

**A Review of Tc Geochemistry:
The Behavior of an Artificial Element in the Natural Environment —9384**

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ABSTRACT

Technetium-99 (^{99}Tc) is an element of concern for the environment due to its high solubility and low sorption potential ($K_D < 1$) in oxidizing environments, long half-life (2.14×10^5 a = annum), large scale production during fission of uranium fuel rods (6.06%), and moderate radiotoxicity. Nearly 290 metric tonnes of ^{99}Tc have been produced worldwide (2008), and this number is roughly quadruple of that in 1994. The oxidized form of ^{99}Tc is the pertechnetate anion $[\text{Tc}(\text{VII})\text{O}_4^-]$, which migrates in the subsurface at nearly the same velocity as groundwater. In reducing environments (< 200 mV E_{h7}), the soluble $\text{Tc}(\text{VII})\text{O}_4^-$ anion is reduced to the quadravalent state $[\text{Tc}(\text{IV})]$, especially in the presence of reducing agents, such as biogenic $\text{Fe}(\text{II})$ sorbed onto mineral surfaces. The heterogeneous surface-mediated reduction reaction occurs much more rapidly than the homogenous one and yields the relatively insoluble $\text{Tc}(\text{IV})\text{O}_2 \cdot n\text{H}_2\text{O}$ solid ($[\text{TcO}(\text{IV})(\text{OH})_2^{\circ}_{aq}] = 10^{-8.2}$ mol/L). Thus, reduction of $\text{Tc}(\text{VII})$ can take place either through an indirect route via biogenerated $\text{Fe}(\text{II})$ or through direct enzymatic reduction by certain dissimilar metal reducing bacteria (DMRB) that couple the oxidation of H_2 or organic molecules to reduction of metals. However, even for solutions in equilibrium with $\text{Tc}(\text{IV})$ solids, the activity of ^{99}Tc is still above the Drinking Water Standard set by the Environmental Protection Agency (EPA) of 900 pCi/L. Recent investigations have shown that $^{99}\text{Tc}(\text{IV})$ can be immobilized either as a co-precipitate or a trace element in iron sulfides, hydrous iron oxyhydroxides, or perhaps carbonates. This review explores the potential of sequestering Tc into solid phases and addresses the data gaps that must be closed in order to enable efficient subsurface remediation schemes.

INTRODUCTION

Along with the element promethium (Pr; $Z = 59$) technetium ($Z = 43$) is one of two light elements ($Z < 82$) made up entirely of unstable isotopes. Technetium was discovered by Perrier and Segrè in 1937 [1, 2] who investigated a discarded piece of radioactive molybdenum foil from the Berkeley cyclotron. The isotopes isolated by Perrier and Segrè were ^{95}Tc and ^{97}Tc and since that discovery neutron or deuteron bombardment of target samples (consisting mainly of Mo) produced an array of Tc isotopes and isomers. Today, there are 26 known isotopes (mass 88 to 113) and numerous isomers of technetium and little attention would be paid to this element outside of specialized physics laboratories but for the large amount amassed through nuclear energy generation and production of atomic weapons.

Except for a miniscule amount formed through spontaneous fission of ^{238}U [3], all of the technetium present today is anthropogenic. The lack of natural technetium isotopes is a consequence of their relatively short half-lives compared to the age of the Earth. On the other hand, ^{99}Tc is produced in significant quantities during fission of ^{235}U -enriched (~3%) uranium fuel rods. The fission yield of ^{99}Tc is 6.06%, meaning that one ton of enriched uranium fuel will produce approximately 1 kg of ^{99}Tc [4, 5]. Fission of ^{235}U also produces other isotopes of technetium besides ^{99}Tc and some of these possess long half-lives, but their fission yield is very low. Table 1 lists the principal isotopes of Tc, their half-lives, and fission yields. The data in the table indicates that ^{99}Tc is the isotope with the combined characteristics of long half-life and high

fission yield. For example, even though ^{97}Tc and ^{98}Tc have very long half-lives (2.6×10^6 and 4.2×10^6 a, respectively), they are a factor of 10^6 and 10^{11} less abundant than ^{99}Tc [5]. Additional ^{99}Tc is formed during fission of ^{239}Pu . Note also that a small amount of ^{99}Tc comes from medical imaging; the decay of 1 Ci of $^{99\text{m}}\text{Tc}$ ¹ results in 3 nCi of ^{99}Tc [6, 7]. Accordingly, even though there are 150 000 Ci of $^{99\text{m}}\text{Tc}$ used in medical testing, the amount produced in one year is a factor of $\sim 3 \times 10^5$ less than what was released from the Sellafield uranium reprocessing facility in 1980 in the UK. Thus, the principal source of ^{99}Tc is through fission processes and its release to the environment has been through either accidental or approved releases to soils, surface waters, and the atmosphere.

