Cesium Adsorption in Hydrated Iron Oxide Particles Suspensions: An NMR Study

Yves Gossuin,*,[1] Jean-Marie Colet,* Alain Roch,† Robert N. Muller,† and Pierre Gillis*

*Department of Biological Physics and †NMR Laboratory, Department of Organic Chemistry, University of Mons-Hainaut, B-7000 Mons, Belgium

[137]Cs is an important component of nuclear waste which may pollute water. Its migration in natural environments is slowed down by adsorption on minerals. Cesium adsorption on akaganeite (β-FeOOH) particles, dextran-coated ferrihydrite ($5\,Fe_2O_3$–$9H_2O$) particles, and ferritin in aqueous solutions is studied with [133]Cs nuclear magnetic resonance measurements. The longitudinal relaxation time (T_1) of [133]Cs in the presence of such magnetic particles depends on whether the ions bind to the particle or not. T_1 of [133]Cs ions in aqueous solutions containing the same amount of magnetized particles will not depend on cesium concentration if relaxation is governed by diffusion (when cesium is not able to bind), but it will depend on cesium concentration if exchange governs relaxation (when cesium is able to bind). The method is successfully tested using TEMPO, a nitroxide stable free radical whose relaxation is due to diffusion. [133]Cs relaxation in solutions of ferritin, akaganeite, and dextran-coated ferrihydrite particles is found to result from a cationic exchange of cesium ions between particles surface and bulk ions, owing to adsorption. The effect of pH on [133]Cs relaxation in solutions of the particles is consistent with the adsorption properties of cations on hydrated iron oxides. © 2002 Elsevier Science (USA)

Key Words: cesium; adsorption; ferrihydrite; akaganeite; ferritin.

INTRODUCTION

Hydrated iron oxides, like antiferromagnetic ferrihydrite ($5\,Fe_2O_3$–$9H_2O$) and akaganeite (β-FeOOH), are used to remove heavy metals from polluted water ([1]). Indeed, metal ions can be adsorbed on the oxide surface through a complexation reaction with surface hydroxyl groups. The efficiency of this adsorption depends on many parameters: concentration of metal ions in solution, concentration of adsorbent, specific surface of adsorbent, pH, presence of other competing ions, ... ([2–13]). Cesium-137 is a major and hazardous component of nuclear waste, which can pollute soil and water ([14, 15]). Its migration in natural environments is slowed down by adsorption on different clay minerals, as shown by several techniques, namely radiometric determi-

nation and magic angle spinning solid state nuclear magnetic resonance ([16–23]). The adsorption of cesium on some iron oxides, which could constitute interesting adsorbent agents, has already been studied ([23]) but never with NMR techniques. This is achieved here thanks to a nuclear magnetic relaxation study, showing evidence of cesium adsorption on ferrihydrite and akaganeite particles in aqueous solutions. This NMR technique does not require the drying of the adsorbent, which is an advantage over conventional methods. Cesium adsorption by ferritin, the natural iron storage protein of many living systems, is also studied for comparison. Ferritin is constituted by 24 subunits forming a spherical shell of 13 nm in diameter ([24]). Iron is stored in an 8-nm-diameter inner cavity, structuring a ferrihydrite mineral core, which may possibly adsorb cesium ions. Recent studies have shown that hydroxyl groups located at the ferrihydrite core surface of ferritin are involved in water relaxation induced by ferritin in aqueous solution ([25, 26]); this implication could explain the anomalous water relaxation properties exhibited by these solutions. This feature underlies the attempts to use magnetic resonance imaging (MRI) of organs containing ferritin to measure the iron content of tissues ([27–30]). The method described here could provide a useful tool for the study of important environmental contaminants' (cesium, cadmium, arsenic, ...) adsorption on magnetic hydrated iron oxides.

EXPERIMENTAL METHODS

Samples

Ferritin (ref F4503) was obtained from Sigma Chemicals (Bornem, Belgium). The average loading factor (number of iron ions per molecule) of the ferritin sample, as determined from the iron mass fraction, was about 1720. The hydrodynamic size of the protein, as measured by Photon Correlation Spectroscopy (Brookhaven Instruments BI 160, USA), was 13 nm. The average diameter of the spherical ferrihydrite core, measured by transmission electron microscopy (Philips CM 20 Microscope, USA), was 5.4 ± 0.8 nm. The pH of the original ferritin aqueous solutions was about 6.5. Ferritin agglomerated in solution below pH 5.5 and above pH 11.

