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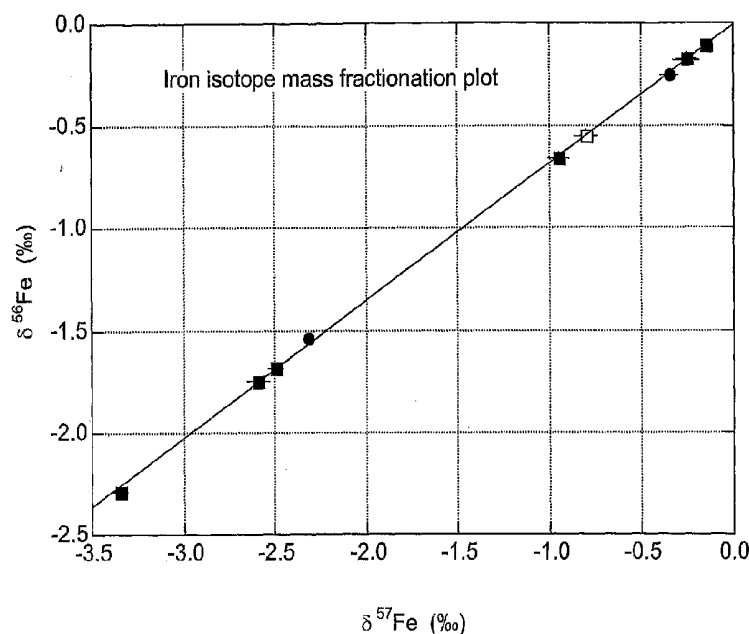
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(54) Title: ELECTROCHEMICAL SEPARATION OF STABLE ISOTOPES OF TRANSITION METAL ELEMENTS



(57) Abstract: An electroplating process for fractionating isotopes of transition metals, particularly iron, where the isotope recovered in enhanced amounts is determined by the voltage used in the electroplating process. The provision of preselected ratios of isotopes utilizing this process provides the capability to construct equipment components from metals having different isotope composition and thus monitor the corrosion of such components by analyzing the metal isotope ratios in solutions in contact with those components.

## ELECTROCHEMICAL SEPARATION OF THE STABLE ISOTOPES OF TRANSITION METAL ELEMENTS

Abby Kavner

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This invention is directed to methods of separating the isotopes of transition metal elements and particularly iron.

As used herein the suffix symbol ‰ (per mille sign) denotes a quantity as "per mil" which means a relative portion represented as a ratio to one one-thousandth ( $1/1,000 = 0.001$ ) of the whole.

### BACKGROUND

The discovery of stable "isotopes" began with J. J. Thomson's identification of neon-22 in 1912. A major advancement in chemistry was the discovery of deuterium and techniques for separation and collection of deuterium (H. C. Urey, F. G. Brickwedde, and G. M. Murphy, A Hydrogen Isotope of Mass 2, *Phys. Rev.* **39**, 164-165 (1932);] H. C. Urey, F. G. Brickwedde, and G. M. Murphy, *Phys. Rev.* **40**, 1-15 (1932)). Electrochemically-driven isotopic fractionation in the hydrogen-deuterium system have been reported (Topley B. and Eyring H., "The separation of the hydrogen isotopes by electrolysis. Part I", *J. Chem. Phys.* **2**, 217-230 (1934), and Urey H. C., "The Thermodynamic properties of isotopic substances", *J. Chem. Soc.*, 562-581 (1947)). The lighter hydrogen isotope having a faster electrochemical reaction rate, leaving behind a liquid enriched in deuterium. Since then the isotopes of numerous other elements and ions have also been separated. More than 90 naturally occurring elements have been identified; they exist as nearly 270 stable isotopes. These isotopes are generally separated by centrifugal techniques or electromagnetic fields, such as used to separate uranium.

Recent developments in mass spectrometry techniques have created opportunities to examine the partitioning behavior of stable isotopes of transition metals (Belshaw N. S., Zhu X. K., Guo Y., and O'Nions R. K. "High Precision Measurement of Iron Isotopes by Plasma Source Mass Spectrometry" *International Journal of Mass Spectrometry* **197**, 191-195 (2000); Hirata T., Hayano Y., and Ohno T. "Improvements in precision of isotopic ratio measurements using laser

ablation-multiple collector-ICP-mass spectrometry: reduction of changes in measured isotopic ratios", *J. Anal. At. Spectrom.* **18**, 1283-1288 (2003); Malinovsky D., Stenberg A., Rodushkin I., Andren H., Ingri J., Ohlander B., and Baxter D. C., "Performance of high resolution MC-ICP-MS for Fe isotope ratio measurements in sedimentary geological materials", *J. Anal. At. Spectrom.* **18**, 687-695, (2003); Albarede F. and Beard B., "Analytical methods for non-traditional isotopes", In *Reviews in Mineralogy and Geochemistry*, **55: Geochemistry of Non-Traditional Stable Isotopes**, (eds. C. M. Johnson, B. L. Beard, and F. Albarede). Mineralogical Society of America, Washington DC, pp. 113-152, (2004); Archer C. and Vance D., "Mass discrimination correction in multiple-collector plasma source mass spectrometry: an example using Cu and Zn isotopes", *J. Anal. At. Spectrom.* **19**, 656-665 (2004); Arnold G. L., Weyer S., and Anbar A. D., "Fe isotope variations in natural materials measured using high mass resolution multiple collector ICPMS", *Anal. Chem.* **76**, 322-327 (2004)), and particularly iron isotopes (Beard, B.L., and C.M. Johnson, "High precision iron isotope measurements of terrestrial and lunar materials", *Geochimica Et Cosmochimica Acta*, **63** (11-12), 1653-1660, 1999; Beard B. L., Johnson C. M., Cox L., Sun H., Nealson K. H., and Aguilar C., "Iron isotope biosignatures", *Science* **285**, 1889-1892, (1999); Johnson, C.M., and B.L. Beard, "Correction of instrumentally produced mass fractionation during isotopic analysis of Fe by thermal ionization mass spectrometry", *International Journal of Mass Spectrometry*, **193** (1), 87-99, (1999), Polyakov V. B. and Mineev S. D., "The use of Mossbauer spectroscopy in stable isotope geochemistry", *Geochim. Cosmochim. Acta* **64**, 849-865, (2000); Brantley S. L., Liermann L., and Bullen T. D., "Fractionation of Fe isotopes by soil microbes and organic acids" *Geology* **29**, 535-538, (2001); Zhang C. L., Horita J., Cole D. R., Zhou J. Z., Lovley D. R., and Phelps T. J., "Temperature-dependent oxygen and carbon isotope fractionations of biogenic siderite", *Geochim. Cosmochim. Acta* **65**, 2257-2271 (2001); Kehm K., Hauri E. H., Alexander C. M. O., and Carlson R. W., "High precision iron isotope measurements of meteoritic material by cold plasma ICP-MS", *Geochim. Cosmochim. Acta* **67**, 2879-2891 (2003); Anbar A. D. "Iron stable isotopes: beyond biosignatures", *Earth Planet. Sci. Lett.* **217**, 223-236, (2004)).

However, the fundamental physical and chemical mechanisms responsible for both natural abiotic and biotic fractionations are not yet well understood (Anbar A. D., "Iron stable isotopes: beyond biosignatures", *Earth Planet. Sci. Lett.* **217**, 223-236 (2004)). The accumulated evidence, including both biotic and abiotic fractionation, points to a strong connection between Fe

oxidation-reduction processes and Fe isotope fractionation (Zhu, X.K., Y. Guo, R.J.P. Williams, R.K. O'Nions, A. Matthews, N.S. Belshaw, G.W. Canters, E.C. de Waal, U. Weser, B.K. Burgess, and B. Salvato, "Mass fractionation processes of transition metal isotopes", *Earth and Planetary Science Letters*, 200 (1-2), 47-62, 2002).

Electron charge transfer in Fe is a fundamental physical chemical process which occurs when an electron travels from one species to another, either via an intermediate complex, or as a single step, such as quantum mechanical tunneling (Barbara P. F., Meyer T. J., and Ratner M. A., "Contemporary issues in electron transfer research", *J. Phys. Chem.* **100**, 13148-13168 (1996), Adams D. M., Brus L., Chidsey C. E. D., Creager S., Creutz C., Kagan C. R., Kamat P. V., Lieberman M., Lindsay S., Marcus R. A., Metzger R. M., Michel-Beyerle M. E., Miller J. R., Newton M. D., Rolison D. R., Sankey O., Schanze K. S., Yardley J., and Zhu X. Y., "Charge transfer on the nanoscale: Current status", *J. Phys. Chem. B* **107**, 6668- Vol 6697 (2003)). Energy derived from charge transfer reactions is central to the existence of life (Devault D., "Quantum-Mechanical Tunnelling in Biological-Systems", *Quarterly Reviews of Biophysics* **13**, 387-564 (1980), Bertrand P., "Application of Electron-Transfer Theories to Biological-Systems", *Structure and Bonding* **75**, 3-47 (1991), Bixon M. and Jortner J., "Electron transfer - From isolated molecules to biomolecules", *Adv. In Chem. Physics*, **106**, 35-202 (1999), Daizadeh I., Medvedev D. M., and Stuchebrukhov A. A., "Electron transfer in ferredoxin: Are tunneling pathways evolutionarily conserved?", *Molecular Biology and Evolution* **19**, 406-415 (2002), Nealson K. H., Belz A., and McKee B., "Breathing metals as a way of life: geobiology in action", *Antonie Van Leeuwenhoek International Journal of General and Molecular Microbiology* **81**, 215-222 (2002)). Because these charge transfer reactions occur at interfaces (Brown G. E., Henrich V. E., Casey W. H., Clark D. L., Eggleston C., Felmy A., Goodman D. W., Gratzel M., Maciel G., McCarthy M. I., Nealson K. H., Sverjensky D. A., Toney M. F., and Zachara J. M., "Metal oxide surfaces and their interactions with aqueous solutions and microbial organisms", *Chem. Rev.* **99**, 77-174 (1999)), analysis of the physical chemistry at interfaces expands our understanding of biochemistry (Eggleston C. M., "The surface structure of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (001) by scanning tunneling microscopy: Implications for interfacial electron transfer reactions", *Am. Miner.* **84**, 1061-1070 (1999)), Eggleston C. M., Stack A. G., Rosso K. M., Higgins S. R., Bice A. M., Boese S. W., Pribyl R. D., and Nichols J. J., "The structure of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) (001) surfaces in aqueous media: Scanning tunneling microscopy and resonant tunneling

calculations of coexisting O and Fe terminations”, *Geochim. Cosmochim. Acta* **67**, 985-1000 (2003)), Neal A. L., Rosso K. M., Geesey G. G., Gorby Y. A., and Little B. J., “Surface structure effects on direct reduction of iron oxides by *Shewanella oneidensis*”, *Geochim. Cosmochim. Acta* **67**, 4489-4503 (2003)). Charge transfer occurs in a wide range of geological processes, biological processes, and geological, biological, and industrial applications. Isotopic markers can be used to elucidate mechanisms for electrochemical processes in several different environments, including biological systems. In addition, isotopic markers can provide a diagnostic test to monitor the corrosion behavior of materials in service. Current mass spectrometry techniques can analyze iron isotope fractionation with natural isotopic abundances, precluding the necessity for specially-doped materials. Still further, the electroplating technique can provide an inexpensive method to isotopically enrich manufacturing materials. When these materials are used to form fabricated components the different isotope ratios can provide a mechanism to selectively monitor corrosion (or degradation) behavior of these components.

