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INSIDE

Evidence for Life in a Martian Meteorite?

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ABSTRACT

The controversial hypothesis that the ALH84001 meteorite contains relics of ancient martian life has spurred new findings, but the question has not yet been resolved. Organic matter probably results, at least in part, from terrestrial contamination by Antarctic ice meltwater. The origin of nanophase magnetites and sulfides, suggested, on the basis of their sizes and morphologies, to be biogenic remains contested, as does the formation temperature of the carbonates that contain all of the cited evidence for life. The reported nanofossils may be magnetite whiskers and platelets, probably grown from a vapor. New observations, such as the possible presence of biofilms and shock metamorphic effects in the carbonates, have not yet been evaluated. Regardless of the ultimate conclusion, this controversy continues to help define strategies and sharpen tools that will be required for a Mars exploration program focused on the search for life.

INTRODUCTION

Since the intriguing proposal last summer that martian meteorite Allan Hills (ALH) 84001 contains biochemical markers, biogenic minerals, and microfossils (McKay et al., 1996), scientists and the public alike have been treated to a variety of claims supporting or refuting this hypothesis. Occasionally, the high visibility of the controversy has overshadowed the research effort (e.g., Begley and Rogers, 1997), but I believe that science will benefit significantly from this experience. If the hypothesis is confirmed, it will rank among the major discoveries of all time. If not, McKay and his colleagues have still demonstrated that microparticles, soluble minerals, and possibly organic matter can survive on the red planet for billions of years, which provides a hopeful outlook for a Mars exploration program focused on the search for life.

This article reviews recently published research bearing on this important topic. Most of this literature exists only as conference abstracts and technical comments in scientific journals. There seems to be virtually no argument, at least within the planetary science community, that ALH84001 is a sample of the ancient (~4.5 Ga) martian crust (e.g., Mittlefehldt, 1994; McSween, 1994; Clayton and Mayeda, 1996; Goswami et al., 1997). This ultramafic igneous rock (Fig. 1) is crosscut by breccia zones containing small carbonate grains, which are the hosts for organic matter as well as reported biogenic materials and microfossils. This article addresses and expands upon the four lines of evidence for possible biologic activity cited by McKay et al. (1996).

