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1 **Incorporation of technetium into spinel ferrites**

2

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14

15 **Abstract**

16 Technetium (<sup>99</sup>Tc) is a problematic fission product for the long-term disposal of nuclear waste  
17 due to its long half-life, high fission yield, and to the environmental mobility of pertechnetate,  
18 the stable species in aerobic environments. One approach to preventing <sup>99</sup>Tc contamination is  
19 using sufficiently durable waste forms. We report the incorporation of technetium into a family  
20 of synthetic spinel ferrites that have environmentally durable natural analogs. A combination of  
21 X-ray diffraction, X-ray absorption fine structure spectroscopy and chemical analysis reveals that  
22 Tc(IV) replaces Fe(III) in octahedral sites and illustrates how the resulting charge mismatch is  
23 balanced. When a large excess of divalent metal ions is present, the charge is predominantly

24 balanced by substitution of Fe(III) by M(II). When a large excess of divalent metal ions is  
25 absent, the charge is largely balanced by creation of vacancies among the Fe(III) sites  
26 (maghemitization). In most samples, Tc is present in Tc-rich regions rather than being  
27 homogeneously distributed.

28

## 29 **Introduction**

30 Technetium ( $^{99}\text{Tc}$ ) is a problematic fission product for nuclear waste disposal due to its long  
31 half-life (211,000 yr), high fission yield (6 %), and to the environmental mobility of  
32 pertechnetate ( $\text{TcO}_4^-$ ), the stable form in aerobic environments.<sup>1-4</sup>  $^{99}\text{Tc}$  migration may be  
33 minimized by disposal in an anaerobic repository since Tc(IV) is stable under these conditions  
34 and is not highly mobile.<sup>3</sup> Alternatively, technetium may be immobilized in a waste form that is  
35 sufficiently durable to prevent release of  $^{99}\text{Tc}$  until an acceptable fraction has decayed. The  
36 current U.S. high-level waste repository is Yucca Mountain, which is aerobic and oxidizing.<sup>5</sup> In  
37 addition, the majority of the  $^{99}\text{Tc}$  from plutonium production at the Savannah River and Hanford  
38 Sites will be disposed in near-surface, aerobic repositories although the Savannah River Site  
39 facility will be reducing initially.<sup>6,7</sup> Disposal of  $^{99}\text{Tc}$  in current and proposed aerobic repositories  
40 underscores the interest in durable waste forms for  $^{99}\text{Tc}$ .

41

42 Even under reducing conditions, the 3 pM solubility of  $\text{TcO}_2 \cdot x\text{H}_2\text{O}$  exceeds the EPA maximum  
43 contaminant level of 900 pCi/L or 0.5 pM.<sup>8-10</sup> Naturally occurring ligands can increase the  
44 solubility of Tc(IV).<sup>11-14</sup> Therefore, durable waste forms are also desirable for  $^{99}\text{Tc}$  disposal in an  
45 anaerobic repository. The most commonly used waste form, borosilicate glass, is durable, but  
46 loss of volatile technetium species during glass vitrification can make it difficult to retain

47 technetium in the glass.<sup>15-18</sup> Alternatives include synthetic mineral phases, such as Synroc.<sup>19</sup>  
48 Likewise, certain mineral phases are both highly durable and could accommodate Tc doping.<sup>20</sup>  
49 The similarity of the six coordinate ionic radii of Tc(IV), Ti(IV), and Fe(III), 0.645 Å, 0.604 Å  
50 and 0.645 Å,<sup>21</sup> respectively, suggests that Tc(IV) can replace Ti(IV) or Fe(III) in an oxide  
51 mineral.<sup>20</sup> Rutile (TiO<sub>2</sub>), hematite (α-Fe<sub>2</sub>O<sub>3</sub>) and goethite (α-FeOOH), are known to be durable  
52 under aerobic conditions.<sup>22-26</sup> Hematite and goethite are unstable under reducing conditions and  
53 could release <sup>99</sup>Tc; however, migration is slow under these conditions.<sup>3</sup> Moreover, Tc(IV) can be  
54 incorporated into mineral phases under these conditions as demonstrated by Kobayashi, et al.  
55 who showed that prolonged contact of magnetite (Fe<sub>3</sub>O<sub>4</sub>) with TcO<sub>4</sub><sup>-</sup> leads to Tc(IV)  
56 incorporation.<sup>27</sup> Iron oxides, particularly goethite, have received attention as waste forms for  
57 stabilizing <sup>99</sup>Tc.<sup>28,29</sup> Other iron oxides can also accommodate Tc(IV). Pepper, et al., incorporated  
58 Tc(IV) into an iron oxide phase resulting from oxidation of green rust.<sup>30</sup> Marshall, et al.  
59 demonstrated that adsorption of Tc(IV) onto ferrihydrite followed by conversion to magnetite  
60 results in Tc doping.<sup>31</sup> Tc-doped magnetite has been studied computationally by Smith, et al..<sup>32</sup>  
61 Lee, et al. demonstrated that Tc(IV) may be incorporated into the lattice of transition metal  
62 doped magnetites.<sup>18</sup>

63  
64 Another family of iron oxides, spinel ferrites (MFe<sub>2</sub>O<sub>4</sub>, where M is Mg(II), Mn(II), Co(II), or  
65 Ni(II)), especially nickel/magnesium ferrite, Mg<sub>x</sub>Ni<sub>1-x</sub>Fe<sub>2</sub>O<sub>4</sub>, are highly durable as evidenced by  
66 their persistence since being deposited widely across earth's surface 65 million years ago by the  
67 Chixulub meteorite impact.<sup>33</sup> These minerals are inverse spinels, but they will be referred to as  
68 "spinel ferrites" for brevity. Synthetic spinel ferrites are attractive potential waste forms for  
69 several reasons. Aqueous synthesis conditions and short reaction times (few hours) make them

70 amenable to processing.<sup>34-38</sup> They are magnetic, potentially allowing magnetic separation of Tc.  
71 Incorporation of Tc(IV) into magnetite,<sup>18,27,31</sup> suggests that other Tc(IV)-doped spinel ferrites  
72 may be prepared. This observation leads the hypothesis that starting from  $\text{TcO}_4^-$ , Tc(IV) will be  
73 homogeneously incorporated into spinel ferrites by replacing Fe(III) on  $M_O$  sites provided that  
74 sufficient Fe(II) is present to reduce  $\text{TcO}_4^-$ .

75  
76 To test the hypothesis and to understand the factors controlling Tc incorporation into spinel  
77 ferrites, we have prepared: (i) a series of Tc(IV)-doped spinel ferrites with the composition  
78  $\text{Tc}_{0.1}\text{M}_{1.1}\text{Fe}_{1.8}\text{O}_4$ , where M is Mn, Co, and Ni; and (ii) a series of magnetites doped with Tc(IV)  
79 and divalent metals having the composition  $\text{Tc}_{0.1}\text{M}_{0.2}\text{Fe}_{2.7}\text{O}_4$  where M is Mg, Mn, Fe, Co, and  
80 Ni. The objectives of this study were (i) to determine whether Tc could be incorporated into the  
81 octahedral sites ( $M_O$ ) of spinel ferrites,  $\text{M}_x\text{Fe}_y\text{O}_4$ , (ii) to determine the effect of ionic radius of the  
82 divalent metal ion, M, on the incorporation of Tc in the spinel ferrite lattice, and (iii) to  
83 determine the effect of different synthetic routes on the incorporation of Tc. The two synthetic  
84 routes examined were the traditional coprecipitation route (samples indicate by “-c”),<sup>34</sup> in which  
85 a mixture of M(II), Fe(II) and Fe(III), and  $\text{TcO}_4^-$  is treated with NaOH to form the ferrite spinel  
86 and a oxidation route (samples indicated by “-o”) in which a mixture of M(II), Fe(II) and  $\text{TcO}_4^-$   
87 is treated with NaOH and  $\text{NaNO}_3$ , and Fe(III) is generated *in situ* by oxidation of Fe(II) by  $\text{NO}_3^-$

88 .<sup>36</sup>

89

## 90 **Experimental Details**

91 **Caution:**  $^{99}\text{Tc}$  is  $\beta$ -emitter. All operations were carried out in a laboratory equipped to handle  
92 this isotope.

