Concerning the Existence of Life on Mars

E. M. Galimov

Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, ul. Kosygina 19,
Moscow, 117975 Russia

Abstract—In a paper published in the August issue of *Science*, the American researchers McKay *et al.* (1996) reported the results of their investigation of the Martian Antarctic meteorite ALH 84001. They regard these results as evidence of the existence (in the past, at any rate) of life on Mars. However, a study of the geochemical data in the paper suggests that simple inorganic processes offer a more plausible explanation of the results. Thermodynamic analysis reveals that a mineral association, including pyrrhotite, magnetite, and magnesite, is quite stable in a hydrothermal system at a temperature of the order of 150°C and does not require invoking a biological mechanism. The interpretation by McKay *et al.* (1996), based on the isotopic compositions of oxygen and carbon, led them to conclude, as Romanek *et al.* (1994) concluded, that the formation of carbonate globules was a low-temperature (from 0 to 80°C) process. This conclusion has been made based on less than convincing assumptions. The very same isotope data suggest that the globules are more likely to have formed as a result of a high-temperature (~700°C) process, with the subsequent superimposition of a hydrothermal alteration process at about 150°C. Polycyclic aromatic hydrocarbons could have arisen abiogenically in the same processes. The intriguing fact remains that the discovered structures have a specific morphology. However, it cannot be ruled out that such structures are trivial in the inorganic world as well on a nanometric scale. Nevertheless, the work of McKay *et al.* (1996) is important since it shows that a combination of state-of-the-art analytical techniques, in principle, provides an approach to both the problem of the existence of extraterrestrial life and the problem of the origin of life on Earth.

INTRODUCTION

A paper by McKay *et al.* (1996), which has had widespread repercussions, contains data that were interpreted by the authors as evidence of the highly probable presence of living organisms on Mars. The case for such a presence is based on the following premises: (1) an unusual combination of minerals, which, in the view of the authors of the paper (McKay *et al.*, 1996), cannot arise in a purely inorganic process; (2) the isotopic compositions of the carbon and oxygen of the carbonates, which points to their low-temperature (from 0 to 80°C) formation and extraterrestrial origin; (3) the presence of polycyclic aromatic hydrocarbons; and (4) an unusual type of microstructure, resembling the remains of microorganisms.

McKay *et al.* (1996) accept that none of these facts are clinching proof of their case, but believe that together, they constitute a solid argument in support of the proposition that the structures they have discovered are relics of the functional activities of organisms. Beyond doubt, the discovery of any life forms on other bodies of the Solar System would be an epoch-making event. But, as we all know, the more significant a discovery, the more unassailable must be its proof.

The goal of this paper is to evaluate how convincing is the evidence presented in the paper by McKay *et al.* (1996).

COULD THE MINERAL STRUCTURES DISCOVERED HAVE FORMED INORGANICALLY?

McKay and co-workers have described structures they found in the meteorite Allan Hills (ALH) 84001. This meteorite was found in the Antarctic and was at first referred to the diogenite subdivision of achondrites. However, Mittlefehldt (1994) identified it as belonging to the SNC suite of meteorites, which, on the basis of a number of features, are considered to be of Martian origin (McSween, 1994). The structures described are carbonate globules of 10–100 μm in an orthopyroxene matrix. The globules, according to microprobe analysis, contain a core represented by carbonate enriched with Fe and Ca (Fig. 1). The core is surrounded by carbonate enriched with Mg. The peripheral part of a globule exhibits traces of dissolution. Microscopic formations (10–100 nm in size), consisting of magnetite (Fe_3O_4) and ferrous sulfide (FeS), occur along the outer margins, in the pore space, and along cracks. The ferrous sulfide was determined by McKay *et al.* (1996) to be the mineral pyrrhotite. McKay and co-workers referred both the carbonate globules themselves and the microscopic mineral structures to biogenic formations. They formed the opinion that, while "simultaneous precipitation of Fe-sulfides and magnetite along with dissolution of carbonates" appears implausible in simple inorganic models, this could, in contrast, "be explained
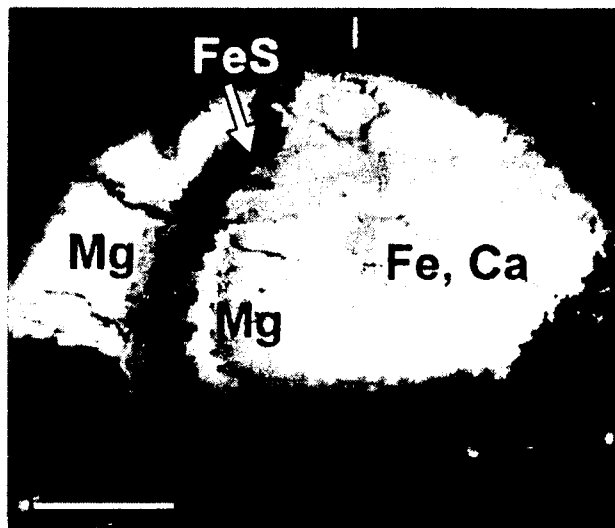
Fig. 1. Chemical zoning in carbonate globule from ALH 84001. Plotted on the basis of the microprobe analysis data cited by McKay et al. (1996).
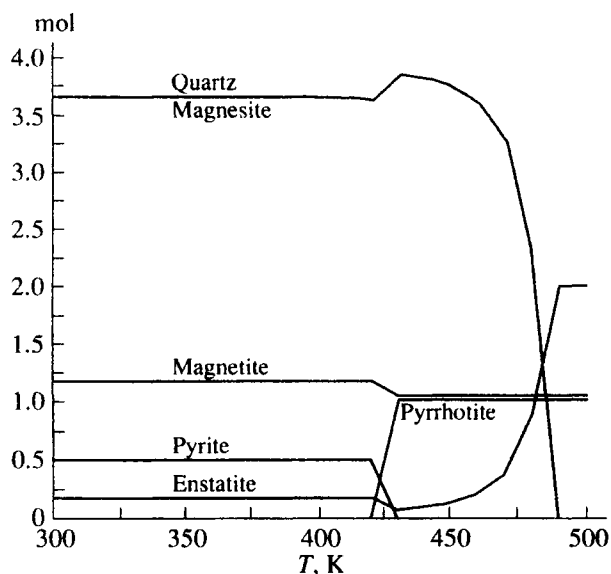

