# I-1. PROJECT RESEARCHES

## Project 4

# PR4

## Project Research on Advances of Mössbauer Spectroscopy in Isotope-Specific Studies

M. Seto[1]

[1] *Institute for Integrated Radiation and Nuclear Science, Kyoto University*

**OBJECTIVES OF RESEARCH PROJECT**

The primary objective of this research project is to leverage the unique capability of Mössbauer spectroscopy to extract precise information regarding electronic states, magnetic properties, and lattice dynamics for specific isotopes. The main objectives of this project research on advanced isotope-specific investigation on the frontier of materials science by the methods of Mössbauer spectroscopy. Developments of Mössbauer spectroscopy provides more useful and valuable methods in modern materials science.

**MAIN SUBJECTS AND RESULTS OF THIS REPORT**

(R7P4-1, K. Kitase) $^{61}$Ni Mössbauer spectroscopy of Fe-Ni Hofmann-type complex

K. Kitase et al. applied $^{61}$Ni Mössbauer spectroscopy to Fe-Ni Hofmann-type complexes, determining Ni isomer shifts and providing rare coordination data for these polymers.

(R7P4-2, Y. Kobayashi) $^{197}$Au Mössbauer Spectroscopy of Au dithiolene complex, Au(4OEt)

Y. Kobayashi et al. analyzed a neutral radical gold dithiolene complex, finding the Au state in the Au(IV) region rather than Au(III), consistent with DFT calculations.

(R7P4-3, Y. Kobayashi) Mössbauer Spectroscopy of Au Microparticle-supported Catalysts

The group estimated the Debye temperature of Au particles on $TiO_2$ and $SiO_2$ using the recoilless fraction to investigate lattice vibrations in catalytic environments.

(R7P4-6, R. Masuda) Analysis of iron compound nanoparticles in Zeolite

T. Kato et al. identified ferrihydrite nanoparticles in HY-zeolite. At 3 K, these showed super-paramagnetic behavior influenced by synthesis temperature and heat treatment.

(R7P4-8, K. Shinoda) Intensity Tensors of Quadrupole Doublet due to $Fe^{2+}$ Ions of Amphibole

K. Shinoda et al. determined Fe intensity tensors using single-crystal hornblende, facilitating peak separation in complex multi-site minerals by relating γ-ray direction to peak intensities.

(R7P4-9, M. Tabuchi) Understanding of valence and local states for Fe ion in Fe and Ni substituted $Li_2MnO_3$ during charge and discharge runs

M. Tabuchi et al. monitored Fe oxidation in battery electrodes, finding significant valency shifts to tetravalent or pentavalent states during activation, depending on the initial calcination atmosphere.

(R7P4-10, M. Satish-Kumar) Pressure-temperature-fluid evolution and oxygen fugacity changes from calc-silicate granulites at Rundvågshetta, Lützow-Holm Complex, East Antarctica

This study estimated iron oxidation states in garnet from high-temperature rocks, finding $Fe^{3+}$ (73.20%) strongly partitioned, slightly below traditional EPMA-based predictions.

(R7P4-12, K. Yonezu) Experimental Preliminary Approach on the Precipitation Mechanism of Banded Iron Formation (BIF) Part 4: Precipitation Behavior of Iron-bearing Siliceous Deposit Formed at Menengai Geothermal Power Plant, Kenya

K. Yonezu et al. modeled Banded Iron Formation (BIF) mechanisms using scale from the Menengai geothermal plant, characterizing iron speciation in modern siliceous deposits via $^{57}$Fe Mössbauer spectroscopy.

(R7P4-14, S. Ishiwata) Spin and charge ordering in perovskite-type oxides $Ca_{1-x}Bi_xFeO_3$ probed by Mössbauer spectroscopy

The evolution of charge disproportionation (CD) and intermetallic charge transfer (CT) was investigated in high-valence iron oxides. The study explored how Bi-doping and high-pressure synthesis influence the formation of layered charge-ordered structures.

(R7P4-15, Y. Kamihara) Magnetism and Electronic Phase in a H-doped Iron-based Superconductor

Y. Kamihara *et al*. reported the first derivation of the Debye temperature (approx. 400 K) for H-doped SmFeAsO (Sm1111). The study combined SQUID magnetometry with $^{57}$Fe Mössbauer spectroscopy to evaluate the material's magnetic and electronic phases.

(R7P4-16, T. Ohta) Mössbauer Characterization of a Non-Heme $Fe^{III}$–OOH Semiquinonate Intermediate

T. Ohta *et al*. performed characterization of an $Fe^{III}$–OOH semiquinonate intermediate. By fitting the spectra with Lorentzian lines, they obtained precise isomer shift and quadrupole splitting parameters to define the electronic state of the non-heme iron complex.

PR4-1

# $^{61}$Ni Mössbauer spectroscopy of Fe-Ni Hofmann-type complex

K. Kitase[1], T. Chiba[1], Y. Shinohara[1], Y. Miura[1], T. Kitazawa[1, 2], S. Kitao[3], Y. Kobayashi[3], T. Kubota[4], M. Seto[3]

[1]*Department of Chemistry, Faculty of Science, Toho University, Japan*
[2]*Research Centre for Materials with Integrated Properties, Toho University*
[3]*Institute for Integrated Radiation and Nuclear Science, Kyoto University*
[4]*Agency for Health, Safety and Environment, Kyoto University*

**INTRODUCTION:** Spin-crossover (SCO) phenomenon is a reversible spin transition between high-spin and low-spin state. Hofmann-type complex is the one of coordination polymer with bridging ligand [M(CN)$_4$]. In Hofmann-type SCO complex, SCO phenomenon usually occurs in Fe center. $^{57}$Fe Mössbauer spectroscopy is useful tool to investigate SCO complex since the isomer shift (IS), quadrupole splitting (QS), and spectrum shape of $^{57}$Fe Mössbauer spectroscopy are sensitive to the coordination environments or spin state of Fe sites, so $^{57}$Fe Mössbauer spectroscopy is widely used by many researchers to investigate SCO phenomenon of Fe center in many complexes. Hofmann-type complex contains other Mössbauer active nuclei such as Ni, Au. Nevertheless, other type of Mössbauer spectroscopy such as $^{61}$Ni Mössbauer spectroscopy is much less resarched than $^{57}$Fe Mössbauer spectroscopy. Now we synthesized Fe-Ni Hofmann-type complex Fe(Ethyl Isonicotinate)$_2$[Ni(CN)$_4$] (Fe-Ethyl Iso-Ni) and Fe(Allyl Isonicotinate)$_2$[Ni(CN)$_4$] (Fe-Allyl Iso-Ni) and researched the properties of this complex by $^{61}$Ni Mössbauer spectroscopy.

