Spontaneous redox continuum reveals sequestered technetium clusters and retarded mineral transformation of iron

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The sequestration of metal ions into the crystal structure of minerals is common in nature. To date, the incorporation of technetium(IV) into iron minerals has been studied predominantly for systems under carefully controlled anaerobic conditions. Mechanisms of the transformation of iron phases leading to incorporation of technetium(IV) under aerobic conditions remain poorly understood. Here we investigate granular metallic iron for reductive sequestration of technetium(VII) at elevated concentrations under ambient conditions. We report the retarded transformation of ferrihydrite to magnetite in the presence of technetium. We observe that quantitative reduction of pertechnetate with a fraction of technetium(IV) structurally incorporated into non-stoichiometric magnetite benefits from concomitant zero valent iron oxidative transformation. An in-depth profile of iron oxide reveals clusters of the incorporated technetium(IV), which account for 32% of the total retained technetium estimated via X-ray absorption and X-ray photoelectron spectroscopies. This corresponds to 1.86 wt.% technetium in magnetite, providing the experimental evidence to theoretical postulations on thermodynamically stable technetium(IV) being incorporated into magnetite under spontaneous aerobic redox conditions.
Natural minerals can host, or incorporate into their crystal structure, different elements and function as sinks attenuating environmental transport of heavy metals and radionuclides. Garnet, gypsum, calcite, muscovite, rutile and other mineral phases are found to contain incorporated Tc, Ru, Cs, U, Np, and Pu. Iron minerals, such as iron oxides (magnetite, maghemite, and hematite), and iron oxyhydroxides (goethite, lepidocrocite, ferrihydrite, etc.) also incorporate various metal cations, in particular, substitution of Fe$^{3+}$ by Al$^{3+}$ can reach up to 33 mol.% in natural weathered goethite and up to 15 mol.% in maghemite in tropical soils. Computational studies on Tc$^{4+}$ incorporation in magnetite revealed thermodynamic feasibility to obtain up to 5 wt.% of incorporated Tc$^{4+}$ with higher stability around 1–3 wt.%3, however, no experimental studies were carried out to support the upper limit of Tc incorporation in the ambient uncontrolled environment. Further, formation of iron minerals is complex as it yields an array of transformation pathways for different stable oxides/oxyhydroxides. This allows for design of plentiful systems targeting a specific mineral formation in which an element of interest is being incorporated. Particularly, there is practical significance to employ widely available metallic iron (Fe$^0$), encouraging investigation of its oxidative transformation with the possibility of concomitant sequestration of radionuclides undergoing simultaneous reduction, e.g., Tc, in a system under ambient conditions where only a limited number of controlled parameters are imposed to resemble natural pathways.

The radioisotope of technetium, $^{99}$Tc, is a $\beta^−$ emitter of predominantly anthropogenic origin that generates environmental risk in sites impacted by cold war era development of nuclear weapons (e.g., Hanford site WA, USA4; Mayak, Russia5) or nuclear accidents (e.g., Chernobyl, Ukraine6), and its environmental impact is amplified by a long half-life (213,000 years) and redox-dependent mobility with high solubility of the pertechnetate anion (TcO$_4^−$) in aerobic conditions. Under anoxic conditions Tc reductively precipitates as hydrous TcO$_2$ and can be retained in iron-rich sediments even upon consequent exposure to air8. The possibility of utilizing iron-based phases as reductive separation and sequestration agents initiated numerous studies on Tc immobilization into iron minerals9–19. The majority of these studies investigated reductive removal of Tc from solution via structural incorporation into in situ formed mineral iron oxide/oxyhydroxide phases, i.e., ferrihydrite, magnetite, hematite, and goethite, starting with soluble homogeneous Fe$^{2+}$ precursors20. Immobilization of Tc within the crystalline structure of a host helps to achieve recalcitrant oxidative leaching of Tc$^{4+}$, and synthesized Tc$^{4+}$-doped magnetite, hematite and goethite that have been evaluated as durable waste forms for long-term geological disposal demonstrated relatively low Tc release rates13,14,21. When structurally incorporated into in situ formed magnetite, Tc$^{4+}$ was prone to remain in the reduced state even upon oxidation of magnetite15. Tc$^{4+}$-doped magnetite (Tc$_{0.01}$Fe$_{2.99}$O$_4$) can be synthesized with 2.5 wt.% Tc by dissolving a small amount of iron powder in a denitrated solution of Tc$^{4+}$, however, incorporation of Tc$^{4+}$ into pre-synthesized magnetite was found to be sensitive to its initial concentration16. Although in situ formed magnetite was more efficient for Tc reductive sequestration than the pre-synthesized one, these studies have been conducted in anoxic conditions. Iron oxidation in anoxic vs. oxic conditions would take a different route with water or dissolved oxygen serving as an oxidant, leading to dissimilar iron oxidation pathways2.

