特別講演等要旨（Ｓ会場）

2S01

外場応答性錯体の創製と物性

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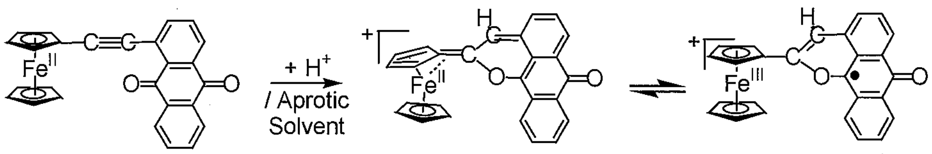
［はじめに］光、電気、化学刺激などに応答して多重の安定状態をとる分子は、分子素子のユニットとして興味深い。多彩な光化学やレドックス化学を示す金属錯体は外場応答性分子として魅力的である。本発表では、この観点から展開している外場応答性錯体の研究の中でフェロセン系を中心に、１）プロトン応答型ドナー(D)-アクセプター(A)共役錯体、および　２）フォトクロミック錯体、のユニークな性質について報告する。

１）プロトン応答型 D-A 共役錯体 [1)]

フェロセンとアントラキノンをπ共役鎖のエチニレンで結合した D-A 錯体にプロトンを共存させると、アントラキノン部位のみプロトン付加してアクセプターレベルが変化するため、分子内電子移動が起き、電子的に揺らいだ状態が生成すると予想される。実際に、最も単純な D/A = 1/1 の **1-FcAQ** では、プロトン付加により Scheme 1 に示したような原子価互変異性の存在が確認された。溶液中においては、プロトン付加体は Fe(II)フルベン錯体型（**[1-FvAqH]$^+$**）として存在するが、固体状態においては、メスバウアースペクトルの温度変化などから、低温では Fe(II)フルベン錯体型（**[1-FvAqH]$^+$**）、室温では Fe(III)フェロセニウム型（**[1-Fc$^•$AqH$^•$]$^+$**）をとるという可逆な磁性変換を起こすことが明らかになった。

Scheme 1.

