Abstract: Sediments with basaltic provenance, such as those at the Hanford nuclear reservation, Washington, U.S.A, are rich in Fe-bearing minerals of mixed valence. These minerals are redox reactive with aqueous O2 or Fe(II), and have the potential to react with important environmental contaminants including Tc. Here, we isolate, identify and characterize natural Fe(II)/Fe(III)-bearing microparticles from Hanford sediments, develop synthetic analogues and investigate their batch redox reactivity with aqueous Tc(VII). Natural Fe-rich mineral samples were isolated by magnetic separation from sediments collected at several locations on Hanford’s central plateau. This magnetic mineral fraction was found to represent up to 1 wt% of the total sediment, and be composed of 90% magnetite with minor ilmenite and hematite, as determined by X-ray diffraction. The magnetite contained variable amounts of transition metal impurities consistent with alio- and isovalent metal substitutions for Fe. X-ray microprobe analysis showed that Ti was the most significant impurity, and that these grains could be described with the titanomagnetite formula Fe3 xTixO4, which falls between endmember magnetite (x = 0) and ulvöspinel (x = 1). The dominant composition was determined to be x = 0.15 by chemical analysis and electron probe microanalysis in the bulk, and by L-edge X-ray absorption spectroscopy and X-ray photoelectron spectroscopy at the surface. Site-level characterization of the titanomagnetites by X-ray magnetic circular dichroism showed that despite native oxidation, octahedral Fe(II) was detectable within 5 nm of the mineral surface. By testing the effect of contact with oxic Hanford and Ringold groundwaters to reduced Ringold groundwater, it was found that the concentration of this near-surface structural Fe(II) was strongly dependent on aqueous redox condition. This highlights the potential for restoring reducing equivalents and thus reduction capacity to oxidized Fe-mineral surfaces through redox cycling in the natural environment. Reaction of these magnetically-separated natural phases from Hanford sediments with a solution containing 10  μmol L-1 Tc(VII) showed that they were able to reduce Tc(VII) to Tc(IV) with concurrent oxidation of Fe(II) to Fe(III) at the mineral surface, as were synthetic x = 0.15 microparticle and nanoparticle analogue phases. When differences in the particle surface area to solution volume ratio were taken into consideration, measured Tc(VII) reduction rates for Fe3 xTixO4 (x = 0.15) natural material, synthetic bulk powder and nanoparticles scaled systematically, suggesting possible utility for comprehensive batch and flow reactivity studies.
Dear Dr Norman,

Please find attached a manuscript entitled ‘Characterization of natural titanomagnetites (Fe$_{3-x}$Ti$_x$O$_4$) for studying heterogeneous electron transfer to Tc(VII) in the Hanford subsurface’, submitted for consideration as a regular article to *Geochimica et Cosmochimica Acta*. The authors of the manuscript are as follows:

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All authors have seen the manuscript and agree to its submission to Geochimica et Cosmochimica Acta.

This manuscript describes the isolation and comprehensive characterization of Fe(II)/Fe(III)-bearing microparticles from sediments at the Hanford nuclear reservation, one of the world’s most contaminated sites, and the development of synthetic analogues, and the measurement of their electron transfer reactivity with respect to the contaminant Tc(VII). The research focuses on investigating the properties of Hanford subsurface sediments to predict their influence on key chemical processes affecting the stability of radioactive contaminants. More broadly it relates to mechanisms of heterogeneous electron transfer across the mineral-water interface, providing new insights into the importance of Fe(II) in the solid-state and its potential to be recharged by redox interaction with groundwater.
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Thank you very much,

Carolyn Pearce, Ph.D.

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Characterization of natural titanomagnetites (Fe$_{3-x}$Ti$_x$O$_4$) for studying heterogeneous electron transfer to Tc(VII) in the Hanford subsurface

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Abstract

Sediments with basaltic provenance, such as those at the Hanford nuclear reservation, Washington, U.S.A, are rich in Fe-bearing minerals of mixed valence. These minerals are redox reactive with aqueous O$_2$ or Fe(II), and have the potential to react with important environmental contaminants including Tc. Here, we isolate, identify and characterize natural Fe(II)/Fe(III)-bearing microparticles from Hanford sediments, develop synthetic analogues and investigate their batch redox reactivity with aqueous Tc(VII). Natural Fe-rich mineral samples were isolated by magnetic separation from sediments collected at several locations on Hanford’s central plateau. This magnetic mineral fraction was found to represent up to 1 wt% of the total sediment, and be composed of 90% magnetite with minor ilmenite and hematite, as determined by X-ray diffraction. The magnetite contained variable amounts of transition metal impurities consistent with alio- and isovalent metal substitutions for Fe. X-ray microprobe analysis showed that Ti was the most significant impurity, and that these grains could be described with the titanomagnetite formula Fe$_{3-x}$Ti$_x$O$_4$, which falls between endmember magnetite ($x = 0$) and ulvöspinel ($x = 1$). The dominant composition was determined to be $x = 0.15$ by chemical analysis and electron probe microanalysis in the bulk, and by L-edge X-ray absorption spectroscopy and X-ray photoelectron spectroscopy at the surface.

Site-level characterization of the titanomagnetites by X-ray magnetic circular dichroism showed that despite native oxidation, octahedral Fe(II) was detectable within 5 nm of the mineral surface. By testing the effect of contact with oxic Hanford and Ringold groundwaters to reduced Ringold groundwater, it was found that the concentration of this near-surface structural Fe(II) was strongly dependent on aqueous redox condition. This highlights the potential for restoring reducing equivalents and thus reduction capacity to oxidized Fe-mineral surfaces through redox
cycling in the natural environment. Reaction of these magnetically-separated natural phases from Hanford sediments with a solution containing 10 μmol. L⁻¹ Tc(VII) showed that they were able to reduce Tc(VII) to Tc(IV) with concurrent oxidation of Fe(II) to Fe(III) at the mineral surface, as were synthetic x = 0.15 microparticle and nanoparticle analogue phases. When differences in the particle surface area to solution volume ratio were taken into consideration, measured Tc(VII) reduction rates for Fe₃₋ₓTiₓO₄ (x = 0.15) natural material, synthetic bulk powder and nanoparticles scaled systematically, suggesting possible utility for comprehensive batch and flow reactivity studies.

**Keywords:** Magnetite, titanomagnetite, electron transfer, iron redox cycling, technetium, X-ray diffraction, electron probe microanalysis, X-ray photoelectron spectroscopy, X-ray microprobe, X-ray magnetic circular dichroism
1. Introduction

The Hanford site is a former nuclear reprocessing facility occupying 1500 km² on the banks of the Columbia River in Washington State, U.S.A. (McKinley et al., 2007). Operations at the site were restricted to specific areas, with nuclear fuel fabrication to the south (300 Area), fuel irradiation to the north (100 Area) and fuel rod processing on the central plateau (200 Area). In the 300 Area, waste fluids and slurries containing U, Al and Cu were stored in process ponds. In the 200 Area, highly-radioactive wastes from Pu production were disposed of in underground tanks. The unintended release of U, Tc and Pu from these storage facilities resulted in contamination of the underlying vadose sediments and the groundwater (McKinley et al., 2007).