93 **General.** Water was deionized using a Milli-Q Gradient A-10 system. Chemicals were ACS  
94 grade or better and were used as received. Fe(II)/total Fe ratios (Fe(II)/ $\Sigma\text{Fe}$ ) in the spinels were  
95 determined colorimetrically.<sup>39,40</sup> In this method, V(V) is reduced to V(IV) by Fe(II) during  
96 dissolution of the sample in acid. When 2,2'-bipyridyl (bipy) and buffer are added, V(IV)  
97 quantitatively reduces Fe(bipy) $_3^{3+}$  to red Fe(bipy) $_3^{2+}$ , which is measured spectrophotometrically.  
98 The Fe(II)/ $\Sigma\text{Fe}$  ratios for the Tc-doped samples were decreased proportionally to the amount of  
99 Tc recovered from the spinel ferrites and the Tc/Fe ratio to account for reduction of three V(V)  
100 by each Tc(IV), e.g., for  $\text{Tc}_{0.1}\text{Mn}_{1.1}\text{Fe}_{1.8}\text{O}_{4-o}$  Fe(II)/ $\Sigma\text{Fe}$  was decreased by  $3 (e^-/\text{Tc(IV)}) \times 0.99$   
101 (Tc recovered from solid)  $\times 0.1/1.8$  (Tc/Fe). Two sets of independently prepared samples were  
102 used for characterization. The initial set was used for XRD and XAFS studies. Later, a second  
103 set was prepared for LSC and Fe(II)/Fe(III) measurements to address questions that arose during  
104 the analysis of the XRD and XAFS results. Both sets were prepared using the same procedures.

105

## 106 **Synthesis of Tc-doped spinel ferrites**

107 Note: The stoichiometry of the samples (e.g., " $\text{Tc}_{0.1}\text{Co}_{1.1}\text{Fe}_{1.8}$ ") are based on the amount of each  
108 metal added during the synthesis. The samples contain 4 wt% Tc.

109 Two approaches were used to prepare samples: coprecipitation and oxidation. In the  
110 coprecipitation approach,  $\text{TcO}_4^-$  was added to a mixture of divalent metal ion and Fe(III).<sup>34</sup> A  
111 five-fold excess of Fe(II) relative to  $\text{TcO}_4^-$  was used to reduce  $\text{TcO}_4^-$  to Tc(IV). The solution was  
112 neutralized with sodium hydroxide and heated. These samples are indicated by a "c" after the

113 formula, e.g.,  $\text{Tc}_{0.1}\text{Fe}_{2.9}\text{O}_4\text{-c}$ . In the oxidation route,  $\text{TcO}_4^-$  was added to a mixture of Fe(II) and a  
114 divalent metal ion; sodium hydroxide and sodium nitrate were added and the solution was  
115 heated.<sup>36</sup> Fe(III) is formed *in situ* through oxidation of Fe(II) by nitrate, hence the term  
116 “oxidation route.” These samples are indicated by an “o” after the formula, e.g.,  $\text{Tc}_{0.1}\text{Fe}_{2.9}\text{O}_4\text{-o}$ .  
117 Following the synthesis, the samples were handled and stored in air, and no attempts were made  
118 to exclude oxygen.

119  
120 **Coprecipitation** (adapted from ref 33).  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  (53 mg, 0.22 mmol) was dissolved in a  
121 mixture of 1.0 M  $\text{FeSO}_4$  (0.10 mL, 0.10 mmol) and 1.0 M  $\text{NH}_4\text{Fe}(\text{SO}_4)_2$  (0.26 mL, 0.26 mmol).  
122 The solution was sparged with argon for 1 minute. A 0.10 M solution of  $\text{TcO}_4^-$  in 0.03 M  $\text{HNO}_3$   
123 (200  $\mu\text{L}$ , 0.02 mmol) was added. The headspace of the tube was purged with argon, and the tube  
124 was vigorously shaken. Aqueous 2.00 M  $\text{NaOH}$  (0.91 mL, 1.81 mmol  $\text{OH}^-$ ) was added. The  
125 headspace of the tube was purged with argon, and the tube was vigorously shaken. The tube was  
126 heated to 95 °C for 90 minutes. After heating, the tube was centrifuged (5 min, 8500 g) and the  
127 solution decanted. The black solid was washed with  $2\times 1.5$  mL water and 1.5 mL acetone.

128  
129 **Oxidation** (adapted from ref. 35).  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  (53 mg, 0.22 mmol) was dissolved in 1.0 M  
130  $\text{FeSO}_4$  (0.36 mL, 0.36 mmol). The solution was sparged with argon for 1 minute. A 0.11 M  
131 solution of  $\text{TcO}_4^-$  in 0.03 M  $\text{HNO}_3$  (200  $\mu\text{L}$ , 0.02 mmol) was added. The headspace of the tube  
132 was purged with argon, and the tube was vigorously shaken. An aqueous solution of 1.00 M  
133  $\text{NaNO}_3$  and 2.00 M  $\text{NaOH}$  (0.61 mL, 1.21 mmol  $\text{OH}^-$ ) was added. The headspace of the tube was  
134 purged with argon, and the tube was vigorously shaken. The tube was heated to 95 °C for 90

135 minutes. After heating, the tube was centrifuged (5 min, 8500 g), and the supernate decanted.  
136 The black solid was washed in air with 2×1.5 mL water and 1.5 mL acetone.

137

138 **Synthesis of undoped spinel ferrites.** Samples with the same transition metal composition, but  
139 without added Tc were prepared. Both the oxidation synthesis and coprecipitation synthesis were  
140 performed as described above except that 200 uL of water was used in place of the  $\text{NH}_4\text{TcO}_4$   
141 solution.

142

143 **Liquid Scintillation Counting (LSC).** Solutions were centrifuged (5 min, 8500 g) to remove  
144 Tc-doped ferrite nanoparticles. 100 uL of this solution was added to 4 mL of Ecolume. Samples  
145 were analyzed using a Wallac 1414 liquid scintillation counter. Results are not corrected for  
146 chemical quench. Comparison of the spectral quench parameter, SQP(E), to a  $^{99}\text{Tc}$  quench curve  
147 prepared using nitromethane showed that quenching was less than 1%.

148

149 **X-ray diffraction (XRD).** An acetone suspension of the sample was dropped onto a silicon zero  
150 background plate. Samples were sealed with Kapton film to control contamination.  
151 Diffractograms were recorded using a Panalytical X'Pert Pro diffractometer with a Cu source  
152 and a silicon strip detector except for sample  $\text{Tc}_{0.1}\text{Ni}_{0.2}\text{Fe}_{2.7}\text{O}_4\text{-c}$ , which was recorded using a Co  
153 source. Data were summed and analyzed using HiScore Plus software. A blank diffraction  
154 pattern from the zero background plate and the Kapton film was subtracted from each diffraction  
155 pattern. An empirical background consisting of a curve through the bases of the peaks at low  $2\theta$   
156 and through the baseline at high  $2\theta$  was removed. The diffraction data were modeled using the



157 crystal structure of magnetite. Rietveld refinement using X'Pert High Score Plus was used to  
158 determine the lattice parameters and to estimate the sizes of the crystallites.