Fig. 2. Changes in the composition of the H–O–S–C–Si–Mg–Fe system with temperature at a pressure of 1 bar. The initial contents of the components conform to the stoichiometry of the reaction in the text. The computation was performed with the aid of the DIANIK software package by the method of minimizing the Gibbs free energy (Shapkin, 1986).

by biogenic processes, which are known to operate under extreme disequilibrium conditions" (McKay et al., 1996, p. 927).

However, judging by this description, there are no grounds for treating the formation of the carbonate globule and the micromineral assemblage, which includes magnetite and ferrous sulfide, as a single process. It is more probable that the primary carbonate

globules with Fe and Ca constituents were present in the orthopyroxene and are of magmatic origin. They later experienced the effect of an aqueous solution bearing Mg ions. As a result of this, the ferrous carbonate was partly replaced by magnesium carbonate (magnesite), and altered relics of the primary globules survived in the central part in the form of Fe-enriched carbonate nuclei. Sulfur, as mentioned by McKay et al. (1996), occurs in measurable quantities throughout the globule. In that case, the process of the initial formation of magnetite and ferrous sulfide (pyrrhotite) together with magnesite may be described by the following reaction:

$$4MgSiO_3 + 4FeCO_3 + H_2O + S$$

$$\Rightarrow 4MgCO_3 + FeS + Fe_3O_4 + H_2O + 4SiO_2.$$
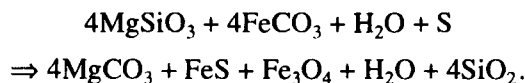
The Fe-enriched carbonate on the left-hand side is represented by siderite $(FeCO_3)$. Present on both the left-hand and the right-hand side of the equation is water (H_2O), which can be cancelled in the overall reaction, but its presence is relevant to computation of the balanced system. Enstatite $(MgSiO_3)$ is present as a source of Mg.

The corresponding system of elements, $4Mg-4Si-25O-4Fe-4C-2H-S$, was subjected to a computational procedure involving the Gibbs principle of free-energy minimization (Shapkin, 1986), in order to identify the mineral compositions corresponding to the state of equilibrium of the above system at different pressures and temperatures $(P-T$ conditions). The question is whether the combination of minerals including magnetite, magnesite, and pyrrhotite is stable, and, if so, in what range of $P-T$ conditions.

Computer analysis produced the following result: At a pressure of 1 bar, magnetite is stable throughout the entire temperature range of the hydrothermal process (Fig. 2). The sulfide coexists with magnetite, but appears in the form of pyrrhotite only at a temperature of about 150°C. Magnesite ceases to be stable at a temperature above 180°C. Hence, at $P = 1$ bar, all three minerals coexist, but in a relatively narrow range of temperatures. At a lower pressure, for example, at 6 mbar, corresponding to the pressure in the present-day atmosphere of Mars, magnesite becomes unstable at relatively low temperatures. On the other hand, when the pressure rises (for example, to 10 bar), the range of the coexistence of magnetite, magnesite, and pyrrhotite broadens. It therefore follows from equilibrium computations, first, that the above mineral composition is stable in a simple inorganic (equilibrium) system; second, that the temperature of the process, if the pyrrhotite is stable, has to be no less than 150°C; and, third, that the process took place at elevated pressures, i.e., not at the surface, but at a certain depth.