Table I. A List of the Principal Technetium Isotopes Produced by Fission of ^{235}U , Their Percent Yields, and Half-Lives. From [8].

Technetium isotope:	^{99}Tc	^{101}Tc	^{102}Tc	^{103}Tc	^{104}Tc	^{105}Tc	^{107}Tc
Yield (%)	6.06	5.6	4.3	3.0	1.8	0.9	0.19
Half-life	2.12×10^5 yr	14.3 min	4.5 min	50 sec	18 min	7.7 min	<1 min

Notes: ^{99}Tc decays at 37,800 dpm/ μg and a specific activity of 1.7×10^{-2} Ci/g

Approximately 160 TBq² of ^{99}Tc were released during atmospheric nuclear tests, and greater than a factor of $10 \times$ more (> 1 PBq) has been released into the marine environment through approved discharge from fuel reprocessing plants [9]. In the typical case ^{99}Tc is distributed in marine sediments in low concentrations (10^{-10} gTc/g sediment) [10] and poses little threat to human life. On the other hand, in areas involved in nuclear weapon production and related facilities (e.g., Hanford, Washington, Paducah, Kentucky, Portsmouth, Ohio, and Oak Ridge, Tennessee) contamination is widespread and at higher concentrations. For example, 930 Ci of ^{99}Tc were intentionally discharged to the subsurface at the Hanford Site and an additional 460 Ci were released because of leaks or accidents. Assays of soil and pore water from beneath tanks SX-108 and T-106 revealed concentration of ^{99}Tc as high as 1.5×10^{-5} mol/L, which is a factor of nearly 10 000 higher than the drinking water standard (5.3×10^{-10} mol/L or 900 pCi/L [11]). Eventually the technetium contamination will migrate through the vadose zone and reach the underlying aquifer. The aquifer beneath the Hanford Site discharges into the Columbia River which supplies drinking water downstream. When consumed, ^{99}Tc has a very short biological half-life (60 hours) [12] and the low energy β^- decay (0.292 MeV) causes little damage to the host. On the other hand, inhalation of ^{99}Tc , through tainted dust or water vapor, may result in lung cancer and other maladies because the biological half-life of technetium in lung tissue is relatively long [12]. Accordingly, a means by which technetium could be immobilized in contaminated sediments and pore water is necessary.

Adding to the massive quantities of extant ^{99}Tc , the continuing use of nuclear power will result in an increase of the technetium stockpile. According to Jan Leen Kloosterman (Delft University

¹ The “m” designates an isomer of technetium, which is a nucleon that possesses a higher energy level than that of the ground state. Isomers decay by means of an isomeric transition, in this case to ^{99}Tc . In order to prevent confusion, the ground state of technetium is commonly designated $^{99\text{g}}\text{Tc}$. When we refer to ^{99}Tc , it is in the ground state, unless otherwise noted.

² One Becquerel (Bq) is 1 disintegration/second or 2.7×10^{-11} Ci. TBq = terabecquerel (10^{12}); PBq = petabecquerel (10^{15}).

of Technology, the Netherlands), 21 kg of ^{99}Tc (13.2 TBq) are produced annually in a large 1 GWe reactor. His estimated inventory of ^{99}Tc produced in 2007 is 15.1 metric tonnes (MT) [13]. In 1994, there were ~78 MT of ^{99}Tc . Accordingly, if the 2007 production value is roughly average, then there are ~290 MT (182.6 PBq) of ^{99}Tc today. In other words, the inventory of ^{99}Tc has nearly quadrupled between 1994 and today (2008). Future ^{99}Tc production will likely accelerate. In order to simultaneously produce more electrical power and reduce emissions of greenhouse gases to the atmosphere, a three-fold increase of power from nuclear reactors is needed [14] but at the cost of generating more ^{99}Tc in the future. The potential of a “renaissance” of nuclear power alone will require creative ideas to immobilize ^{99}Tc .

The scope of this article is to review the salient data on technetium geochemistry and from this information propose potential immobilization strategies. One potential solution is to sequester Tc(IV) into a chemically durable phase. As we demonstrate below, the mineral goethite [$\alpha\text{-FeO(OH)}$], may be useful in this regard.

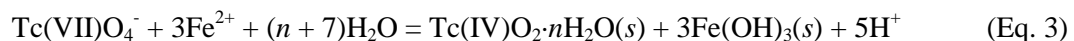
TECHNETIUM GEOCHEMISTRY

The two most prominent oxidation states that technetium possesses are Tc(IV) and Tc(VII) [8]. In oxidizing environments technetium is manifested as the pertechnetate anion [Tc(VII)O_4^-]. In this form, technetium is mobile in the subsurface due to its poor sorption properties. Typical rock-forming minerals that make up the subsurface at circum-neutral pH conditions possess an overall negative charge on their surfaces, which repels the negatively-charged pertechnetate anion [15]. On the other hand, the reduced form of technetium, Tc(IV), is relatively insoluble ($10^{-8.2}$ mol/L)[16] and precipitates out of solution as the $\text{Tc(IV)O}_2 \cdot n\text{H}_2\text{O}$ solid. Oxidation states between IV and VII are possible, but technetium disproportionates rapidly:



The half-life of Tc(VI) in air, for example, is only 10 msec [17]. Lower oxidation states are also possible, but these require ligands such as CO or organic molecules.