There are limitations of utility of the homogeneous in situ synthesis of iron minerals for the practical separation systems design when it utilizes prone-to-oxidation Fe$^{2+}$, as it must be carried out in a controlled pH and redox sensitive environment, and therefore can’t be accomplished in complex aqueous matrices directly, necessitating prior separation of Tc from the original host streams. A valuable alternative is in situ mineral transformation of a metallic iron, Fe$^0$, or zero valent iron (ZVI), potentially offering continuum reductive separation and structural incorporation of Tc under ambient conditions from complex aqueous electrolyte mixtures over wide pH and concentration ranges, albeit via poorly understood mechanisms. Overall, ZVI is a readily available strong reductant that has been proposed for decontamination and remediation strategies, including reductive removal of radioactive contaminants, uranyl and pertechnetate, in groundwater22–24. ZVI (iron powder, nano-iron, and steel coupons) exhibits effective reductive separation of Tc25–27, and is one of the materials compatible with immobilization and stabilization of the separated Tc for long-term disposal, but its application can be modulated by Tc anticorrosive properties28,29, and has not been investigated for high Tc loading. Different iron oxides/oxyhydroxides can be formed during reaction of metallic iron in aerobic conditions, and their transformation pathways are influenced by a variety of factors, including presence of anions30, where effect of Tc$^{4+}$ at moderately high concentration has not been studied yet. In addition, ZVI materials have shown different redox kinetics, depending on particle size and related to their manufacturing method27. Thus, the behavior of an iron system requires additional investigation for each unique setting and contaminant of concern.

Here, we seek a fundamental understanding of the in situ formation of iron oxide phases in the aerobic environment governed by the redox equilibria processes. We study a heterogeneousoxic system containing solid Fe$^0$ and aqueous TcO$_4^−$-initiating surface redox reactions associated with Fe$^0$ dissolution, followed by in situ co-precipitation with Tc$^{4+}$ reduction products. Our previous testing of a wide range of commercial iron products27 shows that granular ZVI exhibits 99% Tc-removal efficiency indicating kinetics suitable for time-dependent structural studies on formation and transformation of iron minerals in the presence of Tc. The NaCl solution matrix is chosen in order to supply an electrolyte that promotes iron oxidation and avoids complexation with TcO$_4^−$, i.e., without interfering with the Tc$^{4+}$ reduction process30. All experiments of reductive sequestration of Tc with granular ZVI and comprehensive characterization of solid phases are conducted at Fe:Tc molar ratio 53:1, or 3.3 wt.% Tc. The results show structural incorporation of Tc$^{4+}$ at the high loading and reveal effect of Tc on transformation of iron mineral phases.

**Results**

**Reductive removal of pertechnetate.** After 25 days of contact time of granular ZVI with 80 mM NaCl solution containing 17 mM TcO$_4^−$, 99.8% of the aqueous Tc was removed from the solution (aqueous fraction of Tc 0.0010 ± 0.0004). In the presence of Tc, ZVI granules exhibited distinct time-dependent changes observable by color (Supplementary Fig. 1a, b), transitioning from brown-yellowish after a week to smaller black granules after a month from the start of the experiment. In the absence of Tc, the sample of ZVI reacted with 80 mM NaCl solution turned black within one week after the start of the experiment (Supplementary Fig. 1c). Both samples with and without Tc had a fraction of newly formed black suspended fines (likely magnetite), separated during several runs of consecutive centrifugation, and analyzed as a bulk solid phase with the rest of solids per each sample. The concentration of Tc in the supernatant was 0.01 mM of TcO$_4^−$. After centrifugation, samples were washed with deionized water, and the washing solution had slightly higher Tc concentration (0.08 mM) compared to the supernatant. This suggested possible re-oxidation or resuspension of Tc$^{4+}$. 

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As investigated previously, ZVI materials manufactured by different methods exhibit different kinetics of Tc removal, attributed to variable surface properties and rates of Fe\(^{0}\) oxidation and dissolution\(^{22}\). Among the wide variety of ZVI materials tested previously, granular iron belonged to a group with superior Tc\(^{2+}\) reduction efficiency, and it exhibited the least propensity for Tc\(^{4+}\) re-oxidation within this group. For this material, the profile of Fe\(^{0}\) solubilization in 80 mM NaCl solution and the corresponding pH and ORP time dependencies had been studied earlier\(^{27}\). Here, the pH value of 10.3 measured 25 days after the start of experiment indicated the prevalence of iron dissolution reactions\(^{2}\).