However, our conclusion about the temperature of 150°C does not agree with the estimates obtained by McKay et al. (1996) from isotope data. Let us consider these data in detail.

DO THE ISOTOPE DATA TESTIFY
TO A DEFINITELY LOW-TEMPERATURE
(FROM 0 TO 80°C) FORMATION
OF THE DISCOVERED STRUCTURES?

McKay *et al.* (1996) themselves did not study the isotopic compositions of the investigated carbonates. They cite data obtained earlier by Romanek *et al.* (1994), who isolated two fractions of carbonates by sequential acid digestion: a Fe,Ca-rich fraction and a Mg-rich fraction. The following isotopic composition values were obtained for $\delta^{13}C$ and $\delta^{18}O$:

Composition	$\delta^{13}C(\permil)$	$\delta^{18}O(\permil)$
Ca, Fe-rich	+39.5	+13.3
Mg-rich	+41.1	+22.3

The isotopic composition of carbonate in equilibrium with high-temperature silicate tends toward a value of $\delta^{18}O$ ranging from +6 to +8‰. Therefore, Romanek *et al.* (1994) assumed in their paper that the observed $\delta^{13}O$ values were a result of low-temperature equilibria.

Romanek *et al.* (1994) assumed that the carbonate precipitated from a carbonate solution. Isotopic fractionation in this case is governed by the molar H_2O/CO_2 ratio and by the precipitation temperature. Romanek *et al.* (1994) accepted a minimal temperature of 0°C at which precipitation is still possible. In that case, the H_2O/CO_2 ratio to which the isotopic composition of the carbonate with the maximal measured value of $\delta^{18}O$ = +22.3‰ corresponds can be determined from the diagram linking the H_2O/CO_2 molar ratios, the temperature, and the isotopic composition of the carbonates (Fig. 2 of Romanek *et al.*, 1994). That ratio was found to be equal to 0.58. On the assumption that the established ratio of H_2O/CO_2 = 0.58 does not change in the course of the process, Romanek *et al.* (1994) determined the temperature to which the fraction with $\delta^{18}O$ = +13.3‰ corresponds, which was found to be 80°C. The estimate of the temperature range by Romanek *et al.* (1994) is thus tentative: it represents a version corresponding to a certain provisional model. Unfortunately, McKay *et al.* (1996) adopted the 0 to 80°C range as an objective estimate supported by isotope data.

These data, however, lend themselves to a different interpretation.

Note, first of all, that Harvey and McSween (1996) published a paper in which they estimated the temperature of the formation of the globules to be 700°C, i.e., they identified them as magmatic rather than biogenic low-temperature formations. To what extent does such an assessment conflict with the isotopic composition data?

From the graph (Fig. 3) of isotopic fractionation as a function of the temperature in the carbonate–enstatite (orthopyroxene) system, it follows that the temperature
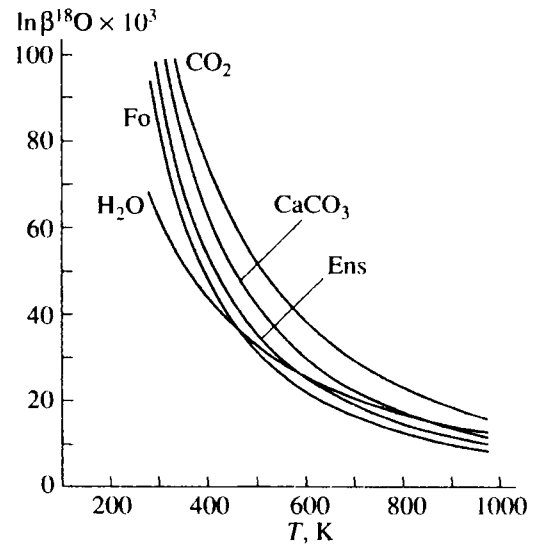

Fig. 3. Temperature dependence of $\beta^{18}O$ factors for forsterite (Fo), enstatite (Ens) (Zheng, 1993), $CaCO_3$ (Clayton and Kieffer, 1991), H_2O and CO_2 (Richet *et al.*, 1977). Isotope fractionation for oxygen is determined as the difference $\Delta^{18}O_{A-B}(\permil) = 10^3 \ln\beta_A - 10^3 \ln\beta_B$.
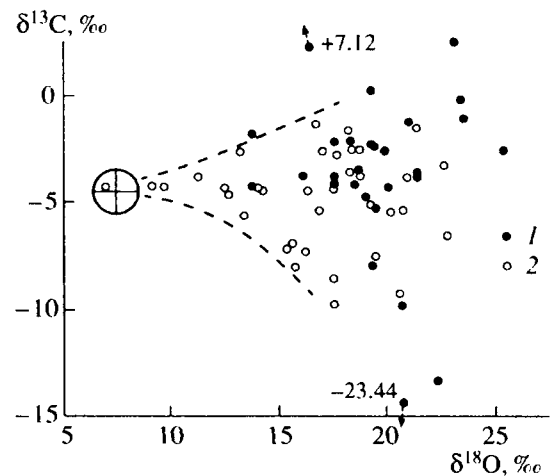