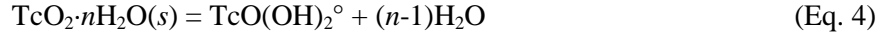
1. Redox Behavior. Reduction of Tc(VII) to Tc(IV) in nature can be slow, even when low E_h conditions prevail. Lieser and Bauscher [18] found that pertechnetate was reduced to Tc(IV) in solutions with E_h values between 200 and 100 mV. Other investigators, however, reported that Tc(VII) is slowly reduced, except when Fe(II) is present as a sorbed species. Cui and Eriksen [19, 20] showed that even when Fe(II) concentrations are high compared to that of pertechnetate, reduction was slow. On the other hand, there are cases in which technetium persists in the oxidized form, even though the E_h of the system is below the reduction threshold. These conditions arise because of the availability and steric distribution of electron donors is more critical than the overall E_h of the system. For example, Cui and Eriksen [20] showed that even under conditions in which ferrous iron [Fe(II)] activity in solution were relatively high, reduction kinetics of Tc(VII) were sluggish. Therefore, even though the reduction reaction:



is thermodynamically feasible ($\log K_{298} = -21.8$; [21]), the kinetics of this homogeneous reaction are rate-limited. In contrast, when Fe(II) is sorbed onto other mineral phases, especially iron oxyhydroxides, surface-mediated heterogeneous catalysis becomes important and reduction of Tc(VII) to Tc(IV) takes place rapidly above pH 6 [22-24].

These data demonstrate that the fate of technetium is intimately tied to the geochemistry of iron and sulfur. Further, the mobility of technetium is affected by biogenic Fe(II), and not simply on Fe(II) produced in inorganic reactions. Therefore, the geochemical behavior of technetium is governed not so much by the overall redox conditions, but by the availability of reducing agents.

2. Solubility. The solubility of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$, written as:



has been measured by several investigators [16, 25] and these results have been reviewed by Rard et al. [26]. The solubility depends on the crystallinity of the $\text{TcO}_2 \cdot n\text{H}_2\text{O}$. Not only does poorly crystalline TcO_2 dissolve more rapidly into solution [18], the solubility of amorphous technetium dioxide [$\text{TcO}_2(\text{am})$] is about a factor of $10\times$ times higher than that of crystalline $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ [26]. In consideration of these observations, the accepted value of solubility of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ at 25°C in dilute solutions between pH 4 to pH 10 is $10^{-8.2}$ mol/L [25] to $10^{-8.44}$ mol/L [26], which overlap in value within experimental uncertainty. This translates into 16,800 pCi/L Tc [as $\text{TcO}(\text{OH})_2^\circ$ in neutral pH waters] in equilibrium with the hydrated crystalline TcO_2 phase, which is about 20 times higher than the Drinking Water Standard (DWS) of 900 pCi/L established by the EPA [11]. Accordingly, any remediation scheme that relies solely on reduction and precipitation of a TcO_2 solid will still result in concentrations of aqueous Tc above the drinking water limit.³

3. Sorption. Sorption relates the quantity of a chemical species associated with solid components of soil to the concentration in the contacting solution. Although “sorption” and “partitioning” are used interchangeably, true sorption takes place under equilibrium conditions and is dependent on the solution composition (pH, concentration of competing ions) and soil characteristics (point-of-zero-charge, surface area). On the other hand, partitioning refers to the sum of contributions that leads to uptake of the chemical constituent in question, irrespective of equilibrium conditions. In other words, partitioning may include surface sorption, co-precipitation, surface precipitation, and inclusion of the chemical constituent within the mineral lattice. Accordingly, partitioning should be regarded as an empirical value rather than a mechanistic description. Partitioning is typically expressed as the distribution coefficient, K_D :

$$K_D = [(C_{\text{initial}} - C_{\text{final}})V_{\text{initial}}/M_{\text{sed}}]/C_{\text{final}} \quad (\text{Eq. 5})$$

in which C_{initial} is the beginning concentration of technetium in solution, C_{final} is the concentration of technetium at the end of the experiment, V_{initial} is the beginning volume of water before soil is added, and M_{sed} is the mass of sediment added. Because technetium is also redox sensitive, its partitioning behavior will also depend on the E_h of the system and the presence of materials that lead to reduction, such as organic matter. The reduction of Tc(VII) to Tc(IV) takes place between 200 and 100 mV over circum-neutral pH values [27].