159

160 **X-ray absorption fine structure (XAFS) measurements.** Samples were dispersed in acetone or  
161 water and centrifuged (5 min, 8500 g), and the liquid was discarded to produce a homogeneous  
162 pellet. Data was obtained at room temperature at the Tc K-edge on Beamline 11-2 or 4-1 of the  
163 Stanford Synchrotron Radiation Lightsource. Most data were obtained during a single  
164 experiment. For samples  $\text{Tc}_{0.1}\text{Co}_{1.1}\text{Fe}_{1.8}\text{O}_4\text{-o}$ ,  $\text{Tc}_{0.1}\text{Mg}_{0.2}\text{Fe}_{2.7}\text{O}_4\text{-o}$ , and  $\text{Tc}_{0.1}\text{Ni}_{0.2}\text{Fe}_{2.7}\text{O}_4\text{-c}$ , the  
165 pellet dried out and disintegrated inside the centrifuge tube. Spectra from these samples were re-  
166 collected during a subsequent experiment using freshly prepared material. X-rays were  
167 monochromatized using a double-crystal monochromator with Si [220]  $\phi = 90$  crystals; the  
168 second crystal was detuned by 70% to reduce the harmonic content of the beam. Spectra were  
169 recorded in transmission mode using argon filled ion chambers.

170

171 Data were analyzed by standard procedures<sup>41</sup> using ifeffit<sup>42</sup> and Artemis/Athena.<sup>43</sup> Theoretical  
172 scattering curves were calculated using Feff6<sup>44</sup> based on the structure of titanomagnetite  
173 ( $\text{Ti}_{0.1}\text{Fe}_{2.9}\text{O}_4$ ) with Tc in the octahedral site.<sup>45</sup> Coordination numbers for the neighboring atoms  
174 were fixed at the values found in the crystal structure except for the oxygen shell at 2 Å. This  
175 shell was split into two shells, one with a short distance (1.5 to 1.75 Å) and another with a longer  
176 distance (2 Å); the sum of the oxygen coordination numbers for these shells was fixed at 6, the  
177 number of oxygen nearest neighbors for the Ti(IV) site in titanomagnetite. The value of  $S_0^2$  was  
178 determined to be 0.80 (rather than 0.90) for fitting the data in this study by fitting several  
179 extended X-ray absorption fine structure (EXAFS) spectra of the  $\text{TcO}_4^-$  reference collected

180 simultaneously with the data. The statistical significance of each scattering shell was evaluated  
181 using an F-test.<sup>46</sup>

182

183 **X-ray magnetic circular dichroism spectroscopy (XMCD).** Sample was placed on a 100 nm  
184 thick Si<sub>3</sub>N<sub>4</sub> window, which was sealed to an identical Si<sub>3</sub>N<sub>4</sub> window with epoxy. Data was  
185 recorded at the Molecular Environmental Science Beamline 11.0.2 at the Advanced Light Source  
186 (ALS) with a scanning transmission X-ray microscope (STXM). XMCD spectra were recorded  
187 at the Fe L<sub>2,3</sub>-edge with the sample in a 0.5 T magnetic field using left and right circularly  
188 polarized X-rays from an elliptically polarizing undulator.<sup>47</sup> Data were recorded as images  
189 obtained at different X-ray energies. The background data was obtained from the portion of the  
190 image with no sample. Data were pre- and post-edge normalized. Data were fit using nonlinear  
191 least-squares analysis with calculated spectra<sup>48,49</sup> for each site as previously described<sup>50,51</sup>

192

## 193 **Results and discussion**

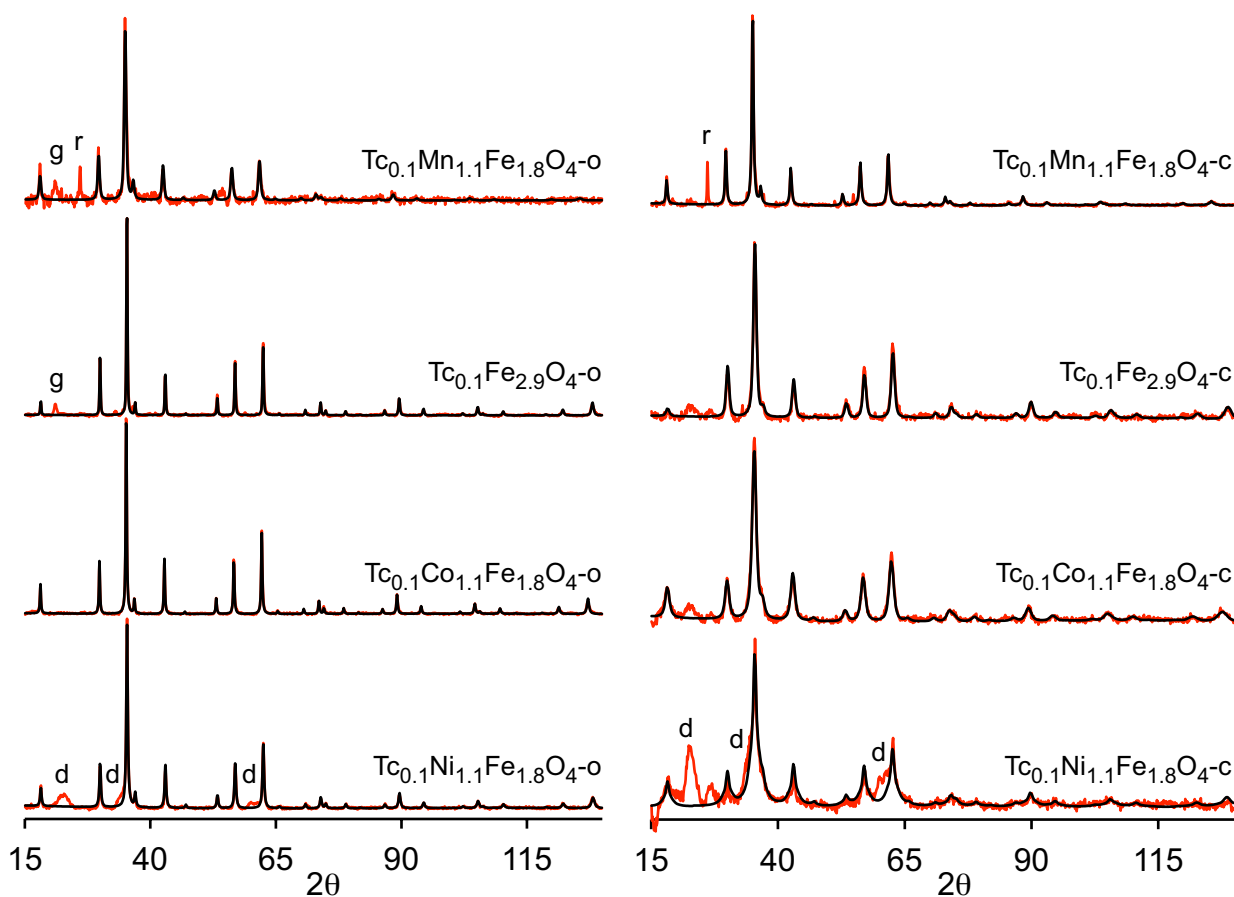
### 194 **Incorporation of Tc into spinel ferrites.**

195 Incorporation of TcO<sub>4</sub><sup>-</sup> was evaluated by LSC analysis of the solution remaining after  
196 preparation of the spinel ferrite (Table S1). More than 99.5 % of the Tc was removed from  
197 solution in all cases; in the oxidation route, more than 99.88 % of the Tc was removed. The Tc  
198 remaining in solution is presumably TcO<sub>4</sub><sup>-</sup>. These results are consistent with work by Livens and  
199 coworkers using green rust to trap TcO<sub>4</sub><sup>-</sup>.<sup>30</sup> Other studies showed that iron metal, magnetite, and  
200 adsorbed Fe(II) can effectively remove TcO<sub>4</sub><sup>-</sup> from solution.<sup>27,52-56</sup> Recovery of Tc from the  
201 spinel ferrites was determined during analysis of Fe(II) and total iron (ΣFe) by determining the  
202 amount of <sup>99</sup>Tc using LSC. The recovery of Tc varied from 81% to 100% (Table S1).

