Systematic XAS study on the reduction and uptake of Tc by magnetite and mackinawite†

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The mechanisms for the reduction and uptake of Tc by magnetite (Fe3O4) and mackinawite (FeS) are investigated using X-ray absorption spectroscopy (XANES and EXAFS), in combination with thermodynamic calculations of the Tc/Fe systems and accurate characterization of the solution properties (pHm, pe, [Tc]). Batch sorption experiments were performed under strictly anoxic conditions using freshly prepared magnetite and mackinawite in 0.1 M NaCl solutions with varying initial Tc(υ) concentrations (2 × 10⁻⁵ and 2 × 10⁻⁴ M) and Tc loadings (400–900 ppm). XANES confirms the complete reduction of Tc(υ) to Tc(ν) in all investigated systems, as predicted from experimental (pHm + pe) measurements and thermodynamic calculations. Two Tc endmember species are identified by EXAFS in the magnetite system, Tc substituting for Fe in the magnetite structure and Tc−Tc dimers sorbed to the magnetite (III) faces through a triple bond. The sorption endmember is favoured at higher [Tc], whereas incorporation prevails at low [Tc] and less alkaline pH conditions. The key role of pH in the uptake mechanism is interpreted in terms of magnetite solubility, with higher [Fe] and greater recrystallization rates occurring at lower pH values. A TcS₄-like phase is predominant in all investigated mackinawite systems, although the contribution of up to 20% of TcO₂·H₂O(s) (likely as surface precipitate) is observed for the highest investigated loadings (900 ppm). These results provide key inputs for an accurate mechanistic interpretation of the Tc uptake by magnetite and mackinawite, so far controversially discussed in the literature, and represent a highly relevant contribution to the investigation of Tc retention processes in the context of nuclear waste disposal.

Introduction

Technetium-99 is a β-emitting fission product highly relevant in the safety assessment of repositories for radioactive waste disposal due to its significant inventory in spent nuclear fuel, long half-life (t₁/₂ > 2.1 × 10⁷ a) and redox-sensitive chemical behaviour. Although several oxidation states of Tc are reported in the literature (from 0 to +VII),¹⁻⁵ Tc(ν) and Tc(υ) are the prevailing redox states in the absence of any complexing ligand other than water under non reducing and reducing conditions, respectively. Tc(υ) is the most stable oxidation state of Tc in suboxic/oxidising environments, it is found as the highly mobile TcO₄²⁻ anion over the entire pH range and shows very high solubility and weak sorption properties.³⁻⁵ Under reducing conditions, Tc(ν) forms sparingly soluble hydrous oxides TcO₂·xH₂O(s) and is strongly sorbed onto mineral surfaces.⁶⁻¹³ Because of the large differences in the aquatic chemistry of Tc(υ) and Tc(ν), an accurate knowledge of Tc redox chemistry is necessary for an appropriate assessment of Tc retention/mobilization processes under repository-relevant conditions.

As for other redox-sensitive radionuclides, Fe(ν) solid phases play a relevant role in the (geo)chemistry of Tc, often involving a combination of reduction and uptake processes. Indeed, the release of Fe(ν) through the anoxic corrosion of metallic iron/steel canisters and the corresponding formation of Fe(ν) minerals play a very important role in defining the redox boundary conditions of deep underground repositories for the disposal of radioactive waste, whilst having also a great impact on the uptake of radionuclides. Magnetite (Fe₃O₄) and mackinawite (FeS) are corrosion products of Fe expected to form under repository-relevant conditions. Magnetite is the most relevant Fe(ν)–Fe(υ) mixed oxide and shows a very large stability field ranging from near-neutral to hyperalkaline pH conditions. In spite of this, relevant uncertainties still exist for the thermodynamic data available for this compound, mainly resulting from kinetically controlled solubility behaviour at T = 25 °C and with regard to crystallinity and particle size. Mackinawite is an Fe(ν)–sulphide phase found in certain types¹⁴,¹⁵ of clay formations (e.g. Callovo Oxfordian) and

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forming in sulphide-rich reducing groundwaters. It occurs naturally as Fe$_{1+x}$S due to the non-stoichiometric contribution of Ni or Cu (among other) impurities, although it is readily produced as stoichiometric FeS under laboratory conditions.

The role of Fe-containing minerals in the reduction of Tc(IV) has been intensively investigated over the last decades. Cui et al. (1996a, b) studied the reduction of Tc(IV) by Fe(II) and the uptake of Tc by magnetite in the presence of synthetic ground water. The authors assessed the effect of ionic strength and pH (7.8–9.5), investigated the rate of the sorption reaction, and concluded that the uptake was controlled by a ligand exchange mechanism with a very strong pH-dependency. A number of studies were also dedicated to the intercalation of Tc(IV) with a very strong pH-dependency and concluded that the uptake was controlled by an intercalation mechanism with a very strong pH-dependency.