Applicant has found that the Marcus theory for the kinetics of electron transfer can be applied to show that isotope fractionation is associated with electron transfer and is not a result of diffusion. This discovery has been substantiated by measuring a voltage dependent isotope fractionation effect in the  $\text{Fe}^{+2}/\text{Fe}_{(\text{metal})}$  system, the results comparing favorably with the theoretical predictions.

#### SUMMARY

Applicant has discovered that the stable isotopes of iron ( $^{54}\text{Fe}$ ,  $^{56}\text{Fe}$ ,  $^{57}\text{Fe}$ ,  $^{58}\text{Fe}$ ) can be readily separated by using electrochemical techniques. The process is also applicable to separation of isotopes with a reasonable half life. Isotope fractionation of electroplated Fe was measured as a function of applied electrochemical potential. As plating voltage is varied from -50 mV to -2.0 mV the isotopic distribution of the electroplated iron is depleted in heavy Fe when compared to the starting solutions with  $\delta^{56}\text{Fe}$  values ranging from -0.106( $\pm 0.01$ ) to -2.290( $\pm 0.006$ ) ‰, and corresponding  $\delta^{57}\text{Fe}$  values of -0.145( $\pm 0.011$ ) and -3.354( $\pm 0.019$ ) ‰. As a consequence, the concentration of the isotopes in solution also changes, with an increase in the concentration of the heavier isotopes. While the increase in concentration of a particular isotope, for example  $^{54}\text{Fe}$ , in relationship to heavier isotopes of iron, on a single pass may be small, by redissolving the recovered isotopes and repeating the process multiple times on the redissolved metal compositions, the concentration of isotopes in the mixture of recovered iron

can be significantly increased. Still further, this invention is not limited to iron but can be applied to any isotopic transition element that can be dissolved to form an electrically conductive solution.

The slope of the line created by plotting  $\delta^{56}\text{Fe}$  vs  $\delta^{57}\text{Fe}$  is equal to  $0.6723(\pm 0.0032)$ , consistent with fractionation due to a kinetic process involving unsolvated iron atoms. The data demonstrates that there is a voltage-dependent isotope fractionation associated with the reduction of iron. Applicant has discovered that the theory of the kinetics of electron transfer can be extended to include the isotope effects of electron transfer, and that the extended theory accounts for the voltage dependence of Fe isotope fractionation. The magnitude of the electrochemically-induced fractionation is similar to that of Fe reduction by certain bacteria, suggesting that electrochemical processes may be responsible for biogeochemical Fe isotope effects. Charge transfer is a fundamental physicochemical process involving Fe as well as other transition metals with multiple isotopes.

#### DRAWINGS

FIGURE 1 is a graph illustrating the energy-reaction coordinate model.

FIGURE 2 is an enlarged view of the circled portion of claim 1 further including the isotope energy differences, with energy curves for a second isotope system depicted as dotted lines, with corresponding reaction coordinate ( $E^{\ddagger}$ ,  $\xi^{\ddagger}$ ).

FIGURE 3 shows the kinetic behavior of charge transfer reactions with three different distance coordinates.

FIGURE 4 is a cyclic voltammetry plot of  $\text{FeCl}_2 + \text{HCl}$  liquid on a glassy carbon electrode using a scan rate of 10 mV/sec.

FIGURE 5 shows  $\delta^{56}\text{Fe}$  values as a function of applied voltage (referenced to the equilibrium potential for the  $\text{Fe}^{+2}/\text{Fe}$  reaction) for the recovered plated iron from potentiostatic (constant voltage) electroplating experiments.

FIGURE 6 is a graph showing  $\delta^{56}\text{Fe}$  values as a function of applied voltage. The different symbols indicate sets of experiments performed a month apart, using different aliquots of the same starting solution.

FIGURE 7 is a graph showing iron isotope fractionation data in a three isotope system from nine different electroplating conditions. Squares and circles indicate sets of experiments performed a month apart, using different aliquots of the same starting solution.

## DETAILED DISCUSSION

Theory For The Kinetic Isotope Effects Of Electron Transfer

The isotopic effects of charge transfer can be derived with reference to the kinetic theory developed by Marcus, R., "On the theory of electron-transfer reactions. VI. Unified treatment for homogeneous and electrode reactions", *J. Chem. Phys.* **43**, 679-701 (1965). That theory, reviewed in several articles in *Chemical Reviews*, vol. 92, issue 3 (1992), is discussed with emphasis on isotope-dependent terms.

The rate constant  $k$  for the electron transfer reaction can be written in the usual way as

$$k = \nu \exp(-\Delta G^* / (k_b T)) \quad (1)$$

The pre-exponential collision frequency term  $\nu$  accounts for translation:

$$\nu = \left( \frac{k_b T}{2\pi m} \right)^{1/2} \quad (2)$$

where  $m$  is the appropriate mass in motion (in the present case  $\nu$  refers to the collision frequency with an electrode),  $k_b$  is Boltzmann's constant and  $T$  is temperature.  $\Delta G^*$  is a free energy of activation, and is analogous to the term  $\Delta F^*$  used by Marcus.  $\Delta G^*$  is composed of three distinct contributions: 1) the work required to bring reactants together; 2) a reorganization energy involving changes in bond lengths and angles as preludes to electron transfer; and 3) the difference in configurational free energy between products and reactants (free energy of reaction). For the purpose of this analysis it is assumed that the work terms are negligible with respect to the observed isotope effects.

Following Marcus, the activation energy was obtained by considering two parabolas representing the energy surfaces for the reactants and products (Fig. 1). The parabolas are one-dimensional representations along a single reaction coordinate  $\xi$  (representing changes in bond distances and reorientation of solvent molecules, for example) of what are actually multidimensional energy surfaces. The equations for the energy parabolas for reactants(r) and products (p) are

$$E_r = f \xi^2 \quad (3)$$

and

$$E_p = f(\xi - \Delta\xi)^2 + \Delta G \quad (4)$$

respectively, where  $E_r$  and  $E_p$  are the energies for the reactants and products;  $\Delta G$  is the free energy difference between products and reactants,  $f$  is a force constant ( $\text{N m}^{-1}$ ), and  $\Delta\xi$  is a displacement along the reaction coordinate  $\xi$  between stable products and reactants (Figures 1 and 2). In Figure 1, reactants and products are parabolic in reaction coordinate space. Electron transfer takes place at the coordinate  $(E^*, \xi^*)$ . The driving force for the reaction is  $\Delta G = KT \ln(Q_p/Q_r) - zeV_{\text{appl}}$ . The isotope energy differences are too small to be viewed on this scale. Figure 2 is an enlarged view of the circled portion of Figure 1 further showing the isotope energy differences, with energy curves for a second isotope system depicted as dotted lines, with corresponding reaction coordinate  $(E^*, \xi^*)$ .

The two parabolas intersect at some value of the reaction coordinate  $\xi^*$  with energy  $E^*$ . The difference in energy between this point of intersection and the stable energy of the reactants defines the activation free energy  $\Delta G^*$ . Equations 3 and 4 can be combined to solve the expression  $E_r = E_p$  for the value of  $\xi^*$  at the crossing point, yielding

$$f\xi^{*2} = f(\xi^* - \Delta\xi)^2 + \Delta G \quad (5)$$

and therefore

$$\xi^* = \frac{1}{2} \left( \Delta\xi + \frac{\Delta G}{f\Delta\xi} \right) \quad (6)$$

Substituting (6) into (3) gives the energy at  $\xi^*$ :

$$E^* = \frac{f\Delta\xi^2}{4} + \frac{\Delta G}{2} + \frac{\Delta G^2}{4f\Delta\xi^2} \quad (7)$$

The value  $E^*$  is seen to be the activation free energy  $\Delta G^*$  since  $E_r$  can be arbitrarily set to zero. In the context of the Marcus theory,  $f\Delta\xi^2$  in equation (7) is the “reorganization energy”,  $\lambda(\text{J})$ , that accounts for the energy required to ready the reactants for electron transfer. Following this convention eqn. 7 can be rewritten as



$$\Delta G^* = \frac{\lambda}{4} + \frac{\Delta G}{2} + \frac{\Delta G^2}{4\lambda} \quad (8)$$

According to this description of the kinetics, the reaction rate increases with increasing driving force until it attains a maximum, after which it begins to decrease with further increases in driving force. This “reverse kinetic” effect (Fig. 3) is a hallmark of Marcus theory and was confirmed experimentally by Miller J. R., Calcaterra L. T., and Closs G. L., “Intramolecular long-distance electron transfer in radical anions. The effects of free energy and solvent on the reaction rates”, *J. Am. Chem. Soc.* **106**, 3047-3049 (1984).

