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Application of EXAFS and XANES for studies of heavy metal/metalloid interaction with mineral surfaces

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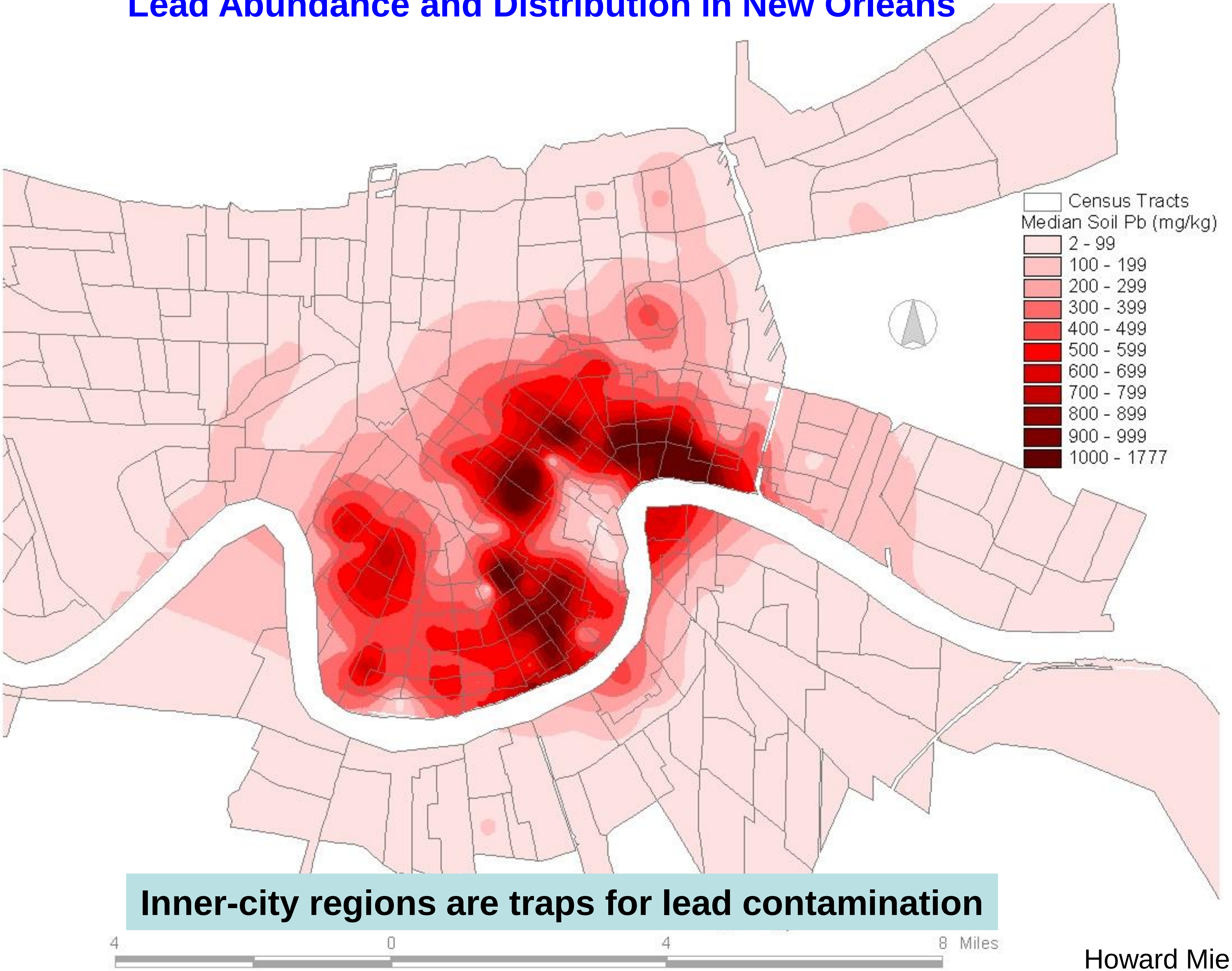
Lead Abundance and Distribution in New Orleans



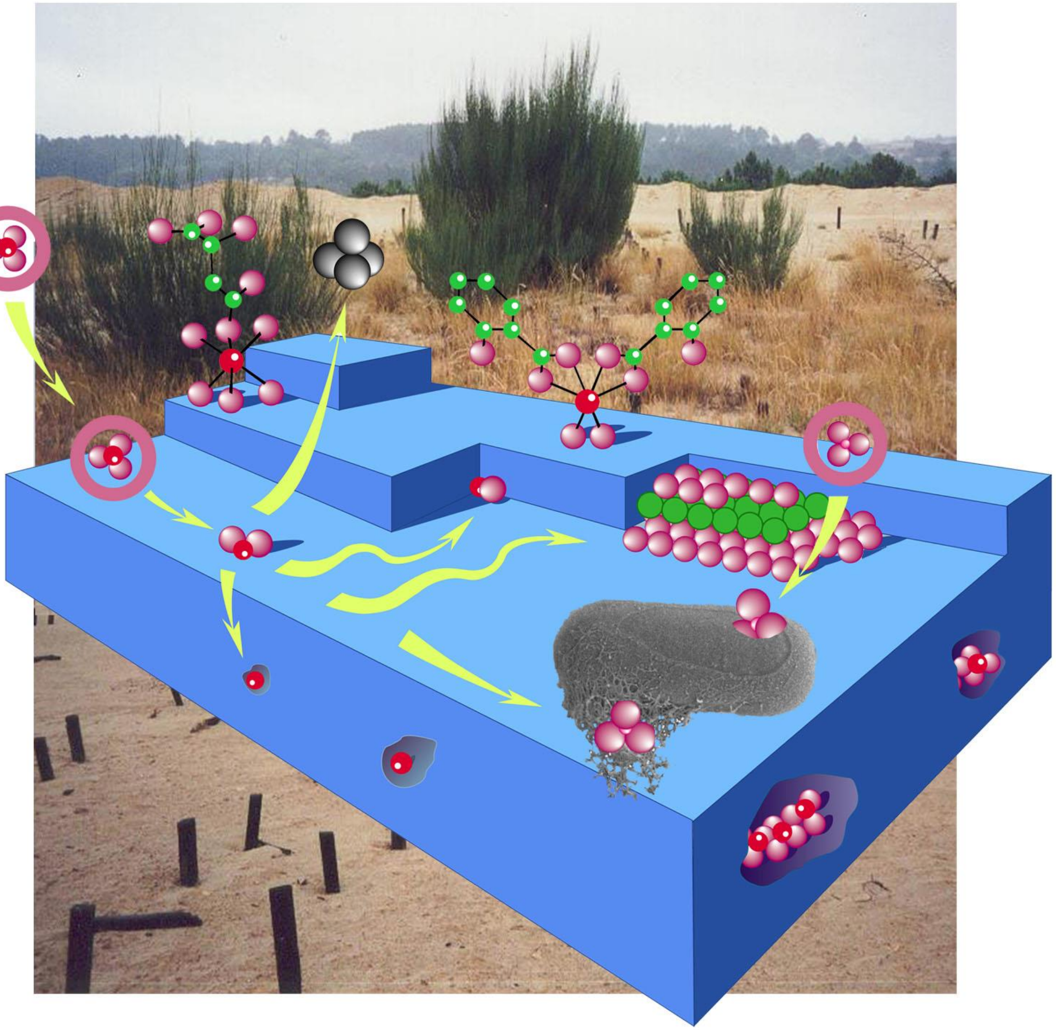
Inner-city regions are traps for lead contamination

Howard Mielke

Why are mineral surfaces important for environmental chemistry?