To predict the distribution and migration potential of these contaminants, it is necessary to understand the geology and mineralogy of the enclosing sediments. To this end, sediment was recovered from boreholes drilled at several locations across the 200 Area on the Central Plateau, and in the 300 Area next to the Columbia River. Table 1 provides details on the geology and the mineralogy of the samples obtained from these locations. The sediments were similar in composition and invariably contained a magnetic, Fe-rich mineral fraction consisting of magnetite, titanomagnetite, ilmenite, Fe(II)/Fe(III) phyllosilicates, and Fe(III) oxides, as well as carbonates, pyroxenes and feldspars, reflecting the underlying basaltic lithology of the Hanford site (Zachara et al., 2007b).

Spinel-type iron oxides such as magnetite (Fe₃O₄) are key mineral phases at the Hanford site because their structural Fe(II) content is able to affect the form and stability of redox-active contaminants through heterogeneous electron transfer. In the absence of surface passivation, magnetites have been shown to spontaneously reduce and effectively immobilize ^99^Tc(VII), a major risk-driving contaminant at Hanford, to less soluble Tc(IV) in the form of a mixed Fe(III)-
Tc(IV) co-precipitate (Cui and Eriksen, 1996; Farrell et al., 1999; Ilton et al., 2010; Liu et al., 2012; Skomurski et al., 2011). However, surface passivation is prevalent in oxic aquifer zones as a result of exposure to oxygen from the atmosphere or oxygenated water. The Hanford subsurface also contains reduced zones where there is potential for restoring reducing equivalents to mineral surfaces by exposure to aqueous Fe(II). These oxidation-reduction processes are strongly dependent on the inherent bulk-mineral Fe(II) content and on the Fe(II) distribution and accessibility at the mineral surface.

The objective of this study was to obtain fundamental information about the structure and chemical composition of Hanford sediment-derived iron oxides and to assess their potential for electron transfer reactions with contaminants, e.g. Tc(VII), at the oxide-solution interface. To achieve this, natural Fe(II)/Fe(III)-containing mineral samples were isolated by magnetic separation from three sediments collected at two different locations on the Central Plateau of the Hanford site; the Environmental Restoration Disposal Facility (ERDF) and the coarse (SC) and fine (SF) fractions from the Trench 94 Subpit (the excavated site used for storage of scrapped submarine reactor compartments). The magnetic mineral fraction of these sediments was characterized in terms of mineralogy, chemical composition, particle size and morphology, and presence of impurities, by micro-X-ray diffraction (µ-XRD), wet chemical analysis, electron probe microanalysis (EPMA), scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) and X-ray microprobe/X-ray absorption near edge spectroscopy (XMP/XANES).

Due to the importance of the mineral surface when considering the potential for interaction with solution species, the surface composition was examined by L-edge X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS). The magnetic mineral fraction was also analyzed using X-ray magnetic circular dichroism (XMCD), which is the only
technique that allows a clear distinction between possible Fe oxidation states and
crystallographic sites at the reactive surface due to the ~4.5 nm (~5 unit cells) probing depth of
these measurements in total electron yield mode (Gota et al., 2000).

We focused on magnetite-containing Ti(IV) as a major structural substituent, so-called
titanomagnetites (Fe$_{3-x}$Ti$_x$O$_4$), because this naturally-occurring phase was dominant within the
magnetic mineral fraction. Substitution of Fe(III) by Ti(IV) in the lattice yields solid-solution
intermediates along the binary join from end-member magnetite (Fe$_3$O$_4$, x = 0) to ulvöspinel
(Fe$_2$TiO$_4$, x = 1). This substitution is accompanied by reduction of lattice Fe(III) to Fe(II) for
charge balance; therefore, a proportional increase in the Fe(II)/Fe(III) ratio to values greater than
that in magnetite (1:2) is expected. Because the Ti-content dictates the solid-state Fe(II)/Fe(III)
ratio, it also “tunes” the bulk thermodynamic redox potential and thereby controls the rate and
extent of electron transfer to contaminant species of interest (Liu et al., 2012).

We also examined heterogeneous Tc(VII) reduction by these Hanford titanomagnetites to
assess their reducing capacity, a reaction that involves concurrent oxidation of Fe(II) to Fe(III) at
the mineral surface. Reduction of Tc(VII) by titanomagnetite could thus be written:

\[
\frac{y}{3} \text{TcO}_4^- + \text{Fe}_{2-2x}^{3+} \text{Fe}_{1+x}^{2+} \text{Ti}_x^{4+} \text{O}_4^{2-} + \frac{4}{3} y \text{H}_2 \text{O} \rightarrow \frac{y}{3} \left[ \text{TcO}_2 \cdot 2 \text{H}_2 \text{O} | \text{Fe(OH)}_3 \right] + \\
\text{Fe}_{2-2x}^{3+} \text{Fe}_{1+x}^{2+} \text{Ti}_x^{4+} \text{O}_4^{2-} + \frac{y}{3} \text{OH}^- + \frac{2}{3} \text{H}_2 \text{O},
\]

yielding titanomaghemite and a relatively insoluble Tc(IV)-Fe(III) phase as expected products,
the latter of which is similar to a structurally unspecified mixture of TcO$_2$ hydrate and
ferrihydrite (Liu et al., 2012), consistent with previous work (Lukens et al., 2002; Zachara et al.,
2007a). Tc(VII) reduction rates were compared with those obtained for complementary synthetic
microparticle and nanoparticle analogue Fe$_{3-x}$Ti$_x$O$_4$ phases developed for this comparative
purpose. We took advantage of the uniquely well-suited power of XMCD to characterize the
oxidation state and site occupancy of Fe present at the titanomagnetite surfaces before and after reactivity with Tc(VII), and also before and after exposure to groundwater extracted from different depths in the Hanford subsurface, to determine the potential for oxidation or Fe(II)-recharge of the surface as a result of changes in aqueous redox conditions.

2. Experimental Method

2.1 Sediment source and separation

Two operating waste-disposal areas on the Hanford Central Plateau were selected for sediment collection. Five gallons of (i) silty fine sand (SF); (ii) pebbly coarse sand (SC) were collected from the north wall of the trench 94 Subpit (218-E-12B Submarine Burial Ground), 12.2 m below ground surface; and five gallons of (iii) interstratified fine, medium and course sands of the Hanford formation (Ice Age flood deposits) of Pleistocene age (15,000-20,000 years old), with occasional finer layers of silty sand were collected from the Environmental Remediation Disposal Facility (ERDF), 12.2 m below ground surface. The sediment separation procedure developed by Baer et al. (2010) was employed to obtain the magnetic mineral fraction. The sediments were (i) dried and riffle split to produce homogeneous sub-splits; (ii) sieved to obtain the -20 mesh (<840 µm) fraction; (iii) elutriated and sonicated to remove the fines; and (iv) passed twice through a free-fall magnetic separation apparatus (Frantz Magnetic Barrier Laboratory Separator LB1) to separate the magnetic mineral fraction.

