Mineralogical consideration of possible microfossils in martian meteorite ALH84001

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Abstract

Antarctic meteorite ALH84001 is a member of twelve martian meteorites that are widely believed to have originated on planet Mars based upon several lines of evidence. ALH84001 is an ancient orthopyroxenite rock of 4.5 billion years old that contains abundant Ca-Fe-Mg carbonates, unlike other martian meteorites. Recently, it has been reported that ALH84001 contains (1) unique mineral compositions and biominerals, (2) polycyclic aromatic hydrocarbons (PAHs) in association with carbonates, and (3) unique structures and morphologies typical of nannobacteria or microfossils. They are interpreted as a possible relic biogenic activity on early Mars. We review the possibility of alternative explanations for these phenomena, especially for mineralogical features in the carbonate globules. Although it may be possible to consider that such phenomena in carbonates are biogenic rather than inorganic in origin, we show more difficulty in the biogenic interpretation than has been discussed. Because it is very difficult to conclude that they are biogenic or non-biogenic from present data, it is necessary to further study ALH84001 and other martian meteorites. We also need to consider future Mars missions, especially sample return missions. In this consequence, we should start to think about a curation system and analytical facilities in Japan in cooperation with other related communities.

Introduction

The possibility of past life on Mars has been proposed by McKay *et al.* (1996). The summary of this work was given by Gibson *et al.* (1996) as follows. “An igneous Mars meteorite, ALH84001, of unknown geologic context, was penetrated by fluids along fractures and pore spaces, which then became the sites of secondary mineral formation. Freshly broken fracture surfaces display carbonate globules with associated abundant polycyclic aromatic hydrocarbons (PAHs). Studies by others have shown that the igneous material crystallized 4.5 Ga, and that the carbonate globules formed 3.6 Ga. ALH84001 was removed from the martian surface 16 My ago by an impact and arrived on Antarctica 13,000 years ago. It appears to be essentially free of terrestrial weathering. The PAHs are present at concentrations $\sim 10^3$ to 10^5 times higher than are found in the surrounding terrestrial ice, and contamination studies indicate that the observed organic material is indigenous to the meteorite. The carbonate globules are rimmed by fine-grained, secondary phases of single-domain magnetite and iron sulfides, that could have resulted from oxidation and reduction reactions known to be important in terrestrial microbial systems. SEM and TEM images of the carbonate globules show features resembling terrestrial microorganisms, terrestrial biogenic carbonate structures, or microfossils. Although there are alternative explanations for each of the above phenomena taken individually, when they are considered collectively, particularly in view of their spatial association, we conclude that they may be evidence for primitive life on early Mars.” Furthermore, new evidence of life on Mars was announced lately in some newspapers based on an earlier study by Wright *et al.* (1989), although details are not known. They found “organic material” up to 1000 ppm in the martian meteorite EETA79001 (basaltic shergottite).

Four lines of evidence are given in McKay *et al.* (1996); (1) the presence of carbonate globules (Mittlefehldt, 1994) showing infiltration by fluids and their textural resemblance to terrestrial microorganisms, (2) the discovery of PAHs associated with carbonate globules, (3) the presence of the microscopic mineral grains (magnetite-iron sulfide-carbonate at the 10-100 nm scale), and (4) the discovery of shapes that resemble bacteria. The first, third and fourth lines of evidence are based on mineralogical or biomineralogical studies. In this review, mineralogical (and biomineralogical) considerations on the features recorded in the carbonate globules are made as well as reconsideration of mineralogical and geochemical features of ALH84001 as a martian meteorite (also see Yanai, 1997, in this volume). The second line of evidence is important for life. However, organic materials are beyond the scope of this review, and are not considered in detail here.

ALH84001 as a martian meteorite

Evidence for martian origin of SNC meteorites

Twelve martian meteorites have been identified up to date. Since discovery of a large

TABLE 1. Martian meteorites.