X-ray absorption near edge structure (XANES) analysis from different locations (A and B) on two iron granules (ZVI-1 and ZVI-2) showed that both Tc\(^{4+}\) and Tc\(^{2+}\) were present in the solid phase after one month of contact with ZVI (Table 1); however, partial oxidation of Tc\(^{4+}\) during sample preparation, storage, and analysis cannot be ruled out. Linear combination fitting (LCF) was performed for XANES (21 to 21.4 keV) and extended X-ray absorption fine structure (EXAFS) spectra (3 < k < 12), and LCF combinatorics showed better statistical results for three components, with R-factor and Chi\(^{2}\) almost two times smaller for three components vs. two components (Supplementary Table 1). Moreover, principal component analysis (PCA) was supportive of three components (Supplementary Fig. 2); hence, three standards were kept for LCF (Fig. 1a; Table 1), two of which were Tc\(^{4+}\) with different coordination environments (Tc\(^{4+}\) hydrated oxide and Tc\(^{4+}\) in magnetite). These results revealed that approximately 50% of Tc was present as TcO\(_2\) and Tc\(^{2+}\) in magnetite. The remaining small fraction of Tc was associated with adsorbed Tc\(^{4+}\) phases with a larger fraction present in B locations of both granules, where more Tc was associated with the solid phase, as seen from the false-color abundance maps, Fig. 1b (11–13% in A locations vs. 20–21% in B locations, Table 1).

We further performed high-resolution X-ray photoelectron spectroscopy (XPS) analysis of the ZVI granules (Fig. 2). Peak fitting of the Tc 3d spectrum required three pairs of doublets, whose lower binding energies (3d\(_{5/2}\)) were determined to be 256.4 eV, 257.4 eV, and 259.6 eV. While the peaks at 256.4 eV and 259.6 eV were assigned to Tc\(^{4+}\) (35.3%) and Tc\(^{2+}\) (32.8%), respectively\(^{31,32}\), the peak at 257.4 eV suggested Tc\(^{4+}\) in a different local environment (~31.9%) that is supported by XANES analysis (Fig. 1a and Table 1).

### Table 1 Linear combination fitting.

|          | XANES weight fraction (one SD error on the last significant figure) | XANES Chi\(^{2}\) | EXAFS weight fraction (one SD error on the last significant figure) | EXAFS Chi\(^{2}\) |
|----------|---------------------------------------------------------------------|------------------|---------------------------------------------------------------------|------------------|
| ZVI-1-A  | TcO\(_{2}\)\(^{-}\)                                                   | 0.011 (1)        | TcO\(_{2}\)                                                      | 0.10 (1)         |
|          | TcO\(_{2}\)\(\cdot\)nH\(_{2}\)O                                      | 0.55 (6)         |                                                                    | 0.48 (3)         |
|          | Tc\(^{4+}\) in Fe\(_{3}\)O\(_{4}\)                                  | 0.34 (6)         |                                                                    | 0.42 (4)         |
| ZVI-1-B  | TcO\(_{2}\)\(^{-}\)                                                   | 0.21 (2)         |                                                                    | 0.15 (2)         |
|          | TcO\(_{2}\)\(\cdot\)nH\(_{2}\)O                                      | 0.45 (9)         |                                                                    | 0.45 (4)         |
|          | Tc\(^{4+}\) in Fe\(_{3}\)O\(_{4}\)                                  | 0.34 (9)         |                                                                    | 0.40 (4)         |
| ZVI-2-A  | TcO\(_{2}\)\(^{-}\)                                                   | 0.13 (1)         |                                                                    | 0.10 (1)         |
|          | TcO\(_{2}\)\(\cdot\)nH\(_{2}\)O                                      | 0.55 (6)         |                                                                    | 0.52 (3)         |
|          | Tc\(^{4+}\) in Fe\(_{3}\)O\(_{4}\)                                  | 0.32 (6)         |                                                                    | 0.39 (3)         |
| ZVI-2-B  | TcO\(_{2}\)\(^{-}\)                                                   | 0.20 (2)         |                                                                    | 0.15 (1)         |
|          | TcO\(_{2}\)\(\cdot\)nH\(_{2}\)O                                      | 0.46 (9)         |                                                                    | 0.47 (3)         |
|          | Tc\(^{4+}\) in Fe\(_{3}\)O\(_{4}\)                                  | 0.34 (9)         |                                                                    | 0.38 (4)         |

Structural characterization of solid phase. Powder X-ray diffraction (PXRD) analysis of ZVI granules contacted with 80 mM NaCl solution with and without TcO\(_{4}\)\(^{-}\) was indicative of magnetite in all samples, with a more prominent magnetite pattern in samples without Tc, Fig. 3ab (data with Rietveld refinement are in Supplementary Fig. 3). Here, PXRD patterns did not allow for the discrimination between magnetite and maghemite, hence, maghemite formation was not excluded. In addition, the single crystal diffractogram of the one-month contacted ZVI sample without Tc revealed an additional iron phase, ferrithyrdate (Supplementary Fig. 4); the sample with Tc did not produce a good signal.

