

## THE BIOGEOCHEMISTRY OF TECHNETIUM: A REVIEW OF THE BEHAVIOR OF AN ARTIFICIAL ELEMENT IN THE NATURAL ENVIRONMENT

JONATHAN P. ICENHOWER<sup>\*,\*\*†</sup>, NIKOLLA P. QAFOKU<sup>\*</sup>, JOHN M. ZACHARA<sup>\*</sup>,  
and WAYNE J. MARTIN<sup>\*</sup>

**ABSTRACT.** Interest in the chemistry of technetium has only increased since its discovery in 1937, mainly because of the large and growing inventory of  $^{99}\text{Tc}$  generated during fission of  $^{235}\text{U}$ , its environmental mobility in oxidizing conditions, and its potential radiotoxicity. For every ton of enriched uranium fuel (3%  $^{235}\text{U}$ ) that is consumed at a typical burn-up rate, nearly 1 kg of  $^{99}\text{Tc}$  is generated. Thus, the mass of  $^{99}\text{Tc}$  produced since 1993 has nearly quadrupled, and the pace of generation will likely increase if more emphasis is placed on nuclear power to slow the accumulation of atmospheric greenhouse gases. In order to gain a comprehensive understanding of the interaction of  $^{99}\text{Tc}$  and the natural environment, we review the sources of  $^{99}\text{Tc}$  in the nuclear fuel cycle and its biogeochemical behavior. We include an evaluation of the use of Re as a chemical analog of Tc, as well as a summary of the redox potential, sorption, colloidal behavior, and interaction of humic substances with Tc, and the potential for re-oxidation and remobilization of Tc(IV). What emerges is a more complicated picture of Tc behavior than that of an easily tractable transition of Tc(VII) to Tc(IV) with consequent immobilization. Reducing conditions (+200 to +100 mV $E_h$ ) and the presence of Fe(II) sorbed onto Fe(III) (oxy)hydroxides will bring the mobile Tc(VII) species to a lower oxidation state and will form the relatively insoluble Tc(IV) $\text{O}_2 \cdot n\text{H}_2\text{O}$ , but even as a solid, equilibrium concentrations of aqueous Tc are nearly a factor of 20 $\times$  above the EPA set drinking water standards. However, sequestration of Tc(IV) into Fe(III)-bearing phases, such as goethite, iron-bearing phyllosilicates and, perhaps, siderite, may ameliorate concerns over the mobility of Tc. A key factor, elucidated through experiment, in retarding the mobility of Tc in the environment is isolation from exposure to oxygen. One way to achieve isolation from oxygen occurs when Tc is locked in a crystallographic position in a solid phase.

### INTRODUCTION

When Perrier and Segrè discovered a new element in 1937 (Perrier and Segrè, 1937a; Perrier and Segrè, 1937b), it is unlikely that they could have foreseen the impact that it would have on environmental chemistry. The new element, which they named technetium, derived from the Greek word “technetos” (τεχνητος) or artificial, was produced synthetically by deuteron activation of molybdenum metal at the Berkeley cyclotron. Technetium turned out to be the lightest element ( $Z = 99$ ) comprised of only unstable isotopes, none of which are long-lived enough to be present from the formation of the Earth, and would merely be a chemical curiosity were it not for its large-scale production during nuclear power generation and atomic weapons manufacturing and testing. Fission of enriched uranium (fuel rods of uranium dioxide that contain  $\sim 3\%$   $^{235}\text{U}$ ) yields several isotopes of technetium, with the heavier ones favored ( $^{99}\text{Tc}$  to  $^{107}\text{Tc}$ ) (Katcoff, 1958; Kotegov and others, 1968), and of these  $^{99}\text{Tc}$  has the highest yield (6.03%). The other high-yield isotopes of technetium have short half-lives (18 min. to  $<60$  s), but  $^{99}\text{Tc}$  has a half-life of  $2.13 \times 10^5$  years, making it the most important technetium isotope in the nuclear fuel cycle (Luykx, 1986) (table 1).

\* Pacific Northwest National Laboratory, P.O. box 999, Richland, Washington, 99352

\*\* Present address: VSI, LLC, 12100 Hiram Clarke Road, Houston, Texas 77045

† Corresponding author: jonathan@vsianalytics.com; (713) 728-9221

TABLE 1

*Yield and half-lives of technetium isotopes produced during fission genesis*

Technetium isotope:	<sup>99</sup> Tc <sup>1</sup>	<sup>101</sup> Tc	<sup>102</sup> Tc	<sup>103</sup> Tc	<sup>104</sup> Tc	<sup>105</sup> Tc	<sup>107</sup> Tc
Yield (%)	6.03	5.6	4.3	3.0	1.8	0.9	0.19
Half-life	2.12×10 <sup>5</sup> yr	14.3 min	4.5 min	50 sec	18 min	7.7 min	<1 min

Notes: 1. <sup>99</sup>Tc decays at 37,800 dpm/μg and a specific activity of 1.7×10<sup>-2</sup> Ci/g.

Estimates of the quantity of <sup>99</sup>Tc that has been released to the environment are variable, but surveys indicate that atmospheric nuclear testing resulted in ~100 to 140 TBq (1 TBq = 10<sup>12</sup> Bq<sup>1</sup>) of <sup>99</sup>Tc released, much of which has subsequently been deposited and incorporated into sediments. An additional 1000 TBq of <sup>99</sup>Tc (1 PBq), or an order of magnitude more than that released by atmospheric tests, has been released through reprocessing of spent fuel (Schulte and Scoppa, 1987). However, this amount is small in comparison to the stock of <sup>99</sup>Tc that is awaiting final disposition. For example, at the Hanford Site, Washington State, alone nearly 1990 kg of <sup>99</sup>Tc (or 1.25 PBq) was produced between 1943 and 1987 (Darab and Smith, 1996). In addition to that which has already been produced, technetium continues to accumulate in large amounts due to active nuclear power generation. According to Jan Leen Kloosterman (Delft University of Technology, the Netherlands), 21 kg of <sup>99</sup>Tc (13.2 TBq) are produced annually in a large 1 GWe reactor. His estimated inventory of <sup>99</sup>Tc produced in 2007 is 15.1 metric tonnes (MT) (Kloosterman, 2008). In 1994, there were ~78 MT of <sup>99</sup>Tc in total. Accordingly, if the 2007 production value is roughly average, then there are ~305 MT (~190 PBq) of <sup>99</sup>Tc today. In other words, the inventory of <sup>99</sup>Tc has nearly quadrupled between 1994 and today (2010) so technetium pollution will continue to be a source of concern well into the future.

Although the inventory of <sup>99</sup>Tc is growing, we would be remiss if we did not point out that considerable effort is being devoted to strategies for transmuting <sup>99</sup>Tc into stable ruthenium isotopes, as discussed by V. F. Peretrakhin and co-workers (for example, Kozar and others, 2002; Tarasov and others, 2007). For example, stable <sup>100</sup>Ru can be produced by <sup>99</sup>Tc neutron capture to form <sup>100</sup>Tc followed by γ-decay with a half-life of 15.8 seconds. Heavier Ru isotopes, as well as those of palladium, can also be produced during successive neutron capture events with or without subsequent radioactive decay (Tarasov and others, 2007). For this strategy to succeed economically, the transmutation process cannot consume more energy than that originally produced through fission. Further, new reactor types, separation and extraction processes, and preparation methods will need to be developed. Progress in realizing these changes can be followed in such papers as Mashkin and others (2002), Ozawa and others (2003), Poineau and others (2008), Poineau and others (2009), Tomlin and others (2007) and Zilberman and others (2007). In sum, the feasibility of <sup>99</sup>Tc transmutation on an industrial scale is far from certain and may not ultimately represent the panacea that it was once pronounced.

When exposed to the atmosphere or any moderately oxidizing environment (>200 mV) technetium is manifested as the pertechnetate anion (<sup>99</sup>TcO<sub>4</sub><sup>-</sup>), which is highly soluble in aqueous solution (~11 mol/L; Boyd, 1978). Even when reduced, Tc(IV) solubility (Tc = 3.08×10<sup>-9</sup> M or ~5200 pCi/L; ~190 Bq/L; Meyer and others, 1991) does not restrict technetium concentrations to below the drinking water

<sup>1</sup> Becquerel = 1 disintegration per second = 2.7×10<sup>-11</sup> Curie. TBq = terabecquerel (10<sup>12</sup>); PBq = petabecquerel (10<sup>15</sup>).

standard of 900 pCi/L (or  $5.3 \times 10^{-10}$  mol/L;  $\sim 33$  Bq/L; EPA, 2002). In a number of settings where production of atomic weapons or waste from nuclear energy is stored or processed, the accidental or approved release of  $^{99}\text{TcO}_4^-$  to the environment has led to widespread contamination of seawater (Aarkrog and others, 1987; Aarkrog and others, 1988; Brown and others, 1999; Lindahl and others, 2003; Dahlggaard and others, 2004; Keith-Roach and Roos, 2004; McCubbin and others, 2006), rivers (Aarkrog and others, 1997; Standring and others, 2002), estuaries (Morris and others, 2000; Burke and others, 2005; Burke and others, 2006; Burke and others, 2010), subsurface pore waters (Serne and others, 2002; Serne and others, 2004; Hartman and others, 2004; Brown and others, 2006; Brown and others, 2007) and the sediments with which they are associated. Because typical sediments in temperate climates possess an overall negative charge at circum-neutral pH conditions, the pertechnetate anion is electrostatically repelled and its travel through the sub-surface is poorly attenuated (Wildung and others, 1974; Wildung and others, 1984; Sheppard and Sheppard, 1986; Kaplan and Serne, 1998). Because of the lack of interaction with sediment particles,  $^{99}\text{Tc}$  has been used as an excellent tracer of oceanic currents (Aarkrog and others, 1987; Aarkrog and others, 1988) and is transported in the subsurface at nearly the same velocity as groundwater (Rudin and others, 1992).

When released to the environment, a number of plants and animals uptake  $^{99}\text{Tc}$  to an appreciable extent (Bonotto and others, 1985; Van Loon and others, 1985; Lembrechts and Desmet, 1989; Brown and others, 1999; Hattink and others, 2000; Hattink and Wolterbeek, 2001; Bennett and Willey, 2003; Thorne, 2003; Oliver and others, 2006) and the biomagnification of  $^{99}\text{Tc}$  in the food chain is an obvious concern. When consumed, however, the biological half-life of  $^{99}\text{Tc}$  is typically short ( $\sim 60$  hours for humans) and, coupled with the low-energy beta decay (294 keV), it is unlikely to pose a significant radiological threat under most conceivable exposure scenarios (EPA, 2008). On the other hand, aspiration of  $^{99}\text{Tc}$  and resultant accumulation in lung tissue, which has a much longer biological excretion half-life, does present a significant risk. For this exposure pathway, inhalation of dust or vapor tainted with  $^{99}\text{Tc}$  could lead to lung cancer and related maladies (EPA, 2008). Therefore, due to its high mobility, high fission yield in nuclear energy production, long half-life, and moderate radiotoxicity,  $^{99}\text{Tc}$  is an element of intense concern for the environment.

This review is divided into sections that discuss the sources of technetium, its distribution in the environment, aspects of its geochemical behavior, and its interaction with microorganisms. All of these topics are discussed with the aim that understanding the chemistry of technetium on a fundamental level is essential to environmental interests. We preface this review by noting that, in the past, a number of excellent reviews have already been published. Colton (1965) and Peacock (1966) published monographs on technetium, and Kotegov and others (1968) provided a cogent summary in the form of a book chapter. Other books on the behavior of technetium include Technetium in the Environment (Desmet and Myttenaere, editors, 1986) and Chemical Thermodynamics of Technetium (Rard and others, 1999), the latter of which provides a comprehensive appraisal thermodynamics of technetium. A year later, Schwochau (2000) completed a book on the radiopharmaceutical aspects of technetium (Technetium: Chemistry and Radiopharmaceutical Applications), which is a response to the widespread use of the isomer (defined below)  $^{99\text{m}}\text{Tc}$  in medical imaging. It is not our intention to merely replicate the information contained in these reviews, but to summarize the salient data and to update the state of knowledge of technetium behavior in the environment.

## SOURCES OF TECHNETIUM IN THE ENVIRONMENT

*Technetium Due to Spontaneous Fission of  $^{238}\text{U}$* 

Nearly all of the technetium in existence today is the result of either neutron or deuteron activation of molybdenum isotopes or from fission of  $^{235}\text{U}$  and  $^{239}\text{Pu}$ . Only very small concentrations of “natural” technetium exists in nature and, because of relatively short half-lives compared to the age of the Earth, no primordial technetium is present today. However, small quantities of technetium can be produced by spontaneous fission processes in  $^{238}\text{U}$ . In one kg of pitchblende ore of sufficient age, there can be  $\sim 2.5 \times 10^{-10}$  g of Tc (or 10.5 disintegrations per minute or 0.175 Bq). With this as a guide, Kenna and Kuroda (1961) were able to demonstrate the first natural occurrence of Tc in a terrestrial sample. The fact that technetium was observed in spectra from relatively young stars outside our solar system (Merrill, 1952) nearly 10 years before its discovery on Earth is testament to its elusive terrestrial distribution.

*Technetium from “Natural Reactors”*

Present day uranium is made up of only  $\sim 0.72$  percent  $^{235}\text{U}$ , but in the past, the proportion of  $^{235}\text{U}$  to  $^{238}\text{U}$  was higher, owing to the relatively shorter half-life of  $^{235}\text{U}$  compared to  $^{238}\text{U}$ . Under the right geochemical conditions and if the geometry of the ore deposit is favorable, then natural fission can induce a nuclear chain reaction.

There have been several localities in which “natural reactors” were known to exist, the most studied of which are the deposits at Oklo, in the central West African country of Gabon (Curtis, 1986; Curtis and others, 1989; Brookins, 1990; Gauthier-Lafaye and others, 1996; Janeczek, 1999). In all, fifteen natural reactors are known to have operated for various durations in the  $\sim 2.0$  Ga uranium deposits. In total, nearly 730 kg of  $^{99}\text{Tc}$  were thought to be produced in the reactors, and today that technetium is represented by  $^{99}\text{Ru}$ , the stable daughter of  $^{99}\text{Tc}$ .

In the Oklo deposits, the principal phase containing the daughter of  $^{99}\text{Tc}$  are metallic grains containing Ru, Rh, Te, As, S, Pb and Pd and bear resemblance to the metallic “epsilon” phases (Ru, Rh, Pd, Mo, and Tc) in spent nuclear fuel (Buck and others, 2004). These observations are consistent with a lack of large-scale migration of  $^{99}\text{Tc}$  after fission genesis, because most of the  $^{99}\text{Ru}$ -bearing “metal aggregates” are within 10 meters of their respective reactor “cores” (Gancarz and others, 1980; Hidaka and others, 1993; Hidaka and others, 1999; Janeczek, 1999). The apparent lack of mobility of  $^{99}\text{Tc}$  in this setting has led some investigators to conclude that loss of technetium from spent fuel rods disposed in geologic formations will be unimportant, since so little mobility was observed in a deposit of  $\sim 2.0$  Ga. This may be somewhat misleading, however, because the Oklo deposits are bounded by organic-rich sediments (Parnell, 1996) that not only impose a reducing oxidation state on the lithologies, but may also provide sorption sites for uranium and other radionuclide elements (Janeczek, 1999). The potential for organic matter (OM) to immobilize Tc will be discussed more fully below.

*Technetium from Nuclear Weapons Testing*

In a nuclear detonation, Tc forms from fission of  $^{235}\text{U}$  or  $^{239}\text{Pu}$ , and by the activation of isotopes of Mo, Nb, and Ru. The predominant form of technetium is  $\text{Tc}_2\text{O}_7$ , which rapidly reacts with water vapor to form pertechnetic acid ( $\text{HTcO}_4$ ). Technetium sorbs onto particles in the atmosphere and settles through precipitation. The concentration of  $^{99}\text{Tc}$  in rainwater has steadily decreased from its peak of 1 pg/L (or 0.017 pCi/L or  $6.3 \times 10^{-4}$  Bq/L; a factor of  $\sim 5300\times$  less than the Drinking Water Standard) in 1963, when atmospheric testing was banned (Schulte and Scoppa, 1987).

TABLE 2

*Half-lives, decay mechanisms, energies of emission, and decay products of the principal industrial and geochemical isotopes of technetium*

Technetium isotope	half-life	decay mechanism	energy (MeV)	decay product
<sup>95m</sup> Tc	61 d	EC	--	<sup>95</sup> Mo
		γ	0.204, 0.582, 0.835	--
		IT	0.0389, e	<sup>95</sup> Tc
<sup>96</sup> Tc	4.3 d	EC	--	<sup>96</sup> Mo
		γ	0.778, 0.849, 0.812	--
<sup>97</sup> Tc	2.6×10 <sup>6</sup> y	EC	--	<sup>97</sup> Mo
<sup>97m</sup> Tc	90 d	IT	0.965, e	<sup>97</sup> Tc
<sup>98</sup> Tc	4.2×10 <sup>6</sup> y	β <sup>-</sup>	0.4	<sup>98</sup> Ru
		γ	0.745, 0.652	--
<sup>99</sup> Tc	2.12×10 <sup>5</sup> y	β <sup>-</sup>	0.294	<sup>99</sup> Ru
<sup>99m</sup> Tc	6.01 h	IT	0.142, 0.002	<sup>99</sup> Tc
		γ	0.14	--

EC = electron capture; IT = isomeric transition; m = metastable isomer; e = electron.

#### *Medical Isotopes of Technetium*

A number of the longer-lived isotopes, such as <sup>95m</sup>Tc and <sup>99m</sup>Tc<sup>2</sup>, have a plethora of research applications, especially in the medical field. Table 2 lists the principal isomers and isotopes of technetium, their half-lives, decay mechanism, the energies of their radiation, and their stable decay products. Most artificially-produced Tc, including <sup>99m</sup>Tc, results from neutron or deuteron bombardment of various isotopes of Mo, and to a lesser extent, Nb and Ru. Even though 150 000 Ci (or 5.6×10<sup>15</sup> Bq = 5.6 PBq) of medical tests are performed with <sup>99m</sup>Tc each year (with the decay product of <sup>99</sup>Tc), medical isotopes represent only a small fraction of <sup>99</sup>Tc (1 Ci <sup>99m</sup>Tc decays to 3 nCi or 110 Bq <sup>99</sup>Tc) that could potentially be released to the environment (Wildung and others, 1979; Jurisson and others, 2004). For example, the average amount of <sup>99</sup>Tc released by the Sellafield, United Kingdom, reprocessing plant to the sea after 1980 is 4.6 TBq/y, which is a factor of 2.8×10<sup>5</sup> more than that released through yearly medical diagnostic testing worldwide.

