Alkali technetium oxides and their relation to Tc loading in nuclear waste glasses

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Sydney, Australia

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Acknowledgements

Pacific Northwest NATIONAL LABORATORY
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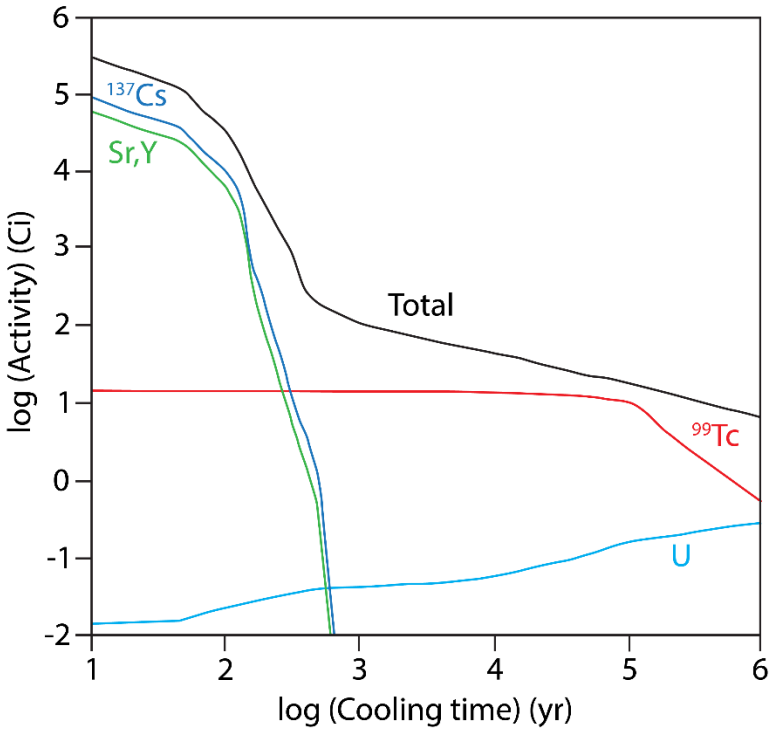
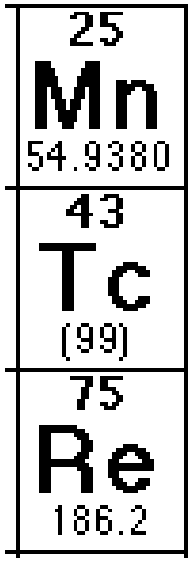
Outline

- Motivation
- Tc in glass
- TcO_4 compounds
- TcO_5, TcO_6 compounds
- Simulations & ongoing work

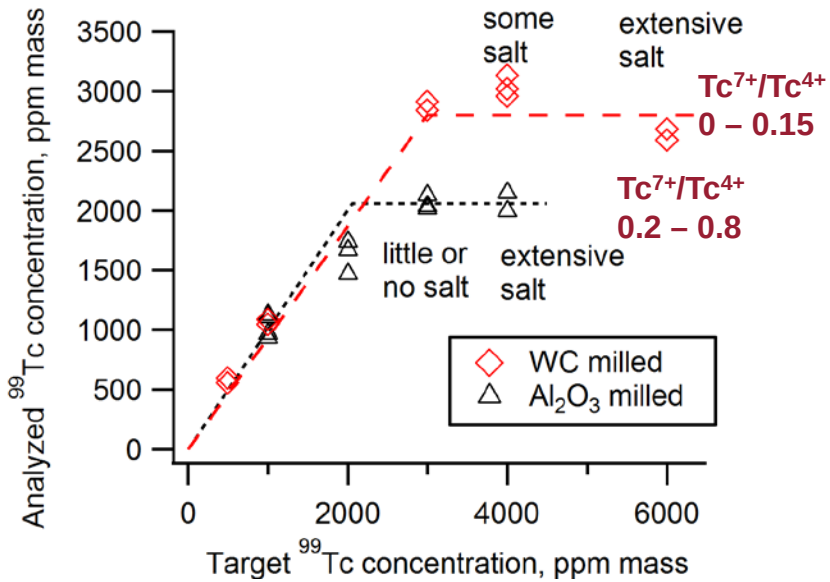
Technetium – why do we care?

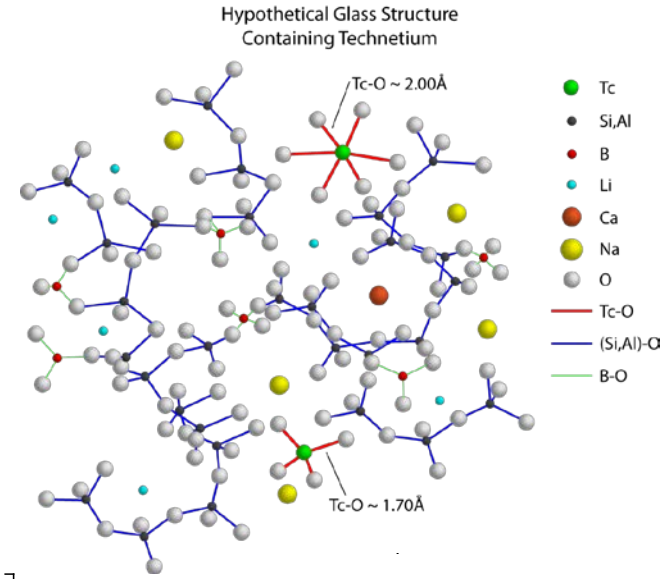
- Tc-99 is problematic radionuclide
  - Half life 213,000 years
  - TcO_4^- highly mobile in ground water
  - Redox quite different than surrogate Re
- For Hanford mission, Tc-99 is concern
  - Hanford site: ~1500 kg (~25,000 Ci) of ^{99}Tc, 50-90+% to be immobilized in LAW glass
  - Low retention of Tc: Solubility? Volatility?