XPS core level Fe 2p spectrum (Supplementary Fig. 5) showed a profile characteristic of Fe\(^{3+}\)\(^{33,34}\), with an Fe 2p\(_{3/2}\) peak at 711.2 eV and a signature satellite peak at ~719 eV, which may belong to maghemite. It should be noted that XPS is a surface sensitive technique with a sampling depth of ~10 nm, and oxidized surface layers, i.e., magnetite oxidized to maghemite, may not be representative of the bulk.

Mössbauer spectroscopy confirmed the presence of non-stoichiometric, or partially oxidized, magnetite. Magnetite (Fe\(_{3}\)O\(_{4}\)) is an inverse spinel which has stoichiometry of 8 tetrahedral Fe\(^{3+}\), 8 octahedral Fe\(^{3+}\), 8 octahedral Fe\(^{2+}\), and 32 O atoms with Fe\(^{2+}\)/Fe\(^{3+}\) ratio equal to 0.5. Oxidation of magnetite leads to formation of maghemite (γ-Fe\(_{3}\)O\(_{4}\)) with a unit cell of 8 tetrahedral Fe\(^{3+}\), 13 1/3 octahedral Fe\(^{3+}\), 32 O atoms, and 2 1/3 vacancies for charge balance at octahedral sites, and its stoichiometric Fe\(^{2+}\)/Fe\(^{3+}\) ratio is 0 at complete oxidation of magnetite. The experimental Fe\(^{2+}\)/Fe\(^{3+}\) stoichiometry can be determined using Mössbauer signals as Fe\(^{2+}\)/Fe\(^{3+}\) = 0.5 oct Fe\(^{2+}\)\(=\) 0.5 oct Fe\(^{3+}\)\(=\) octFe\(^{2.5+}\), where octFe\(^{2.5+}\) is an overlapped sextet signal from tetFe\(^{3+}\) and octFe\(^{3+}\) in partially oxidized samples, and octFe\(^{2.5+}\) is a sextet of octahedrally coordinated Fe\(^{2+}\) and Fe\(^{3+}\).
increase of the magnetite-maghemite content in the samples without Tc was accompanied by the expected decrease of the Fe$^{0}$ phase (Supplementary Table 2).

Room temperature Mössbauer spectra of the ZVI samples contacted with Tc for one week and one month were both dominated by Fe$^{3+}$ doublets at 0–0.78 mm/s (Supplementary Fig. 6b) and at 0–0.72 mm/s (Supplementary Fig. 6c), respectively, that could be attributed to a mixture of phases, such as nano-sized magnetite$^{36}$, nano-sized maghemite$^{37}$, lepidocrocite$^{38}$, nano-sized goethite$^{39}$, or ferrihydrite$^{10}$. The PXRD analysis excluded the dominant presence of goethite and lepidocrocite (Fig. 3); ferrihydrite was not easily evident due to its poorly crystalline nature, but its presence was supported by the results from single crystal analysis for the ZVI sample without Tc (Supplementary Fig. 4). Liquid nitrogen Mössbauer spectroscopy measurements allow identification of nano-sized magnetite and poorly crystallized maghemite resolved as a sextet due to superparamagnetic relaxation$^{36,37}$. For this purpose, additional spectra of the one-month aged sample were taken at 77 K and provided evidence of a Fe$^{3+}$ doublet at 0–0.81 mm/s, comprising 27% of total iron and proving presence of ferrihydrite; the remaining spectral features were resolved as the sextets of octahedral-tetrahedral Fe$^{3+}$ and octahedral Fe$^{2+}$ (Fig. 4b). Decrease of the Fe$^{3+}$ doublet area and

Fig. 1 X-ray absorption near edge structure analysis. a Tc K-edge XANES spectra for granular ZVI reacted with 17 mM TcO$_4^-$ in 80 mM NaCl for one month. Dotted black lines are data, solid red lines are fit; Tc$^{4+}$ in Fe$_2$O$_4$ (magnetite), Tc$^{4+}$ as TcO$_2$$\cdot$nH$_2$O, and Tc$^{7+}$ as TcO$_4^-$ are standards. b X-ray fluorescence false-color images showing XAFS scans’ spatial locations (indicated by the circle) and Tc abundance on ZVI particles. XAFS data were collected on two ZVI particles, 1 and 2, in two locations, A and B. The color scales are arbitrary intensities of fluorescent X-rays with the highest intensity assigned red color and number 1.0, and the lowest intensity—dark blue color and number 0.001.