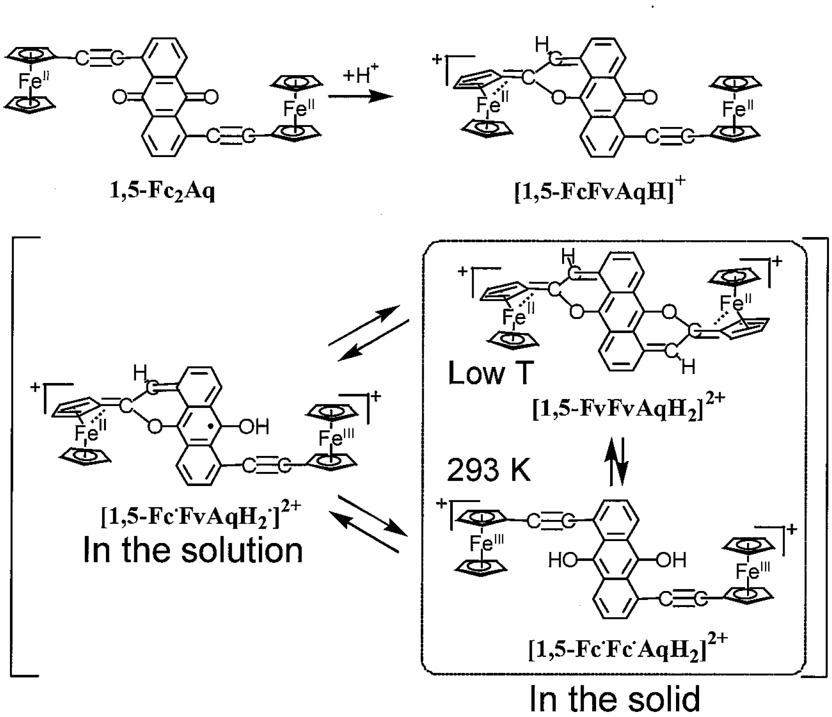


1-FcAq　**[1-FvAqH]$^+$**　**[1-Fc$^•$AqH$^•$]$^+$**

さらに D と A の数を変化させていくと、DA 数、D/A 比、キノン上の結合位置などの違いによって、プロトン付加に伴う様々な構造物性変換を示す。たとえば、2 分子のフェロセンが対照的にアントラキノンに接合された分子である **1,5-Fc$_2$Aq** の酸添加による構造変化は２段階に起こり、その１段階目の吸収スペクトル変化は **1-FcAq** と同様であることなどから、Fe(II)フルベン錯体型の**[1,5-FcFvAqH]$^+$**が生じることが示された。２段階目ではアントラセミキノン類に特徴的な強い吸収が 748nm と 850nm に現れた。またこの酸添加物の凍結溶液の 5K での ESR スペクトルは鋭いセミキノンラジカルの信号を示すと同時にフェロセニウムに起因する信号も観測され、スピン分離型の**[1,5-Fc$^•$FvAqH$_2$$^•$]$^{2+}$**が生成していることが示された。このことからフェロセン部位がともに隣接酸素原子へのプロトン付加との協奏的構造変換を起こしていることが

明らかになった。2プロトン付加体のメスバウアースペクトルは、広い温度範囲で変化を示し、ESRと磁化率測定の結果を合わせると、2プロトン付加体の固体状態では、Scheme 2に示すように3種の原子価互変異性体が存在し、それらの存在比は、溶液と固体では異なり、また温度に依存して変化することが示された。

Scheme 2.

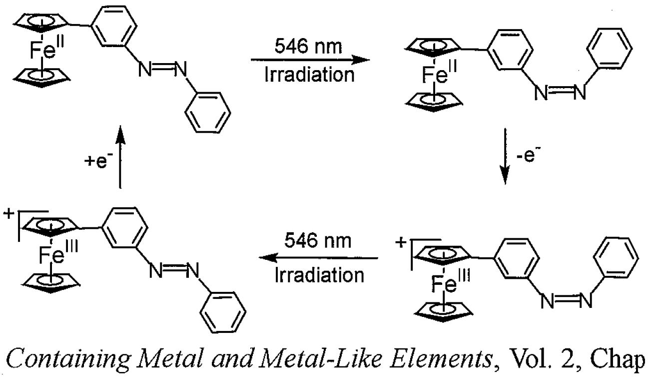


2）フォトクロミック錯体[2)]

フォトクロミック分子と金属錯体の融合，すなわち“フォトクロミック錯体”は興味深い研究対象と考えられる。フォトクロミズム現象が、結合した金属の種類に大きく依存するようであれば，金属イオンセンシングに有用である。また光以外の外部刺激を連動した可逆的構造変化を発現できたり，構造変化によって色のみならず磁性やレドックス特性なども変わったりすれば，分子メモリとしての応用範囲が広がる．この観点からアゾ共役フェロセンの研究をおこなった。

3-フェロセニルアゾベンゼンは，500 nm 付近に MLCT バンドを有するが、このバンドを励起する緑色光照射によりトランス体からシス体への異性化を起こすことを見出した。フェロセンを 1 電子酸化したフェロセニウムでは、緑色光照射により、逆にシス体からトランス体への異性化が起こる。これらを組合せることにより、緑色光照射とフェロセン／フェロセニウムのレドックス変化による可逆な異性化を実現した（Scheme 3)。

Scheme 3.



1) M. Murata and H. Nishihara, *Macromolecules Containing Metal and Metal-Like Elements*, Vol. 2, Chap. 8, Wiley InterScience, 135-159 (2003).

2) H. Nishihara, *Bull. Chem. Soc. Jpn.* **77**, 407-428 (2004).

Synthesis and properties of external-stimuli responsive complexes

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Mössbauer Exploration of the Surface of Mars with MIMOS II and the Mars-Exploration-Rovers

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Introduction:

For the first time in history a Mössbauer spectrometer was placed on the surface of another planet. Our miniaturized Mössbauer spectrometer MIMOS II [1,2] (see fig. 1.b) is part of the Athena payload of NASA's twin Mars Exploration Rovers (MER) "Spirit" and "Opportunity" (see fig.1.a). It determines the Fe-bearing mineralogy of Martian soils and rocks at the Rovers' respective landing sites, Gusev crater and Meridiani Planum. In January 2004 the NASA twin MERs Spirit and Opportunity landed successfully at the Gusev crater and at the Meridiani Planum landing sites, respectively. The main goals of this planetary twin mission are to: (i) identify hydrologic, hydrothermal, and other processes that have operated and affected materials at the landing sites; (ii) identify and investigate the rocks and soils at both landing sites, as there is a possible chance that they may preserve evidence of ancient environmental conditions and possible pre-biotic or biotic activities. Both rovers are carrying the Mössbauer spectrometer MIMOS II, which is part of the Athena instrument suite consisting of remote sensing instruments [1], and the In-Situ instruments mounted on an robotic arm (IDD): (i) Rock Abrasion Tool (RAT), (ii) Mössbauer (MB) spectrometer MIMOS II [2], (iii) Microscopic Imager [1], and (iv) Alpha Particle X-ray Spectrometer (APXS) [3]. The IDD instruments are used to determine the chemistry and mineralogy of rocks and soils.

Instrument design:

MIMOS II operates in backscatter geometry, detecting the reemitted 14.4 keV Mössbauer and 6.4 keV X-ray radiation. Because of the complexity of sample preparation, this is the choice for an in situ planetary Mössbauer instrument [2]. No sample preparation is required, the instrument is simply presented to the sample for analysis. Because of mission constrains for minimum mass, volume, and power consumption, the MIMOS II is extremely miniaturized (without loss in capability) compared to standard laboratory Mössbauer spectrometers and is optimized for low power consumption and high detection efficiency. All components were selected to withstand high acceleration forces and shocks, temperature variations over the Martian diurnal cycle, and cosmic ray irradiation. Because of restrictions in data transfer rates, most instrument functions and data processing capabilities, including acquisition and separate storage of spectra as a function of temperature, are performed by an internal dedicated microprocessor and memory. The dedicated CPU is also required because most Mössbauer measurements will be done at times (for instance during night) when the rover CPU is turned off to conserve power. High detection efficiency is extremely important in order to minimize experiment time. Experiment time is also minimized by using as strong a main 57Co/Rh source as possible.

Physically, the MIMOS II Mössbauer spectrometer has two components that are joined by an interconnect cable: the sensor head (fig. 1.b) and electronics printed-circuit board. On MER, the sensor head is located at the end of the IDD and the electronics board is located in an electronics box inside the rover body. The sensor head contains the electromechanical transducer (mounted in the center), the main and reference 57Co/Rh sources, multi-layer radiation shields, detectors and their preamplifiers and main (linear) amplifiers, and a contact plate and contact sensor. The contact plate and sensor are used in conjunction with the IDD to apply a small preload when it places the sensor head, holding it firmly against the target. The contact plate also carries a temperature sensor measuring the sample temperature allowing to perform temperature dependent measurements. The