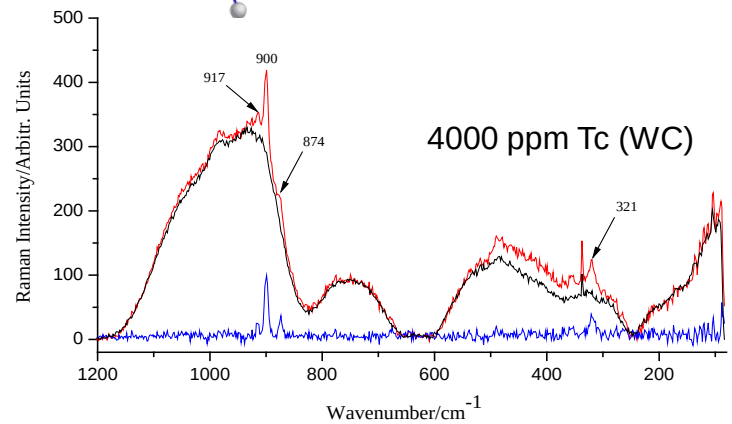




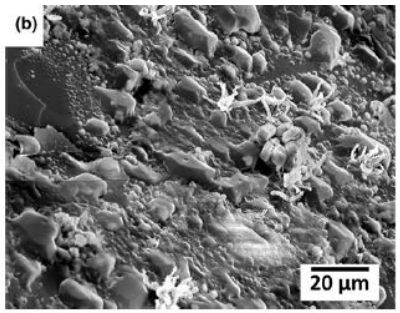
Tc in glass

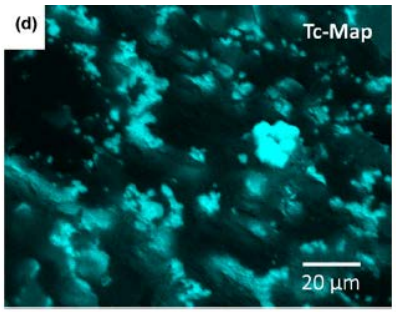


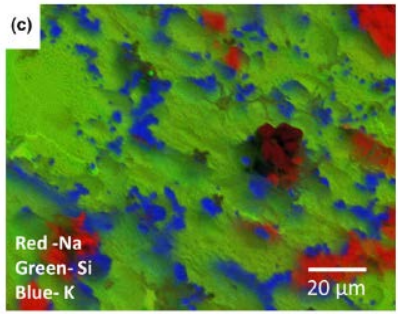




- A lot of Tc can go into glass
- In glass, structure may be more complicated than traditional view
- Not clear if Tc is clustering or crystallizing in glass
- Salt phase formation

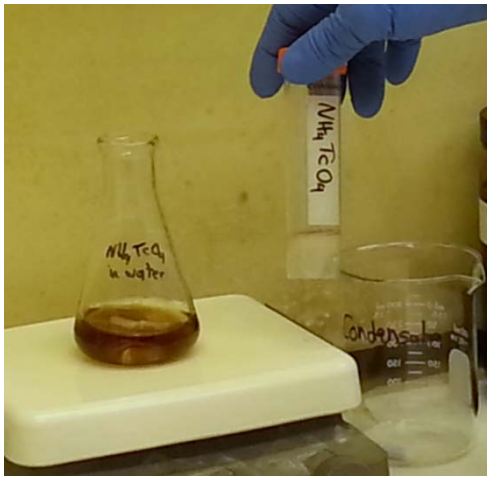






Soderquist et al, *J. Nuclear Materials*, 449, 173 (2014).
Gassman et al, *J. Raman Spectroscopy*, 45, 139 (2014).
Soderquist et al, *J. Nuclear Materials*, 99, 3924 (2016).

Pertechnetate Synthesis



- Synthesis completed in a specialized hood in the Radiochemical Processing Laboratory (RPL) at Pacific Northwest National Laboratory
- Batch sizes 0.5 – 20.0 grams of solid Tc oxides

1. NH_4TcO_4

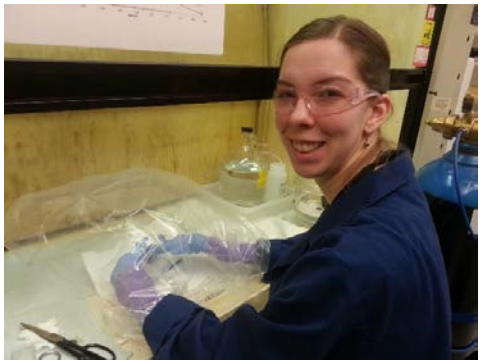
2. Cation Exchange Column

3. Distillation & Crystallization

$HTcO_4$
$LiTcO_4$
$NaTcO_4$
$KTcO_4$
$RbTcO_4$
$CsTcO_4$
Na_3TcO_5
K_3TcO_5
Na_5TcO_6
K_5TcO_6
Li_5TcO_6