**EXPERIMENTS:** The complex was synthesized using Mohr's salt $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, citric acid, $K_2[Ni(CN)_4] \cdot H_2O$, and pyridine-type ligand ethyl nicotinate or Allyl Isonicotinate. First, Mohr's salt and ligand were dissolved into water. Then aqueous solution of $K_2[Ni(CN)_4]$ was dropped into this solution. The powder sample was obtained as two types of colors, large amount of yellow powder and small amount of orange powder. We can separate yellow powder from orange powder. We confirmed that both types of powder are same formula and isostructural by elemental analysis and powder X-ray diffraction measurement. We charged powder of complexes into a 10 mm diameter holder for $^{61}$Ni Mössbauer spectroscopy.

Table 1. Parameter of $^{61}$Ni Mössbauer spectroscopy

| | δ / mm s$^{-1}$ | FWHM | Peak area | Ni thickness |
|---|---|---|---|---|
| $V_{86}Ni_{14}$ alloy | 0 | 0.95 | 0.0416 | 0.0794 |
| Fe-Ethyl Iso-Ni | -0.06 | 1.21 | 0.0208 | 0.116 |
| Fe-Allyl Iso-Ni | -0.002 | 1.07 | 0.0329 | 0.270 |

**RESULTS:** Fig. 1 shows $^{61}$Ni Mössbauer spectroscopy of $Ni_{86}V_{14}$ alloy, Fe-Ethyl Iso-Ni and Fe-Allyl Iso-Ni. These spectra have singlet peak. The parameter of spectra is shown in table 1. The thickness of the latter two complexes is thicker than the $Ni_{86}V_{14}$ alloy sample. Nevertheless, the absorption intensity of the spectrum of both complexes are smaller than $Ni_{86}V_{14}$ alloy. This result could be explained as Hofmann-type coordination polymers contains organic long ligands and flexible framework. As result, the recoil fraction in both complexes is smaller than that of $Ni_{86}V_{14}$ alloy.

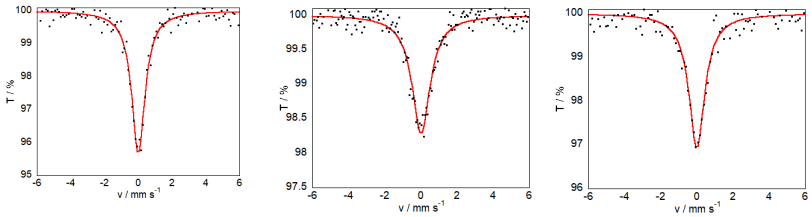


Fig. 1. $^{61}$Ni Mössbauer spectroscopy of $Ni_{86}V_{14}$ alloy (left), Fe-Ethyl Iso-Ni (center) and Fe-Allyl Iso-Ni (right).

**REFERENCE:** K. Kitase, T. Kitazawa, S. Kitao, T. Kubota, Y. Kobayashi, M. Seto, J. Radioanal. Nucl. Chem., 335 (2026) https://doi.org/10.1007/s10967-026-10820-4

PR4-2

# $^{197}$Au Mössbauer Spectroscopy of Au dithiolene complex, Au(4OEt)

Y. Kobayashi[1], S. Yokomori [2], N. Kojima [3], N. Matsushita[3] and M. Seto[1]

[1] *Institute for Integrated Radiation and Nuclear Science, Kyoto University*
[2] *Graduate School of Science and Engineering, Ibaraki University*
[3] *Research Center for Smart Molecules, Rikkyo University*

**INTRODUCTION:** Metal dithiolene complexes are a class of redox-active molecules whose frontier orbitals are composed of metal-centered d orbitals and ligand-based π orbitals. In general, oxidation in these complexes is considered to occur predominantly on the ligand framework, with only a slightly minor change in the formal oxidation state of the metal center. In the gold dithiolene complexes as well, one-electron oxidation from a monoanionic Au(III) complex to a neutral radical species has been interpreted as essentially ligand-centered, because no significant change indicative of partial oxidation at the Au site was detected in the $^{197}$Au Mössbauer spectra,[1] despite theoretical predictions of a small contribution of Au d orbitals to the SOMO. Notably, the neutral radical gold dithiolene complex Au(4OEt), which we recently synthesized, exhibits a canted antiferromagnetic transition below approximately 8 K, raising the possibility that Au-derived spin–orbit coupling contributes to the emergence of this magnetic order. In addition, theoretical calculations have suggested the presence of a small but non-negligible spin density on the Au atom, implying that, in this system, the one-electron oxidation may still be predominantly ligand-centered while being accompanied by a detectable change in the electronic state in the vicinity of the Au nucleus. In order to investigate the valence state of the Au in Au(4OEt), we investigated the $^{197}$Au Mössbauer spectra of this complex system.

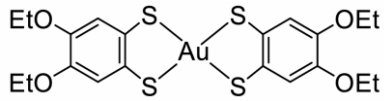


Fig. 1. Molecular structure of Au(4OEt).

**EXPERIMENTS:** The Mössbauer spectroscopic measurement of the 77.34 keV transition in $^{197}$Au was carried out with both source and absorber cooled down to 18 K. A $^{197}$Pt source was obtained by the neutron irradiation for 98% enriched $^{196}$Pt metal by the nuclear reaction of $^{196}$Pt(n,γ)$^{197}$Pt in the Kyoto University Reactor. The isomer shift of Au foil was referenced as 0 mm/s. The spectra was calibrated by using six lines of α-Fe foil at r.t.

**RESULTS:** The isomer shift (δ) and the quadrupole splitting ( Δ ) of Au(4OEt) are δ = 4.50 mm/s, and Δ = 2.76, respectively. On the other hand, δ and Δ of (Ph4P)[Au(4OEt)] are δ = 4.24 mm/s, and Δ = 2.84, respectively. As shown in Fig. 2, these positions are deviated from the δ - Δ correlation belt of Au(III) state and are situated in the area of the Au(IV) state, which is consistent with our DFT calculation.

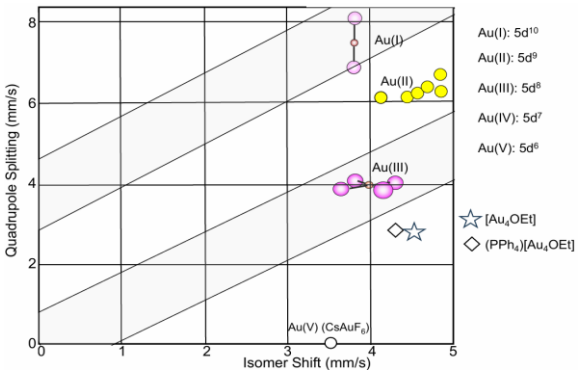


Fig. 2. Quadrupole splitting vs. isomer shift for Au complexes.