203

204 **X-ray diffraction (XRD).** Tc-doped spinel ferrites were characterized using XRD to determine  
205 the oxide phases present, the lattice parameters, and the crystallite sizes of the major phase. XRD  
206 patterns and Rietveld fits for the Tc-doped spinel ferrites are given in Figure 1. Samples prepared  
207 by the coprecipitation route have broader peaks than samples produced by the oxidation route  
208 due to the smaller crystallites produced by more rapid nucleation of nanoparticles in the  
209 coprecipitation synthesis.<sup>57</sup> These results are consistent with the original magnetite syntheses  
210 from which the procedures to prepare Tc-doped spinel ferrites were adapted.<sup>34,36</sup> Undoped spinel  
211 ferrites, prepared under identical conditions, but adding water instead of  $\text{TcO}_4^-$ , were also  
212 characterized. These undoped samples allow the effect of Tc doping on the lattice parameters  
213 and  $\text{Fe(II)}/\Sigma\text{Fe}$  to be determined.

214



215  
 216 **Figure 1:** X-ray powder patterns (in red) and Rietveld fits (black) of spinel ferrites. Data are  
 217 normalized so that the largest peaks have the same height. Data for  $Tc_{0.1}M_{0.2}Fe_{2.7}O_4$  are given in  
 218 the SI and are similar to those of  $Tc_{0.1}Fe_{2.9}O_4$ . Impurity peaks are labeled with g for goethite, r  
 219 for  $\alpha$ -MnOOH, and d for the layered double hydroxide. Diffraction peaks of the coprecipitation  
 220 samples are broader than those produced by the oxidation route due to the smaller crystallite  
 221 sizes of the coprecipitation samples.

222  
 223 The major phase was spinel ferrite in all samples. The most common impurity was goethite,  
 224 which forms in the presence of oxygen.<sup>36</sup> Its presence suggests that the short sparging period did  
 225 not remove all of the oxygen. When Mn(II) was used,  $\alpha$ -MnOOH, was observed. When Ni(II)

226 was used, an impurity was indicated by broad peaks at  $2\theta = 22.5^\circ$ ,  $35^\circ$ , and  $60^\circ$ , which is  
227 consistent with the presence of a lamellar nickel/iron layered double hydroxide (LDH) phase.<sup>58,59</sup>

228

229 **Effects of charge compensation on lattice parameters and Fe(II)/ $\Sigma$ Fe ratio.** Tc-doping

230 affects the lattice parameters of the spinel ferrites (Figure 2), which provides information about

231 the mechanism that balances the charge mismatch created when Tc(IV) replaces Fe(III). While

232 other mechanisms are possible,<sup>32</sup> the charge mismatch may be balanced in two main ways: M(II)

233 could replace Fe(III) (divalent substitution) or one vacancy at a Fe(III) site could be created for

234 every three Tc(IV) (maghemitization). In  $\text{TiFe}_2\text{O}_4$  (ulvöspinel), the charge mismatch is balanced

235 by divalent substitution leading to a lattice expansion to  $8.521 \text{ \AA}$  relative to magnetite,  $8.397 \text{ \AA}$ .<sup>45</sup>

236 Lattice expansion occurs because M(II) ions are larger than the Fe(III) that they replace. In

237 contrast, maghemitization decreases the lattice parameter, i.e. to  $8.341 \text{ \AA}$  in of Ti-doped

238 maghemite,  $\text{Ti}_{0.42}\text{Fe}_{2.18}\text{O}_4$ .<sup>60</sup> Previous studies of iron oxides doped with tetravalent ions suggest

239 that divalent substitution occurs under reducing conditions and maghemitization occurs under

240 oxidizing conditions.<sup>61-64</sup>

241

242 The lattice parameters of the Tc-doped and undoped spinel ferrites are compared in Figure 2. To

243 explain the results, the samples are categorized by the amount of M(II) and Fe(II) present during

244 synthesis. Samples prepared by the oxidation route are “high Fe(II)” while coprecipitation

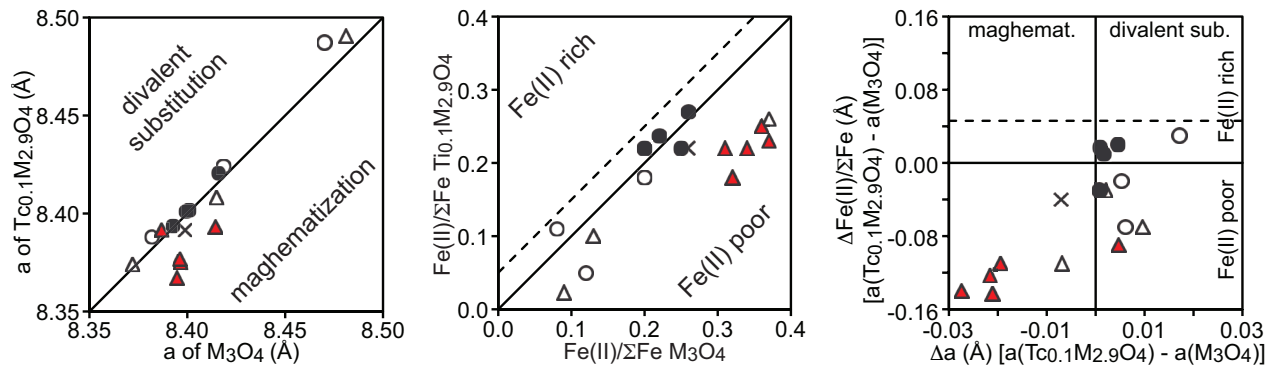
245 samples are “low Fe(II)”. Spinel ferrites,  $\text{Tc}_{0.1}\text{M}_{1.1}\text{Fe}_{1.8}\text{O}_4$ , are “high M(II),” and doped magnetite

246 samples,  $\text{Tc}_{0.1}\text{M}_{0.2}\text{Fe}_{2.7}\text{O}_4$ , are “low M(II).” For example,  $\text{Tc}_{0.1}\text{Co}_{1.1}\text{Fe}_{1.8}\text{O}_4\text{-c}$  is high M(II), low

247 Fe(II). In samples with high M(II) and/or high Fe(II), Tc-doping increases the lattice parameters

248 with the exception of  $\text{Tc}_{0.1}\text{Co}_{1.1}\text{Fe}_{1.8}\text{O}_4\text{-c}$  and  $\text{Tc}_{0.1}\text{Fe}_{2.9}\text{O}_4\text{-o}$ . The increased lattice parameter in

249 these samples suggests that charge is mainly balanced by divalent substitution, which is  
 250 consistent with the large excess of divalent metal ions, either M(II) or Fe(II), present during  
 251 these syntheses. On the other hand, except for  $Tc_{0.1}Ni_{0.2}Fe_{2.7}O_4-c$  and  $Tc_{0.1}Mn_{0.2}Fe_{2.7}O_4-c$ ,  
 252 samples with low M(II) and low Fe(II) show a decrease in the lattice parameter upon Tc-doping.  
 253 This decrease suggests that the charge mismatch is predominantly balanced by maghemitization,  
 254 which is consistent with the smaller amounts of divalent metal ions present during synthesis.



