

特別講演

特別講演 1

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特別講演 2

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"Radiogeochemistry: 1936-1986"

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ABSTRACT

The history of radiochemistry is analogous to that of organic chemistry. At the beginning of the 19th century, it was considered that inorganic and organic substances were sharply differentiated by the circumstance that, whereas the former might be prepared by artificial means, the latter could only be formed in the bodies of animals and plants as the result of vital force. In 1928, Freiderich Wöhler (1800-1882) showed, however, that urea, preeminently a product of animal metabolism, could be prepared synthetically from inorganic materials. A spectacular advancement of organic chemistry then followed throughout the 19th century.

At the beginning of the 20th century, chemists believed that the natural radioactivity was created somewhere in the Universe long before the earth came into existence and the radioactive elements could not be prepared by artificial means. In 1934, Irène Joliot-Curie (1896-1956) and Frédéric Joliot (1900-1958) showed, however, that radioactive isotopes could be prepared artificially. A spectacular advancement of radiochemistry then followed the discovery of artificial radioactivity.

I was a student in 1934, but two years later, I had the good fortune of attending a special lecture given by Dr. F. W. Aston on

the subject of isotopes which was held at the Imperial University of Tokyo on June 12, 1936. I became very much interested in some of the ideas expressed by Dr. Aston and the fact that I spent the next 50 years of my life doing research in the field of studies which may best be described as Radio-Geo-Chemistry is no doubt due to my encounter with Dr. Aston in 1936.

I learned from Dr. Aston's book "Mass-Spectra and Isotopes" (Edward Arnold & Co., London, 1933) that the history of Radio-chemistry can be traced back another 50 years, to the time when Sir William Crookes (1832-1919) in his Presidential Address to the Chemical Section of the British Association which was held at Birmingham, England, in September 1886, expressed his concept of isotopes. He stated: "Is it not possible, or even feasible, that these heavier and lighter atoms may have been in some cases subsequently sorted out by a process resembling chemical fractionation? This sorting out may have taken place in part while atomic matter was condensing from the primal state of intense ignition, but also it may have been partly effected in geological ages by successive solutions and reprecipitations of the various earths." It seems that what Crookes had in mind exactly one hundred years ago was a long-range prediction of not only the discovery of isotopes, but also of the concept of isotopic heterogeneity or isotopic anomalies in the early solar system, which was to become the focus of intense investigation by many researchers in the field of astronomy, physics, chemistry and geology during the second half of the 20th century.

During my early days at the University of Tokyo, I spent much of my time doing research on radioactive disequilibria among naturally-occurring radionuclides in the hydrosphere (for example, Kuroda, Bull. Chem. Soc. Japan 21, 52, 58, 1948; 34, 43, 149, 203, 1949). These studies eventually led to the theory concerning the Oklo phenomenon (Kuroda, J. Chem. Phys. 25, 781, 1956). I also became interested in the behaviors of fission products from nuclear weapons tests in the atmosphere and these studies led to the research concerning the existence of ^{244}Pu in the early solar system (Kuroda, Nature 187, 36, 1960; Rowe and Kuroda, J. Geophys. Res. 70, 709, 1965). During the 1970's, I spent most of my time and energy attempting to develop a unified theory of the isotopic anomalies in the solar system (see for example, Kuroda, "The Origin of the Chemical Elements and the Oklo Phenomenon", Springer-Verlag, Berlin, Heidelberg, New York, 1982). During the past few years, we have been concentrating on the study of alpha-recoil effects of uranium (for example, Sheng and Kuroda, Nature 312, 535, 1984; Radiochim. Acta 37, 93, 1984; in press 1986; J. Radioanalyt. Nucl. Chem. 92, 315, 1985; Geochem. J., in press, 1986). Results from these studies will be reviewed in this report, together with the latest results from the studies which are currently being carried out in our laboratories.

^{57}Fe Mössbauer Spectroscopic Studies of
Electronically Labile Transition Metal Compounds

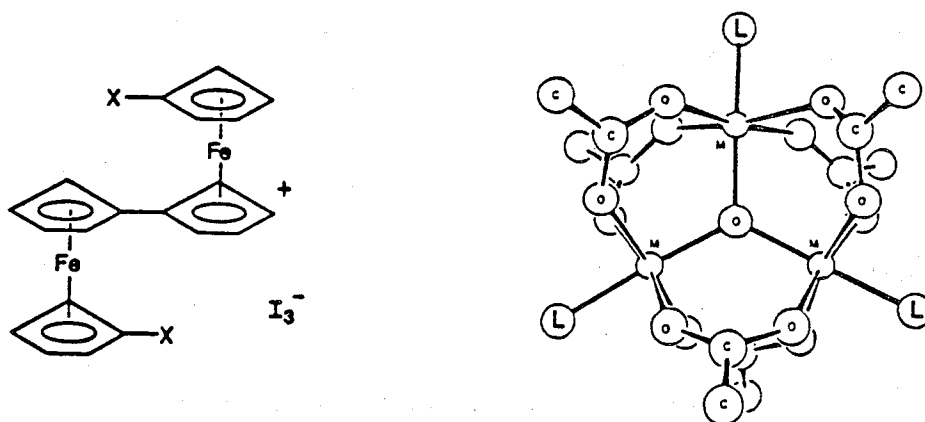
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ABSTRACT