Fercayl is clinically used for intramuscular iron injections and is distributed by Sterop laboratories (Brussels, Belgium). It consists of a colloidal solution of akaganeite (β-FeOOH) particles coated with dextran (information provided by the supplier) with an overall size of 24 nm. The iron oxide particles are rod-like, with a long axis measuring 15 nm log-normally distributed ($\sigma = 0.072$), and a short axis whose length is between 1.5 and 3.5 nm (measured by transmission electron microscopy). Akaganeite, like ferrihydrite, is a hydrated iron oxide. The pH of the original Fercayl aqueous solutions was about 6. Thanks to the dextran coating, Fercayl solutions were stable over a large pH range, from pH 2 to 12. Dextran is used to prevent agglomeration.

Ferrihydrite particles were synthesized by adding 5 g of $Fe(NO_3)_3$–$9H_2O$ to 500 ml of distilled water at 75°C containing 10 g of dextran (MW = 78,000), under rapid stirring. Fe^{3+} and NO_3^+ in excess were eliminated by dialysis (membrane cut-off = 500). The iron concentration of the sample was determined by inductively coupled plasma atomic emission spectroscopy (Jobin Yvon JY70+, Longjumeau, France). The overall size of the particles is 25 nm, while the spherical particles of ferrihydrite have a radius of 5.3 ± 1.2 nm, measured by transmission electron microscopy. The sample was shown to be 6-line ferrihydrite by electronic diffraction: the diffraction pattern was composed of 6 rings. Thanks to the dextran coating, ferrihydrite particles solutions are stable from pH 2 to 12.

TEMPO (2,2,6,6 tetramethyl-piperidine-1-oxyl; ref 21, 400-0) was obtained from Aldrich Chemicals (Bornem, Belgium) and Cesium chloride (ref 20968) from Fluka (Steinheim, Germany). TEMPO is used in our work as a paramagnetic reference for outer sphere relaxation. Indeed the relaxation of water protons in the presence of this paramagnetic molecule was shown to arise from an outer sphere relaxation mechanism.

NMR Measurements

^{133}Cs longitudinal relaxation time measurements were performed on a 4.7 T MSL-200 Spectrometer (Bruker, Karlsruhe) with a 10-mm broadband coil. The corresponding Larmor frequency of ^{133}Cs is 26.13 MHz. T_1 was determined by an inversion recovery sequence. The repetition time was always longer than 5 T_1. Monoexponential fits were adequate with no evidence of mutiexponential behavior. Temperature regulation (37°C) was ensured by a gas flow BVT 100 unit. The error on relaxation times was less than 2%.

pH Measurement

The pH of the solutions was adjusted by adding minute amounts of concentrated NaOH and HCl and was measured 5 minutes after the addition by a WTW PH597 pH-meter (WTW, Germany), with a SENTIX 41 glass electrode.

Distinction between Diffusion and Exchange Relaxation

In aqueous solutions, the increasing of water relaxation by magnetic particles can be the result of the binding of water to the particles, with an exchange between bulk and hydration water molecules, or the diffusion of water molecules within the magnetic field inhomogeneities created by the magnetic particles (*31, 32*). Adsorption has thus potentially a great impact on the relaxation properties of a given nucleus, for example, ^{133}Cs, in a solution containing magnetic particles.

It is possible to point out parameters whose influence on relaxation differs according to the physical process modulating the relaxation. When binding occurs, the relaxation rate $1/T_1^{EX}$ is proportional to the ratio of the concentration of adsorption sites for cesium ions on the magnetic particles to the concentration of cesium ions present in solution C_{CS}. When diffusion governs relaxation, $1/T_1^{DIF}$ is only proportional to the concentration of magnetic particles C_V, i.e., the number of moles of magnetic particles per liter of solution, without any dependence on C_{CS},

$$\frac{1}{T_1^{DIF}} \propto C_V \qquad [1]$$

$$\frac{1}{T_1^{EX}} \propto \frac{C_V \cdot q}{C_{CS}} \qquad [2]$$

q being the number of Cesium ions adsorbed on one magnetic particle.

