from both the interior and the exterior of the meteorite. Exterior samples include fusion crust surfaces, which are important in determining the extent of terrestrial weathering of meteorites. The focus of this study is weathering features and secondary minerals other than the distinctive carbonate globules that continue to be studied by many researchers.

Both the interior and the fusion crust of ALH 84001 generally show very little evidence of terrestrial weathering. In [1,6], we reported the presence of traces of typical Antarctic secondary minerals (Ca sulfate, Mg sulfate, NaCl, and SiO_2) on the fusion crust surface. The absence of these terrestrial minerals in the chips below the fusion crust surface is a good indicator of the lack of significant Antarctic alteration. We have now found one small occurrence of Ca sulfate slightly (~200 µm) below the fusion crust surface (Fig. 1a). It is most likely of terrestrial origin, since no Ca sulfate has been identified in interior samples. Another weathering feature not previously described is shown in Fig. 1b. It consists of amorphous-looking C-rich material (not carbonate) partly filling a vug in the fusion crust. Traces of this C-rich material are found both on and near the fusion crust (e.g., Fig. 1a). More work is needed to determine if it is identifiable in interior samples with the SEM. Similar C-rich material was found on the fusion crust of Chassigny [2].

Evidence of alteration in the interior of ALH 84001 consists mostly of pitted carbonate globule surfaces, etched silicates (mostly pyroxene), and traces of smectite-type clay associated with pyroxene [1,6]. In addition to the carbonate globules, the interior contains traces of another type of Mg carbonate, as reported in [6]. This Mg carbonate (Fig. 1c) has a distinct blady morphology that is different from that of typical ALH 84001 carbonate globules, and it also has a different composition (higher O, no minor elements).
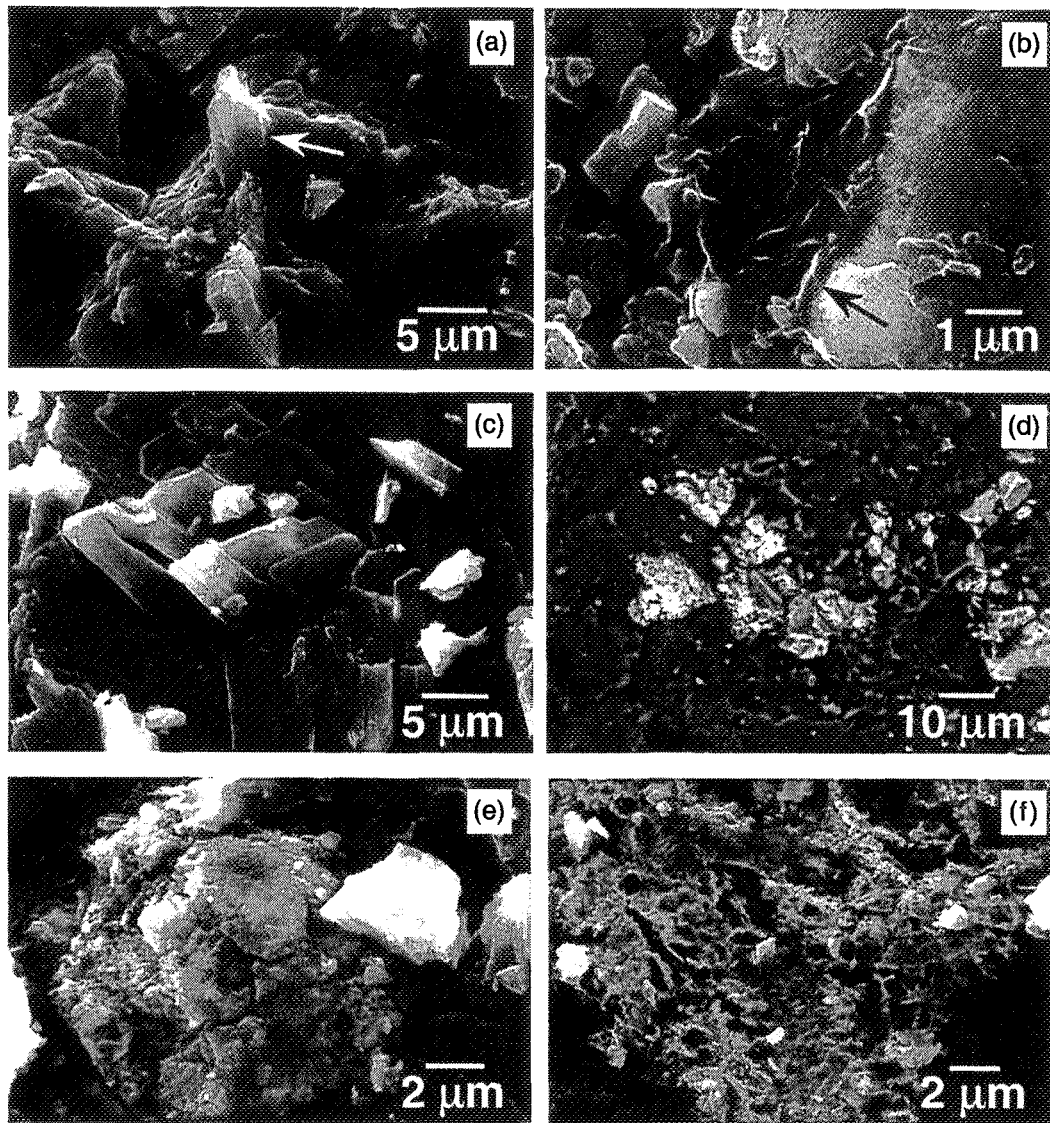
Fig. 1.