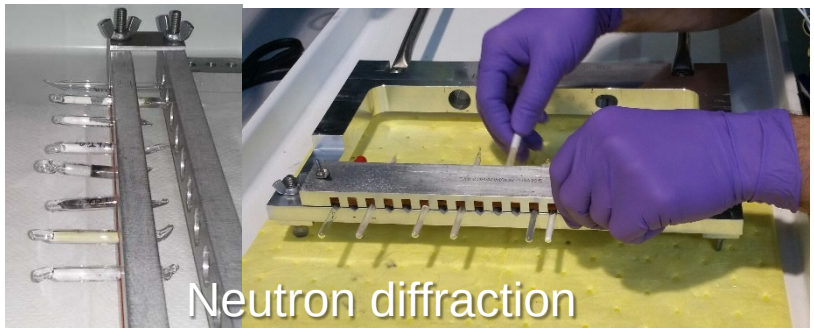
From M^+TcO_4 and M^+OH or $M^+_2CO_3$

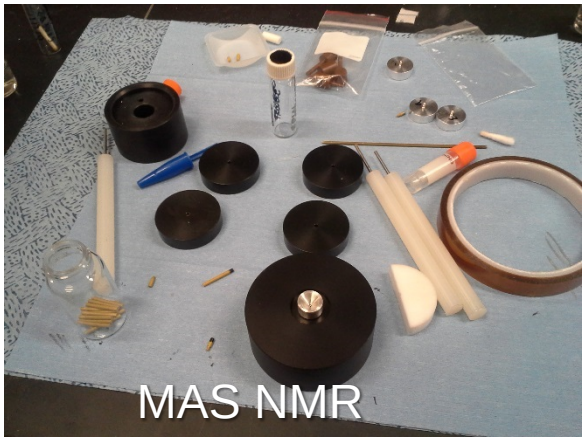
Analysis



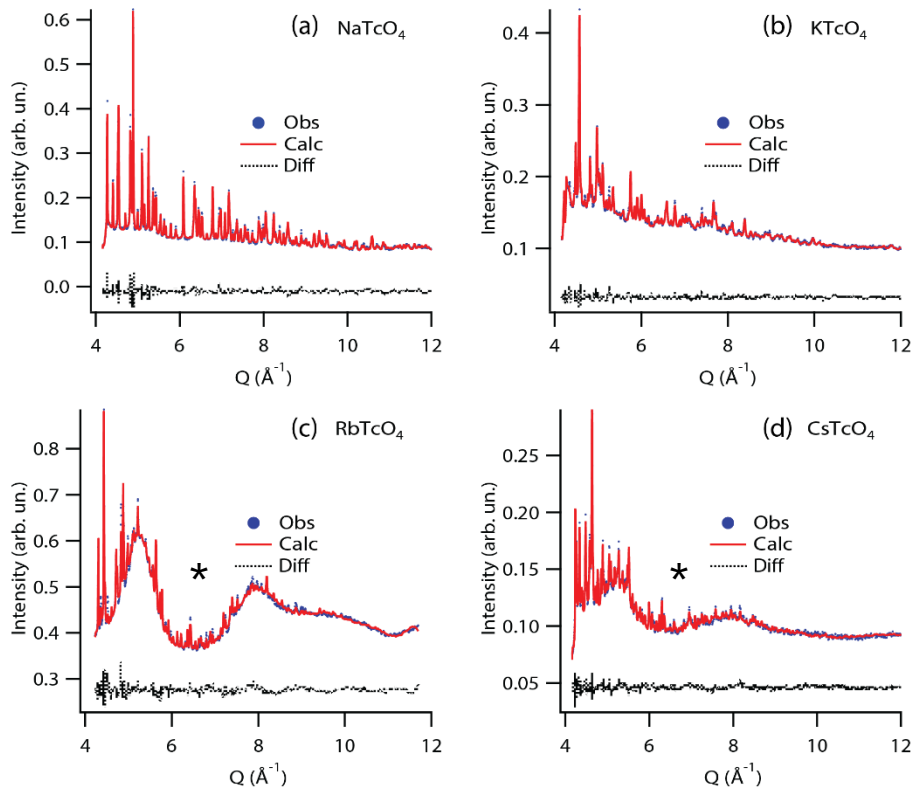
- Special tools and techniques had to be developed for loading & analyzing Tc-99 compounds
- Issues included performing sample loading in **radiological hood** and sometimes inside **glove bag**, all to prevent **dispersibility** & interaction with water

• ND	~1200 µCi	(44.4 MBq)
• NMR	~100	(3.70)
• Raman	~50	(1.85)
• XAS	~43	(1.59)





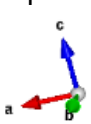
TcO_4 Pertechnetates: Neutron Diffraction