The difference between the two physical mechanisms will be highlighted if one compares two solutions with the same concentration of magnetic particles (C_V) but with different concentrations of cesium ions (C_{CS}). According to Eqs. [1] and [2], if cesium relaxation rates are the same in both solutions, relaxation is assigned to diffusion, while different relaxation rates will be interpreted as the fingerprint of an exchange process. In our results, the iron concentration is used instead of the concentration of magnetic particles. Indeed, the measured concentration is the iron concentration.

Diamagnetic Contribution

The longitudinal relaxation of ^{133}Cs in pure water is slow and independent of the Cs concentration in solution ($1/T_1^{dia} = 0.0730 \pm 0.0007$ s^{-1}). It is due to the interaction between the quadrupolar moment of the nucleus and the electric field gradient created by the surrounding electrons (*33*). This diamagnetic contribution to the relaxation of cesium solutions was taken into account in all the fittings.

RESULTS AND DISCUSSION

Effect of C_{CS} and pH on T_1

Figure 1 shows ^{133}Cs T_1 for different aqueous solutions of TEMPO with the same concentration of TEMPO but with different values of C_{CS}. ^{133}Cs longitudinal relaxation is independent of C_{CS}.

Figure 2 provides the same measurements but for ferritin with a unique iron concentration. ^{133}Cs T_1 is clearly dependent on the
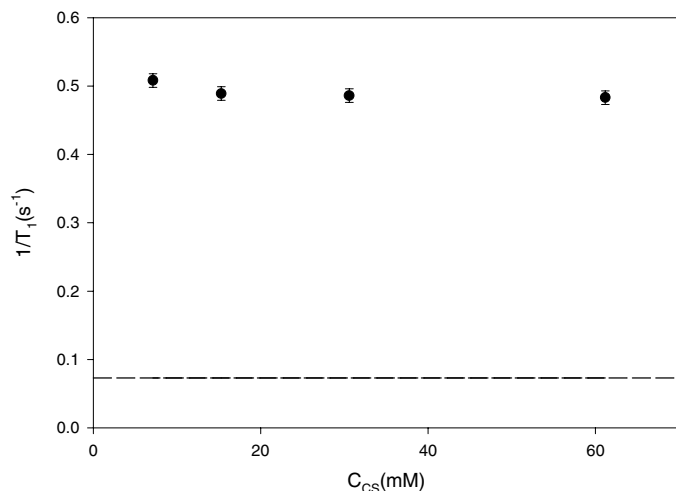
FIG. 1. ^{133}Cs longitudinal relaxation rate as a function of Cesium concentration (C_{CS}) for different aqueous solutions of 26.1 mM TEMPO. T = 37°C and pH = 7. The dashed line represents the longitudinal relaxation rate of cesium in aqueous solution, without any addition of magnetic compounds.

FIG. 3. ^{133}Cs longitudinal relaxation rate as a function of Cesium concentration (C_{CS}) for different aqueous solutions of 36 mM [Fe] Fercayl. T = 37°C and pH = 6. The long dashed line is a fitting of the data with a constant q (Eq. [2]). The plain line is a fitting of the data using a Langmuir isotherm expression for q (Eq. [4]). The short dashed line represents the longitudinal relaxation rate of cesium in aqueous solution, without any addition of magnetic compounds.