**REFERENCES:**

[1] K. Ray et al., *Inorg. Chem*., **42**, 4082 (2003).
[2] M.O. Faltens, D.A. Shirley, *J. Chem. Phys*., **53**, 4249 (1970).

# Mössbauer Spectroscopy of Au Microparticle-supported Catalysts

Y. Kobayashi[1], H. Ohashi[2] and M. Seto[1]

[1]*Institute for Integrated Radiation and Nuclear Science, Kyoto University*
[2]*Faculty of Symbiotic Systems Science, Fukushima University*

**INTRODUCTION:** The recoilless fraction is a parameter that reflects lattice vibrations and provides important knowledge in physics, chemistry, etc. We have succeeded in estimating the Debye temperature not from the absolute amount of spectral absorption area but from its temperature dependence curve and estimated that of some Au compounds [1]. We applied this technique to Mössbauer measurements of Au-supported catalysts and investigated the temperature dependence in more detail.

**EXPERIMENTS:** Prepared samples were Au particles on a $TiO_2$ supporter ($Au/TiO_2$) and Au particles on a $SiO_2$ supporter ($Au/SiO_2$). The Au contents were 2~10wt% in $Au/TiO_2$ and 2wt% in $Au/SiO_2$. The $TiO_2$ or $SiO_2$ powder was put in the $HAuCl_4$ aqueous solution, and $Au(OH)_3$ was precipitated on the powder surface by adjusting the pH while stirring. The obtained powder was dried and calcined at 300°C for 4 hours to prepare the sample. Using KUR, the $^{197}$Pt γ-ray sources for $^{197}$Au Mössbauer measurements were prepared by neutron irradiation to 98%-enriched $^{196}$Pt metal foil. The γ-ray source and samples were cooled to the same temperatures using a helium refrigerator.

**RESULTS:** In the $^{197}$Au Mössbauer spectra of the $Au/TiO_2$ and $Au/SiO_2$ samples, all components showed a single peak like metallic Au. It was found that Au was chemically in the metallic Au state in all samples. Figure 1 shows the temperature dependence of the absorption area, normalized by the absorption area at 20K for each measurement temperature. The Debye temperature of each sample was determined by comparing its temperature dependence with that expected for each Debye temperature. The results showed that the $Au/TiO_2$ 10wt%Au sample, expected to have a large particle size, had a Debye temperature of 159K, similar to that of bulk Au. In contrast, the $Au/TiO_2$ 2.5wt%Au sample, with smaller particle sizes, had a considerably lower Debye temperature of 128K [2]. The Debye temperature of the $Au/SiO_2$ 2wt%Au sample was 168K, and no decrease in Debye temperature was observed compared to $Au/TiO_2$. Lattice vibrations affect molecular adsorption and surface transport, and are therefore thought to be related to catalytic activity.

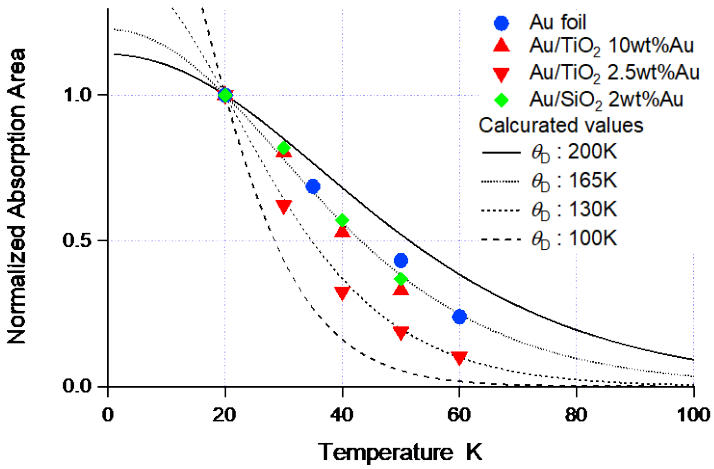


Fig. 1 The temperature dependences of the normalized absorption area obtained from the spectra (markers), together with that calculated using the Debye temperature (lines). The absorption area is normalized to its value at 20 K.

**REFERENCES:**

[1] Yasuhiro kobayashi et al., Interactions, 245, 42 (2024).
[2] Yasuhiro kobayashi et al., Interactions, 247, 19 (2026).

# $^{197}$Au Mössbauer Spectra for Frozen Aqueous Solution of Gold(III) complex

H. Ohashi[1], M. Fujimoto[1], S. Kuwahara[2], A. Yoshizawa[2], A. Nakayama[2], T. Ishida[2], Y. Kobayashi[4], S. Kitao[4]

[1] *Faculty of Symbiotic Systems Science, Fukushima University*
[2] *Faculty of Science, Kyushu University*
[3] *Research Center for Artificial Photosynthesis, Osaka Metropolitan University*
[4] *Institute for Integrated Radiation and Nuclear Science, Kyoto University*

**INTRODUCTION:** As shown in a book published in 1976 [1], the distribution curves and phase diagram for the hydrolysis of $AuCl_4^-$ complex was determined using potentiometry. Recently, ligand exchange for $AuCl_4^-$ complex has been directly observed using the XAFS method. We have studied in order to observe this exchange using XAFS and other methods. $^{197}$Au Mössbauer spectroscopy is widely known to be sensitive to ligand exchange of gold(III) ions. It is able to distinguish between oxygen and chlorine ligands. However, Mössbauer spectroscopy is considered extremely difficult to measure in aqueous solutions due to recoil phenomena. On the other hand, since $^{197}$Au Mössbauer spectroscopy is performed at extremely low temperatures (approximately 20 K), it has been suggested that the aqueous solution may freeze and change its state. We hypothesized that we could achieve measurement by combining these two drawbacks. We conducted research with the aim of obtaining spectra of gold(III) aqueous solutions.

**EXPERIMENTS:** Aqueous solutions of $AuCl_4^-$ complex were prepared at various concentrations. The pH were kept below 1 or above 13. To prevent uneven distribution of the aqueous solution in the cell and subsequent freezing, each solution was rapidly and completely frozen using liquid nitrogen before being placed in the Mössbauer apparatus.

$^{197}$Au Mössbauer spectra were measured at Kyoto University Research Institute of Nuclear Science. The $^{197}$Pt isotope ($T_{1/2}$ = 18.3 h), γ-ray source feeding the 77.3 keV Mössbauer transition of $^{197}$Au, was prepared by neutron irradiation of isotopically enriched $^{196}$Pt metal at the Kyoto University Reactor. The measurement temperature was around 20 K, and the measurement was performed by the transmission method.

**RESULTS:** Figure 1 shows $^{197}$Au Mössbauer spectra for each $AuCl_4^-$ complex solution frozen. It was found that the sufficient ligand changes of $AuCl_4^-$ complex occurred and that it was preserved even in a frozen state.