2.2 Micro X-ray diffraction
Crystalline phases in the magnetic mineral fractions (ERDF, SC and SF) were identified using a Rigaku D/Max Rapid II μ-XRD instrument with a 2D image plate detector. X-rays were generated with a MicroMax 007HF generator fitted with a rotating Cr anode (λ = 2.2897 Å), and focused on the specimen through a 30 μm diameter collimator. μ-XRD patterns were collected for 300 s at 42 kV and 150mA over a 2θ range of 10-150° Cr Kα1 radiation. Magnetic mineral fraction aliquots were ground dry in an agate mortar and pestle, and loaded into an X-ray amorphous silica capillary (Charles Supper Company, 0.5 mm OD). Samples were diluted with cornstarch (5:1 by volume) to alleviate the problem of reduced intensity, especially at low 2θ, due to the relatively high x-ray absorption of iron oxides. 2DP, Rigaku 2D Data Processing Software (Ver. 1.0, Rigaku, 2007) was used to integrate the diffraction rings captured by the 2-D image plate detector. Analysis of diffraction data was done using JADE 8.5 from Materials Data Inc., and the PDF4+ database from ICSD. The background was fitted by a cubic spline function, and diffraction peaks were fitted using the pseudo-Voigt profile shape function. Quantitative analysis and cell refinement was carried out in JADE using whole pattern fitting with the Reference Intensity Ratio (RIR) reported in the database used to scale the overall intensity of each mineral phase.

2.3 Chemical Analysis

The chemical composition of the SF sediment, in terms of Fe(II), and total Fe and Ti was characterized by dissolving in shaken, N2-sparged 5M HCl inside a glovebox overnight. Fe(II) was determined using the ferrozine method (Stookey, 1970) by adding 0.2 mL of diluted acid digest solution to 1.8 mL ferrozine (C20H15N4NaO7S2) reagent (1 g L⁻¹ ferrozine in 50 mM HEPES buffer, pH 7.0), and determining aqueous Fe(II) concentration by measuring the
absorbance at 562 nm using a Shimadzu UV-2501 PC spectrophotometer. Total Fe and Ti were determined using ICP-MS by adding 0.05 mL of the digested sample to 4.95 mL 2% HNO₃ and measuring on an ICP-MS Agilent 7500.

2.4 Electron probe microanalysis

The magnetic mineral fraction from the SF sediment was imbedded in epoxy, wafered using a diamond saw, and prepared as polished 100-μm thin sections on fused quartz slides. Samples were carbon coated (HR208 carbon coater, Ted Pella Inc., Redding, CA) prior to analysis. Compositional analyses were done using a JEOL JXA-8200 (JEOL USA, Peabody, MA) electron microprobe operated at an accelerating potential of 20 KeV and a beam current of 20 nA, focused on the sample surface (ca. 1 μm electron spot size). The instrument was calibrated against commercial mineral and oxide standards (Structure Probe, Inc., West Chester, PA), and data was reduced using a ZAF correction routine (Goldstein et al., 2003).

2.5 Scanning electron microscopy/energy dispersive spectroscopy

Particle morphology, surface topography, and the chemical composition of whole particles and polished mounts of the magnetic mineral fraction from the SF sediments was characterized by SEM/EDS. For the particle mount, the sample was placed on carbon tape attached to an aluminium planchette. Whole particle and polished mounts were carbon coated using a vacuum sputtercoater. A JEOL JSM-5900LV SEM equipped with an Oxford INCA EDS system (Oxford Instruments America Inc., Concord, MA), operating in backscattered electron (BSE) emission mode at 20 keV, was used for imaging and qualitative elemental analysis. Particle size and EDS analysis were conducted using automated particle analysis software on a
JEOL JXA-8530F electron microprobe equipped with an energy-dispersive X-ray spectrometer at 15 keV. Backscattered electron images were acquired on three randomly selected areas of the sample. All particles that were greater than 5 µm were numbered and analyzed automatically. After size analysis (~ 1 s), the electron beam was positioned in the center of the particle to collect an EDS spectrum for 30 seconds. Conventional standard ZAF (atomic number, mass absorption and fluorescence) correction was carried out automatically for semi-quantitative EDS analysis.

2.6 Synchrotron X-ray microprobe/X-ray absorption near edge spectroscopy

A thin section of the SF magnetic mineral fraction was characterized by XMP and XANES. XMP fluorescence imaging was carried out on beamline 20-ID at the Advanced Photon Source, Argonne National Lab. XMP fluorescence images were collected for Fe, Ti, Mn and V with a beam size of 3 µm x 7.5 µm, and at an energy below the Fe edge (7100 eV) to reduce the Fe signal. A Si (111) monochromator provided an energy resolution of 1 eV at the Fe K edge and 0.7 eV at the Ti K edge. X-ray fluorescence images of the thin sections were recorded and used to choose points for subsequent XANES measurements at the Fe and the Ti K-edge. Fe and Ti data were taken in fluorescence mode with an Fe foil used for online energy calibration. The XANES data were analyzed using the Athena interface to the IFEFFIT program package (Ravel and Newville, 2005).

2.7 X-ray photoelectron spectroscopy

The near-surface composition of the SF magnetic mineral fraction was analyzed by X-ray photoelectron spectroscopy (XPS) to determine the Fe chemical state and to measure the overall
particle surface composition. XPS analyses were conducted using a Physical Electronics Quantum 2000 Scanning ESCA Microprobe with a focused monochromatic Al Kα X-ray source (1486.7 eV) source and a spherical section analyzer. Particles were mounted using double-sided plastic tape attached to a Si (100) substrate. Fe 2p photoelectron spectra were compared to reference spectra in Chambers et al. (1998). For large collections of mineral particles, the X-ray beam was operated at approximately 100W power, focused to 100 µm diameter, and rastered over the sample. For the analysis of individual particles, the X-ray beam was focused to ~20 µm to avoid detection of areas away from the particle. Data were collected while using the highly reliable combined electron and ion charge compensation capability that is incorporated on this instrument (Baer et al., 2002; Larson and Kelly, 1998). The spectra were aligned to a carbon peak energy of 284.8 eV (adventitious carbon) which produced highly consistent results for these samples. The compositional results reported in Table S2 for natural and ground surfaces were obtained using standard sensitivity factors in the Phi MultiPak Version 9.1 software package, using peak area intensities after a Shirley background subtraction.