cesium concentration. The corresponding results for Fercayl and dextran-coated ferrihydrite particles are shown respectively in Figs. 3 and 4. pH does not affect the longitudinal relaxation of ^{133}Cs in aqueous solutions of TEMPO. Contrarily, pH considerably influences ^{133}Cs T_1 for ferritin, Fercayl, and dextran-coated ferrihydrite particles. Relaxation is significantly faster at alkaline pH than at acidic pH (Fig. 5).
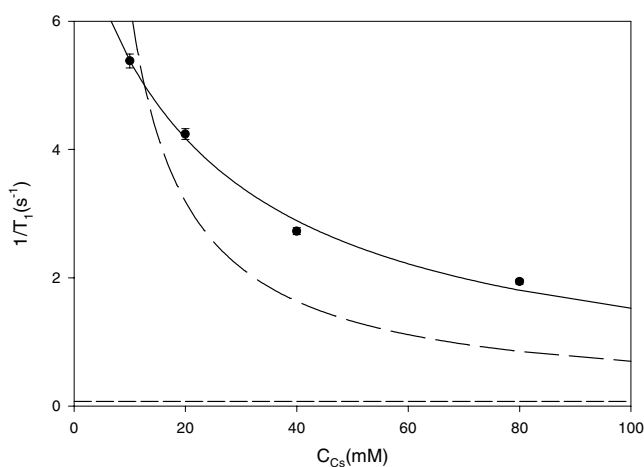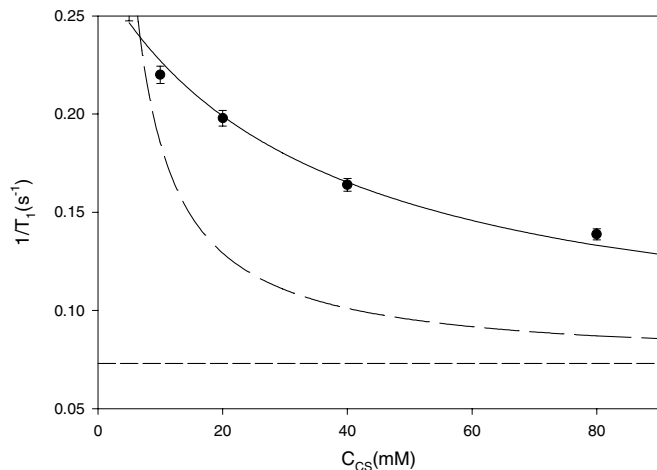
Interpretation of the Results

TEMPO

TEMPO is a neutral organic molecule which does not bind water or protons. The relaxation of water protons in the presence of TEMPO is therefore due to a diffusion mechanism (*34*). Similarly, TEMPO likely does not bind cesium ions. Our result, i.e.,
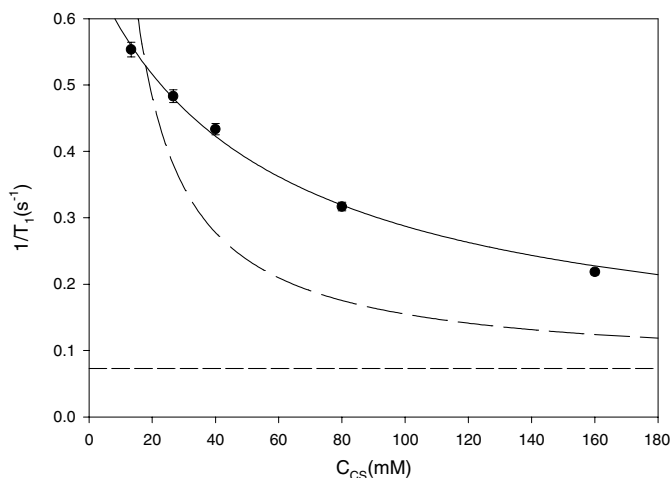

FIG. 2. ^{133}Cs longitudinal relaxation rate as a function of Cesium concentration (C_{CS}) for different aqueous solutions of 25.7 mM [Fe] ferritin. T = 37°C and pH = 8.95. The long dashed line is a fitting of the data with a constant q (Eq. [2]). The plain line is a fitting of the data using a Langmuir isotherm expression for q (Eq. [4]). The short dashed line represents the longitudinal relaxation rate of cesium in aqueous solution, without any addition of magnetic compounds.

FIG. 4. ^{133}Cs longitudinal relaxation rate as a function of Cesium concentration (C_{CS}) for different aqueous solutions of 24.2 mM [Fe] dextran-coated ferrihydrite particles. T = 37°C and pH = 9.25. The long dashed line is a fitting of the data with a constant q (Eq. [2]). The plain line is a fitting of the data using a Langmuir isotherm expression for q (Eq. [4]). The short dashed line represents the longitudinal relaxation rate of cesium in aqueous solution, without any addition of magnetic compounds.

the independence of $1/T_1$ on C_{CS}, proves that ^{133}Cs relaxation is also caused by diffusion and confirms that cesium is not binding to the TEMPO molecule.

