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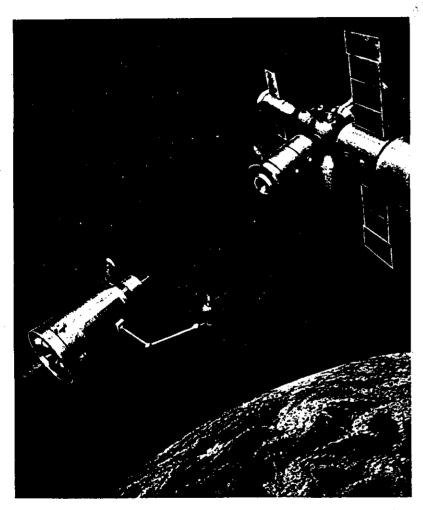
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COLLEGE ON SOIL PHYSICS 9 - 27 October 1989

"Magnetic Soils on Earth and Mars"

Jens M. KNUDSEN
Physics Laboratory
University of Copenhagen
Copenhagen
Denmark

Please note: These are preliminary notes intended for internal distribution only.



From: The USSR in Outer Space.

Docking with the orbital station in terrestrial orbit of the reusable craft bringing samples of Martian soil

Abstract

The main objective of the seminar will be to discuss the soils on Mars, with emphasis on their magnetic properties.

As a background for the study of iron compounds in the martian surface fines a brief introduction to the history of the element iron in the solar system will be given.

To appreciate the significance of terrestrial soil science for the study of Mars, the magnetic properties of some terrestrial soils will be discussed.

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1. Introductory Remarks

During the International Space Research (COSPAR) meeting in Helsinki in July 1988 it was announced that it is under consideration to accommodate a Mössbauer spectrometer on board a rover to be placed on Mars in the Sovjet missions to the planet in the coming decade. The purpose should be to study the distribution of the element iron in the soils and rocks of Mars.

Also in connection with the American planetary program, it has been suggested to construct a Mössbauer spectrometer to be landed on Mars, and a construction of the spectrometer is under way.

Besides there are plans for bringing samples back from Mars to a Space Station, where the samples will be kept for some time, and where they may be studied by various techniques, among these probably Mössbauer spectrometry, Electron Spin Resonance, and Magnetic Susceptibility.

By means of such techniques the magnetic – and other properties – of the iron containing minerals on the planet may be determined.

Thus there is strong motivation for investigating what might be learned about the evolution of Mars by the study of the element iron on the surface of the planet.

In this seminar we shall be especially interested in the socalled martian soils. (Perhaps it would have been better to stick to the name the martian fines — however, the name martian soils is widely used).

To understand the significance of the study of these distant soils it is necessary to have a rudimentary insight into the ideas about the formation of the planets, and some knowledge of meteorites.

The talk therefore starts with a brief introduction to the origin of the Solar System.

2. Formation of the solar system

2.1 Gravitational collapse of an interstellar cloud.

It is generally accepted that our Sun — as any other star — formed from the gravitational collapse of an interstellar cloud containing gas and dust grains. The interstellar clouds participate in the rotation of the Milky Way, and thus the clouds possess an angular momentum. Owing to the conservation of its angular momentum the cloud rotated more rapidly as it collapsed. The whole process resulted in a system consisting of a dense, gaseous body in the center (a protostar) surrounded by a

flattened disk of gas and dust grains. See figure 2.1. These events took place 4.6×10^9 years ago.

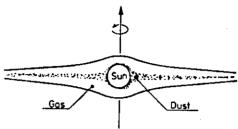


Fig. 2.1. Sketch showing the primordial nebula of gas and dust surrounding the newborn sun. The planets and the meteorites formed by condensation in the dusty nebula.

The disk was evidently formed because the gravitational contraction perpendicular to the angular momentum vector of the cloud was halted by the balance of gravitational and centrifugal forces in the co-rotating reference frame. As the cloud, during contraction, grew denser, some gas condensed into grains, thus adding new grains to the possibly surviving interstellar grains. The grains were pulled to the central plane by the uncompensated component of the gravitational field of the protostar, i.e. the component of the field parallel to the axis of rotation. The dust grains ultimately formed a rather thin disk.

The protostar in the center evolved into our Sun, while the solid bodies in the solar system, i.e. planets, moons and asteroids, accreted in the disk. The processes by which the grains formed and accumulated into larger solid bodies are not known in detail, but are vigourously studied. (1-3).

The planetary orbits all lie nearly in the same plane, i.e. the plane of the original disk. The planets all move in the same direction around the Sun. The structure of the present solar system thus bears wittness to the process of birth.

The disk of gas and dust surrounding the newborn Sun is called the primordial solar nebula, or simply the solar nebula.

Disk shaped, and grain containing, nebulae around young stars have now been observed. See figure 2.2.

The picture shows the star β -pictories, which may be observed from the southern hemisphere. The picture – recorded at 890 nm – shows a flattened disk of dust grains stretching out from the star to a distance of 400 AU. The light detected by the telescope is starlight from β -pictories reflected off the small dust grains in the disk.

For the first time we can here study the birth of a planetary system directly. Indirectly and often in substantial detail we can investigate the process of birth and evolution of planets through the study of meteorites.

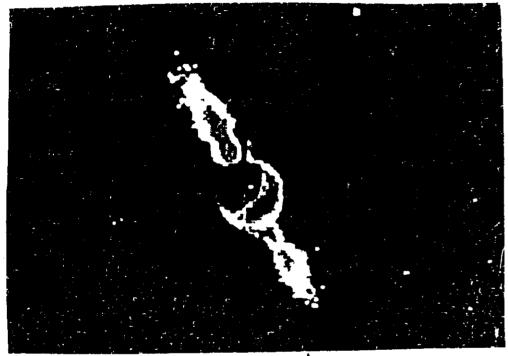


Fig. 2.2. A disk of dust grains surrounding the star β -pictories. The disk, seen nearly edge on, stretches about 400 A.U. out from the star. The picture was taken by Bradford A. Smith (University of Arizone) and Richard J. Terrile (Jet Propulsion Laboratory, Pasadena) at the 2.5 m telescope in Chile. I A.U. = The mean distance of the Earth from the Sun, 149.5 x 10^6 km.

The meteorites are rocks and metal-pieces from interplanetary space that have reached the Earth by chance, captured by the gravitational field of the planet. Most meteorites are believed to come from the belt of asteroids between Mars and Jupiter.

A typical velocity at which meteorites cross the terrestrial atmosphere is 10 km/s. During the less than 1 minute flight through the denser part of the atmosphere, the surface layer of the meteorite is, so to speak, planed off, and the melted particles are scattered over a large area. What we call a meteorite is the entering body that survives the flight and lands on the Earth. Except for a surface layer of a depth of – at

the most -1 cm, the meteorite has not been harmed thermally. The internal part of the meteorite is in the same state, as it was in space. Our precious research material is saved by the fact that the time scale of the conduction of heat is long, compared to the time the meteorite needs to pass through the atmosphere.

From the point of view of the study of the evolution of matter outside the stars, meteorites are unique samples. On the cosmic evolutionary scale they are placed somewhere between interstellar dust clouds and planets.

The chemistry of iron in Cosmos — and for that matter on the Earth — is strongly coupled to the chemistry of abundant elements like hydrogen, carbon, oxygen, and sulphur. Essentially, it is this coupling of chemical cycles of abundant elements that gives us the possibility of understanding some features of the chemical evolution of matter, by a study of the history of the element iron. The element iron is also relevant for the understanding of some aspects of the birth and evolution of planets.