To examine isotope effects, the simplifying assumption was made that  $\lambda$  is isotope independent and therefore focus is on terms that may show a voltage dependent isotope fractionation effect. The effect of isotope substitution on  $\Delta G^*$  is through the difference in free energy between isotopologues at equilibrium (Fig. 2). This difference in  $G$  is well known (Bigeleisen J. and Mayer M. G., “Calculation of Equilibrium constants for isotopic exchange reactions”, *J. Chem. Phys.* **15**, 261-267 (1947), Bigeleisen J., “The relative reaction velocities of isotopic molecules”, *J. Chem. Phys.* **17**, 675-678 (1949), Bigeleisen J., “Statistical mechanics of isotopic systems with small quantum corrections. I. General considerations and the rule of the geometric mean”, *J. Chem. Phys.* **23**, 2264-2267 (1955)) and is equal to  $-k_b T \ln \alpha_{eq}$ . The term  $\alpha_{eq}$  is the isotope fractionation factor defined as  $R_p/R_a$  where  $R_p$  and  $R_a$  are the ratios of the rare isotopologue to the heavy isotopologue for products and reactants, respectively, at equilibrium. Said another way,  $\alpha_{eq}$  is the ratio of reduced partition functions for the product isotopologues ( $Q_p^l/Q_p$  where  $Q_p$  is the reduced partition function for the product and  $l$  designates the rare isotopic species) divided by the analogous reduced partition function ratio for the reactants. In the case of the partitioning between  $^{56}\text{Fe}$  and  $^{54}\text{Fe}$ , for example,  $\alpha_{eq} = (^{56}\text{Fe}/^{54}\text{Fe})_p / (^{56}\text{Fe}/^{54}\text{Fe})_r = (Q^l/Q)_p / (Q^l/Q)_r$ .

From the known energy effects of isotope substitution an equation can be written analogous to eqn. 8 for the activation free energy for the electron transfer reaction but for the different product and reactant isotopologues (values for the new isotope-substituted species are designated with a  $l$  superscript):

$$\Delta G^{*'} = \frac{\lambda}{4} + \frac{(\Delta G - k_b T \ln \alpha)}{2} + \frac{(\Delta G - k_b T \ln \alpha)^2}{4\lambda} \quad (9)$$

The free energy change in the presence of a voltage potential will be

$$\Delta G = -k_b T \ln(Q_p/Q_r) - V z e \quad (10)$$

where  $Q_p$  and  $Q_r$  are the partition functions for the abundant isotopologue of the product and reactant;  $V$  is the applied voltage (with the convention that negative  $V$  is cathodic potential);  $z$  is the number of electrons transferred; and  $e$  is the charge of an electron. Eqn. 10 is equivalent to  $\Delta G = -(V - V_0) z e$ , where  $V_0$  is the equilibrium potential.

The kinetic isotope fractionation factor,  $\alpha_{\text{kinetic}}$ , describes the isotope partitioning arising from kinetics and is related to the ratio of the rate constants for the two different isotopologues in the electron transfer reaction such that

$$\ln \alpha_{\text{kinetic}} = \ln\left(\frac{k'}{k}\right) = \ln\left(\frac{\nu'}{\nu}\right) + \left((\Delta G^* - \Delta G'^*) / (k_b T)\right) \quad (11)$$

The kinetic isotope fractionation factor can be cast into per mil deviations from the original reactant isotopic ratio using the “linearized” delta notation where  $\delta_{p-r} = 10^3 \ln \alpha_{\text{kinetic}}$ . Substitution of equations (2), (8), (9) and (10) into equation (11) yields the equation for per mil fractionation as result of the kinetics of electron transfer:

$$\frac{\delta_{p-r}}{10^3} = \frac{1}{2} \ln\left(\frac{m}{m'}\right) - \frac{Vze}{2\lambda} \ln \alpha_{\text{eq}} + \frac{1}{2} \ln \alpha_{\text{eq}} - \frac{k_b T}{4\lambda} (\ln \alpha_{\text{eq}})^2 - \frac{k_b T}{2\lambda} \ln\left(\frac{Q_p}{Q_r}\right) \ln \alpha_{\text{eq}} \quad (12)$$

Based on equation 12 it is predicted that there should be a kinetic isotope fractionation associated with an electron transfer reaction, and this fractionation will depend on the applied voltage that drives the reaction (Fig. 3).

The extension of the Marcus theory for the kinetics of electron transfer predicts a linear relationship between  $\delta_{p-r}$  and voltage  $V$  where the slope is

$$\frac{\partial \delta_{p-r}}{\partial V} = -10^3 \frac{ze}{2\lambda} \ln \alpha_{\text{eq}} \quad (13)$$

and the intercept  $B$  is

$$B = 10^3 \left[ \frac{1}{2} \ln \left( \frac{m}{m'} \right) + \frac{1}{2} \ln \alpha_{eq} - \frac{k_b T}{4\lambda} (\ln \alpha_{eq})^2 - \frac{k_b T}{2\lambda} \ln \left( \frac{Q_p}{Q_r} \right) \ln \alpha_{eq} \right] \quad (14)$$

The magnitude of the kinetic isotope effect is predicted to be a balance between the fractionation imparted by translation, the maximum value of which is represented by the first term  $\frac{1}{2} \ln \left( \frac{m}{m'} \right)$  in eqn. 14, and the effect of the reduced partition function ratios represented by the  $\ln \alpha_{eq}$  terms. In practice, the translation term will be considerably smaller than the first term in eqn. 14 while the last term in eqn. 14 is generally negligible. The sign of the slope of fractionation vs. voltage depends on the sign of  $\ln \alpha_{eq}$ . When the products are enriched in the rare isotope relative to the reactants at equilibrium,  $\alpha_{eq}$  is greater than 1 and  $\ln \alpha_{eq}$  is positive, resulting in a positive slope. When the products are depleted in the rare isotope relative to the reactants at equilibrium,  $\ln \alpha_{eq}$  is negative and the slope of voltage-dependent fractionation will be negative.

The prediction of a voltage-dependent isotope effect during electron transfer does not result from applying simple equations relating reaction rate to applied voltage (e.g., the overpotential-activated Butler-Volmer equation (Bockris J. O. M. and Reddy A. K. N., *Modern Electrochemistry*, New York, 1432 pp (1970), Bard A. J. and Faulkner L. R., *Electrochemical Methods, Fundamentals and Applications*. Wiley, 718pp (1980). However, it is a natural result of Marcus' theory, making it possible to test the isotope-specific extension to Marcus theory by examining the effects of voltage on isotope fractionation during redox reactions.

As an example, the separation of the isotopes of iron is examined. The Fe metal-Fe<sup>+2</sup> half reaction,



is at chemical equilibrium at a point determined by the standard reduction potential  $\Delta\Phi_e^\circ = -0.65\text{V}$ . An electrochemical cell was set up consisting of two iron metal electrodes submersed in aqueous solutions each solution containing different concentrations of Fe<sup>+2</sup> ions, separated by a salt bridge. The electrodes were attached to a voltmeter and a potential difference was measured, which reflects the difference in chemical potential of each electrode in contact with different concentrations of solution (a "concentration cell"). When the voltmeter is replaced by a current meter, and reactions are allowed to proceed at each electrode, current flows as the reactions take place with oxidation of Fe to produce Fe<sup>+2</sup> at one electrode, and reduction of Fe<sup>+2</sup> to Fe metal at

the other electrode. As the reactions proceed, the chemistry (and therefore potential difference) evolves until equilibrium is reached. The thermodynamics of the system determines which reactions will occur at each electrode; however, kinetics determines how fast the reaction occurs. The measured current reflects the kinetic properties of the reaction, via the Butler-Volmer rate eqn, in which the total current is written as the sum of the oxidation current and the reduction current:

$$i = i_0 (i_{\text{red}} + i_{\text{ox}}) \quad (16)$$

$$i = i_0 \{ \exp(zF\alpha\eta/RT) + \exp(zF(1-\alpha)\eta/RT) \} \quad (17)$$

where  $i$  is reaction current;  $i_0$  is the equilibrium exchange current;  $z$  is the number of electrons transferred in each step (two for the Fe reaction shown above);  $\alpha$  is a transfer term approximately equal to 0.5;  $\eta$  is the overpotential, equal to  $V_{\text{appl}} - \Delta\Phi_e^\circ$ ;  $R$  is the gas constant,  $T$  is temperature, and  $F$  is Faraday's number, which relates chemical and electrical energy, is equal to 96,485 coulombs/mole (Bard, A.J., and L.R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, 718 pp., Wiley, New York, 1980). This equation emphasizes the relationship between kinetics of a charge transfer reaction and its thermodynamic driving force, given by the overpotential  $\eta$ . Ion isotope fractionation was examined as a function of the electrochemical driving force.

### **Example 1**

Iron plating was performed in a standard three-electrode electrochemical cell in conjunction with an EG&G Potentiostat model 273 using glass carbon electrode counter cells. All voltages were recorded with respect to the silver-silver chloride electrode (Ag/AgCl). The electroplating bath consisted of a 2M FeCl<sub>2</sub> solution with 1 M HCl at a pH of 1.5. Twenty ml aliquots from two initial batches of 1L were used for each procedure. Prior to each procedure, the solution was de-oxygenated by bubbling Ar or N<sub>2</sub> through the solution for 20 minutes. Cyclic voltammetry (CV) tests of the plating bath (Fig. 4) show voltage-activated kinetics, with cathodic reactions below -0.9 V and iron oxidation above -0.5 V with a strong reduction current observed during the cathodic scan starting at -0.7 V vs. Ag/AgCl. In all cases, the cathodic reaction was a combination of H<sup>+</sup> reduction to hydrogen (gas bubbles were observed on the electrode surface) and the reduction of the Fe<sup>+2</sup> to metal.

Fig. 4 shows current varying as a function of applied voltage (with respect to a standard electrode) for the starting plating solution, during two cycles. During the anodic scan the

oxidation peak or metallic iron deposited in the previous cathodic sweep at -0.4 V vs. Ag/AgCl can be seen. Cyclic voltammetry tests of the plating bath (Fig. 4) show voltage-activated kinetics, with cathodic reactions below -0.9 V/SCE and iron oxidation above -0.5 SCE. This plot shows how current varies as a function of applied voltage (with respect to a standard electrode) for the starting plating solution, during two cycles. At the larger negative voltages, the current increase (absolute value) is due to both plating of iron and reduction of  $2\text{H}^+$  to  $\text{H}_2$  gas. The hump of positive current at voltages between -0.5 and 0 V is due to oxidation of the iron plated in the previous reduction cycle.

As shown in Figure 3, several different plating conditions were evaluated. The top three figures show the reaction coordinate diagram with identical driving force, and decreasing  $\lambda$  proceeding from left to right. The bottom three plots depict the corresponding reaction rates as a function of driving force for each case. The inset shows the corresponding predicted voltage dependent isotope fractionation for Fe 56/54.