A number of studies were also dedicated to the intercalation of Tc(IV) with Fe-bearing sediments (Wildung et al. (2004), Burke et al. (2005), Burke et al. (2006), McBeth et al. (2007), Morris et al. (2008), Burke et al. (2010), Peretyazhko et al. (2012)). All these studies reported the precipitation of TcO$_2$-OH$_2$O(s) as main mechanism for the immobilization of Tc. Geraedts et al. (2002, 2008) and Maes et al. (2004) studied the system magnetite-Tc in the presence of natural and synthetic Gorleben groundwater. The authors reported the predominance of TcO$_2$ solid phases in synthetic cement leachates under alkaline pH conditions. Marshall et al. (2014) investigated the sorption and incorporation of Tc on magnetite in the presence of Fe(II) (magnetite, mackinawite) and siderite (Fe(III) (goethite and hematite)) and Fe(III) (Fe(II) minerals). The authors reported the predominance of TcO$_2$ solid phases in the sorption samples. The relevant contribution of Tc-Fe bonds confirmed by EXAFS hinted towards the sorption of Tc chains on the surface of magnetite, possibly in combination with a partial incorporation in the structure of magnetite. On the contrary, the very large Fe–Co coordination numbers observed in the coprecipitation samples suggested that incorporation of Tc(IV) into the magnetite structure was the main retention mechanism in this case. In our recent study on the redox behaviour of Tc in the presence of different reducing systems, complete and fast reduction of Tc(IV) to Tc(II) was observed in the presence of magnetite, mackinawite and siderite in highly saline systems (5.0 M NaCl and 4.5 M MgCl$_2$). XANES analysis of these samples suggested O-coordination in the first shell of all investigated samples. Recently, Smith et al. (2016) performed quantum chemical calculations to assess the charge-compensation mechanism governing Tc(IV) incorporation in the structure of magnetite. The authors reported that incorporation of Tc(IV) by removing two octahedral Fe(II) ions is energetically favoured. Wharton et al. (2000) studied the coprecipitation of Tc(IV) and Tc(II) with mackinawite and characterized the resulting solid phases by X-ray absorption spectroscopy. Tc was immobilized as a Tc$^{IV}$S$_2$ like phase regardless of the initial oxidation state of Tc.

In spite of the number of publications dedicated to the study of Tc uptake by magnetite and mackinawite, significant contradictions arise in the retention mechanisms proposed in the literature. The lack of extensive studies with systematic variation of key parameters such as [Tc], solid-to-liquid ratio (S : L) or loading importantly hinders a correct and complete evaluation of these mechanism. These uncertainties are tackled in the present work with a combination of classical wet-chemistry methods, thermodynamic calculations (involving Tc/Fe) and advanced spectroscopic techniques.

**Experimental**

**Chemicals**

All the experiments and sample preparation were performed in an Ar-glovebox at $T = 22 \pm 2 \, ^\circ\mathrm{C}$. All solutions were prepared with purified water (Milli-Q academic, Millipore) and purged with Ar before use to remove traces of oxygen. A purified and radiochemically well-characterized $^{99m}$Tc stock solution (1.3 M NaTcO$_4$) was used for the experiments after dilution to 20 mM with Milli-Q water. NaCl (p.a.) and Na$_2$S were obtained from Merck; FeCl$_3$$\cdot$6H$_2$O, Fe(NH$_4$)$_2$(SO$_4$)$_2$$\cdot$6H$_2$O and NH$_4$OH were obtained from Sigma-Aldrich, and FeCl$_3$ from Alfa Aesar.

**Fe minerals**

Magnetite and mackinawite were synthesized following the well-established methods reported in ref. 29–32 (experimental description summarized in Table S1 in the ESI†). Both solid phases were equilibrated for 4 weeks in the original synthesis solution, washed three times with the corresponding background electrolyte (0.1 M NaCl) and equilibrated in this solution for 3 weeks. The resulting solids were characterized by powder X-ray diffraction (D8 ADVANCE, Bruker) before and after washing with the respective background electrolyte solutions to confirm that solids remained the same during the equilibration. XRD measurements were performed at $10^\circ \leq 2\theta \leq 78^\circ$ with incremental steps of 0.015$^\circ$ and a measurement time of 1.7 seconds per step. The XRD patterns of the Fe phases synthesized in this work are shown in Fig. S1 in the
Sample preparation

The uptake of Tc by magnetite and mackinawite suspensions was investigated as a function of the initial TcO$_4^-$ concentration (2 × 10$^{-4}$ M and 2 × 10$^{-5}$ M) and Tc loading on Fe minerals (400 ppm, 600 ppm and 900 ppm, obtained by decreasing solid-to-liquid ratios). Experimental conditions used in the sample preparation are summarized in Table 1. After the addition of Tc, samples were equilibrated under Ar atmosphere for 6 weeks and pH$_m$, $E_h$ and [Tc] (after 10 kDa ultrafiltration) were measured. Magnetite and mackinawite samples with the highest amount of Tc ([TcO$_4^-$])$_b = 2 × 10^{-4}$ M and 900 ppm loading) (~0.5 mg each) were analysed by SEM to assess the morphology of the Fe phases responsible for the retention of Tc.