#### *Technetium in Spent Fuel Rods*

The greatest source of <sup>99</sup>Tc is its artificial production by neutron-induced fission and because the fission yield of <sup>99</sup>Tc is 6.06 percent, one ton of <sup>235</sup>U-enriched fuel (3% enrichment) will produce ~1 kg of <sup>99</sup>Tc at a typical burn up rate (Chen and others, 2000). Similar estimates were provided by Till (Till, 1986). He estimated the amount <sup>99</sup>Tc generation in one reference reactor year (RRY), which is based on irradiation of 40 MT of enriched UO<sub>2</sub> (3.2 wt% <sup>235</sup>U). Other fissile isotopes will also be produced and irradiation of these will contribute to the production of <sup>99</sup>Tc. For example,

<sup>2</sup> The designation “m” refers to the metastable isomer. An isomer possesses a higher energy state in its nucleon than the lower-energy isotope of the same mass and decays to the ground state isomer by means of an isomeric transition. In this case, the isotope <sup>99</sup>Tc is the ground state, and is sometimes designated as “<sup>99g</sup>Tc” in the literature.

thermal neutron-induced fission of  $^{233}\text{U}$  and  $^{239}\text{Pu}$  produces 4.8 percent and 5.9 percent  $^{99}\text{Tc}$ , respectively, and fast neutron fission will yield 6.3 percent  $^{99}\text{Tc}$  from  $^{238}\text{U}$  and 2.7 percent from  $^{232}\text{Th}$ . When normalized on the RRY basis, the amount of  $^{99}\text{Tc}$  produced is between 12 and 15 Ci/MT ( $\sim 400$  and  $500$  GBq/MT), depending on the type of reactor.

Without human intervention, technetium in spent nuclear fuel (SNF) is immobilized in metallic (“epsilon,” “ $\epsilon$ ” or “white”) phases that form in void spaces within fuel rods (Kleykamp, 1985). A detailed analysis of spent fuel shows that very little Tc is sequestered in the  $\text{UO}_2$  lattice or is found in gaps between phases (Buck and others, 2004). Therefore, in order to mobilize technetium, a great deal of uranium dioxide would have to be dissolved to expose the  $\epsilon$ -phases to aqueous solution (Buck and others, 2004). The thermodynamic stability and dissolution behavior of  $\epsilon$ -phases are discussed in Cui and others (2001), Cui and others (2004), Kaye and others (2007), Utsunomiya and Ewing (2006), and Wronkiewicz and others (2002).

#### *Technetium Associated with Reprocessing*

Reprocessing of spent uranium fuel rods to recover  $^{235}\text{U}$ ,  $^{239}\text{Pu}$ , and other fissile elements is the chief means by which Tc becomes part of the waste stream. Technetium has found its way into the environment over the last 40 years principally through the approved or accidental discharge of processing fluids (Schulte and Scoppa, 1987). Three examples of these points of release include Sellafield, United Kingdom, and LaHague, France, reprocessing centers, and the Hanford Site, USA. When “burned” at a rate of 33 000 MWd/MT (mega watt day per metric tonne), spent fuel still contains  $\sim 0.84$  weight percent  $^{235}\text{U}$ . Reprocessing the spent fuel and re-irradiation will produce more  $^{99}\text{Tc}$  as well as other isotopes of Tc whose half-lives are short. Use of chelating agents to separate metals during reprocessing of SNF or to isolate plutonium produced in irradiated uranium targets for atomic weapons production typically results in soluble forms of Tc (Colton, 1965; Lieser and Bauscher, 1987). For every 34 MT of U returned for re-enrichment, there will be a total of 100 Ci ( $\sim 176$  ppm) of Tc. Regulations specify that only 4 ppm  $^{99}\text{Tc}$  can be present in reprocessed fuel (2.3 Ci/RRY or 3.7 TBq/RRY). Thus, the rest of the  $^{99}\text{Tc}$  (or  $\sim 97$  Ci/RRY) must go to the high level waste stream (Till, 1984).

Dissolution of U during reprocessing and fluorination to produce  $\text{U(VI)F}_6$  also produces fluoride complexes of Tc, such as  $\text{Tc(VI)F}_6$  and  $\text{Tc(VII)O}_3\text{F}$ , with the former more abundant than the latter. Although these species are volatile and potentially mobile to the atmosphere, most of the contamination caused by technetium fluorides is due to accidental release into water, where it hydrolyzes and disproportionates into Tc(IV) and Tc(VII). In localities where gaseous diffusion operations occurred, such as Paducah, Kentucky, and Oak Ridge, Tennessee, nearly 97.5 percent  $^{99}\text{Tc}$  was discharged to the environment through aqueous solution and only 2.5 percent by gaseous pathways (Till, 1984).

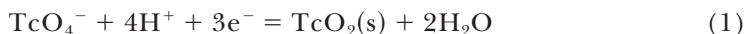
### ENVIRONMENTAL GEOCHEMISTRY

#### *Redox Chemistry*

Because technetium is a redox-sensitive element and its solubility and mobility in subsurface pore waters depends strongly on its oxidation state, a great deal of effort has gone into quantifying stability fields of the various technetium species in terms of  $E_h$ , pH, and oxidation potential. The fundamental measurement that describes the stability of reduced and oxidized technetium is the electromotive force (EMF) of the  $\text{TcO}_4^-/\text{TcO}_2$  couple.

A number of investigators have attempted to measure the EMF of the  $\text{TcO}_4^-/\text{TcO}_2$  couple, including Cobble and others (1953), Cartledge and Smith (1955),

Liebscher and Münze (1975) and Meyer and Arnold (1991). Rard and others (1999) reviewed these studies and pointed out that several measurements were plagued by the presence of oxygen in the reaction cell, the lack of demonstrated achievement of steady-state conditions, or lack of evidence of reversibility. The most reliable data were obtained by Meyer and Arnold (1991), who determined by experiment, the standard potential of the  $\text{TcO}_4^-/\text{TcO}_2$  couple as expressed by:



They carefully minimized the oxygen fugacity by conducting the experiments in a controlled atmosphere argon box. Further, they kept the concentration of  $\text{TcO}_4^-$  low and precipitated  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  by electrodeposition on a platinum mesh. Steady-state values were demonstrated, further lending credence to the measurements. The value of  $E^\circ$  was reported to be  $0.747 \pm 0.004$  V, and this value overlaps with the one advocated by Rard and others (1999), which is  $E = 0.746 \pm 0.012$  V.

While the predominance of reducing conditions is a necessary condition for Tc reduction, the availability and steric distribution of electron donors is far more critical. For example, Cui and Eriksen (1996a) showed that even under conditions in which ferrous iron ( $\text{Fe}^{2+}$ ) activity in solution were relatively high, reduction kinetics of Tc(VII) were sluggish. Therefore, even though the oxidation—reduction reaction:



has a standard free-energy of reaction ( $\Delta G_R^\circ$ ) of 77.06 kJ/mol (Zachara and others, 2007), the kinetics of this reaction are rate-limited. In contrast, when  $\text{Fe}^{2+}$  is sorbed onto other mineral phases, especially iron (oxy)hydroxides, surface-mediated heterogeneous catalysis becomes important and reduction of Tc(VII) to Tc(IV) takes place rapidly above pH 6 (Zachara and others, 2007; Peretyazhko and others, 2008a; Peretyazhko and others, 2008b).

The rapid disproportionation of Tc in valence states between (VII) and (IV) also inhibits the reduction of Tc(VII). Equations like (2) above likely describes the overall, and not the elementary, reaction that takes place. As discussed by Peretyazhko and others (2008a), reduction of Tc(VII) likely occurs through a set of parallel or sequential single electron transfers, but the disproportionation of Tc(VI) and Tc(V):



hinders complete transformation to Tc(IV) unless other factors come into play, such as surface-mediated catalysis. For example, the half-life of Tc(VI) in air is  $\sim 10$  msec (Cotton and Wilkinson, 1980), so it is therefore likely that only Tc(VII) and Tc(IV) species will be found in nature, unless the reduced species forms a complex with an organic ligand.

A diagram illustrating the stability fields of the technetium species as a function of pH and  $E_h$  is displayed in figure 1. Note that nearly the entire field for the species  $\text{TcO}(\text{OH})_2^\circ$  is congruent with the stability field of  $\text{TcO}_2 \cdot 2\text{H}_2\text{O}(\text{am})$ .

#### *Precipitation and Solubility*

Metallic technetium ( $\text{Tc}^0$ ) is 12-fold coordinated and possesses the hcp structure. The average radius of  $\text{Tc}^0$  is 1.358 Å (135.8 pm; Mooney, 1948; Plekhanov and others, 2003) and Tc possesses some chemical similarities with adjacent elements in the Periodic Table, such as Re and Mo. The dioxides  $\text{TcO}_2$ ,  $\text{ReO}_2$  and  $\text{MoO}_2$  all crystallize as the distorted rutile structure (Colton, 1965; Rogers and others, 1969). For  $\text{TcO}_2$  and  $\text{ReO}_2$ , the metal—oxygen bond lengths are nearly identical at 1.98 Å (198 pm;

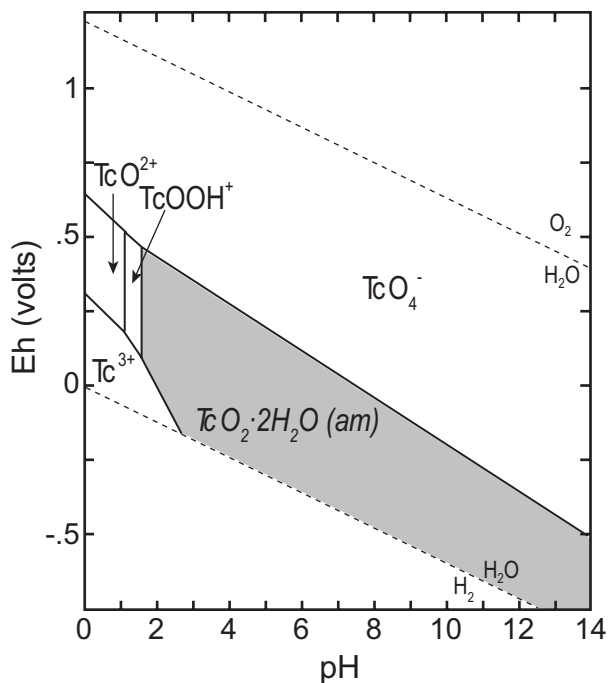


Fig. 1.  $E_h$ -pH diagram for technetium constructed using *Geochemist's Workbench* program. The shaded area represents the region in which the amorphous solid,  $\text{TcO}_2 \cdot 2\text{H}_2\text{O}(\text{am})$  is stable. Concentration of  $\text{Tc} = 10^{-8} \text{ M}$ .

Almahamid and others, 1995) and  $2.00 \text{ \AA}$  (200 pm; Wharton and others, 2000), respectively. The bond lengths for the  $\text{Tc}(\text{IV})\text{—O}$  and  $\text{Re}(\text{IV})\text{—O}$  are longer than those for the corresponding  $\text{Tc}(\text{VII})\text{—O}$  and  $\text{Re}(\text{VII})\text{—O}$  compounds (1.711 and  $1.719 \text{ \AA}$ , or 171.1 and 171.9 pm, respectively; Krebs and Hasse, 1976). The principal difference in structure is that the coordination number for Tc is 6, but is 4 for Re. A divergence of coordination structure is also manifested in the sulfides of  $\text{Tc}(\text{IV})$  and  $\text{Re}(\text{IV})$ ;  $\text{TcS}_2$  possesses an atomic arrangement akin to  $\text{Cd}(\text{OH})_2$ , but  $\text{ReS}_2$  has a layer structure like  $\text{CdCl}_2$  (Wharton and others, 2000). As a consequence of this atomic arrangement,  $\text{Tc}(\text{IV})$  is surrounded by 6 S(-II) anions, 3 between  $2.30$  and  $2.36 \text{ \AA}$  (230 and 236 pm), and the remaining 3 between  $2.41$  and  $2.50 \text{ \AA}$  (241 and 250 pm). On the other hand,  $\text{Re}(\text{IV})$  is surrounded by 3 pairs of S(-II) anions between  $2.30$  to  $2.50 \text{ \AA}$  (230 to 250 pm; Wharton and others, 2000). However, the initial precipitation of  $\text{Tc—O}$  (and likely  $\text{Tc—S}$ ) compounds occurs by the formation of short (monomeric to trimeric) chains that attach to mineral surfaces under most environmentally relevant conditions ( $\text{Tc} < 10^{-5} \text{ M}$ ) (for example, Fredrickson and others, 2009). In hydrous  $\text{Tc}(\text{IV})$  oxides monomers and polymers the atomic arrangement of Tc and O are different from the  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  crystals precipitated biotically or abiotically from strongly supersaturated solutions; octahedra of  $\text{Tc—O}$  have an edge-sharing arrangement and a  $\text{Tc—Tc}$  distance of  $2.59 \text{ \AA}$  (259 pm) in the chains. Thus, the formation of hydrated  $\text{TcO}_2$  compounds with the distorted rutile configuration apparently occurs through a complex rearrangement of these incipient molecular structures.

A number of investigators have undertaken measurements to determine the solubility of  $\text{Tc}(\text{IV})$  in aqueous solution. Solubility determinations were made in a variety of different solutions, including natural and synthetic groundwater. Concentra-



tions of technetium in equilibrium with hydrated  $\text{TcO}_2$  solid compounds vary from  $1 \times 10^{-8}$  M (Kunze and others, 1996; Baston and others, 2002) to  $2.4 \times 10^{-10}$  M (Farrell and others, 1999). The most commonly cited solubility values are those reported by Eriksen and others, 1992 ( $7 \times 10^{-9}$  M), Meyer and others, 1987 ( $2.6 \times 10^{-9}$  M), and Meyer and others, 1991 ( $3.08 \times 10^{-9}$  M). Note that these experiments were conducted over a pH interval in which the solubility is not dependent upon the hydronium ion activity (pH 4-10). Note also that the value of the solubility concentration depends on the nature of the substrate onto which the  $\text{TcO}_2$  material precipitates. In the study of Meyer and others (1991) precipitation of a  $\text{TcO}_2$ -like phase was aided by a substrate of noble metal (platinum).

At high pH values ( $>9.5$ ), there were hints in the data from some studies that the solubility of  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  increased, although a definitive statement could not be made at the time (Eriksen and others, 1992). Recently, the solubility of  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  was determined at high pH values (11.8 to 14.4) by Warwick and others (2007). They reported that above pH 13.5, the solubility of  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  increases linearly due likely to the formation of the  $\text{TcO}(\text{OH})_3^-$  species. The formation constant for the reaction:



is  $\log K_2 = -21.6$  (the value of  $\log K_2$  for the Sn-reduced Tc, which appear to be more robust, is  $-20.7$ ; see Warwick and others, 2007). Because the Nuclear Energy Agency (NEA) database was derived from the work of Eriksen and others (1992), it is clear that the NEA data over-predicts Tc(IV) solubility with pH. The presence of carbonate species in the alkaline pH range can also increase the solubility of  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ ; formation of  $\text{Tc}(\text{OH})_2\text{CO}_3^\circ$ ,  $\text{Tc}(\text{OH})_3\text{CO}_3^-$ ,  $\text{Tc}(\text{OH})(\text{CO}_3)_2^-$ , and  $\text{Tc}(\text{OH})_2(\text{CO}_3)_2^{2-}$  complexes may increase the solubility by a factor of  $\sim 2.5 \times$  (Liu and others, 2007) to  $10 \times$  (Langmuir, 1997).

Although Meyer and others (1991) did not find evidence for an increase in solubility because of the presence of chloride in solution, Hess and others (2004) concluded otherwise. The latter investigators showed that in chloride solutions of  $1 \times 10^{-3}$  to 5 M NaCl, technetium likely forms  $\text{TcCl}_6^{2-}$  and  $\text{TcCl}_4^\circ$  complexes. An increase in the solubility of technetium in chloride solutions was also reported by Lieser and others (1987), although only at relatively low pH values. In general, the data reported by Hess and others (2004) are consistent with those of Lieser and others (1987).

The solubility of Tc(IV) is also complicated by the proclivity of amorphous technetium dioxide [ $\text{TcO}_2(\text{am})$ ] to form more readily than its crystalline analog under most pH conditions. Like  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ , the solubility of  $\text{TcO}_2(\text{am})$  is pH-independent from acidic to alkaline conditions, but is a factor of  $10 \times$  more soluble (Baston and others, 2002). Further,  $\text{TcO}_2$  solubility is strongly influenced by heterogeneous precipitation kinetics on the surfaces or within Fe(II)-bearing phases. Principally, Fe(II) oxide, hydroxide and sulfide phases have been reported to facilitate the precipitation of Tc(IV) compounds. Investigations have shown that  $\text{TcO}_2$  compounds will precipitate on the surfaces of magnetite ( $[\text{Fe}^{2+}\text{Fe}_2^{3+}]_2\text{O}_4$ ) (Cui and Eriksen, 1996b; Farrell and others, 1999), goethite [ $\alpha\text{-FeO}(\text{OH})$ ] (Peretyazhko and others, 2008a), ferrihydrite [ $\text{Fe}(\text{OH})_3$ ] (Zachara and others, 2007), "green rust" [Fe(II)/Fe(III) hydroxides containing sulfate, carbonate or chloride] (Pepper and others, 2003), mackinawite (tetragonal FeS) (Wharton and others, 2000; Livens and others, 2004), pyrrhotite ( $\text{Fe}_7\text{S}_8$ ) and greigite ( $\text{Fe}_3\text{S}_4$ ) (Watson and others, 2001), amorphous FeS (Liu and others, 2008), and pyrite ( $\text{FeS}_2$ ) (Bruggeman and others, 2007). Precipitation also has been reported on solids that are structurally similar to Fe(II) oxides, hydroxides and sulfides, including stibnite ( $\text{As}_2\text{S}_3$ ) (Peretroukhine and others, 2006), corundum ( $\alpha\text{-Al}_2\text{O}_3$ ) and diaspore [ $\alpha\text{-AlO}(\text{OH})$ ] (Peretyazhko and others, 2008b). Silicates

containing Fe(II) have also been found to cause reduction and precipitation of Tc(IV) compounds, including amphibole and chlorite (Cui and Eriksen, 1996b), and phyllosilicates (Fredrickson and others, 2004b; Fredrickson and others, 2009; Jaisi and others, 2009). Precipitation is preceded by reduction of Tc(VII) to Tc(IV) and the rate of reduction is strongly controlled not only by the form of Fe (II) (aqueous, structural, or sorbed), but also the identity of the phase associated with reduced iron (phyllosilicates v. iron oxides and hydroxides). The ability of Fe(II) to reduce Tc(VII) therefore depends on whether Fe(II) is a dissolved species, sorbed onto mineral surfaces, or is manifested in a structural role in the mineral. The relative power of Fe(II) in its various forms to reduce Tc(VII) was given by Peretyazhko and others (2008a) in this order: Fe(II) aqueous  $\sim$  Fe(II) sorbed onto phyllosilicates  $\ll$  structural Fe(II) in phyllosilicates  $\ll$  Fe(II) sorbed onto hematite and goethite. The association of Tc(IV) with structural Fe(II) has a profound influence on the rate of re-oxidation of technetium, and will be discussed below.

### Sorption

Sorption relates the quantity of a chemical species associated with solid components of soil to its concentration in the contacting solution. Partitioning between solids and solution is generally assumed to take 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). Partitioning is typically expressed as an empirical distribution coefficient,  $K_D$ :

$$K_D = [(C_{\text{initial}} - C_{\text{final}})V_{\text{initial}}/M_{\text{sed}}]/C_{\text{final}} \quad (6)$$

in which  $C_{\text{initial}}$  is the beginning concentration of Tc in solution,  $C_{\text{final}}$  is the concentration of Tc at the end of the experiment,  $V_{\text{initial}}$  is the beginning volume of water before soil is added, and  $M_{\text{sed}}$  is the mass of sediment added.