Fig. 2 X-ray photoelectron spectroscopy analysis. Scan of granular ZVI contacted with 17 mM TcO$_4^-$ in 80 mM NaCl for one month (Tc 3d spectrum).
increase of the Fe$^{3+}$ and Fe$^{2+}$ sextet areas relative to the room temperature measurements is attributed to the presence of nano-sized magnetite and/or maghemite. Another interesting observation is that the Fe$^{2+}$/Fe$^{3+}$ ratio in the room temperature spectrum was 0.33 compared to 0.39 for the analogous sample without Tc (Supplementary Table 2), which signifies a higher fraction of octahedral Fe$^{2+}$ oxidized to Fe$^{3+}$, hence, higher content of non-stoichiometric magnetite or magnetite-maghemite mixture in the sample with Tc. Distinction between non-stoichiometric magnetite and magnetite-maghemite mixture is known to be problematic$^{40}$, and we further refer to it here as non-stoichiometric magnetite. The maghematization process is accompanied by the formation of vacancies during oxidation and loss of Fe$^{2+}$. This process is energetically favorable for Tc$^{4+}$ incorporation, where Tc$^{4+}$ substitutes Fe$^{2+}$ in the octahedral sites, and loss of two Fe$^{2+}$ atoms satisfies the charge balance$^{3}$. Moreover, as shown by Marshall et al.$^{15}$, Tc$^{4+}$ incorporated into magnetite is recalcitrant to oxidation and release during long-term transformation of magnetite to maghemite.

Microscopy analysis. Cubo-octahedral morphology pertinent to magnetite$^{2,41}$ was observed by scanning electron microscopy (SEM) in the sample contacted with Tc for one month (Fig. 5). The surface of the iron oxide, formed as a result of ZVI dissolution and reprecipitation, was uniformly covered with Tc, as seen via energy dispersive X-ray spectroscopy (EDS) on particles contacted with Tc for one week (Supplementary Fig. 7) and on particles contacted with Tc for one month (Fig. 5). Moreover, Tc association with iron oxide (i.e., non-stoichiometric magnetite) was both on the surface and within iron oxide particles. Analysis of the lamella prepared by focused ion beam (FIB) showed that Tc was incorporated and homogeneously distributed well below the particle surface (Fig. 6). However, EDS performed at the nano scale revealed heterogeneous areas with local enrichment of Tc (Fig. 7).
High resolution scanning transmission electron microscopy (HR-STEM) analysis identified regions with the crystal structure consistent with maghemite or magnetite which cannot be distinguished because of close structural similarities (Fig. 7c). According to the Mössbauer spectroscopy results, the material in the images could be non-stoichiometric magnetite or a magnetite-maghemite mixture. In addition, EDS analysis of the edge of a particle revealed an area (approximately 100 × 200 nm) with little to no Tc present (Supplementary Fig. 8) which was also confirmed via HR-STEM to be either magnetite or maghemite.

Further, HR-STEM analysis of the ZVI sample contacted for one month without Tc was consistent with the presence of magnetite or maghemite (Supplementary Fig. 9).

The presence of other iron mineral phases was not detected with STEM analysis, however the lamella did not represent the bulk sample (Supplementary Fig. 10). The amorphous powder-like solids were not suitable for FIB extraction, thus, additional iron mineral phases cannot be excluded. Scanning electron micrographs of ZVI samples with and without Tc showed larger particles in the sample without Tc, and more of the powder-like iron oxidation product (i.e., ferrihydrite) in the sample with Tc (Supplementary Fig. 11). Possibly, retarded transformation of ferrihydrite to magnetite resulted in smaller particles in the sample with Tc.

**Extended X-ray absorption fine structure analysis.** Extended X-ray absorption fine structure (EXAFS) data analysis and modeling were performed to clarify Tc⁴⁺ association with iron oxides (Fig. 8, Table 2). Even though non-stoichiometric magnetite or magnetite and maghemite mixture is referred to here, due to their structural similarities, a modified crystal structure of magnetite was used for the fitting model. The octahedral atom of iron (Fe1) was set as a core atom substituted by Tc. The coordination number (CN) of both octahedral Fe1 and tetrahedral Fe2 was fixed at 6.0 in accord with the crystal structure of magnetite. Theoretically, the first shell of octahedrally coordinated Tc⁴⁺ is represented by six O atoms in both oxide and magnetite. The majority of the EXAFS studies on Tc incorporation into magnetite fixed CN to 6.0[15,16,30,42], however, our data did not result in a good fit with 6O atoms, possibly due to a fraction of the Tc being on the surface of the iron oxide nanoparticles where its coordination numbers can be reduced. While the CN for ZVI-1-A and ZVI-2-A (4.4 and 4.1, respectively) are reasonable, accounting for the mixture of Tc⁷⁺ and Tc⁴⁺ and surface fraction of Tc⁴⁺, the CN for ZVI-1-B and ZVI-2-B are quite low (3.1 and 2.7, respectively), but the data for these scan locations correspond to the elevated amounts of Tc (false-color images with Tc abundance on ZVI granules, Fig. 1b).

**Fig. 5 Microscopy analysis.** Granular ZVI reacted with 17 mM TcO₄⁻ in 80 mM NaCl for one month. a SEM micrograph of the iron oxide as a result of ZVI granules dissolution/reprecipitation; b–d EDS maps of Tc (b), Fe (c), and O (d). The maps were collected from the area outlined in white on the SEM image (a).