It is probably secondary to the globule carbonate. This O-rich carbonate is found in the interior of the meteorite and within a few hundred micrometers of the fusion crust surface, but it has not been found on the fusion crust itself. In [1] we reported that Fe sulfates were present in the interior of ALH 84001. It is not clear, however, that they are actually sulfates because the amount of O present is not well defined; TEM and diffraction work still need to be done. Examples of these Fe-,S-rich occurrences are shown in Figs. 1d–f. Figure 1d is a backscattered electron image of a typical occurrence (the brightest patches with fine-grained granular to fibrous textures are the Fe-,S-rich phase, the smoother medium gray grains are chromites, and the dark gray masses are silicates). The Fe-,S-rich material is commonly found in clusters closely associated with chromite grains. The equant occurrence in Fig. 1e appears to be a partly weathered equant pyrite grain. EDS indicates that the proportion of S to Fe decreases with increased alteration (Fig. 1f).

It is clear that the interior of the ALH 84001 meteorite has interacted with aqueous fluids, but the fluids are not obviously the same as those that deposited salts on the fusion crust. Further studies of these types of features may allow us to determine where they originated and how they formed. It may also be possible to use mineralogical and textural evidence of the degree of terrestrial weathering to help determine the amount of terrestrial biological contamination. Distinctions between terrestrial and preterrestrial weathering effects should prove to be useful in determining the origins of possible biogenic features [7] in the martian meteorites.

References: [1] Wentworth and Gooding (1995) *LPS XXVI,* 1489. [2] Wentworth and Gooding (1994) *Meteoritics, 29,* 860. [3] Treiman et al. (1993) *Meteoritics, 28,* 86. [4] Gooding et al. (1991) *Meteoritics, 26,* 135. [5] Gooding et al. (1988) *GCA, 52,* 909. [6] Wentworth et al. (1998) *LPS XXIX,* Abstract #1793. [7] McKay et al. (1996) *Science, 273,* 924.

TERRESTRIAL BIOMARKERS FOR EARLY LIFE ON EARTH AS ANALOGS FOR POSSIBLE MARTIAN LIFE FORMS: EXAMPLES OF MINERALLY REPLACED BACTERIA AND BIOFILMS FROM THE 3.5–3.3-Ga BARBERTON GREENSTONE BELT, SOUTH AFRICA.