The simple model of sorption described above is probably inadequate for making long-term predictions of aqueous Tc behavior in the subsurface. Sophisticated models describing sorption of anionic complexes to mineral surfaces have appeared in the literature (for example, Dzombak and Morel, 1990) and this subject, by itself, deserves a comprehensive overview. However, a correct mechanistic model is difficult to construct for technetium, for the following reasons. In oxidizing systems, where pertechnetate is the dominant species, there is virtually no sorption between dissolved  $\text{TcO}_4^-$  and typical geologic materials, as discussed below. Accordingly, there is no interaction between pertechnetate and a solid surface that can be measured (equation 6 is undefined). On the other hand, when Tc(VII) is reduced to Tc(IV), the concentration of technetium is well above that of saturation, and surface precipitates and colloids, rather than an aqueous complex, form. Unfortunately, concentrations of Tc(IV) below the saturation value ( $10^{-8}$  to  $10^{-9}$  M) are poorly determined, even when measured by high-energy synchrotron radiation, because the limit of quantification by Extended X-Ray Fine Structure (EXAFS) analysis ( $10^{-8}$  M), is on the same order as the solubility.

As discussed above, results of partitioning experiments have demonstrated that pertechnetate sorbs weakly onto solid phases. For example, Wildung and others (1974) 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. Sheppard and Sheppard (1986) reported small values of  $K_D$  ( $<0.005$  mL/g) measured on soils in lysimeter tests. El-Wear and others (1992) measured  $K_D$  values of pertechnetate on a variety of geologic materials and reported values of  $\leq 2$  mL/g. These results reflect the electrostatic repulsion between the negatively-charged pertechnetate anion ( $\text{TcO}_4^-$ ) and the

negative surface charge carried by sedimentary materials in temperate climates at near-neutral pH values. Kaplan and Serne (1998) 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 the 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 6).

Partition coefficient values for Tc(IV) tend to be larger than those measured for Tc(VII). For example, Baston and others (2002) report  $K_D$  values of 0.8 to 1.8 mL/g for experiments with low  $E_h$  values ( $-230$  mV), well below the threshold of Tc(VII) reduction. Because of the low solubility of amorphous compared to crystalline Tc compounds, experiments carried out under reducing conditions typically contain Tc concentrations that exceed the solubility limit. Lower Tc concentrations could be used, but this imposes heavy analytical challenges to experiments, typically precluding this option. Some of these analytical challenges were overcome by Gu and Ruan (2007), who used a Surface-Enhanced Raman Spectroscopy (SERS) technique. Low concentrations of Tc(IV) (aq) can be detected by Raman spectroscopy when technetium sorbs onto nanoparticles of gold that have had their surfaces modified with positively-charged dimethylamine functional groups. The gold particles enhance the Raman signal such that concentrations as low as  $10^{-7}$  M Tc can be detected and the valence state determined. It is likely that future refinements of this technique will result in much lower detection thresholds.

Another technique for determining Tc behavior at very low concentrations involves gamma-camera imaging of  $^{99m}\text{Tc}$ . As discussed in a previous section (*Medical Isotopes of Technetium*),  $^{99m}\text{Tc}$  decays to  $^{99}\text{Tc}$  via an isomeric transition and emits a gamma ray whose energy (140 KeV) is easily detected (see also table 2). Picomolar concentrations of Tc ( $1 \times 10^{-12}$  M) can thus be quantified. In the studies conducted by Lear and others (2010) and Burke and others (2010), 10 MBq of  $^{99m}\text{Tc}$ -spiked solutions were added to bottles containing estuarine sediments that were either oxidic or were reduced by naturally occurring microorganisms (sulfate reduction). Imaging of the bottles using a gamma-camera showed that for reducing conditions, Tc was associated with the sediments, but the oxidizing experiments revealed that Tc was evenly distributed in the solution and was thus likely manifested as the pertechnetate anion. Note that the concentration of Tc in these experiments was well below that required for precipitation (Tc =  $3.08 \times 10^{-9}$  M or  $\sim 5200$  pCi/L;  $\sim 190$  Bq/L; Meyer and others, 1991), so sorption to particles is an important mechanism for immobilizing Tc in reducing environments. This technique could be used with other isotopes and isomers of technetium. For example,  $^{95m}\text{Tc}$  has a much longer half-life than  $^{99m}\text{Tc}$  (61 days versus 6 hours) and decay of  $^{95m}\text{Tc}$  involves emission of a 204 keV gamma ray. Currently,  $^{95m}\text{Tc}$  is commercially available and perhaps future experiments will elucidate the behavior of Tc partitioning more clearly.

In contrast to the fairly coherent pattern of Tc distribution discussed above, there are several cases where the behaviors of Tc runs counter to expectation. Zhang and others (2000) conducted a series of experiments with aluminum-bearing solids [boehmite, Al-(oxy)hydroxide gels, and simulated tank wastes] and Tc and Re (the non-radioactive surrogate for Tc). Measured  $K_D$  values vary from 5 to 105 mL/g, depending on nitrate concentration, solution pH, and identity of the solid. In boehmite [ $\text{AlO}(\text{OH})$ ]

suspensions, the highest  $K_D$  values were measured in pH = 5 solutions with low nitrate concentrations. Competition between nitrate and perrhenate sorption was fairly strong; increasing activities of nitrate caused a decrease in perrhenate sorption, but in a non-linear fashion (higher activities of nitrate had a small effect on  $K_D$  values). High  $K_D$  values were also found for aluminum-rich gels (21 to 111 mL/g). This might be an important scenario describing nuclear waste tanks leaking into the environment; the alkaline solutions (as at the Hanford Site, Washington State) may partially dissolve aluminum-bearing phases resulting in the formation of amorphous Al-(oxy)hydroxides that sequester Tc. Similar findings were reported by Luo and others (2009), who found that Tc (and U) could be immobilized by Al-(oxy)hydroxides in low pH (<5) and low carbonate systems.

### *Colloids*

In experiments with relatively high concentrations of technetium ( $>10^{-5}$  M Tc), several investigators have reported formation of colloids of technetium at moderately acidic (pH 4) conditions (Maes and others, 2004). Other investigators have reported the presence of Tc colloids in alkaline media containing high concentrations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  (Vichot and others, 2002). In these experiments, in which technetium was reduced to Tc(IV), the formation of colloidal particles increased the apparent solubility of hydrated  $\text{TcO}_2(\text{s})$  by a factor of 100 $\times$ . The structure of the colloid particles was revealed by EXAFS to be one-dimensional chains of Tc(IV) in octahedral coordination that connect through edge-sharing of the polyhedra (Vichot and others, 2002). The Tc—Tc distance is 2.53 Å (253 pm), and the Tc—O bond lengths alternate between short (1.80 Å = 180 pm) and long (1.98 Å = 198 pm). Double bonds between Tc and O are excluded, because a double bond would have a bond length of 1.63 to 1.64 Å (163–164 pm). The single bond and chain-like structure is similar to dimers  $[(\text{H}_2\text{EDTA})_2\text{Tc}_2(\mu\text{—O})_2]$  synthesized in the presence of EDTA (Bürgi and others, 1981). In these molecules, Tc(IV) are arranged in octahedral coordination that connect to proximate octahedrons through edge-sharing (as described above), rather than by direct metal—metal bonding. Experiments by Poineau and others (2006) at acidic (pH = 0 to 1.5) and saline conditions also yielded dimers with the  $[\text{Tc}_2(\mu\text{—O})_2]^{4+}$  structure, but the Tc(IV) are coordinated mainly by chloride ions, such as  $\text{Tc}_2\text{OCl}_{10}^{4-}$ . Sekine and others (2002) and Sekine and others (2004) showed that colloids of Tc will condense from pertechnetate solutions exposed to radiolysis at acid to near-neutral pH values. Radiolysis caused reduction of Tc(VII) and formation of Tc(IV) polymers and colloids, first as Tc(IV), then as  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  nanoparticles as the solution pH increased. On the other end of the pH scale, Lukens and others (2002) also showed that radiolysis of alkaline pertechnetate solutions can produce polymers similar to the  $(\text{H}_2\text{EDTA})_2\text{Tc}_2(\mu\text{—O})_2$  structure. Because of the tendency for colloids of Tc to form at concentrations above saturation over a wide range of pH conditions, it is best to approach solubility measurements from undersaturated conditions.

### *Interaction with Organic Matter*

A number of investigators have reported that Tc is less mobile in soils containing natural solid organic matter (OM) (Stalmans and others, 1986; Van Loon and others, 1986; Wolfrumm and Bunzl, 1986; Bors and others, 1999). These studies proposed that the presence of solid OM provides “sites” onto which technetium can bind, thereby restricting its mobility. Immobilization of Tc by OM appears to be very strong; addition of complexing agents, such as EDTA and DTPA, results in only minor re-solubilization of technetium (Stalmans and others, 1986). This same study proposed that particularly strong bonds between Tc(IV) and humic acids occur on hydroxyl sites that are adjacent to carboxylic groups.

It was not clear from these earlier studies, however, what the mechanism for attachment of Tc to solid OM entailed. More recent work (Geraedts and others, 2002; Maes and others, 2004; Geraedts and Maes, 2008) has shown that Tc(IV) precipitates as short chains of Tc—O—Tc at the surfaces of minerals, and these polymeric chains bear little resemblance to the hydrous TcO<sub>2</sub>(s) precipitate that is manifested as the distorted rutile structure (Rogers and others, 1969). EXAFS measurements (Maes and others, 2004) reveal that the polymers are manifested as edge-shared Tc(IV) octahedra with water in the *trans* position, and that this form is similar or identical to precipitates in other settings, such as alkaline (Lukens and others, 2002) and NaCl/NaSO<sub>4</sub> solutions (Vichot and others, 2002). Thus far, modeling of EXAFS data is inconsistent with carbon as a nearest neighbor to Tc; only bridging oxygen atoms or oxygen from water molecules can be successfully modeled (for example, Maes and others, 2004). Further, chromatographic data have not yielded evidence for strong Tc—C bonds (Maset and others, 2006). Therefore, the precipitation of short, hydrated Tc—O—Tc chains appears to be a general rule, and may serve as a precursor to TcO<sub>2</sub> · nH<sub>2</sub>O formation. The small, uncharged particles that attach themselves to primary mineral surfaces (“hydrophobic sorption”; Maes and others, 2004) appear to be relatively resistant to re-oxidation early on, but over time are susceptible to oxidation and mobilization (for example, Fredrickson and others, 2009).

In contrast to the behavior of Tc(IV) with *solid* OM, the solubility and, therefore, the mobility of Tc(IV) may be increased due to complexation with *dissolved* OM. Because of the widespread occurrence of humic acids (HA) in natural groundwaters, investigators have focused on the effects that these substances exert on the chemistry of dissolved reduced technetium [principally Tc(IV)O(OH)<sub>2</sub><sup>o</sup>]. These studies (Sekine and others, 1993; Sekine and others, 1997; Rößler and others, 2000; Tkac and others, 2000; Geraedts and others, 2002; Maes and others, 2004; Maset and others, 2006; and Geraedts and Maes, 2008) revealed an increase in solubility of Tc(IV) solids by up to a factor of 10<sup>4</sup>× with increases in natural dissolved HA, indicating the importance of some types of OM on the geochemical behavior of technetium. Evidence consistent with the hypothesis of strong complexation includes partition coefficients for Tc(IV) between magnetite and solution that decrease linearly with increasing concentrations of dissolved HA (Bruggeman and others, 2007; Geraedts and Maes, 2008). Geraedts and others (2002) and Maes and others (2004) also showed that reduction rates of Tc(VII) to Tc(IV) are inhibited by the presence of dissolved OM. Although technetium in a number of lower valence states (0 through V) are stabilized by organic complexants (Schwochau, 2000), mobility of Tc(IV) does not appear to be enhanced in the presence of anthropogenic organic compounds commonly co-disposed with technetium. Maset and others (2006) reported no increase in Tc(IV) solubility or mobility when contacted by ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), or isosaccharinic acid (ISA). A lack of interaction between EDTA and Tc(IV) was also reported by Begg and others (2007) (see also review by Keith-Roach, 2008). Further, Liu and others (2009) reported that the presence of low molecular weight organic acids (LMWOAs) and EDTA did not inhibit reactions between technetium and sulfide to precipitate Tc<sub>2</sub>S<sub>7</sub>.

Contrary to the studies on reduced Tc, investigators have not found a quantifiable difference in mobility of oxidized technetium (that is, pertechnetate, TcO<sub>4</sub><sup>-</sup>) associated with relatively high concentrations of OM in soils. For example, Kaplan (2003) conducted an experimental study to determine the pH-dependent *K<sub>D</sub>* values of pertechnetate and iodine on two different soils, one a wetland sample with a relatively high OM content, the other an upland soil with virtually no OM. The two soil samples exhibited similar particle size distributions, mineralogy, and pH values. Further, the soil samples had relatively similar cation exchange capacities (CECs) and Point-of-Zero-

Salt Effect (PZSE or  $\text{pH}_o$ ). The results of the tests showed that Tc(VII) partitioning was weak with low or even negative  $K_D$  values. Negative  $K_D$  values indicate that anions are being electrostatically repulsed (Kaplan and Serne, 1998), as discussed in the previous section on sorption. Therefore, the presence of OM in the wetland soil had no effect on Tc partitioning. The lack of interaction between  $\text{Tc(VII)O}_4^-$  and OM in natural soils was also discussed by Maset and others (2006). It appears, therefore, that a condition for immobilization of Tc is that it must first be reduced; it does not appear that OM directly causes reduction and then precipitation of Tc.

#### *Technetium in the Marine Environment*

In the Atlantic Ocean, the principal source of technetium contamination has come from releases from reprocessing plants in the United Kingdom (Sellafield) and France (La Hague), with the former discharging more than the latter (102 versus 42 TBq in the years 1982-1991; Brown and others, 1999). In the case of the Sellafield plant, two pronounced spikes in concentration of released  $^{99}\text{Tc}$  occurred in 1978 and from 1994 to 2002. The higher-than-normal concentrations of Tc can be traced in the Irish and North Seas and, looking at the positive side of things, have proven to be an unexpected boon to scientists studying sea currents (Aarkrog and others, 1988; Smith and others, 2001; Lindahl and others, 2003; Dahlgard and others, 2004) and contaminant redistribution in marine sediments (Keith-Roach and Roos, 2004; McCubbin and others, 2006).

As in the case of other redox-sensitive metals, the distribution of Tc in seawater depends on the activity of  $\text{O}_2$  with depth. In near-surface waters, conditions are oxidizing and technetium remains in the pertechnetate form. Attachment of  $\text{TcO}_4^-$  to suspended material in the water column appears to be limited, unless the material contains organic matter. For example, distribution coefficients of  $<1$  mL/g have been reported for pertechnetate in seawater and suspended particles (McCubbin and others, 2006). In near-shore sediments, anoxic and reducing environments are common (likely due to the agency of reducing bacteria) and rapid reduction of Tc(VII) to Tc(IV) occurs (Keith-Roach and Roos, 2004). Following deposition, incorporation of Tc in marine sediments, by binding to sediments or by co-precipitating with iron monosulfides, becomes strong but a fraction remains reversibly bound. Typical  $K_D$  values for Tc partitioning between marine sediments and seawater are between  $\sim 10^2$  and  $10^3$  (Harvey and Kershaw, 1984; IAEA, 2004; McCubbin and others, 2006), which are about an order of magnitude larger than those obtained from laboratory experiments. Investigators attribute this discrepancy to non-equilibrium binding between sedimentary particles and Tc(IV) in seawater, with the implication that  $K_D$  values are kinetically governed and that the greatest source of Tc to seawater in the future is the re-oxidation and re-dissolution of Tc. Thus, it is likely that Tc will be a persistent contaminant in the Atlantic and in the Irish Sea for years to come.

The uptake of technetium into marine biota and its biomagnifications has been a topic of considerable importance and a number of investigators have pursued it with vigor (for example, Brown and others, 1999; Smith and others, 2001; Lindahl and others, 2003). The level of Tc contaminant uptake can be appraised through the harvest and analysis of  $^{99}\text{Tc}$  in brown seaweed (*Fucus vesiculosus* and *Fucus serratus*). Not only were concentration factors high in these species of seaweed, they were also reported to be high in a variety of crustaceans, shell fish, and fish. However, Smith and others (2001) showed that the maximum dose imparted to consumers from animals harvested from the Irish Sea were 0.061 to 0.24  $\mu\text{Sv}$ , or  $<0.01$  percent of the total annual average dose, 90 percent of which is natural background radiation. Therefore, exposure to  $^{99}\text{Tc}$  by ingestion of seafood, even in the presently most heavily contaminated areas, is not considered to be a threat to human health.

TABLE 3  
Comparison of properties of Tc and Re

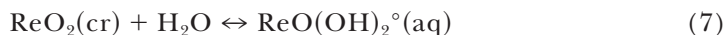
M = Tc or Re	Tc	Re
Principal oxidation states:	IV, VII	III, IV, VII
Cation (VII) size (pm)	51 <sup>a</sup>	52 <sup>a</sup>
Cation (IV) size (pm)	78.5 <sup>a</sup>	77 <sup>a</sup>
M(VII)—O Å	1.702 <sup>f</sup>	1.719 <sup>j</sup>
M(IV)—O Å	1.98 <sup>b</sup>	2.00 <sup>i</sup>
M(IV)—S Å	2.33 <sup>e</sup>	2.36 <sup>c</sup>
E <sub>hyd</sub> (eV)	-2.4 <sup>g</sup>	-2.5 <sup>g</sup>
Binding energy (eV)	-388.7 <sup>g</sup>	-371.1 <sup>g</sup>
MO <sub>2</sub> /MO <sub>4</sub> <sup>-</sup> (V)	-0.747 <sup>d</sup>	-0.510 <sup>h</sup>

Sources: a. (Shannon, 1976), b. (Almahamid and others, 1995), c. (Murray and others, 1994), d. (Meyer and Arnold, 1991), e. (Lamfers and others, 1996), f. (Faggiani and others, 1980), g. (Anderson and others, 2007), h. (Kotegov and others, 1968), i. (Wharton and others, 2000), j. (Krebs and Hasse, 1976).

USE OF Re AS A GEOCHEMICAL ANALOG OF Tc

Due to the constraints on working with radioisotopes, the chemical analogue rhenium is typically substituted for technetium in experiments. Both Re and Tc are manifested as septavalent cations (7+) of similar size that combine with oxygen to form water soluble anionic species: the pertechnetate (TcO<sub>4</sub><sup>-</sup>) and perrhenate (ReO<sub>4</sub><sup>-</sup>) species. Despite the similarities in cationic size and other chemical properties (table 3), there may be some reasons that use of Re as an analog of Tc in experiments or tracer studies might yield incorrect conclusions, as outlined below.