Hydrated Iron Oxide Particles

The influence of C_{CS} on ^{133}Cs relaxation rate in ferritin, akaganeite, and dextran-coated ferrihydrite particles solutions demonstrates that relaxation is due to an exchange of cesium ions between particle surface and free ions in solution. Cesium ions are thus adsorbed on the particles, confirming the well known ability of hydrated iron oxides to adsorb cations (2–11). In the case of ferritin, the adsorption could occur on the inner ferrihydrite core or maybe on the proteic shell. Indeed, Cesium ions must be able to pass through the proteic shell to adsorb on the inner crystal. The access channels of ferritin are quite small and maybe not large enough for a Cesium ion. For the dextran-coated particles, the presence of dextran is not affecting the binding of Cesium ions, because dextran is only covering a small part of the surface of the particle.

However, the results must be carefully interpreted. Indeed, Eq. [2] predicts that if q is independent of C_{CS}, there is a $1/C_{CS}$ dependence of $1/T_1$. However, as shown in Figs. 2, 3, and 4, the experimental dependence is different because q, the number of cesium ions adsorbed on one particle, depends on C_{CS}. When there is only a single type of adsorption site, this dependence is described by a Langmuir isotherm (1, 6):

$$q = Q \cdot \frac{K \cdot C_{CS}}{1 + K \cdot C_{CS}}. \qquad [3]$$

Q is the maximum number of adsorbed cesium ions on one particle, while K is the adsorption equilibrium constant. Taking
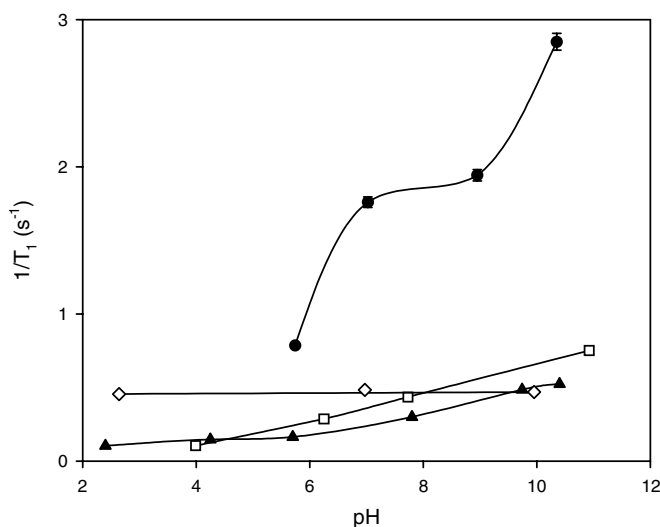
TABLE 1
Adsorption Equilibrium Constants Calculated from the Fittings

	Ferritin (pH = 8.95)	Fercayl akaganeite particles (pH = 6)	Dextran-coated ferrihydrite particles (pH = 6.3)
K (L/mole)	(42 ± 6)	(28.7 ± 4.4)	(18.2 ± 1.4)

this dependence into account, one obtains for the longitudinal relaxation rate

$$\frac{1}{T_1^{EX}} \propto Q \cdot \frac{K \cdot C_V}{1 + K \cdot C_{CS}}. \qquad [4]$$

Fitting Eq. [4] to the experimental data, rather than Eq. [2], yields a much better agreement (see Figs. 2, 3, and 4) and allows the determination of the adsorption equilibrium constants K of the different compounds (Table 1).

The effect of pH on T_1 can be related to the acid-base properties of the surface of the hydrated iron oxide particles. Indeed, surface hydroxyl groups of hydrated iron oxides exhibit an amphoteric behavior:

$$\equiv\!\!-O^- + H^+ \rightleftharpoons \equiv\!\!-OH \qquad [5]$$

$$\equiv\!\!-OH + H^+ \rightleftharpoons \equiv\!\!-OH_2^+ \qquad [6]$$
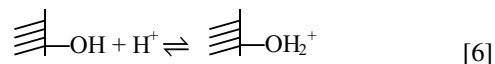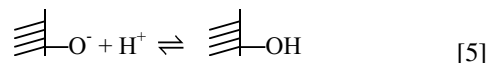
The surface is protonated at low pH, and thus positively charged, while at high pH it is negatively charged. As a consequence, the adsorption of a positive ion, like Cs^+, is easier at alkaline pH than at acidic pH. In Eq. [2], q is thus pH dependent and longitudinal relaxation is faster at high pH than at low pH, as observed experimentally for all hydrated iron oxide particles (Fig. 5).