**Fig. 6 Microscopy analysis of the lamella at micron scale.** Granular ZVI reacted with 17 mM TcO₄⁻ in 80 mM NaCl for one month. a HAADF STEM micrograph of Tc-containing lamella; b higher magnification HAADF image of the area outlined in white on the image (a); c bright field STEM image collected concurrently with (b); d–f EDS maps of the area shown in b and c indicate homogeneous distribution of Tc within oxidized ZVI. The mineral phases shown in this area could not be identified.
with a higher fraction of TcO$_4^-$, i.e., 0.21 and 0.20, respectively (Table 1), the contribution from which is not included in the fit. The path Tc—Tc (Table 2) implies the existence of Tc$^{4+}$ oxide monomers and dimers.$^{11}$ Similar results were obtained for TcO$_2$ sorbed to magnetite,$^{16}$ Tc$^{4+}$ partially incorporated into magnetite,$^{18}$ and surface-precipitated TcO$_2$$\cdot$$x$H$_2$O (not incorporated into goethite, or magnetite)$^{13}$ with the respective Tc—Tc atomic distances at 2.57, 2.56, and 2.51 Å and CN of 0.9, 1.2, and 0.5.

The obtained Tc-Fe1 and Tc-Fe2 atomic distances (Table 2) are in excellent agreement with the respective 3.12 and 3.52 Å reported by Yalçintaş et al.$^{16}$ These distances are very similar to those reported in the studies on sorbed and incorporated Tc in magnetite$^{13,15,18,30}$, implying an impossible differentiation of the paths between sorbed vs. incorporated Tc in the magnetite structure. Note that the large value of $\sigma^2$ for the Tc-Fe1 path is an indication that the average CN of this path is lower, and is supportive of the heterogeneous system, where Tc has next-near neighboring Fe ions from the iron mineral, as well as Tc in a Tc$^{4+}$ oxide. Moreover, distances between iron atoms in different iron minerals are very similar, and the EXAFS spectra of hematite, goethite, and ferrihydrite were found to be almost identical.$^{10,11}$ In such cases conclusive statements should not be made from EXAFS analysis alone, but in conjunction with other techniques.$^{20}$ As such, STEM and EDS results confirm association of Tc with iron oxide, i.e., non-stoichiometric magnetite, not only on

![HAADF STEM image](image_url)

Fig. 7 Microscopy analysis of the lamella at nano scale. Granular ZVI reacted with 17 mM TcO$_4^-$ in 80 mM NaCl for one month. a HAADF STEM image of the sample; b higher magnification image of the area outlined in white on the image (a); c higher magnification image of the area outlined in white on the image (b), indicating the presence of magnetite or maghemite structure as seen along the [−1 1 2] zone axis; d-f EDS maps of Tc (d), Fe (e), and O (f).

![Extended X-ray absorption fine structure analysis](image_url)

Fig. 8 Extended X-ray absorption fine structure analysis. ZVI granules reacted with 17 mM TcO$_4^-$ in 80 mM NaCl for one month: (a) $k^2$-weighted EXAFS spectra of Tc K-edge; (b) corresponding Fourier transform of $k^2$-weighted EXAFS; dotted black lines are data, solid red lines are fit; fitting $k$-range from 2 to 10 Å$^{-1}$; Fourier transform fitting range from 1.0 to 3.3 Å; amplitude reduction factor $S_0^2 = 0.8.$
the surface (Supplementary Fig. 6), but in the vertical profile of the lamella cut from the iron oxide with FIB technique (Figs. 6 and 7), showing a clustered Tc environment within the maghemite nanostructure. Possibly, the areas of local enrichment are mixtures of TcO₂ monomers and dimers incorporated in the iron oxide’s crystal structure, where incorporation of mononuclear Tc⁴⁺ at the octahedral Fe site cannot be excluded. This is also supported by the XPS results, demonstrating two distinct environments for Tc⁴⁺. In addition, a model with contribution from the multiple scattering paths as an alternative to the iron phase, e.g., siderite or green rust, that could separate Fe²⁺ from Fe³⁺. As mentioned previously, the addition of foreign species, i.e., anions, in the system retards the transformation of ferrihydrite, and our observations relate pertechnetate to the category of such species. The maghemite fraction was noticeably suppressed in the samples of ZVI with Tc (Supplementary Table 2), resulting in slower transformation of ferrihydrite into maghemite, which was also supported by PXRD data, with the amount of maghemite comprising 2–7% in the Tc-loaded samples vs. amount of maghemite in the range of 15–26% in the samples without Tc (Supplementary Fig. 3). Moreover, in the presence of Tc, samples of ZVI granules did not oxidize as fast, as evidenced by the larger fraction of Fe²⁺ detected in the Tc-loaded samples via Mössbauer and PXRD analyses (Supplementary Table 2; Supplementary Fig. 3). These results are in accord with the fact that Tc is known for its anticorrosion properties.⁵⁸,⁵⁹