TeO$_2$·xH$_2$O used as reference material in the fitting procedure was prepared by acidifying a pertechnetate solution with concentrated HCl, then adding Zn to generate nascent hydrogen. After the reaction was completed, 20 M NaOH solution as added to obtain a black precipitate, which was aged for one week.

XANES/EXAFS measurements

| Fe minerals | Background electrolyte | [TcO$_4^-$]$_b$ [M] | Solid/liquid ratio (g L$^{-1}$) | Loading (ppm) | Loading' (μmol m$^{-2}$) |
|-------------|------------------------|---------------------|------------------------|--------------|------------------------|
| Mag-0 | 0.1 M NaCl | 2 × 10$^{-5}$ | 5 | 400 | 0.04 |
| Mag-1 | 0.1 M NaCl | 2 × 10$^{-4}$ | 50 | 400 | 0.04 |
| Mag-2 | 0.1 M NaCl | 2 × 10$^{-4}$ | 50 | 400 | 0.04 |
| Mag-3 | 0.1 M NaCl | 2 × 10$^{-4}$ | 50 | 400 | 0.04 |
| Mag-4 | 0.1 M NaCl | 2 × 10$^{-5}$ | 3 | 600 | 0.06 |
| Mag-5 | 0.1 M NaCl | 2 × 10$^{-5}$ | 3 | 600 | 0.06 |
| Mag-6 | 0.1 M NaCl | 2 × 10$^{-5}$ | 3 | 600 | 0.06 |
| Mack-1 | 0.1 M NaCl | 2 × 10$^{-4}$ | 50 | 400 | 0.01 |
| Mack-2 | 0.1 M NaCl | 2 × 10$^{-4}$ | 33 | 600 | 0.02 |
| Mack-3 | 0.1 M NaCl | 2 × 10$^{-4}$ | 22 | 900 | 0.03 |
| Mack-4 | 0.1 M NaCl | 2 × 10$^{-5}$ | 5 | 400 | 0.01 |
| Mack-5 | 0.1 M NaCl | 2 × 10$^{-5}$ | 3 | 600 | 0.02 |
| Mack-6 | 0.1 M NaCl | 2 × 10$^{-5}$ | 2 | 900 | 0.03 |

* Data taken from Kobayashi et al. (2013). b Initial Tc(vii) concentration. c Calculated based on specific surface area of 110 m$^2$ g$^{-1}$ for magnetite and 270 m$^2$ g$^{-1}$ for mackinawite.
Results and discussion

Quantitative evaluation of the wet chemistry data

Table 2 summarizes the experimentally measured $pH_m$, $E_h$, and Tc concentrations in the Fe mineral suspensions after 6 weeks of equilibration time. Experimental $pH_m$ and $E_h$ values are also plotted in the Tc Pourbaix diagram shown in Fig. 1. The figure shows that $E_h$ values measured in magnetite samples are slightly below the thermodynamically calculated Tc(vii)/Tc(iv) redox borderline, whereas significantly lower $E_h$ values are found in the mackinawite system. In both cases, Tc concentrations measured in solution decrease to values below the detection limit of LSC (Liquid Scintillation Counting) within 6 weeks, suggesting that TcO$_4^-$ is completely reduced to Tc(iv) and quantitatively removed from the aqueous phase.

Structural interpretation of Tc uptake: EXAFS/XANES

Magnetite.

Fig. 2a shows the Tc K-edge XANES spectra of Tc sorbed magnetite samples (labelled Mag-1 to 6) along with the spectra of three references, an amorphous TcO$_2$-xH$_2$O(s) representing the tetravalent oxidation state, Tc(iv) structurally incorporated by magnetite (Mag-0)$^{22}$ and the TcO$_4^-$ aquo-complex representing the heptavalent oxidation state of Tc.$^{47}$ The XANES spectra of all magnetite samples show edge positions similar to that of Tc(iv) structurally incorporated by magnetite, confirming the reduction of Tc(vii) to Tc(iv). Note that small contributions of Tc(vii) can be excluded, since both the pre-edge peak of Tc(vii) at about 21.05 keV and the white line at 21.10 keV would be easily discernible when exceeding about 5 atom%. The fine structure of all magnetite samples is also very similar, suggesting a Tc coordination similar to Tc(iv) in magnetite, and different from TcO$_2$-xH$_2$O(s). The $k^3$-weighted EXAFS spectra and the Fourier Transform Magnitudes (FTM) are shown in Fig. 2b and c, respectively. To derive the number of chemically different Tc species in all seven samples based on their short range structure, their EXAFS spectra were inves-