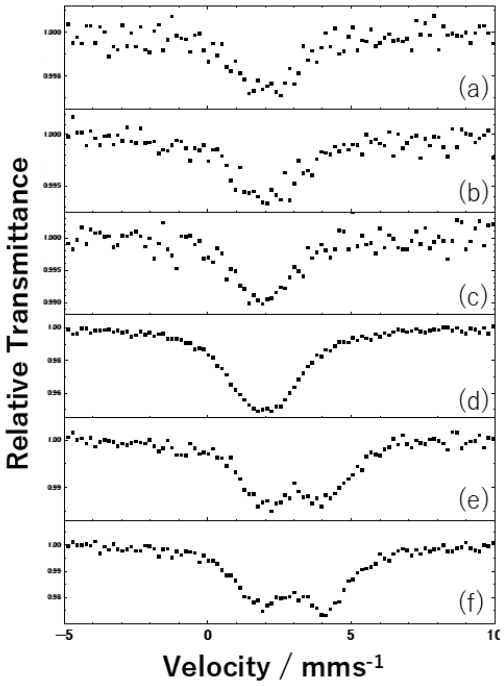


Fig. 1. $^{197}$Au Mössbauer spectra for $HAuCl_4$aq solution frozen. (a) 200 mM, pH<1, (b) 500 mM, pH<1, (c) 1000 mM, pH<1, (d) $HAuCl_4 \cdot 4H_2O$ solid, (e) 250 mM, pH>13, (f) 500 mM, pH>13.

**REFERENCE:**

[1] C. F. Baes, Jr. and R. E. Mesmer. "The Hydrolysis of Cations", 279-286 (1976).

**PR4-5**

# Analysis of iron compound nanoparticles in Zeolite

T. Kato[1], R. Masuda[1], Y. Suzuki[1], and S. Kitao[2]

[1] *Graduate school of Science and Technology, Hirosaki University*
[2] *Institute for Integrated Radiation and Nuclear Science, Kyoto University*

**INTRODUCTION:** Zeolites are a series of porous materials whose general formula is $M_{1/n}(AlO_2)(SiO_2)_x \cdot yH_2O$ (M: an element with valence n+). They adsorb various substances within their pores and are used for deodorization and water purification. They are also used as hosts for the formation of nanoparticles. When nanoparticles are synthesized in zeolites, element-selective measurements are extremely effective for analyzing the nanoparticles, because the nanoparticles are indivisible from zeolites. Therefore, Mössbauer spectroscopy has been employed for the analysis of iron-compound nanoparticles in zeolites and elucidated that a variety of compounds are formed depending on the type of zeolites and the preparation methods [1]. Here, we studied the properties of nanoparticles synthesized by a chemical exchange method.

**EXPERIMENTS:** The sample nanoparticles were prepared using the powders of HY-zeolite $H(AlO_2)(SiO_2)_{7.35}$ and an aqueous solution of ferric chloride tetrahydrate $FeCl_2 \cdot 4H_2O$. The ion-exchange was performed at 50 ℃ or 70 ℃. The zeolite powders including nanoparticles were dried in the air and a part of them were heat-treated in the air at 400 ℃. Thus, we have four samples depending on the synthesis process: exchange temperature (50 ℃ or 70 ℃) and heat-treat (none or 400 ℃). The Mössbauer spectra of the samples were measured at room temperature in the air or at 3 K in the vacuum.

**RESULTS:** All the Mössbauer spectra at room temperature showed doublet pattern with the isomer shift of ~ 0.35 mm/s (relative to metal iron) and quadrupole splitting of ~ 0.9 mm/s. On the other hand, the spectra at 3 K were analyzed with one quadrupole doublet and one magnetic sextet. An example of the spectra at 3 K is shown in Fig. 1. There spectra agree that the nanoparticles were ferrihydrite $mFe_2O_3 \cdot nH_2O$ and showed super-paramagnetic behavior partially due to the small particle size even at 3 K [2]. The size of nanoparticles depends on the synthesis process: it would be larger at the temperature of ion-exchange process $T_{exchange}$ = 50 ℃ or with the heat treatment.

**REFERENCES:**

[1] Frank J. Berry, in *Mössbauer spectroscopy Applied to Inorganic Chemistry* vol. 3 ed. by G. J. Long (Plenum Press, New York, 1989), Chap. 7, 331-369.
[2] X. Wang *et al.*, Environ. Sci.: Nano, **3** (2016) 190-202.

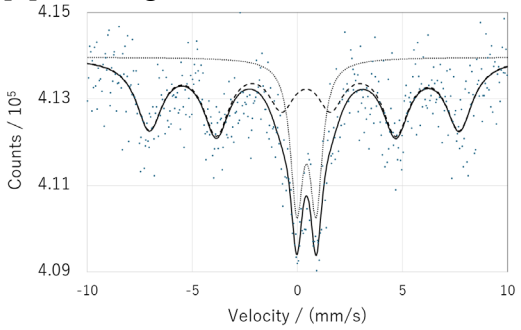


Fig. 1 The Mössbauer spectrum of iron nanoparticles with $T_{exchange}$ = 50 ℃ without heat treatment. The spectrum was measured at 3 K.

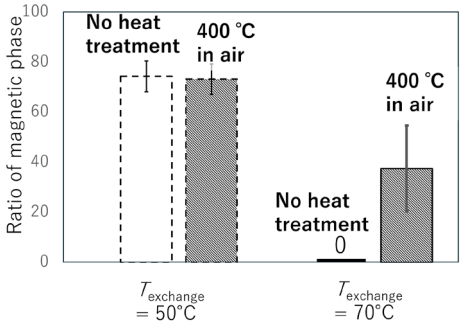


Fig. 2 The Ratio of magnetic components for each samples.

# Intensity Tensors of Quadrupole Doublet due to $Fe^{2+}$ Ions ofAmphibole

K. Shinoda[1], M. Tanaka[1], Y. Kobayashi[2]

[1]*Department of Geosciences, Graduate School of Science, Osaka Metropolitan University*
[2]*Institute for Integrated Radiation and Nuclear Science, Kyoto University*

**INTRODUCTION:** A peak intensity ($I$) of quadrupole doublets of Mössbauer spectra is defined as $I_h/(I_h+I_l)$, where $I_l$ and $I_h$ are the lower and higher peak's intensity of quadrupole doublets, respectively [1]. The peak intensity of Mössbauer spectra of single crystal varies depending on the direction of γ-ray relative to crystal axes. The intensity tensor relates the direction of γ-ray to the peak intensity. This indicates that peak intensity can be calculated from intensity tensor and incident γ-ray direction. Amphibole is a multi-sites solid solution mineral that includes four *M*-sites. Thus, single crystal of amphibole shows complex Mössbauer spectra where multiple quadrupole doublets are overlapping. Peak separation of such a complex Mössbauer spectra is difficult, because it often results in multiple solutions of peak separation. Although intensity tensors due to Fe ions at *M*-sites is essential properties to select an appropriate fitting result from multiple solutions, intensity tensors due to Fe ions in amphibole are unknown. We reported an intensity tensor of Mössbauer quadrupole doublet due to $Fe^{3+}$ at *M* site of oxyhornblende [2]. In this study, we report Mössbauer spectra of amphibole including $Fe^{2+}$ and $Fe^{3+}$ ions, its peak separation, and an intensity tensor due to $Fe^{2+}$ and $Fe^{3+}$of amphibole.