Our experiments, carried out with initial Fe to Tc molar ratio 53, or 3.3 wt.% Tc, indicated the feasibility of near complete reduction of Tc⁷⁺ (TcO₄²⁻) determined via XANES analysis could be explained by surface oxidation during sample handling and/or exposure to the photon beam) with consequent incorporation of at least 32% Tc, as determined from XANES analysis (Table 1) and supported by XPS analysis, which identified ~32% Tc⁴⁺ in the local environment different from Tc⁴⁺ in the precipitated oxide (Fig. 2). This amount comprises an estimated 1.86 wt.% Tc in the maghemite (magnetite fraction was estimated via Mössbauer measurements of the one-month reacted sample). Interestingly, these results, corresponding to the thermodynamically spontaneous system, support theoretical calculations defining 5 wt.% as the energetically feasible, but unstable, upper limit for Tc incorporation into magnetite with increasing stability at 1.3 vs. 2.6 wt. % for Tc incorporation into hematite. It is important to note that spinel ferrite with 4 wt.% Tc was synthesized by Lukens...
et al.\textsuperscript{17}, however it pertains to a system under a controlled environment, i.e., TcO\textsubscript{4}\textsuperscript{-} dissolved in Fe\textsuperscript{2+} solution followed by neutralization and heating. We emphasize the importance of a spontaneous system, analyzed here, as it relates to practical needs and may pave the way for remediation technologies and waste form development.

Further, our results showed heterogeneous distribution of Tc within the iron oxide (Fig. 7). Similar observations of clustered Tc in spinel ferrites have been reported previously for Tc\textsubscript{2}O\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{4}\textsuperscript{-}, and Tc\textsuperscript{4+} dimers were estimated to be the most stable clusters in doped rutile (TiO\textsubscript{3})\textsuperscript{4+}. The study by Yalcintas et al.\textsuperscript{16}, reported Tc\textsuperscript{4+} dimers bonded to the surface of pre-synthesized magnetite at 0.2 mM Tc as opposed to partial incorporation of Tc\textsuperscript{4+} at 0.02 mM Tc (Fe:Tc molar ratios 1300–3200). It is known that substitution of magnetite is enhanced when the metal coprecipitates with ferrihydrite vs. when the metal is added after ferrihydrite precipitation\textsuperscript{2}; that is why results for Tc incorporation are sensitive to relatively low Tc concentration of 0.2 mM\textsuperscript{16}, when there is no in situ synthesis of iron oxides/oxyhydroxides. In contrast, we observed significant fractional incorporation of Tc\textsuperscript{4+} into iron oxide formed in situ during oxidation of Fe\textsuperscript{0} at elevated Tc loading. 17 mM TcO\textsubscript{4}\textsuperscript{-} (Fe:Tc molar ratio 53). Such successful results can be explained by the compounded processes of Tc\textsuperscript{4+} reduction and ferrihydrite formation with further transformation to non-stoichiometric magnetite or magnetite and maghemite mixture during oxidation of ZVI.

Methods

Caution

\textsuperscript{99m}Tc emits \beta\textsuperscript{-} radiation (0.29 MeV\textsuperscript{27}). All radioactive samples were prepared at a nonreactor nuclear facility by certified personnel inside of a fume hood designed for radiological contamination control.

Batch experiments. The samples were prepared with granular ZVI (Alfa Aesar, electrolytic, 1–2 mm particle size, 99.98% purity) at a concentration of 50 g/L in 80 mM NaCl (Sigma Aldrich, \(+99.5\%\); neutral solution (pH 6.9 \pm 0.1) was used to prepare a solution of 17 mM Tc\textsuperscript{4+} in magnetite\textsuperscript{17}, Tc\textsuperscript{4+} oxide\textsuperscript{17} and Tc\textsuperscript{4+} adsorbed onto Purolite AS30E resin. ICSD files of Fe\textsubscript{3}O\textsubscript{4} and Tc\textsubscript{O}\textsubscript{2} were used for FEFF6.0 calculations for fitting the EXAFS region; the magnetite input file was modified with a core Tc atom in an octahedral Fe site.

Scanning electron microscopy (SEM) images were obtained using a Quanta 250 FEG SEM (Thermo Fisher Inc., Hillsdale, MI) equipped with an EDAX Genesis™ (EDAX Inc., Mahwah, NJ) analytical energy dispersive X-ray spectroscopy (EDS) system. Scanning transmission electron microscopy (STEM) was performed on a cold field emission JEM ARM 200 F operated at 200 kV and equipped with a Noran™ (Thermo Scientific, Waltham, MA) EDS system. The microscope is aberration-corrected with a hexapole-type probe Cs corrector (Cryo-Corr, CEOS). STEM maps and EDS spectra were collected with a 0.78\textdegree-Å probe at an emission current of 15 μA, with a high-angle annular dark-field (HAADF) detector inner angle of 82.6 mrad. A lamella from the sample contacted with Tc for one month was prepared using a focus ion beam (FIB) on a Quanta 200 FEG (FEI). The lamella was attached to a copper Omniprobe liftout with Tc for one month was prepared using a focus ion beam (FIB) on a Quanta 200 FEG (FEI). The lamella was attached to a copper Omniprobe liftout grid using Pt welds. The sample aged without Tc was prepared using low-copper TEM grid coated with a holey carbon film (Electron Microscopy Supplies, Inc) and tapping off the excess.