255 **Figure 2.** (Left panel) comparison of lattice parameters of Tc doped spinel ferrites (vertical axis)  
 256 with the lattice parameters of undoped samples (horizontal axis) (left). (Center) comparison of  
 257 the Fe(II)/total Fe values for Tc-doped spinel ferrites (vertical axis) with the undoped analogs  
 258 (horizontal axis). (Right) Change in Fe(II)/ $\Sigma Fe$  (vertical axis) and lattice parameter (horizontal  
 259 axis) as a result of Tc-doping. The dashed line indicates the Fe(II)/total Fe value for a Tc-doped  
 260 spinel ferrite if the charge is balanced by replacing Fe(III) by Fe(II). Open circles:  
 261  $Tc_{0.1}M_{1.1}Fe_{1.8}O_4-o$  (high M(II), high Fe(II)). Filled circles:  $Tc_{0.1}M_{0.2}Fe_{2.7}O_4-o$  (low M(II), high  
 262 Fe(II)). Open triangles:  $Tc_{0.1}M_{1.1}Fe_{1.8}O_4-c$  (high M(II), low Fe(II)). Filled triangles:  
 263  $Tc_{0.1}M_{0.2}Fe_{2.7}O_4-c$  (low M(II), low Fe(II)).

264

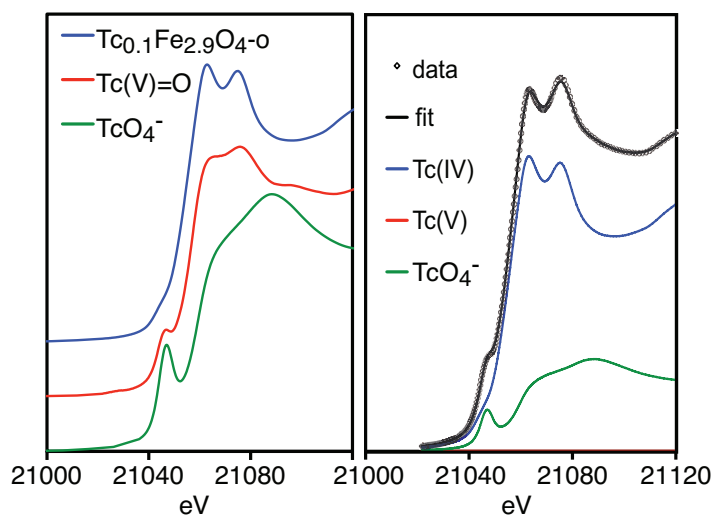
265 The XRD data suggests that the charge mismatch created by Tc doping is predominantly  
 266 balanced by divalent substitution in high Fe(II) or high M(II) samples. The identity of the

267 divalent cation may be inferred from the ratio of Fe(II) to total iron (Fe(II)/ $\Sigma$ Fe) (Table S1 and  
268 Figure 2). If the divalent cation is Fe(II), Fe(II)/ $\Sigma$ Fe will increase upon Tc doping as determined  
269 by stoichiometry (dashed lines in Figure 2 for  $\text{Tc}_{0.1}\text{Fe}_{2.9}\text{O}_4$ ). With some exceptions, Fe(II)/ $\Sigma$ Fe is  
270 smaller for Tc-doped samples, indicating that M(II) rather than Fe(II) replaces Fe(III) during  
271 divalent substitution in the high M(II) samples. The relationship between the change in lattice  
272 parameter and change in Fe(II)/ $\Sigma$ Fe is illustrated in the right panel of Figure 2. In the low M(II)  
273 samples (filled symbols) the changes in lattice parameter and Fe(II)/ $\Sigma$ Fe are generally correlated  
274 since either Fe(II) replaces Fe(III) to balance the charge and expand the lattice or the samples are  
275 maghemitized and the lattice shrinks. High M(II) samples show less correlation because  
276 replacing Fe(III) by M(II) expands the lattice but has little effect on Fe(II)/ $\Sigma$ Fe.

277

278 **XAFS results.** Representative Tc K-edge XANES and EXAFS spectra are shown in Figures 3  
279 and 4, respectively (the other EXAFS spectra are similar to  $\text{Tc}_{0.1}\text{Fe}_{2.9}\text{O}_4\text{-o}$  and are included in the  
280 SI). The model used to fit the EXAFS spectra is the octahedral site ( $M_O$ ) of titanomagnetite  
281 ( $\text{Ti}_{0.1}\text{Fe}_{2.9}\text{O}_4$ ) occupied by Ti(IV). Tc(IV) and Ti(IV) are similar in size, so the local structure of  
282 Ti(IV) in the  $M_O$  site is an appropriate model for the structure of Tc(IV) in spinel ferrites.  
283 Coordination numbers for the metal neighbors were fixed at the value in the crystal structure, e.g.  
284 6 nearest octahedral site ( $M_O$ ) neighbors. A minor contribution from a short Tc-O distance at  
285 either  $<1.7 \text{ \AA}$  or  $\sim 1.72 \text{ \AA}$  was used to obtain the best fit (Table 1). The  $1.72 \text{ \AA}$  Tc-O distance is  
286 consistent with  $\text{TcO}_4^-$ .<sup>65</sup> The shorter Tc-O distance is ascribed to a fitting artifact. In some cases,  
287 the shorter Tc-O distance is consistent with the distance of a terminal oxo group of Tc(V),  $1.64$   
288  $\text{ \AA}$ .<sup>66</sup> However, the shorter Tc-O distance varies widely from  $1.51 \text{ \AA}$  to  $1.69 \text{ \AA}$ . This variation is  
289 inconsistent with the presence of a well-defined Tc(V) species for which the same Tc-O distance

290 should be observed in all samples as seen in the samples that contain  $\text{TcO}_4^-$ . Moreover, XANES  
291 analysis, Table 1, does not confirm the presence  $\text{Tc(V)}$  in any of the samples with very short Tc-  
292 O distances. Only two samples contain  $\text{Tc(V)}$  greater than  $3\sigma$  in the XANES analysis:  
293  $\text{Tc}_{0.1}\text{Mn}_{1.1}\text{Fe}_{1.8}\text{O}_4\text{-c}$  and  $\text{Tc}_{0.1}\text{Ni}_{1.1}\text{Fe}_{1.8}\text{O}_4\text{-c}$ , and both have Tc-O bond distances consistent with  
294  $\text{TcO}_4^-$ . In contrast, EXAFS and XANES analysis show better agreement for  $\text{TcO}_4^-$ . In all cases  
295 but one,  $\text{TcO}_4^-$  is found in materials produced by the low Fe(II), coprecipitation route. For most  
296 samples produced by the oxidation route, the only significant oxidation state is  $\text{Tc(IV)}$ ,  
297 presumably due to the large excess of Fe(II) used in these syntheses. Based on the XANES  
298 analyses, the main oxidation state of Tc in all samples is  $\text{Tc(IV)}$  although some contain  $\text{TcO}_4^-$ .  
299



300  
301 **Figure 3.** XANES standard spectra (left) and deconvoluted XANES fit for  $\text{Tc}_{0.1}\text{Co}_{1.1}\text{Fe}_{1.8}\text{O}_4\text{-c}$   
302 (right).  
303