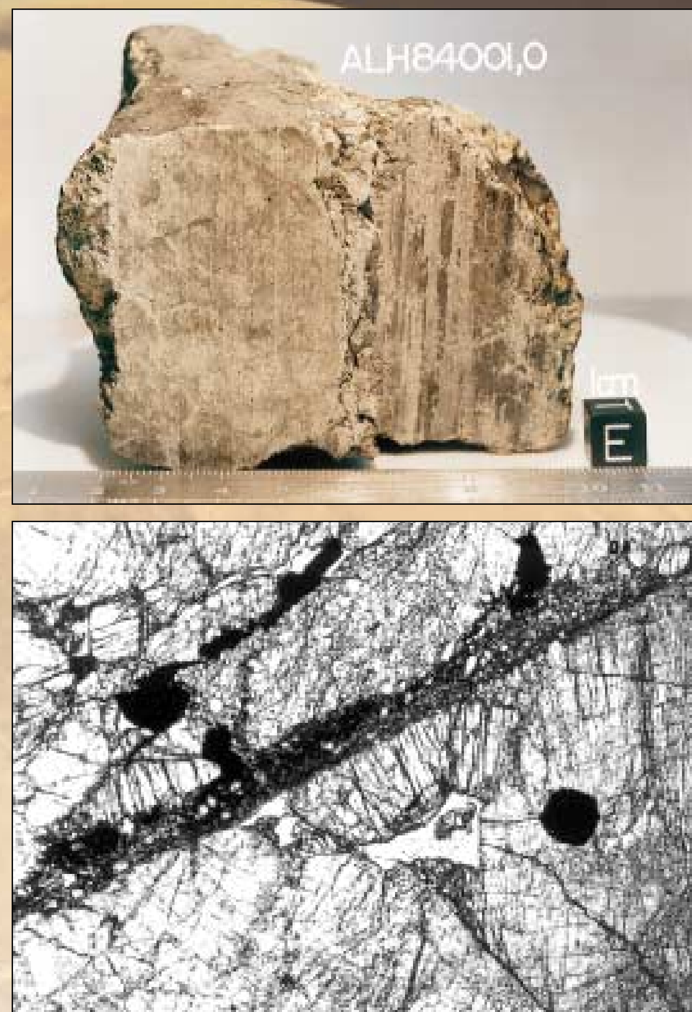

Figure 1. **Mars is thought to be the parent body of a dozen igneous meteorites (achondrites). The ALH84001 achondrite was recovered in Antarctica in 1984, but it was not recognized as a martian sample until a decade later. This orthopyroxene cumulate rock (cube is 1 cm) is crosscut by fracture zones (see thin section view; long axis is ~0.5 cm), within which tiny carbonate globules were deposited. The carbonate grains are associated with organic matter and contain microparticles suggested to be martian nanofossils and biogenic minerals.** ***Photographs courtesy of NASA.***

ORGANIC MATTER

McKay et al. (1996) described fused hydrocarbon rings (polycyclic aromatic hydrocarbons, or PAHs) associated with the carbonates in ALH84001. The identification of specific molecules in a sample containing ~1 ppm PAHs ranks as a triumph of analytical ingenuity. Although PAHs do not play a significant role in the biochemistry of terrestrial organisms, they can form by geochemical transformation of certain hydrocarbons present in decayed organisms. PAHs also form by abiotic processes such as the combustion of fossil fuels, and they are common constituents of chondritic meteorite kerogens (Zenobi et al., 1989). Anders (1996) noted that PAHs are produced by pyrolosis (thermal decomposition) whenever graphite formation is kinetically inhibited. He further pointed out that the "few specific PAHs" from C_{14}

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In Memoriam

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Portland, Oregon
December 17, 1996

Harold W. Dailey
Franklin, Georgia
January 27, 1997

John J. DeBenedetti
Laguna Hills, California
January 1996

James M. Kirby
Vallejo, California
April 16, 1997

G. Edward Lewis
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Waclaw Ryka
Warsaw, Poland
1996

William J. Stuart
South Australia
April 16, 1996

Livio Trevisan
Pisa, Italy
March 1997

Correction

In the April *GSA Today* (v. 7, no. 4) article "Global Seismic Tomography: A Snapshot of Convection in the Earth" by Stephen P. Grand, Rob D. van der Hilst, and Sri Widiyantoro, the beginning of the caption for Figure 1 (p. 1) should be: "Cross sections of mantle S-wave (A) and P-wave (B) velocity variations along a section through the southern United States." The published description reverses the S-wave and P-wave images.

Meteorite *continued from p. 1*

to C_{22} in ALH84001 suggested to be biogenic by McKay et al. (1996) comprise all homologs in this carbon number range, and thus do not require a selective (biological) source. Clement and Zare (1996) countered that differences in alkylation (the addition of side chains) of the low-mass and high-mass envelopes of the PAHs suggest both low- and high-temperature processing, which might arise through diagenesis of decomposed biologic matter. Bell (1996) suggested that abiotic PAHs could have accreted to Mars as constituents of organic-rich asteroid impactors, several of which still remain in martian orbit as the moons Phobos and Deimos.