We shall see that the magnetic properties of the soils on Mars are significant for the understanding of the evolution of the surface of the planet.

2.2. Condensation Sequence in the Solar Nebula.

By means of calculations based on thermodynamics it has been possible to establish the sequence in which different minerals formed in the cooling solar nebula (4-5). The results obtained may be compared with the analysis of the various classes of meteorites in an attempt to find the conditions in the solar nebula at the time of the formation of the meteorites.

We shall here limit ourselves to give a brief description of the results of the calculations of the condensation sequence in a gas of solar composition.

CLUIC#	ARGINANCE	Log _{ie} (Allumbants)
	2.66 a 10 ¹⁶	19.425
No	1.6 a 16 ⁹	1.215
•	1.86 # 10 ⁷	7.341
e	1.16 o 16 ³	7.845
-	2.6 m 10 ⁶	4.411
	8.35 m 18 ⁶	4.364
***	1.00 m 10 ⁸	6.628
64	1.00 x 10 ⁶	6.001
Pa .	918 H 18 ⁸	1.014
	5/8 at 28 ⁸	1.41)
Ar	1.06 s to ⁶	1.635
AL	8.3 a to ⁶	4.835
Ca	6.35 a 16 ⁶	1,716
M-	8.6 a 16 ⁶	0,778
4	4-70 A 10 ⁶	4.479

Table 2.1. Cosmic abundances of the 15 most abundant elements in atoms per 10⁶ atoms Si [adapted from A.W. Cameron, after ref.6]

Take a gram of the material of the Sun; more than 99.9% of its weight is due to the 15 most abundant elements. See table 2.1.

Note: For a heavy metal, iron has a very high abundance. This is due to the fact that of all nuclei ⁵⁶Fe has the highest binding energy per nucleon.

The main results of the thermochemical calculations are summarized in figure 2.3

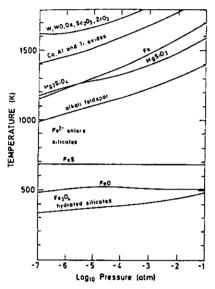


Fig. 2.3.

Stability limits for some condensates in the primitive solar nebula. The Fe—curve shows the temperature under which metallic iron—nickel is stable. At temperatures below about 800 K the metallic iron is oxidized to Fe²⁺ by water vapour, and the oxidized iron enters the magnesium silicates Mg₂SiO₄ and MgSiO₃. Solid solutions, [MgFe]₂SiO₄ (olivine) and [Mg,Fe]SiO₃ (pyroxene) are thus formed. This process stops at about 500 K, shown by the curve marked FeO. At lower temperatures magnetite (Fe₃O₄) and iron containing hydrosilicates are formed. Adapted from ref.7.

Due to low pressures ($\approx 10^{-4} atm$) the condensation in the solar nebula took place directly from the gaseous phase to solids. The sequence of condensation is nearly independent of pressure.

In the high–temperature range, $T>1000~\mathrm{K},$ we distinguish three groups of condensates:

around 1600 K some highly refractory compounds like oxides of Ca, Al, and Ti condense,

at approximately 1400 K metallic iron appears, carrying with it the less abundant transition metal nickel, and

below 1400 K the magnesium silicates Mg2SiO4 and MgSiO3 appear.

In the medium-temperature range, 1000 K>T>500 K, important reactions take place. The gases remaining at such temperatures are dominated by the elements H,C,O, and S. These elements control the fate of the iron. The details are rather involved, but the essentials are as follows:

Below about 900 K carbonmonoxide starts to react with hydrogen to form water (steam):

$$CO + 3H_2 \neq CH_4 + H_2O$$

The water vapour formed in this process oxidizes the metallic iron to Fe²⁺, which somehow enters the magnesium silicates. A bulk reaction scheme could be the following:

$$MgSiO_3 + Fe + H_2O \neq [Mg,Fe]_2SiO_4 + H_2$$

The thermodynamical constants (Gibbs free energy) have such values that both reactions mentioned proceed towards the right, as the temperature decreases. The conversion of CO into CH₄ and water increases the ratio $\rm H_2O/H_2$ in the solar nebula, thus promoting the oxidation of iron in the second process. At about 900 K oxidized iron (Fe²⁺) begins to enter the magnesium silicates, to form the minerals olivine [(Mg,Fe) $\rm 2SiO_4$] and pyroxene [(Mg,Fe)SiO₃]. As the temperature decreases the amount of iron in the silicates increases. The details of the incorporation of iron into olivine and pyroxene is not known. In many meteorites the iron in olivine and pyroxene grains seems to be inhomogenously distributed.

While the iron does not form oxides at higher temperatures, this becomes possible when the temperature drops below 400 K. At such temperatures the oxidation of iron in the nebula is controlled by the chemical reaction:

$$3\text{Fe} + 4\text{H}_2\text{O} \neq \text{Fc}_3\text{O}_4 + 4\text{H}_4$$

This equilibrium is determined by the relative abundance of H₂O and H₂ in the solar nebula. In the low temperature range iron is also oxidized by H₂S to FeS (troilite), which is a widespread mineral in meteorites.

According to the condensation sequence the iron thus appears in the oxidation state 3+ below about 400 K. This oxidized iron should be found in the mineral magnetite, and also in hydrosilicates (clay-like compounds).

3. Meteorites

The classified meteorites are divided into three main groups:

Stones, 92.8% of observed falls Irons, 5.7% of observed falls Stony-irons, 1.5% of observed falls

Stony meteorites are subdivided into three groups

chondrites carbonaceous chondrites achondrites.

Below follows a brief description of meteorites. For more detailed information see f.inst. references 8-14.

3.1 Chondrites

The meteorites called chondrites are the least altered samples we know of the material which evolved into our solar system. The chondrites are stony meteorites that owe their name to the fact that they generally contain chondrules (from Greek: khondros = small grain). Chondrules are rounded or subrounded grains, which appear to have been molten droplets of rocks that solidified rapidly. See figure 3.1. Chondrules are often composed of olivine ([Mg,Fe]2SiO₄) and pyroxene ([Mg,Fe]SiO₃) in varying proportions. The material outside the chondrules is called the matrix of the meteorites.

Generally the chondrites are rather reduced. Most of them contain reduced iron in the form of inclusions of metallic iron-nickel alloys. No Fe³⁺ is found in ordinary chondrites, and no volatile elements. The ordinary chondrites are medium temperature condensates.

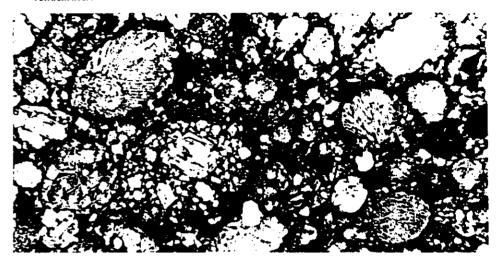


Fig. 3.1. The surface of a thin slice of a meteorite of the class called chondrites. Note the more or less round (spherical) inclusions called chondrules. The width of the picture is 8 mm.

The most primitive, i.e. the best preserved, among the chondrites belong to the group called carbonaceous chondrites (CC). These meteorites probably accumulated in the solar nebula at low temperatures, around 350 K. After the accumulation, the processes causing differentiation (melting, interdiffusion, chemical reactions) have been very gentle.

The carbonaceous chondrites contain low temperature consensates, including water and carbon compounds (organic molecules including aminoacids). The carbonaceous chondrites are highly oxidized, and Fe³⁺ is found in minerals like magnetite and hydrosilicates. Also ferrihydrite is present [15–17].