In conclusion, evidence of cesium adsorption on ferrihydrite and akaganeite particles in aqueous solutions has been shown, thanks to a ^{133}Cs NMR relaxation time study. The same method could be used to study the adsorption of other ions producing an NMR signal, like cadmium-113, arsenic-75, . . . , on hydrated iron oxides in aqueous solutions. A more detailed study, with ions whose adsorption properties are well known, may help to validate the method.

ACKNOWLEDGMENTS

FIG. 5. Effect of pH at 37°C on ^{133}Cs T_1 of aqueous solutions of 26.1 mM TEMPO (◇) with $C_{CS} = 60$ mM; 25.7 mM [Fe] ferritin (●) with $C_{CS} = 80$ mM; 36 mM [Fe] Fercayl (▲) with $C_{CS} = 40$ mM; and 24.2 mM [Fe] dextran-coated ferrihydrite particles (□) with $C_{CS} = 80$ mM.

REFERENCES

1. R. M. Cornell and U. Schwertmann, "The Iron Oxides," VCH, New York (1996).

2. J. A. Davis and J. O. Leckie, Surface ionization and complexation at the oxide/water interface. II. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions, *J Colloid. Interface Sci.* **67,** 90–107 (1978).

3. C. O. Cowan, J. M. Zachara, and C. T. Resch, Cadmium adsorption on iron oxides in the presence of alkaline-earth elements, *Environ. Sci. Technol.* **25,** 437–446 (1991).

4. K. P. Raven, A. Jain, and R. H. Loeppert, Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes, *Environ. Sci. Technol.* **32,** 344–349 (1998).

5. K. F. Hayes and J. O. Leckie, Modeling ionic strength effects on cation adsorption at hydrous oxide/solution interfaces, *J. Colloid Interface Sci.* **115,** 564–572 (1987).

6. D. A. Dzombak and F. M. Morel, "Surface Complexation Modeling: Hydrous Ferric Oxide," Wiley, New York (1990).

7. M. M. Benjamin and J. O. Leckie, Multiple-site adsorption of Cd, Cu, Zn and Pb on amorphous iron oxyhydroxide, *J. Colloid Interface Sci.* **79,** 209–221 (1981).

8. M. M. Benjamin, K. F. Hayes, and J. O. Leckie, Removal of toxic metals from power-generation waste steams by adsorption and coprecipitation, *J. WPCF* **54,** 1472–1481 (1982).

9. M. F. Shultz, M. M. Benjamin, and J. F. Ferguson, Adsorption and desorption of metals on ferrihydrite: Reversibility of the reaction and sorption properties of the regenerated solid, *Environ. Sci. Technol.* **21,** 863–869 (1987).

10. J. M. Zachara, D. C. Girvin, R. L. Scmidt, and C. T. Resch, Chromate adsorption on amorphous iron oxyhydroxide in the presence of major groundwater ions, *Environ. Sci. Technol.* **21,** 589–594 (1987).

11. Y. Gao, A. K. Sengupta, and D. A. Simpson, A new hybrid inorganic sorbent for heavy metals removal, *Water Res.* **29,** 2195–2205 (1995).

12. T. E. Payne, J. A. Davis, and T. D. Waite, Uranium adsorption on ferrihydrite—Effects of phosphate and humic acid, *Radiochim. Acta* **74,** 239–243 (1996).

13. T. E. Payne, G. R. Lumpkin, and T. D. Waite, *in* "Adsorption of Metals by Geomedia: Variables, Mechanisms and Model Applications" (E. A. Jenne, Ed.), Chap. 2, pp. 75–97, Academic Press, San Diego (1998).

14. T. M. Beasley and D. Jennings, Inventories of ^{239,240}Pu, ^{241}Am, ^{137}Cs and ^{60}Co in Columbia River sediments from Hanford to the Columbia River Estuary, *Environ. Sci. Technol.* **18,** 207–212 (1984).

15. J. J. Alberts and M. A. Wahlgren, Concentrations of ^{239,240}Pu, ^{137}Cs and ^{90}Sr in the waters of the Laurentian Great Lakes, *Environ. Sci. Technol.* **15,** 94–98 (1981).

16. A. Yllera de Llano, A. Hernandez Benitez, and M. Garcia Guiterrez, Cesium sorption studies on spanish clay materials, *Radiochim. Acta* **82,** 275–278 (1998).

17. A. M. Hansen, A. Cerezo-Roman, and V. Ortega-Lara, Interactions of cesium with sediments from Mexican aquatic environments, *Aquatic Ecosyst. Health Manage.* **1,** 221–235 (1998).