New research has focused mostly on characterization of the organic matter in EETA79001, another martian meteorite found in Antarctica. Becker et al. (1997) extracted PAHs using a laser ionization technique similar to that used by McKay et al. (1996) for ALH84001. EETA79001 also contains a low-mass assortment of unalkylated PAHs with masses from C_{14} to C_{22}, as well as a weaker high-mass envelope. The abundance of PAHs (~1 ppm) is similar to that in ALH84001, although the relative proportions of specific PAHs inferred from the spectra are slightly different, possibly resulting from differences in ionization efficiencies for the distinct laser wavelengths used in the analyses. Becker et al. (1997) also performed experiments demonstrating that PAHs are selectively adsorbed onto carbonate. This finding, along with the determination that the assortment of PAHs in both martian meteorites is similar to that measured in Antarctic ice, suggests that the PAHs in both meteorites may result from organic contamination by ice meltwater. On the

Meteorite *continued on p. 3*

Meteorite *continued from p. 2*

basis of the low abundances of PAHs in ice, Wright et al. (1997a) suggested that the quantity of meltwater that would have to be flushed through the meteorite was prohibitive; however, Antarctic meteorites are sometimes found in puddles, and evaporation of this water would concentrate PAHs. The presence of optically active amino acids (almost exclusively L-enantiomers, the same forms found in terrestrial proteins) in EETA79001 (McDonald and Bada, 1995) supports the idea of organic contamination in the polar environment, and the measured carbon isotopic compositions of organic matter in both meteorites ($\delta^{13}C$ = –22‰ to –25‰; Wright et al., 1989; Grady et al., 1994) are indistinguishable from terrestrial values. The carbon isotopic composition of the carbon source (presumably the atmosphere, with $\delta^{13}C$ = ~ +40‰) implies a fractionation of >60‰ between it and organic matter (Grady et al., 1996). Isotopic effects of this magnitude on Earth require a complex community of organisms that includes methane-producing bacteria and methylotropic bacteria that convert methane into biomass. Such an interpretation for ALH84001 depends on the assumption that both the atmosphere and organic matter equilibrated with the same fluid. A previous announcement of even more extreme carbon isotopic fractionation in ALH84001 carbonate (widely reported in the British press as evidence for life) can now be explained as possible laboratory contamination (Wright et al., 1997b).

BIOGENIC MATERIALS

Another line of evidence for life in ALH84001 cited by McKay et al. (1996) is the presence within carbonates of nanophase magnetite grains morphologically similar to those produced by terrestrial magnetotactic bacteria. Coexisting sulfides (pyrrhotite and greigite were tentatively identified) within the carbonates were also suggested to be biogenic. McKay et al. (1996) argued that coprecipitation of magnetite and sulfides, with concomitant dissolution of carbonate (inferred from its porous microtexture), indicates disequilibrium and thus points to biologic mediation. The geochemical basis for this argument has been criticized by Anders (1996) and Browning and Bourcier (1997).

Bradley et al. (1996) presented transmission electron microscopic images of a variety of tiny magnetite whiskers (rods and ribbons) and platelets in ALH84001 carbonates, adding to the assortment of cuboid, teardrop, and irregular grains described by McKay et al. (1996). The morphologies of bacterially produced magnetite grains are generally species-specific (Bazylinski, 1995), so the diverse magnetite morphologies in this meteorite would imply a rich community of organisms. Bradley et al. (1996) suggested that the whisker morphologies containing internal structural defects (Fig. 2) and twins are unlike the characteristics of biogenic magnetite. Thomas-Keprta et al. (1997) noted that twinning does sometimes occur in biologically induced magnetite, and that at least one bacterium is known to produce magnetite rods, although the specific dislocations seen in ALH84001 magnetite whiskers have not yet been observed in biogenic grains.

Magnetotactic bacteria string crystallographically oriented magnetite grains together into chains (magnetosomes; Fig. 2) that increase the net magnetic moment, used for sensing Earth's geomagnetic field. Thomas-Keprta et al. (1997) interpreted five or six aligned cuboid particles in ALH84001 as a possible magnetosome, but without data on crystallographic orientations of the grains or evidence for the former existence of an organic membrane holding the chain together. However, the preservation of intact fossil magnetosomes is uncommon (Chang and Kirschvink, 1989).