Perhaps the two small martian moons, Phobos and Deimos, are composed of carbonaceous chondrite material.

3.2. Achondrites

It is generally believed that the meteorites called achondrites are fragments of asteroids that were shattered by collisions. See figure 3.2.

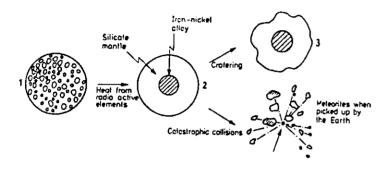


Fig. 3.2. Evolution from asteroid to meteorite.

- 1. Newly formed asteroid
- Asteroid separated in iron—nickel core and silicate mantle due to heating.
- 3. Asteroid partly or completely destroyed by collisions with other bodies.

Soon after forming, some of the asteroids were melted, probably by short-lived radioactive isotopes (e.g. ^{26}Al , $T_{1/2}\approx 0.7\times 10^6$ years). After the melting, the heavy iron-nickel alloys were drawn to the center by gravity, forming the core of the small planet, while the lighter silicate materials floated to form the mantle.

After the short-lived isotopes had decayed, the asteroid started to cool. Due to the low thermal conductivity of the silicate rocks, the metal core cooled very slowly, probably with a cooling rate of the order of magnitude $1 \text{K}/10^5$ years.

Later in its history the solidified asteroid collided with other planetoids. The socalled iron meteorites are believed to be pieces of the core of an asteroid, while the stony meteorites called achondrites come from the mantle of the small planet.

We shall here be mainly interested in the achondrites and we proceed to give a brief description of these for the study of Mars so important class of meteorites.

The Class of the Achondrites.

Achondrites are mineralogically and chemically similar to the terrestrial igneous rocks called basalts. The term achondrite refers to the absence of chondrules in these meteorites. There are seven main groups of achondrites:

basaltic achondrites (eucrites, diogenites, howardites) shergottites nakhlites chassignites enstatite achondrites ureilites angrite.

The groups of shergottites, nakhlites and chassignites are collectively known as the SNC achondrites. These SNC-meteorites are especially interesting from our point of view because they are believed to come from the planet Mars. [18-21].

Terrestrial Basalts, Basaltic Achondrites and SNC Achondrites.

Basalts are igneous rocks which solidify from molten samples (magmas) of the upper mantle of the Earth.

Basalts consist mostly of plagioclase (mixing of approximately equal amount of calcic and sodic feldspars, $CaAl_2Si_2O_8 + NaAlSi_3O_8$) and pyroxenes (augite, $Ca[Mg,Fe]Si_2O_6$). As minor components, terrestrial basalts contain small amounts of iron-titanium oxides as ilmenite (FeTiO₃) and the so-called titanomagnetite (Fe_{3-x}Ti_xO₄, a solid solution of the end members Fe₃O₄ and Fe₂TiO₄).

We shall not go into details of the rather complicated processes of magma crystallization, but the presence of Fe-Ti oxides in terrestrial basalts is an important factor in evaluating the oxidizing conditions under which the igneous rocks solidified.

Pyroxenes from terrestrial basalts usually contain iron in the oxidation state $III+(Fe^{3*})$.

Basaltic Achondrites (Eucrites, Diogenites and Howardites)

Basaltic achondrites are igneous rocks which crystallized $\sim 4.5 \times 10^9$ years ago. The basaltic achondrites known as eucrites are chemically and mineralogically similar to terrestrial basalts. There are, however, some essential differences. The pyroxene in eucrites is mainly pigeonite (a ferromagnesian pyroxene with a small amount of

calcium), whereas the dominant pyroxene in terrestrial basalts is augite (see above), a Ca-rich pyroxene. Eucrites are depleted in alkali volatiles (compared with terrestrial basalts), so that their plagioclase is almost pure anorthite, CaAl₂Si₂O₈.

The absence of titanomagnetite in eucrites shows that these meteorites formed under less oxidizing conditions than did the terrestrial basalts. This fact is confirmed by the presence of metallic grains of iron in some eucrites.

We have previously shown that there seems to be no Fe³⁺ in the pyroxenes from eucrites, confirming their reduced state compared with terrestrial basalts.

Diogenites are brecciated achondrites of basaltic origin, consisting of nearly pure orthopyroxene $[Mg_xFe_{1-x}]SiO_3$, with typical $x \sim 0.75$). Despite this apparently simple mineralogical composition, diogenites are believed to be metamorphosed samples of a magma similar to that where eucrites came from.

Howardites appear to be essentially mixtures of eucritic and diogenitic fragments.

SNC Achondrites.

SNC achondrites (Shergottites, Nakhlites and Chassignites) form a rare group of the achondrites. In several aspects SNC achondrites are close to terrestrial basalts. Referring to shergottites and terrestrial basalts, McSween and Stolper [22] stated that they 'are so similar in composition and mineralogy that it is difficult to conceive that the shergottites could have originated elsewhere in the solar system'. The oxidation state of SNC meteorites as well as the presence of hydrous minerals (in nakhlites and chassignites, table 3.1) are consistent with an origin on the Earth. But there are some strong reasons for rejection this hypothesis, especially, the systematic differences in oxygen isotopic ratios between terrestrial basalts and SNC achondrites. A minor difference in mineralogy is the presence of maskelinite (in shergottites), a shock—produced, high pressure form of plagioclase.

	Ewe Filed	Sherwort free	<u> </u>	
Systellization ago	4.4 × 10° years		.3 = 10 ⁹ years —	
motions these	pigognite + sugiti	pigoomite-cugito	angito	elirine
Taidages composition	A34-18	A#44-48	8434 + 01.31	4416-17 * OF 21
midetion atore	free motel		- TI emidee —	
lydrous phases			1 dd ingal to	haerputita
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	EFTA 79886	ALMA 77608	Gaveraster	
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Table 3.1 Comparison of Eucrites and SNC Achondrites (adapted from WOOD and ASHWAL, 23).

Table 3.1 summarizes some important features of the SNC achondrites and (for comparison) the basaltic meteorites (eucrites). Concerning the feldspar composition, SNC meteorites reveal a high content of alkali volatiles (Na and K) relative to eucrites. Eucrites are water—free whereas SNC contain some hydrous minerals. SNC achondrites are rather oxidized compared with eucrites.

The most striking difference between SNC meteorites and eucrites is perhaps the age difference. Eucrites (as most of the meteorites) date from the beginning of the solar system, i.e. they crystallized about 4.5×10^9 years ago, whereas SNC achondrites crystallized about 10^9 years ago. This fact implies that, unlike the eucrites, SNC achondrites seem not to have originated in an asteroidal body. Asteroids are not big enough to sustain igneous activity $\sim 3.5 \times 10^9$ years after their formation.

Taken together, the content of volatiles (alkali and water), the high oxidation state and the crystallazation age, indicate that SNC achondrites are pieces of the mantle of a planet—sized body.

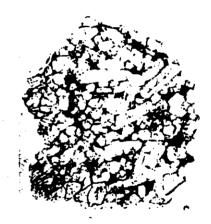


Fig. 3.3. Photomicrograph of Governador Valadares. Most of the grains are pyroxenes (augite). Note that the grains display a preferred direction. Width = 3 mm. From ref. 24.

The subgroup of the SNC-meteorites called Nakhlites are what the geologists call cummulates:

Let us imagine a molten magma cooling slowly. The cooling occurs at the top, thus causing crystals to form there. These crystals sink to the bottom of the molten rock, where they accumulate. A good example is the brazilian meteorite, Governador Valadares, which is classified as a Nakhlite. Figure 3.3 shows a photomicrograph of a slice of Governador Valadares. Most of the grains are augite [Ca-rich pyroxene]. The

prismatic grains show a preferred orientation caused by the settling of crystals in a gravitational field.