- Most geochemically relevant reactions occur at interfaces
- Fate and transport of minor chemical components (including most contaminants) controlled by <u>sorption</u> and <u>precipitation</u> at solid surfaces
- Bulk concentrations don't tell whole story
- Chemical speciation controls mobility, toxicity, and bioavailability
- X-ray absorption spectroscopy has become essential tool for studying speciation of metals and metalloids
- Here we will focus on metal interactions with mineral surfaces

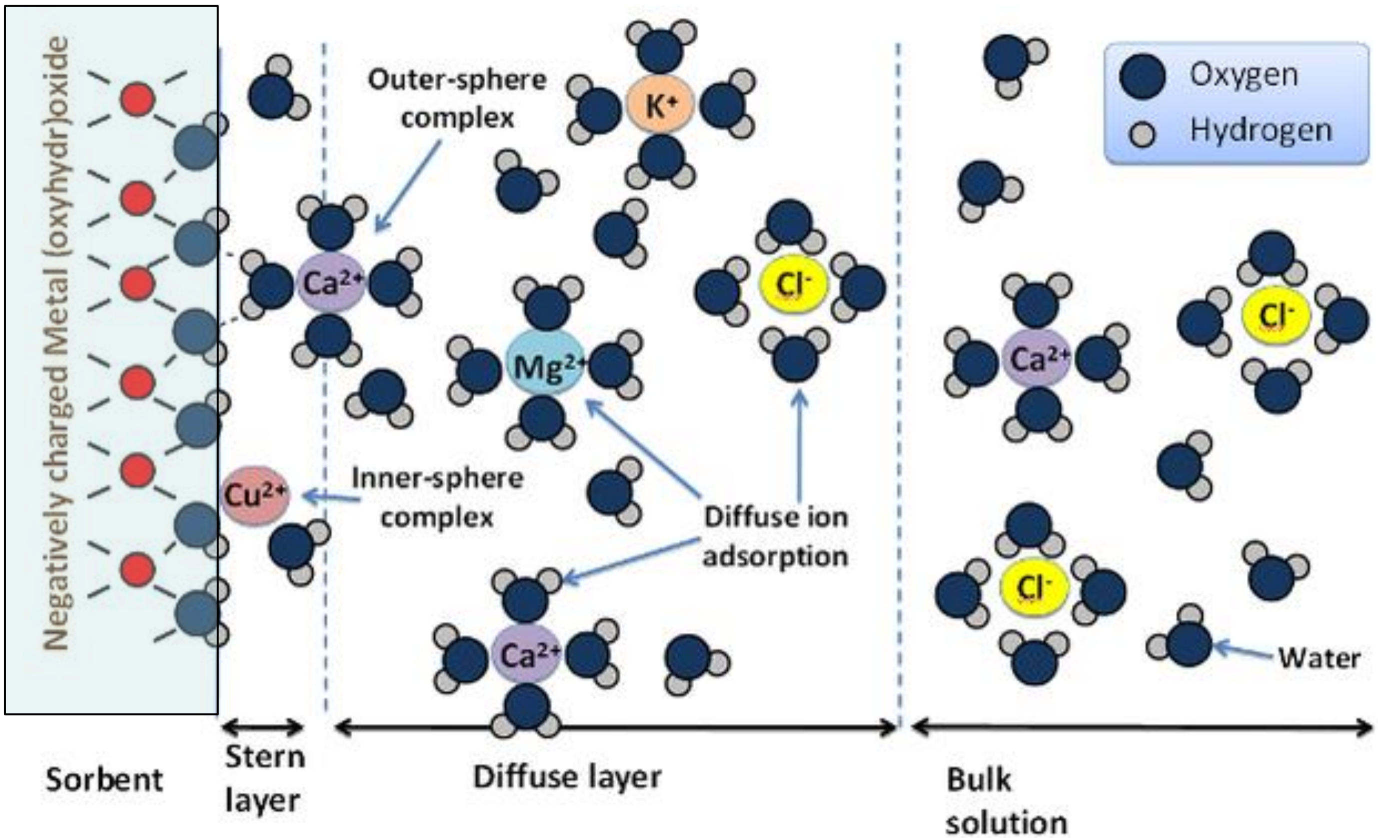
Processes at mineral-water interfaces



http://en.wikipedia.org/wiki/User:Alain_Manceau

- Bulk precipitation/dissolution
- Sorption:
  - Adsorption
  - Desorption
  - Surface precipitation
  - Co-precipitation
- Redox reactions

Molecular-scale understanding of interfacial processes



http://www.nature.com/scitable/knowledge/library/introduction-to-the-sorption-of-chemical-constituents-94841002

Three examples using EXAFS and XANES to study interfaces

1) Pb^{2+} interaction with calcite

   Distinguishing between adsorption and coprecipitation

2) Tungstate sorption onto boehmite

   Surface-induced polymerization

3) Arsenic and chromium redox reactions on ferrihydrite

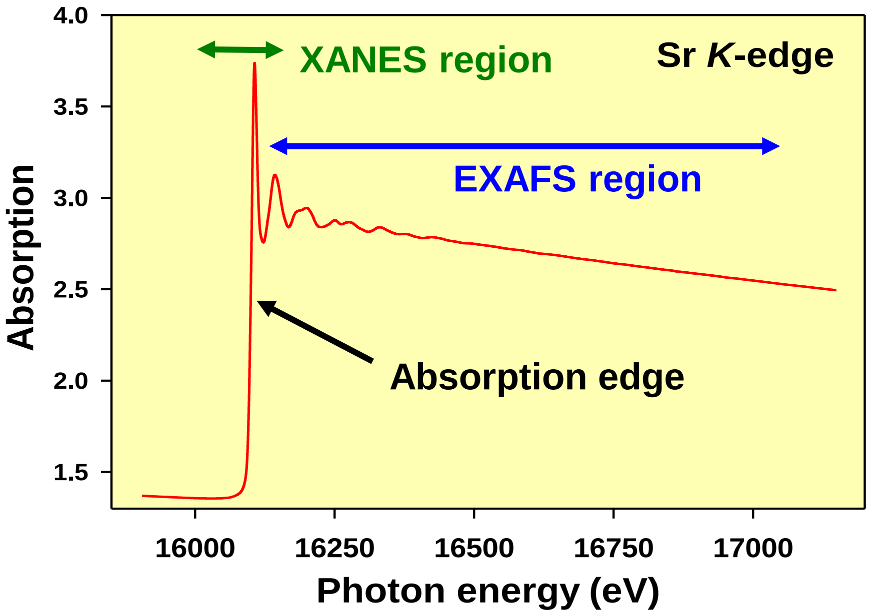
   Surface-facilitated, coupled redox reactions