A first set of evaluations were performed at either -0.9V or -1.25 V. A second set of evaluations were performed with deposition potentials of -0.7, -0.9, -1.1, -1.25, -1.5, and -2.0 V. Plating times were controlled so that the same amount of total charge density ( $\sim 75\text{-}100 \text{ C/cm}^2$ ) was exchanged in all cases. Electroplating times were varied from 9 minutes with the deposition potential at -2.0 V to over 7 hours with the deposition potential at -0.9 V. The amount of electrodeposited iron was consistent under each set of conditions, with the 0.9V being slightly more efficient ( $\sim 1\text{-}2 \text{ mg}$ ) than -1.25 V ( $\sim 0.1\text{-}0.3 \text{ mg}$ ). The amount plated is 0.03% of the initial concentration of Fe within the plating bath for the first set of experiments, and 0.002-0.005% for the second set. The small amount plated, compared with the 80 Coulombs of charge passed for each operating condition indicates the low efficiency of the iron plating process, compared with hydrogen evolution. The plating efficiency did not vary as a function of plating potential. As a further evaluation an additional procedure was performed at -1.25 V with continuous  $\text{N}_2$  sparging. The purpose of the  $\text{N}_2$  sparging was to provide a simple constraint on the effects of mixing. However, it was discovered that this resulted in several unexpected changes, including different hydrodynamics, water chemistry, and relative hydrogen reduction/iron reduction rates. This was manifested by 1) the noisy CV plot showing 10% rms variations in current and 2) the significant decrease in recovered plated iron (a photograph shows the electrode to be bare, as

opposed to the other electrodes, which show a layer of iron). Therefore the data from the evaluation using the N<sub>2</sub> sparging technique was not included with the other data.

In each instance, the cathode was collected and gently washed with distilled water to remove the plating bath solution. The cathodes were then placed in clean Teflon beakers and the electroplated iron was removed from the electrodes using hot concentrated HNO<sub>3</sub> acid for about six hours followed by hot concentrated HCl acid for about ten hours, in each instance at about 60 – 80°C. Each acid solution was evaporated to dryness, and then re-dissolved in 0.3 N nitric acid for analysis. The samples were diluted so the iron concentration was ~5 ppm Fe in the first set of evaluations, and ~3.8 ppm in the second set. In addition, to provide a control the starting FeCl<sub>2</sub> material was dissolved in hot concentrated HNO<sub>3</sub> acid and then diluted to 0.3 N for analysis.

The isotopic concentrations in the various compositions of resultant Fe/HNO<sub>3</sub> solutions were determined by sample-standard comparisons using a multi-collector inductively-coupled plasma mass spectrometer (MC-ICPMS) (ThermoFinnegan Neptune). The solutions were found to be substantially pure, with trace amounts of <sup>52</sup>Cr, the most abundant Cr isotope (>83%), considered to be insignificant and to not result in mass interference at mass 54 (e.g., background <sup>52</sup>Cr signals of 5 mV corresponded to a 0.1 mV <sup>54</sup>Cr background signal compared with sample <sup>54</sup>Fe signals of several volts). Peak heights for sample and standard were matched to minimize background effects. Mass interferences from Argon complexes ArO<sup>+</sup>, Ar-OH<sup>+</sup> and ArN<sup>+</sup> were resolved from the <sup>56</sup>Fe, <sup>57</sup>Fe and <sup>54</sup>Fe peaks by operating at a mass resolving power of ~ 12,000 (corresponding to a flat-top peak mass resolution of 4000 (Arnold G. L., Weyer S., and Anbar A. D., "Fe isotope variations in natural materials measured using high mass resolution multiple collector ICPMS", *Anal. Chem.* **76**, 322-327 (2004)). Potential instrumental mass bias due to inter-element matrix effects was not an issue because measurements were made on dilute, essential pure Fe solutions. Each solution was analyzed 5 to 6 times. Mean values for δ<sup>56</sup>Fe and δ<sup>57</sup>Fe and their corresponding standard deviations for the means (standard errors) are listed in Table 1.

**TABLE 1.**  
**DATA FROM EXAMPLE 1.**

| Plate<br>Potential <sup>1</sup> | $\delta^{56}\text{Fe}$<br>‰ | $\delta^{57}\text{Fe}$<br>‰ | amount<br>deposited <sup>5</sup><br>(mg) | efficiency<br>(%) | average<br>current<br>(A/cm <sup>2</sup> ) | total time (sec) |
|---------------------------------|-----------------------------|-----------------------------|------------------------------------------|-------------------|--------------------------------------------|------------------|
| Starting<br>material 1          | -0.184(14) <sup>2</sup>     | -0.252(31)                  |                                          |                   |                                            |                  |
| 1.25 (1)                        | -1.543(10)                  | -2.320(11)                  | 1.5                                      | 5.5               | 0.02                                       | 4508             |
| 0.9 (1)                         | -0.252(8)                   | -0.349(21)                  | 1.5                                      | 6.3               | 0.008                                      | 10600            |
| Starting<br>material 2          | -0.171(13)                  | -0.249(25)                  |                                          |                   |                                            |                  |
| -2.0                            | -2.290(6)                   | -3.354(19)                  | 0.2                                      | 0.9               | 0.15                                       | 540              |
| -1.5                            | -1.753(7)                   | -2.591(27)                  | 0.3                                      | 0.9               | 0.10                                       | 970              |
| -0.9                            | -0.106(10)                  | -0.145(11)                  | 0.1                                      | 0.9               | 0.002                                      | 26330            |
| -1.1                            | -0.655(12)                  | -0.951(23)                  | 0.3                                      | 0.9               | 0.03                                       | 3210             |
| -1.25                           | -1.686(10)                  | -2.498(20)                  | 0.2                                      | 0.7               | 0.052                                      | 1550             |
| -0.7 <sup>3</sup>               | N/A                         | N/A                         | N/A                                      | N/A               | 0.00003                                    | 35990            |
| -1.25 <sup>4</sup>              | -0.546(13)                  | -0.802(29)                  | 0.09                                     | 0.4               | 0.05                                       | 1400             |
|                                 | -0.552(14)                  | 0.784(21)                   |                                          |                   |                                            |                  |

<sup>1</sup>Potentials are given versus the Ag/AgCl reference electrode

<sup>2</sup>Ranges in ( ) are delta values are one-sigma error bars

<sup>3</sup>Experiment terminated after ten hours—too low a voltage to electroplate

<sup>4</sup>Experiment agitated by N<sub>2</sub> bubbling during plating. H<sub>2</sub> evolution efficiency greater

<sup>5</sup>Efficiency was decreased due to possible flaking off of electroplated iron during plating

Isotope ratios are plotted in Fig. 7 for all of the iron isotope fractionation data from the nine electroplating experiments. The measurement performed during N<sub>2</sub> bubbling is depicted as an open symbol. This plot shows one-sigma error bars on the measurements. This plot shows one-sigma error bars on the data points. The  $^{56}\text{Fe}/^{54}\text{Fe}$  and  $^{57}\text{Fe}/^{54}\text{Fe}$  ratios of reactant and product Fe are reported as per mil deviations from the IRMM-14 Fe isotope standard (Mass fraction  $^{54}\text{Fe} = 5.645\%$ ;  $^{56}\text{Fe} = 91.902\%$ ,  $^{57}\text{Fe} = 2.160\%$  and  $^{58}\text{Fe} = 0.292\%$ ) using the  $\delta$  notation where:

$$\delta^{56}\text{Fe} = ((^{56}\text{Fe}/^{54}\text{Fe})_{\text{sample}} / (^{56}\text{Fe}/^{54}\text{Fe})_{\text{IRMM-14}} - 1)1000 \quad (18)$$

and

$$\delta^{57}\text{Fe} = ((^{57}\text{Fe}/^{54}\text{Fe})_{\text{sample}} / (^{57}\text{Fe}/^{54}\text{Fe})_{\text{IRMM-14}} - 1)1000 \quad (19)$$

Based on this data generated for the electrochemical separation of isotopes obtained from these single pass procedures it has been determined that a significant increase of the concentration of a lighter isotope from the heavier isotopes of iron, for example  $^{54}\text{Fe}$  when compared to  $^{57}\text{Fe}$ , can be obtained by collecting the isotope mixture deposited on the cathode, redissolving that mixture and then performing a second electrochemical separation of that recovered mixture. The enhancement numbers, relative to starting isotope composition, are based on the use of 1000 Liters of 2M  $\text{FeCl}_2$  as a starting solution having a concentration, in per cent by weight, of

#### STARTING SOLUTION

|                  |        |
|------------------|--------|
| $^{54}\text{Fe}$ | 5.645  |
| $^{56}\text{Fe}$ | 91.902 |
| $^{57}\text{Fe}$ | 2.160  |
| $^{58}\text{Fe}$ | 0.292  |

**TABLE 2**  
**CONCENTRATION ENHANCEMENT**

| # pass | Permil $^{54}\text{Fe}$<br>enrichment <sup>2</sup> | Permil $^{57}\text{Fe}$<br>enrichment | Amt Fe<br>deposited (mg) | Surface Area<br>covered (cm <sup>2</sup> ) |
|--------|----------------------------------------------------|---------------------------------------|--------------------------|--------------------------------------------|
| 1      | 2.21                                               | -1.24                                 | $5.6 \times 10^6$        | $7.116 \times 10^6$                        |
| 2      | 4.41                                               | -2.48                                 | $2.8 \times 10^5$        | $3.558 \times 10^5$                        |
| 3      | 6.61                                               | -3.72                                 | 14,000                   | 17,789                                     |
| 4      | 8.82                                               | -4.96                                 | 700                      | 889                                        |
| 5      | 11.05                                              | -6.21                                 | 35                       | 44.5                                       |

In regard to Table 2, 5% of the total Fe in solution was electroplated per pass, plated iron was strip off, and then redissolve. Relative to the starting solution permil  $^x\text{Fe} = 1000 * (^x\text{Fe}_{\text{dep}} - ^x\text{Fe}_{\text{start}}) / ^x\text{Fe}_{\text{start}}$ . It was assumed that an electroplated coating 1  $\mu\text{m}$  thick was produced.



That procedure can be repeated multiple times, with each pass further increasing the concentration of the lighter isotope in relationship to the heavier isotope. Table 2 sets forth the per mil increase of  $^{54}\text{Fe}$  for a 5 pass procedure, the  $^{54}\text{Fe}$  isotope being enriched 5 times from 2.21 to 11.05 per mil relative to the starting concentration.

In Figure 5, the two separate sets of experiments are depicted as circles and squares. Calculated fractionations for three different values of  $\lambda$  are also displayed on this plot. The dashed gray line is the best-fit regression through the portion of the data lying on the linear part of the CV curve.