Partitioning behavior is starkly different for Tc(VII) and Tc(IV). Pertechnetate partitions poorly onto typical soil materials whereas Tc(IV) partitions well onto a variety of materials. If Tc(VII) could be reduced to Tc(IV), the partitioning (mostly irreversible) will increase by a factor of 10^3 [27]. Further, Tc(IV) is also prone to partition onto FeS_2 [28], although it is not clear if the technetium forms a Tc—S bond. Because most aquifers are assumed to be in contact with the atmosphere and because most arable soils display E_h values in the mildly oxidizing to oxidizing

³In vadose zone sediments, the concentration of ^{99}Tc will indeed be greater than that of the DWS, but the rate of transfer to underlying aquifer may be such that the concentration of ^{99}Tc will be below the DWS.

range [29], most partitioning experiments are conducted under aerobic conditions. These experimental conditions seem justified because of the observed fast transit (90 percent of the groundwater velocity) of technetium in aquifers [30].

The basis for the lack of interaction between pertechnetate and mineral surfaces is well established through experimentation. Wildung et al. [31] for example, reported that 22 different soils were equilibrated with pertechnetate for 24 hours and yielded K_D values (pCi sorbed per g soil/pCi solute per mL solution) of 0.007 to 2.8 mL/g. Subsequent studies have yielded similar results. El-Wear et al. [32] reported low K_D values for technetium on a variety of rock types while Sheppard and Sheppard [33] determined low values of K_D (<0.005 mL/g) measured on soils. Kaplan and Serne [15] reported small positive to negative K_D values (-0.16 to +0.11 mL/g) for soils sampled from the Hanford Site, Washington State. Negative K_D values are possible because of the principle of excluded water. Water molecules will orient themselves with the positive end of their dipole towards the negatively charged mineral surface and, depending on the properties of the metal—oxygen surface species and ambient solution pH, a zone of structured water develops that repels negatively charged species, such as pertechnetate. Solution extracted from the experiment will typically not include the water sorbed at the surface of the mineral grains, so pertechnetate is concentrated in the sampled “excluded” bulk solution. Thus, the concentration of pertechnetate in the final compared to the beginning solution may be higher, yielding negative K_D values (see Equation 5).

Notably, there are several cases in which technetium partitioning does not conform to the patterns described above. For example, Zhang et al. [34] conducted a series of tests with aluminum-bearing solids (boehmite, Al-oxyhydroxide gels, and simulated tank wastes) in order to measure the partitioning of rhenium (the chemical analogue of Tc) and technetium between solids and solution. Measured K_D values varied from 5 to 105 mL/g, depending on nitrate concentration, solution pH, and identity of the solid. X-ray diffraction confirmed that boehmite was the main phase in the high-aluminum sludge. In boehmite [γ -AlO(OH)] suspensions, the highest K_D values were measured in pH = 5 solutions with low nitrate concentrations. Relatively high K_D values were also measured for aluminum-rich gels (21 to 111 mL/g). This might be an important scenario for tanks leaking into the environment; the alkaline solutions may partially dissolve aluminum-bearing phases resulting in the formation of amorphous Al-oxyhydroxides that sequester technetium.

Although the results of the experiments performed by Zhang et al. [34] seem to stand alone, it is important to note that higher values of K_D are implied by other investigations. Soil scientists, for example, have shown that despite the relatively oxidizing conditions of most farm lands, technetium appears to be bound up in soil, especially in periodically wet conditions [35-38]. The relative immobility of technetium in soils was noted early by Henrot [39], who proposed that microbial activity may cause reduction with consequent partitioning of Tc(IV), which is more prone to sorption than Tc(VII) in soil. In this model microbial activity in the soil causes depletion of oxygen in the interstices of mineral grains, and diffusion of O₂ through a layer of water becomes rate-limiting. Therefore, technetium immobility may occur, even in soils in which overall oxidizing conditions are assumed. Accordingly, biogeochemical reactions are important to the fate of technetium and are discussed next.

BIOGEOCHEMISTRY OF TECHNETIUM

Microbial organisms are ubiquitous in the subsurface and in water. Recent estimates of the number of microorganisms are in the range of 10^6 to 10^9 per gram of soil [40], and these numbers are consonant with earlier estimates ([39] and references therein). A large variety of bacteria are able to couple oxidation of H_2 and organic material to metal reduction during anaerobic respiration, including the dissimilatory metal reducing bacteria (DMRB) [41-44]. Among these anaerobic microbes, several have been shown to reduce Tc(VII), including *Geobacter metallireducens* [45], *Geobacter sulfurreducens* [46], *Escherichia coli* [42], *Desulfovibrio desulfuricans* [47], *Shewanella putrefaciens* [44], and *Desulfovibrio fructosovorans* [48]. The ability for microbes to reduce metals in anaerobic environments is one potential way to limit migration of radionuclide elements, especially pertechnetate, because the metabolic processes involved in respiration yields products that are reactive towards technetium. Table II lists the soil aeration status and the corresponding biogeochemical zones in which reduction occurs.