Magnetotactic bacteria produce magnetite within their cells, but some other terrestrial bacteria form extracellular magnetite (Stolz et al., 1990). Vali et al. (1997) described extracellular magnetite produced in the laboratory by thermophilic bacteria; the diamond-shaped grains in these cultures show a wide range in size distribution and random arrangement, and were argued to be similar in size and morphology to magnetites in ALH84001 carbonates.

McKay et al. (1996) suggested that tiny grains of pyrrhotite inside the carbonates in ALH84001 may have formed by sulfate-respiring bacteria. Biogenic sulfides typically contain isotopically light sulfur, as terrestrial bacteria preferentially utilize ^{32}S in making excreted sulfide. Small grains of pyrite occurring outside the carbonates in ALH84001 have been inferred, on the basis of textural criteria, to have coprecipitated with carbonate (although Gibson et al. [1996] suggested that these were unrelated to the sulfides within carbonates). Measured sulfur isotopic compositions of the pyrite grains ($\delta^{34}S$ = +2‰ to +8‰; Shearer et al., 1996; Greenwood et al., 1997) appear to be inconsistent with biologic formation, unless the sulfate precursor was extremely isotopically heavy, the supply of sulfate was limited, or martian organisms utilized sulfur via different biochemical pathways.

McKay et al. (1997) recently proposed yet another kind of biogenic material in ALH84001—lacy network structures in acid-etched carbonates and pyroxenes which resemble microbially secreted organic polymers (biofilms). Although they contain carbon, an organic composition for these curious structures has not yet been established.

Meteorite *continued on p. 4*

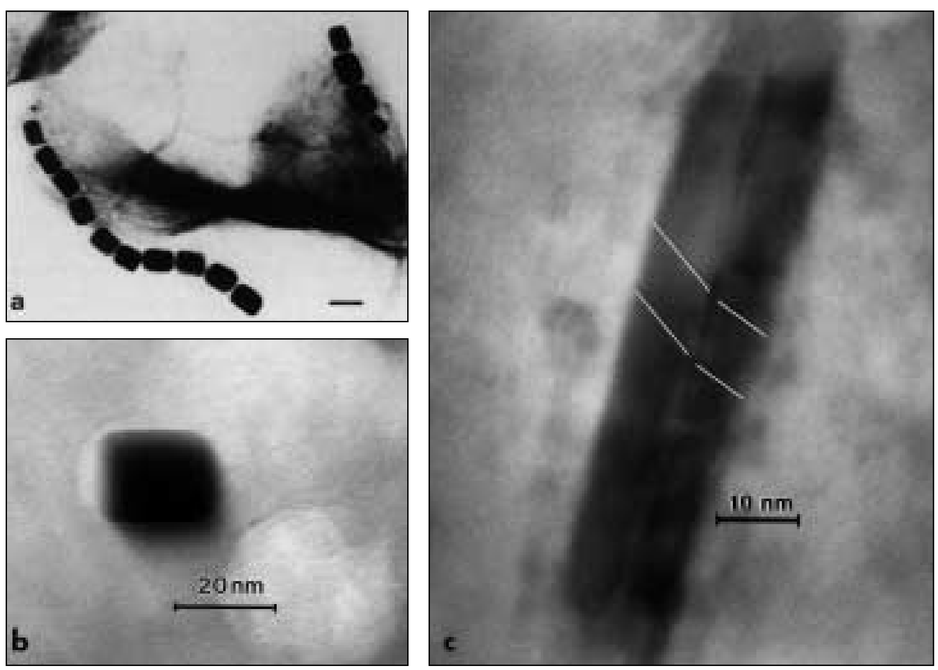

Figure 2. TEM images of single-domain magnetite grains within ALH84001 carbonates and in magnetotactic bacteria. a: Chains of crystallographically oriented nanophase magnetites in *Magnetococcus* bacterium are linked by lipid membranes (scale bar is 100 nm; from Stolz et al., 1990). b: Well-formed magnetite platelet in ALH84001 appears morphologically similar to some biogenic magnetites. c: Magnetite whisker in ALH84001 contains an axial screw dislocation, indicative of spiral growth, probably from a vapor. Lattice fringe orientations on either side of the dislocation (marked by white lines) are distinct. Platelet and whisker images from John Bradley (MVA, Inc.).