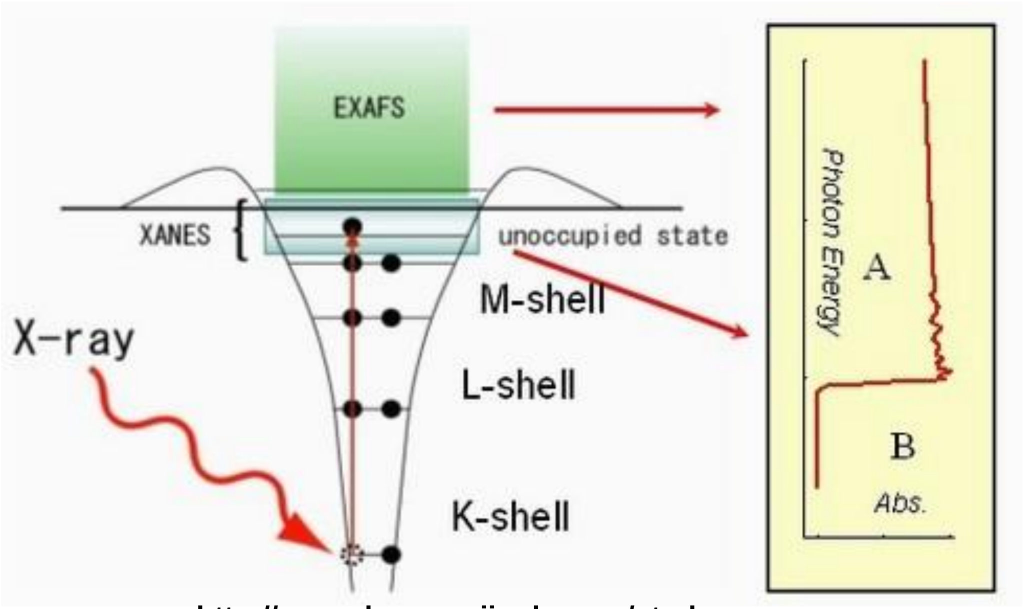
1 H 1.00794																	2 He 4.002602
3 Li 6.941	4 Be 9.012182											5 B 10.811	C 12.0107	7 N 14.00674	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
11 Na 22.989770	12 Mg 24.3050											13 Al 26.581538	14 Si 28.0855	15 P 30.973761	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938049	26 Fe 55.845	27 Co 58.933200	28 Ni 58.6534	29 Cu 63.545	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92160	34 Se 78.96	35 Br 79.504	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 196.56655	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.90447	54 Xe 131.29
55 Cs 132.90545	56 Ba 137.327	57 La 138.9055	72 Hf 178.49	73 Ta 180.94.79	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.56655	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.58038	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)		114 (289) (287)		116 (289)		118 (293)

EXAFS and XANES Spectroscopy

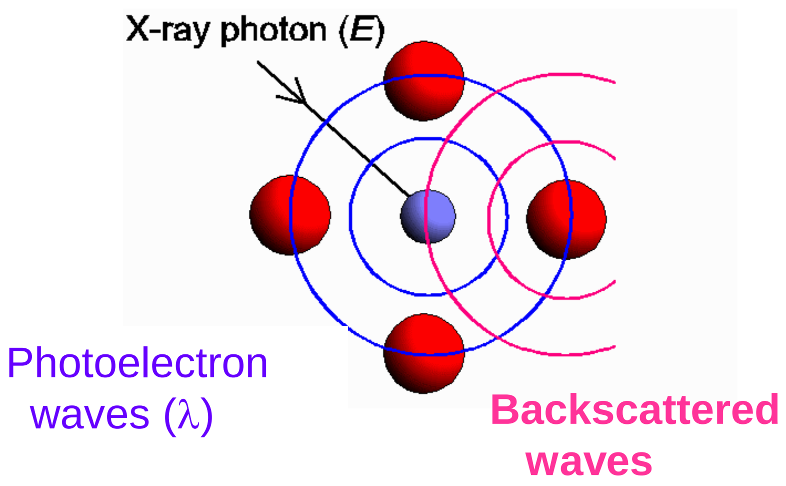
EXAFS:
- Element specific
- Identity, distance and number of near neighbor atoms
- Degree of local structural disorder

