Investigation of Technetium Redox Cycling in FRC Background Sediments using EXAFS and Gamma Camera Imaging

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Introduction
Technetium occurs in a variety of inorganic Tc(VII) and Tc(IV) forms. Tc(VII) is a heavy actinide; its redox chemistry is well understood, and a significant amount of Tc(VII) is found in aquatic systems. Tc(VII) is of concern due to its long half-life (215 yr) and high mobility in the environment. As a result, Tc is a significant contributor to global radiological impact, particularly in the nuclear waste disposal process. Technetium redox cycling in the environment is influenced by the availability of electron donors and acceptors, reaction rates, reaction mechanisms, and redox status. This study focuses on the microbial reduction of Tc(VII), an important process in the biogeochemical cycling of Tc in the environment. There is increasing awareness of the impact of anaerobic processes on the movement and transformation of Tc, and the need for better understanding of the factors controlling Tc redox cycling.

Aims and Objectives
The objective of this project is to probe the site-specific biogeochemical controls underpinning biogeochemical processes occurring in a site-specific context. This includes the identification of: (i) Tc(VII) reduction and precipitation in FRC sediments under anaerobic conditions in batch experiments; (ii) the rate of reduction of Tc(VII) by Fe(III)-reducing bacteria; (iii) the relative amount of Tc(VII) in Tc(VII) phases. The objective is to probe the site-specific processes underpinning biogeochemical controls and the factors controlling Tc redox cycling.

Hypotheses
1. Sediment and groundwater from FRC background area can be used as model systems for anaerobic conditions. This hypothesis focuses on the identification of Tc(VII) phases under anaerobic conditions, in particular biogenic magnetite control against a more complex biogeochemical background provided by the site-specific context.
2. The redox state of reduced Tc can be determined using X-ray absorption spectroscopy (XAS), EXAFS, and gamma camera imaging. This hypothesis focuses on the determination of the redox state of reduced Tc using XAS and EXAFS.
3. Tc(VII) will be reduced and precipitated in FRC sediments under anaerobic conditions in batch experiments. This hypothesis focuses on the identification of Tc(VII) phases under anaerobic conditions, in particular biogenic magnetite control against a more complex biogeochemical background provided by the site-specific context.

Microbiological Analyses
Analysis of the site microbial community (Figure 2) showed that the site is dominated by Tc(VII)-reducing bacteria. The community also included a large number of Tc(VII) reducers, which would be expected to be present in Tc(VII)-reducing environments.

EXAFS Analyses
Table 1. EXAFS data reduction and results for reduced Tc(VII).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reduced Tc(VII)</th>
<th>% Reduction</th>
<th>Tc-O/Oxalate Distance (Å)</th>
<th>Tc-O/Oxalate Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) 1</td>
<td>1.908 0.029</td>
<td>80.4%</td>
<td>1.732 ± 0.005</td>
<td>1.732 ± 0.005</td>
</tr>
<tr>
<td>(B) 2</td>
<td>1.908 0.029</td>
<td>80.4%</td>
<td>2.512 ± 0.005</td>
<td>2.512 ± 0.005</td>
</tr>
<tr>
<td>(C) 3</td>
<td>1.908 0.029</td>
<td>80.4%</td>
<td>2.996 ± 0.005</td>
<td>2.996 ± 0.005</td>
</tr>
</tbody>
</table>

Figure 3. EXAFS and outer Transform for Fe(III)-reducing sediment, and 100 y of reduced biologically sample.

Conclusions
- **Tc** reduction in FRC background sediments is associated with Fe(III)-reducing conditions. The proportion of Tc(VII) reducing bacteria isolated from these sediments is high, and is in agreement with the hypothesis that Tc(VII) reduction occurs in Tc(VII)-reducing environments.
- **EXAFS** analysis of reduced Fe(III)-reducing sediment indicates that Tc(VII) is reduced to Tc(IV) in Fe(III)-reducing environments, with Tc(IV) remaining in Tc(VII)-reducing environments. Further characterization is necessary to confirm the redox state of reduced Tc(VII).

Future Directions
- We are currently developing additional progressive microcosm experiments and EXAFS analyses using sediments and groundwater from both FRC background and contaminated areas, to address the effect of iron reduction on Tc redox cycling in sediments. Tc(IV) will be used as a model system to identify the factors controlling Tc redox cycling.
- We will also use gamma camera imaging to evaluate the biogeochemical processes occurring in sediments.

References

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