Fig. 4. Isotopic compositions of oxygen and carbon of magmatic carbonates from the Udachnaya kimberlite pipe in Yakutia: (*1*) brecciated carbonates; (2) unaltered massive carbonates (Galimov, 1991).

700°C corresponds to a value of $\delta^{18}O$ = +2.3‰. If, for the ALH 84001 orthopyroxene, we accept the value of $\delta^{18}O$ = +4.6‰ (Romanek *et al.*, 1994), the isotopic composition of the carbonate becomes equal to +6.9‰. This differs from the value of +13.3‰ for the Fe,Ca-rich phase, which can be regarded as a relic of the primary magmatic globule. However, it should be borne in mind that ideal relations of equilibrium rarely occur in nature. Usually, even unaltered carbonates in kimberlites and carbonatites, i.e., unquestionably magmatic carbonate formations, exhibit a scatter of $\delta^{18}O$ values in the +7...+15‰
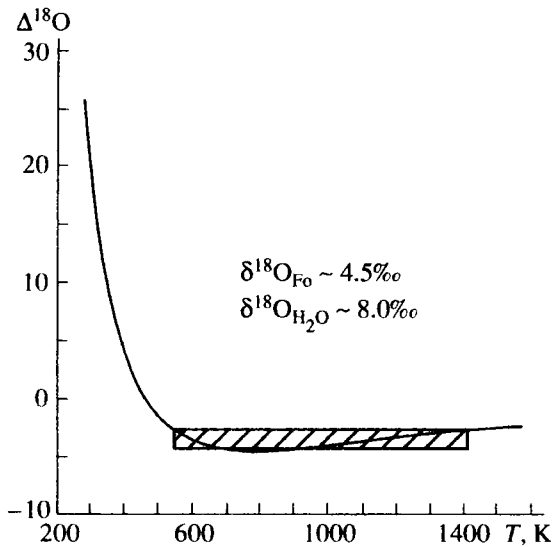
Fig. 5. Temperature dependence of isotopic fractionation for oxygen in the forsterite–H_2O system. Computed according to data for $\beta^{18}O$ factors of forsterite (Clayton and Kieffer, 1991) and water (Richet et al., 1977).
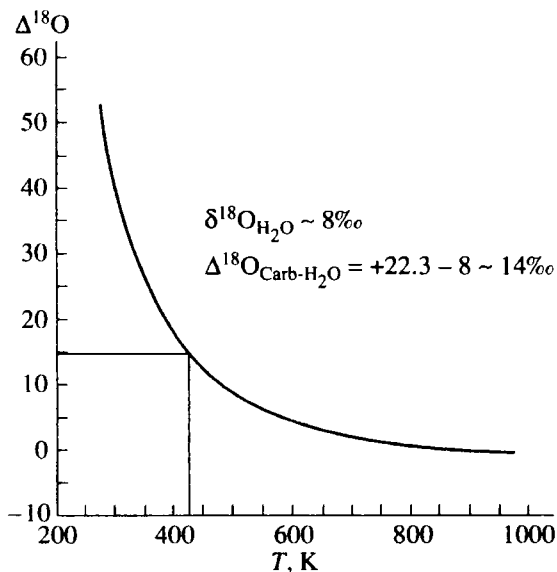

Fig. 6. Temperature dependence of isotopic fractionation for oxygen in the carbonate ($CaCO_3$)–water system. Computed according to data for $\beta^{18}O$ factors of $CaCO_3$ (Clayton and Kieffer, 1991) and water (Richet et al., 1977).

range. An example of this is provided by the results of my investigation of $\delta^{18}O$ and $\delta^{13}C$ carbonates from the Udachnaya kimberlite pipe in Yakutia (Fig. 4). In addition to this, it should be remembered that the Fe, Ca-rich fraction of carbonates is not intact magmatic material, but to some extent, an altered product, affected by a hydrothermal process and corresponding isotope exchange. Therefore, the value of +13.3‰ for this frac-

tion is in agreement with the option of a high-tempera-ture magmatic origin of this carbonate.