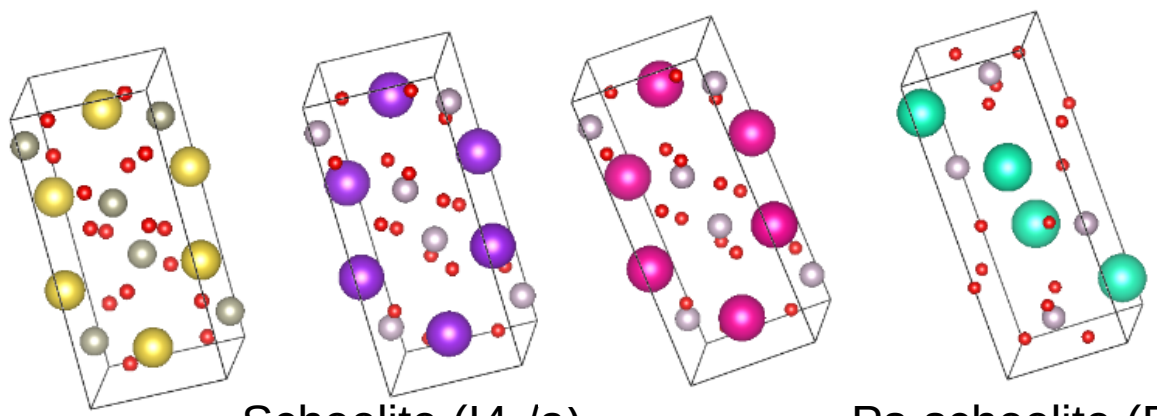


Compound	Tc -O bond length (Å)	O-Tc-O Angle (degrees)	Alkali-O bond length (Å)	χ^2
$NaTcO_4$	1.71(2)	107.29(1); 113.92(6)	2.56(1), 2.61(1)	20.160
$KTcO_4$	1.74(8)	109.02(4); 110.0(5)	2.83(5); 2.86(8)	21.530
$RbTcO_4$	1.72(3)	109.18(4); 110.04(74)	3.02(1)	1.210
$CsTcO_4$	1.66(1); 1.70(3)	109.33(12); 113.6(4); 107.29(18); 109.9(4)	3.05(9), 3.31(9), 3.24(6), 3.64(5) 3.13(9), 3.67(7), 3.08(9), 3.17(4), 3.77(4), 3.07(7), 3.46(6), 3.26(5)	4.840

Initial difficulties with capillary XRD led to the use of ND

*Hump is SiO_2 glass background from sealed tube holder due to having less Tc powder for these





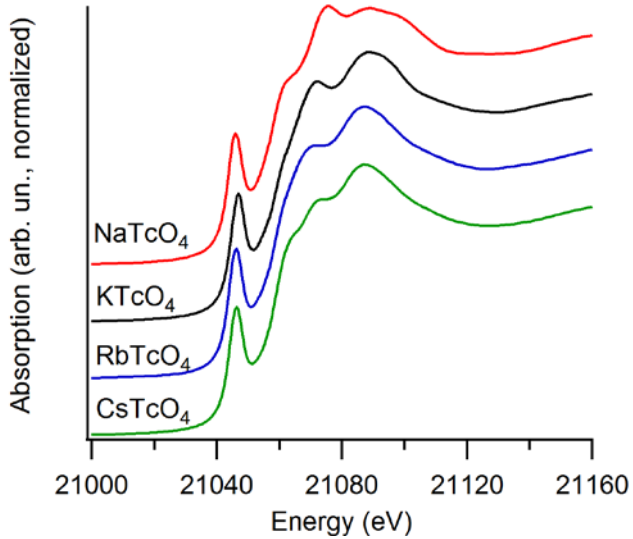
Gray = ^{99}Tc
Red = O

Scheelite ($I4_1/a$)

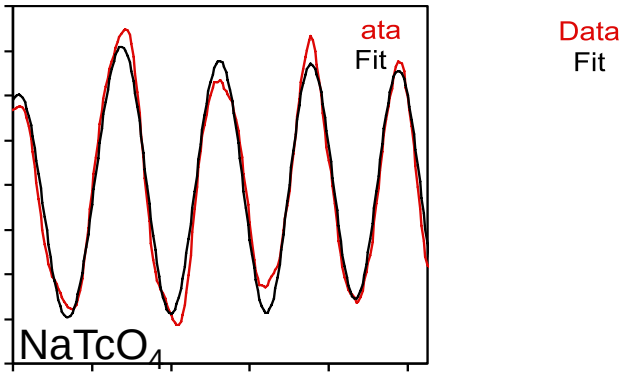
Ps-scheelite (Pnma)

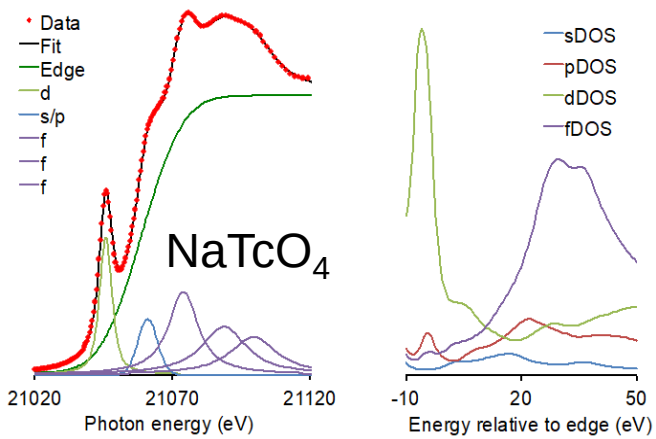
TcO_4 Pertechnetates: Tc K-edge XAS

XANES



EXAFS





Compound	# Neighboring O Atoms	σ^2 (Å^2)	Tc-O Distance (Å)
$NaTcO_4$	3.6(2)	0.0007(3)	1.731(3)
$KTcO_4$	4.1(2)	0.0010(3)	1.736(3)
$RbTcO_4$	4.3(3)	0.0011(5)	1.713(5)
$CsTcO_4$	4.1(2)	0.0011(3)	1.723(5)