The SNC-meteorites seem to have formed by volcanic activity on a body large enough to sustain igneous activity relatively late in solar system history.

For the time being the planet Mars is assumed to be the mother body of the SNC-meteorites. Plausible models for how it is possible to accelerate the rocks to martian escape velocity [5 km/s] without creating marks of strong shocks have been presented in the literature [25,26].

For a description of the SNC-meteorite association and its possible relation to the planet Mars one may consult the following issue of Geochimica and Cosmochimica Acta: Vol 50, no 6, 1986. [27].

The groups of SNC-meteorites consist of 4 Shergottites, 3 Nakhlites and Chassigny. Table 3.2 below show dates of fall (or find), location and the actual recovered mass of the SNC-meteorites.

Meteorite	7,94	Fall Date	incaling	Original Mass (Eg)
Shermotty	5	August 25, 1955	India	5.0
	ŝ	October 3, 1962	Nigeria	23
Zagom1 ALNA 77005	Š	Find - 1977	Anterchica	0.48*
EETA 79001	s	Find - 1979	Amterctice	7.9*
Nakh)a		June 29, 1911	Egypt	40
Lafayette	i	Find - 1932	Indiana, U.S.A.	0.40*
Gavernador Valedares	N	Find - 1958	#razil	0.16*
Chassigny	c	October 3, 1815	France	4.0

Table 3.2 SNC meteorites. From J.C. Laul in ref. 27.

4. Iron in the Planets

The planets were somehow assembled from dust grains in the primitive nebula that surrounded the newborn sun.

According to the generally accepted theory of condensation and accretion in the solar nebula, the farther away from the Sun a planet formed, the more oxidized its iron should be. Thus according to theory the amount of oxidized iron is higher in Mars than it is in the Earth.

An interesting comparison of the formation and composition of the Earth and Mars has been given by G. Dreibus and H. Wänke [28]. These authors consider two components of solar system material: The volatile-free and reduced component A which formed at or inside the orbit of the Earth, and the volatile-containing and more oxidized component B which formed farther out. Component A is similar to the chondrites and component B is similar to carbonaceous chondrites. Component B contains Fe³⁺ in magnetite, ferrihydrite and in other compounds. Mars is thought to have accreted both components in roughly equal amounts, while in the case of the Earth the material of component B was added only during a late phase of the accretion of the planet, and in a smaller proportion. The mantle of Mars should thus be more oxidized than the mantle of the Earth.

From the moment of inertia of Mars, it has been inferred that the mantle of the planet has a density of 3.55 gcm⁻³ while the density of the mantle of the Earth is 3.3-3.4 gcm⁻³. The difference is probably due to a high content of the element iron in the rocks of Mars.

Iron thus plays a rather fundamental role in the study of the formation, and, as we shall see, in the study of the evolution of the planets.

5. Mossbauer Spectroscopy of SNC-meteorites.

We have previously shown that the pyroxenes from ordinary achondrites (i.e. meteorites coming from broken asteroids) do not contain Fe³⁺, a result which is in accordance with their rather reduced state [29].

In the meteorite Nakhla, believed to come from Mars, the pyroxenes contain some Fe^{3+} . See figure 5.1.

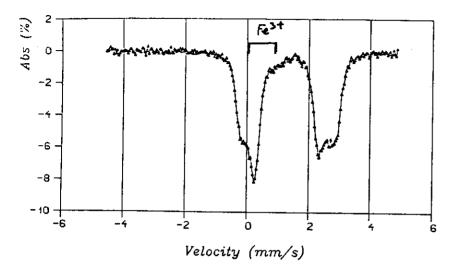


Fig. 5.1. Mossbauer spectrum of pyroxenes separated from the meteorite Nakhla. Liquid nitrogen temperature. Note the presence of Fe³⁺. Nakhla is the only achondritic meteorite, where Fe³⁺ has been detected in the pyroxenes.

The composition of the pyroxenes in Nakhla is approximately $[Ca_{0.39}Mg_{0.38}Fe_{0.23}]SiO_3$ (augite). The presence of Fe³⁺ in these pyroxenes indicates that the meteorite originated in a rather oxidized magma.

We have furthermore separated the magnetic grains from Zagami (a shergottite) and from Nakhla (a nakhlite), and Fig. 5.2 shown the Mössbauer spectra of these magnetic separates.

The spectrum in Fig. 5.2 demonstrates the presence of magnetite in Nakhla. Line two from the left – i.e. the first line in the B-sextet – is broad, implicating an impurity. This impurity is probably titanium. Elemental composition analysis of the magnetic grains shows 12% of Ti (ilmenite, FeTiO₃, accounts for part of the titanium, but some is probably left for the magnetite). Nakhla is the only achondrite in which the presence of (titano)magnetite has been demonstrated by means of Mössbauer spectroscopy. The amount of titanomagnetite in Nakhla has been estimated to about 2%. This result also shows that the meteorite Nakhla originated in a rather oxidized parent body

(Mars). With its content of titanomagnetite the meteorite Nakhla becomes rather similar to terrestrial basaltic rocks.

For the time being we have access to only about 1 g of the meteorite Zagami. In this sample we have not been able to find any (titano)magnetite. The magnetic fraction in our sample of Zagami seems to be an iron sulphide (pyrrhotite, Fe_{1-x}S). [30].

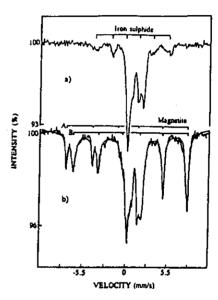


Fig. 5.2. Room temperature Mossbauer spectra of the magnetic fractions of a) Zagami and b) Nakhla.

6. The Viking Missions

In the Viking missions (1976) two chemical laboratories were successfully landed on the planet Mars. The Viking landers analyzed the elemental composition of the martian soil by means of X-ray fluorescence. The two landing sites (~ 2000 km apart) yielded very similar results of the elemental analysis of the fine-particle material: silicon and iron in large amounts, followed by magnesium, aluminum and calcium in significant amounts. Rather surprisingly sulphur was also found in substantial quantity.

	Sample 1 Wi%	Sample 2 Wife	Shergotty W(%
SiO2	44.7	43.9	49.5
AJ:O3	5.7	5.5	7.6
Fe ₂ O ₃	18.2	18.7	•
FŧO	•	•	19.8
MgO	8.3	1.6	9.0
CaO	5.6	5.6	9.6
K,O	< 0.3	0.3	0.2
TiO ₂	0.9	0.9	0.9
so,	7.7	9.5	•
a	0.7	0.9	
Sum	91 8	93.6	96.6

Table 6.1. Composition of selected martian samples. The third column shows the main constitution of the meteorite Shergotty (class: SNC). Compounds of light elements, like H₂O, CO₂, Na₂O and NO₃, could not be detected, and such elements probably make up for the lacking 7-8 weight %.

The results of the analysis of two of the samples are shown in Table 6.1. Following tradition the elements are presented as combined with oxygen. This does not imply that the metals are present as oxides in the martian dust. In the table we also show the elemental composition of Shergotty, a SNC-meteorite.

The most anomalous feature of the composition of the martian fines — when compared to terrestrial weathering products — is the low content of aluminum. Compared to the average composition of igneous (granitic) rocks in the near-surface part of the continental crust of the Earth, the martian samples are depleted in Al_2O_3 by a factor of about 2.5, while Fe_2O_3 is enriched by a factor of 4 and MgO by a factor of 3.8. The martian fines seem to be derived from basaltic rocks, with no evidence for admixture of granitic rocks.