| Table 2 | Experimentally measured pH$_m$, $E_h$, and $|\text{Tc}|_{\text{final}}$ in magnetite (Mag) and mackinawite (Mack) samples after 6 weeks of equilibration time |
|---------|-----------------|-----------------|-----------------|
| Fe mineral | pH$_m$ | $E_h$ (mV) | $|\text{Tc}|_{\text{final}}$ [M] |
| Mag-0$^a$ | 6.00 | -120 | $\leq 1 \times 10^{-9}$d |
| Mag-1 | 9.28 | -149 | $\leq 4 \times 10^{-10}$d |
| Mag-2 | 9.16 | -146 | $\leq 4 \times 10^{-10}$d |
| Mag-3 | 9.08 | -139 | $\leq 4 \times 10^{-10}$d |
| Mag-4 | 9.12 | -138 | $\leq 4 \times 10^{-10}$d |
| Mag-5 | 8.90 | -121 | $\leq 4 \times 10^{-10}$d |
| Mag-6 | 8.68 | -109 | $\leq 4 \times 10^{-10}$d |
| Mack-1 | 9.07 | -315 | $\leq 4 \times 10^{-10}$d |
| Mack-2 | 9.16 | -381 | $\leq 4 \times 10^{-10}$d |
| Mack-3 | 8.99 | -309 | $\leq 4 \times 10^{-10}$d |
| Mack-4 | 9.02 | -289 | $\leq 4 \times 10^{-10}$d |
| Mack-5 | 8.91 | -280 | $\leq 4 \times 10^{-10}$d |
| Mack-6 | 8.83 | -271 | $\leq 4 \times 10^{-10}$d |

$^{a}$ ±0.05, $^{b}$ ±50 mV. $^c$ Data taken from Kobayashi et al. (2013).$^{22}$
$^d$ Detection limits.
tigated by principal component analysis using the ITFA software package (version 1.3.12). The Malinowski indicator as well as the good reconstruction of the experimental EXAFS spectra with 2 principal components (red lines in Fig. 2b and c) suggest that two structurally different Tc species are present in the magnetite samples. Based on the VARIMAX loadings, magnetite species 1 prevails in sample Mag-0, i.e. the structurally incorporated Tc, while magnetite species 2 prevails in sample Mag-5.

Assuming that the spectra of samples Mag-0 and -5 represent the pure endmember species, we are able to extract the noise-filtered endmember spectra of magnetite species 1 and 2 and determine their structure by shell fitting (Table 3) and to determine at the same time the relative proportions of the two species in the other samples by iterative target test (ITTT) (Table 4).

Subsequent shell fits are shown in Fig. S3 in the ESI.† The spectrum of magnetite species 1 could be fitted as expected by the magnetite model, with Tc(IV) residing in the 16d position of the Fd3m cubic space group. Tc is hence coordinated to 6 oxygen atoms forming the corners of a TcO6 octahedron, which is then linked to 6 neighbouring FeO6 octahedra by sharing edges (shorter Tc–Fe distance of 3.08 Å), and to 6 next-neighbouring FeO6 tetrahedra sharing corners (longer Tc–Fe distance of 3.49 Å). A fit with floating CNs resulted in the same interatomic distances, CNs which deviated by less than 15% from the crystallographic values, hence within the typical error range, and only slightly better fit statistics (%R reduced from 6.1 to 5.3). Hence the spectrum of magnetite species 1 is fully in line with Tc(IV) residing in the 16d position of the cubic magnetite structure, i.e. substituting for octahedral Fe, in line with previous work. Note that the Tc–O distance is 2% smaller than the Fe–O distance in magnetite (2.01 vs. 2.05 Å), in line with the ionic radius of Tc(IV) being smaller than that of Fe with an average oxidation state of 2.5. In contrast, the shorter Tc–Fe distance is about 4% longer than the corresponding Fe–Fe distance in magnetite (3.08 vs. 2.97 Å), while the longer Tc–Fe distance is almost identical (3.49 vs. 3.48 Å). The similarity with the fit data by Um et al. suggests that these authors might have also observed Tc incorporation into magnetite rather than into goethite.