- XANES transitions quite different, especially in *sp* and *f* transitions
- For EXAFS, Tc-O bond distances very similar, but Na seems undercoordinated

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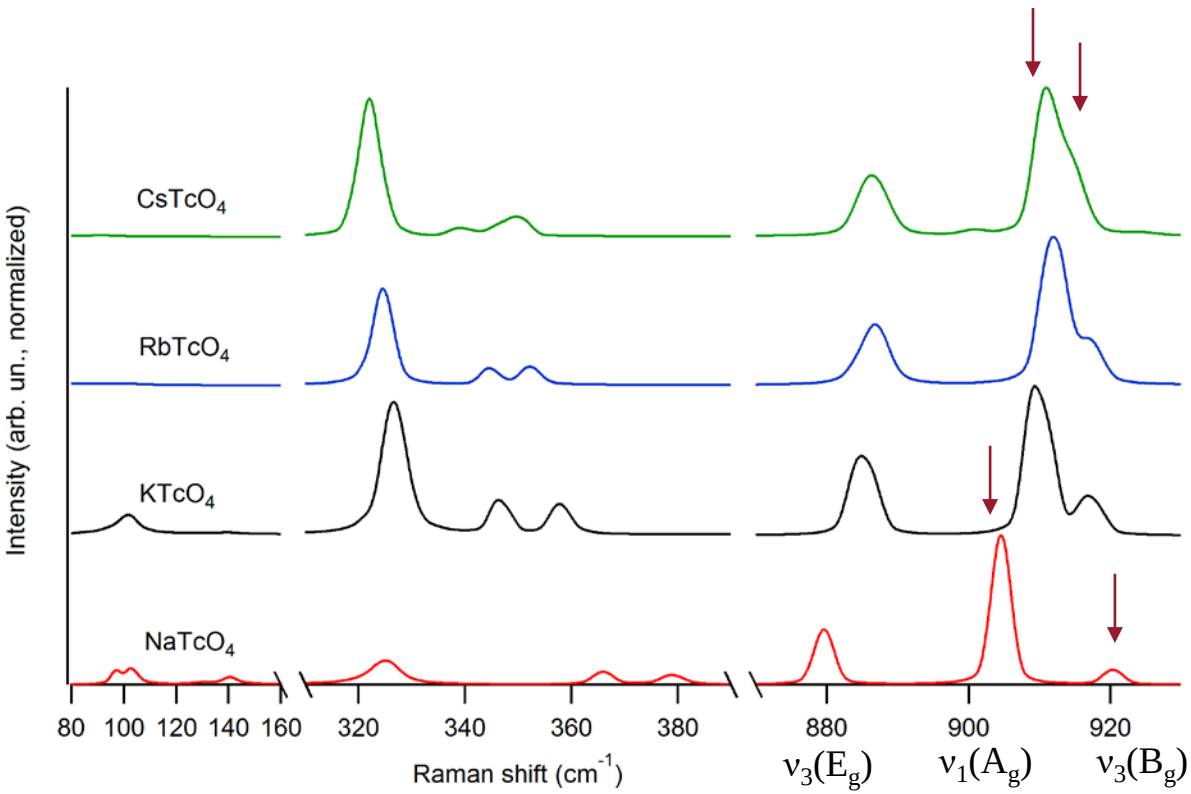
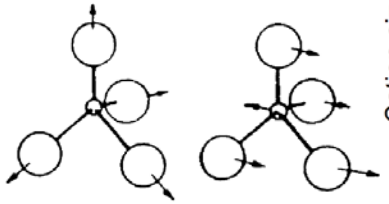
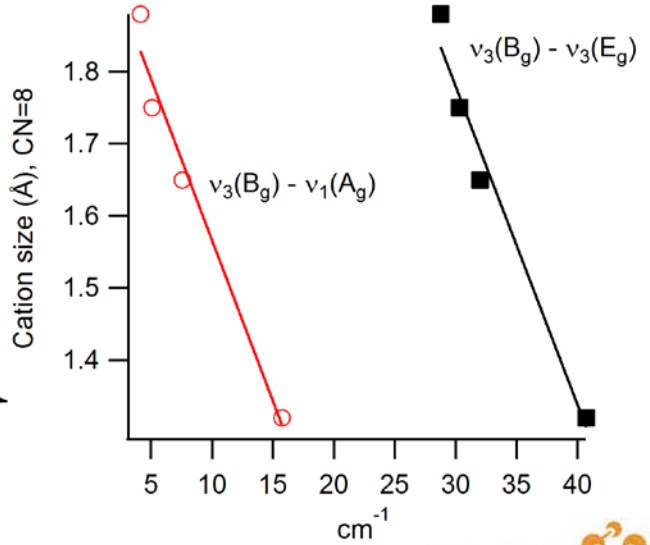
TcO_4 Pertechnetates: Raman