2.8 Synchrotron X-ray absorption spectroscopy/X-ray magnetic circular dichroism

A ground sample of the SF magnetic mineral fraction was characterized by XA and XMCD analysis to characterize the mineral surface in terms of Ti content and Fe(II)/Fe(III) ratio. XMCD is the difference in absorption of circularly polarized x rays depending on the relative orientation of magnetization and x ray polarization. XMCD was measured with fixed circular polarization reversing the external magnetic field point by point in an X-ray absorption experiment. XMCD is uniquely sensitive to the oxidation state and local structure of magnetically ordered iron cations near solid surfaces (Chen et al., 1995; Stohr, 1995; van der
Laan and Thole, 1991; van der Laan et al., 1986). Fe $L_{2,3}$ XA spectra were obtained on beamline 4.0.2 at the Advanced Light Source (ALS), Berkeley, CA, using the eight-pole resistive magnet endstation (Arenholz and Prestemon, 2005). Samples were loaded onto carbon tape attached to the sample manipulator in an anoxic N$_2$ glovebox. XA was monitored in total-electron yield (TEY) mode, which has an effective probing depth of 50 Å (Gota et al., 2000). At each energy point, XA spectra were measured for two opposite magnetization directions by reversing the applied field of 0.6 T. After normalization to incident beam intensity, the XMCD spectrum was obtained as the difference between the two XA spectra (Pattrick et al., 2002). To obtain cation distribution over the two structural Fe site types, the experimental XMCD was fit by means of a nonlinear least-squares analysis, using the calculated spectra for each site. In these calculations, described in van der Laan and Kirkman (1992) and van der Laan and Thole (1991), the 10Dq crystal field parameters were taken as 1.2 and 0.6 eV for Fe $Oh$ and $Td$ sites. Results were convoluted by a Lorentzian of $\Gamma = 0.3$ (0.5) eV for the $L_3$ ($L_2$) edge to account for intrinsic core-hole lifetime broadening and by a Gaussian of $\sigma = 0.2$ eV to account for instrumental broadening. The Ti $L_{2,3}$ XAS was also recorded and was not sensitive to the magnetic field. The Ti/Fe ratio was calculated from the integrated area of the XA spectra for the Fe and Ti $L_{2,3}$-edges taken at the same point on the sample, after background subtraction as described in Droubay (1999).

2.9 Effect of aqueous environment on natural titanomagnetite surfaces

Groundwater samples were collected over distinct geological strata corresponding to the Hanford formation (12.21 m bgs), the oxidized zone of the Ringold formation (15.90 m bgs) and the reduced zone of the Ringold formation (16.99 m bgs) at the Integrated Field-Scale.
Subsurface Research Challenge (IFRC) site within the 300 Area of the Hanford Site. Unground ‘as separated’ samples of the SF magnetic mineral fraction (300 mg) were contacted with the groundwater samples (1 mL) in an anoxic N₂ glovebox, with shaking for one week. Samples were dried onto carbon tape, attached to a sample manipulator in an anoxic N₂ glovebox for XA/XMCD measurement. The cation composition of the groundwater samples was determined by HNO₃ acidification followed by ICP-OES. ICP-OES analysis was carried out on a Perkin Elmer Optima 2100 DV ICP-OES with an AS93 auto sampler using a Helix Tracey 4300 DV spray chamber and a SeaSpray nebulizer at 1.5 mL/min flow rate in double distilled 2 % nitric acid (GFS Chemicals, Inc. Cat. 621, lot C141305). Calibrations were made using Ultra Scientific ICP standards (Kingstown, RI) in a dilution range of 0.5 to 3000 ug/L.

2.10 Synthesis of titanomagnetite microparticles and nanoparticles (Fe₂.₈₅Ti₀.₁₅O₄)

Titanomagnetite microparticles of composition consistent with that dominant in the natural samples (Fe₂.₈₅Ti₀.₁₅O₄) were prepared as described in Pearce et al. (2010). A stoichiometric mixture of TiO₂, Fe₂O₃, and Fe metal were ground under acetone, loaded into silver foil and heated at 1170 K in evacuated, sealed quartz tubes for seven days. Titanomagnetite nanoparticles of the same composition were prepared as described in Pearce et al. (2012). A stoichiometric mixture of dissolved FeCl₂, FeCl₃ and TiCl₄ in 0.3M HCl (pH<1) was co-precipitated through the addition of a NH₄OH solution under ambient conditions and in aqueous suspension, in an anoxic N₂ glovebox.

2.11 Reactivity studies with Tc(VII)
Glassware and plastic bottles were soaked in 1% HNO$_3$ overnight and rinsed several times with distilled and deionized water (DDW) before use. Chemicals and plastic equipment were deoxygenated for 24 hours inside an anoxic glovebox prior to use. Reduction experiments were performed in a 97% Ar/3% H$_2$ atmosphere inside the anoxic glovebox (Thermo, USA) equipped with a palladium catalyst to remove trace O$_2$. DDW was stored in an anoxic glovebox for preparation of all solutions and suspensions. Chemicals were reagent grade or better. Tc(VII) reduction experiments were conducted in 30 mL glass serum bottles with rubber stoppers and crimp seals. Titanomagnetite was added to HEPES buffer solution, giving a solid : solution ratio of 382 mg : 5 mL for natural materials, 993 mg : 13 mL for microparticles and 1.3 mg : 30 mL for nanoparticles. The bottles were sealed and continuously shaken for 20 hours to allow the titanomagnetites to reach equilibrium with their aqueous environment. A $^{99}$Tc(VII) stock solution (5 mM) was prepared by diluting NH$_4$TcO$_4$ (Perkin-Elmer Life Science Inc., Boston, MA) in DDW. The bottles were spiked with Tc(VII) solution to give a concentration of 10 µM or 30 µM after the 20 hour equilibration period. The Tc-spiked solutions were continuously shaken and sampled over time. For sampling, aliquots of suspension (1.2 mL) were centrifuged (3000 rpm for 5 mins). The supernatant (1 mL) was mixed with anoxic scintillation cocktail (9 mL) in the glovebox. The sample was counted on a Packard 2500TR liquid scintillation counter (Packard Instrument Co. Meriden, CT) for 10 minutes. Background counts were collected by measuring HEPES buffer solution without Tc(VII). The concentration of Tc(VII) in solution was calculated from the background subtracted counts for the samples in dpm/mL. Control experiments were conducted to test for potential Tc(VII) adsorption onto the glass bottles and the syringe filters.