It should be emphasized that the Viking landers were not equiped to determine the minerals present in the martian fines; only the elemental composition of the soil could be determined. It has been guessed that the mineralogical composition of the martian fines would be about 80% of iron-rich clays (nontronite), 10% of MgSO₄, 5% of iron oxide (e.g. γ -Fe₂O₃, (maghemite), see below) and perhaps CaCO₃. [31].

6.1 The Oxidation State of the Surface of Mars and the Viking Biology Experiments.

The Viking landers carried laboratories designed to look for life related molecules and for biological activity on the surface of Mars.

No life was detected, but in connection with the biology experiments some highly interesting results were found, concerning the chemical reactivity of the martian soil.

The conclusions reached from the study of the results of the "Viking Biology Experiments" are summarized in reference 31-33.

Vol. 82 of the Journal of Geophysical Research (1977) contains detailed descriptions.

Below we add a few comments of relevance for the study of iron on the surface of Mars.

One of the Viking instruments looked for organic molecules, and unexpectedly it showed that the Mars soil samples did not contain organic molecules at all, not even the traces of organic molecules expected from the meteorites of the class carbonaceous chondrites that must have hit the surface of the planet. The absence of organic molecules is probably due partly to the destructive effect of the ultraviolet radiation from the Sun and partly to the oxidizing power of the martian soil.

Other instruments looked for biological activity. In one case solutions of organic molecules — nutrients — in water were mized with some martian soil. The organic molecules were labelled with ¹⁴C. The mixing of the solution with the martian soil resulted in the release of ¹⁴CO₂. The conclusion of this experiment is that an oxidizing agent in the martian soil has oxidized the ¹⁴C containing formic acid (HCOOH) in the water solution.

A second biology experiment uncovered another intriguing chemical property of the soil, which perhaps may be said to mimic simple lifelike reactions: A martian surface sample was exposed to a simulated martian atmosphere that had been enriched with a small quantity of radioactively labeled CO₂ and CO. The martian soil appeared capable of — albeit on a small scale — to synthesize organic molecules out of atmospheric ¹⁴CO₂ and ¹⁴CO.

The puzzling results of the biology experiments seem to be explained by inorganic chemical reactions between the crystallites of the soil and organic molecules in the water solutions which were mixed with the soil, and inorganic chemical reactions with the gaseous molecules with which the soil was brought into contact.

The ultraviolet radiation from the Sun interacts with the surface and the atmosphere. Examplewise: By the interaction with the water in the atmosphere the ultraviolet light creates, the hydrozyl radical, OII. This radical is a powerful oxidizing agent, whose production near the martian surface alone can explain the absence of organic matter. The chemical reactivity, and the high oxidation state of the soil, has been created through a complex interplay of the uv-radiation, the atmosphere and the solid surface of the planet.

The martian soil probably harbors iron containing clay minerals and perhaps maghemite, γ -Fe₂O₃. It has been speculated that iron containing minerals in some way acted as catalysts for the chemical reactions and thus contributed to the high chemical reactivity.

The small crystal grains of the martian soil seem to be kept in a highly reactive state, far from chemical equilibrium. The reasons why this is possible are the low temperature (≈ 200-270 K) and the present lack of liquid water on the surface of the planet. On the other hand, liquid water once existed on Mars, during a period of a warmer climate, probably early in the history of the planet.

The Viking landers were equipped to detect magnetic particles in the martian soil, and a remarkable finding was that the martian surface material contains 1–7% of highly magnetic, most probably ferrimagnetic, minerals. Maghemite (γ -Fe₂O₃) and feroxyhite (δ -FeOOH) are strongly magnetic, ferric oxide minerals. Both compounds have been advanced as candidates for the magnetic component of the martian soil [34–36]. For further details see the next section.

It is generally agreed that the red colour of the martian surface is caused by the presence of Fe(III)—compounds. More precisely:

The red colour of Mars is due to the charge transfer band in Fe(III)—compounds. We do not know how the highly oxidized iron on the surface of Mars was formed. The SNC—meteorites, believed to be igneous rocks from Mars, contain iron mainly in the oxidation state +2 (Fe^{2*}). The red colour of Mars suggests resemblance to the colour of the terrestrial, red tropical soils, which form mainly in hot and humid climates. The climate of the present Mars is cold.

Several questions concerning the iron on Mars enforce themselves:

- 1. How did the iron on the surface of Mars become highly oxidized?
- 2. What is the nature of the magnetic minerals on Mars, and how did they form?
- 3. What is the role of the putative iron-containing clays, and how did they form?

- 4. Is the oxidation a surface phenomenon only, or is there a thick layer of rocks that are highly oxidized, i.e. contain most of their iron as Fe³⁺?
- 5. Most of the rocks seen on the surface of Mars are ejecta from large meteorite impacts. Are these strewn rocks similar in composition to SNC-meteorites?
- 6. What is the oxidation state of the iron in the early sediments formed on Mars?

In the concluding remarks we shall briefly touch upon question number 6 and its possible connection with the search for fossil life on the planet. We shall now focus our attention on the problems related to the magnetic phase in the martian soil. We shall try to illustrate that soil science can make essential contributions to the study of Mars, i.e. contributions to the preparation of the coming rover and sample return missions to the planet.

6.2 The Viking Magnetic Properties Experiment.

The results of the "Viking Magnetic Properties Experiment" have been described by Hargraves et al. [34,35].

The investigation was designed to detect magnetic particles and – if possible – their composition and abundance in the martian surface material. The experiment utilized a series of permanent magnets, which were either inserted directly into the surface material or were passively exposed to particles carried by the martian atmosphere. The magnets, which were directly inserted into the soil, were incorporated in the backhoe of the samplers used to collect surface material for analysis. One magnet array was designated strong, another weak. The effective magnetic field and field gradient at the surface of the strong magnets are 2500 G and 10000 G/cm. For the weak array magnets these values are 700G and 3000 G/cm respectively [1 Tesla = 104 Gauss].

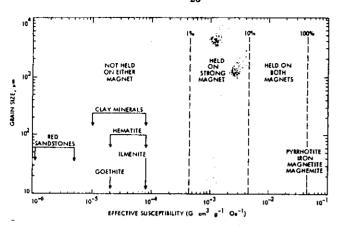


Fig. 6.1. Diagram illustrating the response to the backhoe magnets of the common magnetic minerals, according to their grain size and magnetic susceptibility. The diagram is based on extrapolation of the results of laboratory experiments (with Viking backhoe magnets and natural and synthetic materials) to the conditions which we consider to apply when the magnets are actually deployed during sampling activity on Mars. The vertical broken lines refer to composite particles containing different percentages of any of the four strongly magnetic minerals. The broad stippled bands separate the three main levels of magnetic attraction between which there is no clear division. (G=gauss; Oe=oersted).

[104] Gauss = 1 Teslal. From ref. 34.

Before the Viking mission, the response of the magnets to a variety of terrestrial – synthetic and natural – materials was tested. The results of the laboratory investigations – corrected for the lower gravity on Mars $(0.38~g_{\text{earth}})$ – are shown in figure 6.1.