F. Westall[1], D. S. McKay[1], E. K. Gibson[1], M. J. de Wit[2], J. Dann[2], D. Gerneke[3], and C. E. J. de Ronde[4], [1]Mail Code SN, Earth Sciences and Solar System Exploration Division, NASA Johnson Space Center, Houston TX 77058, USA (frances.westall1@jsc.nasa.gov), [2]Department of Geological Sciences, University of Cape Town, Rondebosch, South Africa, [3]EM Unit, University of Cape Town, Rondebosch, South Africa, [4]Institute of Geological and Nuclear Sciences, P.O. Box 31-312, Gracefield, Lower Hutt, New Zealand.

Introduction: The search for extraterrestrial life and especially martian life hinges on a variety of methods used to identify vestiges of what we could recognize as life, including chemical signatures, morphological fossils, and biogenic precipitates. Although the possibility of extant life on Mars (subsurface) is being considered, most exploration efforts may be directed toward the search for fossil life. Geomorphological evidence points to a warmer and wetter Mars early on in its history [1], a scenario that encourages comparison with the early Earth. For this reason, study of the early terrestrial life forms and environment in which they lived may provide clues as to how to search for extinct martian life.

As a contribution to the early Archean database of terrestrial microfossils, we present new data on morphological fossils from the 3.5–3.3-Ga Barberton greenstone belt (BGB), South Africa [2]. This study underlines the variety of fossil types already present in some of the oldest, best-preserved terrestrial sediments, ranging from minerally replaced bacteria and bacteria molds of various morphologies (coccoid, coccobacillus, bacillus) to minerally replaced biofilm. Biofilm or extracellular polymeric substance (EPS) is produced by bacteria and appears to be more readily fossilisable than bacteria themselves. The BGB fossils occur in shallow water to subaerial sediments interbedded with volcanic lavas, the whole being deposited on oceanic crust. Penecontemporaneous silicification of sediments and volcanics resulted in the chertification of the rocks, which were later subjected to low-grade metamorphism (lower greenschist).

Results and Discussion: Petrographic and SEM observation of rock chips and thin sections of finely laminated cherts revealed (1) smooth to granular films (fossil biofilm) and strands coating bedding-plane surfaces and embedded within the quartz, and (2) bacterimorph structures (fossil bacteria). A fuller understanding of both of these biogenic features in Archean terrestrial rocks will help us document similar features, if present, in martian rocks and meteorites.

Biofilm. Thin sections of the finely laminated cherts are characterized by fine, wavy, discontinuous, brown-colored texturing of the order of 50–100 µm, parallel to the bedding. These laminae consist of films that irregularly coat bedding planes, sometimes extending over thousands of square micrometers. The films are characterized by either a smooth or a ropy, twisted, interwoven ultrastructure, although they may also be granular.

We interpret these films as representing the EPS slime or biofilm in which bacteria live and grow. Biofilms provide protection against a hostile outer environment and also provide a nutrient and poten-

tial energy source, since biofilms trap nutrients and carbonaceous material. Biofilms are invariably present in modern-day, naturally occurring bacterial colonies. They are as much representative of bacterial presence as the bacterial bodies themselves, since they are produced by bacteria. Both bacteria and biofilms are mineralized by the chelation of mineral ions to the active groups in the polysaccharide-rich polymers that make up the EPS [3]. In this case, the bacteria and biofilms have been silicified. Stromatolites are good examples of mineralized biofilms: In fact, these examples from the BGB can be termed tabular stromatolites. Biofilms are also sinks for heavy metals and may be implicated in the concentration of precious metals in economically significant deposits. The association of heavy minerals with filmlike structures in an unknown sample may therefore be a biomarker for the presence of life forms.

Bacteria. Numerous spherical and rod-shaped bacteriomorph structures and bacteriomorph molds, ranging in size from 0.6 to 4 µm, are embedded in the quartz matrix and in smooth-surfaced biofilm. They have been interpreted as a fossil bacteria following well-defined criteria [4]:

1. Their *sizes* and *shapes* are similar to those of modern bacteria, including rod-shaped (bacillus or coccobacillus) and spherical morphologies (coccoid), and range from <0.2 µm (nanobacteria) to tens of micrometers (cyanobacteria) in size.