**EXPERIMENTS:** A single crystal of hornblende from unknown occurrence was used for this study. Two crystallographically oriented thin sections perpendicular to ***b***-axis were prepared by measuring X-ray diffraction methods. Ten Mössbauer spectra of oriented thin sections and one powder spectrum were measured. Mössbauer measurements were carried out in transmission mode on a constant acceleration spectrometer with an Si-PIN semiconductor detector (XR-100CR, AMPTEK Inc.) and multi-channel analyzer of 1024 channels. A 3.7GBq $^{57}$Co/Rh of 4mmϕ in diameter was used as γ-ray source. An $^{57}$Fe-enriched α-iron foil was used as velocity calibrant. Two symmetric spectra were folded, and velocity range was ± 4mm/s. Mosswinn program was used for peak separation.

**RESULTS:** Fig.1 shows Mössbauer spectrum of amphibole single crystal under γ-ray //***b***-axis and peak separation by fixing isomer shift, peak width and quadrupole doublet obtained from powder spectrum. Doublet peak assignments of Bancroft [3] were adopted. In this experiment, thin sections normal to the ***c***-axis were not completed because of perfect cleavage normal to the ***c***-axis of amphibole. Thus, directions of incident γ-ray relative to the crystal axes were limited to directions around the ***b***-axis. As the result, spectra normal to the ***b***-axis were not measured, and reliable intensity tensors of four quadrupole doublets were not obtained. To compensate uncompleted direction of incident γ-ray, we must measure Mössbauer spectra normal to the ***a***-axis.

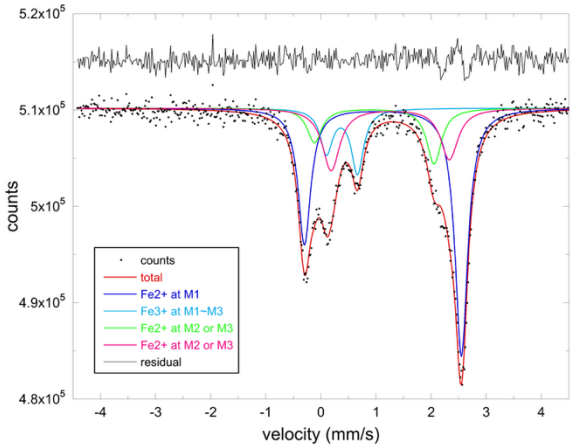


Fig. 1. Mössbauer spectrum of amphibole single crystal under γ-ray parallel to the ***b***-axis and a peak separation of four QS doublets.

**REFERENCES:**

[1] R. Zimmermann (1975) Nucl. Instr. and Meth. **128** 537-543
[2] K. Shinoda and Y. Kobayashi, KURNS Progress Report 2024 (PR9-6) (2025)
[3] G. M. Bancroft and J. R. Brown., Am. Mineral., **60** (1975) 265-272

# Understanding of valence and local states for Fe ion in Fe and Ni substituted $Li_2MnO_3$ during charge and discharge runs

M. Tabuchi[1]and Y. Kobayashi[2],
[1]*National Institute of Advanced Industrial Science and Technology (AIST)*
[2]*Institute for Integrated Radiation and Nuclear Science, Kyoto University*

**INTRODUCTION:** Large scale lithium-ion battery (LIB) is needed for EV and ESS applications. Low-cost positive electrode material is necessary for these applications. Therefore, Fe and Ni substituted $Li_2MnO_3$ is developed for above object [1, 2]. In this report, two $Li_{1+x}(Fe_{0.2}Ni_{0.1}Mn_{0.7})_{1-x}O_2$ ($0<x<1/3$, FNM217) samples were selected to check the change in valence state of Fe ion using $^{57}$Fe Mössbauer spectroscopy during the electrochemical activation process.

**EXPERIMENTS:** The sample was prepared by coprecipitation-calcination method [2]. Final calcination atmospheres was selected to air (217A) or $N_2$ (217N) at 850℃ for 10h. After washing with distilled water, the two samples were prepared for characterization. The electrochemical activation process was constructed as follows; The charged capacity increased from 80 mAh/g (1st) by 40 mAh/g step until 200 mAh/g (4th) after discharged to 2.0 V for Li/sample cell. At 5th cycle, the cell charged to 4.8 V and then discharged to 2.0 V to finish activation process. The active material was sealed in Al-laminate sheet for $^{57}$Fe Mössbauer measurement. The isomer shift (IS) value was calculated using $\alpha$-Fe foil. The Fe valency was examined for first charged samples (217A-1c and 217N-1c) as well as above as-prepared ones (217A and 217N).

**RESULTS:** XRD data showed that all samples were single phase of monoclinic $Li_2MnO_3$-type structure. $^{57}$Fe Mössbauer data fitted by two symmetric doublets with different isomer shits (IS) for 217A. The IS values were +0.3561 (19) mm/s for main (89.6%) component and -0.042 (9) mm/s for minor (10.4%) one. Former and latter components can be assigned as tri and tetravalent Fe ones, respectively [3]. On the other hand, the spectrum for 217N was fitted by a symmetric doublet (IS=+0.3 mm/s), indicating that 217N contains only trivalent Fe. Therefore, Fe valency was reduced by $N_2$ calcination.

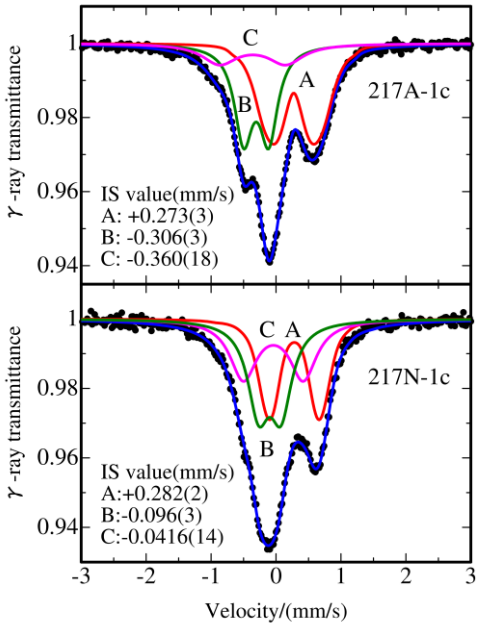


Fig. 1 $^{57}$Fe Mössbauer spectra for 217A-1c and 217N-1c samples.