3. Results and Discussion
3.1 Characterization of magnetic mineral fraction bulk

Figure 1 shows the Environmental Restoration Disposal Facility (ERDF) and the submarine burial ground trenches, from which bulk sediments were collected in the 200 East Area on the Central Plateau at the Hanford site. Bulk texture and mineralogic compositions of the Hanford formation sediments collected from ERDF and the coarse (SC) and fine (SF) horizons of the trenches, compared with that of Hanford formation sediments collected from the 200 West Area Tank Farm on the Central Plateau, and Ringold formation sediments collected from the 300 Area in the Columbia River corridor, are given in Table 1. The mineralogy of the samples was similar, reflecting the basaltic provenance of Hanford site sediments. Based on initial weight of bulk, dry sediment, the magnetic mineral fraction was 1% for SF, 0.5% for EDRF and 0.1% for SC, by weight (Table 1). Representative optical microscopy images of the texture of these fractions, including some authigenic subhedral to euhedral octahedral crystals typical of magnetite, are given in Figure 1. XRD patterns for these SF, ERDF and SC magnetic fractions are shown in Figure S1 and indicate primarily magnetite (~90%) with a smaller quantity of hematite. Sample SF also contained minor ilmenite. A quantitative estimation of the relative abundance of these mineral phases scaled to 100%, ignoring additional remaining trace crystalline or possible undetected amorphous phases, is given in Table 2. The magnetite lattice was consistent for all samples and close to the expected value for pure magnetite (8.396 Å, ICDD 19-629). Due to compositional similarities in the magnetic mineral fraction of these sediments, SF was selected as a representative sample for more detailed subsequent characterization and reactivity experiments, as this sediment contained the highest concentration of magnetic material.
Representative EPMA analyses of a thin section of the magnetic mineral fraction of the SF sediment (Table S1) were used to determine chemical composition and assess purity of the mineral phases. Table 3 shows that the mineral phases predominantly consisted of Fe and O, as expected for magnetite. These natural magnetites contained variable amounts of impurities, including Al, Mg, V, Cr, Mn, but with a substantially higher proportion of Ti, consistent with magnetites derived from igneous rocks such as basalt (Cornell and Schwertmann, 2003). That the Ti comprised primarily a structural substituent in the magnetite lattice, as opposed to an interstitial impurity, was an assumption consistent with expectations for typical basalt-derived magnetites (Frost and Lindsley, 1991). The term titanomagnetite applies to magnetite wherein the substitution of Fe(III) by Ti(IV) in the lattice yields formulae conforming to Fe$_{3-x}$Ti$_x$O$_4$; a complete solid solution exists along the binary join from magnetite (x = 0) to ulvöspinel (x = 1). Exsolution in intermediate compositions along this binary join for crystallization below the consolute temperature (Lilova et al., 2012), yields coherent intergrowths of Ti-rich and Ti-poor phases (Harrison and Putnis, 1999), as can be seen in the darker lamella around Spot 2 in Figure 2A. This phenomenon can also result in formation of very fine-scale microstructures that can only be resolved using TEM (Price, 1980; Smith, 1980). EPMA provided an average composition of grains, but with possible reduced accuracy arising from the likely presence of phase heterogeneity due to fine-scale exsolution in the analysed grains (Goldstein et al., 2003). Nonetheless, the nominal EPMA-based composition of these Fe$_{3-x}$Ti$_x$O$_4$ grains, determined by taking an average of all measured Ti/Fe ratios was x = 0.16.

Chemical analysis, involving acid digestion, ferrozine assay (for Fe(II) content), and ICP-MS, was carried out on the SF magnetic mineral fraction for a measure of the bulk Fe$_{3-x}$Ti$_x$O$_4$ composition, in terms of Fe(II), Fe(III) and Ti(IV). The composition was x = 0.17, within error.
of that determined by EPMA. The measured Fe(II)/Fe(III) ratio was 0.663, slightly lower than
the theoretical Fe(II)/Fe(III) ratio for $x = 0.17$ (0.705). The fact that this measured ratio did not
exceed the theoretical one was consistent with the identity of these phases as titanomagnetites,
i.e., that the Ti was tetravalent and resided in the lattice at cationic sites replacing Fe(III). The
slightly lower ratio suggests that these titanomagnetites were slightly oxidized, and thus fell
along the binary join between titanomagnetite and titanomaghemite, c.f. the titanomaghemite
composition on the right hand side of Equation 1.

To obtain information on spatial distribution of elements within the SF magnetic mineral
fraction, and to assess compositional heterogeneity, polished cross sections were analysed using
SEM-EDS (Fig. 2). EDS of the large, homogeneous particle in the center of Figure 2A (Spot 1)
showed that this was a relatively pure magnetite particle composed of Fe and O with minor
amounts of Mn (Fig. 2B and Table S1). EDS of the particle exhibiting exsolution lamella (Spot
2) showed that it contained a significant amount of Ti, corresponding to a composition of
$\text{Fe}_{2.71}\text{Ti}_{0.29}\text{O}_4$, with minor impurities of Al, V and Mn (Fig. 2C and Table S1). The darker phase
at the edge of the particle (Spot 3) represented a surface coating that was present on some of the
particles. EDS shows that it was mostly composed of SiO$_2$ (Fig. 2D and Table S1).

SEM images were also collected for whole particles to give an indication of size and
shape. Subhedral to euahedral single crystal octahedra consistent with one dominant habit of
magnetite were common; Figure S2 (inset) shows an image of a typical faceted particle. EDS
analysis at particle edges, which should emphasize near-surface information, indicated Fe, O and
Ti with trace amounts of Mg and Al (Fig. S2 and Table S1). Although the particle in Figure S2
was ~200 µm across, size analysis of 102 particles from the SF magnetic mineral fraction
indicated that the average mean particle size was 72 µm and the size distribution was relatively narrow with a normal distribution.

XMP on thin sections of the magnetic mineral fraction of the SF sediments was carried out on ID20 at the APS to image the distribution of Fe and Ti within individual particles (Fig. 3 A, B and C). Sampling points were selected from the images for subsequent XANES measurements to determine the oxidation state of Fe (Fig. 3D) and Ti (Fig. 3E). Figure 3 A and B showed that a significant number of the Fe-containing particles were also Ti rich, consistent with other measurements. Fe K-edge XANES spectra were collected for a particle that was high in both Fe and Ti (Spot 1), a particle that was predominantly Fe with small amounts of Ti (Spot 2) and a particle that contained only Fe (Spot 3). The Fe K-edge XANES spectrum for Spot 1 showed that the edge was shifted to lower energy than in the reference spectrum for magnetite, and was close to the edge position for reference spectra for titanomagnetite (Fe$_{3-x}$Ti$_x$O$_4$, x = 0.9) and ilmenite (FeTiO$_3$), suggesting that this was a more reduced mineral phase containing significantly more Fe(II) than pure magnetite. However, the Spot 1 spectrum did not have a line shape with the characteristic shoulder for titanomagnetite or double peak for ilmenite, so it is possible that this was a mixed phase consistent with fine-scale exsolution lamellae below the resolution of the 3 µm x 7.5 µm focused beam on ID20. The Ti K-edge spectrum in Figure 3E resembled the titanomagnetite spectrum but it is possible that it also included an ilmenite component. The Fe K-edge spectrum for Spot 2 (Fig. 3D) was also shifted to slightly lower energy with respect to the magnetite spectrum and has a low energy shoulder, suggesting that this was a titanomagnetite phase. The Ti K-edge spectrum for Spot 2 (Fig. 3E) was also similar to the reference titanomagnetite spectrum. For Spot 3 (Fig. 3D) the Fe K-edge spectrum was at the same energy as the reference spectrum for magnetite and the line shape was very similar. As
this particle only contained Fe, it can be concluded that it was close to end member magnetite.