The peripheral Mg-rich fraction has a +22.3‰ isotopic composition, which should have arisen through an exchange with water at lower temperatures. To determine this temperature, let us assume that the water that interacted with the rock in the hydrothermal process had a composition characteristic of the primary water of Mars, i.e., the water released by the high-tem-perature outgassing of the planet's mantle. A similar assumption was made by Romanek et al. (1994), and, unfortunately, a more definite estimate, corresponding to specific local conditions, cannot be made. It follows from the temperature dependence for the mantle rock–water (specifically, forsterite–water) system that frac-tionation in this system remains more or less constant and close to +3.5‰ (Fig. 5) in a fairly broad tempera-ture range (300 to 1150°C. Therefore, adopting $\delta^{18}O$ = +4.5‰ for the mantle rock, we obtain the value +8‰ for the $\delta^{18}O$ of the primary water. This is the value, inci-dentally, of the primary water of the Earth as well as of Mars. The contemporary value of $\delta^{18}O$ = 0 was acquired by the World Ocean on the Earth through oxy-gen isotope exchange with sedimentary formations and the isotope balance that was established and that embraces the entire mass of the sedimentary rocks in the Earth's crust (Galimov, 1988).

Turning now to the temperature dependence of isoto-pic fractionation in the H_2O–carbonate system (Fig. 6), we find that at a $\delta^{18}O$ = +8‰ isotopic composition of water, the isotopic composition of carbonate $\delta^{18}O$ = +22.3‰ is attained at a rock temperature of 150°C.

In this way, proceeding from an interpretation of the isotope data, we arrive at the same estimate of the hydrothermal process temperature that we reached by analyzing mineral equilibria.

In my view, the carbonate globules were most prob-ably of a magmatic high-temperature origin (~700°C). They then underwent hydrothermal alteration at a tem-perature of about 150°C.

The observed high enrichment of the carbonate globules with a heavy isotope of carbon (of the order of +40‰) testifies to the extraterrestrial origin of the car-bonate material in ALH 84001. On this point, I agree with McKay and co-workers (1996), although it should be mentioned that carbonate material of such an isoto-pic composition does occur in Earth conditions as well—contrary to the assertion of McKay et al. (1996). Specifically, carbonate globules in kimberlites (so-called autholiths) are characterized by $\delta^{13}C$ values above +30‰ (Galimov, 1991).

Significantly, the Mg-rich fraction, which I consider to be a product of hydrothermal alteration, has an iso-topic composition ($\delta^{13}C$ = +41.1‰) that scarcely dif-fers from the isotopic composition of the Fe, Ca-rich fraction ($\delta^{13}C$ = +39.5‰), which I believe to be a relic of the primary magmatic globule. Consequently, the
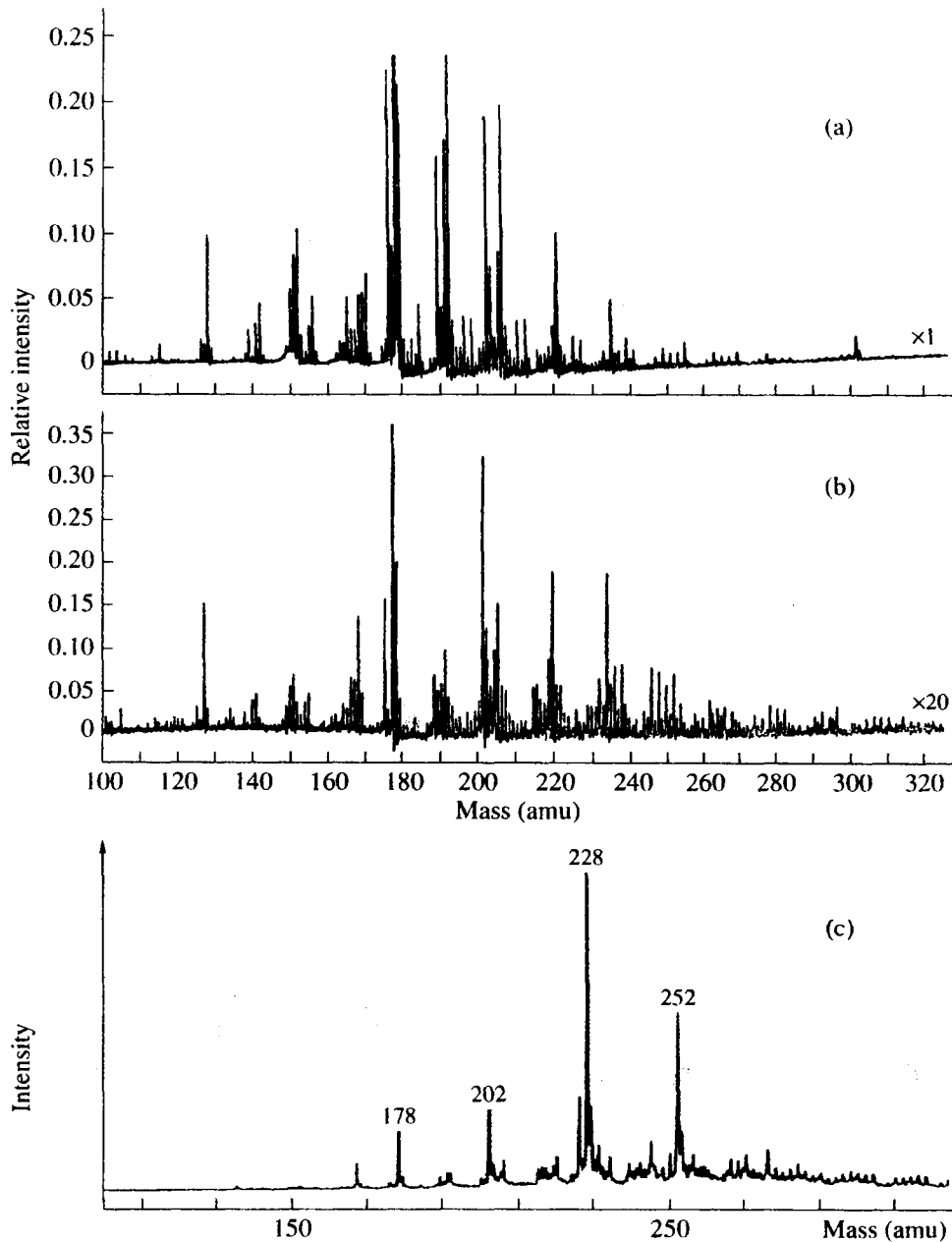
Fig. 7. A comparison of the spectra of polycyclic hydrocarbons from the meteorites (a) Bishanpur, (b) Murchison (Clemett*et al.*, 1992), and (c) ALH 84001 (McKay *et al.*, 1996).