- High resolution confocal Raman
- 532 nm excitation
- 1800 grooves/mm



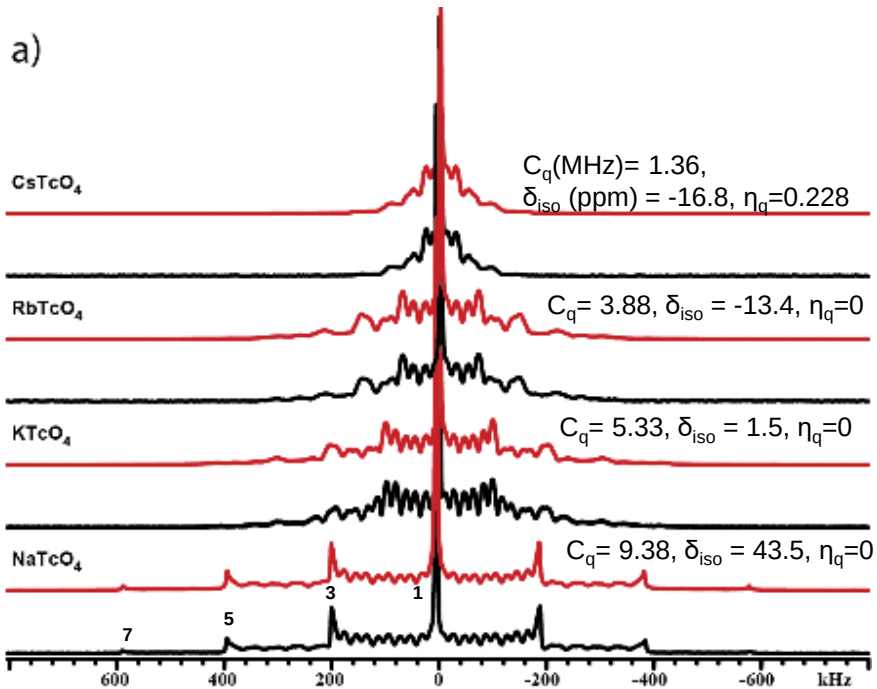


- Some trends evident, particularly in spacing between stretching modes
- $CsTcO_4$ (pseudo-scheelite) closely resembles $RbTcO_4$ (scheelite)
- Large cation: vibrations similar to isolated TcO_4

EMSL

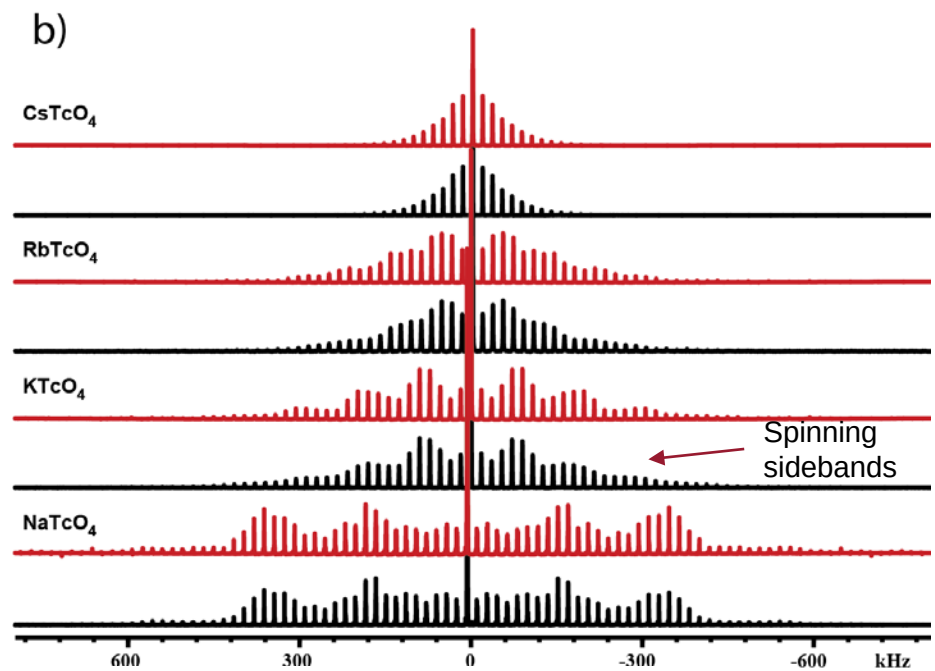
TcO_4 Pertechnetates: Tc-99 NMR

750 MHz (17.6 T) "Static" NMR



Tc-99 referenced to TcO_4^-(aq)

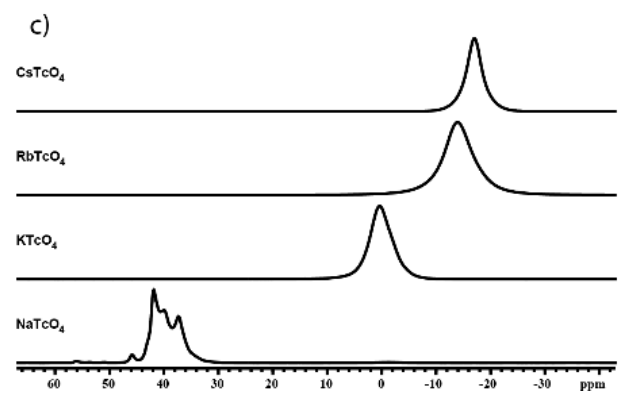
750 MHz (17.6 T)
18 kHz (MAS) MAS NMR



Red (simulation); **Black** (experiment)
Tc-99 is a **spin 9/2 nucleus**:

1: -1/2 ↔ +1/2 ("central transition", left after MAS)
3: -3/2 ↔ -1/2
5: -5/2 ↔ -3/2
7: -7/2 ↔ -5/2
9: -9/2 ↔ -7/2