The XMP and XANES data show that, although the SF magnetic mineral fraction was predominantly magnetite according to bulk XRD, on a micron scale, the sample consisted of a range of mineral phases with different compositions. Other potential impurities in the magnetite were also imaged using XMP and the three most significant (Mn, Ti and V) are plotted in terms of their correlation with Fe in Figure S3 A-C. The energy used to collect the XMP fluorescence images (7100 eV) was below the Fe edge to reduce the Fe signal, and it therefore cannot be directly compared to the signal levels of the other elements. However, Figure S3B shows that Ti constituted the impurity present in the highest concentration and had some degree of correlation with the Fe.

3.2 Surface characterization

The techniques described thus far emphasize information on the bulk characteristics of the magnetic mineral fraction but, in the environment, it is the mineral surface that interacts with groundwater and contaminants. Two highly surface-sensitive techniques, XPS and XMCD, were employed to determine the composition and potential for reactivity, in terms of the Fe(II)/Fe(III) ratio, at the surface of the SF magnetic mineral fraction. The SEM-EDS results indicated that the surface of some of the particles was covered with an SiO$_2$-containing coating. To further investigate this coating, XPS was performed out on the ‘as separated’ material and on material that had been ground in the glovebox under N$_2$ to expose fresh surfaces. Figure 4 shows high resolution normalized photoelectron spectra of the Fe 2p (Fig. 4A) and O 1s (Fig. 4B) regions at three different analysis areas, referenced to the C 1s line at 284.8 eV. In Figure 4A, the Fe 2p$_{3/2}$ peak is at 712.3 eV, similar in energy to goethite, suggesting that the surfaces of the ‘as
separated’ particles were oxidized and predominantly composed of Fe(III). After grinding the SF magnetic mineral fraction under N$_2$ to expose fresh surfaces and limit air oxidation, the Fe 2p$_{3/2}$ peak was shifted to lower binding energy (711.1 eV), as a result of an increase in the Fe(II) component (Fig. 4A). The shape of the O 1s line also changed after grinding (Fig. 4B). The ‘as separated’ material had a single peak at 532.0 eV, consistent with the presence of Al$_2$O$_3$ and SiO$_2$, but after grinding a second peak at 530.2 eV was observed, which is consistent with an Fe oxide. Table S2 includes relative atomic concentrations calculated from peak intensities after Shirley background subtraction. The ratios of Fe to Si, Al and O all increased significantly after grinding, consistent with a decrease in the surface coating. The fact that the Fe 2p peak was measurable, even before grinding, suggested that the Al$_2$O$_3$/SiO$_2$-containing surface coating was less than 1-2 nm thick and/or heterogeneous with incomplete surface coverage. Fe thus remained accessible at the surface of these Fe$_{3-x}$Ti$_x$O$_4$ phases, with the potential to participate in electron transfer reactions with contaminants in the aqueous environment. The Ti/Fe metal ratios calculated from XPS peak intensities before and after grinding were 0.034 and 0.052 respectively. After grinding, the ratio corresponded to a Fe$_{3-x}$Ti$_x$O$_4$ composition of $x = 0.15$, which was in very good agreement with values obtained for the bulk composition from EPMA ($x = 0.16$) and chemical analysis ($x = 0.17$). However, the lower Ti/Fe ratio in the ‘as separated’ material suggested a surface phase that was relatively depleted in Ti and rich in Fe(III), with a bulk composition containing more Ti and more charge-balancing Fe(II)-equivalents consistent with expected stoichiometry in titanomagnetite.

To obtain surface-sensitive information on local coordination, bond distances, and magnetic ordering of Fe in the Fe$_{3-x}$Ti$_x$O$_4$ structure, samples of the SF magnetic mineral fraction both ‘as separated’ and after grinding in the glovebox under N$_2$, were analyzed using XA and
XMCD. XA allows the separation of the Fe and the Ti signal to assess their valence states individually. XMCD is sensitive with site-specificity to distinguish magnetic A- and B-site Fe(II) and Fe(III) in the titanomagnetite structure (inverse spinel), emphasizing that constituency residing within 50 Å of the surface. The background subtracted Fe L-edge XA spectrum for the ‘as separated’ SF magnetic mineral fraction had a more intense peak at 709.5 eV, corresponding to Fe(III), whereas the spectrum for the ground sample had lower overall intensity and a more intense peak at 707.8 eV, corresponding to Fe(II) (van Aken et al., 1998). The peak shapes of the background subtracted Ti L-edge XA spectra for the samples before and after grinding are very similar, indicating that Ti was tetravalent and in octahedral coordination in both samples (Fig. 5B). However, the intensity of the Ti spectrum was much lower for the ‘as separated’ sample. The Ti/Fe metal ratios calculated from the integration of the background subtracted spectra before and after grinding were 0.029 and 0.043 respectively (Table 3). This was in agreement with the trend observed in the XPS data that the surface of the ‘as separated’ particles was depleted with respect to Ti, whereas the fresh surfaces were consistent with the measured bulk stoichiometry. The increased intensity in the low energy peak of the Fe L-edge XMCD for the ground sample, corresponding to Fe(II) in octahedral coordination (Fig. 5C) confirmed that the additional Fe(II) was a structural component of the Fe$_{3-x}$Ti$_x$O$_4$ phase. The Fe(II)/Fe(III) ratios, calculated from the Fe XMCD experimental spectra (Table 3) increased from 0.37 to 0.69 upon grinding, consistent with the XPS data, showing that the Fe at the surface of the ‘as separated’ particles was oxidized.

3.3 Effect of aqueous environment
Despite that fact that the ‘as separated’ titanomagnetite particles isolated from the SF sediment were coated with a heterogeneous layer of Al$_2$O$_3$/SiO$_2$, Fe was measurable within ~5 nm of the surface both by XPS and XMCD. To determine the extent to which this Fe could participate in electron transfer reactions with species in the aqueous environment, ‘as separated’ samples of the SF magnetic mineral fraction were contacted for one week with groundwaters from three different depths across a redox boundary in the Hanford subsurface at the 300 Area; the oxic Hanford formation (12.2 m), the oxidized zone of the Ringold formation (15.9 m) and the reduced zone of the Ringold formation (17.0 m). The compositions of the different groundwaters (Table S3) were very similar except that the reduced Ringold sample was slightly more alkaline and contained less nitrate and more nitrite, consistent with more reducing conditions. The surface Fe(II)/Fe(III) ratio of the samples was measured using XMCD to determine if it was affected by the oxygen content of aqueous environment (Fig. S4). The XMCD spectra were normalized to the intensity of the Fe(III) tetrahedral site for relative comparison and the inset in Figure S4 shows that octahedral Fe(II) peak intensity changes in response to different groundwaters. The octahedral Fe(II) peak increased slightly upon exposure to the oxic Hanford and Ringold groundwater, as compared to the initial ‘as separated’ material. This was expected as the ‘as separated’ material was stored in air, 21% oxygen by volume, whereas air-saturated water contains 8.22 mg L$^{-1}$ oxygen at room temperature. As expected, the Fe(II)/Fe(III) ratios for the samples contacted with the two oxic groundwaters were very similar (0.42 and 0.43 for Hanford and oxidized Ringold respectively). A more significant increase in octahedral Fe(II) was observed upon contact with the reduced Ringold groundwater. The Fe site occupancies and Fe(II)/Fe(III) ratios for the samples are given in Table 3, showing that the Fe(II)/Fe(III) ratio had increased from 0.37 for the ‘as separated’ sample to 0.49 after contact
with the reduced Ringold groundwater. Although the increase did not fully restore the
Fe(II)/Fe(III) ratio to that found for samples exposing fresh surfaces by grinding (0.69), the shift
was significant and in the expected direction. These results showed that structural Fe at the
mineral-solution interface was highly responsive to changes in the aqueous environment, and, if
initially oxidized, could be reduced to electron donating Fe(II) by transition of the aqueous
environment from oxidizing to reducing. In principle, this structural Fe(II) was then capable of
catalysing the reduction of polyvalent contaminant species such as $^{99}$Tc(VII) in the groundwater
by heterogeneous electron transfer at the mineral-solution interface.