2. *Cellular complexity* such as cell division is a fundamental bacterial characteristic and is manifested by our microfossils as simple pairings to multiple linear or pluridimensional cell divisions.

3. The *cell wall texture* of bacteria varies depending on the osmotic gradient between an organism and its external environment: In perfect osmostic conditions, the cell is turgid and the cell wall smooth, whereas where the gradient is steep, the outer wall may be puckered and wrinkled. Both situations are preserved in our bacteriomorphs.

4. The association of large numbers of cells is typical of bacterial *colonies*. We observe large numbers of microfossils as clusters as well as extending in matlike sheets over bedding planes.

5. Bacterial colonies usually consist of a coexisting variety of species (*consortia*). Some of the colonies of bacteriomorphs from the BGB cherts contain a number of different morphotypes, e.g., coccoid, rod-shaped, and linear associations of coccoid forms. Each species, however, presents only a limited size and shape range.

The association of the microfossils with fossil biofilm, as well as the –27‰ [13]C value from these sediments, supports the interpretation of the bacteriomorphs as bacteria.

The above criteria are sufficient to distinguish minerally replaced bacteria from small crystals. Although many of the bacteriomorphs presented rounded cross sections, some of them had slightly crystalline terminations. However, observations of microfossils with one end coated by a wrinkled surface and the other by a smooth surface coated with crystalline termination demonstrate that mineral replacement of bacteria can, in some cases, lead to subeuhedral crystalline structures. This has also been demonstrated in the laboratory [5]. In the case of the BGB fossils, the morphotypes with slightly mineral terminations occur together with rounded morphotypes and satisfy all the other biogenic criteria.

Conclusions: Our data show that minerally replaced bacteria and biofilm can be useful morphofossils. The fossil types in the BGB cherts, together with fossil bacteria and biofilm from the (contiguous) early Archean Warrawoona sequence in northwest Australia [6] show that bacteria were well established on Earth by that
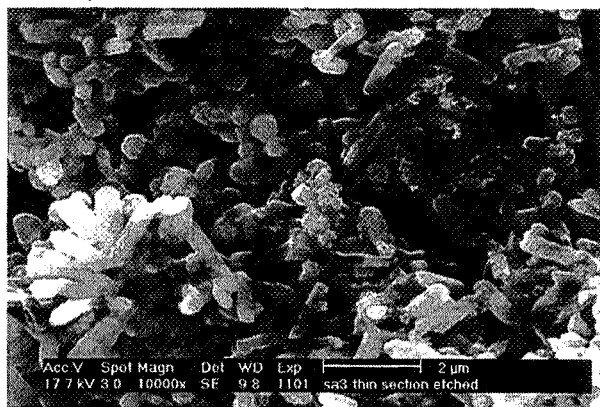
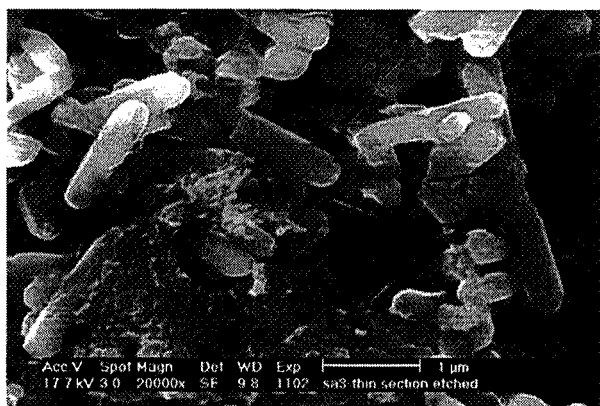**Fig. 1.** Colony of a consortium of rod-shaped and coccoid fossil bacteria from the BGB.