hydrothermal process was not (or was barely) accompanied by the addition of extraneous CO_2.

POLYAROMATIC HYDROCARBONS

The presence of polycyclic aromatic hydrocarbons (PAHs) cannot be considered evidence of the biogenic origin of an organic substance. Polycyclic aromatic hydrocarbons are present in sedimentary rocks of the Earth, where they are partly a product of the diagenesis of biogenic organic matter, and are partly formed and incorporated in sediments through the burning of vegetation massifs.

But PAHs also arise in many processes entirely unrelated to life. They have been identified, for example, in interstellar dust (Clemett *et al.*, 1993), in meteorites (Hahn *et al.*, 1988), and in the atmospheres of Titan and Jupiter (Sagan *et al.*, 1993); they are synthesized in shock waves (Mimura *et al.*, 1994), during the irradiation of graphite by protons in accelerators, etc.

Spectra of PAHs from McKay *et al.* (1996), isolated from the Martian meteorite ALH 84001, are compared in Fig. 7 with spectra of PAHs from meteorites, where their origin is definitely abiogenic.
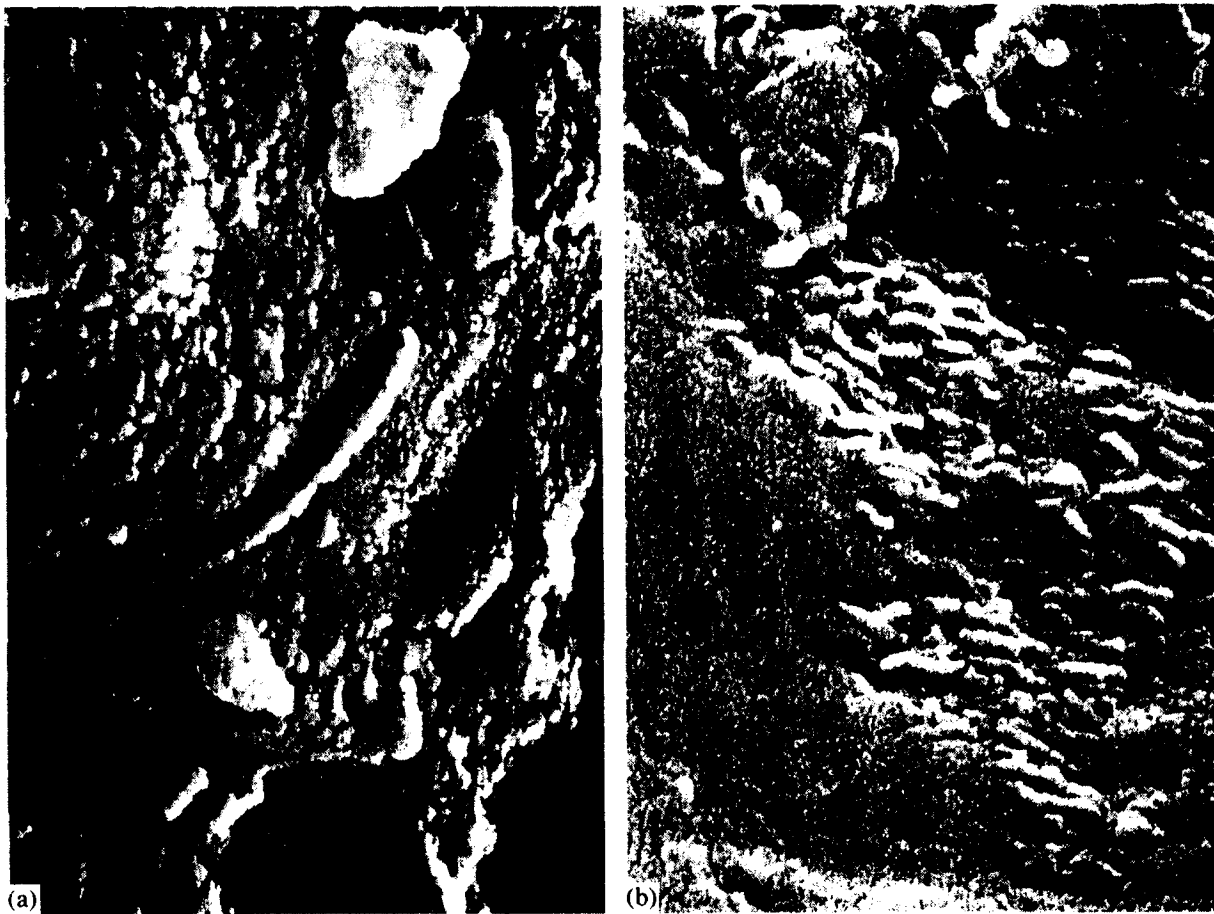
Fig. 8. Electron-microscope image of structures related to carbonate globules from ALH 84001. Borrowed from (a) Kerr (1996) and (b) Gibbs and Powell (1996).