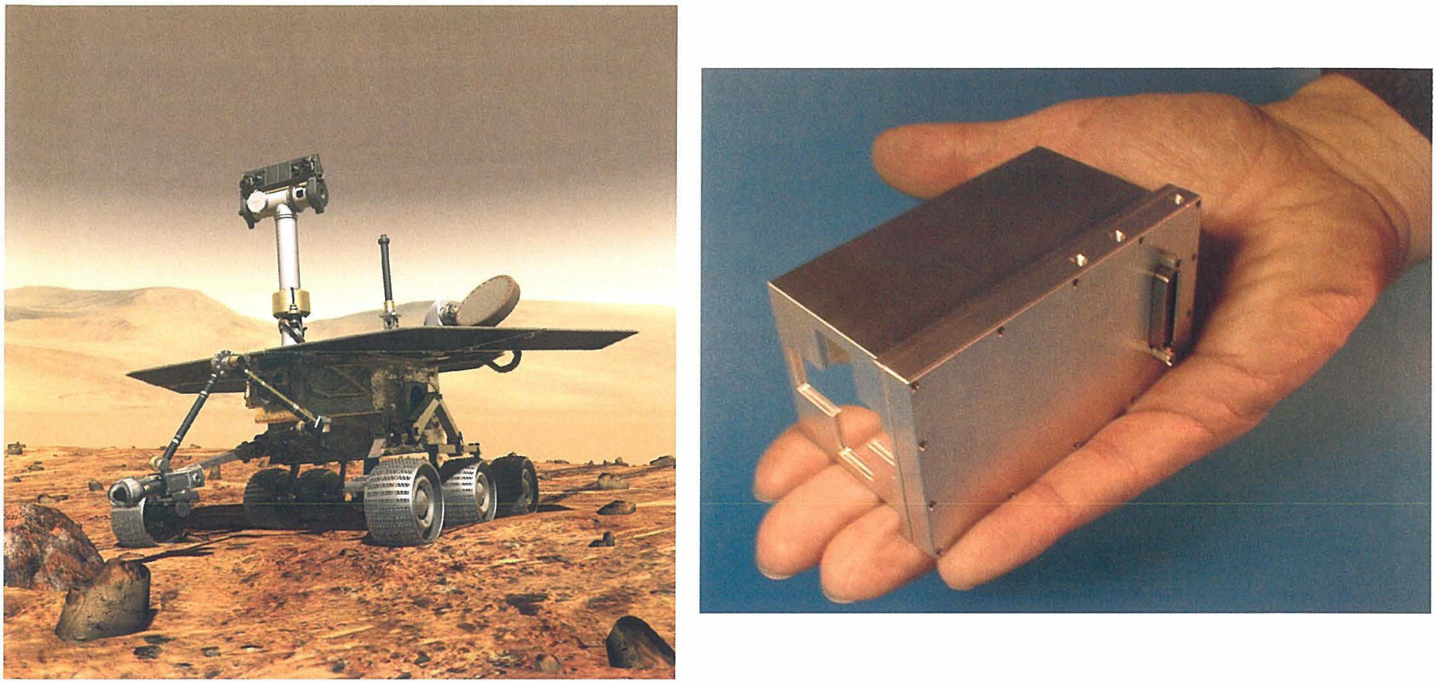

Figure 1. (a) Mars Exploration Rover (left) with robotic arm, carrying MIMOS II (dimensions about 1.5 m x 1.5 m wide); (b) Mössbauer instrument MIMOS II sensor head (picture on the right): dimensions about 9 cm long; 4 cm x 5 cm wide).

electronics board contains power supplies/conditioners, the dedicated CPU, different kinds of memory, firmware, and associated circuitry for instrument control and data processing.

Spirit at Gusev Crater:
The Mars Exploration Rover *Spirit* landed at Gusev Crater, hypothesized to have been a site of possibly past lacustrine and fluvial environments [4]. Therefore, sedimentation may have occurred under such conditions. Mineralogical analysis can reveal evidences of these sedimentary deposits. Columbia Memorial Station (CMS), the Spirit landing site, is situated within the low albedo region, consistent with sand-sized particles. Images of this unit, taken from orbit, show numerous dark, possibly dust devil tracks.

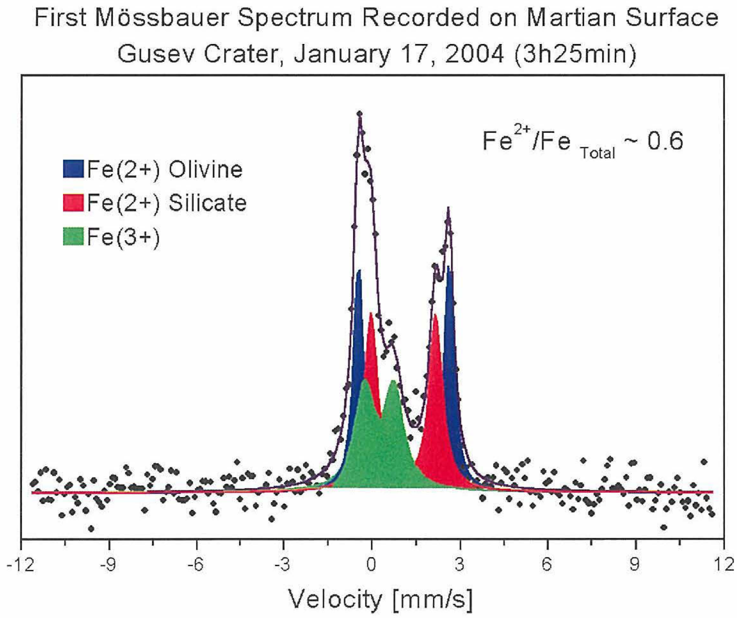

Figure 2. Mössbauer spectrum of soil in Gusev crater.