At alkaline pH conditions (>9) and low concentrations (Re <10<sup>-6</sup> mol/L), the species [Re(IV)O(OH)<sub>3</sub>]<sup>-</sup> forms (Kim and Boulègue, 2003), which is analogous to formation of [Tc(IV)O(OH)<sub>3</sub>]<sup>-</sup> under similar conditions (Eriksen and others, 1992). However, dissolution of ReO<sub>2</sub> showed little dependence on pH (Lieser and others, 1987), and the presence of oxygen did not appear to affect its solubility. The lack of dependence of dissolution on oxygen partial pressure makes the behavior of ReO<sub>2</sub> different from that of TcO<sub>2</sub>; (Lieser and others, 1987) reported that TcO<sub>2</sub> solubility is strongly dependent upon the presence of oxygen. Dissolution in neutral pH regimes releases neutral species of Re, just as in the case of technetium:



Re(III) compounds, such as Re<sub>2</sub>O<sub>3</sub>, ReO<sub>3</sub> are more stable (Kim and Boulègue, 2003) than Tc(III) solids, as indicated by figure 2, which was taken from Darab and Smith (1996). This figure indicates stability fields for ReO<sub>3</sub> and Re<sub>2</sub>O<sub>3</sub> in acidic to neutral waters. Accordingly, ReO<sub>4</sub><sup>-</sup> is mainly in equilibrium with ReO<sub>3</sub> and Re<sub>2</sub>O<sub>3</sub> whereas TcO<sub>4</sub><sup>-</sup> is principally in equilibrium with TcO<sub>2</sub>(s) and [TcO(OH)<sub>2</sub>]<sup>°</sup> over a large pH interval. Thus, oxidative dissolution of Re(III) solids in aqueous solution does not result in the precipitation of ReO<sub>2</sub>(s), although concentrations of aqueous Re are high enough to saturate in this phase. Instead, Kim and Boulègue (2003) argue that oxidation of Re(III) results in the formation of Re(IV) polymers or colloids that forestalls the precipitation of ReO<sub>2</sub>(s). This characteristic is similar (but not identical) to that of technetium, in which dimers [TcO(OH)<sub>2</sub>]<sub>2</sub><sup>°</sup> form at concentrations greater than 10<sup>-5</sup> mol/L (Maes and others, 2004). Note, however, that the stability field for ReO<sub>2</sub> is much smaller than that of TcO<sub>2</sub> (fig. 2). The stability of ReO<sub>2</sub>(cr) in anoxic waters is reflected in its low solubility value of 4×10<sup>-7</sup>–10<sup>-6</sup> mol/L. This compares well

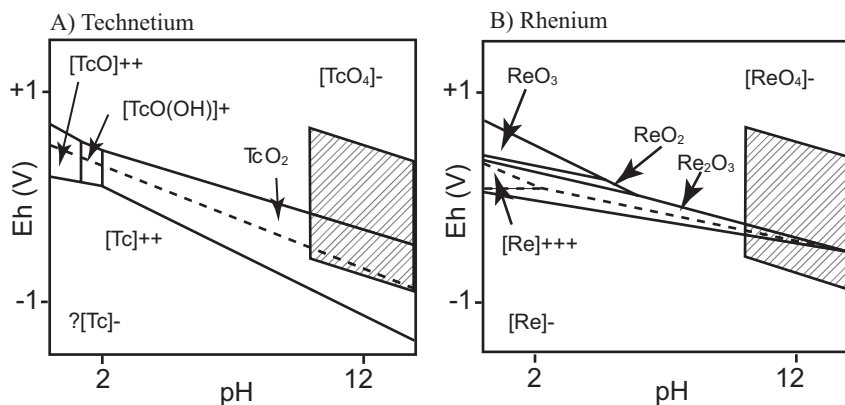


Fig. 2.  $E_h$ -pH diagrams for (A) technetium and (B) rhenium. Note that the stability field of  $TcO_2$  is much larger than that of  $ReO_2$  and that there is no stability field for Tc(III) species. The shaded boxes represent the  $E_h$ -pH conditions expected in the tank waste environment. From (Darab and Smith, 1996).

with the solubility values of  $TcO_2(cr)$  ( $10^{-8}$ - $10^{-6}$  mol/L). Free energies of formation of aqueous species of Tc and that of  $ReO_4^-$  (aq) are listed in table 4 and thermodynamic data for the formation of Tc, Re, and Ru solids in table 5.

Other studies demonstrated that substantial differences between Tc and Re behavior can exist for conditions in which electron transfers become important. A modeling investigation contrasting Tc and Re sorption onto iron and sulfur-bearing minerals was carried out by Anderson and others (2007). The modeling exercise showed that on galena terrace surfaces,  $TcO_4^-$  and  $ReO_4^-$  sorption was similar. On the

TABLE 4

*Free energies of formation of aqueous technetium, perrhenate, and perruthenate species*

Aqueous Species	$\Delta_f G^\circ$ (kcal/mol)	$\Delta_f G^\circ$ (kJ/mol)
$TcO^{2+}$	-24.04 <sup>a</sup>	-100.6 <sup>a</sup>
$TcOOH^+$	-79.18 <sup>a</sup>	-331.3 <sup>a</sup>
$TcO(OH)_2^\circ$	-132.89 <sup>a</sup>	-556.0 <sup>a</sup>
$[TcO(OH)_2^\circ]_2$	-274.67 <sup>a</sup>	-1149.2 <sup>a</sup>
$TcO_4^-$	-152.34 <sup>a</sup>	-637.4 <sup>a</sup>
$TcO(OH)_3^-$	-174.08 <sup>b</sup>	-728.4 <sup>b</sup>
$Tc(OH)_2CO_3^\circ$	-228.04 <sup>b</sup>	-954.1 <sup>b</sup>
$Tc(OH)_3CO_3^-$	-273.45 <sup>b</sup>	-1144.1 <sup>b</sup>
$Tc(OH)(CO_3)_2^-$	-324 <sup>c</sup>	-1355 <sup>c</sup>
$Tc(OH)_2(CO_3)_2^{3-}$	-354 <sup>c</sup>	-1483 <sup>c</sup>
$TcOSO_4^\circ$	-205.27 <sup>b</sup>	-858.9 <sup>b</sup>
$ReO_4^-$	-166.0 <sup>d</sup>	-694.5 <sup>d</sup>
$RuO_4^-$	-59.8 <sup>e</sup>	-250.1 <sup>e</sup>

Sources: a. (Rard and others, 1999), b. (Langmuir, 1997), c. (Lemire and Jobe, 1996), d. (Wagman and others, 1982), e. (Rard, 1985).



TABLE 5  
Thermodynamic data for solids of Tc, Re, and Ru

Compound	$\Delta_f H^\circ$ kJ/mol	$\Delta_f G^\circ$ kJ/mol	$S^\circ$ J/mol/K
TcO <sub>2</sub>	-457.8±11.7 <sup>a</sup>	-401.8±11.8 <sup>a</sup>	50.0±4 <sup>a</sup>
TcO <sub>2</sub> ·1.6H <sub>2</sub> O	--	-758.5±8.4 <sup>a</sup>	--
TcO <sub>2</sub> ·2H <sub>2</sub> O	--	-837.3 <sup>b</sup>	--
Tc <sub>2</sub> O <sub>7</sub>	-1126.5±14.9 <sup>a</sup>	-950.3±15.5 <sup>a</sup>	192.0±15 <sup>a</sup>
Tc <sub>2</sub> O <sub>7</sub> ·H <sub>2</sub> O	-1414.2±14.9 <sup>a</sup>	-1194.3±15.5 <sup>a</sup>	278.9±72.1 <sup>a</sup>
HTcO <sub>4</sub>	-699.0 <sup>b</sup>	--	--
TcS <sub>2</sub>	-223.8±41.0 <sup>a</sup>	-216.1±42.1 <sup>a</sup>	71.1±31.6 <sup>a</sup>
Tc <sub>2</sub> S <sub>7</sub>	-615.0±57.4 <sup>a</sup>	-580.9±60.4 <sup>a</sup>	175.7±63.2 <sup>a</sup>
ReO <sub>2</sub>	-610.9 <sup>b</sup>	-368 <sup>b</sup>	--
ReO <sub>2</sub> ·2H <sub>2</sub> O	-987 <sup>b</sup>	--	--
ReO <sub>3</sub>	-605 <sup>b</sup>	--	--
Re <sub>2</sub> O <sub>7</sub>	-1241.4 <sup>c</sup>	-1066.9 <sup>c</sup>	207.3 <sup>c</sup>
HReO <sub>4</sub>	-762.3 <sup>b</sup>	-656.4 <sup>b</sup>	158.2 <sup>b</sup>
ReS <sub>2</sub>	-180.0 <sup>b</sup>	--	--
Re <sub>2</sub> S <sub>7</sub>	-451.5 <sup>c</sup>	--	--
RuO <sub>2</sub>	-307.2±7.8 <sup>d</sup>	-253.1±8.2 <sup>d</sup>	52.2 8±7 <sup>d</sup>
RuO <sub>2</sub> ·2H <sub>2</sub> O	--	-691.0±13 <sup>d</sup>	--
RuS <sub>2</sub>	-199.5±1.7 <sup>d</sup>	-188.4±1.7 <sup>d</sup>	55.2±1.7 <sup>d</sup>

Sources: a. (Rard and others, 1999), b. (Wagman and others, 1982), c. (Cotton and Wilkinson, 1980), d. (Rard, 1985).

other hand, TcO<sub>4</sub><sup>-</sup> was reduced on galena near step edges, but ReO<sub>4</sub><sup>-</sup> was not. Part of the difference in behavior between the two elements may be a reflection of their chemical properties, such as their binding energies. The binding energy of TcO<sub>4</sub><sup>-</sup> and ReO<sub>4</sub><sup>-</sup> is -388.7 and -371.1 eV, respectively (table 3) and this difference may be decisive in surface mediated reduction. Krupka and others (2006) found that Re sorbs onto or is co-precipitated with corrosion products, such as goethite [ $\alpha$ -Fe(O)(OH)], lepidocrocite [ $\gamma$ -Fe(O)(OH)], and maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) as Re(VII). This behavior contrasts with that of Tc, in which sorption takes place as Tc(IV), rather than Tc(VII). Because of the low solubility of TcO<sub>2</sub>(s)-type compounds, technetium precipitates or forms a co-precipitate with Fe(III) minerals. Krupka and others (2006) suggest that the standard potential of the Re(VII)/Re(IV) couple is significantly lower than that for Tc(VII)/Tc(IV), which indeed it is. The oxidation potential of the former is -0.510 V, whereas the latter has a value of -0.738 V, according to (Kotegov and others, 1968; table 3) and this difference may prove essential in some experimental settings.

In addition, differences in complexation energies between the chloride species of Re and Tc may render the usefulness of the chemical analogy void. Complexation of Tc with chloride results in a higher solubility (Hess and others, 2004), whereas the chloride complexes of Re results in virtually no difference in solubility, as confirmed experimentally by Xiong and Wood (1999). Therefore, in cases where solutions are chlorine-rich, such as certain tank waste chemistries, Tc should be used in experiments

and use of the analogue element, Re, should be avoided. In addition, complexation of Tc and Re by organic ligands appears to be quite different (Jurisson and Murmann, 1999), and experiments aimed at understanding Tc speciation in organic-bearing waste, for example, should use Tc rather than Re, as demonstrated by Xia and others (2006).

#### BIOGEOCHEMISTRY

##### *Microorganisms in the Environment and Bioreduction*

A major breakthrough in biogeochemistry since the earlier reviews of technetium chemistry was the recognition that microbial activity affects the redox state of radionuclide elements and, thereby, affects their mobility in the environment (see review by Simonoff and others, 2007). Early studies underestimated the importance of microorganisms in governing the oxidation state of Tc (for example, Schulte and Scoppa, 1987). It is now well-known that a wide range of endemic bacteria are able to couple oxidation of  $H_2$  and organic material to metal reduction during anaerobic respiration. One such set of microbes are the dissimilatory metal reducing bacteria (DMRB) (Lovely, 1993; Wildung and others, 2000; Liu and others, 2002) and these are well-represented in aquifer (Anderson and others, 2003), marine (Pignolet and others, 1989), and estuarine (Burke and others, 2005; Burke and others, 2006) sediments. Estimates of the number of microbes present in soil varies, but one estimate states that there are up to  $10^8$  to  $10^9$  bacteria per gram of soil, although only a fraction of these are active at any given time (Henrot, 1989 and references therein). Even in relatively oligotrophic sediments in which the sediments are heavily contaminated by radioactive elements, such as the Hanford Site, Washington State, viable populations of microorganisms have been documented (Fredrickson and others, 2004a), although the size of the population is much smaller than those in more hospitable environments. Stimulating the growth and active anaerobic respiration of environmentally-limited population may be possible if the soil were amended with an electron donor source. Therefore, there is a prospect that the oxidized form of technetium,  $Tc(VII)O_4^-$ , may be reduced to hydrous  $Tc(IV)O_2$ -like solids and the mobility of technetium thus hindered.

Henrot (1989) showed, for example, that water-bearing sediments inoculated with the sulfate-reducing obligate anaerobe, *Desulfovibrio vulgaris* and *Desulfovibrio gigas*, resulted in a loss of technetium from solution. She speculated that during sulfate reduction, biologically-aided precipitation of sulfides of technetium ( $TcS_2$  and  $Tc_2S_7$ ) occurred outside the cell outer membrane. Gram-negative and -positive marine bacteria, *Moraxella* sp. and *Planococcus* sp., respectively, reduced technetium, but only under anaerobic conditions (Pignolet and others, 1989), a finding consistent with that of Henrot (1989). Subsequently, a wide variety of anaerobic microbes have been shown to reduce  $Tc(VII)$ , including *Geobacter metallireducens* (Lloyd and Macaskie, 1996), *Geobacter sulfurreducens* (Lloyd and others, 2000), *Escherichia coli* (Lloyd and others, 1997), *Desulfovibrio desulfuricans* (Lloyd and others, 1999), *Shewanella putrefaciens* (Wildung and others, 2000), *Desulfovibrio fructosovorans* (De Luca and others, 2001), and *Deinococcus radiodurans* (Fredrickson and others, 2000).

Because a number of other terminal electron accepting (TEA) species exist in natural sediments, such as  $Fe(III)$  and  $Mn(III,IV)$ , and nitrate in contaminated aquifers that have a higher reduction potential, reduction of  $Tc(VII)$  typically occurs later in the sequence as progressive anoxia develops (for example, Abdelouas and others, 2002; Fredrickson and others, 2004b; and Istok and others, 2004; Abdelouas and others, 2005; Burke and others, 2005). The biogeochemical mechanisms by which Tc is reduced by direct enzymatic processes are discussed below.

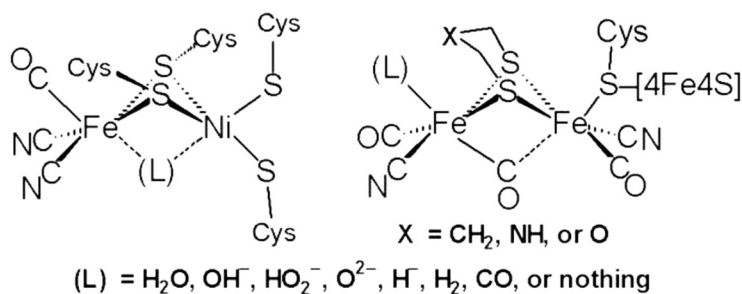


Fig. 3. Structural diagrams of [FeNi] (left) and [FeFe] (right) hydrogenase proteins. The molecular structure was determined through precipitation followed by X-ray diffraction.

#### *Reduction 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 (Lloyd and others, 1997; Lloyd and others, 1999; Lloyd and others, 2000; Wildung and others, 2000; De Luca and others, 2001; Liu and others, 2002). DMRB couple oxidation of H<sub>2</sub> and, to a lesser degree, organic matter to reduction of Tc(VII) via enzymatic electron transfer reactions.

Recent work has centered on understanding the role of a class of hydrogenase enzymes on the metal reduction process (for example, Shi and others, 2006; Shi and others, 2007). In particular, attention has been focused on the sulfur-bridged di-iron and nickel-iron forms (designated as [FeFe] and [FeNi], respectively) (fig. 3). These enzymes catalyze the oxidation of molecular dihydrogen (H<sub>2</sub> oxidation) and reduction of protons (H<sub>2</sub> evolution) that comprises the bi-directional redox reaction of hydrogen. The metal clusters in the [FeFe] and [FeNi] proteins, which consist of Fe and Ni coordinated by carbon monoxide (CO) and cyanide (CN) ligands, are the localities where catalysis takes place. 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 (fig. 4). The close association of Tc 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.

Other lines of evidence strongly indicate that hydrogenase plays a direct role in Tc reduction. Lloyd and others (1999) reported that cells of *Desulfovibrio desulfuricans* poisoned with Cu(II), which deactivates periplasmic, but not cytoplasmic, hydrogenase, were unable to reduce Tc(VII). A similar finding was reported by De Luca and others (2001) for *D. fructosovorans*, and they additionally showed that strains lacking in the [FeNi] hydrogenase operon possessed a strongly diminished ability to reduce Tc(VII).

Intimately involved in redox catalysis are the physiological electron donors or acceptors for hydrogenase, such as ferredoxins, cytochrome c<sub>3</sub>, and cytochrome c<sub>6</sub>. Although De Luca and others (2001) argued that cytochrome c<sub>3</sub>, for example, does not directly reduce technetium, the presence of this enzyme with hydrogenase is considered to be necessary, though not sufficient, for reduction. In contradiction to this evidence, Marshall and others (2008) 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

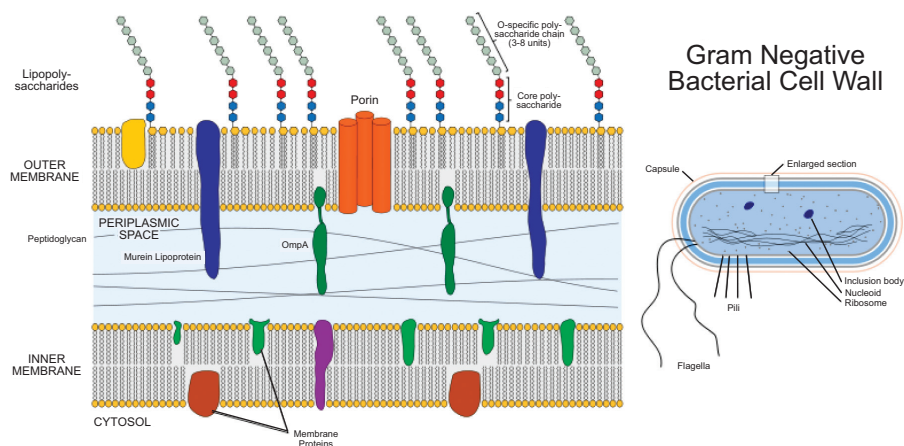


Fig. 4. A cartoon cross-section showing the inner and outer membranes separated by the periplasmic space in a gram-negative bacteria cell wall. Reduction of Tc(VII) occurs through catalysis by hydrogenase and cytochrome enzymes in the periplasm or on the surface of the outer membrane.

and OmcA were oxidized by pertechnetate, thereby providing direct evidence for the electron transfer reaction. It is unclear at this point whether the direct role of OMCs is species-specific to *Shewanella* sp. or if differences in experimental procedures led to different conclusions.