Fig. 2. Two silicified, rod-shaped, dividing bacteria (arrows) with slightly crystalline termination on the lower individual and wrinkled surface on the upper one.
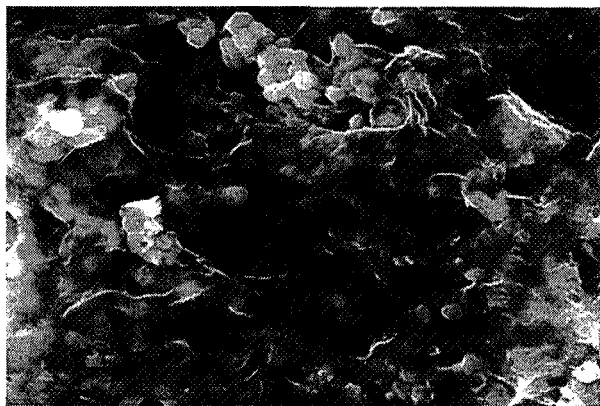

Fig. 3. Smooth, silicified biofilm covering large colony coccoid bacteria.

period, and, not only do they look very similar to modern bacteria, but their intimate association with biofilm is also a fundamental characteristic of modern bacteria.

Similar associations in returned martian samples or meteorites may be the key to documenting early life forms. Deciphering the effects of fossilization, mineralization, and aqueous or metamorphic alteration will be a vital part of the search for ancient life on

Mars, and the study of early Archean samples provides important insights into those processes.

References: [1] Head J. W. et al. (1998) *Meteoritics & Planet. Sci., 33,* A66. [2] Westall F. et al. (1998) *Precambrian Res.,* in press. [3] Westall F. et al. (1995) *Palaeontology, 38,* 495–528. [4] Schopf J. W. and Walter M. R. (1983) in *Earth's Earliest Biosphere* (J. W. Schopf, ed.), pp. 214–239, Princeton Univ. [5] Castanier S. et al. (1989) *Bull. Soc. Geol. Frances. 8V3,* 589–595. [6] Morris P. et al. (1998) *LPS XXIX.*

ABIOTIC SYNTHESIS OF HYDROCARBONS ON MARS: THEORETICAL MODELING OF METASTABLE EQUILIBRIA. M. Yu. Zolotov[1,2] and E. L. Shock[1], [1]Department of Earth and Planetary Sciences, Washington University, St. Louis MO 63130, USA (zolotov@zonvark.wustl.edu; shock@zonvark.wustl.edu), [2]Vernadsky Institute Russian Academy of Sciences, Kosygin Street 19, Moscow 117975, Russia.

Introduction: The martian meteorite ALH 84001 contains polycyclic aromatic hydrocarbons (PAHs) and other hydrocarbons of endogenous origin [1–4]. McKay et al. [1] proposed that the presence of PAHs in carbonate globules of ALH 84001 indicates biological activity on ancient Mars. On the other hand, the presence of hydrocarbons in other meteorites, IDPs, interstellar clouds, and Earth's pristine and altered igneous rocks (e.g., serpentinites) is not attributed to biological sources. In many cases these hydrocarbons are formed abiotically due to reduction of C oxides by H. We used thermodynamic calculations of metastable equilibria to evaluate the possibility of abiotic synthesis of PAHs and n-alkanes in possible hydrothermal fluids and thermal gases on Mars.

Model: Hydrocarbons are thermodynamically unstable compounds and may form if the formation of stable methane or graphite is inhibited [e.g., 5]. On Mars and Earth, this inhibition could have happened in dynamic cooling systems: volcanic/impact gases, fumaroles, and hydrothermal systems around magmatic intrusions or hot impact craters. We considered metastable equilibria among condensed PAHs and n-alkanes with gaseous and aqueous CO_2 and H_2, which could have existed in these systems on ancient Mars. In addition, we considered some aromatization and PAH methylation equilibria. We assumed that the fugacity (f) of H_2(gas) and activity (a) of H_2(aq) are controlled by the quartz-fayalite-magnetite (QFM) or hematite-magnetite (HM) buffers, which represent martian igneous rocks and oxidized soil/sediments. We used 5.4 mbar and 1 bar for f_{CO_2}, corresponding to the present and a possible ancient atmosphere. In the terrestrial analogy, for carbonate-bearing hydrothermal systems we used f_{CO_2} values that are governed by calcite-silicate equilibria [4–7]. We assumed the activity of condensed hydrocarbons and water was in unison. Pressure corresponds to liquid-water vapor saturation. The thermodynamic data for unsubstituted and methylated PAHs and n-alkanes (C numbers 5–20) are from [7] and [8] respectively.