Meteorite name	Recovered location	Recovered date	Weight	Rock type	*Crystal. age	**Cosmic-ray exp. age
Shergotty	Shergotty, India	Aug. 25, 1865	~ 5 kg	Basalt	163 Ma	2.5 Ma
Zagami	Zagami, Nigeria	Oct. 3, 1962	~ 18 kg	Basalt	178-186 Ma	2.6 Ma
EETA79001	Elephant Moraine Antarctica	Jan. 13, 1980	7.9 kg	Basalt	172-177 Ma	0.6 Ma
QUE94201	Queen Alexandra Range Antarctica	Dec. 16, 1994	12.0 g	Basalt	144 ± 23 Ma	2.4 Ma
ALH-77005	Allan Hills, Antarctica	Dec. 29, 1977	482 g	Lherzolite	187 Ma	3.4 Ma
LEW88516	Lewis Cliff, Antarctica	Dec. 22, 1988	13.2 g	Lherzolite	—	3.6 Ma
Yamato-793605	Yamato Mountains Antarctica	1979	16 g	Lherzolite	—	—
Nakhla	Nakhla, Egypt	Jun. 28, 1911	~ 40 kg	Clinopyroxenite	1.3 Ga	10.3-10.7 Ma
Lafayette	Lafayette, Indiana, USA	1931	~ 800 g	Clinopyroxenite	1.3 Ga	10.3-10.7 Ma
Governador Valadares	Governador Valadares Brazil	1958	158 g	Clinopyroxenite	1.3 Ga	10.3-10.7 Ma
Chassigny	Chassigny, France	Oct. 3, 1815	~ 4 kg	Dunite	1.3 Ga	9.9 Ma
ALH84001	Allan Hills, Antarctica	Dec. 27, 1984	1939.9 g	Orthopyroxenite	4.56 Ga	15 Ma

*Crystal. age: Crystallization age. Data from Nakamura *et al.* (1982b), Nyquist *et al.* (1995), Borg *et al.* (1996). **Cosmic-ray exp. age: Cosmic-ray exposure age. Data from Eugster *et al.* (1996).

number of meteorites from Antarctica (Nagata, 1978), 6 Antarctic meteorites (ALH-77005, EETA79001, LEW88516, ALH84001, Y-793605, QUE94201) have been added to the SNC meteorite group of shergottites (Shergotty, Zagami), nakhlites (Nakhla, Lafayette, Governador Valadares), and chassignite (Chassigny). Many workers have extensively discussed the possible martian origin of SNC meteorites for the last two decades, and the hypothesis has been strengthened as new SNC meteorites have been discovered (*e.g.*, McSween 1985; 1994). In 1993, ALH84001 was reclassified as a SNC meteorite rather than a diogenite (Clayton, 1993; Mittlefehldt, 1994), although ALH84001 differs in several respects from the previous SNC meteorites. This reclassification has expanded the range of properties of SNC meteorites. We will first summarize the several lines of evidence for a martian origin of the SNC meteorites that existed before 1993, when ALH84001 was identified as a new member of SNC meteorites. Then, we will discuss mineralogy and chemistry of ALH84001, paying special attention to similarities and differences between ALH84001 and other SNC meteorites.

The previous SNC meteorites have extremely young crystallization ages (180 Ma to 1.3 Ga), whereas those of typical meteorites are normally older than 4.0 billion years ago (*e.g.*, Shih *et al.*, 1982; Nakamura *et al.*, 1982a and b). The SNC meteorites are igneous rocks formed by crystallization of minerals from molten magma, indicating that their parent body had been geologically active until a very recent time of the history of the solar system. The presence of volcanic activity as recently as 180 Ma ago suggests a parent body of large size, such as Venus, Earth, or Mars. It is clear that SNC meteorites have distinct oxygen isotope ratios from terrestrial rocks (*e.g.*, Clayton and Mayeda, 1996), thus ruling out terrestrial origin. It is highly difficult to consider that a rock fragment produced by an impact on Venus could escape through the atmosphere that is 90 times denser than that of the Earth, and then reach the Earth as a meteorite. Thus, Mars becomes plausible as a parent body of the SNC meteorites. The cumulate texture typical of some SNC meteorites also suggests an origin from a planetary body having a large gravitational field.

Another characteristic of SNC meteorites is that they were formed under relatively oxidizing conditions near the QFM (quartz-fayalite-magnetite) buffer. For example, meteorites usually contain metallic iron suggesting that they were formed in an extremely reducing environment around the IW (iron-wustite) buffer. In the SNC meteorites, iron is present as magnetite rather than metallic iron. These magnetites are igneous origin. The SiO_2 -fayalite-magnetite assemblage and the compositions of coexisting Fe-Ti oxides observed in shergottites suggest the formation of the meteorites near the QFM buffer. Nakhlites and Chassigny are also considered to have formed near the QFM buffer.