In most of these studies, bio-reduced technetium [Tc(IV)] was manifested as a dark precipitate formed mainly within the periplasmic space and on the exterior surfaces of the cell outer membrane (Lloyd and others, 1997; Lloyd and others, 2000; Wildung and others, 2000). The black Tc(IV) precipitate that was characterized by Selected Area Electron Diffraction (SAED) (Wildung and others, 2000) and Transmission Electron Microscopy (TEM) in experiments with *S. putrefaciens* (Wildung and others, 2000; Liu and others, 2002; Marshall and others, 2008), *G. sulfurreducens* (Lloyd and others, 2000), and *E. coli* (Lloyd and others, 1997) and was shown to be amorphous to nanocrystalline. A number of atom-specific analytical techniques, including Proton-Induced X-ray Emission (PIXE) (Lloyd and others, 1997) and Energy Dispersive X-ray (EDX) (Wildung and others 2000; Lloyd and others, 2000; Abdelouas and others, 2002; Liu and others, 2002; Marshall and others, 2008) analyses, indicate that Tc and O, and not Fe or S, were the major components of the solid. X-ray absorption spectroscopy (XAS) confirmed that the technetium solid was in a reduced form and had Tc—O bond lengths ( $\sim 2.00$  Å) that are characteristic of hydrous Tc(IV)O<sub>2</sub>-like solids, even in systems that contained sulfur (Burke and others, 2005). In some instances, it appears that Tc co-precipitates with iron sulfide phases (Abdelouas and others, 2002). However, even when sulfide minerals form, other investigations have shown that TcO<sub>2</sub>-like bonding environments persist when the sulfide phase is oxidized (Wharton and others, 2000; Livens and others, 2004). These data indicate that hydrated TcO<sub>2</sub> solids are the long-term reservoir of technetium that forms as a result of biological activity.

#### *Reduction by Indirect Biogenic Iron (II) Catalysis*

Several investigators have argued that the very low concentrations of Tc in the environment ( $<1 \times 10^{-8}$  M) makes it unlikely that direct enzymatic reduction by DMRB will occur (Begg and others, 2007). In these cases, an indirect route for

reduction of Tc(VII) is possible when ferric is reduced to ferrous iron due to anaerobic respiration of DMRB. Although not precisely correlated, the ingrowth of Fe(II) in progressively reducing sediments is roughly coincidental with reduction of Tc(VII) (Lloyd and others, 2000; Fredrickson and others, 2004b; Burke and others, 2005; Begg and others, 2007; Zachara and others, 2007; Begg and others, 2008; Peretyazhko and others, 2008a). Note also that DMRB do not need to be active in order for Tc(VII) reduction. Sediments in which anoxia had developed through activity of DMRB were then pasteurized and, when Tc(VII) was added, precipitation of Tc(IV) occurred (for example, Begg and others, 2007; Burke and others, 2010). The explanation is that Fe(II) is present as a sorbed species and, when present on the surface of iron (oxy)hydroxides, is a potent reductant for Tc(VII) in anoxic environments. Many of the findings from these studies have been highlighted elsewhere in this review and will not be repeated.

#### ENVIRONMENTAL APPLICATION

##### *Potential for Remobilization*

As the preceding paragraphs illustrate, the longevity of reduced Tc may be ephemeral when technetium-bearing sediments, soils, or solutions become exposed to oxidizing conditions. Addressing the issue of re-oxidation and remobilization of Tc is extremely pertinent for understanding the mobility of Tc between sources and sinks in the natural environment. It is also an important topic from the standpoint of fashioning immobilization strategies for environments contaminated with Tc. The activity of Tc in solution will depend upon the *crystallinity* of the solid with which it is in equilibrium (that is,  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  crystalline versus amorphous), the pH of solution, the redox state of the system, and the activities of complexing ligands, such as chloride, carbonate, or humic acids. Further, the mobility of technetium is strongly tied to the *form* of reducing agents, such as Fe(II), (aqueous, structural, or sorbed) and the *identity* of the solid with which it is associated (for example, goethite versus phyllosilicates). The following studies aimed at elucidating this important question.

In terrestrial environments impacted by contamination from nuclear test fallout, the Tc incorporated into soils is generally immobile. In shallow soils containing sufficient organic material, respiration by microorganisms results in depletion of oxygen, thereby imposing reducing conditions (for example, Vandecasteele and others, 1989; Tagami and Uchida, 1997; Tagami and Uchida, 1999; Kock-Steindl and Pröhl, 2001; Ishii and others, 2004a; Ishii and others, 2004b; Begg and others, 2007). Formation of Fe(II) (oxy)hydroxides or sulfides, abiotically or through bioprecipitation, will aid in immobilizing Tc(IV). Water-saturated soils also aid in preventing oxidation of Tc; water forms a diffusion barrier for  $\text{O}_2$ . Even in shallow aquifers where the water table surface fluctuates in elevation, re-oxidation of Tc(IV) does not occur (Ashworth and Shaw, 2005).

The situation is quite different for Tc-contaminated plumes in aquifers and vadose zone environments containing scant organic matter or marine and lacustrine sediments subject to changing redox conditions. Van Loon and others (1986) were one of the first to report experimental evidence that suggested rapid re-oxidation of reduced forms of Tc. Subsequent studies, however, paint a more complex picture. Standring and others (2002) reported that Tc-contaminated freshwater sediments retained ~80 percent of their  $^{99}\text{Tc}$  budget when contacted by seawater. The soil is reported to be black and weakly anoxic, which would be expected if Tc was reduced. Selective sequential extractions showed that most of the  $^{99}\text{Tc}$  was extractable by  $\text{H}_2\text{O}_2$ , indicating that technetium is bound in the organic fraction. However, extractions using  $\text{H}_2\text{O}_2$  may not be releasing Tc bound by organic matter; rather, hydrogen peroxide may be

oxidizing and dissolving discrete  $\text{TcO}_2(\text{s})$  crystals (see also discussion in Burke and others, 2010; p. 237).

Morris and others (2000), Keith-Roach and others (2003), Burke and others (2006), Begg and others (2007), and Begg and others (2008) carried out experimental studies of the re-oxidation and remobilization of Tc in shallow marine and estuary sediments. In general, Tc was strongly retained in the sediments, but the experiments of Burke and others (2006) indicated that the re-mobilization of Tc was dependent on the oxidant. When  $\text{O}_2$  was the oxidant, about 50 percent of the Tc was re-mobilized as pertechnetate. Typically, Fe(II) was oxidized faster than Tc(IV) in these experiments. In sediments that were sulfate-reducing, a fraction of the sulfur was rapidly oxidized, but a sizable fraction remained reduced beyond the experimental duration of two months. The lack of correlation between sulfate oxidation and Tc oxidation and re-mobilization, coupled with XAFS results, which did not show evidence for Tc—S bonding, indicate that sulfide stabilization of Tc is *not* occurring. In contrast to  $\text{O}_2$ , oxidation by nitrate resulted in <10 percent re-mobilization of the Tc, even though extensive Fe(II) and sulfide re-oxidation occurred. These results concur with those of McBeth and others (2007), and Begg and others (2008) who reported rapid and nearly complete oxidation of Tc(IV) by  $\text{O}_2$  in soils that were originally reducing. Exposure of the reduced soils to nitrate, on the other hand, resulted in very little re-oxidation of Tc(IV).

Other investigations have shown that when Tc is associated with iron (oxy) hydroxides and sulfides, Tc can remain in the reduced state, even though the rest of the material becomes oxidized. Studies by Wharton and others (2000) and Livens and others (2004) showed that Tc associated with sulfide phases are resistant to re-oxidation. In the study by Livens and others (2004), reduced technetium is harbored by mackinawite (tetragonal FeS) and EXAFS data indicates the presence of Tc—S bonds. During re-oxidation mackinawite forms goethite [ $\alpha\text{-FeO}(\text{OH})$ ], yet technetium remains in the reduced state. The EXAFS evidence indicates that Tc(IV) bonds switch from S to O and that Tc(IV) may be incorporated into the goethite structure. Because of the identical size of the Tc(IV) and Fe(III) cations (78.5 pm), this is a plausible substitution, provided that a charge-compensating ion is present or the solid forms a defect structure. These results were similar to those reported by Wharton and others (2000) in that FeS oxidized, but Tc remained reduced as was associated with O, rather than S, after re-oxidation.

Experiments carried out by Pepper and others (2003) showed that green rust, layered (oxy)hydroxides containing both Fe(II) and Fe(III) with interlayer sulfate or carbonate anions, reduces surface-sorbed pertechnetate ions and forms  $\text{TcO}_2$ . Upon re-oxidation, the green rust converts into goethite, but Tc remains reduced and effectively immobile. Tc(IV) also appears to be hosted in green rust phases that are associated with siderite ( $\text{FeCO}_3$ ), in experiments performed by Llorens and others (2007). Further experiments carried out by these latter investigators concluded that Tc(IV) is harbored by siderite, based on the quantity of Tc removed from solution, but the identification of Tc by energy dispersive spectroscopy (EDS) was thwarted by low Tc concentrations in the carbonate phase (Llorens and others, 2008).

Assessment of the relative efficacy of abiotic heterogeneous and homogeneous reduction of Tc(VII) by Fe(II) in an anoxic environment was explored by Fredrickson and others (2004b, 2009), Zachara and others (2007), and Peretyazhko and others (2008a). In these experiments, Fe(II) was produced either through bioreduction followed by pasteurization of the sediments, or abiotically by exposing mixtures of Fe-bearing phases (natural phyllosilicate mixtures) to strong reducing agents, such as dithionite-citrate-bicarbonate (DCB). Sediments consisted of well-characterized Ringold formation material from Hanford, Washington, and a clay-rich saprolite from the Oak

Ridge, Tennessee, site. Both sediments contained Fe(II/III) in various forms [(oxy)hydroxides and silicates] and the saprolite contained a relatively high concentration of Mn(III/IV). A generally self-consistent set of results emerged from these comprehensive studies.

Analyses of reaction run products from the experiments of Zachara and others (2007) shows that it is made up of mainly amorphous iron (oxy)hydroxide. The poorly-ordered Fe-phase contains abundant Fe(II) along with Fe(III) and possesses similar properties to ferrihydrite. Spectra from X-ray Absorption Near-Edge Spectroscopy (XANES) analyses show that Tc is in the reduced form [Tc(IV)]. The estimated composition of the solids is  $Fe_{TOT}/Tc(IV) \approx 6$ . Re-oxidation and mobilization of Tc was slow because Tc(IV) is protected from oxidation by the Fe-oxide or its reaction products. They concluded that the cause of rapid reduction of Tc(VII) added to the reduced sediment was due to the presence of sorbed Fe(II) on mineral surfaces, especially those of goethite or ferrihydrite. The relative importance of the heterogeneous compared to homogeneous [by Fe(II) in solution] was confirmed by Peretyazhko and others (2008a). Reduction of Tc(VII) was not limited solely to the presence of Fe(II) sorbed on mineral surfaces, however. Fredrickson and others (2004b, 2009) and Peretyazhko and others (2008a) showed that Tc incorporated into Fe(II)-bearing phyllosilicates along cracks or defect trails could also be reduced to Tc(IV), albeit more slowly than the mineral-surface mediated reduction mechanism. Fe-bearing di- and trioctahedral phyllosilicates in various states of weathering are common in most sedimentary deposits and may be an important sink for reduced Tc. As reported by Fredrickson and others (2009), reduced Tc incorporated into diffusion-limited spaces, such as in phyllosilicates, is resistant to oxidation, whereas Tc(IV) on unprotected mineral surfaces rapidly re-oxidizes when contacted by air or oxidizing solutions.

Collectively, these studies indicate that co-precipitation of Tc with an iron (oxy)hydroxide, sulfide, “green rust” or siderite may be a good alternative immobilization strategy to straight Tc precipitation. It appears that co-precipitation of goethite and  $TcO_2$ -like phases results in an oxidation-resistant compound, whereas  $TcO_2$  by itself [that is, in the absence of organic matter or iron (oxy)hydroxides] oxidizes rapidly and becomes re-mobilized as the pertechnetate anion. Further, these studies indicate that Tc incorporated into phyllosilicates is resistant to re-oxidation. The Tc(IV) in this case is associated with structural Fe and the resistance to re-oxidation appears to be subject to the limitation of oxygen diffusion into the phyllosilicates. Therefore, immobilization of Tc appears to be strongly a function of incorporation into a mineral host that resists the diffusion of oxygen into its structure.

#### RECOMMENDATIONS FOR FUTURE STUDIES

The current state of knowledge regarding technetium chemistry is impressive, yet part of the problem related to remediation of Tc-contaminated materials lies in several unresolved problems. One problem stems from a lack of knowledge concerning the association of Tc in sediments—is Tc sorbed onto or incorporated into solid phases? A number of investigations reveal that experiments aimed at elucidating Tc binding are time-sensitive, such that the identity of the ligand changes due to oxidation or other kinetic factors (Wharton and others, 2000; Livens and others, 2004). Because of the long half-life of  $^{99}Tc$ , there is an unsettling prospect that the experiments do not replicate the future environmental setting.

In some cases, there is evidence for uptake of Tc into solid phases that are resistant to oxidation or dissolution. Because the size of the Tc(IV) atom is nearly identical to that of Fe(III) (both 78.5 pm), there is a prospect that Tc(IV) can be harbored in the lattice of certain iron-bearing phases. The mineral goethite appears to be a good candidate; it is the most stable (oxy)hydroxide of Fe(III) over a wide range of sizes and

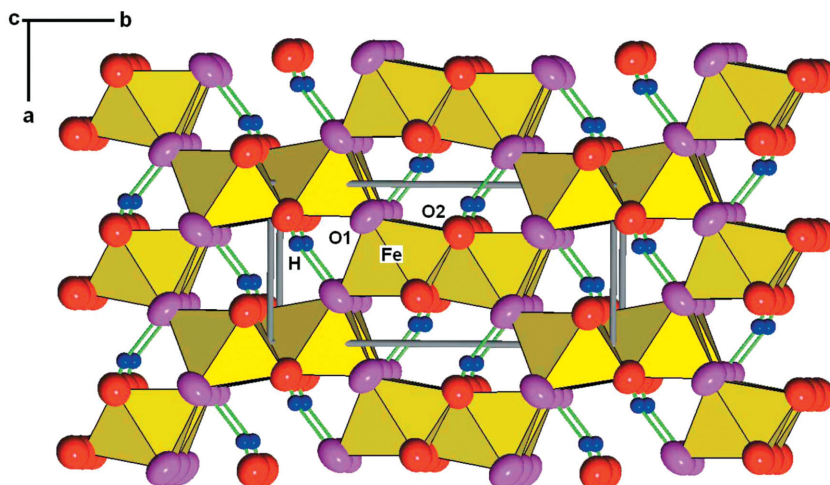


Fig. 5. Crystal structure of goethite,  $\alpha\text{-Fe(III)O(OH)}$ , from Yang and others, 2006.

near-surface environments (Navrotsky and others, 2008). The goethite structure consists of alternating double chains of  $\text{Fe(III)O}_6$  polyhedra (Yang and others, 2006), and these chains are partially linked above and below by H-bonds (fig. 5). The metal—oxygen bond length is 1.99 Å (199 pm) for  $\text{Tc—O}$  (Huheey and others, 1993) and 2.026 Å (202.6 pm) for  $\text{Fe—O}$  in goethite (Yang and others, 2006). In addition, both metals are in octahedral coordination with oxygen, thus making substitution possible. However, because of the charge difference between  $\text{Tc(IV)}$  and  $\text{Fe(III)}$ , the substitution must either be coupled or a defect must be generated.

$\text{Tc(IV)}$  may also be incorporated into iron sulfides, but the proclivity of these phases to oxidize opens questions about how long Tc will remain immobile. Although a number of experiments have shown that Tc remains in the +4 state while the host sulfide oxidizes (Wharton and others, 2000; Livens and others, 2004), there is reasonable concern surrounding the longevity of this state. Long-term experiments in which the paragenetic sequence of sulfide phases evolve towards sulfates, with studies of the corresponding oxidation state of Tc, are needed.

Because of the importance of oxidation-reduction reactions to the mobility of Tc, there should be an emphasis on understanding the chemical fundamentals of these processes. For example, the coupled oxidation-reduction reaction, such as equation (2), above, is an overall, rather than an elementary, kinetic reaction. It is likely that equation (2) is composed of a number of elementary reactions that sum together to the overall reaction. Clearly, it would matter a great deal if the elementary reactions were parallel or sequential, because in the case of the latter, there could be rate-limiting steps that have yet to be identified. On the other hand, if the elementary steps were made up of parallel reactions, it would be very useful to understand the relative importance of the various kinetic pathways by which iron and technetium oxidation states evolve. If catalysts or inhibitors to the reaction pathways could be fashioned, then the overall oxidation-reduction scheme could be modified in an environmentally favorable manner.

On the other hand, if re-oxidation of  $\text{Tc(IV)}$  is kinetically straight-forward and fast, then other studies are needed. The relatively rapid re-oxidation in laboratory experiments appears to contrast to field investigations in which technetium remains in the relatively immobile  $\text{Tc(IV)}$  state. Development of microenvironments, in which the



oxidation state on the local scale contrasts with that of the surrounding, general state, has been discussed in the literature (Hu and Smith, 2004; Hu and others, 2008), but experimental evidence for how these conditions evolve are lacking. Carefully conducted laboratory experiments coupled with field studies and computer modeling may elucidate the evolution of such microenvironments. In this case, the blanket assessment that Tc is always mobile in an overall oxidizing setting deserves greater attention.

#### ACKNOWLEDGMENTS

This work was greatly improved by reviews conducted by Drs. Dawn Wellman, Dan Kaplan, Kath Morris, Matt Marshall and Thomas Albrecht-Schmitt. Funding for this project was provided by the U.S. Department of Energy—Environmental Management, Office of Groundwater and Soil Remediation. This work was conducted at Pacific Northwest National Laboratory, operated by Battelle for the U.S. Department of Energy under Contract DE-AC06-76RL01830.