Meteorite *continued from p. 3*

NANOFOSSILS

Perhaps the most exciting suggestion by McKay et al. (1996) was that tiny "ovoid and elongated forms" in ALH84001 carbonates were nanofossils. Examination of uncoated microparticles in ALH84001 using atomic force microscopy (Steele et al., 1997) demonstrates that they are not artifacts of sample preparation. Although some microparticles in terrestrial carbonates have been described as nanofossils (e.g., Folk, 1993), the evidence is exclusively morphological, and the hypothesis remains controversial.

The microparticles described as nanofossils in ALH84001 are generally 30 to 150 nm in longest dimension, significantly smaller than terrestrial microorganisms. Only viral symbionts and spores that cannot be recultured are commonly of this size. The internal volumes of these microparticles are commonly thought by biologists to be too small to hold sufficient organic solute molecules to carry out the required metabolic and genetic functions (e.g., Morowitz, 1996). However, it is plausible that starved bacteria could have shrunk prior to their encapsulation within the carbonates. Thomas-Keprta et al. (1997) sidestepped the size issue by suggesting that elongated filaments in ALH84001 may be discarded bacterial appendages.

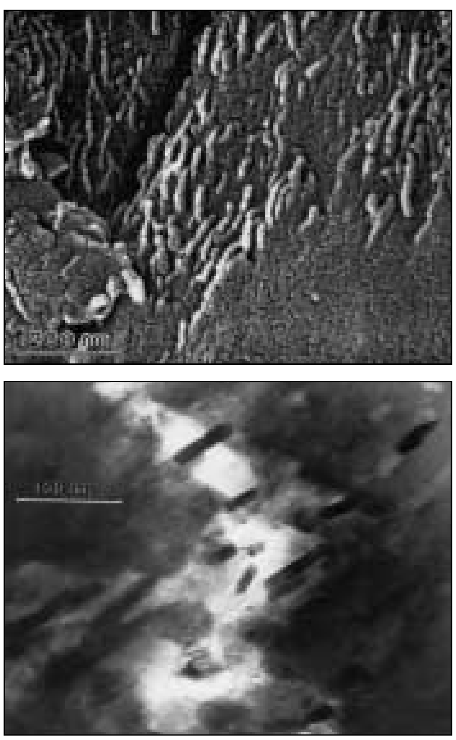

Figure 3. Comparison of an SEM image of putative nanobacteria in ALH84001 carbonates (above) and a TEM image of oriented magnetite whiskers in carbonates (below). Photomicrographs courtesy of NASA and John Bradley (MVA, Inc.), respectively.

The nanofossil controversy, although important in itself, may possibly be moot in the case of ALH84001. Bradley et al. (1997) proposed that the magnetite whiskers and platelets they observed in carbonates are the nanofossils described by McKay et al. (1996). No other microparticles with the sizes and morphologies of the nanofossils have been observed in the carbonates, and fields of oriented magnetite whiskers resemble published SEM images of nanofossils (Fig. 3). The spiral growth mechanism deduced from the presence of axial screw dislocations in magnetite whiskers (Bradley et al., 1996) argues against replacement of microorganisms by magnetite.

CONDITIONS OF CARBONATE FORMATION

The documentation of terrestrial and martian microfossils and biomarkers requires, among other criteria, that the paleoenvironment be a plausible one for biological activity (e.g., Knoll and Walter, 1996). Thus, understanding the formation conditions of the ALH84001 carbonate globules, which are the containers for virtually all of the evidence cited for life, is critical to the argument. Terrestrial organisms survive at temperatures generally below 120 °C, and it seems unlikely that extraterrestrial biota could exist at temperatures far in excess of this value. Constraining the temperature of formation for the carbonates has proved to be the most contentious subject to date.