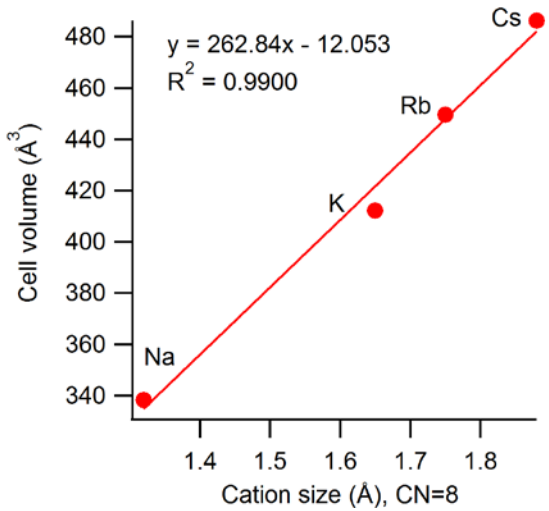
Smaller C_q (MHz), tighter distribution of transitions in frequency space



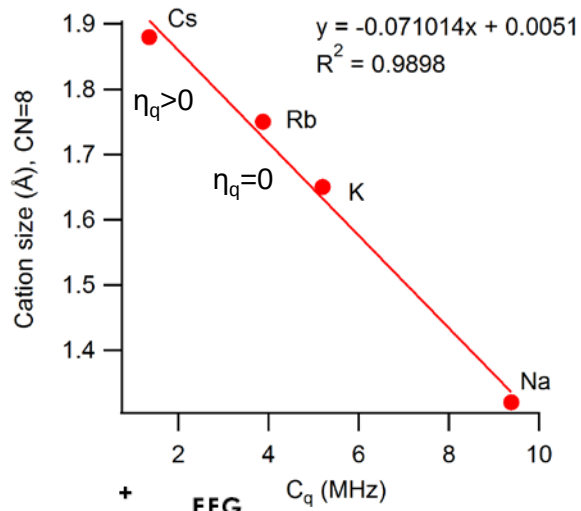
central transition

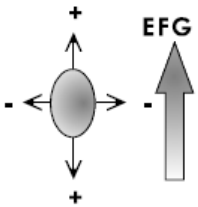
TcO_4 Pertechnetates: "Size matters"

Unit cell volume

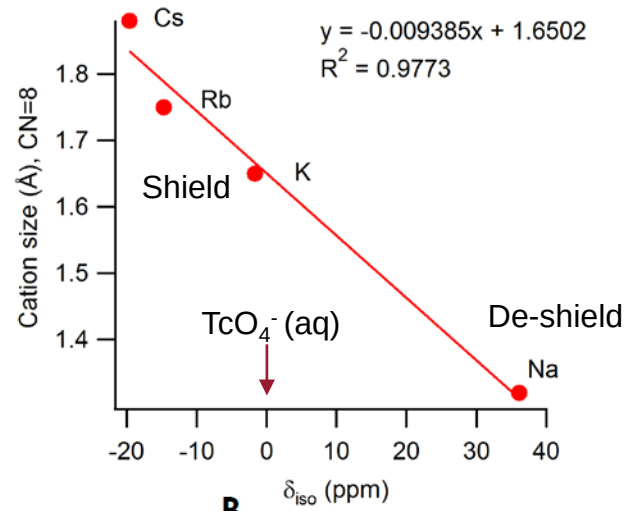


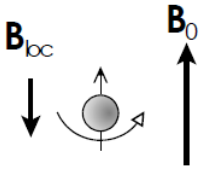
Quadrupolar coupling





Isotropic chemical shift





Bigger counter cation -> bigger unit cell

- despite crystal structure change at Cs

From Tc-99 NMR, alkali size (# electrons) influences O in Tc-O bond, thus influencing Tc-99; for $NaTcO_4$:

- Na higher EN than other alkali thus attracts e-
- charge density relatively higher on alkali side of O
- Tc deshielded relative to TcO_4^-
- Larger difference in O-Tc-O bond angles (more asymmetric) -> larger quadrupolar coupling

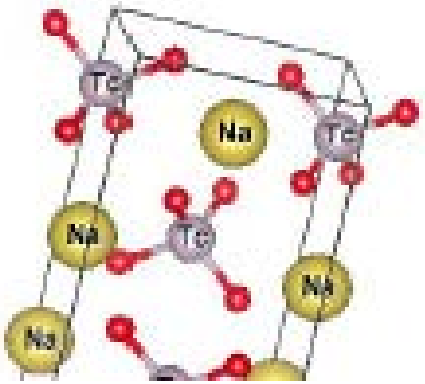
Weaver, J., C.Z. Soderquist, N.M. Washton, A.S. Lipton, P.L. Gassman, W.W. Lukens, A.A. Kruger, N.A. Wall, and J.S. McCloy, "Chemical Trends in Solid Alkali Pertechnetates," *Inorganic Chemistry*, 56(5), 2533-2544 (2017).

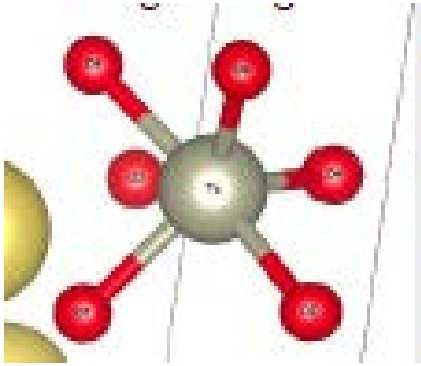
5- and 6-coordinated Tc(VII) Pertechnetates?