The MB results on rocks at the Gusev crater landing site [5] show a primarily olivine-basalt composition (see fig. 2 and 3). For some of the rocks a weathering rind has been detected using the

RAT and subsequently APXS and MIMOS II. Magnetite has been identified in both soils and rocks at Gusev. All rock and soil spectra taken in the vicinity of the Gusev landing site are dominated by the mineral signature of olivine. After a traverse of about 2 km Spirit reached some hills named the

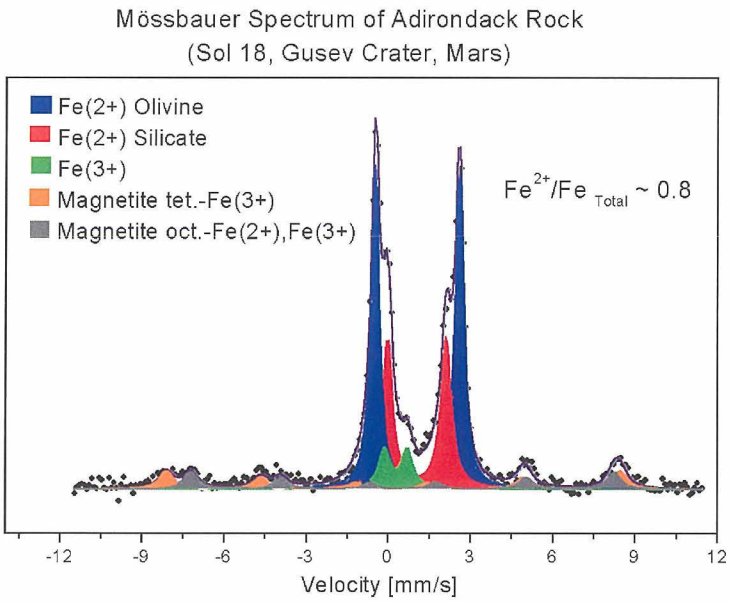

Figure 3. Mössbauer spectrum of Adirondack rock in Gusev crater.

'Columbia hills'. Here first indications for intensive weathering of surface material were found by the Mössbauer spectrometer. A couple of highly weathered rocks, identified with the camera systems of the rover, have been analyzed by MIMOS II and show a strong signal of the mineral hematite, and the absence of olivine. This strongly suggests the presence of water driven processes at this site in the past.

Opportunity at Meridiani Planum:
The Meridiani Planum landing site looks very different from Gusev crater. Opportunity landed inside a shallow crater (Eagle crater), with an outcrop covering part of the crater interior close to the rim. Mössbauer measurements (see fig. 4) show that this outcrop material, and similar material found in the plains around the landing site, consists predominantly of the Fe-sulfate jarosite, hematite, and a basaltic component (olivine, pyroxene). The same material was found again a couple of hundred meters away at the craters Fram and Enduranc suggesting that the whole area is covered with this jarositic material. As jarosite forms under aqueous, acidic conditions, with ph smaller than about 3.5, this finding by the Mössbauer instrument is evidence for the presence of large amounts of acidic water at this site in the past. A second finding is that the plains and large portions of the investigated craters (Eagle, Fram, Endurance) are covered by spherules with a diameter of several mm up to about 1 cm. Mössbauer data clearly show that the composition of these spherules is dominated by the Fe-oxide hematite. The composition of the soil at Meridiani is found to be basaltic, dominated by olivine similar to the Gusev site.