In this section, we explore two possible routes by which anaerobic bacteria can aide in the reduction and immobilization of technetium: a) through direct enzymatic reduction, or b) reduction catalysis on mineral surfaces in the presence of sorbed biogenic Fe(II).

Table II. Summary of Aeration Status of Soils and Corresponding Biogeochemical Zones

Soil Aeration Status	Redox Reaction	$E_{h7}^{(a)}$ (mV)	Biogeochemical Zone	$\Delta G^{(b)}$ (kJ/mol)
Well-aerated soils			Oxic respiration	-856
	Initial nitrate reduction	550-450	Nitrate reduction	-806
	Initial Mn^{2+} formation	450-350	Manganese reduction	-569
Wet soil	O_2 no longer detectable	330		
	Nitrate no longer detectable	220		
	Technetium reduction	200-100	Technetium reduction	-436
Waterlogged soil	Initial Fe^{2+} formation	150	Iron reduction	-361
	Sulfate reduction	-50	Sulfate reduction	-48
	Initial methane production	-120		
	Sulfate no longer detectable	-180		

(a) E_{h7} = the E_h at pH 7

(b) Free-energy change per mole of acetate consumed as electron donor.

Notes: Data from Koch-Steindl and Pröhl [29], Burke et al. [50], and Lieser and Bauscher [27].

1. Reduction of Tc by Direct Enzymatic Activity. A number of investigations have established that a variety of metal- and sulfate-reducing bacteria, especially those of the *Shewanella*, *Desulfovibrio*, *Anaeromyxobacter* and *Geobacter* species, can induce reduction of

Tc(VII) enzymatically [41, 42, 44, 46-49]. Investigators hypothesize that a chain of enzymatic electron transfer reactions directly reduce Tc(VII) when DMRB couple reduction with oxidation of H₂ and organic matter. In experiments designed to illustrate the bioreduction mechanism soluble pertechnetate concentrations decreased rapidly in solution. Control experiments, in which the soil and water mixtures were pasteurized, exhibited no decrease in soluble pertechnetate, thus strongly implicating the role of DMRB in pertechnetate reduction.

The fundamental pathway by which enzymatic reduction takes place has not been worked out in detail, but some recent investigations have highlighted some exciting details. Hydrogenase enzymes appear to be intimately involved with the metal reduction process [49]. There are many types of hydrogenase enzymes, but experiments have focused attention on the sulfur-bridged di-iron and nickel-iron (designated as [FeFe] and [FeNi], respectively) forms. The bi-directional oxidation and reduction of H₂ is also catalyzed by [FeFe] and [FeNi] hydrogenase and appear to be crucial links in the electron transfer chain. Hydrogenase is typically found in the periplasmic and cytoplasmic regions of cells; in gram-negative cells, the periplasm is located between the outer and inner membranes. The close association of technetium solids on the outer membrane or within the periplasm, and not within the cytoplasmic region, is often cited as indirect evidence for the agency of hydrogenase.

Certain strains of bacteria can be genetically manipulated to suppress production of potential reducing enzymes. For example, De Luca et al. [48] showed that strains lacking in the [FeNi] hydrogenase operon in *D. fructosovorans* exhibited a strongly diminished ability to reduce Tc(VII). Results of other experimental investigations strongly indicate that periplasmic hydrogenase plays a direct role in technetium reduction. Lloyd et al. [47] reported that cells of *Desulfovibrio desulfuricans* poisoned with Cu(II), which deactivates periplasmic, but not cytoplasmic, hydrogenase were unable to reduce Tc(VII).

An additional piece of the bioreduction puzzle that is now just becoming understood is the role of physiological electron donors or acceptors for hydrogenase, such as ferredoxins, cytochrome c₃, and cytochrome c₆. De Luca et al. [48] argued that cytochrome c₃, for example, does not directly reduce technetium, but the presence of this enzyme with hydrogenase is considered to be necessary for reduction. In contradiction to this evidence, Marshall et al. [49] argued for a direct role of outer membrane c-type cytochromes (OMCs) in reduction of pertechnetate to Tc(IV). A mutant of *Shewanella oneidensis* MR-1 lacking two decaheme OMCs, MtrC and OmcA, was found to be incapable of reducing pertechnetate in the presence of lactate as an electron donor. Furthermore, when these two OMCs were purified and chemically reduced, both MtrC and OmcA were oxidized by pertechnetate, thereby providing direct evidence for the electron transfer reaction.