The mass spectrum of PAHs from ALH 84001 is very similar to mass spectra of PAHs of carbonaceous chondrites. The fact that PAHs from ALH 84001 are somewhat depleted in low-molecular compounds (naphthalene, phenanthrene) and alkylated homologues may be due to a secondary hydrothermal process, which washed out some of their components.

It should be mentioned that abiogenically synthesized organic compounds are common in magmatic systems. I have, for example, identified hydrocarbons, including high-molecular ones, in fluid inclusions in crystals of olivine and pyroxene from kimberlite pipes (Galimov, 1988). Bitumoids and hydrocarbons are widespread in alkaline igneous rocks. For this reason, organic compounds, including PAHs, certainly could have formed in the process of the evolution of a primary magmatic system.

SPECIFIC STRUCTURES

The most intriguing fact reported by McKay *et al.* (1996) is the peculiar morphology of microscopic discharges observed in the globule. An electron-micro-

scope image of these structures is reproduced in Fig. 8. The image has been borrowed not from McKay *et al.* (1996), but from Kerr (1996) and Gibbs and Powell (1996), where the peculiarities of these microstructures are particularly manifest.

McKay *et al.* (1996) maintain that these ovoids are reminiscent in shape and size of nanobacteria from travertines and limestone, and they "interpret that the carbonate globules have a biogenic origin and were likely formed at low temperatures" (McKay *et al.*, 1996, p. 929).

The discovery of such structures in rock material of Martian origin is undoubtedly of interest and appears to be a weightier fact than the geochemical arguments discussed above.