Next, Fe valency for first charged samples were checked. As shown in Fig. 1, three symmetric doublets needed to fit each spectrum. The IS value for A component for 217A-1c was like that for 217N-1c, whereas those values of B and C components were different from each other. From the IS values of A components, they can be assigned as trivalent Fe ion. The IS values for other B and C components of 217A-1c were highly negative ones (-0.3 mm/s), where those of 217N-1c were nearly zero (-0.1 mm/s). The B and C components of 217A-1c and 217N-1c can be assigned to pentavalent [4] and tetravalent [3] Fe states, respectively. The difference may originate from the difference in initial Fe valency for 217A and 217N, as mentioned before.

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# Pressure-temperature-fluid evolution and oxygen fugacity changes from calc-silicate granulites at Rundvågshetta, Lützow-Holm Complex, EastAntarctica

M. Satish-Kumar[1], A. Koyomi [2], K. Shinoda [3], and Y. Kobayashi[4]

[1] *Department of Geology, Faculty of Science, Niigata University*
[2] *Graduate School of Science and Technology, Niigata University*
[3] *A Department of Geosciences, Graduate School of Science and School of Science, Osaka Metropolitan University*
[4] *Institute for Integrated Radiation and Nuclear Science, Kyoto University*

**INTRODUCTION:** Garnet is a very common mineral in the Earth's crust. It has a peculiar crystal structure and solid solution series which can incorporate $Fe^{2+}$ and $Fe^{3+}$ in varying conditions of its formation. In this study we attempted to estimate the $Fe^{2+}/Fe^{3+}$ ratio of grossular andradite garnet from a natural sample collected from Rundvagshetta in East Antarctica using messbauer spectroscopy. This locality is famous for its occurrence of ultra-high temperature metamorphic rocks, which are supposed to have attained a peak metamorphic temperature condition of >900 $^{o}$C. The sample studies is a garnet bearing calc-silicate rock having a mineral assemblage of scapolite/plagioclase + clinopy-roxene + garnet.

**EXPERIMENTS:** Petrographic observation of the sample revealed 3 types of garnets: i. garnet exhibiting a porphyroblastic texture with a diameter of approximately 2 mm, ii. garnet with an equigran-ular texture with a diameter of approximately 0.3–0.6 mm, and iii. garnet crystallizing in a coronal pattern with a thickness of approximately 0.05–0.2 mm. Of these, type-iii garnet showed the strongest grossular-andradite compositional variations when measured using SEM-EDS. Regardless of the presence or absence of compositional change, we prepared double polished thin slabs of 10 samples to perform local Mössbauer spectral measurements. Measurements were carried out following the previous studies [1,2]

**RESULTS:** As shown in Fig. 1, Mössbauer spectra of garnet were fitted with two doublets for $Fe^{2+}$ and $Fe^{3+}$. The garnet grains in scapolite-rich domain contain on average 73.20 % $Fe^{3+}$, which is approximately 6 % lower than that predicted from the charge-balance calculation of Droop (1987) based on EPMA results. Clinopyroxene grains in scapolite-rich domain show only one doublet of $Fe^{2+}$, indicating all iron exist as ferrous iron. In the garnet-absent domain, clinopyroxene spectra were fit with two doublets for $Fe^{2+}$ and $Fe^{3+}$, and, $Fe^{3+}$ content is limited to 5.83 %. Although the clinopyroxene in scapolite-rich domain may contain few percent of $Fe^{3+}$ within an analytical uncertainty, these results suggest that $Fe^{3+}$ is strongly partitioned into garnet, and the esseneite content of clinopyroxene is only a few percent.

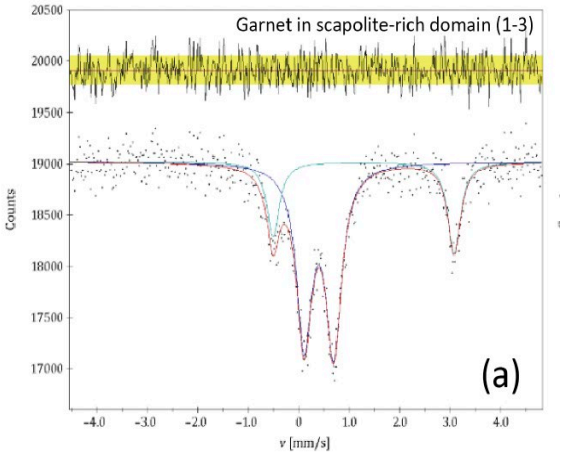


Fig. 1 Representative Mossbauer spectra of garnet

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# Experimental Preliminary Approach on the Precipitation Mechanism of Banded Iron Formation (BIF) Part 4: Precipitation Behavior of Iron-bearing Siliceous Deposit Formed at Menengai Geothermal Power Plant, Kenya

K. Yonezu[1], A. L. Ochieng[1, 2], S. Juhri[1], Y. Kobayashi[3] and T. Yokoyama[4].

[1]*Department of Earth Resources Engineering, Faculty of Engineering, Kyushu University*
[2]*Geothermal Development Company, Kenya*
[3]*Institute for Integrated Radiation and Nuclear Science, Kyoto University*
[4]*Department of Chemistry, Faculty of Sciences, Kyushu University*

**INTRODUCTION:** Banded Iron Formation (BIF) is chemically precipitated sedimentary rock at Precambrian age. Current iron resource widely used in our industries largely depends on BIF. Commonly the hydro-thermal water, anoxic water was mixed with oxic seawater (e.g., [1]). However, the formation mechanism of BIF was not yet clarified. In order to approach the formation mechanism, we have done ambient temperature batch experiments, elevated temperature batch experiments and the experiments using natural system (e.g., [2]). Therefore, this study aims to more understand the formation mechanism of BIF and characterize iron-bearing siliceous deposits in terms of iron speciation from Menengai geothermal power plant in Kenya.

**EXPERIMENTS:** Several scale samples were collected from multiple locations of the Menengai geothermal power plant, including separators, atmospheric silencers, reinjection wells, brine lines and cooling towers. The samples were analyzed by XRD, XRF, petrograph and NMR ($^{29}$Si and $^{27}$Al) prior to Mössbauer analysis.

**RESULTS:** As shown in Fig. 1, $^{57}$Fe Mössbauer spectrum of iron bearing siliceous deposits collected from Menengai geothermal power plant suggested that Fe has 3 different species, $Fe^{3+}$, magnetite and amorphous phases. The ratios of those 3 species are 33.7 %, 22.7 % and 43.5 %, respectively. Still we need to combine the results from $^{27}$Al and $^{29}$Si NMR for identification of possible iron bearing silicate. The results analyzed included the sample formed under both anoxic and oxic conditions. Most of oxix samples do not contain $Fe^{2+}$, while the samples collected from separator or silencer is likely to have $Fe^{2+}$ by the relatively reduced environment. The information is helpful to understand the formation mechanism of siliceous deposits and further of BIF. In addition, the knowledge can be expanded to the mitigation method for the silica scale formation in geothermal industry.