Globular carbonates in ALH84001 are chemically zoned (Fig. 4), with calcite-ankerite cores and magnesite-siderite rims (Harvey and McSween, 1996). Granular carbonates are compositionally similar to globule cores and are concentrated in pockets and veins throughout the rock (McKay and Lofgren, 1997). Romanek et al. (1994) used the oxygen isotopic compositions of carbonates, determined from an acid dissolution model, to argue that they formed by reaction with aqueous fluids at temperatures <80 °C. Hutchins and Jakosky (1997) revised the carbonate formation temperatures to <250 °C on the basis of a model of atmospheric fractionation of oxygen and carbon prior to incorporation in carbonates. New ion microprobe analyses of oxygen isotopes in carbonate globules indicate highly variable compositions. In particular, Valley et al. (1997) reported $\delta^{18}O$ = +9.5‰ to 20.5‰, whereas Leshin et al., 1997 indicated values of +5.6‰ to +21.6‰. Valley et al. (1997) argued that precipitation of carbonates with these compositions suggests nonequilibrium processes at temperatures <300 °C. Leshin et al. (1997) explained a correlation of carbonate mineral chemistries with oxygen isotopes (Fig. 4) as possibly resulting from high-temperature processes.

Harvey and McSween (1996) noted that the apparent absence of hydrous phyllosilicates in ALH84001 was inconsistent with reaction of an aqueous hydrothermal fluid with an orthopyroxenite host rock. They favored a high-temperature reaction involving a CO_2-rich, supercritical fluid. Thomas-Keprta et al. (1997) described several nanometer-sized grains with basal spacings of 10–11 Å, which they interpreted as smectites. Such grains appear to be rare. Valley et al. (1997) described terrestrial carbonate veins that formed at low temperatures from aqueous fluids without producing hydrous minerals.

Comparisons of ALH84001 carbonate elemental compositions and phase equi-

Meteorite *continued on p. 5*

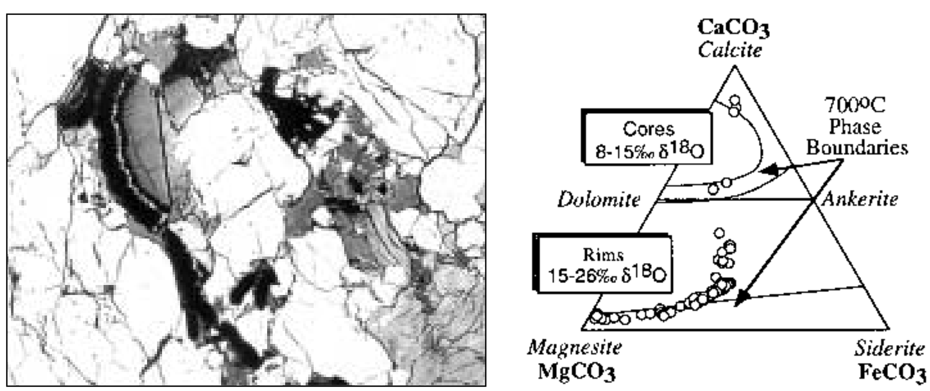

Figure 4. Backscattered electron image (above) of a zoned carbonate globule shows a core of calcite-ankerite (gray) and rim of magnesite (black)-siderite (white) (horizontal axis figure is ~150 µm; courtesy of David Mittlefehldt, Lockheed-Martin Engineering Science Services). Some carbonates have been fractured and disaggregated by shock. Elemental and oxygen isotopic compositional variations (from Harvey and McSween [1996] and L. Leshin [personal commun.], respectively) are illustrated in the figure below. The 700 °C phase boundaries are from Anovitz and Essene (1987); carbonate analyses bridging the gap between ankerite and siderite represent points overlapping several grains. Chemical zoning in carbonates has been cited as evidence for disequilibrium between zones, but the correlation between calcium content and oxygen isotopic composition may also be rationalized by closed-system fractionation within a fluid-poor system.