Reduction of pertechnetate to Tc(IV) in the presence of metal-reducing bacteria resulted in formation of a dark precipitate either within the periplasmic space or on the exterior surfaces of the cell outer membrane [42, 44, 46]. Some of the precipitated materials were analyzed by X-ray Absorption Spectroscopy (XAS), which can determine the oxidation state as well as the number and identity of bonding ligands in crystalline and amorphous materials. X-ray Absorption Near-Edge Spectroscopy (XANES) can easily distinguish between Tc(VII) and Tc(IV) by the presence of a pre-edge feature in the spectra that is indicative of Tc(VII). The data showed that the technetium solid was in a reduced form and had Tc—O bond lengths (approximately 2.00 Å) that

are characteristic of hydrous Tc(IV)O₂-like solids [50]. The data also indicate that even in systems that contained sulfur, the Tc—O bond is the most prevalent. In some instances, it appears that technetium co-precipitates with iron sulfide phases [51]. In other experiments Tc—S bonds are observed, but Tc—O bonds form after the host sulfide phase was oxidized [52, 53]. The data therefore indicate that hydrated TcO₂ solids are the long-term reservoir of technetium that forms as a result of biological activity.

2. Reduction via Biogenic Fe(II) Catalysis. Investigators have noted that an indirect route to reduction of technetium is also possible when ferric iron is reduced to the ferrous form through the agency of DMRB [21, 22, 24, 46, 50]. As discussed previously, the reduction of Tc(VII) by Fe(II) is thermodynamically feasible, although kinetically hindered as a homogeneous reaction [20]. In addition, surface-mediated reduction, such as Tc(VII) on the surface of magnetite (Fe₃O₄), is possible but ferrous iron preferentially reacts with dissolved oxygen such that Tc(IV) does not form. In anoxic environments, Fe(II) that is sorbed onto mineral surfaces, especially iron oxyhydroxides (Fe₃O₄, α-FeO·OH, or γ-FeO·OH) [20, 22-24, 46, 54, 55] causes rapid Tc(VII) reduction in a heterogeneous, surface-mediated reaction. Ferrous [Fe(II)] iron is present in numerous phases typical of sedimentary environments, including magnetite, ilmenite, phyllosilicates (e.g., chlorite, saponite, and biotite), and amphiboles. However, the availability of Fe(II) as a reductant for Tc(VII) in silicate minerals is limited [20, 21].

UPTAKE BY SOLID PHASES AND RETENTION POTENTIAL.

The previous section on Biogeochemistry illustrates that Tc(VII) can be reduced directly or indirectly by DMRB. However, it is still unclear how long Tc(IV) will remain in the reduced state. Addressing the issue of re-oxidation and remobilization of technetium is extremely pertinent for understanding the mobility of technetium between sources and sinks in the natural environment. If the microbial population in a subsurface zone is artificially stimulated how long will it retain the reduced state after the intervention ceases? When technetium-bearing sediments, soils, or solutions become re-exposed to oxidizing conditions or to agents that catalyze oxidation, how long will it take for Tc(IV) to oxidize and re-mobilize? Remobilization of reduced technetium during re-oxidation events has been addressed by Ashworth and Shaw [56], Begg et al. [55], Burke et al. [50, 57], Morris et al. [10, 58]. These investigations, though not necessarily concurring in their conclusions, illustrate the critical connection between Tc redox chemistry and behavior of Fe and S. Further, these investigations reveal the importance of solid phases (crystalline and amorphous) on sequestration of Tc.

Burke et al. [50] explored the retention of technetium in estuarine sediments in which the growth of the indigenous microbial population was stimulated. Populations of nitrate-, iron-, and sulfate-reducing bacteria were separated and sterilized sediments were inoculated with the various microbes. After anoxic conditions developed, the sediments were amended with Tc(VII). Control experiments in which the sediments were sterilized showed that Tc(VII) reduction did not occur, strongly implicating the role of microorganisms on the valence state of technetium. These investigators reported that Tc(VII) reduction occurred when iron- and/or sulfate-reducing bacteria were present, but not when nitrate-reducing bacteria alone were present. Data obtained by x-ray absorption spectroscopy (XAS) reveal that the reduced technetium is manifested as hydrous Tc(IV)O₂ solids. Some Fe(II) was present in the initial material, mostly as Fe(II) in solution, but control experiments indicated that this Fe(II) had no effect on Tc(VII) reduction. These data

indicate that biogenic Fe(II) is somehow more effective as a reducing agent than inorganically-generated Fe(II), in keeping with earlier studies [19, 20].