#### REFERENCES

- Aarkrog, A., Boelskifte, S., Dahlgaard, H., Duniec, S., Hallstadius, L., Holm, E., and Smith, J. N., 1987, Technetium-99 and cesium-134 as long distance tracers in Arctic waters: Estuarine, Coastal and Shelf Science, v. 24, p. 637–647, doi: 10.1016/0272-7714(87)90103-X.
- Aarkrog, A., Carlsson, L., Chen, Q. J., Dahlgaard, H., Holm, E., Huynh-Ngoc, L., Jensen, L. H., Nielsen, S. P., and Nies, H., 1988, Origin of technetium-99 and its use as a marine tracer: Nature, v. 335, p. 338–340, doi: 10.1038/335338a0.
- Aarkrog, A., Chen, Q., Dahlgaard, H., Nielsen, S. P., Trapeznikov, A., and Pozolotina, V., 1997, Evidence of <sup>99</sup>Tc in Ural River sediments: Journal of Environmental Radioactivity, v. 37, p. 201–213, doi: 10.1016/S0265-931X(96)00096-3.
- Abdelouas, A., Fattahi, M., Grambow, B., Vichot, L., and Gautier, E., 2002, Precipitation of technetium by subsurface sulfate-reducing bacteria: Radiochimica Acta, v. 90, p. 773–777, doi: 10.1524/ract.2002.90.9-11\_2002.773.
- Abdelouas, A., Grambow, B., Fattahi, M., Andres, Y., and Leclerc-Cessac, E., 2005, Microbial reduction of <sup>99</sup>Tc in organic matter-rich soils: Science of the Total Environment, v. 336, p. 255–268, doi: 10.1016/j.scitotenv.2004.06.005.
- Almahamid, I., Bryan, J. C., Bucher, J. J., Burrell, A. K., Edelstein, N. M., Hudson, E. A., Kaltsoyannis, N., Lukens, W. W., Shuh, D. K., Nitsche, H., and Reich, T., 1995, Electronic and structural investigations of technetium compounds by X-ray absorption spectroscopy: Inorganic Chemistry, v. 34, p. 193–198, doi: 10.1021/ic00105a032.
- Anderson, B. E., Becker, U., Helean, K. B., and Ewing, R. C., 2007, Perrhenate and pertechnetate behavior on iron and sulfur-bearing compounds, in Dunn, D., Poinssot, C., and Begg, B., editors, Scientific Basis for Nuclear Waste Management XXX: Materials Research Society Symposium Proceedings, v. 985, Paper #: 0985-NN12-09.
- Anderson, R. T., Vrionis, H. A., Ortiz-Bernad, I., Resch, C. T., Long, P. E., Dayvault, R., Karp, K., Marutzky, S., Metzler, D. R., Peacock, A., White, D. C., Lowe, M., and Lovley, D. R., 2003, Stimulating the in situ activity of *Geobacter* species to remove uranium from the groundwater of a uranium-contaminated aquifer: Applied and Environmental Microbiology, v. 69, p. 5884–5891, doi: 10.1128/AEM.69.10.5884-5891.2003.
- Ashworth, D. J., and Shaw, G., 2005, Soil migration and plant uptake of technetium from a fluctuating water table: Journal of Environmental Radioactivity, v. 81, p. 155–171, doi: 10.1016/j.jenvrad.2004.01.033.
- Baston, G. M. N., De Canniere, P. R., Ilett, D. J., Cowper, M. M., Pilkington, N. J., Tweed, C. J., Wang, L., and Williams, S. J., 2002, Technetium behaviour in Boom Clay—A laboratory and field study: Radiochimica Acta, v. 90, p. 735–740, doi: 10.1524/ract.2002.90.9-11\_2002.735.
- Begg, J. D. C., Burke, I. T., and Morris, K., 2007, The behaviour of technetium during microbial reduction in amended soils from Dounreay, UK: Science of the Total Environment, v. 373, p. 297–304, doi: 10.1016/j.scitotenv.2006.10.034.
- Begg, J. D. C., Burke, I. T., Charnock, J. M., and Morris, K., 2008, Technetium reduction and reoxidation behaviour in Dounreay soils: Radiochimica Acta, v. 96, p. 631–636, doi: 10.1524/ract.2008.1547.
- Bennett, R., and Willey, N., 2003, Soil availability, plant uptake and soil to plant transfer of <sup>99</sup>Tc—A review: Journal of Environmental Radioactivity, v. 65, p. 215–231, doi: 10.1016/S0265-931X(02)00098-X.
- Bonotto, S., Kirchmann, R., Van Baelen, J., Hurtgen, C., Cogneau, M., Van der Ben, D., Verthe, C., and Bouqueneau, J. M., 1985, Behaviour of technetium in marine algae, in Bulman, R. A., and Cooper, J. R., editors, Speciation of Fission and Activation Products in the Environment: London, Routledge, p. 382–390.
- Bors, J., Dultz, S., and Riebe, B., 1999, Retention of radionuclides by organophilic bentonite: Engineering Geology, v. 54, p. 195–206, doi: 10.1016/S0013-7952(99)00074-5.
- Boyd, G. E., 1978, Osmotic and activity coefficients of aqueous NaTcO<sub>4</sub> and NaReO<sub>4</sub> solutions at 25°C: Journal of Solution Chemistry, v. 7, p. 229–238, doi: 10.1007/BF00644270.

- Brookins, D. G., 1990, Radionuclide behavior at the Oklo Nuclear Reactor, Gabon: *Waste Management* v. 10, p. 285–296, doi: 10.1016/0956-053X(90)90102-Q.
- Brown, C. F., Serne, R. J., Bjornstad, B. N., Horton, D. G., Lanigan, D. C., Clayton, R. E., Valenta, M. M., Vickerman, T. S., Kutnyakov, I. V., Geiszler, K. N., Baum, S. R., Parker, K. E., and Lindberg, M. J., 2006, Characterization of vadose zone sediments below the C Tank Farm: Borehole C4297 and RCRA Borehole 299-E27-22: Richland, Washington, Pacific Northwest National Laboratory, PNNL-15503.
- Brown, C. F., Valenta, M. M., Serne, R. J., Bjornstad, B. N., Lanigan, D. C., Iovin, C., Clayton, R. E., Geiszler, K. N., Clayton, E. T., Kutnyakov, I. V., Baum, S. R., Lindberg, M. J., and Orr, R. D., 2007, Characterization of direct push vadose zone sediments from the 241-U Single-Shell Tank Farm: Richland, Washington, Pacific Northwest National Laboratory, PNNL-17163.
- Brown, J. E., Kolstad, A. K., Brungot, A. L., Lind, B., Rudjord, A. L., Strand, P., and Føyn, L., 1999, Levels of  $^{99}\text{Tc}$  in seawater and biota samples from Norwegian coastal waters and adjacent seas: *Marine Pollution Bulletin*, v. 38, p. 560–571, doi: 10.1016/S0025-326X(98)00114-3.
- Bruggeman, C., Maes, A., and Vancluysen, J., 2007, The identification of  $\text{FeS}_2$  as a sorption sink for Tc(IV): *Physics and Chemistry of the Earth*, v. 32, p. 573–580, doi: 10.1016/j.pcc.2005.12.006.
- Buck, E. C., Hanson, B. D., and McNamara, B. K., 2004, The geochemical behaviour of Tc, Np and Pu in spent nuclear fuel in an oxidizing environment, in Gieré, R., and Stille, P., editors, *Energy, Waste, and the Environment: a Geochemical Perspective*: The Geological Society, London, Special Publications, v. 236, p. 65–68, doi: 10.1144/GSL.SP.2004.236.01.05.
- Bürgi, H. B., Anderegg, G., and Bläuenstein, P., 1981, Preparation, characterization, and crystal, molecular, and electronic structure of  $(\text{H}_2\text{EDTA})^{99}\text{Tc}^{\text{IV}}(\mu\text{-O})_2^{99}\text{Tc}^{\text{IV}}(\text{H}_2\text{EDTA}) \cdot 5\text{H}_2\text{O}$ . A 2.33-Å Tc-Tc distance which may represent a  $\sigma^2\pi^2\delta^2$  bond: *Inorganic Chemistry*, v. 20, p. 3829–3834, doi: 10.1021/ic50225a046.
- Burke, I. T., Boothman, C., Lloyd, J. R., Mortimer, R. J. G., Livens, F. R., and Morris, K., 2005, Effects of progressive anoxia on the solubility of technetium in sediments: *Environmental Science and Technology*, v. 39, p. 4109–4116, doi: 10.1021/es048124p.
- Burke, I. T., Boothman, C., Lloyd, J. R., Livens, F. R., Charnock, J. M., McBeth, J. M., Mortimer, R. J. G., and Morris, K., 2006, Reoxidation behavior of technetium, iron and sulfur in estuarine sediments: *Environmental Science and Technology*, v. 40, p. 3529–3535, doi: 10.1021/es052184t.
- Burke, I. T., Livens, F. R., Lloyd, J. R., Brown, A. P., Law, G. T. W., McBeth, J. M., Ellis, B. L., Lawson, R. S., and Morris, K., 2010, The fate of technetium in reduced estuarine sediments: Combining direct and indirect analyses: *Applied Geochemistry*, v. 25, p. 233–241, doi: 10.1016/j.apgeochem.2009.11.008.
- Cartledge, G. H., and Smith, W. T., Jr., 1955, Revision of the electrode potential diagram for technetium: *Journal of Physical Chemistry*, v. 59, p. 1111–1112, doi: 10.1021/j150532a032.
- Chen, F., Burns, P. C., and Ewing, R. C., 2000, Near-field behavior of  $^{99}\text{Tc}$  during the oxidative alteration of spent nuclear fuel: *Journal of Nuclear Materials*, v. 278, p. 225–232, doi: 10.1016/S0022-3115(99)00264-0.
- Cobble, J. W., Smith, W. T., Jr., and Boyd, G. E., 1953, Thermodynamic properties of technetium and rhenium compounds. II. Heats of formation of technetium heptoxide and pertechnic acid, potential of the technetium-(IV)-technetium (VII) couple, and a potential diagram for technetium<sup>1,2</sup>: *Journal of American Chemical Society*, v. 75, p. 5777–5782, doi: 10.1021/ja01119a002.
- Colton, R., 1965, *The Chemistry of Rhenium and Technetium*: London, Interscience Publishers, 185 p.
- Cotton, F. A., and Wilkinson, G., 1980, *Advanced Inorganic Chemistry: A Comprehensive Text*, 4th Edition: New York, John Wiley and Sons, 1396 p.
- Cui, D., and Eriksen, T. E., 1996a, Reduction of pertechnetate by ferrous iron in solution: Influence of sorbed and precipitated Fe(II): *Environmental Science and Technology*, v. 30, p. 2259–2262, doi: 10.1021/es9506263.
- 1996b, Reduction of pertechnetate in solution by heterogeneous electron transfer from Fe(II)-containing geological material: *Environmental Science and Technology*, v. 30, p. 2263–2269, doi: 10.1021/es950627v.
- Cui, D., Eriksen, T., and Eklund, U.-B., 2001, On Metal Aggregates in Spent Fuel: Synthesis and Leaching of Mo-Ru-Pd-Rh Alloy, in Hart, K. P., and Lumpkin, G. R., editors, *Scientific Basis for Nuclear Waste Management XXIV*, Materials Research Society: Warrendale, Pennsylvania, Materials Research Society Symposium Proceedings, v. 663, p. 427–434.
- Cui, D., Low, J., Sjöstedt, C. J., and Spahiu, K., 2004, On Mo-Ru-Tc-Pd-Rh-Te alloy particles extracted from spent fuel and their leaching behavior under Ar and H<sub>2</sub> atmospheres: *Radiochimica Acta*, v. 92, p. 551–555, doi: 10.1524/ract.92.9.551.55001.
- Curtis, D. B., 1986, Geochemical controls on  $^{99}\text{Tc}$  transport and retention: *Chemical Geology*, v. 55, p. 227–231, doi: 10.1016/0009-2541(86)90026-4.
- Curtis, D., Benjamin, T., Gancarz, A., Loss, R., Rosman, K., DeLaeter, J., Delmore, J. E., and Maeck, W. J., 1989, Fission product retention in the Oklo Natural Fission Reactors: *Applied Geochemistry*, v. 4, p. 49–62, doi: 10.1016/0883-2927(89)90058-9.
- Dahlgard, H., Eriksson, M., Nielsen, S. P., and Joensen, H. P., 2004, Levels and trends of radioactive contaminants in the Greenland environment: *Science of the Total Environment*, v. 331, p. 53–67, doi: 10.1016/j.scitotenv.2004.03.023.
- Darab, J. G., and Smith, P. A., 1996, Chemistry of technetium and rhenium species during low-level radioactive waste vitrification: *Chemistry of Materials*, v. 8, p. 1004–1021, doi: 10.1021/cm950418+.
- De Luca, G., De Philip, P., Dermoun, Z., Rousset, M., and Verméglio, A., 2001, Reduction of technetium (VII) by *Desulfotomobium fructosovorans* is mediated by the nickel-iron hydrogenase: *Applied and Environmental Microbiology*, v. 67, p. 4583–4587, doi: 10.1128/AEM.67.10.4583-4587.2001.
- Desmet, G., and Myteenaere, C., editors, 1986, *Technetium in the Environment*: Essex, England, Elsevier Applied Science Publishers, 419 p.

- Dzombak, D. A., and Morel, F. M. M., 1990, Surface Complexation Modeling. Hydrous Ferric Oxide: New York, Wiley-Interscience, 393 p.
- El-Wear, S., German, K. E., and Peretrukhin, V. F., 1992, Sorption of technetium on inorganic sorbents and natural minerals: *Journal of Radioanalytical and Nuclear Chemistry*, v. 157, p. 3–14, doi: 10.1007/BF02039772.
- EPA, 2002, EPA Facts about Technetium-99: <http://www.epa.gov/superfund//health/contaminants/radiation/pdfs/technetium.pdf>.
- 2008, U.S. Environmental Protection Agency: Radiation Protection Program. 2008. “Radiation information (technetium-99)”: <http://www.epa.gov/radiation/radionuclides/technetium.html>.
- Eriksen, T. E., Ndalamba, P., Bruno, J., and Caceci, M., 1992, The solubility of  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  in neutral to alkaline solutions under constant  $p\text{CO}_2$ : *Radiochimica Acta*, v. 58–59, p. 67–70.
- Faggiani, R., Lock, C. J. L., and Pocé, J., 1980, The structure of ammonium pertechnetate at 295, 208 and 141 K: *Acta Crystallographia*, v. B36, p. 231–233, doi: 10.1107/S0567740880002993.
- Farrell, J., Bostick, W. D., Jarabek, R. J., and Fiedor, J. N., 1999, Electrosorption and reduction of pertechnetate by anodically polarized magnetite: *Environmental Science and Technology*, v. 33, p. 1244–1249, doi: 10.1021/es980086k.
- Fredrickson, J. K., Kostandarithes, H. M., Li, S. W., Plymale, A. E., and Daly, M. J., 2000, Reduction of Fe(III), Cr(VI), U(VI), and Tc(VII) by *Deinococcus radiodurans* R1: *Applied and Environmental Microbiology*, v. 66, p. 2006–2011, doi: 10.1128/AEM.66.5.2006-2011.2000.
- Fredrickson, J. K., Zachara, J. M., Balkwill, D. L., Kennedy, D., Li, S.-M. W., Kostandarithes, H. M., Daly, M. J., Romine, M. F., and Brockman, F. J., 2004a, Geomicrobiology of high-level nuclear waste-contaminated vadose sediments at the Hanford Site, Washington State: *Applied and Environmental Microbiology*, v. 70, p. 4230–4241, doi: 10.1128/AEM.70.7.4230-4241.2004.
- Fredrickson, J. K., Zachara, J. M., Kennedy, D. W., Kukkadupa, R., McKinley, J. P., Heald, S. M., Liu, C., and Plymale, A. E., 2004b, Reduction of  $\text{TcO}_4^-$  by sediment-associated biogenic Fe(II): *Geochimica et Cosmochimica Acta*, v. 68, p. 3171–3187, doi: 10.1016/j.gca.2003.10.024.
- Fredrickson, J. K., Zachara, J. M., Plymale, A. E., Heald, S. M., McKinley, J. P., Kennedy, D. W., Liu, C., and Nachimuthu, P., 2009, Oxidative dissolution potential of biogenic and abiogenic  $\text{TcO}_2$  in subsurface sediments: *Geochimica et Cosmochimica Acta*, v. 73, p. 2299–2313, doi: 10.1016/j.gca.2009.01.027.
- Gancarz, A., Cowan, G., Curtis, D., and Maeck, W. J., 1980,  $^{99}\text{Tc}$ , Pb and Ru migration around the Oklo natural fission reactors, in Moore, J. G., editor, *Scientific Basis for Nuclear Waste Management II*: New York, New York, Plenum Press, p. 601–608.
- Gauthier-Lafaye, F., Holliger, P., and Blanc, P.-L., 1996, Natural fission reactors in the Franceville basin, Gabon: A review of the conditions and results of a “critical event” in a geologic system: *Geochimica et Cosmochimica Acta*, v. 60, p. 4831–4852, doi: 10.1016/S0016-7037(96)00245-1.
- Geraedts, K., and Maes, A., 2008, Determination of the conditional interaction constant between colloidal technetium (IV) and Gorleben humic substances: *Applied Geochemistry*, v. 23, p. 1127–1139, doi: 10.1016/j.apgeochem.2007.11.007.
- Geraedts, K., Bruggeman, C., Maes, A., Van Loon, L. R., Rossberg, A., and Reich, T., 2002, Evidence for the existence of Tc(IV)-humic substance species by x-ray absorption near-edge spectroscopy: *Radiochimica Acta*, v. 90, p. 879–884, doi: 10.1524/ract.2002.90.12\_2002.879.
- Gu, B., and Ruan, C., 2007, Determination of technetium and its speciation by surface-enhanced Raman spectroscopy: *Analytical Chemistry*, v. 79, p. 2341–2345, doi: 10.1021/ac062052y.
- Hartman, M. J., Morasch, L. F., and Webber, W. D., 2004, Summary of Hanford Site groundwater monitoring for Fiscal Year 2003: Richland, Washington, Pacific Northwest National Laboratory, PNNL-14548-SUM.
- Harvey, B. R., and Kershaw, P. J., 1984, Physico-chemical interactions of long-lived radionuclides in coastal marine sediments and some comparisons with the deep sea environment: La Spezia, Italy, 28–30 September 1983, Proceedings of CEC International Symposium on The Behaviour of Long-lived Radionuclides in the Marine Environment, EUR 9214 en, p. 131.
- Hattink, J., and Wolterbeek, H. T., 2001, Accumulation of  $^{99}\text{Tc}$  in duckweed *Lemna minor* L. as a function of growth rate and  $^{99}\text{Tc}$  concentration: *Journal of Environmental Radioactivity*, v. 57, p. 117–138, doi: 10.1016/S0265-931X(01)00015-7.
- Hattink, J., Goeij de, J. J. M., and Wolterbeek, H. T., 2000, Uptake kinetics of  $^{99}\text{Tc}$  in common duckweed: *Environmental and Experimental Botany*, v. 44, p. 9–22, doi: 10.1016/S0098-8472(00)00045-9.
- Henrot, J., 1989, Bioaccumulation and chemical modification of Tc by soil bacteria: *Health Physics*, v. 57, p. 239–245, doi: 10.1097/00004032-198908000-00001.
- Hess, N. J., Xia, Y., Rai, D., and Conradson, S. D., 2004, Thermodynamic model for the solubility of  $\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{am})$  in the aqueous  $\text{Tc}(\text{IV})\text{-Na}^+\text{-Cl}^-\text{-H}^+\text{-OH}^-\text{-H}_2\text{O}$  system: *Journal of Solution Chemistry*, v. 33, p. 199–226, doi: 10.1023/B:JOSL.0000030285.11512.1f.
- Hidaka, H., Shinotsuka, K., and Holliger, P., 1993, Geochemical behaviour of  $^{99}\text{Tc}$  in the Oklo natural fission reactors: *Radiochimica Acta*, v. 63, p. 19–22.
- Hidaka, H., Holliger, P., and Gauthier-Lafaye, F., 1999, Tc/Ru fractionation in the Oklo and Bangombé natural fission reactors, Gabon: *Chemical Geology*, v. 155, p. 323–333, doi: 10.1016/S0009-2541(98)00173-9.
- Hu, Q., and Smith, D. K., 2004, Field-Scale Migration of  $^{99}\text{Tc}$  and  $^{129}\text{I}$  at the Nevada Test Site, in Hanchar, J. M., Stroes-Gascoyne, S., and Browning, L., editors, *Scientific Basis for Nuclear Waste Management XXVIII*: Warrendale, Pennsylvania, Materials Research Society, Materials Research Society Proceedings Series, v. 824, paper #CC7.7.
- Hu, Q. H., Rose, T. P., Zavarin, M., Smith, D. K., Moran, J. E., and Zhao, P. H., 2008, Assessing field-scale migration of radionuclides at the Nevada Test Site: “mobile” species: *Journal of Environmental Quality*, v. 99, p. 1617–1630.