304 **Table 1:** Tc oxidation state distribution from EXAFS and XANES analyses

Sample <sup>a</sup>	Tc-O (Å) (EXAFS)	# short Tc-O <sup>b</sup> (EXAFS)	TcO <sub>4</sub> <sup>-c</sup> (EXAFS)	Tc(IV) (XANES)	Tc(V) <sup>d</sup> (XANES)	TcO <sub>4</sub> <sup>-</sup> (XANES)
Tc <sub>0.1</sub> Mn <sub>1.1</sub> Fe <sub>1.8</sub> O <sub>4-o</sub>	1.59(1)	0.28(8)	--	1.0(1)	0.0(2)	0.00(6)
Tc <sub>0.1</sub> Co <sub>1.1</sub> Fe <sub>1.8</sub> O <sub>4-o</sub>	1.54(3)	0.3(1)	--	1.0(1)	0.0(2)	0.00(6)
Tc <sub>0.1</sub> Ni <sub>1.1</sub> Fe <sub>1.8</sub> O <sub>4-o</sub>	1.79(3)	--	0.10(2)	0.96(8)	0.0(1)	0.04(4)
Tc <sub>0.1</sub> Mg <sub>0.2</sub> Fe <sub>2.7</sub> O <sub>4-o</sub>	1.54(2)	0.29(9)	--	1.00(9)	0.0(1)	0.00(4)
Tc <sub>0.1</sub> Mn <sub>0.2</sub> Fe <sub>2.7</sub> O <sub>4-o</sub>	1.51(1)	0.38(9)	--	0.93(5)	0.00(8)	0.07(3)
Tc <sub>0.1</sub> Fe <sub>2.9</sub> O <sub>4-o</sub>	1.61(2)	0.20(8)	--	1 <sup>e</sup>		
Tc <sub>0.1</sub> Co <sub>0.2</sub> Fe <sub>2.7</sub> O <sub>4-o</sub>	1.66(2)	0.4(1)	--	0.9(1)	0.0(2)	0.10(6)
Tc <sub>0.1</sub> Ni <sub>0.2</sub> Fe <sub>2.7</sub> O <sub>4-o</sub>	1.57(1)	0.31(8)	--	1.00(6)	0.0(1)	0.00(3)
Tc <sub>0.1</sub> Mn <sub>1.1</sub> Fe <sub>1.8</sub> O <sub>4-c</sub>	1.72(1)	--	0.10(2)	0.62(9)	0.4(1)	0.01(5)
Tc <sub>0.1</sub> Co <sub>1.1</sub> Fe <sub>1.8</sub> O <sub>4-c</sub>	1.718(5)	--	0.21(2)	0.75(5)	0.00(7)	0.25(3)
Tc <sub>0.1</sub> Ni <sub>1.1</sub> Fe <sub>1.8</sub> O <sub>4-c</sub>	1.726(6)		0.30(2)	0.54(3)	0.24(5)	0.22(2)
Tc <sub>0.1</sub> Mg <sub>0.2</sub> Fe <sub>2.7</sub> O <sub>4-c</sub>	1.671(6)	0.33(8)	--	0.84(3)	0.11(4)	0.06(1)
Tc <sub>0.1</sub> Mn <sub>0.2</sub> Fe <sub>2.7</sub> O <sub>4-c</sub>	1.715(7)		0.18(2)	0.80(3)	0.04(4)	0.16(2)
Tc <sub>0.1</sub> Fe <sub>2.9</sub> O <sub>4-c</sub>	1.63(1)	0.29(6)	--	0.89(3)	0.09(5)	0.03(2)
Tc <sub>0.1</sub> Co <sub>0.2</sub> Fe <sub>2.7</sub> O <sub>4-c</sub>	1.716(9)		0.19(2)	0.82(3)	0.01(4)	0.17(1)
Tc <sub>0.1</sub> Ni <sub>0.2</sub> Fe <sub>2.7</sub> O <sub>4-c</sub>	1.720(8)		0.15(2)	0.82(2)	0.00(3)	0.18(1)

- 305 a) Samples with an “o” suffix were prepared by oxidation; “c” by coprecipitation  
306 b) Coordination number of the O neighbors with a Tc-O distance <1.7 Å.  
307 c) Fraction of TcO<sub>4</sub><sup>-</sup> is ¼ of the number of O neighbors with a Tc-O distance between 1.7  
308 and 1.8 Å.  
309 d) Relative to sample Tc<sub>0.1</sub>Fe<sub>2.9</sub>O<sub>4-o</sub>.  
310 e) The XANES spectrum of this sample is the Tc(IV) standard.  
311

312

313

**Table 2.** Local environment of Tc in spinel ferrites from EXAFS<sup>a,b</sup>

Sample <sup>a</sup>	6 O (Å)	$\sigma^2$ (Å <sup>2</sup> )	6 M <sub>O</sub> (Å) <sup>c</sup>	# of Tc <sup>d</sup>	$\sigma^2$ (Å <sup>2</sup> )	6 M <sub>T</sub> (Å) <sup>e</sup>	$\sigma^2$ (Å <sup>2</sup> )	12 M <sub>O</sub> (Å) <sup>b</sup>
M <sub>O</sub> site in Fe <sub>3</sub> O <sub>4</sub>	2.06	--	2.97	--	--	3.48	--	5.15
M <sub>O</sub> site in TiFe <sub>2</sub> O <sub>4</sub> <sup>45</sup>	2.09	--	3.02	--	--	3.54	--	5.22
High M(II), High Fe(II)								
Tc <sub>0.1</sub> Mn <sub>1.1</sub> Fe <sub>1.8</sub> O <sub>4-o</sub>	2.025(3)	0.004	3.087(7)	2.0(1)	0.004	3.565(8)	0.013	5.27(2)
Tc <sub>0.1</sub> Co <sub>1.1</sub> Fe <sub>1.8</sub> O <sub>4-o</sub>	2.009(4)	0.003	3.035(5)	0 <sup>f</sup>	0.006	3.517(7)	0.006	5.19(1)
Tc <sub>0.1</sub> Ni <sub>1.1</sub> Fe <sub>1.8</sub> O <sub>4-o</sub>	2.009(4)	0.003	3.034(6)	1.2(5)	0.003	3.514(7)	0.007	5.19(1)
Low M(II), High Fe(II)								
Tc <sub>0.1</sub> Mg <sub>0.2</sub> Fe <sub>2.7</sub> O <sub>4-o</sub>	2.034(4)	0.003	3.096(9)	1.9(2)	0.004	3.537(7)	0.007	5.22(2)
Tc <sub>0.1</sub> Mn <sub>0.2</sub> Fe <sub>2.7</sub> O <sub>4-o</sub>	2.036(4)	0.004	3.100(8)	2.20(8)	0.002	3.53(1)	0.010	5.25(2)
Tc <sub>0.1</sub> Fe <sub>2.9</sub> O <sub>4-o</sub>	2.027(3)	0.004	3.090(7)	2.1(1)	0.004	3.524(6)	0.008	5.22(2)
Tc <sub>0.1</sub> Co <sub>0.2</sub> Fe <sub>2.7</sub> O <sub>4-o</sub>	2.026(6)	0.005	3.08(1)	2.2(1)	0.003	3.51(1)	0.008	5.20(2)
Tc <sub>0.1</sub> Ni <sub>0.2</sub> Fe <sub>2.7</sub> O <sub>4-o</sub>	2.030(3)	0.003	3.075(7)	1.9(1)	0.003	3.530(6)	0.007	5.21(1)
High M(II), Low Fe(II)								
Tc <sub>0.1</sub> Mn <sub>1.1</sub> Fe <sub>1.8</sub> O <sub>4-c</sub>	2.016(5)	0.004	3.083(1)	2.0(2)	0.003	3.550(3)	0.015	5.26(4)
Tc <sub>0.1</sub> Co <sub>1.1</sub> Fe <sub>1.8</sub> O <sub>4-c</sub>	2.027(5)	0.004	3.069(8)	2.07(8)	0.001	3.54(1)	0.011	5.23(2)
Tc <sub>0.1</sub> Ni <sub>1.1</sub> Fe <sub>1.8</sub> O <sub>4-c</sub>	2.027(8)	0.006	3.10(2)	2.3(2)	0.005	3.50(3)	0.018	f
Low M(II), Low Fe(II)								
Tc <sub>0.1</sub> Mg <sub>0.2</sub> Fe <sub>2.7</sub> O <sub>4-c</sub>	2.027(8)	0.005	3.10(2)	2.27(8)	0.003	3.51(3)	0.012	5.23(1)
Tc <sub>0.1</sub> Mn <sub>0.2</sub> Fe <sub>2.7</sub> O <sub>4-c</sub>	2.019(4)	0.005	3.083(7)	2.10(8)	0.003	3.509(9)	0.012	5.23(2)
Tc <sub>0.1</sub> Fe <sub>2.9</sub> O <sub>4-c</sub>	2.020(3)	0.005	3.086(6)	2.17(6)	0.002	3.511(8)	0.011	5.23(2)
Tc <sub>0.1</sub> Co <sub>0.2</sub> Fe <sub>2.7</sub> O <sub>4-c</sub>	2.020(5)	0.005	3.077(9)	2.16(9)	0.003	3.51(1)	0.011	5.22(2)
Tc <sub>0.1</sub> Ni <sub>0.2</sub> Fe <sub>2.7</sub> O <sub>4-c</sub>	2.019(5)	0.005	3.074(9)	1.93(4)	0.004	3.509(9)	0.011	5.21(2)