In a subsequent study Burke et al. (57) carried out similar experiments that were aimed at determining the length of retention of Tc(IV) that were exposed to oxidizing conditions or agents. During progressive anoxia, concentrations of Fe(II) and sulfide began to increase in the sediments as the result of bacterial activity. As in the previous experiments, nearly all of the Tc(VII) was rapidly reduced and disappeared from solution during iron and sulfate reduction. In sterilized control experiments, Tc(VII) reduction did not occur. These investigators [57] reported that remobilization of technetium in re-oxidation experiments was dependent upon the oxidant. For O₂ as the oxidant, about 50 percent of the technetium was remobilized as pertechnetate. Rapid remobilization of technetium (in approximately 66 days) occurred in both the iron- and sulfate-reduced sediments, but the balance of technetium (35 to 45 percent) remained recalcitrant. In the iron- and sulfide-reduced experiments, a fraction of Fe(II) and sulfide were both rapidly re-oxidized, but not at the same rate and extent as Tc(IV). The fraction of sulfide that remained in the reduced state did so for the duration of the experiment. Thus, the lack of correlation between sulfate and technetium oxidation on the one hand and re-mobilization on the other, in addition to the XAFS results, which did not show evidence for Tc—S bonding, indicate that sulfide stabilization of technetium was *not* occurring.

The mineralogical character and the relationship of the sulfide lattice to reduced technetium in experiments with bioprecipitated FeS has been elusive. In response to this gap in understanding, co-precipitation of technetium (and rhenium) with iron sulfide minerals was studied by Wharton et al. [53]. The mineral mackinawite (tetragonal FeS) was synthesized in the presence of either reduced or oxidized technetium or rhenium. Mackinawite was chosen because it is the first iron sulfide mineral that forms in a redox-driven paragenetic sequence. The synthesis materials and the products of re-oxidation experiments were studied using XAS to characterize the technetium and rhenium bonding environments and oxidation states.

Formation of mackinawite under reducing conditions resulted in reduction of Tc(VII) and Re(VII) and co-precipitation of a TcS₂ or ReS₂ phase. Synthesis of FeS in the presence of either Tc(IV) or Re(IV) resulted in no change in the oxidation state of either metal. When exposed to an oxidizing atmosphere, the coordinating atoms around Tc(IV) switch from sulfur to oxygen. Bond lengths and coordination numbers of the technetium compound are characteristic of TcO₂-like structure, even though iron is oxidized and secondary goethite forms [53]. These data show that when iron is oxidized, technetium remains in a reduced state, although it is not entirely clear why this happens or how long Tc(IV) will remain reduced.

Similar experiments were carried out by Livens et al. [52], in which mackinawite was synthesized inorganically and then reacted with a solution containing Tc(VII)O₄⁻. Contact of the technetium-bearing solution with mackinawite crystals resulted in the surface sorption and co-precipitation of Tc(IV)S₂-like phases. In accord with the experiments of Wharton et al. [53], oxidation caused the FeS phase to be transformed into goethite (α -FeO·OH), and the Tc—S bond was replaced by Tc—O, but technetium remained in a reduced form. Livens et al. [52] speculated that because Tc(IV) is six-fold coordinated, just like Fe(III) in goethite, that technetium was incorporated into the goethite lattice.

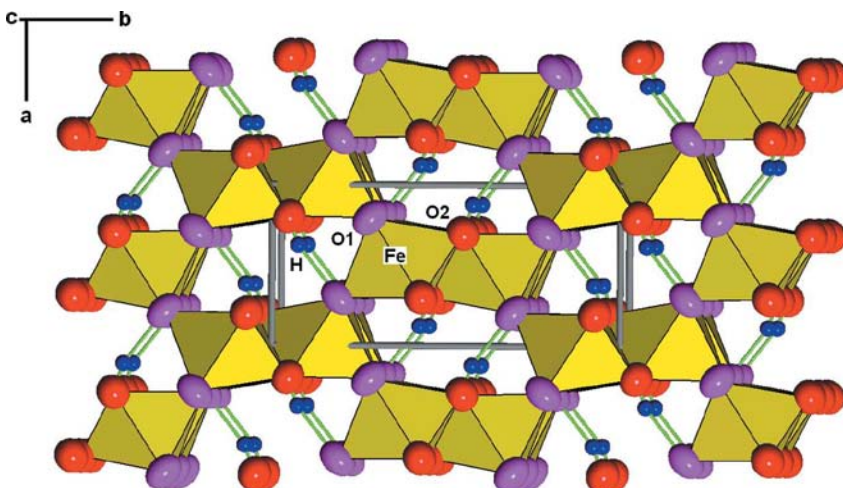


Figure 1. A representation of the crystal structure of α -FeO(OH) (goethite). Oxygen atoms are red and purple, representing two different sites (O_1 and O_2). The small blue spheres represent hydrogen and the yellow octahedral iron. From Yang et al. [59]