XANES:
- Average oxidation state
- Coordination geometry





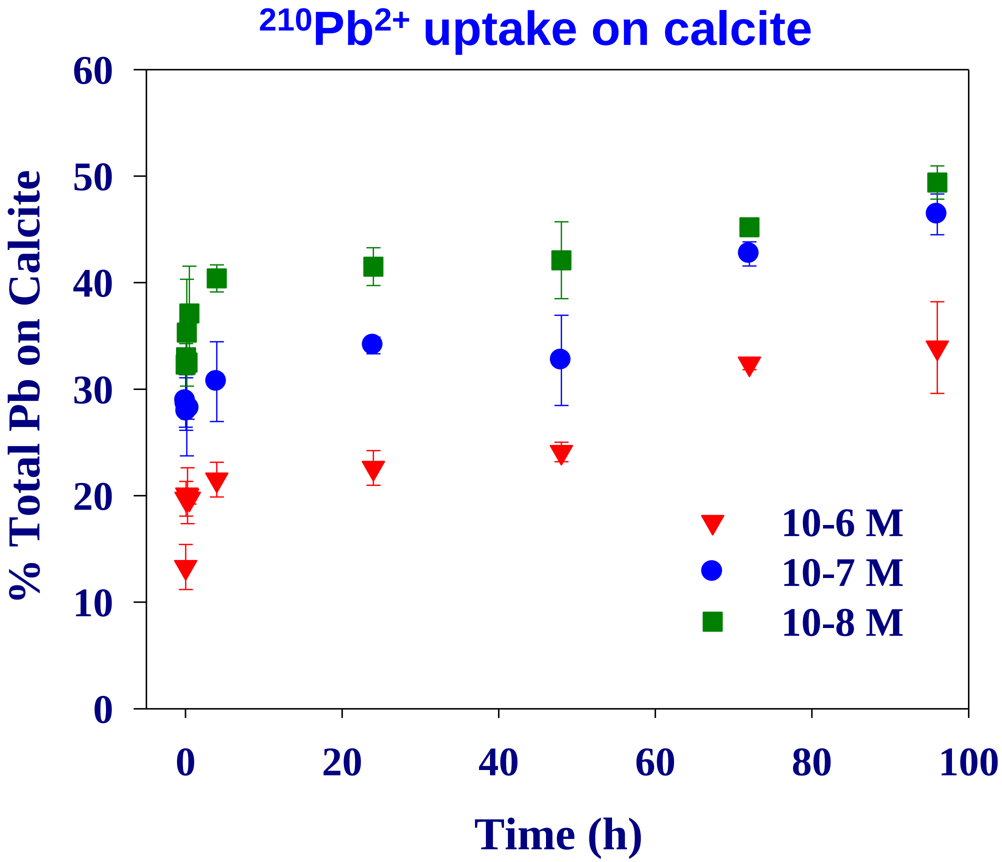
http://mmnakayama.jimdo.com/study



Pb^{2+} interaction with calcite surfaces

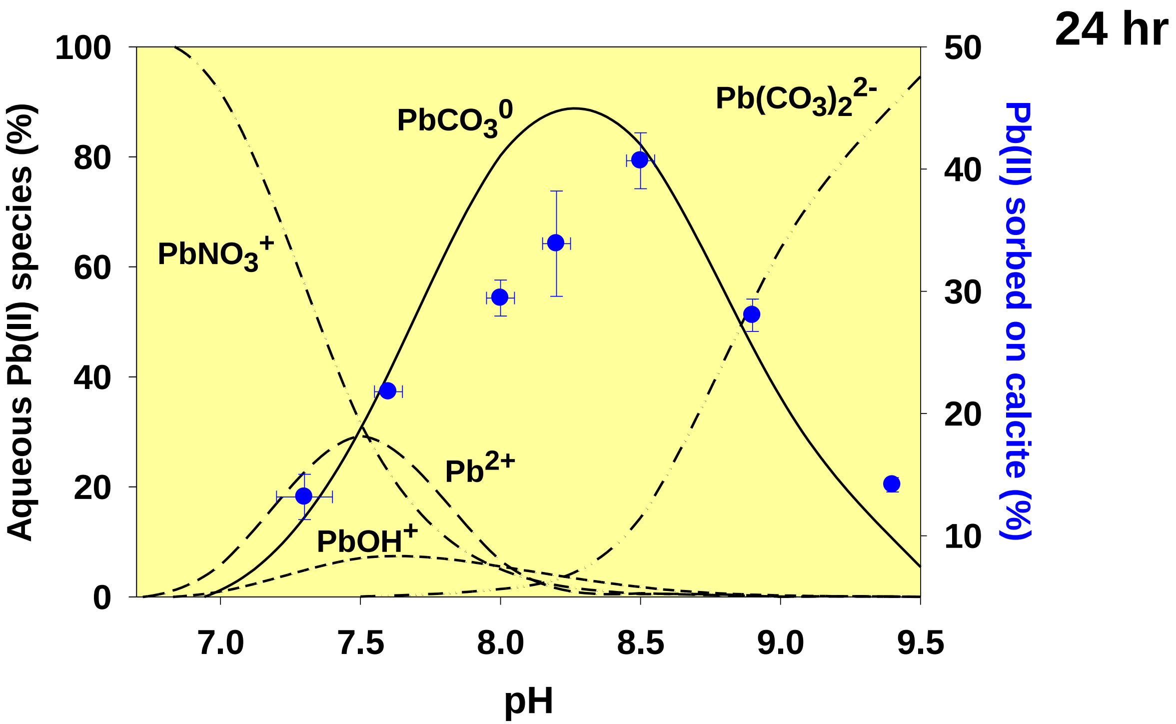
Batch sorption experiments show dual uptake kinetics

- **Initial rapid uptake (adsorption?)**
- **Slow continued uptake (coprecipitation?)**



Pb^{2+} uptake by calcite shows strong pH dependence

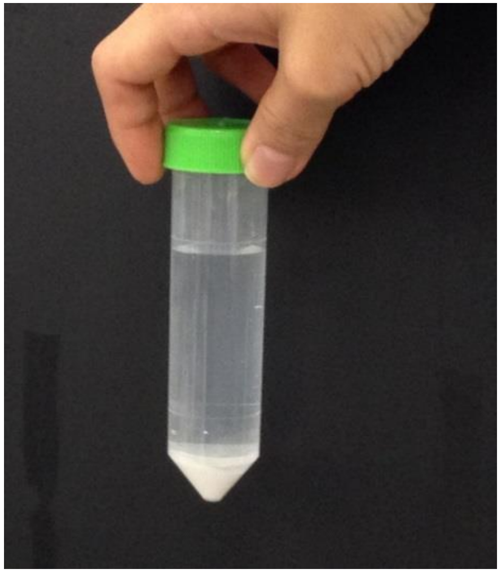
- Sorption maximum at pH 8.4
- Pb^{2+} forms stable aqueous complexes with CO_3^{2-}
- Pb^{2+} sorption maximum corresponds to $PbCO_3^0$(aq) speciation field
- $PbCO_3^0$(aq) thought to be primary species to sorb at calcite surface
- Sorption mechanism unclear

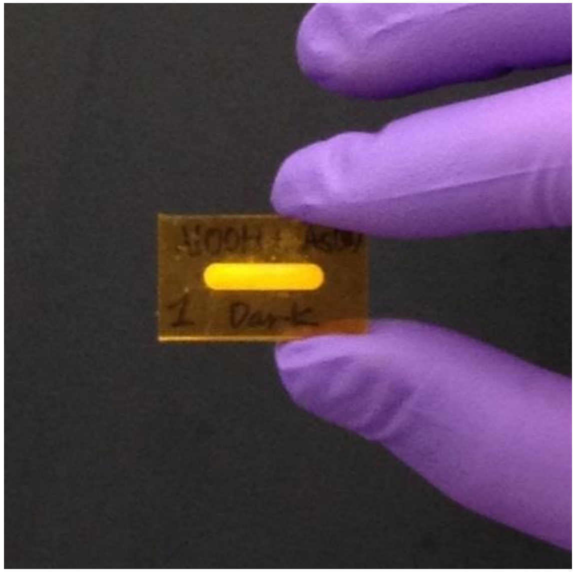


How do we study species sorbed at mineral-water interface? (and not those in the solution)