Results: The calculated activities/fugacities of H_2 and CO_2 for the following metastable equilibria

$$aH_2 + bCO_2 = cHC \text{ (PAH or n-alkane)} + dH_2O$$

are plotted in Figs. 1–3 as saturation lines. PAHs and n-alkanes can be formed if a and f exceed the metastable equilibria values.
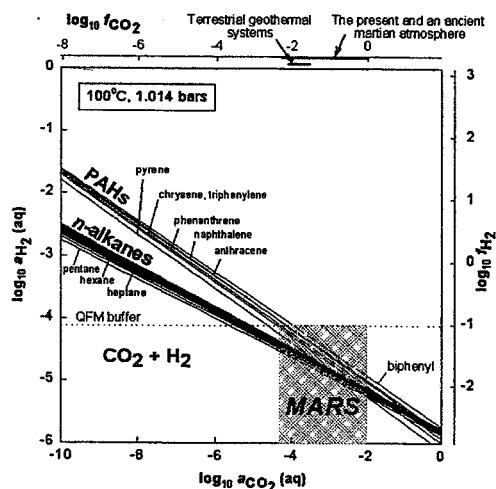
Fig. 1. The metastable equilibrium saturation lines for PAHs and n-alkanes at 100°C. The shaded box represents the proposed conditions in martian thermal systems.
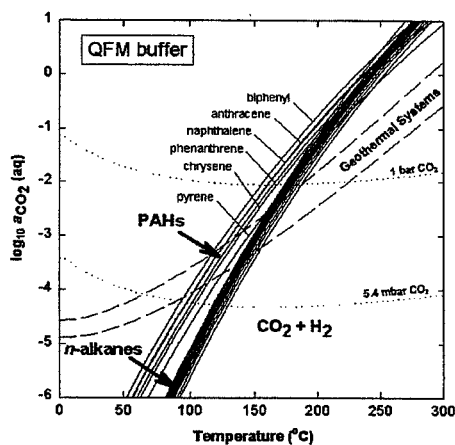

Fig. 3. The metastable equilibrium hydrocarbon saturation lines at the CaCO₃-silicate equilibria [6,7].

Fig. 2. The metastable equilibrium saturation lines for hydrocarbons at the QFM buffer. Dashed lines show CO_2 in terrestrial [6] and proposed martian geothermal systems. Dotted lines show aCO_2 equilibrated with the present and possible ancient atmosphere of Mars.

Fig. 4. The metastable equilibrium conditions between pairs of n-alkanes and PAHs with the same C number as a function of $\log aH_2$ and temperature. The hexadecane to pyrene curve is indicated, other curves are labeled by the PAHs.

Saturation lines for PAHs and n-alkanes lie close to each other; therefore, the formation of a metastable mixture is more likely.

At the f_{H_2} controlled by the QFM buffer, the saturation conditions for hydrocarbons match with the f_{CO_2} conditions proposed for Mars (Fig. 1). However, the HM buffer is too oxidized to stabilize hydrocarbons.