In the FTM spectrum of magnetite species 2, most purely expressed in samples Mag-4 to -6, we observe a peak triplet from 2.0 to 3.3 Å (Fig. 2c). To elucidate the elemental identity of backscattering atoms in this region, we applied Morlet wavelet analysis. The two peaks at shorter distance did not resolve in the wavelet plots, but the intensity of this unresolved wavelet peak increased up to the maximum k-range of 12.5 Å⁻¹, in line with backscattering atoms significantly heavier than Fe. With the known elemental composition of our system, this double peak hence can arise only from Tc–Tc backscattering. In contrast, the third peak at 3.0 Å showed a maximum at about 7.5 Å⁻¹, in line with backscattering by Fe. Fitting this region with only two shells was, however, not sufficient: in addition to a short Tc–Tc and a long Tc–Fe2 path, also a shorter Tc–Fe1 path was required to obtain a satisfying fit, while a second Tc–Tc path corresponding to the structure of TcO2·xH2O could not be fitted (Table 3). The CN of 0.8 and the distance of 2.57 Å for the Tc–Tc path suggest formation of a Tc–Tc dimer linked through the typical short, quasi-metallic bond. The two Tc–Fe distances are with 3.13 and 3.54 Å similar to the ones of structural Tc in magnetite, albeit slightly longer. Furthermore, the CN are roughly half of what would be expected for structural incorporation. The most consistent structural model based on these fit data is that of a Tc–Tc dimer, which forms on one side of the chain a tridentate sorption complex with the magnetite {111} faces, similar to that observed for trivalent Pu, As or Sb. One could argue also, that the observed structure is not that of a limiting species, but represents rather a mixture of Tc-doped magnetite on one hand, and a Tc oxide species on the other hand. TcO2·xH2O(s) as limiting species can be excluded, however, since principal component analysis of its spectrum together with those of the magnetite samples increased the number of statistically significant components from 2 to 3. Crystalline...
TcO$_2$ can also be excluded as limiting species, since this compound has long Tc–Tc distances at 3.6–3.7 Å arising from corner-sharing linkages between the chains, which are absent in our magnetite spectra. Therefore, we maintain that the most likely structural explanation for magnetite species-2 is a Tc–Tc dimer triple-bonding to the magnetite {111} faces. This species bounds in edge-sharing bidentate mode to the ferrihydrite surface$^6$ and to titanomagnetite,$^5$ with one significant difference: while Zachara et al. obtained 2.57 Å for both the Tc–Tc and of the shorter Tc–Fe1 paths, and Liu et al. obtained 2.56 Å for Tc–Tc and 2.59 Å for Tc–Fe1, such a fitting scheme was not successful in our case, and we obtained instead much longer 3.12 Å for the shorter Tc–Fe1 path (in contrast, the distance of the longer Tc–Fe2 path is again similar, 3.50 Å [ref. 6] vs. 3.52 Å). This difference is not only arising from a potentially different fitting approach, but is also reflected by differences in the chi- and FTM spectra. The reason for this difference is, however, not evident.

In our magnetite series, the contribution of structural Tc(IV) increases from 1/3 to 1/2 for samples Mag-1 to -3, i.e. increases with Tc loading for the samples prepared with the lower initial TcO$_4^{2-}$ concentration of 2 × 10$^{-5}$ M, while the contribution of the sorption complex decreases correspondingly. In the samples Mag-4 to -6 with the higher TcO$_4^{2-}$ concentrations, the sorption complex prevails. Our hypothesis is that the amount of Tc–Tc dimers increases at the given pH of ~9 with initial Tc concentration, thereby competing with the sorption of monomers or their structural incorporation. In principle, these dimers may form either in solution or at the magnetite surface. However, reduction of Tc(VII) to Tc(IV) by Fe(II) in solution is unlikely and known as kinetically hindered process.$^{17}$ Therefore, dimer formation should proceed prevalently at the (semiconducting to conducting) magnetite surface. This, however, seems to be in contradiction to the increase of structural Tc with increasing Tc surface loading as observed for samples Mag-1 to -3.

As discussed in the introduction, both complete incorporation of Tc into the magnetite structure and formation of TcO$_2$-like dimers/polymers on the surface were reported by different authors.$^6,7,21,22,55$ However, none of the available studies has systematically investigated the effect of initial Tc concentration and solid to liquid ratio (or loading) as accomplished in the present work, but rather focussed on a given [Tc] and loading. Kobayashi and co-workers$^{22}$ conducted Tc uptake experiments with magnetite under analogous [Tc]$_0$ and loading (2 × 10$^{-5}$ M and 400 ppm, respectively), but significantly lower pH values (6–7.5). The authors observed the complete incorporation of Tc(IV) in the structure of magnetite. The differences in the prevailing uptake mechanism observed in this work and in Kobayashi et al. are interpreted in connection