Meteorite *continued from p. 4*

libria, suggesting formation temperatures of >650 °C (Mittlefehldt, 1994; Harvey and McSween, 1996), have been criticized by some workers (McKay and Lofgren, 1997; Shearer et al., 1996; Treiman, 1997; Valley et al., 1997), who stressed that extensive zoning and isotopic heterogeneity make any attempt to use mineral-exchange geothermometry suspect. Disequilibrium would presumably also invalidate temperature constraints imposed by stable isotope fractionation (Romanek et al., 1994; Leshin et al., 1997). Kinetic control of growth might offer an explanation as to why different lines of evidence suggest distinct formation conditions.

Several other assessments of temperature have reached conflicting conclusions. The assemblage of tiny magnetite whiskers and platelets described in ALH84001 carbonates by Bradley et al. (1996) resemble grains of many substances condensed from vapors, and the spiral growth mechanism documented for some magnetite whiskers (Fig. 2) is consistent with vapor-phase growth. Natural magnetite whiskers have been described in terrestrial volcanic sublimates and grown experimentally from hot (<800 °C) fumarole gases.

Kirschvink et al. (1997) marshaled magnetic evidence in support of a low-temperature origin of ALH84001 carbonates. From a breccia zone they separated two joined orthopyroxene grains, one of which contained carbonate globules on its surface. Each pyroxene grain had stable natural remnant magnetization (NRM) with directions differing by 50° to 80°. These researchers concluded that the grains were not significantly heated after rotation in the breccia zone. Since the carbonates precipitated from fluids percolating through this crushed zone at some later time, they must have formed at low temperature. The NRM temperature constraint assumes that no rotation of grains occurred after carbonate formation. However, the carbonate globules themselves are sometimes fractured and fragmented (Fig. 4), allowing the possibility that associated pyroxene grains were rotated by shock following carbonate formation.

Scott et al. (1997) described shock-melted veins of plagioclase and silica glasses containing carbonate in ALH84001. They envisioned the carbonates having formed at high temperatures during an impact event. Their sample apparently did not contain the carbonate globules studied by McKay et al. (1996), but chemical zoning patterns suggest that these carbonates were part of the same generation. McKay and Lofgren (1997) likewise noted the presence of feldspathic glass, but their observation that the glass intrudes carbonate globules argues that shock melting postdated carbonate formation. The observation of shock metamorphism synchronous with or postdating carbonate formation implies that, however the carbonates in ALH84001 formed, they must have undergone significant temperature excursions.

CONCLUSIONS AND OUTLOOK

The question of whether ALH84001 contains evidence for early martian life remains unresolved. Part of the difficulty in addressing this problem relates to the highly interdisciplinary nature of the arguments, involving complex and sometimes arcane aspects of mineralogy, igneous and carbonate petrology, isotope geochemistry, microbiology and micropaleontology, organic chemistry, shock metamorphism, hydrogeology, and paleomagnetism. Another difficulty derives from the fact that we do not commonly observe and analyze rocks or, for that matter, fossilized or living organisms at these scales. As a result, there are not enough studies of terrestrial analogs to allow adequate interpretations of the data. There is now a serious attempt to supplement the terrestrial database with studies at these scales (e.g., Allen et al., 1997; Vali et al., 1997).

My own assessment is that two of the four lines of evidence cited by McKay et al. (1996)—the presence of extraterrestrial organic matter and of nanofossils in ALH84001—have been seriously challenged and possibly refuted, although others will disagree. Even if some martian organic matter is present, it may be impossible to disentangle its properties from the apparent overprint of terrestrial contamination. The mineralogical characterization of the nanofossils as magnetite whiskers and platelets requires independent confirmation. Before we can constrain the temperature of formation of the carbonates, it will be necessary to ascertain whether they formed by equilibrium or disequilibrium processes. In any case, the recognition that shock has affected this meteorite after carbonate formation suggests that the temperature history of the carbonates was more complex than has been appreciated. More studies of the morphology, structure, and chemistry of proposed biominerals and biofilms in ALH84001 are necessary before the origin of these materials can be specified.