^{57}Fe Mössbauer spectroscopy is useful in studying the fluctuations of valence electron density in electronically labile compounds such as mixed-valence $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ complexes and Fe^{II} and Fe^{III} spin-crossover complexes. Electronically labile complexes have an electronic degeneracy or near-degeneracy, which results in a strong coupling of the electronic coordinates to certain vibrational coordinates. A double-well potential-energy diagram results. In the case of the mixed-valence complex the molecule can interconvert between the two different vibronic states $\text{Fe}_A^{\text{II}}\text{Fe}_B^{\text{III}}$ and $\text{Fe}_A^{\text{III}}\text{Fe}_B^{\text{II}}$. The spin-crossover complex can interconvert between low- and high-spin states. As a result of this vibronic coupling, electronically labile complexes are very sensitive to environmental effects. The presence of a solvate molecule can dramatically rate of interconversion. Intermolecular interactions in the solid state lead to cooperativity

in the dynamics and phase transitions are seen.

Mössbauer spectroscopic data form an important part of the data base on mixed-valence iron compounds such as the two types which are pictured below:



In the case of the mixed-valence biferrocenes (on left side) the molecule has present both Fe^{II} and Fe^{III} ions. Mössbauer spectroscopy can be used to study the intramolecular electron transfer from the Fe^{II} to the Fe^{III} ion in the cation. In the solid state there is a dramatic dependence of the rate of electron transfer on the biferrocene substituent X as well as in changes in the counteranion. The X = Cl triiodide compound is valence-localized on the ⁵⁷Fe Mössbauer time scale at 340K, as indicated by the appearance of both Fe^{II} and Fe^{III} quadrupole-split doublets in the Mössbauer spectrum. This slow rate of electron transfer is rationalized by the results of the X-ray structure which show the I₃⁻ counteranion sits closer to one iron ion (Fe^{III}) than the other in the mixed-valence cation. On the other hand, the X = I or X = Br triiodides transfer electrons faster than

the Mössbauer technique can sense even at 4.2K. In the solid-state structures of these two compounds the environment, including the position of the I_3^- anion, is equivalent for both iron ions in the mixed-valence cation. Rapid electron tunneling occurs.

The mixed-valence biferrocenes with alkyl groups as X exhibit a temperature dependence in their Mössbauer spectra. At temperatures below -200K, each compound shows both an Fe^{II} and an Fe^{III} doublet. An increase in temperature eventually leads to the two-doublet spectrum changing to a spectrum with a single average-valence doublet. A sample-history dependence in the temperature dependence of these spectra has been noted.

Changing the anion from I_3^- to Br_2I^- or to other anions can lead to a dramatic change in the electron-transfer characteristics of the mixed-valence biferrocenes. For example, if the I_3^- anion of the X = H compound is changed to the very similar Br_2I^- anion, the temperature at which the electron-transfer rate is faster than can be sensed by the Mössbauer technique is reduced by ~150 degrees.

It is likely that the electron-transfer processes in the mixed-valence biferrocenes are coupled to phase transitions in the solid state. Evidence for this comes from the sample-history dependence and anion dependence of the electron-transfer rates, as well as heat-capacity measurements on the X = H triiodide compound.

Mixed-valence trinuclear iron acetate complexes (see drawing above) formally contain one Fe^{II} and two Fe^{III} ions. The ligand L is pyridine or a substituted pyridine. Usually these uncharged com-

plexes crystallize with a solvate molecule in the lattice. Mössbauer spectroscopy has played a significant role in the interesting observations which have been made for these iron acetate complexes:

- 1) Simply changing the solvate molecule dramatically affects the rate of intramolecular electron transfer.
- 2) For several of these complexes there is a change in the vibrational nature of the solid which apparently reflects the onset of dynamics associated with the ligand L and/or the solvate molecules. ^2H NMR data support this.
- 3) For several of the complexes the molecular dimensions change appreciably with changes in temperature.
- 4) Phase transitions which affect the rate of electron transfer have been seen for several complexes.

A detailed theoretical model has been formulated to delineate the type of phase transitions that can be seen in these trinuclear mixed-valence iron acetate complexes. The intrinsic electronic structure of the complex, together with the nature of intermolecular interactions present in the solid state, dictate the types of phase transitions which are seen.

Finally, an overview of results bearing on the factors which control the rate of conversion of an iron spin-crossover complex between its low-spin ground state and high-spin excited state will be given. ^{57}Fe Mössbauer spectroscopy has again proved to be a powerful technique in studying the spin-state interconversion in these complexes.