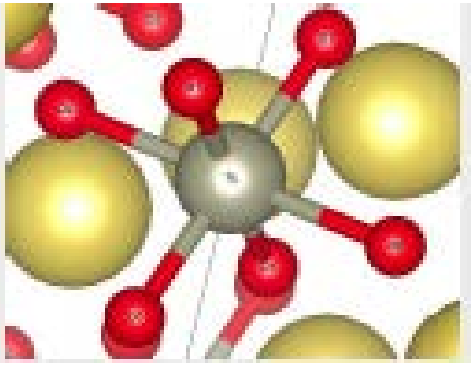
Tc(VII)
Tc(VI)
Tc(V)

- $2Li_2O + LiTcO_4 \rightarrow Li_5TcO_6$ (250-450°C)
  $2Li_2CO_3 + LiTcO_4 \rightarrow Li_5TcO_6 + 2CO_2$ (600-650°C)
- $Li_2O + LiTcO_4 \rightarrow Li_3TcO_5$ (reaction T unknown)
- $4Li_5TcO_6 \rightarrow 2Li_6TcO_6 + Tc_2O_{7(gas)} + 4Li_2O + ½O_{2(gas)}$ (>650°C)
- $Li_6TcO_6 \rightarrow Li_4TcO_5 + Li_2O$ (750°C)

- $2Na_2O + NaTcO_4 \rightarrow Na_5TcO_6$ (250-450°C)
- $Na_2O + NaTcO_4 \rightarrow Na_3TcO_5$ (250-450°C)
- $K_2O + KTcO_4 \rightarrow K_3TcO_5$ (250-450°C)







Tc(VII) TcO_4^- TcO_5^{3-} TcO_6^{5-}

- B. Kanellakopulos, The ternary oxide of 3-to 7-valent technetium with alkalis, Kernforschungszentrum. Inst. Radiochem., Karlsruhe, Germany, IssueAEC Accession No. 31424, Rept. No. KFK-197 (1964).
- Keller, C. and B. Kanellakopulos, "Ternary oxides of tri- to septivalent technetium and alkali metals," *Journal of Inorganic and Nuclear Chemistry*, 27(4), 787-95 (1965).

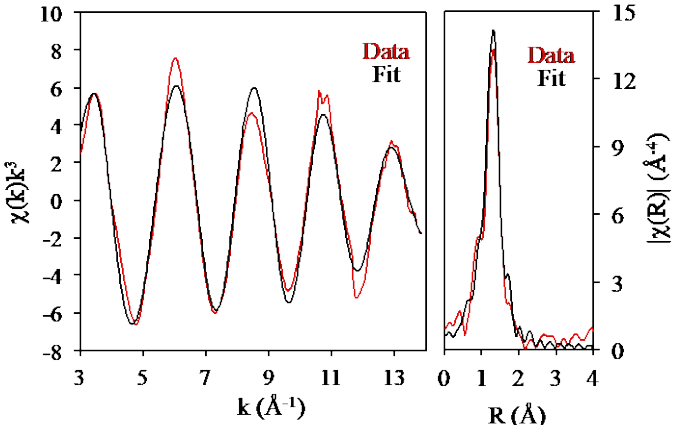
TcO5 and TcO6

- Several synthesis approaches: Very hygroscopic, difficult to characterize
- Probably impure: Na3, K3, Li5, Na5, K5
- XAS: appear to be different than TcO4
- EPR: some even Tc states due to impurity? radiolysis?
- Raman: Li_5ReO_6 successful & matched literature
- NMR: Li_5TcO_6 has strange Tc-99 pattern

Compounds are difficult to make in pure state; not very stable so hard to characterize; crystal structures not generally known

K_3TcO_5

Neighbor	# of Neighbors	Distance (Å)	σ^2 (Å^2)
O	4	1.72(1)	0.0031(4)[a]
O	1	2.03(3)	0.0031(4)[a]

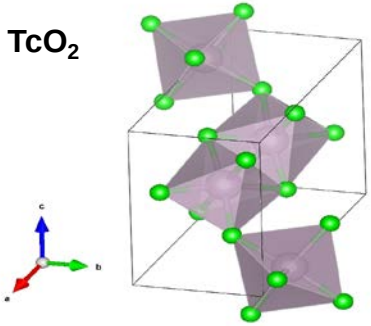


Weaver, J., C. Soderquist, P. Gassman, E. Walter, W. Lukens, and J.S. McCloy, "Synthesis and Characterization of 5- and 6- Coordinated Alkali Pertechnetates," *MRS Advances*, 2(10), 525-542 (2017).

Current and future work

- Establish DFT methods on TcO_2, Tc_2O_7 and compare to literature & spectroscopy

TcO_2



Electronic DOS

Phonon DOS

- Calculate $KTcO_4$, $NaTcO_4$ and compare cal/exp Raman, NMR
- Calculate "unknowns" $LiTcO_4$ and "$HTcO_4$"
- In parallel, synthesize & characterize ReO5 and ReO6 compounds to refine methods

Thanks for staying to (almost) the bitter end of MRS 2017!