315

a)

316

b) Standard deviations are given in parentheses in the same units as the last digit

317

c) M<sub>O</sub>: octahedral sites

318

d) # of nearest octahedral neighbor that are Tc rather than Fe, Mg, Mn, Co, Ni

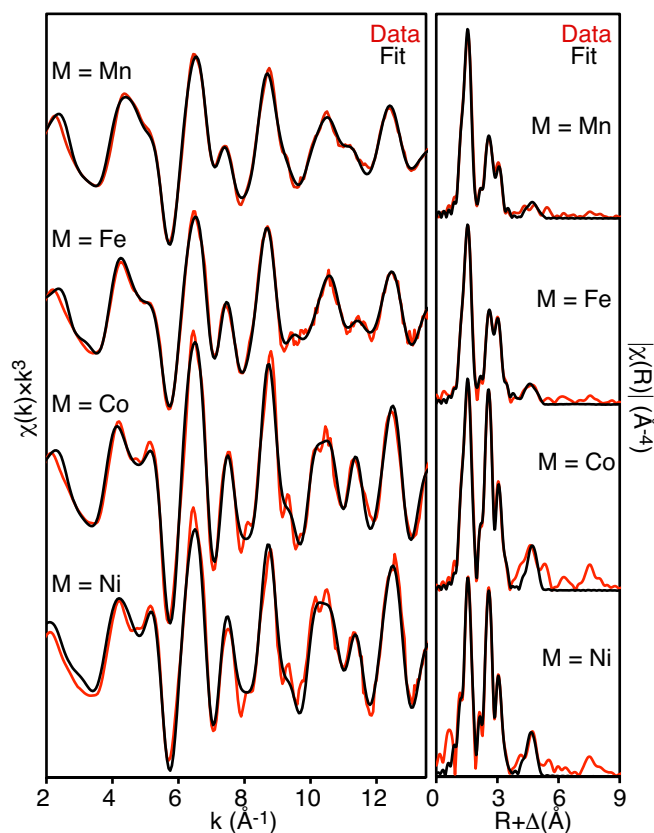
319

e) M<sub>T</sub>: tetrahedral sites

320

f) Inclusion of this set of atoms did not improve the fit.

321



322

323 **Figure 4.** Tc K-edge EXAFS spectra of  $\text{Tc}_{0.1}\text{M}_{1.1}\text{Fe}_{1.8}\text{O}_{4-o}$  (left) and Fourier transforms (right).

324 Data are shown in color and EXAFS fits are shown in black. The spectra of  $\text{Tc}_{0.1}\text{M}_{0.2}\text{Fe}_{2.7}\text{O}_4$  are  
 325 similar to that labeled M = Fe.

326

327 The EXAFS results, Table 2, are consistent with the bulk of Tc in the sample existing as Tc(IV)  
 328 occupying the octahedral spinel site ( $M_O$ ) site as previously seen for Tc-doped magnetite.<sup>27,31</sup>

329 The local environment of Tc is more similar to the  $M_O$  site of ulvöspinel ( $\text{TiFe}_2\text{O}_4$ ) than that of  
 330  $\text{Fe}_3\text{O}_4$  as shown in Table 2. The oxygen neighbors at 2.0 Å are characteristic for Tc(IV)  
 331 octahedrally coordinated by oxygen.<sup>67</sup> The Tc and Fe atoms at 3.1 Å are consistent with the six,  
 332 edge-sharing  $M_O$  neighbors at 3.02 Å in  $\text{TiFe}_2\text{O}_4$ . The six Fe atoms at 3.5 Å are in agreement  
 333 with the six, corner-sharing  $M_T$  neighbors at 3.53 Å in  $\text{TiFe}_2\text{O}_4$ . Scattering from more distant  
 334 iron  $M_O$  sites at 5.2 Å was observed in most cases, which is consistent with the next-nearest

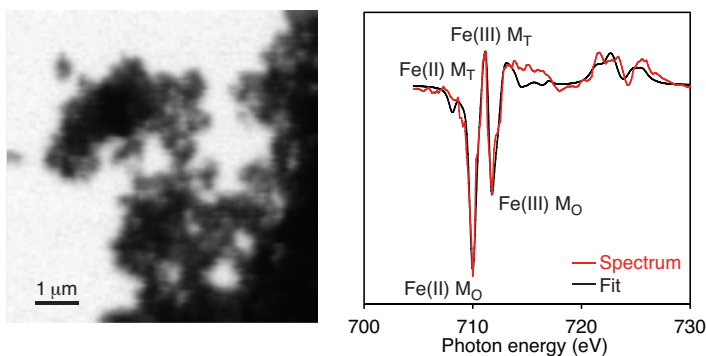
335 neighbor  $M_O$  sites at 5.22 Å in  $TiFe_2O_4$ . In some samples, scattering from more distant atoms can  
336 be observed at  $\sim 8$  Å in the Fourier transformed spectra, which presumably corresponds to 42 Fe  
337 neighbors that are 7.9 and 8.2 Å from  $M_O$ . The presence of Fe and/or Tc neighbors<sup>27</sup> at 3.1 Å, 3.5  
338 Å, and 5.2 Å is sufficient to show that the bulk of the Tc is doped into the  $M_O$  site. This result is  
339 consistent with previous EXAFS studies of magnetite doped with Sn(IV) or Ti(IV) and to the  
340 previously mentioned results for Tc(IV) doped magnetite.<sup>62,68,69</sup>

341  
342 The most surprising result is that Tc is strongly clustered, which was not previously observed,  
343 presumably because the Tc/Fe ratio was much lower in those studies. At the doping level used  
344 here, each Tc would have 0.3 Tc neighbors if Tc were homogeneously distributed. Instead, each  
345 Tc has  $\sim 2$  Tc neighbors. The local environment of Tc again resembles that of Ti in  $TiFe_2O_4$   
346 where each Ti has 3 Ti(IV)  $M_O$  neighbors, and the remaining  $M_O$  and  $M_T$  sites are occupied by  
347 Fe(II). The level of Tc clustering in the Tc-doped spinel ferrites implies that the  $M_O$  sites  
348 surrounding each Tc site contain approximately two Tc(IV) and four M(II) and that the  
349 neighboring  $M_T$  sites contain approximately three Fe(III) and three M(II).