3.4 Pertechnetate reactivity studies

Batch reactivity studies were conducted to measure the extent and rate of Tc(VII) reduction
by the natural titanomagnetite particles. To provide sufficient reactive surface area to observe a
reaction on accessible laboratory time scales, SF magnetic mineral was ground under N$_2$. The
results in Figure 6 A show that the exposed surfaces of these titanomagnetites were reactive with
respect to the reduction of Tc(VII) to Tc(IV), as indicated by a progressive decrease in Tc(VII)
in solution using LSC, compared with a control that contained no mineral phase. Samples of the
natural titanomagnetite particles before and after reaction for 114 days were analyzed using
XMCD, which confirmed that reduction of Tc(VII) to Tc(IV) occurred with concurrent oxidation
of Fe(II) to Fe(III) at the mineral surface, c.f., Equation 1. The decrease in intensity of the peak
corresponding to Fe(II) in octahedral coordination in the XMCD spectrum after reaction (Fig. 6
B) showed that reduction of Tc(VII) resulted in a measurable decrease in surface Fe(II)/Fe(III)
ratio from 0.69 before reaction to 0.63 after reaction.

To approximate the redox reactivity of natural titanomagnetites with respect to groundwater
contaminants such as Tc(VII) more comprehensively as a function of Ti content, surface
composition, and degree of pre-oxidation, and to characterize the products of reduction, it was necessary to generate synthetic analogue mineral phases. Taking an average of the values obtained from all of the characterization techniques for the SF magnetic mineral fraction, for bulk (EPMA and chemical analysis) and surface (XPS and XAS), the general formula for this natural material on average was Fe_{2.85}Ti_{0.15}O_4. Synthetic titanomagnetite nanoparticulate materials of the same composition (x = 0.15) were thus prepared using an aqueous-based, ambient temperature synthesis to provide high surface area pristine material compatible with batch reactivity studies (Pearce et al., 2012). To provide an intermediate-length-scale material between the high surface area nanomaterials and the coarse natural materials, micron-sized x = 0.15 titanomagnetites were also prepared using a high temperature synthesis route (Pearce et al., 2010). To link reaction rates observed using nanoparticles, microparticles, and natural materials, the influence of surface area on reactivity with Tc(VII) must be included. SEM images of natural particles (Fig. S5 A), synthetic microparticles (Fig. S5 B) and synthetic nanoparticles (Fig. S5 C) illustrate differences in particles size and surface area between the samples. A summary of the characteristics of the different titanomagnetite particles determined from previous work is given in Table 4. When differences in experimental conditions, specifically particle surface area to solution volume ratio, are taken into consideration as described in Cui and Eriksen (1996), the measured reduction rate for natural particles (0.032µM day\(^{-1}\)) was found to be slower than that for microparticles (0.38µM day\(^{-1}\)), which in turn was found to be slower than that for nanoparticles (2.868 µM day\(^{-1}\)). While this suggested nonlinearity in the relationship between particle size and reduction rate, the effect appeared constant and predictable by length scale. The effect may arise from coupling of outermost surface electron transfer reactivity to a sustaining resupply of reducing equivalents from the underlying near-surface region, a process
that may require simultaneous solid-state diffusion of e– and Fe(III) (Pearce et al., 2012), becoming disproportionately more efficient with decreasing particle size. K-edge XA spectroscopy was used to determine the Tc oxidation state and bonding environment in the reacted titanomagnetite x=0.15 nanoparticles (Liu et al., 2012). The line shape of the XANES spectra was consistent with a Tc oxidation state of 4+. The radial transforms of the Tc-EXAFS data for the Tc(IV) precipitate on the Fe$_{2.85}$Ti$_{0.15}$O$_4$ nanoparticle samples was modeled with a TcO$_2$·nH$_2$O linear chain developed by Lukens et al. (2002), which was extended to include edge sharing octahedral interactions with an Fe–O surface in Zachara et al. (2007a). It consists of variable length edge-sharing chains of Tc–O octahedra at R = 1.99Å bonded in an edge-sharing fashion to Fe–O octahedra located on the surface of the host Fe(III) oxide substrate (Liu et al., 2012).

4. Conclusions

Hanford sediments contain a magnetic mineral fraction (~2 wt%) composed of 90% titanomagnetite (Fe$_{3-x}$Ti$_x$O$_4$; where x~0.15). Solid-phase Fe(II), measurable within 5 nm of the mineral surface using L-edge XAS and XPS, was highly responsive to changes in the aqueous environment, such as exposure to 300 area groundwater taken above and below the redox boundary. Reaction with a 10 µM Tc(VII) solution showed that natural magnetic isolates reduced Tc(VII) with concurrent oxidation of Fe(II) to Fe(III) at the mineral surface, as did compositionally pristine synthetic microparticle and nanoparticle analogue phases. When particle surface area to solution volume ratio was taken into consideration, Tc(VII) reduction rates for natural particles and synthetic microparticles and nanoparticles could be predicted by a scaling relationship, supporting utility of the synthetic nanoparticles and microparticles for batch and
flow reactivity studies to comprehensively studies of titanomagnetite reactivity in environmental systems such as the Hanford site.

Acknowledgements

This work was funded by PNNL Science Focus Area (SFA), Subsurface Biogeochemical Research (SBR) program, the DOE Office of Biological and Environmental Research (OBER), U.S. Department of Energy (DOE). μ-XRD, TEM and SEM measurements were performed in Environmental Molecular Science Laboratory (EMSL), a national user facility supported by the OBER and located at PNNL. Use of the Advanced Photon Source, an Office of Science User Facility operated by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357. XA and XMCD measurements were performed at the Advance Light Source supported by the DOE Office of Science, Office of Basic Energy Sciences under contract No. DE-AC02-05CH11231.