Results (Table 1, Fig. 5) show that isotopically light iron is preferentially electroplated, and the amount of light isotope enrichment depends on applied voltage with higher voltage providing better separations.  $\delta^{56}\text{Fe}$  values range from  $-0.18(\pm 0.02)$  ‰ at a potential of  $-0.9$  V to  $-2.290(\pm 0.006)$  ‰ at a potential of  $-2.0$  V. Corresponding values for  $\delta^{57}\text{Fe}$  are  $-0.247(\pm 0.014)$  ‰ and  $-3.354(0.019)$  ‰. The  $\delta^{56}\text{Fe}$  and  $\delta^{57}\text{Fe}$  values for the  $\text{Fe}^{+2}$  in the starting solution are  $-0.176(0.014)$  ‰ and  $-0.251(0.030)$  ‰, respectively. Results from two separate sets of experiments are in good agreement (as shown by the values at  $-0.9$  V and  $-1.25$  V) despite greater than an order of magnitude difference between the plating efficiency in the experiments, and slight differences in experimental procedures, including different starting solutions (mixed from different aliquots of the same starting materials), some differences in wet chemistry technique, and a month-long timescale between experimental sets. These results demonstrate a quantitative link between the driving force for a charge transfer reaction, and a resulting geochemical signature. This voltage-dependent fractionation effect seen here has never before been observed in Fe or any other transition metal system.

The relationship demonstrated between  $^{56}\text{Fe}/^{54}\text{Fe}$  ( $^{56}R$ ) and  $^{57}\text{Fe}/^{54}\text{Fe}$  ( $^{57}R$ ) constitutes an exponential mass fractionation law among the three isotopes which is characterized by an exponent  $\beta$ , the values of which are diagnostic of the type of process, (e.g., kinetic or equilibrium) that caused the fractionation (Young E. D., Galy A., and Nagahara H., "Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance", *Geochim. Cosmochim. Acta* **66**, 1095-1104 (2002)). This value is similar to, but not exactly, the slope of the three isotope plot (Fig. 7). The  $\beta$  for processes governed by reduced partition function ratios has a high temperature limit of  $(1/m_{54} - 1/m_{56})/(1/m_{54} - 1/m_{57})$  where  $m_i$  is the atomic mass of the indicated Fe isotope. Slopes with this

functional form are referred to as “equilibrium” slopes in three isotope space since they arise solely from the partition function ratios responsible for equilibrium isotope partitioning. For kinetic processes involving collective masses in motion the values for  $\beta$  are  $\ln(M_{54}/M_{56})/\ln(M_{54}/M_{57})$  where  $M_i$  are the masses of species involved in the rate-limiting process. Slopes with this functional form arise from momentum effects independent of the reduced partition function ratio. However, the kinetic isotope effect incurred during the electroplating process does not necessitate a purely kinetic slope. For example, if isotope fractionation were to arise only from the voltage-dependent kinetic effect (e.g. eqn. 13 or all but the 1<sup>st</sup> terms in eqn. 12), the three isotopes would define a so-called “equilibrium” slope in three isotope space because the dominant term is a reduced partition function ratio.

The  $\beta$  values reported here were obtained by regressing the experimental data cast in terms of  $\ln(^{56}\text{R}/^{56}\text{R}_{\text{IRMM-14}})*1000$  and  $\ln(^{57}\text{R}/^{57}\text{R}_{\text{IRMM-14}})*1000$  (e.g., Young E. D., Galy A., and Nagahara H., “Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance”, *Geochim. Cosmochim. Acta* **66**, 1095-1104 (2002)). Each sample was weighted by its associated standard error and the correlation coefficient between the individual replicate  $\delta^{56}\text{Fe}$  and  $\delta^{57}\text{Fe}$  measurements. The best-fit  $\beta$  value for the electroplating experiments is  $0.6723(\pm 0.0032)(95\%)$ . This value is statistically indistinguishable from the predicted kinetic  $\beta$  of 0.6720 where the masses in motion are Fe atoms (or ions) and is significantly different from the predicted high-temperature limit of reduced partition function effects. This result indicates that there is a component of molecular translation involved in the kinetics, and that the first term in eqn. 12 is important. However, the precise  $\beta$  value for the low-temperature reduced partition function ratio (often lower temperatures tend to lower the  $\beta$  value for the partition function ratios) is not known making it difficult to extract quantitatively the contribution of the first term in eqn. 12 to the overall fractionation effect.

In chemical kinetics theory, in a multistep process with a single rate-determining step, all of the other steps can be considered to be at equilibrium. Equilibrium fractionation can be ruled out on the basis of three arguments. First, calculations of equilibrium exchange between  $\text{Fe}^{+2}$  and  $\text{Fe}_{\text{metal}}$  [Schauble, *ibid*], show fractionations of less than 1 per mil, much smaller than as set forth herein, especially at higher over potentials. This implies that although there might be a contribution to the total effect from equilibrium exchange, the majority of the observed effect

arises from a single step in the reaction, the rate-determining step. The behavior of the three isotope system, described by the exponent  $\beta$ , is also consistent with a kinetic source. The predicted  $\beta$  for a kinetic process is equal to 0.6720, and 0.6780 for an equilibrium process. The observed  $\beta$  (0.6723( $\pm$ 0.0032)) is consistent with a kinetic process.

In summary, the discussion of the theoretical basis set forth above elucidates the mechanism for the observed fractionation amounts. To determine the rate-limiting step for this electroplating process consistent with the constraints imposed by the isotope data, the general rate of an electroplating process is given by:

$$i_{\text{plate,volt}} = D i_0 \exp (\alpha F(V_{\text{appl}} - \Delta\Phi_{\text{eq}})/RT) \quad (20)$$

where the  $D$  term is the mass transport diffusivity term, and the other terms are defined above.

Mass transport, i.e., diffusion or electromigration, can cause isotopic fractionation that scale roughly with the masses of diffusing species. In this case, the diffusing species is most likely  $\text{Fe}^{+2}(\text{H}_2\text{O})_6$ , resulting in a  $^{56}\text{Fe}/^{54}\text{Fe}$  fractionation factor of  $(M_{^{54}\text{Fe}+2(\text{H}_2\text{O})_6}/M_{^{56}\text{Fe}+2(\text{H}_2\text{O})_6})^{1/2}$ , or  $-6.2$  per mil. It appears that mass transport is not the mechanism underlying the observed fractionation. One reason for this conclusion is that the electroplating examples were not performed in a diffusion-limited regime. This is known from examining the CV plot (Fig. 1) which shows voltage activated cathodic current throughout the range of the electroplating experiments. In addition, there is active  $\text{H}_2$  bubbling at the electrodes throughout the various conditions in the example above, which provides active mixing of solution, and would destroy any significant stagnant layer. Third, information from the three-isotope system can again provide constraint. The observed value of the exponent, 0.6723 is consistent with the mass ratio of Fe alone, whereas the  $\text{Fe}^{++}$  species being transported through the solution is most likely solvated by  $\text{H}_2\text{O}$  and/or by  $\text{Cl}^-$  ions. If solvated by six water molecules, the  $\beta$  value would be lower by 0.0043 to 0.6680. Chlorine speciation reduces the  $\beta$  value even more. The rate-limiting step involves Fe atoms or ions alone rather than solvated or chlorinated species. Finally, neither time independent nor time dependent diffusion models can generate a voltage-dependent fractionation. Therefore, it is concluded that although diffusion may play some role in the observed fractionation, it cannot be responsible for fractionation and its observed voltage dependence. Diffusion related fractionation cannot explain the observed fractionation because it is small (approximately 3% and not voltage dependent (Rodushkin I. et al., "Isotopic

Fractionation during Diffusion of Transition Metal Ions in Solution,” *Anal. Chem.*, **76**, p2148-2151 (2004)).

To investigate the charge transfer effects, equation (20) is written for two isotopes, and the ratio is obtained. Since the ratio of the currents is equal to the ratio of the reaction rates, the fractionation can be written as:

$$\delta^{56}\text{Fe} = 1000 \cdot \ln(i^{56}/i^{54}) = 1000 [\ln(^{56}\text{C}_1/^{54}\text{C}_1) + F/RT(\alpha_1(V_{\text{appl}} - \Delta\Phi_{\text{eq},1}) - \alpha_2(V_{\text{appl}} - \Delta\Phi_{\text{eq},2}))] \quad (21)$$

A voltage-dependent isotopic fractionation implies a mass dependence in the constant  $\text{C}_2$  since  $\text{C}_1$  effects do not depend on voltage.  $\text{C}_2$  is the factor that describes voltage-activated processes occurring directly adjacent the electrode, including formation and behavior of the activated complex, surface adsorption, and electron transfer from the electrode to the Fe ion (Koryta J., “Polarographic methods of investigation of the kinetics of metal deposition from complex compounds,” *Electrochim. Acta* **1**, 26-31 (1959)).

Therefore, it is concluded that, for Fe isotopes, the isotope fractionation results from a voltage-dependent kinetic process directly involved in electron charge transfer at the electrode aqueous interface. In other words, the constant  $\text{C}_2$  in equation 2 and 3 is mass-dependent. Assuming values of  $10^{-7}$  for  $\text{C}_1$  and 0.5 for  $\text{C}_2$ , consistent with observed values for Fe electroplating (Koryta J., “Polarographic methods of investigation of the kinetics of metal deposition from complex compounds,” *Electrochim. Acta* **1**, 26-31 (1959)) a variation of 100 ppm in  $\text{C}_2$  is necessary to account for the observed voltage-dependent fractionation.

Electroplating consists of a large number of single step processes required to bring the solvated or other aqueo-complexed transition metal ion (for example  $\text{Fe}^{+2}$ ) to the electrode surface, to generate the activated complex, to perform the transfer of electrons (two electrons in the case of  $\text{Fe}^{+2}$ , and to nucleate and grow the metal on the electrode. (Koryta J., “Polarographic methods of investigation of the kinetics of metal deposition from complex compounds,” *Electrochim. Acta* **1**, 26-31 (1959), Bockris J. O. M. and Reddy A. K. N., *Modern Electrochemistry*, New York, 1432 pp (1970), Bard A. J. and Faulkner L. R., *Electrochemical Methods, Fundamentals and Applications*. Wiley, 718pp (1980)). The theory described above does not capture the full complexity of the reaction; however, it provides a first-order prediction for the slope and intercept for the voltage-dependent isotope fractionation in the electroplating reaction, as shown by the data on Fe isotope fractionation.