It is also important that hydrous minerals are present in the SNC meteorites along with the formation under an oxidizing condition. It has been reported that nakhlites have iddingsite or "rust" that was formed by aqueous alteration of olivines (*e.g.*, Gooding *et al.*, 1991; Treiman *et al.*, 1993). Other clay minerals such as hydrous Al silicates have been found in some SNC meteorites (*e.g.*, Gooding and Muenow, 1986). The SNC meteorites often contain magmatic inclusions in olivine and pyroxene crystals (*e.g.*, Treiman, 1985). These inclusions have been intensely studied in order to estimate parent magma composi-

tions of the SNC meteorites. Kaersutitic amphibole has been reported from such inclusions (*e.g.*, Treiman, 1985), suggesting that the SNC meteorites had crystallized from water-bearing magma at somewhat elevated pressure (> 1 kbar). Aqueously altered minerals have also been observed in carbonaceous chondrites. However, alteration in chondrites occurred early in solar system history, whereas altered minerals in SNC meteorites occurred very recently, at some time after their crystallization from magmas as recently as 180 Ma ago. The only planetary body other than Earth that is known to have supported water until recently is Mars.

These facts have made us a hypothesis that a parent body of SNC meteorites is Mars. The discovery of lunar meteorites in the 1980s further supports the martian origin hypothesis of SNC meteorites. Also, the heavily shocked nature of shergottites (*e.g.*, Stöffler *et al.*, 1986) is consistent with the idea that SNC meteorites escaped from the martian gravitation field.

The most definitive evidence comes from Mars exploration by robotic spacecraft. Although we have not yet brought back any martian rock samples from Mars, the Viking 2 probe landed on Mars in the late 1970s and analyzed its atmospheric composition. The isotopic compositions of noble gases of the martian atmosphere are indistinguishable from those of the trapped gas in the shock melt of EETA79001 (*e.g.*, Bogard and Johnson, 1983).

From many lines of evidence as described above, it is now widely accepted that SNC meteorites have originated on Mars.

Comparison of ALH84001 with other martian meteorites

We have examined the evidence for a martian origin of SNC meteorites. What are the differences between ALH84001 and SNC meteorites? One of the largest differences is in the petrography of ALH84001; it is an orthopyroxenite. The previous SNC meteorites had been divided into 3 groups, shergottites, nakhlites, and chassignite. Now we usually classify them into 5 groups based primarily upon their petrology and mineralogy (*e.g.*, McSween, 1994; Yanai, 1997): basaltic shergottites (basalts), lherzolitic shergottites (lherzolites/harzburgites), nakhlites (clinopyroxenites/wehrlites), chassignite (dunite), and ALH84001 (orthopyroxene). It has been proposed to call them "martian meteorites" rather than SNC meteorites (Mittlefehldt, 1994).

ALH84001 is mainly composed of cataclastic, coarse-grained (~ 1 cm) Mg-rich orthopyroxenes that are usually joined at 120° triple junctions, indicating slow cooling (*e.g.*, Mittlefehldt, 1994). Their chemical composition is relatively homogeneous ($\text{Wo}_3\text{En}_{69}\text{Fs}_{27}$). This is contrary to the fact that other martian meteorites usually contain chemically-zoned pyroxenes. Accessory phases are maskelynitized plagioclase, augite, apatite, carbonate, and pyrite. Euhedral chromite is poikilitically enclosed by orthopyroxene, and contains Fe^{3+} like other martian meteorites.

As described above, mineral assemblages of ALH84001 were difficult to distinguish from HED (howardite-eucrite-diogenite) meteorites that are the largest group of achondrite and are commonly believed to have originated on asteroid, 4 Vesta. In fact, because the texture and pyroxene composition of ALH84001 are very similar to those of a diogenite, ALH84001 was originally classified as a diogenite (MacPherson, 1985). However, minor

differences were apparent. Maskelynite is rarely observed from HED meteorites. Only 2 HED meteorites (ALHA81313 and Padvarninkai) contain maskelynites (McSween, 1985). The Na-rich nature of ALH84001 maskelynite (about $\sim\text{An}_{40}$) is also different in HED meteorites, whose anorthite content is typically around An_{90} . The presence of Fe^{3+} -bearing chromite is also very unusual for HED meteorites. Due to these curiosities, ALH84001 was re-examined (Mittlefehldt, 1994), and its oxygen isotope composition confirmed that it is a member of SNC meteorites as described above (Clayton, 1993).