**Fig. 2** Tc-K edge XAS spectra of Tc sorbed on magnetite in 0.1 M NaCl. (a) XANES, (b) $k^3$-weighted EXAFS spectra, (c) corresponding Fourier Transform Magnitude (FTM). Black lines represent the experimental data, the red lines in (b) and (c) represent their reconstruction with two principal components. The ITFA-derived FTM spectra of the two endmembers (magnetite species 1 and magnetite species 2) are also plotted on top and bottom, respectively.
with differences in magnetite solubility in both systems. As shown in Fig. 3, the solubility of magnetite in the pHm range 6–7.5 (pe + pHm = 4, see Fig. 1) (Kobayashi et al., 2013) is significantly larger than at pHm ∼ 9 (pe + pHm = 7, see Fig. 1) (this work). Higher concentrations of Fe in solution are expected to promote a greater recrystallization rate, thus facilitating the incorporation of Tc(IV) in the structure of magnetite. These observations strongly suggest that the mechanism driving the retention of Tc by magnetite strongly depends on the initial Tc concentration and pH, and to a lesser extent on the loading on the surface of magnetite.

**Mackinawite.** Fig. 4a shows the Tc K-edge XANES spectra of Mack-1 to Mack-6, corresponding to Tc sorbed on mackinawite. As in the case of Tc uptake by magnetite, all investigated mackinawite samples do not show the pre-edge feature at 21.05 keV characteristic of Tc(VII), thus indicating the complete (>95%) reduction of Tc(VII) to Tc(IV) within the timeframe of the experiment. The XANES spectral features are, however, different from those of the magnetite samples in several aspects, most notably the absence of the splitting of the white line peak. The spectral differences between the magnetite and the mackinawite samples are even more pronounced when looking at the EXAFS spectra (Fig. 4b and c). As before, the series of EXAFS spectra was analysed by ITFA to derive the number of spectral components present. The Malinowski indicator values and the reconstruction of the experimental spectra suggested the presence of two spectral components

### Table 3 EXAFS-derived structural parameters for Tc in the magnetite and mackinawite series

| Sample                  | Path        | CN$^a$ | R (Å)  | σ² (Å²) | ΔE° (eV) (%) | %R$^a$ |
|-------------------------|-------------|--------|--------|---------|-------------|--------|
| Magnetite Species 1     | Tc-O        | 6$^f$  | 2.01   | 0.0043  | 3.0         | 6.1    |
| (Structural Tc(IV))     | Tc-Fe$_1$   | 6$^f$  | 3.08   | 0.0113  |             |        |
|                         | Tc-Fe$_2$   | 6$^f$  | 3.49   | 0.0093  |             |        |
| Magnetite Species 2     | Tc-O        | 5.7    | 2.02   | 0.0037  | 3.9         | 6.7    |
| (Sorbed Tc(IV) dimers)  | Tc-Tc       | 0.9    | 2.37   | 0.0018  |             |        |
|                         | Tc-Fe$_1$   | 2.9    | 3.12   | 0.0100$^c$ |           |        |
|                         | Tc-Fe$_2$   | 4.4    | 3.52   | 0.0100$^c$ |           |        |
| Mackinawite Species 1   | Tc-S        | 5.8    | 2.38   | 0.0092  | 8.2         | 9.7    |
| (TcS$^x$)               | Tc-Tc       | 0.8    | 2.83   | 0.0032  |             |        |
| Mackinawite Species 2   | Tc-O$_1$    | 4$^f$  | 2.00   | 0.0025  | −0.9        | 9.3    |
| (TcO$_2$·xH$_2$O(s))    | Tc-O$_2$    | 2$^f$  | 2.38   | 0.0010  |             |        |
| Model 1                 | Tc-Tc       | 2$^f$  | 2.55   | 0.0032  |             |        |
|                         | MS          | 4$^f$  | 4.03   | 0.0071  |             |        |
| Mackinawite Species 2   | Tc-O$_1$    | 4$^f$  | 2.00   | 0.0024  | −0.7        | 8.4    |
| (TcO$_2$·xH$_2$O(s))    | Tc-O$_2$    | 2$^f$  | 2.38   | 0.0015  |             |        |
| Model 2                 | Tc-Tc$_1$   | 1$^f$  | 2.54   | 0.0040  |             |        |
|                         | Tc-Tc$_2$   | 1$^f$  | 3.01   | 0.0099  |             |        |
|                         | MS          | 4$^f$  | 4.01   | 0.0051  |             |        |
| TcO$_4$$^-$(aq)$^{47}$  | Tc-O        | 4      | 1.72   | 0.0014  | 9.5         | 9.2    |

$^a$ CN (coordination number). $^b$ R (residual). Fit errors: CN: ±25%; R: 0.01 Å, σ²: 0.002 Å², f: fixed, c: constrained.