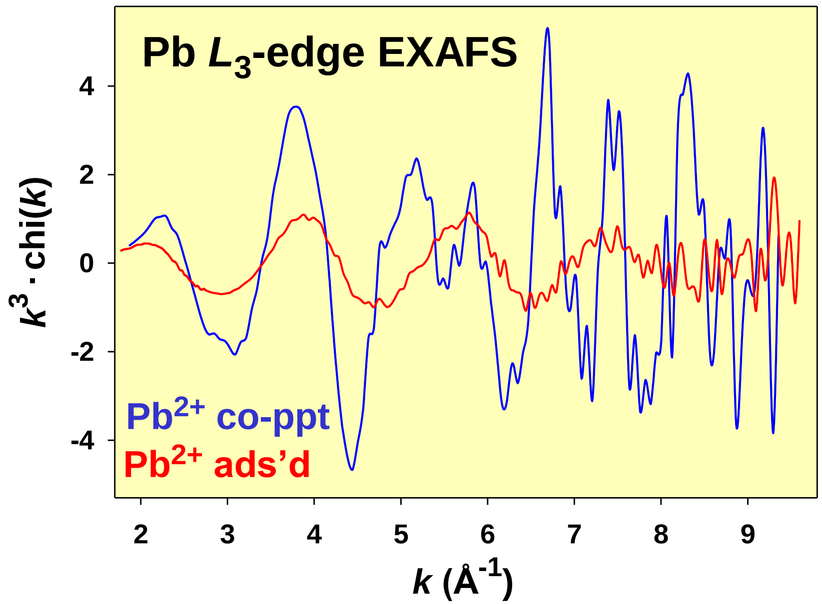
After batch reaction:

- Separate solids from suspension by centrifuge or filtration
- Retain moist solids for X-ray absorption
- Seal moist solids in sample holder



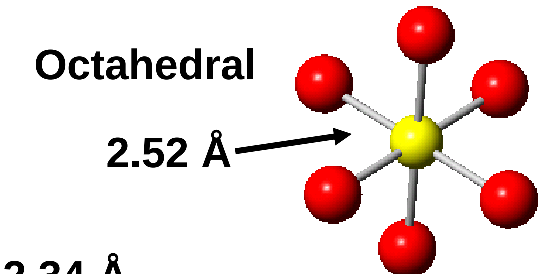


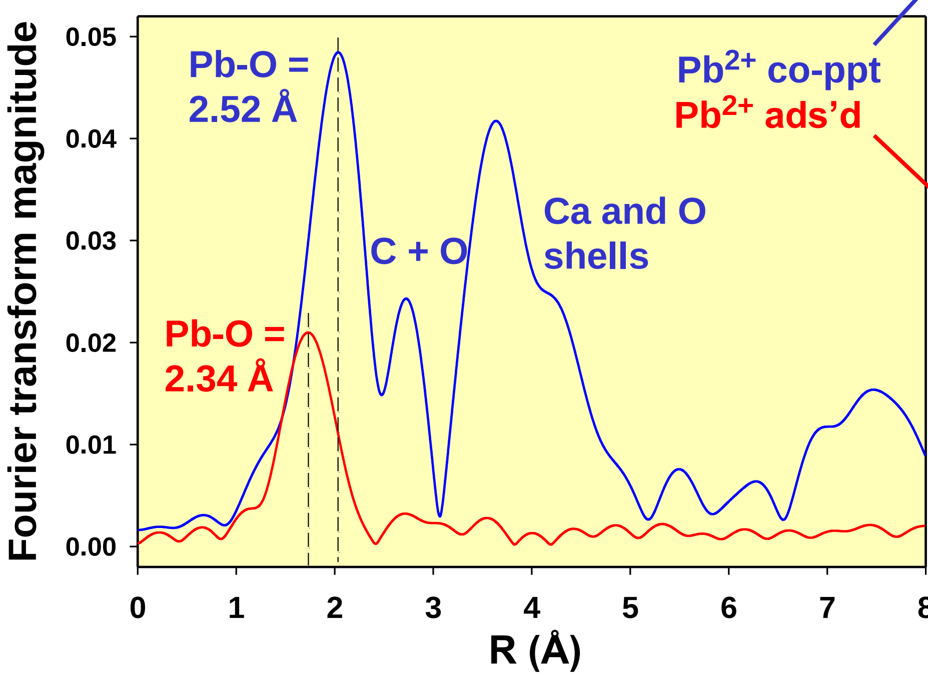
Can we distinguish Pb^{2+} adsorption from co-precipitation

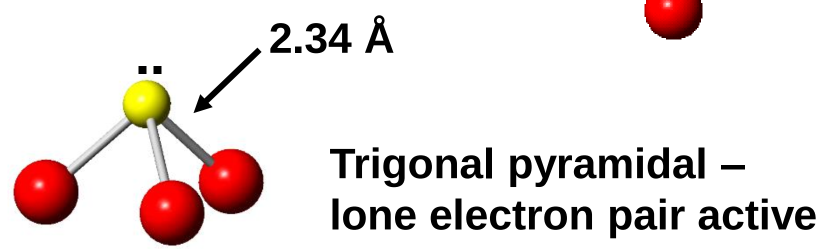


Calcite: Pb^{2+} co-ppt with calcite

Shell	N	R (Å)	σ^2 (Å^2)
Pb-O	5.9	2.52	0.009
Pb-C	6*	3.28	0.005
Pb-O	6*	3.79	0.016
Pb-Ca	6*	4.09	0.005







Pb^{2+} adsorbed on calcite (1 μM)