Another major difference from other martian meteorites is that ALH84001 shows a remarkably old crystallization age of about 4.5 Ga (Jagoutz *et al.*, 1994; Nyquist *et al.* 1995). On the basis of textures, Treiman (1995) suggested that the history of ALH84001 must include: crystallization from magma, a first shock metamorphism (the igneous rock is cut by melt-breccia or cataclastic veinlets), thermal metamorphism (annealing the melt-breccia or cataclastic veinlets to their present granoblastic texture and permitting chemical homogenization of all mineral species present), low-temperature chemical alteration (carbonates and pyrite replaced plagioclase in both clasts and granular bands), and a second shock metamorphism (producing microfault offsets of minerals, radial fractures, and strain birefringence in pyroxene). Thus, ALH84001 has recorded a multiple impact history, suggesting it was formed on an old martian surface, probably Noachian age. As Noachian-age surfaces cover $\sim 40\%$ of Mars (Tanaka *et al.*, 1992), we might expect to have at least one sample derived from such an old region among 12 martian meteorites. Shock ages of this rock were also given by K-Ar or Ar-Ar methods; about 3-4 Ga (*e.g.*, Ash *et al.*, 1996). Wadhwa and Lugmair (1996) obtained a similar Rb-Sr isochron age of 3.84 ± 0.05 Ga. Grady *et al.* (1996) recently reported a much younger shock age of 0.76-1.28 Ga based on the K-Ar system. Many studies have been performed on cosmic-ray exposure ages of this meteorite. Results indicate that the exposure age is about 15 Ma (*e.g.*, Eugster, 1994). This exposure age is clearly longer than those of other martian meteorites. The shergottites cluster around 3 Ma, and the nakhlites and Chassigny around 10 Ma (Eugster *et al.*, 1996), suggesting that ALH84001 was ejected by a different event than the other samples.

The third difference between ALH84001 and other martian meteorites is presence of abundant carbonates, a most important feature in any consideration of biological evidence in this rock. Minute carbonate grains of up to 10 μm have been reported from basaltic shergottite EETA79001 (Gooding *et al.*, 1988); however, ALH84001 is the first martian meteorite that contains carbonate grains exceeding 100 μm . The carbonate in ALH84001 is magnesite-siderite-ankerite (*e.g.*, Mittlefehldt, 1994), while that in EETA79001 is calcite. Carbonate mineralogy is discussed in detail in the next chapter.

As discussed above, ALH84001 shows obvious differences from other martian meteorites. However, it has some common characteristics such as formation under an oxidizing and aqueous environment as observed in other SNC meteorites. It also includes pyrite as do nakhlites and Chassigny (*e.g.*, Gooding *et al.*, 1991; Treiman *et al.*, 1993). It is enriched in D, ^{15}N , ^{40}Ar , and ^{129}Xe as other martian meteorites (*e.g.*, Miura *et al.*, 1995; Leshin *et al.*, 1996), this enrichment characteristic of the martian atmosphere as measured by the Viking

spacecraft (*e.g.*, Marti *et al.*, 1995). Stable isotopic study of martian meteorites also indicates that the martian hydrosphere experienced only limited exchange with the lithosphere as $\delta^{18}\text{O}$ is in disequilibrium between igneous minerals and secondary hydrous phases (*e.g.*, Romaneck *et al.*, 1994a). But, the martian hydrosphere is isotopically in equilibrium with the atmosphere.

Especially, the presence of carbonates is important because it suggests that they are the major sink for CO_2 in the martian atmosphere rather than scapolite or hydrous carbonate. Carbonate also plays a significant role in providing information about the atmosphere and even possible biological activity on Mars.

Mineralogical features in the carbonate globules of ALH84001

Presence of carbonates

As described by many workers (*e.g.*, Mittlefehldt, 1994; Treiman, 1995), ALH84001 contains ~1 vol% of carbonates. The carbonates are globular in shape, and their size ranges from 1 to ~250 μm . The carbonate globules are present along fractures and in pore spaces. The carbon and oxygen isotopic compositions of carbonate globules suggest that they were formed on Mars and indigenous to the meteorite (Romaneck *et al.*, 1994a). Shock-faulted textures as seen in some carbonates also rule out a terrestrial origin. The carbonates are uniquely zoned in chemical composition from Fe-Ca-rich cores to nearly pure magnesite rims (*e.g.*, Harvey and McSween, 1996). McKay *et al.* (1996) also reported a complex zoning pattern of carbonates; the Ca-rich (also highest Mn) core is surrounded by alternating Fe- and Mg-rich bands, and several sharp thin bands are present near the edge of the globule. The first band is enriched in Fe and S, the second is enriched in Mg and is nearly Fe-free, and the third is again enriched in Fe and S. The presence of S was detected by electron microprobe in patchy areas throughout the globule (McKay *et al.*, 1996).