350  
351 The distances determined by EXAFS are slightly different from those determined by  
352 crystallography because EXAFS measures the local structure of Tc while XRD measures the  
353 average structure. The 2.02 Å Tc-O distance is shorter than  $M_O$ -O distance in  $TiFe_2O_4$ , which  
354 includes both Ti(IV)-O and Fe(II)-O distances. Using the ionic radius of four coordinate  $O^{2-}$   
355 (1.24 Å),<sup>21</sup> the Tc-O distance is predicted to be 2.025 Å. In  $TiFe_2O_4$ , the average radius of  $M_O$  is  
356 0.832 Å, and the predicted  $M_O$ -O distance is 2.07 Å. The longer Tc- $M_O$  distance relative to  
357  $TiFe_2O_4$  largely results from Tc clustering. Each Tc has  $\sim 2$  Tc neighbors and  $\sim 4$  M(II) neighbors.

358 In  $\text{Tc}_{0.1}\text{Fe}_{2.9}\text{O}_{4-o}$ , the average ionic radius of the  $\text{M}_\text{O}$  neighbors of Tc is 0.875 Å, about 0.04 Å  
359 larger than in  $\text{TiFe}_2\text{O}_4$ , so the Tc- $\text{M}_\text{O}$  distance determined by EXAFS should be longer than that  
360 determined by diffraction.

361  
362 **Fe L-edge XMCD spectroscopy.**  $\text{Tc}_{0.1}\text{Fe}_{2.9}\text{O}_{4-o}$  was studied using XMCD at the Fe  $\text{L}_{2,3}$ -edge in  
363 an attempt to determine the distribution of Fe(II) and Fe(III) on the octahedral and tetrahedral  
364 sites. This technique has been widely used to study substituted magnetites including  
365 titanomagnetites.<sup>50,51,68</sup> The normal contrast X-ray image and the XMCD spectrum are shown in  
366 Figure 5. The cation distribution from the fit, normalized for 2.9 Fe and an  $\text{M}_\text{T}$  occupancy of 1,  
367 shows that the  $\text{M}_\text{O}$  sites contain 0.7 Fe(III) and 1.2 Fe(II) and  $\text{M}_\text{T}$  contains 1 Fe(III). This  
368 occupancy is similar to that predicted if the charge is balanced by diamagnetic substitution ( $\text{M}_\text{O}$   
369 sites contain 0.1 Tc(IV), 0.8 Fe(III) and 1.1 Fe(II), and  $\text{M}_\text{T}$  sites contain 1 Fe(III)). The XMCD  
370 results suggest a Fe(II)/ $\Sigma\text{Fe}$  ratio of 0.4, which is somewhat larger than measured  
371 colorimetrically, 0.21(1).



372  
 373 **Figure 5.** Normal contrast X-ray micrograph (STXM, left) of  $\text{Tc}_{0.1}\text{Fe}_{2.9}\text{O}_{4-o}$  illustrating the small  
 374 particle size. X-ray magnetic circular dichroism spectrum (XMCD, right) of  $\text{Tc}_{0.1}\text{Fe}_{2.9}\text{O}_{4-o}$   
 375 obtained at the Fe  $L_{2,3}$ -edge. The XMCD spectrum is the difference between absorption of right  
 376 and left circularly polarized X-rays when the sample is in a magnetic field.

377  
 378 The Tc-doped spinel ferrites consist of Tc-rich regions and Tc-poor regions. This behavior  
 379 closely mirrors that of titanomagnetite where Ti(IV) mainly replaces Fe(III) on  $M_O$ , and the  
 380 charge is balanced by divalent substitution. Ti(IV) is homogeneously distributed above 600 °C.<sup>70</sup>  
 381 At lower temperatures, titanomagnetite undergoes spinodal decomposition forming titanium-  
 382 poor regions that resemble magnetite and titanium-rich regions that resemble ulvöspinel.<sup>70</sup>  
 383 Recent work by Lilova, et al. shows that the enthalpy of mixing for the ulvöspinel/magnetite  
 384 system is positive, consistent with the observed spinodal decomposition.<sup>71</sup> The behavior of the  
 385 Tc-doped spinel ferrites appears to be similar, and may explain why the local structure of Tc(IV)  
 386 more closely resembles ulvöspinel than magnetite.

387  
 388 **Implications for durability of Tc-doped spinels.** The spinel ferrites in this study are effective  
 389 at stabilizing Tc(IV) in the solid state and preventing its oxidation to  $\text{TcO}_4^-$ . Only the initial step  
 390 of the synthesis was performed under inert atmosphere. All subsequent operations, including

391 washing, storage, and spectroscopic studies, were performed in air. Nevertheless, Tc remained in  
392 the reduced state. While the ability to stabilize Tc(IV) is necessary for these materials to be  
393 effective waste forms for <sup>99</sup>Tc, the spinel ferrite matrix also must be sufficiently durable towards  
394 dissolution or alteration.

395  
396 The main concern, therefore, is the durability of the Tc-doped spinel ferrites. As prepared herein,  
397 these materials are nanoparticles with high specific surface areas. In addition, the materials  
398 contain Fe(II), which may adversely affect their durability. The effect of Fe(II) on durability is  
399 best illustrated by magnetite and titanomagnetite. In aerobic environments, these materials are  
400 oxidized to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (maghemite) and titanomaghemite, respectively.<sup>69,72</sup> This transformation is  
401 topotactic and unlikely to release doped Tc, as observed by Marshall et al.<sup>31</sup> While somewhat  
402 durable, maghemite is unstable with respect to transformation to hematite or goethite. This  
403 transformation is not topotactic and could lead to the loss of Tc to the environment. Work by  
404 Um, et al. suggest that Tc(IV) can still be trapped in goethite during the oxidation of magnetite.<sup>28,29</sup>  
405 As in magnetite, the Fe(III) site in goethite is octahedral, and Tc(IV) can replace Fe(III) provided  
406 that the charge mismatch is balanced. Ultimately, the best approach for determining how well  
407 these materials immobilize <sup>99</sup>Tc is measuring the release of <sup>99</sup>Tc when these materials are re-  
408 suspended in water.

409  
410

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425

426 **Supplemental Information.** XANES spectra, larger diffraction patterns, larger EXAFS spectra  
427 and detailed fitting results, and combined analytical data are given in the SI.

428

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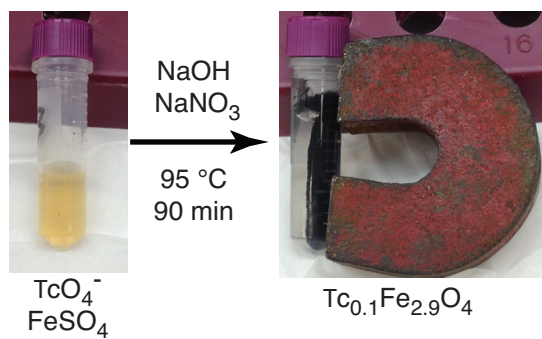
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611 TOC Figure:

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