Regardless of whether or not ALH84001 is ultimately judged to contain relics of ancient martian organisms, the report of McKay et al. (1996) has focused scientists' concentration (not to mention the attention of the rest of the world) on the possibility of extraterrestrial life. Mars is the most Earthlike of planets, and it is certainly within the realm of possibility that it once harbored microorganisms. NASA's planned Mars exploration program will directly address the question of life,

Meteorite *continued on p. 6*

GSAF UPDATE

Valerie G. Brown, Director of Development, GSA Foundation

From the Ground Up

In May, we reported on the 1996 fund-raising results. The accompanying chart shows the cumulative fund-raising results from the inception of the Second Century Fund campaign in 1992 to the end of April 1997, summarizing both the total gifts received and the sources of the gifts. The revenues include cash, pledges, program grants, and deferred gifts, reflecting the considerable variety not only of those who support GSA but also of the ways in which support can be given.

Revenue	1992–1995	1996	1997	Total
Second Century Fund				
Members	$2,278,375	$ 262,313	$ 50,816	$2,591,505
Other Individuals	$ 1,300	$ 3,226	$ 200	$ 4,726
Government	$ 544,512	$ 594,869	$ 0	$1,139,381
Foundations	$ 513,165	$ 16,000	$ 10,000	$ 539,165
Industry	$ 693,500	$ 74,712	$ 500	$ 768,712
Annual Campaign	$ 480,391	$ 104,522	$ 8,746	$ 593,659
Pardee Bequest	$2,677,309			$2,677,309
Total Revenues	**$7,188,552**	**$1,055,642**	**$ 70,262**	**$8,314,457**

Dummett Joins Foundation Board

The GSA Foundation is honored to welcome Hugo T. Dummett as its newest trustee. A member of GSA since 1985, Dummett has established an important career and reputation in minerals exploration.

A graduate of South Africa's University of Witwatersrand, Dummett worked in South Africa and Canada before pursuing postgraduate education at the University of Queensland in Australia. He came to the United States in 1977 as a senior geologist for Superior Oil's Minerals Division. Since 1989, Dummett has been affiliated with BHP Minerals, where he now serves as senior vice president and group general manager of the Exploration Group.

Dummett's contributions to his profession have been equally wide-ranging. He is a member of the Association of Exploration Geochemists, the Society of Economic Geologists, which named him as the 1996 Thayer Lindsley Distinguished Lecturer, the American Institute of Mining Engineers, the Geological Society of South Africa, and the USGS resource program advisory board to the National Academy of Sciences. In 1997, he was awarded the William L. Saunders Gold Medal by the Society for Mining, Metallurgy and Exploration.

The GSA Foundation is truly fortunate to be the beneficiary of such excellence and experience.

A Milestone

Since beginning the program in 1988, the GSA Foundation has awarded over $125,500 to the GSA sections for matching student travel grants. Each year, the grants assist college students to attend the section meetings and GSA's Annual Meeting. In 1997, the Foundation increased the amount of its awards to $4,000 per section.

The awards are paid from the unrestricted gifts GSA members make to the Foundation. This is another important benefit made possible by your generosity! ■

Meteorite *continued from p. 5*

among other topics, over the next decade. The controversy about possible biological activity in a martian meteorite is allowing the scientific community to reexamine its thinking and hone its skills for that effort.

ACKNOWLEDGMENTS

I appreciate thoughtful and constructive reviews by Peter Buseck, Andy Knoll, and John Valley.

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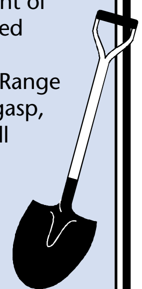

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