Eqn. 13 shows that the voltage-dependent contribution to the electrochemical isotope fractionation is a function of both the equilibrium fractionation ( $1000\ln\alpha_{eq}$ ) and reorganization energies ( $\lambda$ ) for the rate limiting step. For typical ionic stretching force constants of 500 to 900  $\text{Nm}^{-1}$  and interatomic distances of  $2 \times 10^{-11}$  m, the reorganization energies are on the order of 60 to 100 KJ/mol. In aqueous solutions with  $[\text{Cl}^-]$  greater than 4M, (the solution chemistry employed in the Fe experiments uses  $[\text{Cl}^-]=5\text{M}$ )  $\text{Fe}^{+2}$  likely exists as  $\text{Cl}^-$  complexed ferrous ions (e.g., Snoeyink V. L. and Jenkins D., *Water Chemistry*, J. Wiley & Sons, New York (1980)). Calculations for equilibrium fractionation in many Fe-complexes and Fe metal (Schauble E. A., Rossman G. R., and Taylor H. P., "Theoretical estimates of equilibrium Fe-isotope fractionations from vibrational spectroscopy", *Geochim. Cosmochim. Acta* **65**, 2487-2497 (2001)) use vibration energies from spectroscopy measurements. The per mil reduced partition function ratios  $1000\ln(Q^{56}/Q^{54})$  relative to dissociated atoms are  $4.0 (\pm 0.2)$  for  $(\text{Fe}^{\text{II}}\text{Cl}_4)^{-2}$  and  $5.3 (\pm 1.0)$  for  $\text{Fe}_{\text{metal}}$  at  $25^\circ\text{C}$  (i.e. the equilibrium partitioning favors  $^{56}\text{Fe}$  in the metal). Since  $1000\ln\alpha_{eq}$  for two substances a and b is  $1000\ln(Q^{56}/Q^{54})_a - 1000\ln(Q^{56}/Q^{54})_b$ , these values yield a  $1000\ln\alpha_{eq}$  for the metal/chloro complex of 1.3. Using these values, the predicted slopes in  $\delta^{56}$  vs. V space (eqn. 12) range from 1.2 to 2.1. The data on the linear portion of the CV curve (absolute values of applied voltages greater than 1.0 V) yield a best-fit slope of  $0.89 (\pm 0.33)$  (95%). The agreement between the predicted slope from Marcus' theory for electron transfer and the experiments leads to the conclusion that the voltage driven electron transfer process is controlling the isotope kinetics.

The intercept predicted on the basis of the dominant term in eqn. 12 is  $10^3 (1/2) \ln\alpha_{eq}$ , or +0.65 ‰. The data comprising the linear portion of the CV curve yield an intercept of -0.5 ‰. The difference can be attributed to a contribution from the pre-exponential component in the rate equation (i.e., first term in eqn. 12). The maximum that translation of  $\text{FeCl}_2$  isotopologues can contribute to the intercept is -8‰, suggesting that the contribution need not be great to significantly affect the intercept.

One uncertainty in the data is the relative contribution to the overall plating rate contributed by the Fe electroplating reaction compared with hydrogen evolution. Hydrogen evolution dominates the overall rate as shown on the CV plots but Fe plating is in strong competition. As a result, it is unknown whether plating is occurring in the "forward" or "reverse" kinetics regimes in the context of Marcus theory. The observed fractionations would

be smaller (but still comparable) in the forward regime; in the reverse regimes, larger fractionation effects might be observed. This prediction suggests that there are classes of reactions in which very large isotope effects can be expected.

The major alternative hypothesis for the observed fractionation, mass transport effects, can be ruled out. The electroplating experiments were not performed in a diffusion-limited regime as evidenced by the CV plot (Fig. 4), which shows voltage activated cathodic current throughout the range of the electroplating experiments. In addition, there is active H<sub>2</sub> bubbling at the electrodes throughout each experiment, which provides active mixing of solution, and would destroy any significant stagnant layer. Finally, and most importantly, neither time independent nor time dependent diffusion models can generate a voltage-dependent fractionation. Therefore, it can be concluded that although diffusion may play some role in the observed fractionation, it is not the primary process responsible for the overall fractionation and it does not explain the observed voltage dependence.

Based on the data set forth above it was concluded that iron isotope fractionation occurs during the reduction reaction  $\text{Fe}^{+2} + 2\text{e}^- \rightarrow \text{Fe}_{(\text{metal})}$  with isotopically light iron preferentially electroplated, the amount of light isotope enrichment depending on applied voltage.  $\delta^{56}\text{Fe}$  values as a function of applied voltage (referenced to the Ag/AgCl standard electrode) for the recovered plated iron from the potentiostatic (constant voltage) electroplating experiments are plotted in Fig. 6. The two points (very close together) at the equilibrium potential are of the two aliquots of the starting plating solution. The average  $\delta^{56}\text{Fe}$  values range from  $-0.18(\pm 0.02) \text{‰}$  at a potential of  $-0.9 \text{ V}$  to  $-2.290(\pm 0.006) \text{‰}$  at a potential of  $-2.0 \text{ V}$  (Fig. 6). Corresponding values for  $\delta^{57}\text{Fe}$  are  $-0.247(\pm 0.014) \text{‰}$  and  $-3.354(.019) \text{‰}$ . The average  $\delta^{56}\text{Fe}$  and  $\delta^{57}\text{Fe}$  values for the  $\text{Fe}^{+2}$  in the starting solution are  $-0.176(0.014) \text{‰}$  and  $-0.251(0.030) \text{‰}$ , respectively. Results from the two separate sets of experiments are in good agreement (as shown by the values at  $-0.9 \text{ V}$  and  $-1.25 \text{ V}$ ) despite use of greater than an order of magnitude difference between them in plating efficiency, and slight differences in experimental procedures, including different starting solutions (mixed from different aliquots of the same starting materials), some differences in wet chemistry technique, and a month-long timescale between experimental sets.

While observations of isotopic fractionation in electrochemical systems were made by Urey for the hydrogen-deuterium-tritium system, this voltage-dependent fractionation effect has never before been observed in a transition metal system. In Urey's experiments, the lighter

hydrogen isotope had a faster electrochemical reaction rate, leaving behind a liquid enriched in deuterium. The hydrogen-deuterium-tritium isotope electrochemical studies system showed an electrochemical fractionation effect that was attributed to a mass dependence in the electron transfer process.

The tests described herein show a voltage dependent Fe isotope fractionation. In other words, Fe isotopes can be fractionated by electroplating and the ratio and quantity of the various isotopes recovered is voltage dependent. The specific isotope recovered at the electrode in higher concentrations, when compared with normal, starting solutions, can be established by setting the voltage used in the electroplating process. In particular, the above results show that the fractionation can be traced to the charge transfer processes rather than to transport. Tracing Fe isotope fractionation to the charge transfer processes is relevant to a wide variety of natural and industrial processes that may give rise to Fe isotope partitioning. As a result, the connection between charge transfer voltage dependence and Fe isotopic fractionation is a powerful tool applicable to enhancing the understanding of redox mechanisms, industrial forensics, the separation and/or concentration of particular isotopes and the use of the isotopes, particularly Fe isotopes, as markers of bio-geological pathways or in fabrication of materials with pre-engineered isotope ratios.

One particular application of the technology described herein is in the field of corrosion analysis. Corrosion can be a considerable problem in industrial plants and manufacturing procedures. The results of corrosion may not be readily visible and therefore not conveniently corrected before a catastrophic failure. For example, a nuclear power plant has many steel parts, many of which are in contact with water. By fabricating different components with different but unique isotopic iron ratios, corrosion of specific parts can be monitored or located by measuring the abundance of the particular isotopes in the water stream. Similar techniques can be used in naval vessels and the food preparation industry.

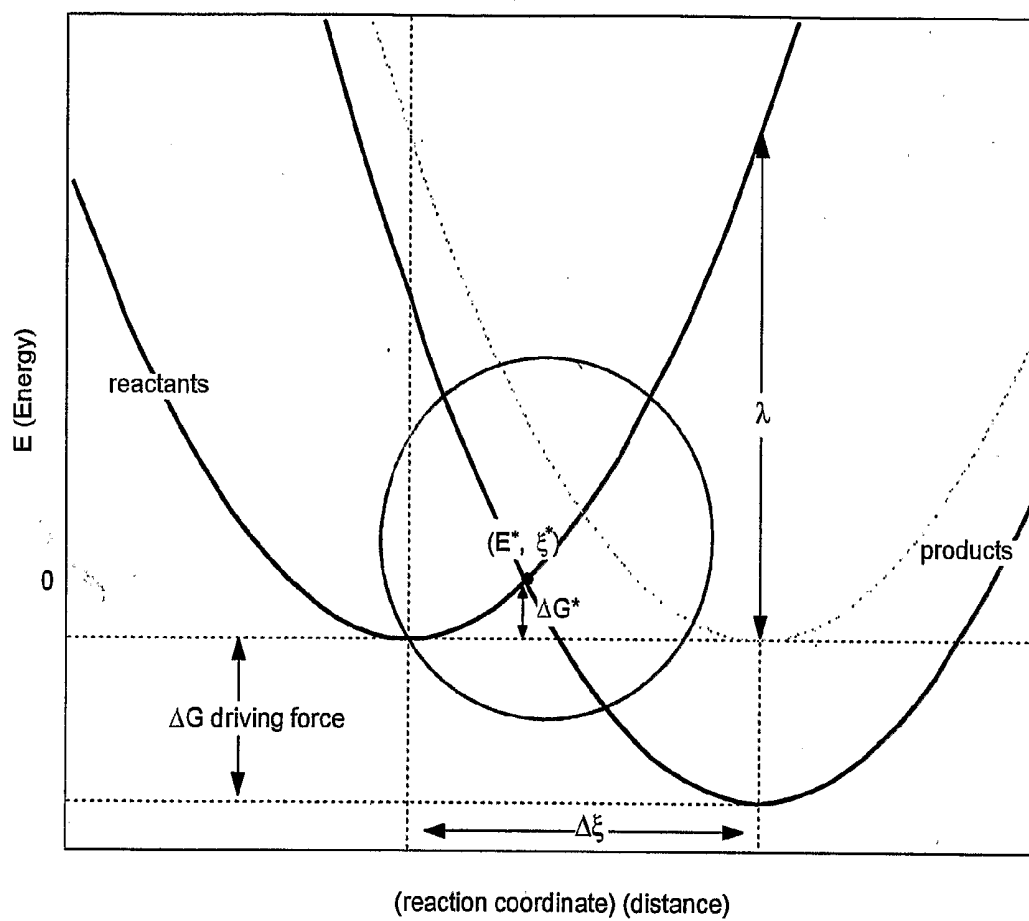
While the process has been described in regard to the isotopes of iron, the invention is not so limited and may in fact be applied to the separation of the isotopes, primarily the stable isotopes, of many different elements, and particularly the transition metals. A primary criteria for the use of said electrochemical separation process is that a conductive solution of soluble salts of said element must be formed and the element isolated at the cathode must be capable of being separated from the electroplating solution and recovered as an isolated element.