Two distinctive models have been proposed for the carbonate formation temperature. Romaneck *et al.* (1994b) measured oxygen isotope compositions of carbonates and proposed that carbonate precipitated from a low-temperature aqueous fluid of 0–80°C, suggesting that carbonates were perhaps formed in a near-surface hydrothermal system of the martian crust. $\delta^{13}\text{C}$ data of the carbonates also suggest a precipitation temperature below ~300°C (Sokki *et al.*, 1995). On the other hand, Mittlefehldt (1994) and Harvey and McSween (1996) propose formation of carbonates at a temperature higher than 650°C on the basis of the major-element composition of zoned carbonates, and suggested that carbonate formed by reactions between the high temperature, CO_2 -rich fluids and the ultramafic host rock during an impact event. Absence of hydrous phases in ALH84001 may support the high-temperature formation of carbonate. Harvey and McSween (1996) imply that O and C isotope relationships were not in equilibrium because of disturbance due to shock, whereas McKay *et al.* (1996) pointed out that if carbonate was of biogenic origin, its major element composition could not be used to determine formation temperature as Mittlefehldt (1994) and Har-

vey and McSween (1996) proposed.

The formation age of carbonate is also controversial. Knott *et al.* (1995) reported a preliminary ^{40}Ar - ^{39}Ar age of 3.6 Ga. As discussed in McSween (1996), Knott *et al.* (1995) might have measured ^{39}Ar release from maskelynite rather than carbonate. Wadhwa and Lugmair (1996) recently proposed a 1.39 ± 0.10 Ga Rb-Sr age for the carbonate, based on the assumption that all the Sr in carbonate was derived from maskelynite during the carbonate formation by partial replacement of the original plagioclase. The young carbonate age causes further discussion about possibility of life on Mars. There is no doubt that textures resembling microorganisms was present after the carbonate formation. If the 1.39 Ga age is correct, this is probably after the time when there was significant water on the martian surface, and therefore provides some difficulty for the biogenic interpretation of McKay *et al.* (1996). However, recently Pillinger *et al.* (1996) suggested that EETA79001 also indicates biogenic characteristics in the isotopes of carbon from carbonates, based on their earlier study (Wright *et al.*, 1989). The crystallization and cosmic-ray exposure ages of EETA79001 are estimated to be 180 Ma and 0.6 Ma, respectively, suggesting the possibility of present life on Mars (Pillinger *et al.*, 1996).

Magnetite-Fe sulfide-carbonate assemblage

McKay *et al.* (1996) interpreted that Fe sulfide (pyrrhotite and possibly greigite) could have formed by sulfur reduction by microorganisms. Coexistence of Fe sulfide with an oxidized phase (magnetite) may be explained by both organic and inorganic processes. Moreover, as Treiman (1996) pointed out, magnetite-iron sulfide could replace another mineral phase other than carbonates.

In some carbonaceous chondrites, especially in CI chondrites, magnetite-carbonate assemblages are often observed, and they are never considered to be of biological origin. Furthermore, organic materials are contained in these meteorites. Such minerals occur in CI chondrites in a variety of sizes and shapes, sometimes minute in size and rounded in shape (Tomeoka *et al.*, 1989; Kimura and Ikeda, 1992). So CI chondrites should also be examined in detail to compare with the results from ALH84001.

Conventional stability relations of magnetite, Fe sulfide and carbonate indicate that the aquatic environment for these minerals might be slightly alkaline and strongly reducing (Garrels and Christ, 1965). Under these conditions iron sulfides such as pyrite and pyrrhotite can coexist with magnetite. Ferrous iron carbonate, siderite, also has a stability field overlapping those for pyrite and magnetite. Partial pressures of gases for the formation of these minerals might be very low for oxygen and sulfur and high for CO_2 (Garrels and Christ, 1965). Consequently, these mineral assemblages can be explained by conventional aquatic geochemistry, although the pH-Eh-partial pressure fields for their coexistence are very restricted. However, it should be noted that these arguments are based on the earth's surface aquatic environment at 25°C and 1 atm total pressure. The real stability relations for ALH84001 should be discussed by redrawing these diagrams for the martian environment.

McKay *et al.* (1996) suggested a biogenic origin for the formation of these iron-con-

taining minerals by means of bacterial redox reactions. However, these minerals can be formed by redox reactions without any biological activities. For example, iron sulfides can be rapidly precipitated from low temperature aqueous solutions containing ferrous iron and sulfide anion without bacteria. In one study, amorphous framboids consisting of fine FeS grains of less than 1 μm were first formed and they transformed to crystalline pyrite after about 60 hours at 120°C (Saito *et al.*, 1995).