### Table 4 Quantitative speciation of the Tc magnetite samples based on EXAFS-ITFA. Bold numbers indicate fixed values

| Sample | Fraction magnetite species 1: structural Tc(IV) | Fraction magnetite species 2: sorbed Tc(IV) dimers | Sum |
|--------|-----------------------------------------------|--------------------------------------------------|-----|
| Mag-0  | 1.00                                          | 0.00                                             | 1.00|
| Mag-1  | 0.33                                          | 0.59                                             | 0.92|
| Mag-2  | 0.42                                          | 0.53                                             | 0.95|
| Mag-3  | 0.54                                          | 0.47                                             | 1.01|
| Mag-4  | 0.15                                          | 0.82                                             | 0.97|
| Mag-5  | **0.00**                                      | **1.00**                                         | **1.00**|
| Mag-6  | 0.02                                          | 0.97                                             | 0.99|

**Fig. 3** Solubility of magnetite (Fe$_3$O$_4$(cr)) calculated for pe + pH$_m$ = 4 (red, Kobayashi et al., 2013) and pe + pH$_m$ = 7 (blue, this work) using ThermoChimie TDB.$^{56}$

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**Table 3** EXAFS-derived structural parameters for Tc in the magnetite and mackinawite series

**Table 4** Quantitative speciation of the Tc magnetite samples based on EXAFS-ITFA. Bold numbers indicate fixed values

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**Fig. 3** Solubility of magnetite (Fe$_3$O$_4$(cr)) calculated for pe + pH$_m$ = 4 (red, Kobayashi et al., 2013) and pe + pH$_m$ = 7 (blue, this work) using ThermoChimie TDB.$^{56}$
and hence Tc species (Fig. 4b and c). Also in contrast to the magnetite samples, the addition of the TcO$_2$·xH$_2$O(s) reference did not increase the number of factors, demonstrating that TcO$_2$·xH$_2$O(s) is one of the two components present, albeit as a relatively small fraction, since none of the mackinawite (XANES and EXAFS) spectra is a close match of the TcO$_2$·xH$_2$O(s) reference.

The spectral component of the non-TcO$_2$-species is most purely expressed in sample Mack-4 based on the VARIMAX factor loading. This EXAFS spectrum – as well as that of the other mackinawite samples – is dominated by a FTM peak at about 1.9 Å (labelled “S”), i.e. about 0.3 Å more than that of the Tc(IV)–O coordination peak (labelled “O”), suggesting sulphur instead of oxygen coordination. The EXAFS shell fit of the ITFA-derived endmember spectrum (Mackinawite species 1, see also Fig. S4†) using FEFF 8.2 calculated paths of an atomic cluster based on the structure of TcS$_2$ confirmed sulphur in sixfold coordination to Tc at a distance of 2.38 Å, which is very close to the average distance of the TcS$_2$ coordination shell at 2.393 Å (Table 4). A second FTM peak at about 2.6 Å (labelled “Tc$_2$”) could be fitted with one Tc atom at 2.83 Å, i.e. only one of the expected three Tc neighbours in the distal range 2.79–2.90 Å of TcS$_2$ could be fitted. Indeed, the local structure of the species formed in presence of mackinawite is more similar to Tc$_2$S$_2$ or TcS$_2$ previously observed in comparable systems. This is corroborated by the Tc–S distance of 2.38 Å in line with that of Lukens et al. and an only slightly longer Tc–Tc distance of 2.83 Å, which has been reported as 2.77 Å by Lukens et al. Our coordination numbers are also slightly smaller (6 instead of 7, and 1 instead of 2 for Tc–S and Tc–Tc, respectively). Whether these small discrepancies arise from shell fit uncertainties or from small structural differences is not easy to decide, but there is no doubt that mackinawite species 1 is largely in line with the previously observed TcS$_x$, and not with the high-temperature phase TcS$_2$.60