The figure illustrates the response to the backhoe magnets — the strong and the weak — of the common magnetic minerals, according to grain size (ordinate) and magnetic susceptibility (abscissa). The vertical straight and broken lines refer to particles consisting of mixtures of magnetic and non-magnetic phases, according to the different percentages of any of the strongly magnetic minerals. By strongly magnetic minerals are meant the ferro— or ferrimagnetic minerals:

metallic iron—nickel alloy magnetite, Fe₃O₄ titanomagnetite, Fe₃* Fe₂* Ti⁴*O₂* maghemite, γ —Fe₂O₃ feroxyhite, δ —FeOOH pyrrhotite, Fe_{1-x}S.

The broad stippled bands shown on figure 6.1 separate three main levels of magnetic attraction.

Examplewise: A particle of linear dimensions of 1 mm ($10^3 \mu m$) and having an effective susceptibility of 2 x 10^{-4} (cgs—units) cannot be held by any of the backhoe magnets. (The effective susceptibility is the magnetic moment per gram of the whole, possibly composite particle. Ferromagnetic (ferrimagnetic) particles will be saturated in the fields applied.)

A particle of a linear dimension of 0.1 mm and of the same effective susceptibility as above will stick to the strong magnet, but not to the weak magnet.

Figure 6.2 shows a photograph of the sample aquisition arm with the magnets visible. The magnets are the two small circular disks on the sampler arm.

The magnets were periodically photographed with the lander imaging system.

Photos were taken between the various sample aquisitions, and the resulting pictures are the primary data on which conclusions have to be based.

By means of this equipment alone it has not been possible to identify with certainty the magnetic compound — or compounds — present on the surface of Mars, but some very important results were obtained.

Below follows a brief description of these results – and the conclusions reached – by Hargraves et al. [34–35]. The conclusions drawn by these authors are based on very careful reasoning, which we cannot reproduce in all detail here. We give the main lines.

A considerable amount of magnetic particles were attracted to both the strong and the weak backhoe magnets from the surface material of Mars. A general — and conspicuous — feature was the similarity (approaching equality) in the amount of material adhering to the weak and the strong magnets.

From spectroscopic evidence there seems to be no difference between the material clinging to either of the backhoe magnets, and the adhering material also seems to have the same spectroscopic properties as the general red soil on the surface of Mars.

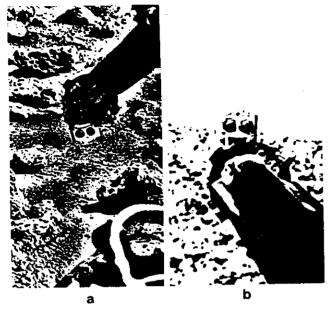


Fig. 6.2. Direct view images of the backhoe after a total of three insertions (a) and 11 insertions (b) into the surface. Note the similar amount of material adhering to both strong and weak magnets: in (a) the weak magnet is to the right and in (b) to the left. From ref. 34.

In a few pictures of the magnets, individual particles of linear dimensions of a couple of mm stuck to the strong magnet. The particles survived several sample aquisitions, suggesting a substantial effective magnetic susceptibility. The fact that such particles were seen on the strong magnet only, suggests that they are composite particles, a — perhaps intergrown — mixture of ferro(ferri)magnetic and non-magnetic compounds. By comparing with figure 6.1 it is suggested that the particles may contain between 1 and 10% of a ferro(ferri)magnetic phase.

In another picture of the magnet array it was possible – from the shadow cast – to measure the pile of material adhering to a strong magnet. The pile was 2–4 mm high. If this height reflects the maximum amount of martian surface particles which can be held by the strong magnet, it makes a rough evaluation of effective susceptibility possible.

The main conclusion of Hargraves et al. [34-35] is that the bulk of the particles clinging to both types of backhoe magnets are composite, each particle containing a small percentage of highly magnetic minerals.

Magnets exposed to airborne dust also attracted magnetic particles. The reflectance spectrum of the material clinging to these magnets is similar to the reflectance spectrum of the material on the backhoe magnets. The martian fines all seem to be similar in composition.

Composition of the particles.

Let us first remark that the results of the inorganic chemical analysis (see table 6.1) shows the presence of more than a sufficient amount of iron to account for the magnetic component evidently present on the surface of Mars.

Next: Minerals with low magnetic susceptibility, say haematile(α -Fe₂O₃), ilmenite FeTiO₃, goethite α -FeOOH or lepidocrocite γ -FeOOH can be excluded. They could not adhere to the weak magnets in the amount that is observed. (Perhaps it cannot be excluded that very small, superparamagnetic particles of α -Fe₂O₃ could be present). The spectrophotometric studies show the particles to be red. The reddish hue is attributed to the presence of ferric iron oxides or hydroxides. Could the reddish colour be due to a coating of metallic iron-nickel particles (reduced iron) or perhaps magnetite (containing Fe²⁺)? From the penetration of the X-rays used in the inorganic chemical analysis it has been concluded that if such a coating exists, it must be very thin (< 0.25 μ m) or discontinuous.

The surface material of Mars is fine-grained, less than 100 μ m in average grain size. The airborne particles are less than 10 μ m in diameter. With the comparatively high partial pressure of oxygen (0.13% of free oxygen in the atmosphere) it seems unlikely that small particles containing reduced iron or Fe²⁺ (metallic iron, pyrrhotite, Fe_{1-x}S, or magnetite) could avoid being oxidized completely to ferric iron. The coating theory therefore seems rather unlikely.

If such arguments hold, the best candidate for the highly magnetic mineral on the surface of Mars seems to be maghemite.

Let us for a moment assume that maghemite is present on the surface of Mars in the supposed amount of between 1 and 10% by weight. This maghemite could be present in various forms, for example:

as grains of γ -Fe₂O₃ mixed with non-magnetic particles as igneous rock particles, intrinsically non-magnetic, but coated by γ -Fe₂O₃,

as igneous rock particles, intrinsically non-magnetic, but coated by 7-re203, which could account for the yellowish to reddish-brown colour.

as grains of γ -Fe₂O₃ intergrown with clay minerals or adsorbed on the crystallites of the clay minerals. Perhaps the particles of γ -Fe₂O₃ could be so small that they are superparamagnetic.

The fundamental question is: How (and when) was the maghemite formed? Was the maghemite on Mars formed billions of years ago, when the planet for a brief period harbored liquid water [31]? Has the ultraviolet light had anything to do with the formation of the maghemite?

On the Earth maghemite occurs in some oxidized basalts and in oceanic red clays. Not much is known with certainty of how terrestrial maghemite forms. One possibility is that it forms by low-temperature oxidation of preexisting magnetite [37].

If the maghemite on Mars formed through oxidation of magnetite, it has interesting implications. The magnetite, as a precursor to maghemite, could have formed in various ways. It could, for instance, have been derived from preexisting igneous rocks. In this respect it may be useful to recall that the meteorites of the class nakhlites contain titanomagnetite. These meteorites are believed to have originated on Mars. See the Mössbauer spectrum on figure 5.2.

If the precursor magnetite on the surface of Mars was derived from martian igneous rocks, one would expect it to contain some titanium, and the maghemite resulting from the oxidation process would then also contain titanium? As seen from table 6.1 the martian fines contain a little less than 1% of titanium.

For the litterature on the Fe-Ti-O system, see reference [37].

There are other pathways to the formation of maghemite. The mineral lepidocrocite, γ -FeOOH, which contains ferric iron only, transforms to γ -Fe₂O₃ by dehydration. The lepidocrocite, as precursor, could have formed by aqueous alteration of ferromagnesian silicates at an earlier stage of evolution of the martian surface. Mössbauer spectroscopy should be applied to the study – in the laboratory and in terrestrial, martian analogue samples – of lepidocrocite production, in connection with the oxidation and hydration of iron bearing silicates. See for instance the studies of "Mars Sample Analogues" in the references 38–41.