A decrease in temperature facilitates the condensation of hydrocarbons (Figs. 2 and 3). At the QFM buffer and CO_2 governed either by the CaCO₃-bearing systems or atmospheric CO_2, PAHs and n-alkanes can be metastably formed below 90°–180°C. Light PAHs can condense together with heavy alkanes. More reduced conditions and more CO_2 raise the condensation temperatures. In addition, possible high-temperature quenching of H_2 (see dotted line in Fig. 3) increases the condensation temperatures and facilitates hydrocarbon synthesis.
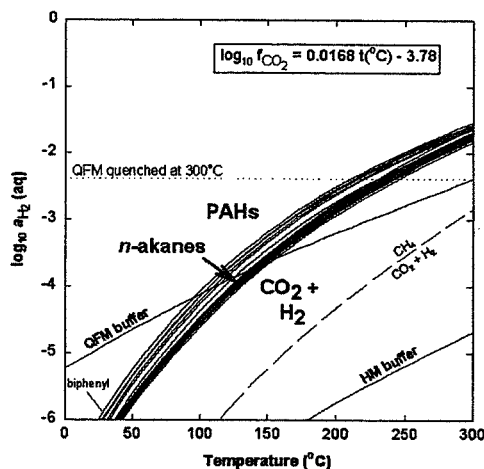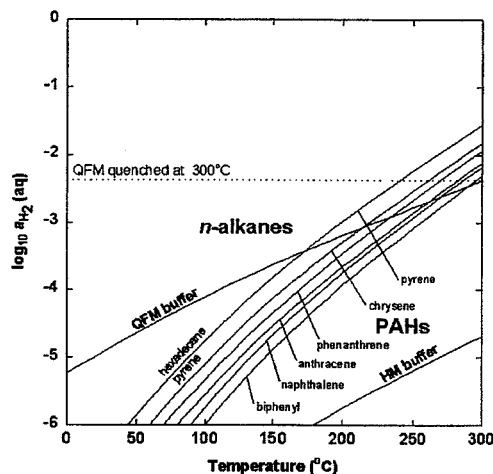
High temperature and/or oxidizing conditions favor aromatization of n-alkanes (Fig. 4). At QFM, aromatization can proceed above ~170°C.

Calculations of equilibria for methylation reactions for PAHs show that low temperature and reduced conditions favor alkylation of parent compounds. At QFM and at temperatures < ~350°C, methylated PAHs are more stable than the unsubstituted species.

Discussion: The predominance of mafic and ultramafic rocks on Mars would favor high f_{H_2} in magmatic gases and high aH_2 in aqueous solutions formed during the alteration of these rocks (e.g., serpentinization). High CO_2 contents proposed in martian thermal systems favor the synthesis of hydrocarbons and provide high $(a, f)CO$ due to high-temperature CO-CO_2 equilibrium. In dynamic systems, C-O-H gases may quench below 300°–700°C and produce higher disequilibrium amounts of CO and H_2, which favors the

Fischer-Tropsch (FT) type synthesis of hydrocarbons. The FT synthesis and the proposed CO_2-H_2 interaction could be catalyzed by magnetite [9,10] in igneous rocks and the martian regolith.

Conclusion: Thermodynamic analysis of metastable equilibria show that PAHs could be formed abiotically together with n-alkanes in dynamic cooling gaseous (volcanic/fumarolic/impact) and aqueous geothermal systems on Mars below ~180°C. Reduced compositions, high initial temperature of gases/fluids, and quick quenching facilitate the synthesis of hydrocarbons. However, the oxidized martian regolith and O_2-bearing subsurface fluids do not favor such synthesis.

The possibility of joint formation of PAHs and n-alkanes indicates that these hydrcarbons in ALH 84001 could be formed in a single process. Our calculations for the aromatization and methylation equilibria also support the suggestions of Anders [11] that magmatic or impact heating on Mars could increase the PAH content and drive their dealkylation.

References: [1] McKay D. S. et al. (1996) *Science, 273,* 924–930. [2] Stephan T. R. D. et al. (1998) *LPS XXIX,* Abstract #1263. [3] Flunn G. J. et al. (1998) *LPS XXIX,* Abstract #1156. [4] Clement S. J. et al. (1998) *Farady Discussions (Royal Soc. Chem.), 109,* in press. [5] Eck R. V. et al. (1966) *Science, 153,* 628–633. [6] Giggenbach W. F. (1997) *GCA, 61,* 3763–3785. [7] Richard L. and Helgeson H. C. (1988) *GCA, 68,* in press. [8] Helgeson H. C. et al. (1998) *GCA, 68,* 985–1081. [9] Anderson R. B. (1984) *The Fischer-Tropsch Synthesis.* [10] Berndt M. E. et al. (1996) *Geology, 24,* 351–354. [11] Anders E. (1996) *Science, 274,* 2119–2120.