- Huheey, J. E., Keiter, E. A., and Keiter, R. L., 1993, *Inorganic Chemistry: Principles of Structure and Reactivity*, fourth edition: New York, Harper Collins College Publishers, 964 p.
- IAEA, 2004, *Sediment Distribution Coefficients and Concentration Factors for Biota in the Marine Environment*: Vienna, Austria, Technical Report Series, n. 422, International Atomic Energy Association, 95 p.
- Ishii, N., Tagami, K., Enomoto, S., and Uchida, S., 2004a, Influence of microorganisms on the behavior of technetium and other elements in paddy soil surface water: *Journal of Environmental Radioactivity*, v. 77, p. 369–380, doi: 10.1016/j.jenvrad.2004.04.006.
- Ishii, N., Tagami, K., and Uchida, S., 2004b, Physicochemical form of technetium in surface water covering paddy and upland field: *Chemosphere*, v. 57, p. 953–953, doi: 10.1016/j.chemosphere.2004.07.027.
- Istok, J. D., Senko, J. M., Krumholz, L. R., Watson, D., Bogle, M. A., Peacock, A., Chang, Y.-J., and White, D. C., 2004, In situ bioreduction of technetium and uranium in a nitrate-contaminated aquifer: *Environmental Science and Technology*, v. 38, p. 468–475, doi: 10.1021/es034639p.
- Jaisi, D. P., Dong, H., Plymale, A. E., Fredrickson, J. K., Zachara, J. M., Heald, S., and Liu, C., 2009, Reduction and long term immobilization of technetium by Fe(II) associated with clay mineral nontronite: *Chemical Geology*, v. 264, p. 127–138, doi: 10.1016/j.chemgeo.2009.02.018.
- Janeczek, J., 1999, Mineralogy and geochemistry of natural fission reactors in Gabon, in Burns, P. C., and Finch, R., editors, *Uranium: Mineralogy, Geochemistry and the Environment: Reviews in Mineralogy and Geochemistry*, v. 38, p. 321–382.
- Jurisson, S. S., and Murmann, R. K., 1999, Oxygen exchange on  $\text{ReO}_4^-$  by  $^{17}\text{O}$ -NMR: *Inorganic Chemistry*, v. 38, p. 3919–3921, doi: 10.1021/ic9902830.
- Jurisson, S., Gawenis, J., and Landa, E. R., 2004, Sorption of  $^{99\text{m}}\text{Tc}$  radiopharmaceutical compounds by soils: *Health Physics*, v. 87, p. 423–428, doi: 10.1097/01.HP.0000128583.33124.7d.
- Kaplan, D. I., 2003, Influence of surface charge of an Fe-oxide and an organic matter dominated soil on iodide and pertechnetate sorption: *Radiochimica Acta*, v. 91, p. 173–178, doi: 10.1524/ract.91.3.173.19977.
- Kaplan, D. I., and Serne, R. J., 1998, Pertechnetate exclusion from sediments: *Radiochimica Acta*, v. 81, p. 117–124.
- Katcoff, S., 1958, Fission product yields from U, Th and Pu: *Nucleonics*, v. 16, p. 78–85.
- Kaye, M. H., Lewis, B. J., and Thompson, W. T., 2007, Thermodynamic treatment of noble metal fission products in nuclear fuel: *Journal of Nuclear Materials*, v. 366, p. 8–27, doi: 10.1016/j.jnucmat.2006.11.014.
- Keith-Roach, M. J., 2008, The speciation, stability, solubility and biodegradation of organic co-contaminant radionuclide complexes: A review: *Science of the Total Environment*, v. 396, 1–11, doi: 10.1016/j.scitotenv.2008.02.030.
- Keith-Roach, M. J., and Roos, P., 2004, Redox-dependent behaviour of technetium-99 entering permanently stratified anoxic fjord (Framvaren fjord, Norway): *Estuarine, Coastal and Shelf Science*, v. 60, p. 151–161, doi: 10.1016/j.j.ecss.2003.12.005.
- Keith-Roach, M. J., Morris, K., and Dahlgaard, H., 2003, An investigation into technetium binding in sediments: *Marine Chemistry*, v. 81, p. 149–162, doi: 10.1016/S0304-4203(03)00014-8.
- Kenna, H. W., and Kuroda, P. K., 1961, Isolation of naturally occurring technetium: *Journal of Inorganic Nuclear Chemistry*, v. 23, p. 142–144, doi: 10.1016/0022-1902(61)80098-5.
- Kim, E., and Boulégu, J., 2003, Chemistry of rhenium as an analogue of technetium: Experimental studies of the dissolution of rhenium oxides in aqueous solutions: *Radiochimica Acta*, v. 91, p. 211–216, doi: 10.1524/ract.91.4.211.19968.
- Kleykamp, H., 1985, The chemical state of the fission products in oxide fuels: *Journal of Nuclear Materials*, v. 131, p. 221–246, doi: 10.1016/0022-3115(85)90460-X.
- Kloosterman, J. L., 2008, *Nuclear Waste Production: The Netherlands*, Delft University of Technology, <http://www.janleenkloosterman.nl/NuclearWaste>.
- Koch-Steindl, H., and Pröhl, G., 2001, Considerations on the behaviour of long-lived radionuclides in the soil: *Radiation and Environmental Biophysics*, v. 40, p. 93–104, doi: 10.1007/s004110100098.
- Kotegov, K. V., Pavlov, O. N., and Shvedov, V. P., 1968, Technetium, in Emeleus, H. J., and Sharpe, A. G., editors, *Advances in Inorganic Chemistry and Radiochemistry*: New York, Academic Press, v. 12, p. 2–72.
- Kozar, A. A., Peretrukhin, V. F., Karelin, E. A., Radchenko, V. M., Toporov, Yu. G., Tarasov, V. A., and Romanov, E. G., 2002, Transmutation of metallic  $^{99}\text{Tc}$  into ruthenium under irradiation in high-flux SM reactors: *Radiochemistry*, v. 44, p. 284–286, doi: 10.1023/A:1020362908689.
- Krebs, B., and Hasse, K.-D., 1976, Refinements of the crystal structure of  $\text{KTCO}_4$ ,  $\text{KReO}_4$  and  $\text{OsO}_4$ . The bond lengths in tetrahedral oxo-anions and oxides of the  $d^0$  transition metals: *Acta Crystallographica*, v. B32, 1334–1337, doi: 10.1107/S056774087600530X.
- Krupka, K. M., Brown, C. F., Schaefer, H. T., Heald, S. M., Valenta, M. M., and Arey, B. W., 2006, Rhenium uptake as analogue for  $^{99}\text{Tc}$  by steel corrosion products, in Sagar, B., editor, *Proceedings of the 11th International High-Level Radioactive Waste Management Conference (IHLRWM)*: Las Vegas, Nevada, 30 April–4 May 2006, American Nuclear Society.
- Kunze, S., Neck, V., Gompfer, K., and Fanghänel, Th., 1996, Studies on the immobilization of technetium under near field geochemical conditions: *Radiochimica Acta*, v. 74, p. 159–163.
- Lamfers, H. J., Meetsma, A., Wiegers, G. A., and DeBoer, J. L., 1996, The crystal structure of some rhenium and technetium dichalcogenides: *Journal of Alloys and Compounds*, v. 241, p. 34–39, doi: 10.1016/0925-8388(96)02313-4.
- Langmuir, D., 1997, *Aqueous Environmental Geochemistry*: Upper Saddle River, New Jersey, Prentice Hall, 600 p.

- Lear, G., McBeth, J. M., Boothman, C., Gunning, D. J., Ellis, B. L., Lawson, R. S., Morris, K., Burke, I. T., Bryan, N. D., Brown, A. P., Livens, F. R., and Lloyd, J. R., 2010, Probing the biogeochemical behavior of technetium using a novel nuclear imaging approach: *Environmental Science and Technology*, v. 44, 156–162, doi: 10.1021/es802885r.
- Lembrechts, J. F., and Desmet, G., 1989, Reaction mechanisms responsible for transformation of pertechnetate in phototrophic organisms: *Health Physics*, v. 57, p. 255–262, doi: 10.1097/00004032-198908000-00003.
- Lemire, R. J., and Jobe, D. J., 1996, Predicted behaviour of technetium in a geological disposal vault for used nuclear fuel—ramifications of a recent determination of the enthalpy of formation of  $\text{TcO}_2(\text{cr})$ , in Murphy, W. M., and Knecht, D. A., editors, *Scientific Basis for Nuclear Waste Management XIX: Materials Research Society Symposium Proceedings*, v. 412, p. 873–880.
- Liebscher, L., and Münze, R., 1975, Bestimmung des standardpotentials der halbkette  $\text{TcO}_4^-/\text{TcO}_2 \cdot x\text{H}_2\text{O}$ , Zentralinstitut für Kernforschung: German Democratic Republic, Rossendorf, Technical Report ZFK-294.
- Lieser, K. H., and Bauscher, C., 1987, Technetium in the hydrosphere and in the geosphere. I. Chemistry of technetium and iron in natural waters and influence of the redox potential on the sorption of technetium: *Radiochimica Acta*, v. 42, p. 205–213.
- Lieser, K. H., Bauscher, C. H., and Nakashima, T., 1987, Dissolution of  $\text{TcO}_2$  in aqueous solutions under various conditions: *Radiochimica Acta*, v. 42, p. 191–200.
- Lindahl, P., Ellmark, C., Gäfvert, T., Mattsson, S., Roos, P., Holm, E., and Erlandsson, B., 2003, Long-term study of  $^{99}\text{Tc}$  in the marine environment on the Swedish west coast: *Journal of Environmental Radioactivity*, v. 67, p. 145–146, doi: 10.1016/S0265-931X(02)00176-5.
- Liu, C., Gorby, Y. A., Zachara, J. M., Fredrickson, J. K., and Brown, C. F., 2002, Reduction kinetics of Fe(III), Co(III), U(VI), Cr(VI), and Tc(VII) in cultures of dissimilatory metal-reducing bacteria: *Biotechnology and Bioengineering*, v. 80, p. 637–649, doi: 10.1002/bit.10430.
- Liu, D. J., Yao, J., Wang, B., Bruggeman, C., and Maes, N., 2007, Solubility study of Tc(IV) in a granitic water: *Radiochimica Acta*, v. 95, p. 523–528, doi: 10.1524/ract.2007.95.9.523.
- Liu, Y., Terry, J., and Jurisson, S. S., 2008, Pertechnetate immobilization with amorphous iron sulfide: *Radiochimica Acta*, v. 96, p. 823–833, doi: 10.1524/ract.2008.1528.
- 2009, Potential interferences on the pertechnetate-sulfide immobilization reaction: *Radiochimica Acta*, v. 97, p. 33–41, doi: 10.1524/ract.2009.1569.
- Livens, F. R., Jones, M. J., Hynes, A. J., Charnock, J. M., Mosselmans, J. F. W., Hennig, C., Steele, H., Collison, D., Vaughn, D. J., Patrick, R. A. D., Reed, W. A., and Moyes, L. N., 2004, X-ray absorption spectroscopy studies of reactions of technetium, uranium and neptunium with mackinawite: *Journal of Environmental Radioactivity*, v. 74, p. 211–219, doi: 10.1016/j.jenvrad.2004.01.012.
- Llorens, I., Fattahi, M., and Grambow, B., 2007, New synthesis route and characterization of siderite ( $\text{FeCO}_3$ ) and coprecipitation of  $^{99}\text{Tc}$ , in Dunn, D., Poinssot, C., and Begg, B., editors, *Scientific Basis for Nuclear Waste Management XXX: Materials Research Society, Proceedings of Symposium on Scientific Basis of Nuclear Waste Management*, v. 985, p. 419–423.
- Llorens, I. A., Denlard, P., Gautron, E., Olicard, A., Fattahi, M., Jobic, S., and Grambow, B., 2008, Structural investigation of coprecipitation of technetium-99 with iron phases: *Radiochimica Acta*, v. 96, p. 569–574, doi: 10.1524/ract.2008.1538.
- Lloyd, J. R., and Macaskie, L. E., 1996, A Novel PhosphorImager-Based Technique for Monitoring the Microbial Reduction of Technetium: *Applied and Environmental Microbiology*, v. 62, p. 578–582.
- Lloyd, J. R., Cole, J. A., and Macaskie, L. E., 1997, Reduction and removal of heptavalent technetium from solution by *Escherichia coli*: *Journal of Bacteriology*, v. 179, p. 2014–2021.
- Lloyd, J. R., Ridley, J., Khizniak, T., Lyalikova, N. N., and Macaskie, L. E., 1999, Reduction of technetium by *Desulfovibrio desulfuricans*: Biocatalyst characterization and use in a flowthrough bioreactor: *Applied and Environmental Microbiology*, v. 65, p. 2691–2696.
- Lloyd, J. R., Sole, V. A., Van Praagh, C. V. G., and Lovley, D. R., 2000, Direct and Fe(II)-mediated reduction of technetium by Fe(III)-reducing bacteria: *Applied and Environmental Microbiology*, v. 66, p. 3743–3749, doi: 10.1128/AEM.66.9.3743-3749.2000.
- Lovely, D. R., 1993, Dissimilatory metal reduction: *Annual Reviews in Microbiology*, v. 47, p. 263–290, doi: 10.1146/annurev.mi.47.100193.001403.
- Luo, W., Kelly, S. D., Kemner, K. M., Watson, D., Zhou, J., Jardine, P. M., and Gu, B., 2009, Sequestering uranium and technetium through co-precipitation with aluminum in a contaminated acidic environment: *Environmental Science & Technology*, v. 43, p. 7516–7522, doi: 10.1021/es900731.
- Lukens, W. W., Bucher, J. J., Edelstein, N. M., and Shuh, D. K., 2002, Products of pertechnetate radiolysis in highly alkaline solution: Structure of  $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ : *Environmental Science & Technology*, v. 36, p. 1124–1129, doi: 10.1021/es015653+.
- Luyckx, F., 1986, Technetium Discharges Into the Environment, in Desmet, G., and Myttenaere, C., editors, *Technetium in the Environment*: Essex, England, Elsevier Applied Science Publishers, p. 21–27.
- Maes, A., Geraedts, K., Bruggeman, C., VanCluysen, J., Roßberg, A., and Henning, C., 2004, Evidence for the interaction of technetium colloids with humic substances by X-ray Absorption Spectroscopy: *Environmental Science and Technology*, v. 38, p. 2044–2051, doi: 10.1021/es034720s.
- Marshall, M. J., Plymale, A. E., Kennedy, D. W., Shi, L., Wang, Z., Reed, S. B., Dohnalkova, A. C., Simonson, C. J., Liu, C., Saffarini, D. A., Romine, M. F., Zachara, J. M., Beliaev, A. S., and Fredrickson, J. K., 2008, Hydrogenase- and outer membrane  $\epsilon$ -type cytochrome-facilitated reduction of technetium(VII) by *Shewanella oneidensis* MR-1: *Environmental Microbiology*, v. 10, p. 125–136, doi: 10.1111/j.1462-2920.2007.01438.x.