Let us finish this section with the remark that it has by no means been proved that maghemite is responsible for the magnetic properties of the martian surface materials as mentioned. Another possible candidate has been suggested by Burns [36]: δ -FeOOH (feroxyhite). Feroxyhite is ferrimagnetic. The magnetic moment is probably due to an antiferromagnetic sublattice with uncompensated moments, due to vacancies in one of the sublattices and because of this is somewhat variable. The saturation moment is substantially less than the saturation moment of maghemite. In table 6.2 we show the magnetic saturation moments per gram of the known magnetic minerals.

Room temperature	$M_{saturation} \left[\frac{erg}{Gq} \right]$	$M_{saturation} \left[\frac{J}{Tkq} \right]$
Metallic iron	220	220
Magnetite, Fe ₃ 0 ₄	93	93
Maghemite, v-Fe ₂ 0 ₃	85	85
Feroxhite, &-FeOOH	20 (variable)	20
Pyrrhotite, Fe ₇ S ₈ α-Fe ₂ O ₃	20 (variable) 0,4	20 0,4

Table 6.2. Saturation magnetization per gram at $T \approx 300$ K. Ti in magnetite and magnetite lowers the saturation magnetization [37].

Very small antiferromagnetic particles in the superparamagnetic state may have a substantial number of uncompensated surface spins and thereby an increased magnetic susceptibility. If each particle contain N magnetically active spins, the number of uncompensated surface spins is of the order of \sqrt{N} . Low temperature oxidation of iron often results in small particles. Superparamagnetism, even in antiferromagnetic particles, might play a role in the magnetic properties of the soil on the surface of Mars. The terrestrial red tropical soil generally contains α -Fe₂O₃ and α -FeOOH in the superparamagnetic state.

7. Magnetic Properties of Tropical Soils from Brazil.

We shall finish by a brief discussion of the study of Brazilian soils, which perhaps in some respects may be considered as a Mars Sample Analogue.

The Martian bedrocks contain the key to the understanding of the evolution of the surface of Mars. From the Viking Mission soil analysis — and from the constitution of the SNC meteorites — it is concluded that the Martian soil is a weathering product of hasaltic rocks.

Tropical and subtropical regions of the Earth are often covered with red soil. In tropical and subtropical regions the weathering processes are advanced: Rocks that crystallized at high pressure and temperature, and under low oxygen fugacity, come to equilibrium in the terrestrial surface conditions, i.e. under low pressure, low temperature and high oxygen partial pressure.

Some of the red tropical soils are – like the martian fines – derived from basalt. As has been shown by Coey, Resende and coworkers, terrestrial basalts often weathers to yield a highly magnetic soil [42,43].

Extensive investigations by these authors indicate that as much as 5% of the surface of Brazil may be covered by soil with a spontaneous magnetization $\sigma_8>1$ JT⁻¹kg⁻¹, which is sufficient for the soil to be attracted by a hand magnet. [1 JT⁻¹kg⁻¹ = 1 ergG⁻¹g⁻¹].

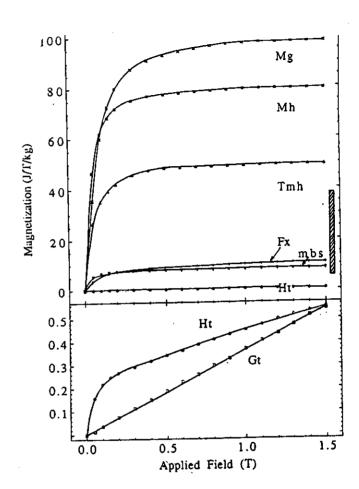
Mineralogical analysis and Mössbauer spectroscopy have revealed that the magnetic phase in the Brazilian soil is fully oxidized titanomagnemite, inherited from the underlying basalt.

In one instance the magnetic phase was found to be [44]: $[Fe_{0.77}Ti_{0.22}Zn_{0.01}] \{Fe_{1.19}Ti_{0.26}Mn_{0.02}Al_{0.04} \quad _{0.49}\}O_4.$

The titanomaghemite has the spinel structure, AB₂O₄. The A (tetrahedral) and B (octahedral) sites are indicated in the formula. The spontaneous magnetization of this mineral is 36 JT⁻¹kg⁻¹.

The titanomaghemite is presumably derived from primary titanomagnetite. Figure 7.1 compares the magnetization curve of a titanomagnemite with the curve for the whole soil, and those determined for some pure iron oxide and hydroxide minerals.

The surface conditions on Mars are different from those on Earth. Nevertheless, the weathering processes must be proceeding basicly in the same sense. Basalts on Mars are tending to equilibrium in the surface conditions of much lower temperature and pressure — and greater oxygen fugacity — than those prevailing when the basalts solidified.



30

Fig. 7.1. Magnetization curves of pure iron oxides magnetite (Mg), maghemite (Mh), feroxyhite (Fx), hematite (Ht) and goethite (Gt), together with those of soil titanomaghemite (Tmh) and a sample of magnetic Brazilian soil (mbs). Magnetization is expressed as JT⁻¹(kg of Fe₂O₃⁻¹), and is uncorrected for the demagnetizing field. An estimate of the magnetization of the Martian soil is indicated by the hatched bar [45].

Due to the fact that the magnetic properties of some weathered terrestrial basalts are caused by titanomaghemite, it has been suggested that titanomaghemite should be considered as a possible candidate for the magnetic mineral on Mars [45]. Let us in this connection remind ourselves about the fact that the meteorite Nakhla — believed to come from Mars — contains titanomagnetite.

From figure 7,1 — and from several articles in ref. 48 — it is seen that Ti has a strong influence on the magnetic properties of maghemite. If the presence of titanomaghemite on Mars is assumed to be a possibility, it is evidently of significance to obtain detailed knowledge of titanomaghemite in terrestrial soils before the (expensive!) rover missions to the planet.

If the putative maghemite on Mars does not contain Ti, the mineral has probably formed via another process. Could lepidocrocite, i.e. γ -FeOOH, somehow form as precipitate when abundant water was present on Mars? Maghemite is a decomposition product of lepidocroite.

Has the ultraviolet light played any role in the formation of the Martian soil? [31,46,47].

Iron compounds are indicators of pedogenic processes. Before the rover missions and the sample return missions to Mars deepgoing investigations of the magnetic properties of highly oxidized red tropical soils should be undertaken. What is the detailed structure of the ferrimagnetic iron—oxides in terrestrial soils? Does the γ -Fe₂O₃ always contain Ti? Apart from being inherited form basaltic rocks, the mineral maghemite also seems to occur on the Earth as secondary, Al-substituted crystallites. How do they form? Does feroxyyhite occur as magnetic mineral in soils?

Many other questions could be asked, but we finish here and proceed to the concluding remarks.

8. Concluding remarks.

The Earth formed about 4.5×10^9 years ago. Life originated on Earth perhaps 3.8×10^9 years ago. It is generally assumed that the Earch at that time had a reducing atmosphere rich in hydrogen compounds and perhaps CO_2 . No free, atmospheric oxygen was present in the first 2.5×10^9 years of the history of the Earth.

Perhaps the early atmosphere on Mars likewise lacked free oxygen. At that time liquid water was present on Mars, and some of the same chemistry that took place on Earth might have occurred on Mars.

We must even consider the possibility that life originated on Mars, and that this life later died out as the climate changed. Might there be fossil life on Mars to be discovered by some future expedition?