PAHs found in ALH84001 showed various degrees of dehydrogenation for their side aliphatic branches (McKay *et al.*, 1996). Some terrestrial organic materials such as humic substances (high molecular weight PAH polymers with aliphatic branches) have been experimentally known to dehydrogenate upon reduction of some heavy metals such as uranium at about 100-200°C. Uranium minerals precipitated from hexavalent uranyl aqueous ions have mixed valence states from U_3O_8 to UO_2 (Nakashima *et al.*, 1984; Nakashima, 1992a and b). On the other hand, the possible presence in ALH84001 of various valence states of iron and sulfur for sulfides ranging from mackinawite FeS_{1-x} , greigite (Fe_3S_4), smythite (Fe_3S_4) to pyrite (FeS_2) were suggested by McKay *et al.* (1996). Dehydrogenation of PAHs can then be linked to reductive formation of minerals having various degrees of reduction. Therefore, the coexistence of dehydrogenated PAHs, iron sulfides and magnetite can be explained readily by means of non-biogenic organic-inorganic interactions.

Biom mineralogical aspects

(i) Small magnetite grains in carbonates

McKay *et al.* (1996) observed magnetite grains in ALH84001 carbonates of ~10-100 nm in size. They suggest that they are similar to bacterially produced grains in chemistry, structure and morphology, although both possibilities of inorganic products and bacterial products are discussed. Magnetotactic bacteria which are believed to swim using magnetite as a magnetic sensor were found relatively recently in the Earth (Blakemore, 1975). They produce well-ordered magnetite grains which are called magnetosome (*e.g.*, Blakemore and Blakemore, 1991). In general, biomineralization processes can be classified into the following two types: "Biologically-Induced Mineralization (BIM)" in which the mineralization is a by-product of the organism's biological activity and "Biologically Controlled Mineralization (BCM)" in which minerals with strictly controlled forms and sizes are formed under biological action. Magnetite formation process in magnetotactic bacteria can be classified to BCM. They are mostly in magnetically single domain sizes (*ca.*, 30~150 nm) and are arranged in chain forms. Compositions are almost pure Fe_3O_4 . Three main morphological types of magnetosome magnetite are known: octahedral, hexagonal prism and tear-drop types (Fig. 1) (*e.g.*, Iida and Akai, 1996). Among them the tear-drop type is very characteristic in contrast with magnetite shapes of an inorganic origin. Well shaped tear-drop type grains can hardly be formed as primary grains in inorganic process, although secondary processes, for example, erosion, mechanical polishing, etc. may modify the original shape to some rounded shapes. In sedimentary environments, the tear-drop shape of magnetite grains and chain-like aggregates of magnetite grains may be conclusive indicators for a biogenic

FIG. 1. Schematic illustrations of three main types of magnetosomes (after Iida and Akai, 1996). (a) Octahedral type crystal (a1) and twinned crystals (a2). (b) Hexagonal prism type crystal. (c) Tear-drop type crystal.

origin (Fig. 2) (*e.g.*, Akai *et al.*, 1991; Iida and Akai, 1996). McKay *et al.* (1996) reported the presence of tear-drop shaped magnetite. However, it is not described in detail and its photograph does not appear in their paper, and so that we cannot give further discussion. Furthermore, chain-like aggregate patterns are not reported in the paper at all.

Search for terrestrial bacterial magnetite grains from sediments of the Western Pacific Ocean, the Japan Sea, fresh water sediments of Japanese lakes and ponds, are not always so easy (*e.g.*, Akai *et al.*, 1991; Sato *et al.*, 1993), because such sediments are composed of many detrital mineral fragments and clay minerals. Even within magnetic grains, bacterial magnetite cannot be easily identified in some cases. The occurrence of magnetite and pyrrhotite grains in the martian carbonate is very homogeneous and they do not accompany with the other mineral grains. In aquatic environments on the Earth, sedi-

mentary environments are not calm and often contain clay minerals.

Magnetotactic bacteria first appeared as the result of bacterial evolution around 2.0 Ga on the Earth (Chang *et al.*, 1989). If the formation age of carbonate containing the magnetite grains in ALH84001 is 3.6 Ga, how can these circumstances be interpreted? Pyrrhotite and greigite are formed by magnetotactic bacteria under sulfur-rich environments on the Earth.

Nanophase magnetite was absent from some of the carbonate globules that they examined as their preliminary study of ALH84001 (Thomas *et al.*, 1996), and magnetite was also

FIG. 2. Magnetofossils found from deep-sea sediments. Scale bar indicates 100 nm. (a) Tear-drop type magnetite grains found in deep-sea sediments from the Japan Sea. (b) and (c) Stereopair EM images of magnetofossils found in deep-sea sediments from Western Pacific Ocean. Chain-like aggregates of octahedral type magnetofossils (b) and hexagonal prism type (c).

present within orthopyroxene, clearly indicating a non-biologic origin as observed in other martian meteorites. The shape of magnetite is sometimes inconclusive for determining its origin because it can be deformed or altered by secondary processes.