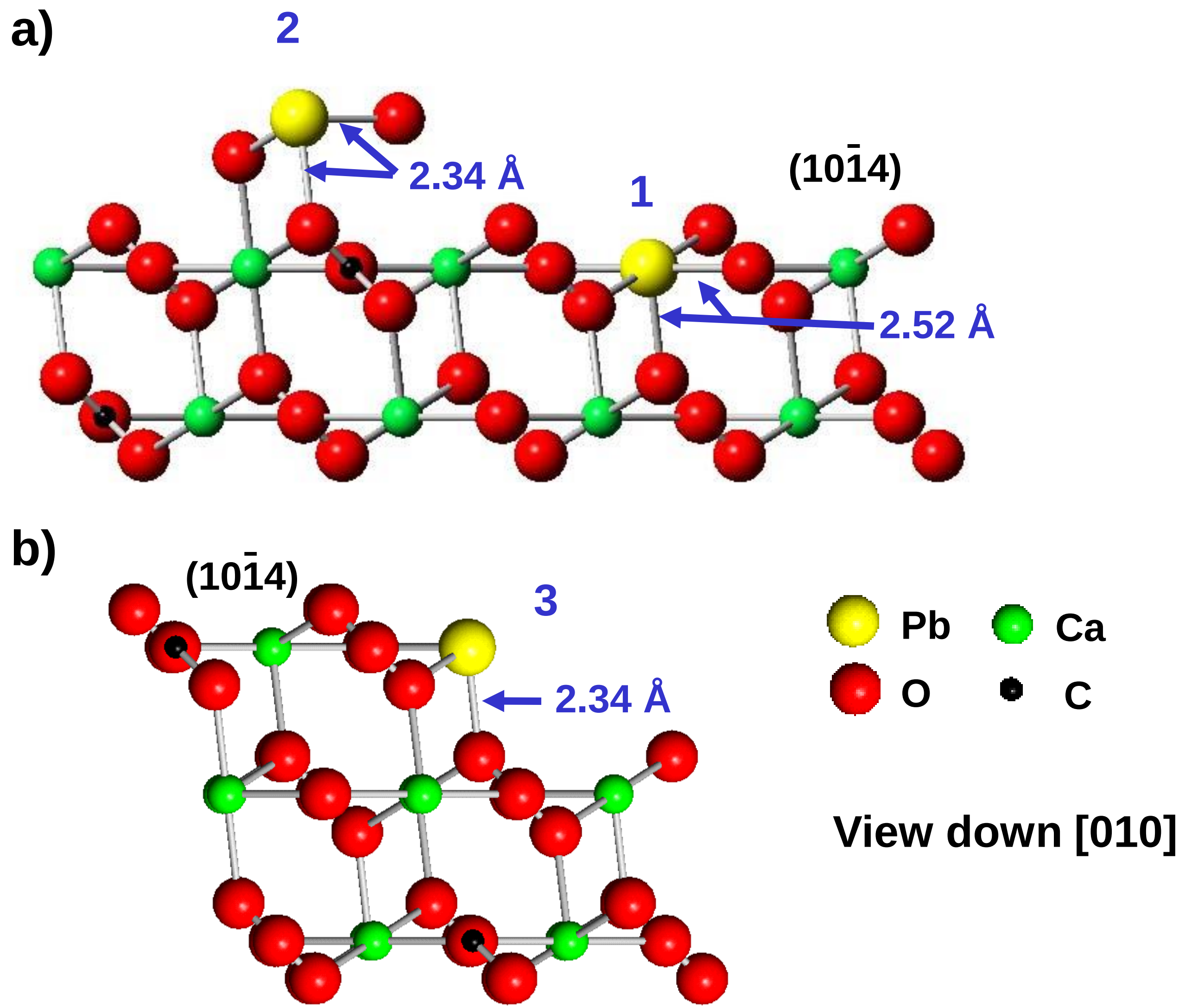
Shell	N	R (Å)	σ^2 (Å^2)
Pb-O	4.3	2.34	0.013
Pb-C	3.3	3.39	0.01*
Pb-O	3.8	3.62	0.01*
Pb-Ca	1.4	4.08	0.01*

Rouff et al. (2003)

Pb^{2+} sorption sites on calcite $(10\bar{1}4)$ surface

Terrace sites

Step edge sites



Rouff et al. (2003)

Tungstate polymerization on the boehmite surface

1 H 1.00794																	2 He 4.002602
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58 Ce 140.116	59 Pr 140.50765	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04	71 Lu 174.967
90 Th 232.0381	91 Pa 231.035888	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

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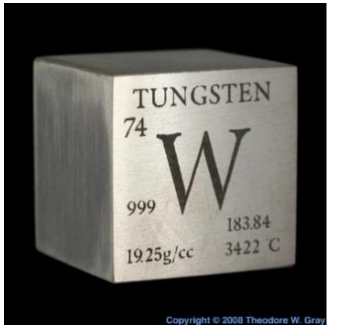
Oxidative dissolution of tungsten alloys releases tungstate – W(VI)

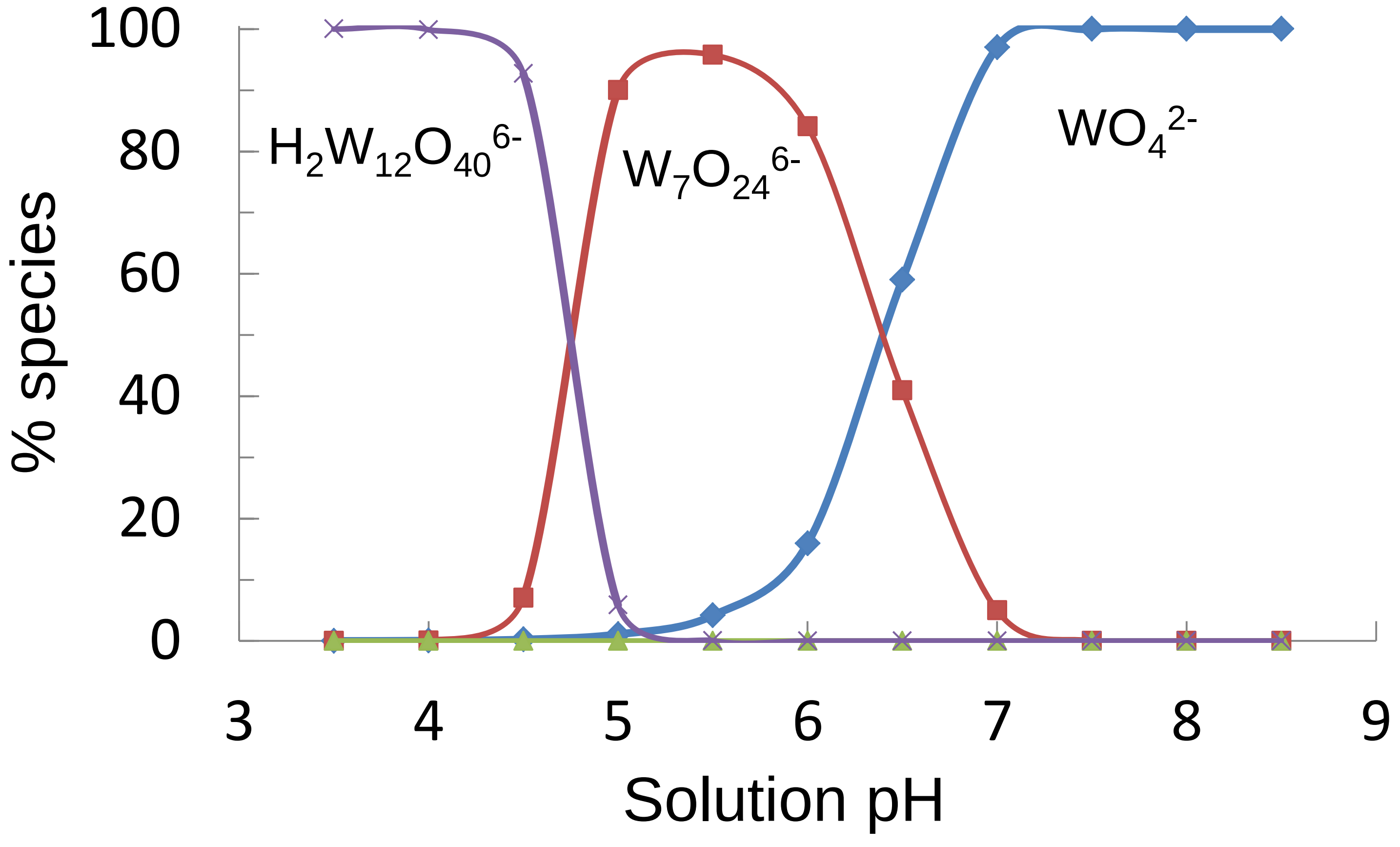
- Common anion form is WO_4^{2-} (occurs at basic pH)
- Below pH 7 WO_4^{2-} polymerizes to form polytungstates