Data availability

Data supporting these findings are available within the article and supplementary information files.

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Mössbauer spectra were collected at room temperature for all samples, and, additionally, 77 K temperature analysis was used for the ZVI sample reacted with Tc-free broth. The 50 mM Tc\textsuperscript{4+} solution and velocity transducer in MVT-1000 (WissEL) operated in a mode of constant acceleration (25 Hz, ±12 mm/s). The signal was transmitted through a holder where radiation was detected by Ar-Kr proportional counter. The counts were stored in a multichannel scaler as a function of energy, utilizing a 1024-channel analyzer. Data were folded to 512 channels to give a flat background and a zero-velocity position corresponding to the center shift (CS or Δ) of a metal Fe foil at room temperature. A 25-μm thick Fe foil (Amersham, England) was placed in the same position as the samples to obtain calibration spectra. The Mössbauer data were modeled using the Recoil software (University of Ottawa, Canada) and a Voigt-based structural fitting routine.

X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Kratos AXIS Ultra DLD system equipped with a monochromatic Al Kα X-ray source (1486.7 eV) at 10 mA, 15 kV for excitation and a hemispherical analyzer. Data were corrected relative to the reference 285.0 eV carbon 1 s peak. The software CasaXPS (version 2.3) with Shirley type background and 20% Gaussian–Lorentzian ratio was used for peak fitting.

X-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) measurements of the Tc K-edge were obtained at the X-ray Science Division beamline 20-ID-C at the Advanced Photon Source (APS, Argonne National Laboratory). In addition, 2-D elemental maps were collected based on x-ray fluorescence mapping (XRM). Thin sections were prepared for the analysis. Dried solids were prepared in a 1.6 cm (ID) aluminum tubing with slow drying overnight at room temperature. Slices were cut with an Isomet 1000 diamond blade thin sectioning saw with Isocut blade (Buehler, Lake Bluff, IL) to a thickness of approximately 150 μm. After mounting on a glass microscope slide, thin sections were sanded with carbide sand paper with Isocut fluid followed by 400 grit sand paper, then 600 grit sand paper, and finally 1200 grit sand paper (Ted Pella, Inc.) all using a figure eight pattern. Final polishing was conducted with a Nylon polishing cloth and 1 μm diamond polish (Metadi II, Buehler). Samples were washed with methanol and dried prior to analysis. Samples of ZVI granules contacted with Tc were encased in epoxy resin and cut into thin sections. The sample was doubly encapsulated in mylar and Kapton films.

Scanning electron microscope (SEM) images were obtained using a Quanta 250 FEG SEM (Thermo Fisher Inc., Hillsdale, MI) equipped with an EDAX Genesis™ (EDAX Inc., Mahwah, NJ) analytical energy dispersive X-ray spectroscopy (EDS) system. Scanning transmission electron microscopy (STEM) was performed on a cold field emission JEOI ARM 200 F operated at 200 kV and equipped with a Noran™ (Thermo Scientific, Waltham, MA) EDS system. The microscope is aberration-corrected with a hexapole-type probe Cs corrector (Cryo-Corr, CEOS). STEM maps and EDS spectra were collected with a 0.78\textdegree-Å probe at an emission current of 15 μA, with a high-angle annular dark-field (HAADF) detector inner angle of 82.6 mrad. A lamella from the sample contacted with Tc for one month was prepared using a focus ion beam (FIB) on a Quanta SEM (Thermo Fisher FEI). The lamella was attached to a copper Omniprobe liftout grid using Pt welds. The sample aged without Tc was prepared using low-copper TEM grid coated with a holey carbon film (Electron Microscopy Supplies, Inc) and tapping off the excess.
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Author contributions
T.G.L. directed overall research, designed experiments, and guided manuscript preparation. Y.K. and H.P.E. supervised the study. J.A.S. carried out STEM/EDS analysis; R.K.K. collected Mössbauer data and performed modeling; Y.D. carried out XPS analysis with modeling; L.E.S. carried out PXRD analysis with modeling; E.C.B. collected SEM data; V.E.H. collected XAFS data at APS; C.U.S. contributed to EXAFS modeling; G.B.H. prepared samples for analyses; D.B. executed experiments, analyzed data, and wrote the manuscript. All the authors reviewed the manuscript.
Competing interests
The authors declare no competing interests.

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