References


Figure legends

**Figure 1.** Source and texture of magnetic mineral fractions isolated from sediments at the submarine burial ground and the Environmental Restoration Disposal Facility at the Hanford site, Washington, U.S.A.

**Figure 2.** SEM images of particles from the SF magnetic mineral fraction in polished cross section (A), showing EDS analysis from a magnetite-rich area (Spot 1, B), a titanomagnetite-rich area (Spot 2, C) and the surface coating (Spot 3, D).

**Figure 3.** X-ray fluorescence microprobe analyses of the SF magnetic mineral fraction showing Fe (A), Ti (B) and Fe-Ti (C) distribution, although with Fe K-edge (D) and Ti K-edge (E) XANES spectra for different points on the XMP map, along with magnetite, titanomagnetite and ilmenite reference spectra.

**Figure 4.** High resolution photoelectron spectra of the Fe 2p region (A) and the O 1s region (B) for three different analysis areas on the ‘as separated’ SF magnetic mineral fraction (grey lines) and on N2-ground SF magnetic mineral fraction (black lines).

**Figure 5.** XA spectra at the Fe L-edge (A) and the Ti L-edge (B), along with Fe L-edge XMCD difference spectra (C) for the ‘as separated’ SF magnetic mineral fraction (black lines) and on N2-ground SF magnetic mineral fraction (red lines).
Figure 6. Reduction in Tc(VII) concentration with time (A) for the control (black line) and after exposure to the N$_2$-ground SF magnetic mineral fraction (red line) with corresponding Fe L-edge XMCD difference spectra (B), before (black line) and after (red line) Tc(VII) reduction.
Table 1: Analyses of sediments from the Hanford Site

<table>
<thead>
<tr>
<th>Sample Site</th>
<th>Geology</th>
<th>Mineralogy</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Environmental Restoration Disposal Facility (ERDF)</strong></td>
<td>Interstratified fine, medium and course sands of the Hanford formation (Ice Age flood deposits) of Pleistocene age (15-20 K years old). Occasional finer layers of silty sand ranging to sandy silt slackwater deposits.</td>
<td>Feldspar, quartz, 0.5 wt. % magnetite</td>
<td>This work</td>
</tr>
<tr>
<td><strong>200 East Area: Trench 94 Subpit (218-E-12B Burial Ground) - silty, fine sand (SF)</strong></td>
<td>Silty, fine sand from 12.2 m below ground surface (bgs). 3 m above bedrock.</td>
<td>Feldspar, quartz, 1 wt. % magnetite</td>
<td>This work</td>
</tr>
<tr>
<td><strong>200 East Area: Trench 94 Subpit (218-E-12B Burial Ground) - pebbly sand (SC)</strong></td>
<td>Pebbly sand from 12.2 m bgs. 3 m above bedrock.</td>
<td>Feldspar, quartz, 0.1 wt. % magnetite</td>
<td>This work</td>
</tr>
<tr>
<td><strong>200 West Area: Borehole 299-W22-50 (South East corner of S-SX Tank Farm)</strong></td>
<td>Fine-grained silty sediments (&lt;2 mm) of the Hanford formation from 66-72 m bgs, just above water table.</td>
<td>43.0 wt.% quartz, 30.0 wt.% plagioclase, 7.4 wt.% orthoclase, 4.5 wt.% mica, 2.0 wt.% amphibole, 1.0 wt.% chlorite, 0.1 wt.% magnetite</td>
<td>(Baer et al., 2010; McKinley et al., 2007)</td>
</tr>
<tr>
<td><strong>300 Area: 55m borehole (South Processing Pond)</strong></td>
<td>Pliocene-age Ringold formation at 51.5-51.8 m bgs consisting of fine-grained deposits. Basalt bedrock exists below Ringold Formation at ~58 m bgs.</td>
<td>Quartz, cristobalite, feldspar, calcite, hematite, magnetite; traces of smectite</td>
<td>(Peretyazhko et al., 2012)</td>
</tr>
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</table>
Table 2: Quantitative estimation of mineral phases present in magnetic mineral fractions isolated from Hanford sediments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Estimated fractions</th>
<th>Magnetite cell /Å</th>
<th>Other phases</th>
</tr>
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<tbody>
<tr>
<td>SC</td>
<td>92% 8%</td>
<td>8.3981(13)</td>
<td></td>
</tr>
<tr>
<td>ERDF</td>
<td>93% 7%</td>
<td>8.3968(11)</td>
<td></td>
</tr>
<tr>
<td>SF</td>
<td>80% 11%</td>
<td>8.3955(12)</td>
<td>Ilmenite (10%)</td>
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Table 3. Site occupancies from XMCD for SF magnetic mineral fraction

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe$^{3+}$ d$^6$O$_h$</th>
<th>Fe$^{3+}$ d$^5$T$_d$</th>
<th>Fe$^{3+}$ d$^5$O$_h$</th>
<th>Fe(II)/Fe(III)</th>
<th>Ti/Fe</th>
</tr>
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<tr>
<td>Unground</td>
<td>0.77</td>
<td>0.95</td>
<td>1.13</td>
<td>0.37</td>
<td>0.029</td>
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<tr>
<td>Ground</td>
<td>1.16</td>
<td>0.87</td>
<td>0.81</td>
<td>0.69</td>
<td>0.043</td>
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<tr>
<td>Hanford</td>
<td>0.84</td>
<td>0.98</td>
<td>1.02</td>
<td>0.42</td>
<td>0.022</td>
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<tr>
<td>Ringold Oxidized</td>
<td>0.85</td>
<td>0.95</td>
<td>1.05</td>
<td>0.43</td>
<td>0.017</td>
</tr>
<tr>
<td>Ringold Reduced</td>
<td>0.94</td>
<td>0.92</td>
<td>1.00</td>
<td>0.49</td>
<td>0.015</td>
</tr>
<tr>
<td>Ground (after Tc(VII) exposure)</td>
<td>1.1</td>
<td>0.89</td>
<td>0.86</td>
<td>0.63</td>
<td>-</td>
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Table 4. Characteristics of natural and synthetic titanomagnetite reactivity

<table>
<thead>
<tr>
<th>Material</th>
<th>Size</th>
<th>Cell parameter</th>
<th>solid/solution m/V</th>
<th>rate of TcO$_4^-$ reduction µM day$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural particles</td>
<td>72.0</td>
<td>8.3940</td>
<td>0.000888</td>
<td>0.0315</td>
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<tr>
<td>Microparticles</td>
<td>8.2</td>
<td>8.4161</td>
<td>0.00932</td>
<td>0.380</td>
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<tr>
<td>Nanoparticles</td>
<td>0.0094</td>
<td>8.4155</td>
<td>0.00461</td>
<td>2.868</td>
</tr>
</tbody>
</table>
Figure 1

Submarine burial ground trenches

Environmental Restoration Disposal Facility
Figure 4

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