The role of iron oxyhydroxides, both amorphous and crystalline, in sequestering Tc(IV) was also investigated by Zachara and co-workers [24]. In the experiments discussed above in the section “Biogeochemistry of Technetium: Reduction via Biogenic Fe(II) Catalysis” Zachara et al. [24] reported that Tc(IV) appeared to be co-precipitated with amorphous to

nanocrystalline iron oxyhydroxides. Recall that the source of the Fe(II) is through biogenesis and that ferric iron sorbed onto the surfaces of sediment solids catalyzes the reduction of pertechnetate in solution. Significantly, the technetium showed little tendency for remobilization when the run product materials were exposed to oxidizing conditions, suggesting that a biologically indirect process could favorably affect the transport and fate of technetium in contaminated sediments. In these experiments, the concentration of re-mobilized Tc(VII) in solution was below the DWS of 900 pCi/L.

The results discussed above are consonant with an earlier investigation in which characterization of the technetium solids by XAS techniques indicated the presence of a reduced TcO_2 -like phase [21]. Technetium could be reduced and manifested as a co-precipitate with an iron oxide phase or as a surface precipitate, if the local concentration of Tc(IV) is high enough. On the other hand, it is plausible that the Tc(IV) may be incorporated directly into the goethite lattice. A model of the goethite lattice is shown in Figure 1.

Table III lists the radii of cations that are similar in size or behavior to technetium. Note first that Tc(IV) is six-fold coordinated (octahedral polyhedra) and that the size of Tc(IV) is roughly equivalent to that of ferrous [Fe(II)] and ferric [Fe(III)] iron, both of which are also six-fold coordinated. The similarity in size and coordination makes substitution of Tc(IV) into the goethite lattice plausible. Further, bond lengths between Fe(III) or Tc(IV) and oxygen are approximately the same. The Fe(III)—O bond in goethite is 2.026 Å [59], and that of Tc(IV)—O is 1.99 Å (both in octahedral coordination). In amorphous FeO-OH solids, the bond length between Fe(III) and O is nearly the same: 3 O at 1.95 Å and 3 O at 2.10 Å [61]. However, the thermodynamics and kinetics of this substitution have yet to be evaluated so there may be constraints on replacement of Fe(III)O₆ by Tc(IV)O₆. Further, the difference in charge between Tc(IV) and Fe(III) means that either a coupled substitution must operate or a defect structure must be generated. The compensation of charge may limit the extent of this substitution.

In carbonate-rich systems Tc(IV) may also find a host in calcite-aragonite CaCO_3 or siderite FeCO_3 phases [62, 63]. Recent work indicates that Tc(IV) may be sequestered in systems that are crystallizing siderite, but the exact location of Tc(IV) has yet to be identified. Calcite has the capacity to sequester a wide variety of cations (e.g., divalent Mg, Sr, Ba, Fe, Cd, Mn, Zn) [64], but not through equilibrium partitioning [65]. Calcite and aragonite have also been identified as hosts for U(IV). Although the size difference between U(IV) and Tc(IV) are quite different (103 vs. 78.5 pm in octahedral coordination), the smaller size of Tc(IV) may allow for more favorable partitioning of Tc(IV). Partitioning of Tc(IV) or U(IV) into the carbonate structure may take place via the coupled substitution:



where M^{4+} represents U(IV) or Tc(IV). This possibility has yet to be evaluated in a rigorous way and warrants further investigation.

Table III. List of Cationic Radii of the VI, VII, and VIII B Block Elements in picometers (pm). The coordination number refers to the number of associated ligands and LS and HS stand for “low spin” and “high spin” configurations, respectively. Data from [60].

Element	Cation	Coordination Number	Radii (pm)
Iron	Fe^{2+}	6, LS	75
		6, HS	92
	Fe^{3+}	6, LS	69
		6, HS	78.5
Chromium	Cr^{3+}	6	75.5
	Cr^{4+}	4	55
	Cr^{6+}	6	69
Manganese	Mn^{2+}	6, LS	80
		6, HS	90
	Mn^{3+}	6, LS	72
		6, HS	78.5
	Mn^{4+}	4	53
		6	67
Mn^{7+}	4	39	
	6	60	
Molybdenum	Mo^{4+}	6	79
	Mo^{6+}	4	55
		6	73
Osmium	Os^{4+}	6	77
	Os^{6+}	6	68.5

Rhenium	Re ⁴⁺	6	77
	Re ⁷⁺	4	52
		6	67
Ruthenium	Ru ⁴⁺	6	76
	Ru ⁷⁺	4	52
Technetium	Tc ⁴⁺	6	78.5
	Tc ⁷⁺	4	51
		6	70

In summary, the mobility of technetium in the environment may be controlled by sequestration into crystalline phases, including ferrihydrite, goethite, siderite, aragonite or calcite. If such harboring by a solid phase takes place, then the mobility of Tc may depend on the stability of the host phase and not necessarily upon the re-oxidation kinetics.

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