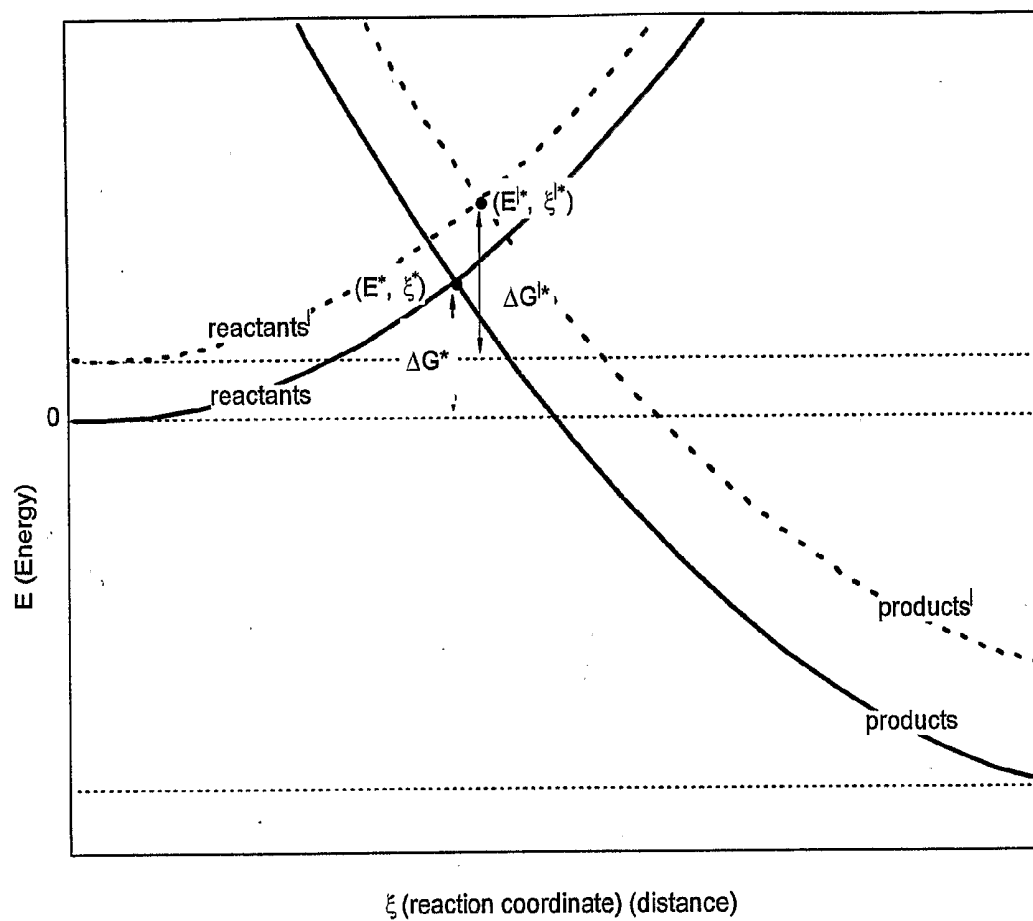
I claim:

1. A method of separation or concentrating the isotopes of a transition metal mixture or changing the ratio of the isotopes of an element in a transition metal mixture comprising;
  - a) dissolving a mixture of isotopes of an element in a solvent to form an electrically conductive solution,
  - b) placing that electrically conductive solution in an electrochemical cell, said electrochemical cell comprising an anode and a cathode and a source of electrical current connected to said anode and cathode such that said electrical current flows through said conductive solution,
  - c) allowing the electrical current to flow through the conductive solution for a period of time, and
  - d) removing the cathode and dissolving the element collected on the surface of the cathode, said dissolved element comprising a ratio of isotopes different from the ratio of isotopes in the conductive solution.
2. The method of claim 1 wherein the ratio of isotopes recovered from the cathode is dependent on the level of voltage applied across the cathode and anode.
3. The method of claim 1 wherein the transition metal is iron and the isotopes comprise  $^{54}\text{Fe}$ ,  $^{56}\text{Fe}$ ,  $^{57}\text{Fe}$  and  $^{58}\text{Fe}$ .
4. A method of monitoring the corrosion of metallic components of an assembly in contact with a corrosive or reactive liquid media comprising fabricating different components of the assembly from a metal, selected components being formed from metals having a different ratio of isotopes, and analyzing the liquid media for the ratio of isotopes contained therein.
5. The method of claim 4 wherein the metal is iron and the selected components contain different ratios of  $^{54}\text{Fe}$ ,  $^{56}\text{Fe}$ ,  $^{57}\text{Fe}$  and  $^{58}\text{Fe}$ .



6. The method of claim 5 wherein the liquid media iron isotope concentration and ratio of iron isotopes is indicative of the component or components corroding.

**FIG. 1**

**FIG. 2**

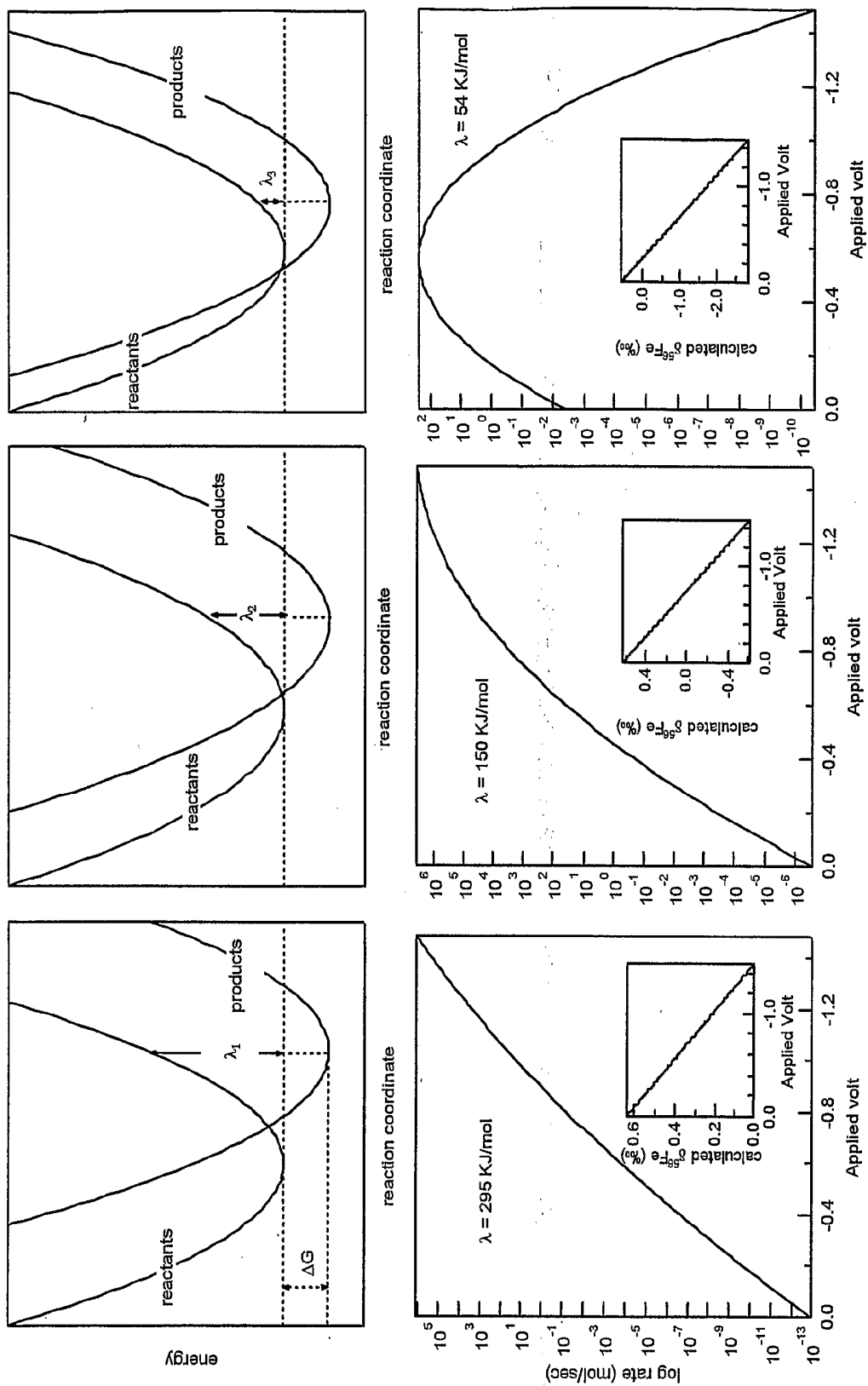
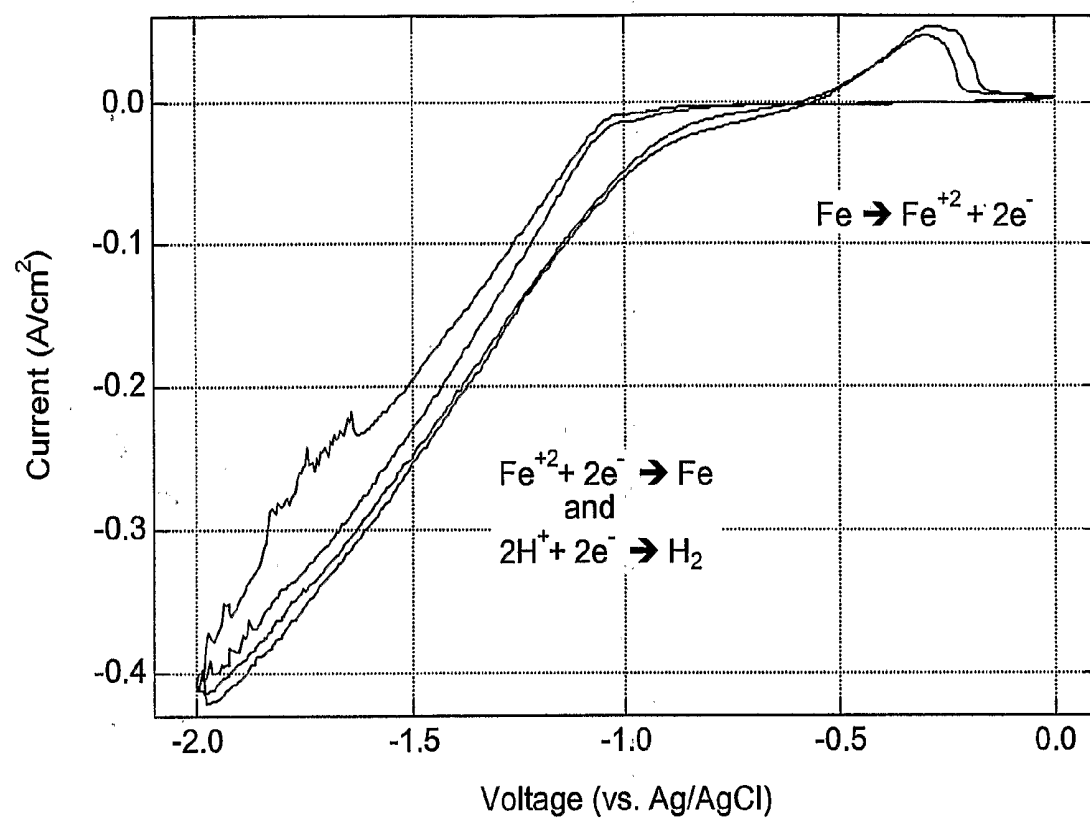