- Maset, E. R., Sidhu, S. H., Fisher, A., Heydon, A., Worsfold, P. J., Cartwright, A. J., and Keith-Roach, M. J., 2006, Effect of organic co-contaminants on technetium and rhenium speciation and solubility under reducing conditions: *Environmental Science & Technology*, v. 40, p. 5472–5477, doi: 10.1021/es061157f.
- Mashkin, A. N., Korchenkin, K. K., and Svetlakova, N. A., 2002, Technetium distribution throughout Purex process cycles at RT-1 Plant: *Radiochemistry* v. 44, p. 35–41, doi: 10.1023/A:1014871000568.
- McBeth, J. M., Lear, G., Lloyd, J. R., Livens, F. R., Morris, K., and Burke, I. T., 2007, Technetium reduction and reoxidation in aquifer sediments: *Geomicrobiology Journal*, v. 24, p. 189–197, doi: 10.1080/01490450701457030.
- McCubbin, D., Kinson, S. L., McDonald, P., Bonfield, R., and Boust, D., 2006, Distribution of technetium-99 in sub-tidal sediments of the Irish Sea: *Continental Shelf Research*, v. 26, p. 458–473, doi: 10.1016/j.csr.2005.12.010.
- Merrill, P. W., 1952, Spectroscopic observations of stars of class S: *Astrophysics Journal*, v. 116, p. 21–26, doi: 10.1086/145589.
- Meyer, R. E., and Arnold, W. D., 1991, The electrode potential of the Tc(IV)-Tc(VII) couple: *Radiochimica Acta*, v. 55, p. 19–22.
- Meyer, R. E., Arnold, W. D., and Case, F. I., 1987, The Solubility of Electrodeposited Tc(IV) Oxides: Oak Ridge, Tennessee, Oak Ridge National Laboratory, ORNL 6374.
- Meyer, R. E., Arnold, W. D., Case, F. I., and O'Kelley, 1991, Solubilities of Tc(IV) oxides: *Radiochimica Acta*, v. 55, p. 11–18.
- Mooney, R. C. L., 1948, Crystal structure of Element 43: *Acta Crystallographia*, v. 1, p. 161–162, doi: 10.1107/S0365110X48000466.
- Morris, K., Butterworth, J. C., and Livens, F. R., 2000, Evidence for the remobilization of Sellafield waste radionuclides in an intertidal salt marsh, West Cumbria, U. K: *Estuarine, Coastal and Shelf Science*, v. 51, p. 613–625, doi: 10.1006/ecss.2000.0705.
- Murray, H. H., Kelty, S. P., Chianelli, R. R., and Day, C. S., 1994, Structure of rhenium disulfide: *Inorganic Chemistry*, v. 33, p. 4418–4420, doi: 10.1021/ic00097a037.
- Navrotsky, A., Mazeina, L., and Majzlan, J., 2008, Size-driven structural and thermodynamic complexity in iron oxides: *Science*, v. 319, p. 1635–1638, doi: 10.1126/science.1148614.
- Oliver, L. R., Perkins, W. T., and Mudge, S. M., 2006, Detection of technetium-99 in *Ascophyllum nodosum* from around the Welsh Coast: *Chemosphere*, v. 65, p. 2297–2303, doi: 10.1016/j.chemosphere.2006.05.014.
- Ozawa, M., Ishida, M., and Sano, Y., 2003, Strategic separation of technetium and rare metal fission products in spent nuclear fuel: Solvent extraction behavior and partitioning by catalytic electrolytic extraction: *Radiochemistry*, v. 45, p. 225–232, doi: 10.1023/A:1026099707043.
- Parnell, J., 1996, Petrographic relationships between mineral phases and bitumen in the Oklo Proterozoic natural fission reactors, Gabon: *Mineralogical Magazine*, v. 60, p. 581–593, doi: 10.1180/minmag.1996.060.401.04.
- Peacock, R. D., 1966, The chemistry of technetium and rhenium: New York, New York, Elsevier Publishing Company, 137 p.
- Pepper, S. E., Bunker, D. J., Bryan, N. D., Livens, F. R., Charnock, J. M., Pattrick, R. A. D., and Collison, D., 2003, Treatment of radioactive wastes: An X-ray absorption spectroscopy study of the reaction of technetium with green rust: *Journal of Colloid and Interface Science*, v. 268, p. 408–412, doi: 10.1016/j.jcis.2003.08.024.
- Peretroukhine, V., Sergeant, C., Devès, G., Poulain, S., Vesvres, M. H., Thomas, B., and Simonoff, M., 2006, Technetium sorption by stibnite from natural water: *Radiochimica Acta*, v. 94, p. 665–669, doi: 10.1524/ract.2006.94.9.11.665.
- Peretyazhko, T., Zachara, J. M., Heald, S. M., Jeon, B.-H., Kukkadapu, R. K., Liu, C., Moore, D. A., and Resch, C. T., 2008a, Heterogeneous reduction of Tc(VII) by Fe(II) at the solid-water interface: *Geochimica et Cosmochimica Acta*, v. 72, p. 1521–1539, doi: 10.1016/j.gca.2008.01.004.
- Peretyazhko, T., Zachara, J. M., Heald, S. M., Kukkadapu, R. K., Liu, C., Plymale, A. E., and Resch, C. T., 2008b, Reduction of Tc(VII) by Fe(II) sorbed on Al (hydr)oxides: *Environmental Science and Technology*, v. 42, p. 5499–5506, doi: 10.1021/es8003156.
- Perrier, C., and Segrè, E., 1937a, Radioactive isotopes of element 43: *Nature*, v. 140, p. 193–194, doi: 10.1038/140193b0.
- 1937b, Some chemical properties of element 43: *Journal of Chemical Physics*, v. 5, p. 712–716, doi: 10.1063/1.1750105.
- Pignolet, L., Auvray, F., Fonsny, K., Capot, F., and Moureau, Z., 1989, Role of various microorganisms on Tc behavior in sediments: *Health Physics*, v. 57, p. 791–800, doi: 10.1097/00004032-198911000-00013.
- Plekhanov, Yu. V., German, K. E., and Sekine, R., 2003, Electronic structure of technetium metal, calculated in the approximation of the  $X_\alpha$ -Discrete Variation Method: *Radiochemistry*, v. 45, p. 237–242, doi: 10.1023/A:1026004007952.
- Poineau, F., Fatthi, M., Montavon, G., and Grambow, B., 2006, Condensation mechanisms of tetravalent technetium in chloride media: *Radiochimica Acta*, v. 94, p. 291–299, doi: 10.1524/ract.2006.94.5.291.
- Poineau, F., Mazubrun, J. Du., Ford, D., Fortner, J., Kropf, J., Silva, G. W. C., Smith, N., Long, K., Jarvinen, G., and Czerwinski, K., 2008, Uranium/technetium separation for the UREX process—synthesis and characterization of solid reprocessing forms: *Radiochimica Acta*, v. 96, p. 527–533, doi: 10.1524/ract.2008.1533.
- Poineau, F., Hartmann, T., Silva, G. W. C., Jarvinen, G., and Czerwinski, K., 2009, Preparation of technetium metal by thermal treatment under argon/H<sub>2</sub>O: *Journal of Radioanalytical and Nuclear Chemistry*, v. 279, p. 43–48, doi: 10.1007/s10967-007-7259-z.

- Rard, J. A., 1985, Chemistry and thermodynamics of ruthenium and some of its inorganic compounds and aqueous species: *Chemical Reviews*, v. 85, p. 1–39, doi: 10.1021/cr00065a001.
- Rard, J. A., Rand, M. H., Anderegg, G., and Wanner, H., 1999, Chemical Thermodynamics of Technetium, *in* Sandino, M. C. A. and Östholts, E., editors, *Chemical Thermodynamics*: Amsterdam, Elsevier, v. 3, 568 p.
- Rogers, D. B., Shannon, R. D., Sleight, A. W., and Gillson, J. L., 1969, Crystal chemistry of metal dioxides with rutile-related structures: *Inorganic Chemistry*, v. 8, p. 841–849, doi: 10.1021/ic50074a029.
- Rößler, D., Franke, K., Süß, R., Becker, E., and Kupsch, H., 2000, Synthesis and chromatographic characterization of [Tc-99m] technetium-humic acid species: *Radiochimica Acta*, v. 88, p. 95–100, doi: 10.1524/ract.2000.88.2.095.
- Rudin, M. J., Stanton, C., Patterson, R. G., and Garcia, R. S., 1992, National Low-Level Waste Management Program Radionuclide Report Series, v. 2, Technetium-99: Idaho Falls, Idaho, INEL, Idaho National Engineering Laboratory Technical Report DOE/LLW-118, 20 p.
- Schulte, E. H., and Scoppa, P., 1987, Sources and behavior of technetium in the environment: *Science of the Total Environment*, v. 64, p. 163–179, doi: 10.1016/0048-9697(87)90129-X.
- Schwobach, K., 2000, Technetium: Chemistry and Radiopharmaceutical Applications: Weinheim, Germany, Wiley-VCH Verlag, 446 p.
- Sekine, T., Watanabe, A., Yoshihara, K., and Kim, J. I., 1993, Complexation of technetium with humic acid: *Radiochimica Acta*, v. 63, p. 87–90.
- Sekine, T., Asai, N., Muine, T., and Yoshihara, K., 1997, Complexation of technetium traces with humic acid: *Radiochemistry*, v. 39, p. 309–311.
- Sekine, T., Narushima, H., Kino, Y., Kudo, H., Lin, M., and Katsumura, Y., 2002, Radiolytic formation of Tc(IV) oxide colloids: *Radiochimica Acta*, v. 90, p. 611–616, doi: 10.1524/ract.2002.90.9-11\_2002.611.
- Sekine, T., Narushima, H., Suzuki, T., Takayama, T., Kudo, H., Lin, M., and Katsumura, Y., 2004, Technetium(IV) oxide colloids produced by radiolytic reactions in aqueous permanganate solution: *Colloids and Surfaces A*, v. 249, p. 105–109, doi: 10.1016/j.colsurfa.2004.08.074.
- Serne, R. J., Last, G. V., Schaeff, H. T., Lanigan, D. C., Lindenmeier, C. W., Ainsworth, C. C., Clayton, R. E., Legore, V. L., O'Hara, M. J., Brown, C. F., Orr, R. D., Kutnyakov, I. V., Wilson T. C., Wagnon, K. B., Williams, B. A. and Burke, D. S., 2002, Geologic and geochemical data collected from vadose zone sediments from borehole SX 41-09-39 in the S/SX waste management area and preliminary interpretations: Richland, Washington, Pacific Northwest National Laboratory, PNNL-13757-3.
- Serne, R. J., Bjornstad, B. N., Horton, D. G., Lanigan, D. C., Lindenmeier, C. W., Lindberg, M. J., Clayton, R. E., Legore, V. L., Orr, R. D., Kutnyakov, I. V., Baum, S. R., Geiszler, K. N., Valenta, M. M., Vickerman, T. S., and Schaeff, H. T., 2004, Characterization of vadose zone sediments below the T Tank Farm: Boreholes C4104, C4105, 299-W10-196 and RCRA Borehole 299-W11-39: Richland, Washington, Pacific Northwest National Laboratory, PNNL-14849.
- Shannon, R. D., 1976, Revised effective ionic-radii and systematic studies of interatomic distances in halides and chalcogenides: *Acta Crystallographica Section A*, v. 32, p. 751–767, doi: 10.1107/S0567739476001551.
- Sheppard, M. I., and Sheppard, S. C., 1986, Technetium behavior in soils of the Canadian Shield, *in* Desmet, G., and Myttenarere, C., editors, *Technetium in the Environment*: Essex, England, Elsevier Applied Science Publishers, p. 131–141.
- Shi, L., Chen, B., Wang, Z., Elias, D. A., Mayer, M. U., Gorby, Y. A., Ni, S., Lower, B. H., Kennedy, D. W., Wunschel, D. S., Mottaz, H. M., Marshall, M. J., Hill, E. A., Beliaev, A. S., Zachara, J. M., Fredrickson, J. K., and Squier, T. C., 2006, Isolation of high-affinity functional protein complex between OmcA and MtrC: Two outer membrane decaheme c-type cytochromes of *Shewanella oneidensis* MR-1: *Journal of Bacteriology*, v. 188, p. 4705–4714, doi: 10.1128/JB.01966-05.
- Shi, L., Squier, T. C., Zachara, J. M., and Fredrickson, J. K., 2007, Respiration of metal (hydr)oxides by *Shewanella* and *Geobacter*: A key role for multihaem c-type cytochromes: *Molecular Microbiology*, v. 65, p. 12–20, doi: 10.1111/j.1365-2958.2007.05783.x.
- Simonoff, M., Sergeant, C., Poulain, S., and Pravikoff, M. S., 2007, Microorganisms and migration of radionuclides in environment: *Comptes Rendus Chimie*, v. 10, p. 1092–1107, doi: 10.1016/j.crci.2007.02.010.
- Smith, V., Fegan, M., Pollard, D., Long, S., Hayden, E., and Ryan, T. P., 2001, Technetium-99 in the Irish marine environment: *Journal of Environmental Radiation*, v. 56, p. 269–284, doi: 10.1016/S0265-931X(00)00209-5.
- Stalmans, M., Maes, A., and Cremers, A., 1986, Role of organic matter as a geochemical sink for technetium in soils and sediments, *in* Desmet, G., and Myttenarere, C., editors, *Technetium in the Environment*: Essex, England, Elsevier Applied Science Publishers, p. 91–113.
- Standing, W. J. F., Oughton, D. H., and Salbu, B., 2002, Potential remobilization of <sup>137</sup>Cs, <sup>60</sup>Co, <sup>99</sup>Tc, and <sup>90</sup>Sr from contaminated Mayak sediments in river and estuary environments: *Environmental Science and Technology*, v. 36, p. 2330–2337, doi: 10.1021/es0103187.
- Tagami, K., and Uchida, S., 1997, Concentration of global fallout <sup>99</sup>Tc in rice paddy soils collected in Japan: *Environmental Pollution*, v. 95, p. 151–154, doi: 10.1016/S0269-7491(96)00124-8.
- 1999, Chemical transformation of technetium in soil during the change of soil water conditions: *Chemosphere*, v. 38, p. 963–971, doi: 10.1016/S0045-6535(98)00361-0.
- Tarasov, V. A., Romanov, E. G., Toporov, Yu. G., Radchenko, V. M., Rotmanov, K. V., Lebedeva, L. S., Kozar, A. A., and Peretrukhin, V. F., 2007, Transmutation of <sup>99</sup>Tc and preparation of artificial stable ruthenium: I. Transmutation of metallic <sup>99</sup>Tc in a high-flux SM reactor: *Radiochemistry*, v. 49, p. 289–292, doi: 10.1134/S1066362207030149.
- Thorne, M. C., 2003, Estimation of animal transfer factors for radioactive isotopes of iodine, technetium, selenium and uranium: *Journal of Environmental Radioactivity*, v. 70, p. 3–20, doi: 10.1016/S0265-931X(03)00126-7.

- Till, J. E., 1986, Source terms for technetium-99 from nuclear fuel cycle facilities, in Desmet, G., and Myttenaere, C., editors, *Technetium in the Environment*: Essex, England, Elsevier Applied Science Publishers, p. 1–20.
- Tkác, P., Kopunec, R., Macásek, F., and Skrašková, S., 2000, Sorption of Tc(IV) and Tc(VII) on soils: influence of humic substances: *Journal of Radioanalytical and Nuclear Chemistry*, v. 246, p. 527–531, doi: 10.1023/A:1006776503353.
- Tomilin, S. V., Radchenko, V. M., Rotmanov, K. V., Lebedeva, L. S., Yakovenko, A. G., Pichuzhkina, E. M., Kryukov, F. N., and Nikitin, O. N., 2007, Transmutation of <sup>99</sup>Tc and preparation of artificial stable ruthenium: II. Examination of Tc-Ru alloys obtained by irradiation of metallic technetium: *Radiochemistry*, v. 49, p. 624–629, doi: 10.1134/S106636220706015X.
- Utsunomiya, S., and Ewing, R. C., 2006, The fate of the epsilon phase (Mo-Ru-Pd-Tc-Rh) in the UO<sub>2</sub> of the Oklo natural fission reactors: *Radiochimica Acta*, v. 94, p. 749–753, doi: 10.1524/ract.2006.94.9-11.749.
- Van Loon, L. R., Desmet, G. M., and Cremers, A., 1985, The Influence of the Chemical Form of Technetium on its Uptake by Plants, in Bulman, R. A., and Cooper, J. R., editors, *Speciation of Fission and Activation Products in the Environment*: London, England, Elsevier Applied Science Publishers, p. 352–360.
- Van Loon, L., Stalman, M., Maes, A., Cremers, A., and Cogneau, M., 1986, Humic Acid Complexes of Technetium: Synthesis and Characterization, in Desmet, G., and Myttenaere, C., editors, *Technetium in the Environment*: Essex, England, Elsevier, Elsevier Applied Science Publishers, Ltd., p. 143–153.
- Vandecasteele, C. M., Dehut, J. P., Van Laer, S., Depriens, D., and Myttenaere, C., 1989, Long-term availability of Tc deposited on soil after accidental releases: *Health Physics*, v. 57, p. 247–254, doi: 10.1097/00004032-198908000-00002.
- Vichot, L., Ouard, G., Montavon, G., Fattahi, M., Musikas, C., and Grambow, B., 2002, XAS study of technetium (IV) polymer formation in mixed sulphate/chloride media: *Radiochimica Acta*, v. 90, p. 575–579, doi: 10.1524/ract.2002.90.9-11\_2002.575.
- Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., Churney, K. L., and Nuttall, R. L., 1982, *The NBS Tables of Chemical Thermodynamic Properties*: New York, American Chemical Society and the American Institute of Physics, 405 p.
- Warwick, P., Aldridge, S., Evans, N., and Vines, S., 2007, The solubility of technetium (IV) at high pH: *Radiochimica Acta*, v. 95, p. 709–716, doi: 10.1524/ract.2007.95.12.709.
- Watson, J. H. P., Croudace, I. W., James, P. A. B., Charnock, J. M., and Ellwood, D. C., 2001, Adsorption of radioactive metals by strongly magnetic iron sulfide nanoparticles produced by sulfate-reducing bacteria: *Separations Science and Technology*, v. 36, p. 2571–2607, doi: 10.1081/SS-100107214.
- Wharton, M. J., Atkins, B., Charnock, J. M., Livens, F. R., Patrick, R. A. D., and Collison, D., 2000, An X-ray absorption spectroscopy study of the coprecipitation of Tc and Re with mackinawite (FeS): *Applied Geochemistry*, v. 15, p. 347–354, doi: 10.1016/S0883-2927(99)00045-1.
- Wildung, R. E., Garland, T. R., McFadden, K. M., and Cowan, C. E., 1984, Technetium Sorption in Surface Soils, in Desmet, G., and Myttenaere, C., editors, *Technetium in the Environment*: Essex, England, Elsevier Applied Science Publishers, p. 115–130.
- Wildung, R. E., Routson, R. C., Serne, R. J., and Garland, T. R., 1974, Pertechmetate, iodide and methyl iodide retention by surface soils, in *Pacific Northwest National Laboratory Annual Report for 1974*, BNWL-1950, Pt. 2: Richland, Washington, Pacific Northwest National Laboratory, p. 37–40.
- Wildung, R. E., McFadden, K. M., and Garland, T. R., 1979, Technetium sources and behavior in the environment: *Journal of Environmental Quality*, v. 8, p. 156–161, doi: 10.2134/jeq1979.00472425000800020004x.
- Wildung, R. E., Gorby, Y. A., Krupka, K. M., Hess, N. J., Li, S. W., Plymale, A. E., McKinley, J. P., and Fredrickson, J. K., 2000, Effect of electron donor and solution chemistry on products of dissimilatory reduction of technetium by *Shewanella putrefaciens*: *Applied and Environmental Microbiology*, v. 66, p. 2451–2460.
- Wolfrumm, C., and Bunzl, K., 1986, Sorption and desorption of technetium by humic substances under oxic and anoxic conditions: *Journal of Radioanalytical and Nuclear Chemistry*, v. 99, p. 315–323, doi: 10.1007/BF02037591.
- Wronkiewicz, D. J., Watkins, C. S., Baughman, A. C., Miller, F. S., and Wolf, S. F., 2002, Corrosion Testing of a Simulated Five-Metal Epsilon Particle in Spent Nuclear Fuel, in McGrail, B. P., and Cragnolino, G. A., editors, *Scientific Basis for Nuclear Waste Management XXV*: Warrendale, Pennsylvania, Materials Research Society, v. 713, p. 625–632.
- Xia, Y., Hess, N. J., and Felmy, A. R., 2006, Stability constants of technetium(IV) oxalate complexes as a function of ionic strength: *Radiochimica Acta*, v. 94, p. 137–141, doi: 10.1524/ract.2006.94.3.137.
- Xiong, Y., and Wood, S. A., 1999, Experimental determination of the solubility of ReO<sub>2</sub> and the dominant oxidation state of rhenium in hydrothermal solutions: *Chemical Geology*, v. 158, p. 245–256, doi: 10.1016/S0009-2541(99)00050-9.
- Yang, H., Lu, R., Downs, R. T., and Costin, G., 2006, Goethite, α-FeO(OH), from single-crystal data: *Acta Crystallographica*, v. E62, p. 250–252, doi: 10.1107/S1600536806047258.
- Zachara, J. M., Heald, S. M., Jeon, B. H., Kukkadapu, R. K., Liu, C. X., McKinley, J. P., Dohnalkova, A. C., and Moore, D. A., 2007, Reduction of pertechmetate [Tc(VII)] by aqueous Fe(II) and the nature of solid phase redox products: *Geochimica et Cosmochimica Acta*, v. 71, p. 2137–2157, doi: 10.1016/j.gca.2006.10.025.
- Zhang, P.-C., Krumhansl, J. L., and Brady, P. V., 2000, Boehmite sorbs perrhenate and pertechmetate: *Radiochimica Acta*, v. 88, p. 369–373, doi: 10.1524/ract.2000.88.6.369.
- Zilberman, B. Ya., Pokhitonov, Yu. A., Kirshin, M. Yu., Ozawa, M., and Blokhin, A. A., 2007, Prospects for development of a process for recovering technetium from spent fuel of nuclear power plants: *Radiochemistry*, v. 49, p. 156–161, doi: 10.1134/S1066362207020105.