Mackinawite species 2, which corresponds to TcO$_2$·xH$_2$O(s) demonstrated by ITFA as described before, was fitted following the model first suggested by Lukens et al.61 In this one-dimensional chain structure, strongly distorted TcO$_4$(OH$_2$)$_6$ octahedra are linked by uniform Tc–Tc bonds of about 2.57 Å and two Tc–O bonds of about 2.02 Å in a square planar arrangement. Two longer Tc–O paths of about 2.47 Å arise from bonding water molecules above and below the TcO$_4$ squares, which complete the octahedral coordination of Tc(IV). The fit requires also a four-legged multiple scattering path (MS) arising from the square planar arrangement of the TcO$_4$ units. The resulting bond lengths and corresponding Debye–Waller factors, reported in Table 3 as model 1, are largely in line with previously published results. In an alternative attempt, we adopted again the square planar configuration including the split of the TcO$_6$ coordination shell in two Tc–O distances
and the arising MS path, but allowed for the alternating longer and shorter Tc–Tc distances along the chains like in crystalline TcO$_2$. While the Tc–O distances remain identical to those of model 1, the Tc–Tc distances show a clear splitting, a shorter at 2.54 Å and a longer at 3.01 Å (model 2 in Table 3). The shorter distance is within the error limit identical to that of model 1, and both distances are 2–3% smaller than those of crystalline TcO$_2$ (2.62 and 3.08 Å). Both models provide a good fit in terms of fit statistics and physically meaningful data; the second model is slightly better, however, based on the smaller error and the length of the MS path being closer to the value of 4.00 Å expected from the fitted average Tc–O distance of 2.00 Å. From a crystal-chemical point of view, the short-long Tc pairing scheme is based on a sensitive balance between crystal field stabilization (favoring an even distribution of Tc–Tc distances by stabilizing a more symmetric TcO$_6$ octahedron, $t_{2g}^3$ configuration) and valence electrons available to form a Tc–Tc metal bond (shortening one of the two Tc–Tc distances).

In contrast to the EXAFS-ITFA-derived Tc speciation in the magnetite system, which showed an effect of the initial Tc concentration, the Tc speciation of the mackinawite series established in the same way shows rather an effect of Tc surface loading: samples Mack-3 and Mack-6 with the highest loading of 900 ppm have the highest contribution of TcO$_2$·xH$_2$O(s), although it never exceeds 20%, while the TcS$_2$-like phase prevails in all systems (Table 5).

| Sample  | Fraction mackinawite species 1: Te$_{\text{IV}}$S$_2$ | Fraction mackinawite species 2: TeO$_2$·xH$_2$O(s) | Sum     |
|---------|---------------------------------|---------------------------------|---------|
| Mack-1  | 0.93                            | 0.07                            | 1.00    |
| Mack-2  | 0.99                            | 0.01                            | 1.00    |
| Mack-3  | 0.79                            | 0.21                            | 1.00    |
| Mack-4  | 1.00                            | 0.00                            | 1.00    |
| Mack-5  | 0.89                            | 0.11                            | 1.00    |
| Mack-6  | 0.82                            | 0.18                            | 1.00    |
| TcO$_2$·xH$_2$O(s) | 0.00                            | 1.00                            | 1.00    |

and loadings used by Liu and co-workers (99 000 ppm). Note that the method of mackinawite synthesis used in our work is identical to that of Kobayashi et al. (2013) and Liu et al. (2008). In contrast to these observations, Livens et al. reported the formation of a TcS$_2$-like phase ($d_{\text{Te–S}} = 2.42 \pm 0.02$ Å and CN = 6) in the presence of relatively high loadings (10 000 ppm) of Tc on 300 mg mackinawite. A direct comparison of the data by Livens and co-workers with the present study cannot be accomplished, provided the different method used for the synthesis of mackinawite and the very limited experimental description provided by the authors, which omits (among others) information on S : L, [Tc]$_0$ and pH.

**Conclusions**

Tc reduction and uptake mechanisms by Fe(II) minerals (magnetite and mackinawite) were investigated in 0.1 M NaCl systems. The results show that Tc($\text{VII}$) is reduced to Tc($\text{IV}$) in contact with magnetite and mackinawite in all investigated systems regardless of initial [Tc]$_0$ and solid-to-liquid ratio. The observed reduction is also consistent with the thermodynamically calculated Tc($\text{VII}$)/Tc($\text{IV}$) borderline.

EXAFS data evaluation indicates that the mechanisms of Tc($\text{VII}$) retention by magnetite and mackinawite are strongly dependent on the loading, [Tc]$_0$ and pH$_m$. Tc($\text{VII}$) partly incorporates into the structure of magnetite at low [Tc]$_0$ ($2 \times 10^{-5}$ M), but forms Tc–Tc dimers bonding to the magnetite (111) face at [Tc]$_0 = 2 \times 10^{-4}$ M. A full incorporation of Tc into the magnetite structure is triggered by boundary conditions enhancing magnetite solubility (and thus promoting a greater recrystallization degree), e.g. lower pH$_m$ and $E_h$ values. In contrast to magnetite, [Tc]$_0$ has no clear impact on the uptake of Tc by mackinawite. A TcS$_2$-like phase prevails in all investigated mackinawite systems, although the contribution of up to ~20% of TcO$_2$·xH$_2$O(s) (likely as surface precipitate) is observed for the highest investigated loadings (900 ppm).

These results provide key inputs for the understanding of the mechanisms driving the reduction and retention of Tc by magnetite and mackinawite under repository-relevant conditions, whilst highlighting the need of coupling classical wet-chemistry techniques, thermodynamic calculations and advanced spectroscopic methods when investigating complex processes or systems such as redox and mineral interfaces.

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