Tungsten Toxicology

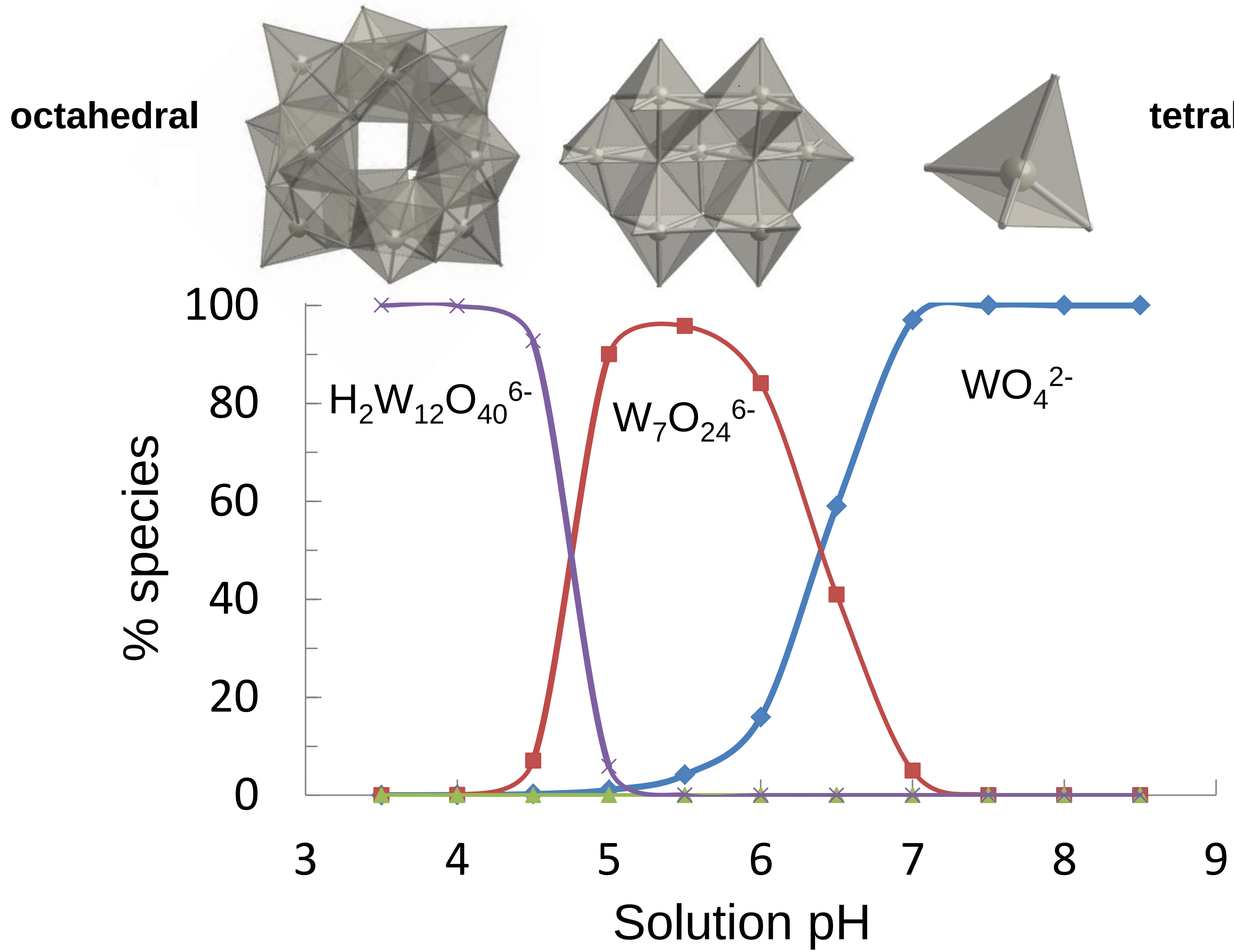


- Metallic forms of tungsten considered to be nontoxic
- Leukemia cluster in Fallon, NV, linked to tungsten refinery
- Polymeric tungstate found to be more toxic than monomeric species
- Tungstate unregulated by US EPA and WHO (regulated in Russia)
- Tungstate concentration in aquatic and soils systems likely controlled by sorption onto mineral surfaces