An important task for Mössbauer spectroscopy of martian samples will be to study the oxidation state of iron in ancient martian sediments. These rocks might have a story to tell about the history of the atmosphere of Mars. We will probably be able to establish if free atmospheric oxygen was present on early Mars. If free oxygen was present life could (probably) not have developed.

Did ancient Mars have a reducing atmosphere that allowed life to develop?

A discussion of this highly interesting subject is, however, a whole new seminar in itself.

Be that as it may we finish by making the following remarks of iron in nature. The geochemical cycle of the element iron – be it on Earch or on Mars – is strongly coupled to the cycles of abundant elements like O, H, C, and S.

Fe occurs in nature in (at least) three oxidation states, metallic, i.e. Fe(0), Fe(II), and Fe(III). There is, perhaps, a remote possibility of Fe(IV) on Mars. Furthermore: The element iron occurs as the essential ion in magnetically ordered compounds, both in the ferro(ferri)-magnetic, antiferromagnetic, and superparamagnetic state.

Due to these properties, and due to its high abundance on Mars, both in the surface fines and in the igneous rocks, the element iron is of fundamental importance for the understanding of the evolution of the planet.

The manned mission to Mars, whenever it will take place, will be one of the greatest endeavours humans have ever undertaken.

Let us learn as much as possible about the planet and its two interesting moons before this epic event.

References.

- R.V. Morris, D.G. Agresti, T.D. Shelfer and T.D. Wdowiak Abstract presented a the Twentieth Lunar and Planetary Science Conference
- 2. George W. Wetherill Ann.Rev. of Astronomy and Astrophysics 18, 77 (1980)
- 3. S.F. Dermott (editor)
 The Origin of the Solar System
 (John Wiley, New York, 1978)
- 4. S.S. Barshay and J.S. Lewis, Ann.Rev.Astron.Astrophysics 14, 81 (1976)
- J.S. Lewis
 "The Chemistry of the Solar System"
 Scientific American
 no 3, 51 (1974)
- B. Mason and C.B. Moore "Principles of Geochemistry" (4 Edt. John Wiley, New York, 1982.
- R.W. Wood
 "The Formation of the solar system" in E.H. Avrett (edt)
 "Frontiers of Astrophysics" (Harvard Univ. Press, 1976)
- 8. Robert T. Dodd
 "Meteorites. A petrologic—
 chemical Systhesis
 (Cambridge University Press,
 1981)

- B. Nagy
 "Carbonaceous Meteorites"
 (Elsevier Scientific
 Publishing Company,
 Amsterdam 1975)
- John T. Wasson Meteorites. Their Record of Early Solar-System History (W.H. Freeman and Company, New York 1985)
- Robert T. Dodd
 Thunderstones and Shooting Stars
 The Meaning of Meteorites.
 (Harvard University Press, Cambridge Massachusetts, 1986)
- Robert Hutchison
 The search for our beginning.
 An enquiry, based on meteorite research, into the origin of our planet and of life.
 (Oxford University Press, Oxford, 1983)
- Harry. Y. Mc Sween, Jr.
 Meteorites and their parent planets.
 (Cambridge University Press, Cambridge, 1987)
- John A. Wood
 Meteorites and the Origin of
 Planets.
 (Mc Grawhill Book Compagny,
 New York, 1968)
- 15. T.J. Wdowiak and D.G. Agresti Nature 311, 140 (1984)
- 16. M.B. Madsen, S. Mørup, T.V.V. Costa, J.M. Knudsen, and M. Olsen Nature 321 (1986)
- 17. K. Tomeoka and P.R. Buseck Geochim.Cosmochim. Acta, Vol 52, 1627 (1988)

- J.T. Wasson and G.W. Wetherill, Page 926-974 in
 T. Gehrels (edt) Asteroids (University of Arizona, 1979)
- 19. D. Walker, E.M. Stolper, and Proc.Lunar Planet. Sci.Conf 10th (1979) page 1995-2015
- D.W. Sears
 The Nature and Origin of Meteorites
 (Oxford Univ. London 1978)
- 21. E. Stolper and H.Y. Mc Sween Geochim.Cosmochim.Acta 43, 1475 (1979)
- 22. H.Y. Mc Sween and E. Stolper Sci.Amer. 242, no 6,54-63 (1980)
- C.A. Wood and L.D. Ashwal Proc.Lunar Planet Sci. 12B, 1359 (1981)
- Celso B. Gomes and Klaus Keil Brazilian Stone Meteorites (Univ. of New Mexico Press, Albuquerque, 1980)
- John D. O'Keefe and Thomas J. Ahrens Science, Vol 234, p. 346 (1986)
- 26. A.M. Vickery and H.J. Melosh Science, Vol 237, p. 738 (1987)
- Geochim. Cosmochim. Acta 50, no 6. (1986)
 This issue contains several articles on SNC-meteorites.

- 28. G. Dreibus and H. Wänke Meteorites 20, 367 (1985)
- V.W.A. Vieira, J.M. Knudsen N.O. Roy-Poulsen, and J. Campsie Phys.Scrip. 27, 437 (1983)
- V.W.A. Vieira, T.V.V. Costa, H.G. Jensen, J.M. Knudsen, M. Olsen, L. Vistisen, Phys.Scrip. 33, 180 (1986)
- 31. M.H. Carr
 "The Surface of Mars"
 (Yale University Press, 1981)
- 32. Norman H. Horowitz
 To Utopia and Back:
 The Search for Life in the
 Solar System
 [N.H. Freeman, New York, 1986]
- 33. Norman H. Horowitz Sci.Amer. Vol 237, no 5 (November 1977)
- P.B. Hargraves, D.W. Collinson R.E. Arvidson, and C.R. Spitzer Science 194, 1303 (1976) and J. Geophys.Res. 84, 4547 (1977)
- 35. R.B. Hargraves, D.W. Collinson, R.E. Arvidson, and P.M. Cates J.Geophys.Res. 84, 8379 (1979)
- 36. R.G. Burns Nature 285, 647 (1980)
- 37. W. O'Reilly Rock and Mineral Magnetism (Blackie, Glasgow 1984)
- 38. R.G. Burns Nature, vol 320, 55 (1986)

- 39. A. Banin and L. Margulies Nature, vol 305, 523 (1983)
- 40. Carlton C. Allen, James L. Gooding, M. Jercinovic, and Klaus Keil Icarus 45, 347 (1981)
- 41. A. Banin
 Clays on Mars, in
 A.G. Cairns-Smith and
 H. Hartman (edt)
 Clay Minerals and the
 Origin of Life
 (Cambridge Univ. Press, 1986)
- 42. M.A. Resende, J.E.M. Allan, and J.M.D. Coey Earth Planetary Sci.Lett. 78, 322 (1986)
- 43. J.E.M. Allan, J.M.D. Coey, M.A. Resende, and J.D. Fabris Phys. Chem. Minerals 15, 470 (1988)
- 44. J.E.M. Allan, J.M.D. Coey, I.S. Sanders, U. Schwertmann, G. Friedrich, and A. Wiechowski Min.Mag. 53 (in press)
- 45. J.M.D. Coey, S. Mørup,
 M.B. Madsen, and J.M. Knudsen
 Accepted for publication in
 Journal of Geophysical Research
 (a special issue on Mars)
- 46. R.L. Huguenin J.Geophys.Res. 79, 3895 (1974)
- 47. B. Lundgreen, H.G. Jensen, J.M. Knudsen, M. Olsen L. Vistisen Phys.Scr. 39, 670 (1989)
- 48. J.W. Stucki, B.A. Goodman, and U. Schwertmann Iron in Soils and Clay Minerals NATO ISI series, vol 217

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