18. M. Todorovic, S. K. Milonjic, J. J. Comor, and I. J. Gal, Adsorption of radioactive ions ^{137}Cs$^+$, ^{85}Sr^{2+}, and ^{60}Co^{2+} on natural magnetite and hematite, *Sep. Sci. Technol.* **27,** 671–679 (1992).

19. C. A. Weiss, R. J. Kirkpatrick, and S. P. Altaner, The structural environments of cations adsorbed onto clays: ^{133}Cs variable temperature MAS NMR spectroscopic study of hectorite, *Geochim. Cosmochim. Acta* **54,** 1655–1669 (1990).

20. Y. Kim, R. J. Kirkpatrick, and R. Cygan, ^{133}Cs NMR study of cesium on the surfaces of kaolinite and illite, *Geochim. Cosmochim. Acta* **60,** 4059–4074 (1996).

21. Y. Kim, R. T. Cygan, and R. J. Kirkpatrick, ^{133}Cs NMR and XPS investigation of cesium adsorbed on clay minerals and related phases, *Geochim. Cosmochim. Acta* **60,** 1041–1052 (1996).

22. Y. Kim and R. J. Kirkpatrick, ^{23}Na and ^{133}Cs NMR study of cation adsorption on mineral surfaces: local environment, dynamics, and effects of mixed cations, *Geochim. Cosmochim. Acta* **61,** 5199–5208 (1997).

23. R. M. Cornell, Adsorption of cesium on minerals: A review, *J. Radioanal. Nucl. Chem.* **171,** 483–500 (1993).

24. P. M. Harrison and P. Arosio, The ferritins: Molecular properties, iron storage function and cellular regulation, *Biochim. Biophys. Acta* **1275,** 161–203 (1996).

25. Y. Gossuin, A. Roch, R. N. Muller, and P. Gillis, Relaxation induced by ferritin and ferritin-like magnetic particles: The role of proton exchange, *Magn. Reson. Med.* **43,** 237–243 (2000).

26. Y. Gossuin, A. Roch, F. Lo Bue, R. N. Muller, and P. Gillis, Nuclear magnetic relaxation dispersion of ferritin and ferritin-like magnetic particle solutions: A pH-effect study, *Magn. Reson. Med.* **46,** 476–481 (2001).

27. G. Bartzokis, J. L. Cummings, C. H. Markham, P. Z. Marmarelis, L. J. Treciokas, T. A. Tishler, S. R. Marder, and J. Mintz, MRI evaluation of brain iron in earlier and later-onset Parkinson's disease and normal subjects, *Magn. Reson. Imaging* **17,** 213–222 (1999).

28. N. Gelman, J. M. Gorell, P. B. Barker, R. M. Savage, E. M. Spickler, J. P. Windham, and R. A. Knight, MR imaging of human brain at 3.0 T: Preliminary report on transverse relaxation rates and relation to estimated iron content, *Radiology* **210,** 759–767 (1999).

29. F. Q. Ye, W. R. Wayne Martin, and P. S. Allen, Estimation of brain iron in vivo by means of the interecho time dependence of image contrast, *Magn. Reson. Med.* **36,** 153–158 (1996).

30. J. Vymazal, A. Righini, R. A. Brooks, M. Canesi, C. Mariani, M. Leonardi, and G. Pezzoli, T_1 and T_2 in the brain of healthy subjects, patients with Parkinson disease and patients with multiple system atrophy: Relation to iron content, *Radiology* **211,** 489–495 (1999).

31. L. Banci, I. Bertini, and C. Luchinat, "Nuclear and Electron Relaxation," VCH, New York (1991).

32. I. Bertini and C. Luchinat, NMR of paramagnetic substances, *Coord. Chem. Rev.* **150** (1996).

33. F. W. Wehrli, Spin–lattice relaxation of some less common weakly quadrupolar nuclei, *J. Magn. Reson.* **30,** 193–209 (1978).

34. P. Vallet, Y. Van Haverbeke, P. A. Bonnet, G. Subra, J.-P. Chapat, and R. N. Muller, Relaxivity enhancement of low molecular weight nitroxisz stable free radicals: Importance of structure and medium, *Magn. Reson. Med.* **32,** 11–15 (1994).