Here too, however, a few remarks should be made. First, as reported by McKay *et al.* (1996), the structures are tens of nanometers in size, which is 2–3 orders of magnitude smaller than the size of terrestrial microorganisms. To be sure, Martian microorganisms could differ from terrestrial ones, but McKay *et al.* (1996) to such an extent base their reasoning on an analogy
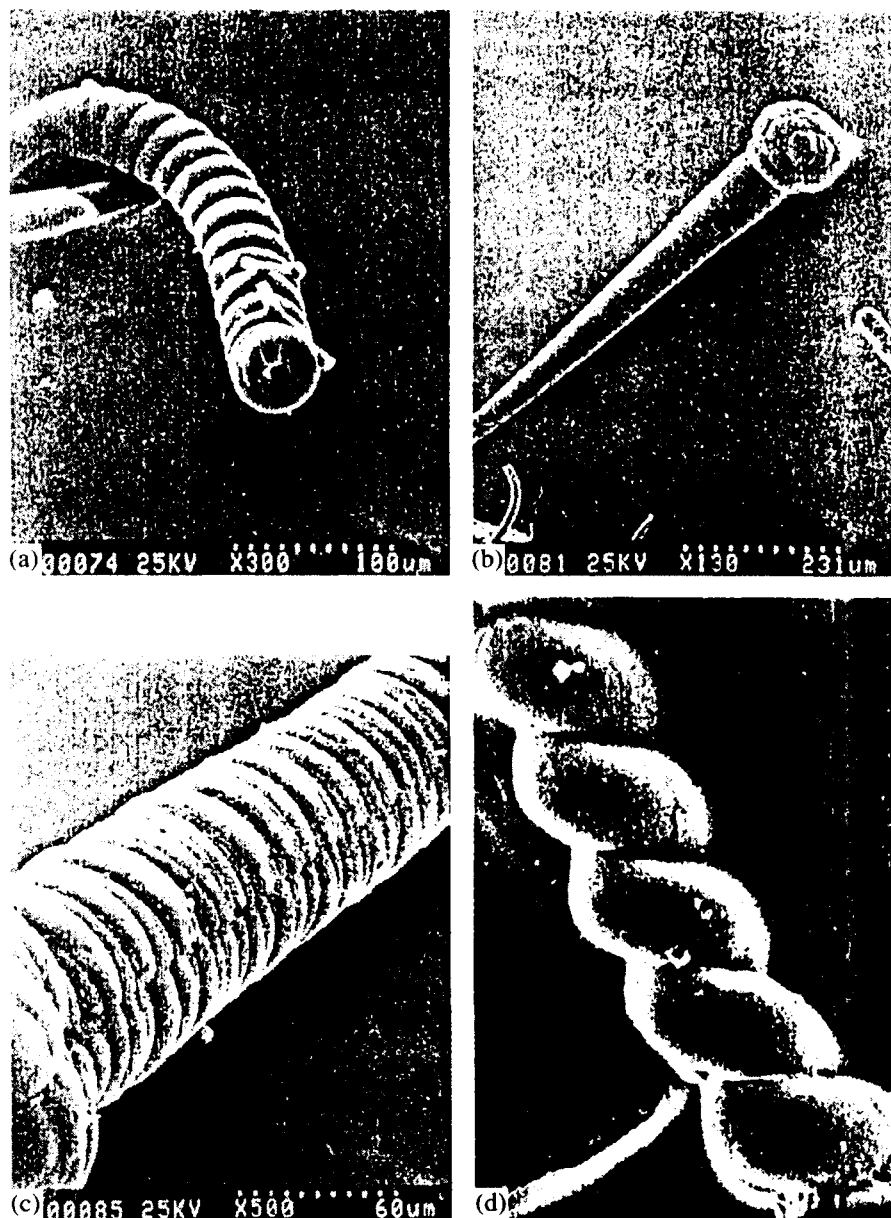
Fig. 9. Structures in kerite from pegmatites in Volyn' granites (Yushkin, 1996).

between the observed life forms and terrestrial ones that this substantial distinction merits attention. Second, terrestrial rocks, including mineral discharges in the inorganic kingdom, have never been studied in detail on a nanometric scale. Accordingly, it cannot be ruled out that the structures observed by McKay *et al.* (1996) are trivial in the context of the inorganic microworld on that scale. Finally, it seems appropriate to note that among inorganic structures formations of very intricate and unusual shape occur, e.g., the illustration (Fig. 9) from a paper by Yushkin (1996), reporting structures of a highly exotic appearance discovered in kerite from pegmatites.

CONCLUSIONS

An examination of the geochemical data presented by McKay *et al.* (1996) as evidence of the existence of microscopic life on Mars thus reveals that, contrary to the interpretation of those authors, they are not only compatible with an inorganic model, but are far more plausibly explained by common inorganic processes. Thermodynamic analysis shows that a mineral association including pyrrhotite, magnetite, and magnesite is quite stable in a hydrothermal system at temperatures of the order of 150°C. As for the interpretation of the isotope data for oxygen and carbon by McKay *et al.* (1996), which led them to conclude, as had Romanek *et al.*

(1994), that the formation of the carbonate globules had been a low-temperature process, this rests upon doubtful assumptions. It follows from the same isotope data that a high-temperature (~700°C) formation of the globules with a subsequent superimposition of a process of hydrothermal alteration at a temperature of about 150°C is more probable. Polycyclic aromatic hydrocarbons could have arisen in the same processes abiogenically.

Therefore, the observations of McKay et al. (1996) scarcely bring us any closer to a conclusion about the existence of life on Mars.

At the same time, the work of McKay et al. is important in that it shows that a combination of state-of-the-art analytical techniques does, in principle, enable us to make progress in investigating both the problem of the existence of extraterrestrial life and the problem of the origin of life on Earth. Mars appears to be the only place in the Solar System, apart from the Earth, where life could have existed—in the past, at any rate. Hence, every earnest scientific investigation in this area—even if its results are controversial—is invaluable.

The work of McKay et al. (1996) shows that science has attained the practical capability of solving one of its most fundamental problems.

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