Summarizing all these data reported in McKay *et al.* (1996), it is difficult to suggest that the magnetite and pyrrhotite grains in ALH84001 are of magnetotactic bacterial origin. In addition, magnetite grains would be useless to a martian bacterium because Mars has hardly any magnetic fields at least now (*e.g.*, Luhmann *et al.*, 1992). Additional study of more martian samples is necessary to ascertain the origin of these magnetite and pyrrhotite grains: biogenic or inorganic. The best way would be to examine materials obtained by direct sampling on Mars.

(ii) *Microfossil-like structure in carbonates*

McKay *et al.* (1996) suggest that the high-resolution scanning electron microscope (SEM) images taken by a field emission SEM (Fig. 6 of their paper) show microfossils of bacteria. The study of bacteria in terrestrial rocks and sediments has been extensively investigated for the last two decades, and they have found that terrestrial samples even from extreme environments on the Earth contain bacteria. Bacteria are typically ~1,000 nm, while Folk (1993) proposed presence of “nannobacteria” that range from 20 to 200 nm in size. Although it is very difficult to identify nannobacteria because the size of the organism is extremely small, and X-ray analysis is nearly impossible due to its small size, Folk (1993) proposed 5 criteria to substantiate a bacterial presence; (1) Clusters of bodies separated by large unpopulated area, (2) Bodies with same sizes as living bacteria, including nannobacteria. Populations within a sample same as those of living bacteria, (3) Bodies in a similar shape to living bacteria: smooth to somewhat lumpy surfaces with shapes of cocci, ellipses, bacilli, or long filaments. The bacteria can appear as chains of spheres or rods, (4) Bodies do not contain Fe, but may have Ca or Si, (5) Bodies must not be confused with minerals or artifacts. In the light of these 5 criteria, it seems that the tubular and ovoid shapes in ALH84001 carbonate match the criteria of (2), (3), and (5). Colonial presence of ovoid structures are also reported and matches the criterion (1). However, it is not clear whether tubular structures of ALH84001 carbonate applies to the criterion (4), because chemical analysis of the ovoid and tubular structures have not been performed. Furthermore, this criterion is not appropriate, because Folk (1993) does not take magnetosome into his consideration. Other criteria can also be considered. For example, Takasu and Tazaki (1994) observed the compaction of aggregates of ovoid structures in terrestrial rocks that resemble the aligned ovoid structures in ALH84001 (Fig. 3). This compaction produced textures that are very similar to textures in the matrix of ALH84001. It is reported that apatite is associated with carbonates in ALH84001. Apatite is one of the most important biogenic materials. However, it is not clear whether this is a biogenic material, because apatite from an igneous origin is often observed in mesostasis areas of shergottites (*e.g.*, McCoy *et al.*, 1992).

It is very difficult to distinguish between biological or non-biological origin only from their shapes. In the 1960s, there was an argument concerning “microfossil-like” structures

FIG. 3. Scanning electron micrograph of graphite in the metamorphic rock sample from Sri Lanka, showing small spheres on the granular surface (after Tazaki, 1994).

observed in carbonaceous chondrite, and it was concluded that they were of non-biological origin (Nagy, 1975). Furthermore, the small size of “nanobacteria” has also been controversial. The structures that resemble bacteria are hundred times smaller than ancient bacteria on the Earth as pointed out by many researchers (*e.g.*, Treiman, 1996). It is necessary to find a cell structure in order to conclude these objects as microfossil by plucking the “microfossil” off the surface of the carbonate.

Summary

As discussed above, there is little doubt that ALH84001 is from Mars as well as eleven other SNC meteorites. It is almost certain that the carbonate globules and microscopic magnetite-iron sulfide grains were formed in Mars (it should be noted that the formation age of the carbonate globule is not clear, 3.6 Ga or 1.39 Ga). However, the mineralogical and biomineralogical evidence for martian bacteria given by McKay *et al.* (1996) is controversial, and could be formed by non-biogenic processes. Carbonate globules can be formed by reaction between CO₂-rich fluid and the ultramafic host rock at high temperatures (Harvey and McSween, 1996). Precipitation of magnetite and iron sulfide with dissolution of carbonates could be possible by a non-biogenic process, and coexistence of dehydrogenated PAHs, iron sulfides and magnetite can be explained by a non-biogenic organic-inorganic interaction as already discussed. The single-domain magnetites do not have distinct features that terrestrial magnetosomes possess. Moreover, inorganic processes can sometimes produce elliptical and tubular structures that resemble bacteria (Treiman, 1996) although the shapes are not inconsistent with the criteria for microbacterial presence of Folk (1993).