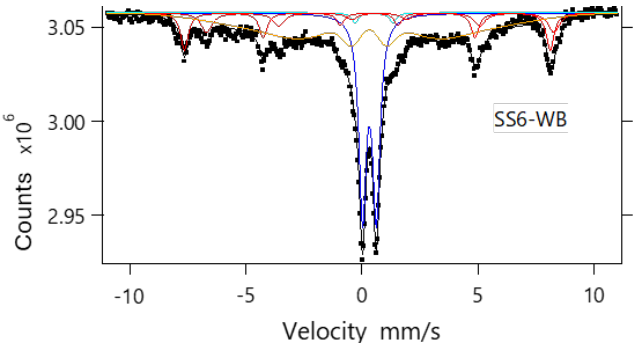


Fig. 1. An example of $^{57}$Fe Mössbauer spectrum of iron bearing siliceous deposits collected from Menengai geothermal power plant.

**REFERENCES:**

[1] T. Otake and Y. Otomo, Shi-gen-Chishitsu, **71** (2021) 57-73.
[2] E. Wanyonyi *et al.,* Geothermics **117** (2024), 102871

# Spin and charge ordering in perovskite-type oxides $Ca_{1-x}Bi_xFeO_3$ probed by Mössbauer spectroscopy

Z. Ma[1], H. Takahashi[1], S. Kitao[2], M. Seto[2], S. Ishiwata[1]

[1] *Graduate school of engineering science, Osaka University*
[2] *Institute for Integrated Radiation and Nuclear Science, Kyoto University*

**INTRODUCTION:** Perovskite-type iron oxides with anomalously high valence have attracted wide attention due to the versatile magnetic properties. The orthorhombic perovskite $CaFeO_3$ with $Fe^{4+}$ exhibits a G-type spiral spin ordering and charge disproportionation (CD) described as $2Fe^{4+} \rightarrow Fe^{3+}+Fe^{5+}$ [1]. Recent research revealed that $Ca_{0.5}Bi_{0.5}FeO_3$ with $Fe^{3.5+}$ exhibits a CD with a $Fe^{3+}/Fe^{4.5+}$ layered charge ordered (CO) structure and intermetallic charge transfer (CT) described as $3Bi^{3+}+4Fe^{4.5+} \rightarrow 3Bi^{5+}+4Fe^{3+}$ [2,3]. The CD and localized electrons in $CaFeO_3$ facilities the emergence of CO phases upon doping. Additionally, the hybridization in Bi-O bonds potentially affects the formation of CO phases. In this study, we focused on $CaFeO_3$, which exhibits more localized electrons and $Ca_{1-x}Bi_xFeO_3$ was synthesized systematically, in order to explore the evolution of CO phases and CT.

**EXPERIMENTS:** Polycrystalline samples of $Ca_{1-x}Bi_xFeO_3$ were synthesized by annealing the nominal $Ca_{1-x}Bi_xFeO_{3-\delta}$ samples with oxidizing agent ($KClO_4$) at 1000 °C and 8 GPa for 1h in a cubic-anvil-type high-pressure apparatus. The $^{57}Fe$ Mössbauer spectra were measured with a $^{57}Co$ source in Rh. The velocity was calibrated with $\alpha$-Fe.

**RESULTS:** As shown in Figure 1(a) and (b), the Mössbauer spectra for $Ca_{0.8}Bi_{0.2}FeO_3$ and $Ca_{0.67}Bi_{0.33}FeO_3$ at 300 K exhibits clear singlets, indicating few oxygen vacancies. Below the phase transition temperature, both samples show two sextets corresponding to $Fe^{3+}$ and $Fe^{5+}$, indicating onset of CD, $2Fe^{4+} \rightarrow Fe^{3+} + Fe^{5+}$. The relative areas of $Fe^{3+}$ and $Fe^{5+}$ are consisted with the nominal Fe valence at room temperature, revealing that no CT occurs during phase transition. Interestingly, unlike $Ca_{0.8}Bi_{0.2}FeO_3$, the $Ca_{0.67}Bi_{0.33}FeO_3$ sample shows an intermediate metastable phase at 190 K, where the $Fe^{3+}$ sites are spin-ordered while the $Fe^{5+}$ sites remain spin-disordered. The discrepancy suggests that the Bi doping level plays a significant role in stabilizing phases with novel spin and charge ordering. By combing the Mössbauer spectra with the structural, magnetic and electronic characterizations, we established a comprehensive phase diagram for $Ca_{1-x}Bi_xFeO_3$. This demonstrates that the hybridization of Bi-O bonds facilitates versatile phases with extraordinary magnetic and order ordering.

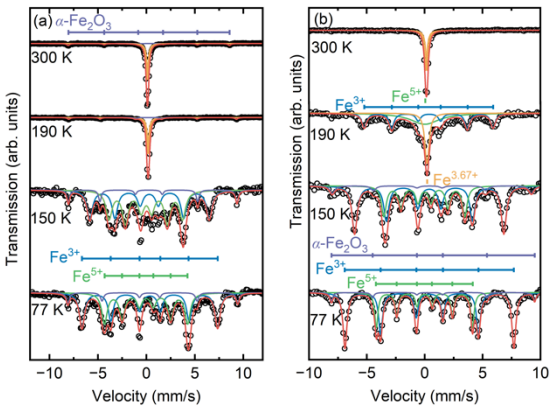


Fig. 1. The Mössbauer spectra for (a) $Ca_{0.8}Bi_{0.2}FeO_3$ and (b) $Ca_{0.67}Bi_{0.33}FeO_3$ at various temperatures.

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# Research on Magnetism and Electronic Phase in a H-doped Iron-based Superconductor IV

Y. Kamihara[1], H. He[1], Y. Kobayashi[2], S. Kitao[2], and M. Seto[2]

[1] *Department of Applied Physics and Physico-Informatics, Faculty of Science and Technology, Keio University*

[2] *Institute for Integrated Radiation and Nuclear Science, Kyoto University*

**INTRODUCTION:** The research in 2022-2024. The magnetic moment of a polycrystalline H-doped SmFeAsO (Sm1111) [1-6] was measured using SQUID magnetometer (Quantum Design MPMS). The magnetic critical-current-density ($J_c$) of the Sm1111 is 22.3 kA/cm$^2$. The lattice constants and volume as a function of H-doped Sm1111 samples. The F contents are determined for the Sm1111 sample using Volume Vegard's rule. Paramagnetic $^{57}$Fe Mössbauer spectra at $T$ = 4.2, 10, 20, 50, 77, 300 K were demonstrated for H-doped Sm1111 with ~10 at.% H contents.