FIG. 3

**FIG. 4**

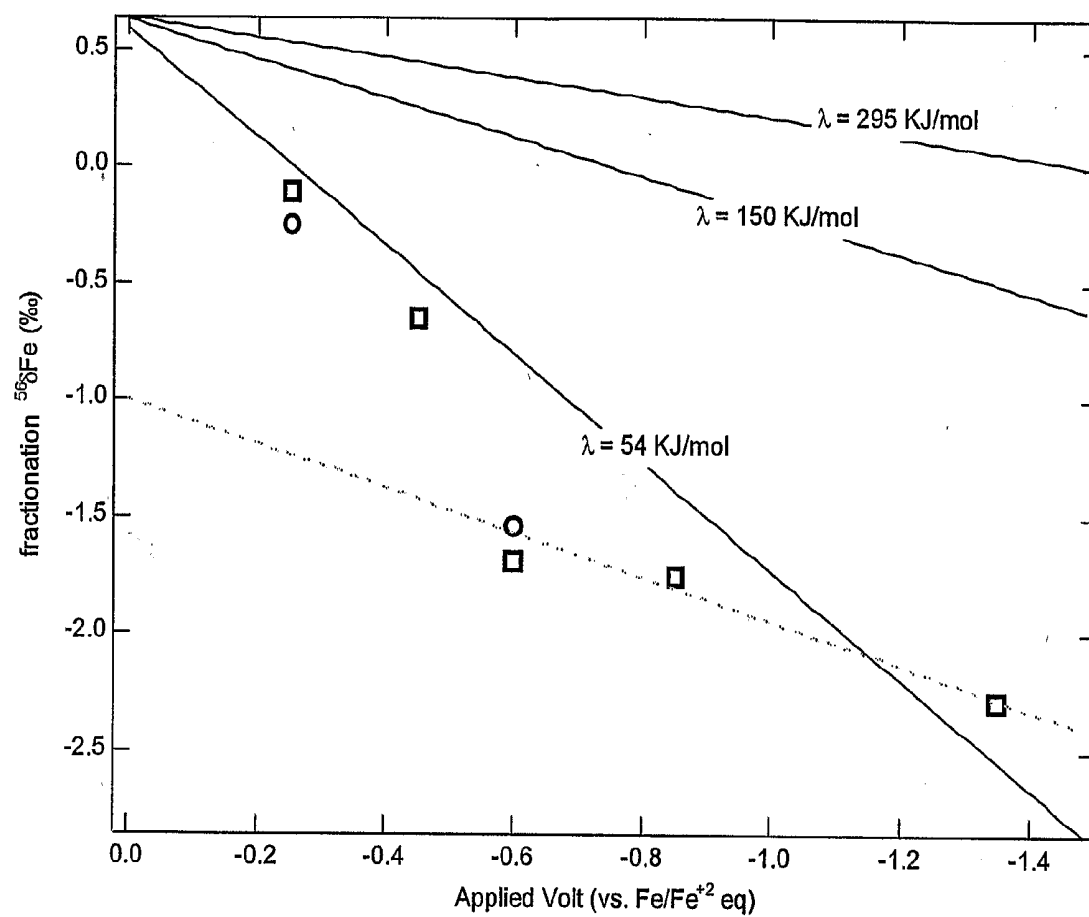
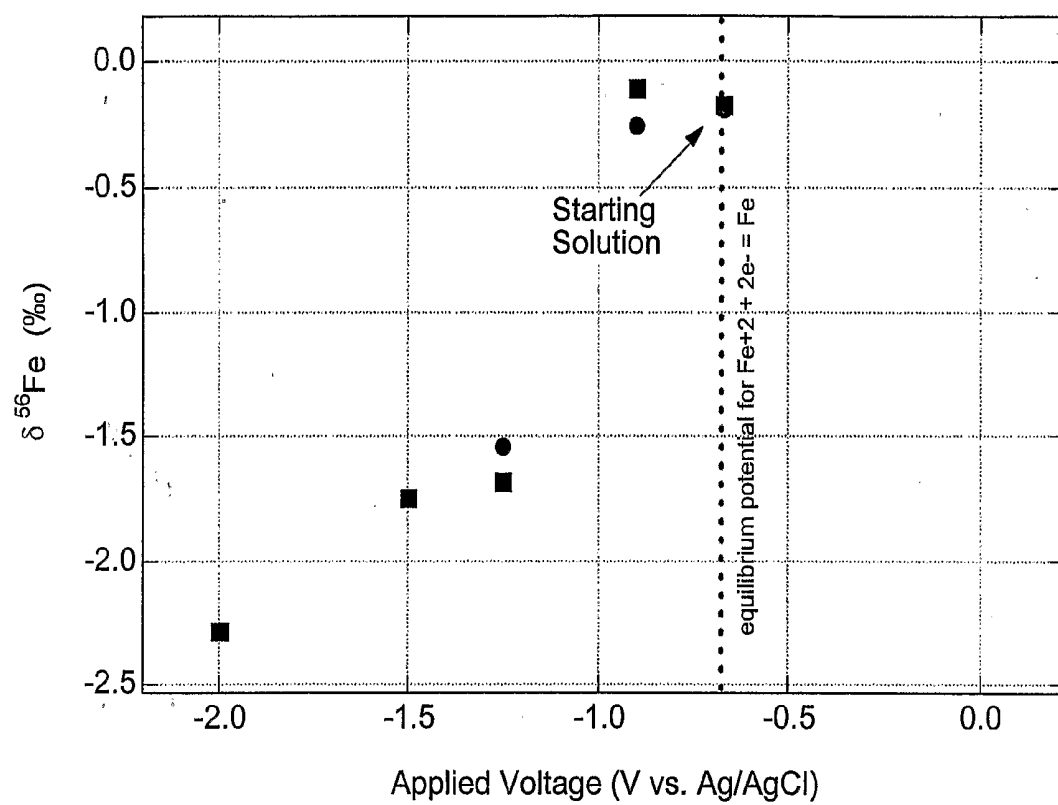
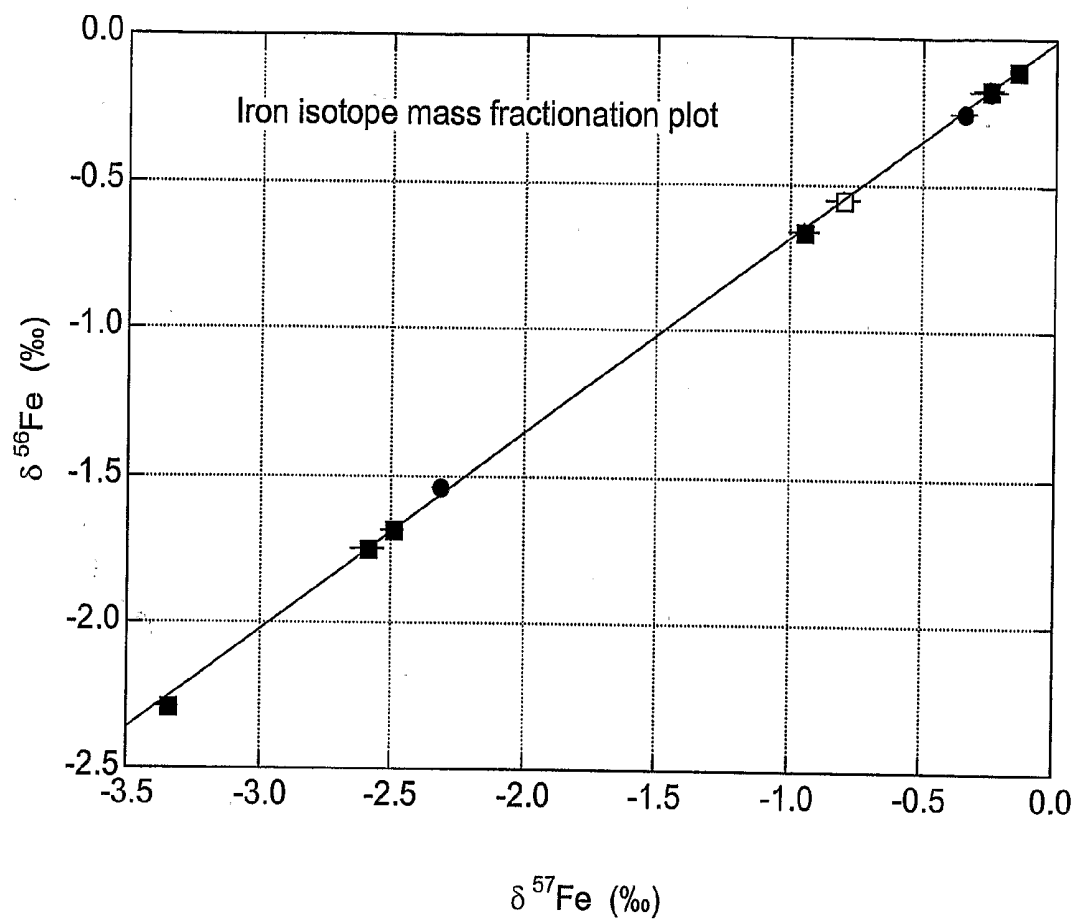


FIG. 5

**FIG. 6**

**FIG. 7**