Summary and Conclusions:
The first Mössbauer measurements on Mars at both the Gusev Crater and the Meridiani Planum landing sites confirm the general basaltic nature of Martian surface materials. All soil Mössbauer spectra and the rock spectra at Gusev crater are dominated by the mineral olivine (composition ~Fo_{60}) [5]. Olivine has also been detected in the Nilli Fosse region from orbit by the Mars Global Surveyor Thermal Emission Spectrometer. Detection of olivine at three widely spaced locations on Mars implies its widespread occurrence on the planet and the inefficiency of alteration processes (at least in recent times) that would act to reduce this highly-alterable mineral to weathering products. It was also found non-stoichiometric

magnetite, the rock forming mineral pyroxene, and octahedrally coordinated Fe^{3+}. Because of the

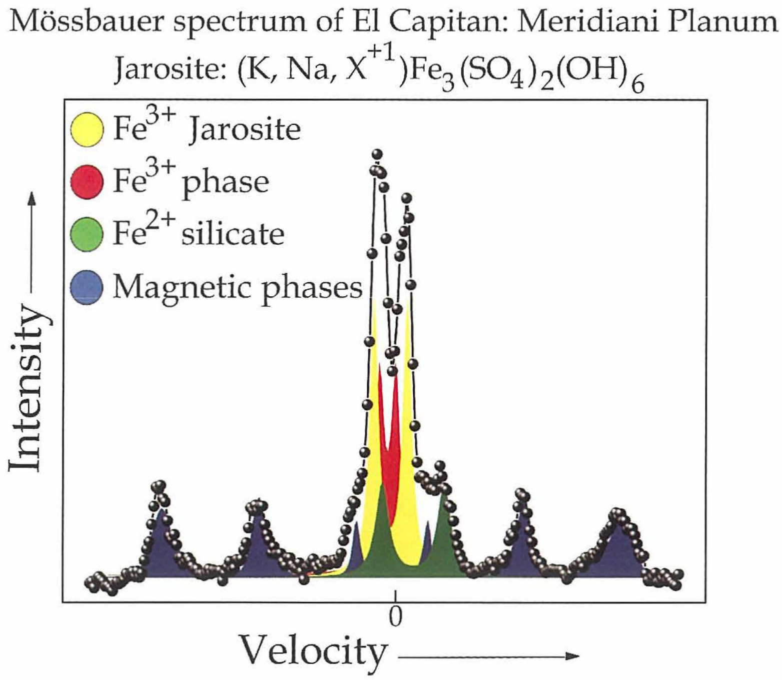

Figure 4. Mössbauer spectrum of Jarositic outcrop material at the 'Eagle crater' landing site of Opportunity in Meridiani Planum. The velocity range was about 11.5 mm/sec, and the temperature range The magnetic phase has been assigned to hematite.

presence of magnetite (possibly containing Ti), the Mössbauer spectrua of Adirondack and other rocks at Gusev crater are unlike that for any bulk sample of known SNC meteorites assumed to originate from Mars. From our observations, soils seem to be derived from basaltic rocks. First measurements at a hilly region called Columbia hills, show a mineral assemblage with a high proportion of hematite, indicative of the presence of aqueous processes in this region in the past .

The Meridiani Planum landing site is characterized by olivine, jarosite and hematite. The octahedrally coordinated Fe^{3+} material could also be detected. Hematite rich spherules, possibly concretions, were identified. Jarosite, which was identified by the Mössbauer instrument on the MER Opportunity rover and whose presence is consistent with the observations of the other MER instruments, has the equivalent of ~10 wt. % H_2O present in its structure as the OH anion. The mineral is thus direct mineralogical evidence for the presence of water on Mars and for aqueous, likely acid sulfate processes under oxidizing conditions that lead to jarosite precipitation in the distant past. The alteration of basaltic material under sulfate-rich and oxidizing conditions to form jarosite and other phases could have occurred under a wide range of aqueous conditions, including shallow seas and interaction with groundwater.

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Reference:

[1] Squyres S. W. et al. (2003), *J. Geophys. Res.*, 108(E12), 8062, doi:10.1029/2003JE002121.
[2] Klingelhöfer et al. *J. Geophys. Res.*, 108(E12), 8067, doi: 10.1029 /2003 JE 002138, 2003.
[3] Rieder et al. *J. Geophys. Res.*, 108(E12), 8066, doi:10.1029/2003JE002150.
[4] S.W. Squyres et al, *Science*, **305** (2004) 794-799.
[5] R.V. Morris, G. Klingelhöfer et al., *Science*, **305** (2004) 833-836.
[6] G. Klingelhöfer, R.V. Morris et al, *Science* (2004), submitted August 2004-10-04
[7] S.W. Squyres et al., *Science* (2004), submitted August 2004-10-04