It is significant that ALH84001 contains the organic materials because any organic materials have not been detected from lunar and other martian meteorites so far (we cannot comment organic materials found in EETA79001 by Pillinger *et al.* (1996) here because of the lack of information). However, again, PAHs can be formed by inorganic processes as seen in carbonaceous chondrites. McKay *et al.* (1996) mentioned that mass distribution of PAHs observed in ALH84001 is similar to that in CM2 carbonaceous chondrites although

some details are different. Furthermore, the higher values of the carbon isotopic composition of ALH84001 are similar to those of CM2 carbonaceous chondrites (Grady *et al.*, 1988) although the sources of carbon might be different. Is there any possibility that PAHs found in ALH84001 was originally from CM2 or CM2-like carbonaceous chondrites that had hit on the martian surface? It should be noted that magnetite-carbonate assemblage is usually observed in carbonaceous chondrites. There are also many controversial problems from the biological viewpoint; any metabolic products intrinsic for life have not been found (Murae, 1996), and only a few kinds of creatures can produce magnetite and iron sulfide by metabolism (Kawasaki, personal communication).

In this review, criticism against martian life was lined up. Many problems are present. However, we cannot deny the possibility of martian life as well. We cannot say yes or no with 100% of certainty on this issue at present. Individual researchers may be located somewhere in this wide spectrum of opinion between yes and no. The work by McKay *et al.* (1996) should rather be recognized as a new starting point in searching for extraterrestrial life in the solar system.

As for further mineralogical investigations, besides detailed observation of minerals for their textures and chemistry, many experimental studies are needed for clarifying roles of non-biogenic organic-inorganic interactions for mineral formation. Precipitation experiments of fine-grained carbonates and iron sulfides in the presence of organic compounds without biological activities should be conducted under conditions similar to the martian environment in order to compare their textures and chemistry with those formed under biological conditions.

Further exploration in connection with martian life is divided into two categories; one is exploration of new martian meteorites in Antarctica, and the other is exploration by mission to Mars. There might be no more candidates for martian meteorites among the meteorites already in hand, because interesting meteorites have been re-examined. National Institute of Polar Research (NIPR) of Japan has a project to search for meteorites in Antarctica in 1998 and 1999. However, it should be noted that only about 10 out of 10,000 meteorites (about 0.1%) are from Mars. There are several mission projects to Mars being planned, including a Japanese project (Table 2). Sample return should be critical to the present problem if a human mission is not realistic at the present stage. Institute of Space and Astronautical Science (ISAS) of Japan is now going to have a sample return mission to an asteroid (MUSES-C). Japan is also considering sample return exploration for Mars. However, it should be noted that we do not have any good curation system in Japan, both facilities and the system itself, available for such returned samples. For example, there are no curation facilities for returned samples, where the samples are stored and processed under a clean environment to avoid contamination with both organic and inorganic materials, described mineralogically, petrologically and geochemically, and distributed systematically for further research. High-tech analytical instruments under smoothly running conditions are not set up sufficiently in research institutes of earth and planetary sciences in Japan for further study (*e.g.*, we cannot determine three oxygen isotope compositions precisely). Moreover, a further problem for us

TABLE 2. Ongoing and future missions to Mars.

Mission name	Launch	Nationality	Note
Mars Global Surveyor	Nov. 6, 1996	USA	5 observational apparatuses of Mars Observer
Mars 96	Nov. 11, 1996	Russia	Failed
Mars Pathfinder	Dec. 2, 1996	USA	Lander and micro-rover
Planet B	Summer, 1998	Japan	Analysis of interaction of solar wind with martian atmosphere
Mars Surveyor 98	Dec., 1998	USA	Orbiter
Mars Surveyor 98-2	Jan. 4, 1999	USA	Lander on polar region, micro-penetrator
Mars 01	2001	Russia	
	2001	USA	Orbiter
	2005	USA	Sample return mission

is a lack of smoothly running curation system itself. The only Japanese curation system working officially is that for meteorites in NIPR. However, their system is not ideal due to lack of both money and understanding of its importance by many other scientists. Our community should start to think about such a curation system and analytical facilities immediately and seriously in cooperation with other communities, such as planetary science, geochemistry, geophysics and astronomy, especially about curation of samples.

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