**EXPERIMENTS:** The phase purity, lattice constants, and crystal structure of the sintered powders were examined by powder x-ray diffraction (XRD) Rigaku Rint2500 using Cu K alpha radiation from a rotating anode. The magnetic moment (M) of polycrystalline H-doped Sm1111 was measured using a SQUID magnetometer (Quantum Design MPMS) at several temperatures (T) and magnetic fields (H). The 57Fe Mössbauer spectroscopy was performed using 14.4 keV Gammna-rays from a 57Co source. The Mössbauer spectra of H-doped Sm1111 were analyzed using the code Mosswinn [7].

**RESULTS:** Figure 1 exhibits Isomer shift as a function of temperature for the Sm1111 polycrystalline sample. The obtained isomer shift (δ) values, which were obtained at each $T$, were used along with the theoretical formula to refine the Isomer shift-$T$ plot. We derived and refined the Debye temperature ~400 K for the H-doped Sm1111. This value is first report for H-doped Sm1111.[8]

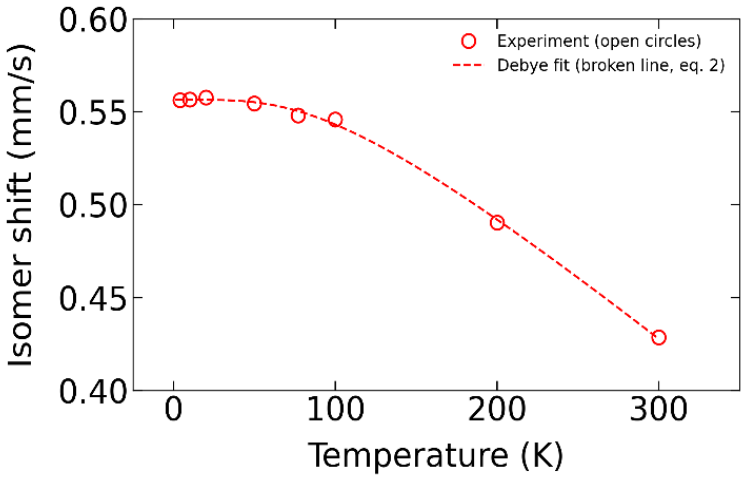


Fig. 1. Isomer shift as a function temperature for the H-doped Sm1111.

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[8] H. Hao, et al., to be submitted

# Mössbauer Spectroscopic Characterization of a Non-Heme $Fe^{III}$–OOH Semiquinonate Intermediate

T. Ohta[1], R. Masui[1], T. Yoshikawa[1], Y. Kobayashi[2], S. Kitao[2], and M. Seto[2]

[1]*Department of Applied Chemistry, Sanyo-Onoda City University, Yamaguchi 756-0884, Japan*
[2]*Institute for Integrated Radiation and Nuclear Science, Kyoto University, Osaka 590-0494, Japan*

**INTRODUCTION:** Studies on transient organic radicals in catalysis attracts significant interests due to the functional importance of such species in the active site of metalloproteins. In this study, an $Fe^{III}$–OOH semiquinonate intermediate, generated via reaction of ferric hydroquinone complex with potassium superoxide under cryogenic conditions, was characterized by Mössbauer spectroscopy.

**EXPERIMENTS:** Conventional transmission $^{57}$Fe Mössbauer spectra were recorded using $^{57}$Co in a Rh matrix as a γ-ray source at 4.2 K. The Doppler velocity and isomer shift ($\delta_{Fe}$) for $^{57}$Fe Mössbauer spectra were calibrated using the sextet of an α-Fe foil. The recorded spectra were fitted using Lorentzian lines to obtain Mössbauer parameters, i.e., $\delta_{Fe}$ and quadrupole splitting ($\Delta E_Q$).

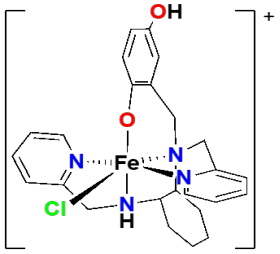


Fig. 1. Fe_HqBPCA (**1**)

**RESULTS:** The characterization of complex **1**, **Int-1**, and **Int-2** was performed using Mössbauer spectroscopy. The zero-field Mössbauer spectra of $^{57}$Fe-enriched samples were measured at 4.2 K. The Mössbauer spectrum of complex **1** exhibits two distinct species with a quadrupole doublet characterized by an isomer shift $\delta_{Fe}$ of 0.51 $mms^{-1}$ and a quadrupole splitting $\Delta E_q$ of 1.24 $mms^{-1}$ and a quadrupole doublet characterized by an isomer shift $\delta_{Fe}$ of 1.38 $mms^{-1}$ and a quadrupole splitting $\Delta E_q$ of 3.37 $mms^{-1}$. The former parameters are characteristic of a ferric species with $S = 5/2$, whereas the later are typical of a ferrous species with $S = 2$. These observations suggest that complex **1** may undergo valence tautomerism between ferric-hydroquinone and ferrous-semiqunonate forms under measurement conditions. The major component of **Int-1** demonstrates Mössbauer quadrupole doublet characterized by an isomer shift $\delta_{Fe}$ of 0.50 $mms^{-1}$ and a quadrupole splitting $\Delta E_q$ of 0.78 $mms^{-1}$, parameters that are characteristic of ferric species with $S = 5/2$. These observations indicate that the $Fe^{III}$ oxidation state of **1** remains unchanged upon reaction with superoxide. It is therefore plausible that antiparallel coupling of semiquinonate radical with the $Fe^{III}$ center ($S = 5/2$) yields a total spin state of $S = 2$, rendering **Int-1** EPR silent under X-band excitation. The Mössbauer spectrum of **Int-2** reveals involvement of $Fe^{III}$ center ($S = 5/2$), as evidenced by an isomer shift $\delta_{Fe}$ of 0.47 $mms^{-1}$ and a quadrupole splitting $\Delta E_q$ of 0.72 $mms^{-1}$.

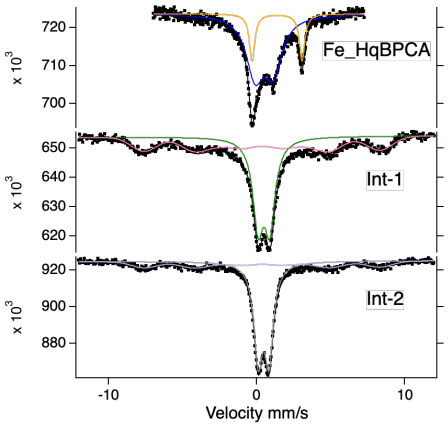


Fig. 2. Mössbauer spectra of **1**, **Int-1**, and **Int-2**.