Tungstate polymerization favored at low pH conditions

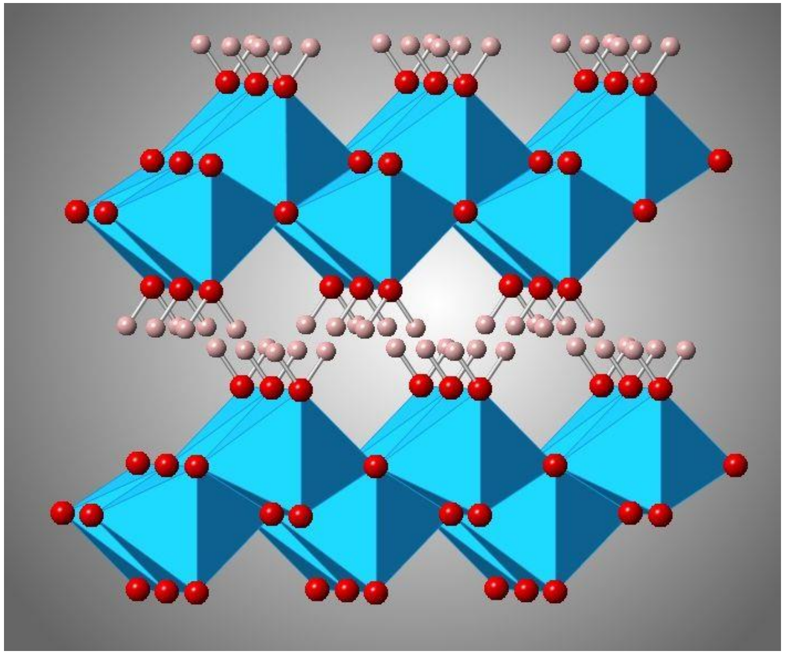


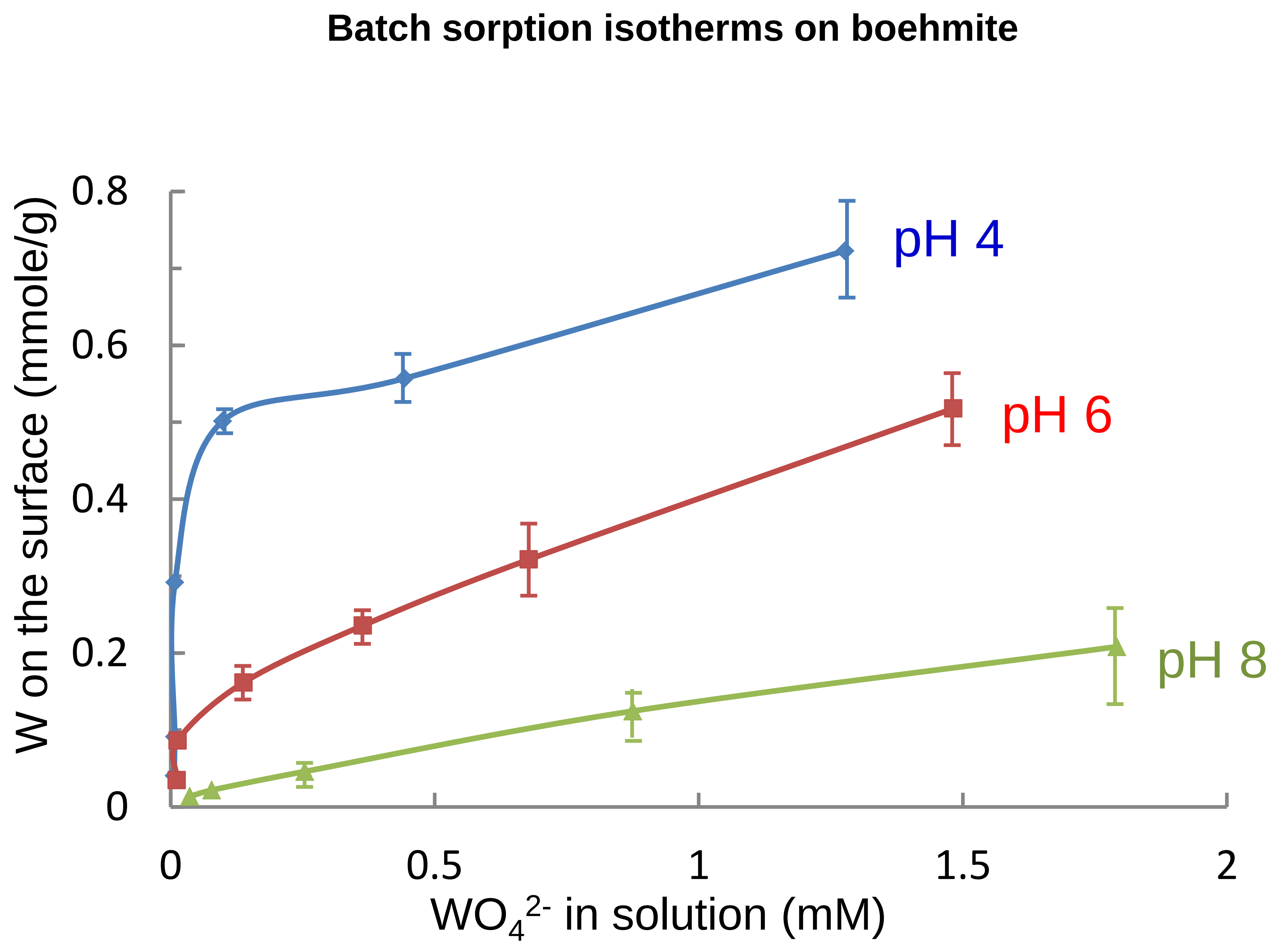
Tungstate polymerization favored at low pH conditions



Boehmite, γ-AlOOH

- Effective sorbent
- Edge-sharing Al octahedra
- Particle Size : ~50 nm
- Surface area : 134 m^2/g
- Zero point of charge : pH 8.7

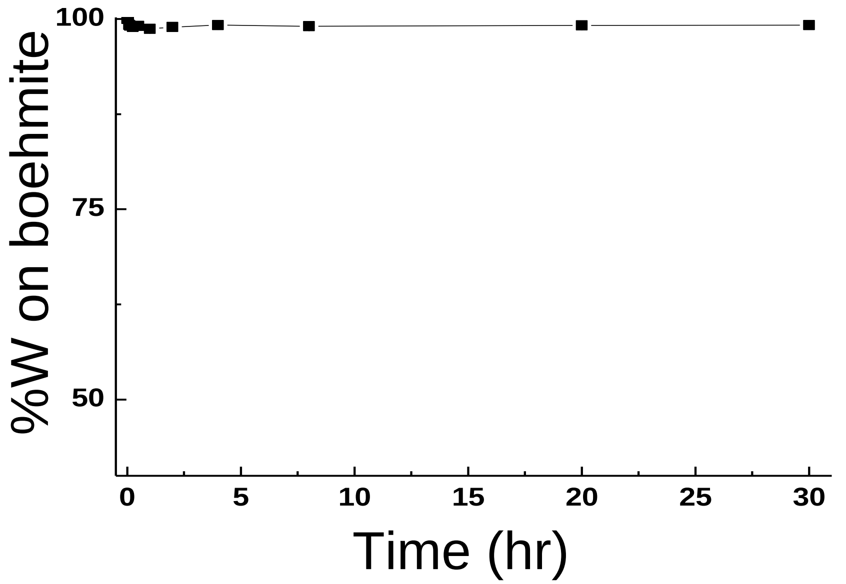



Batch sorption isotherms on boehmite
W on the surface (mmole/g)
0.8
0.6
0.4
0.2
0
0
0.5
1
1.5
2
WO4 2- in solution (mM)
pH 4
pH 6
pH 8

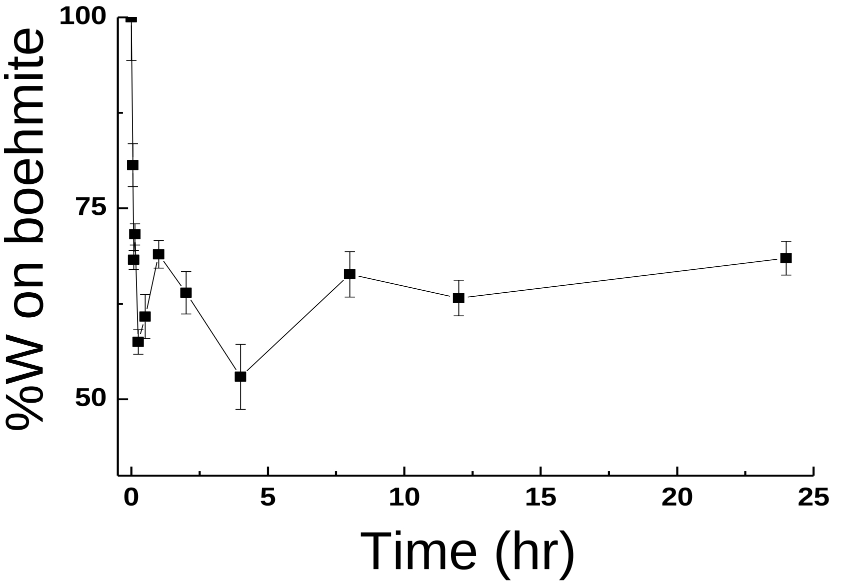
Tungstate desorption from boehmite

Initial [W] = 200 µM

pH 4



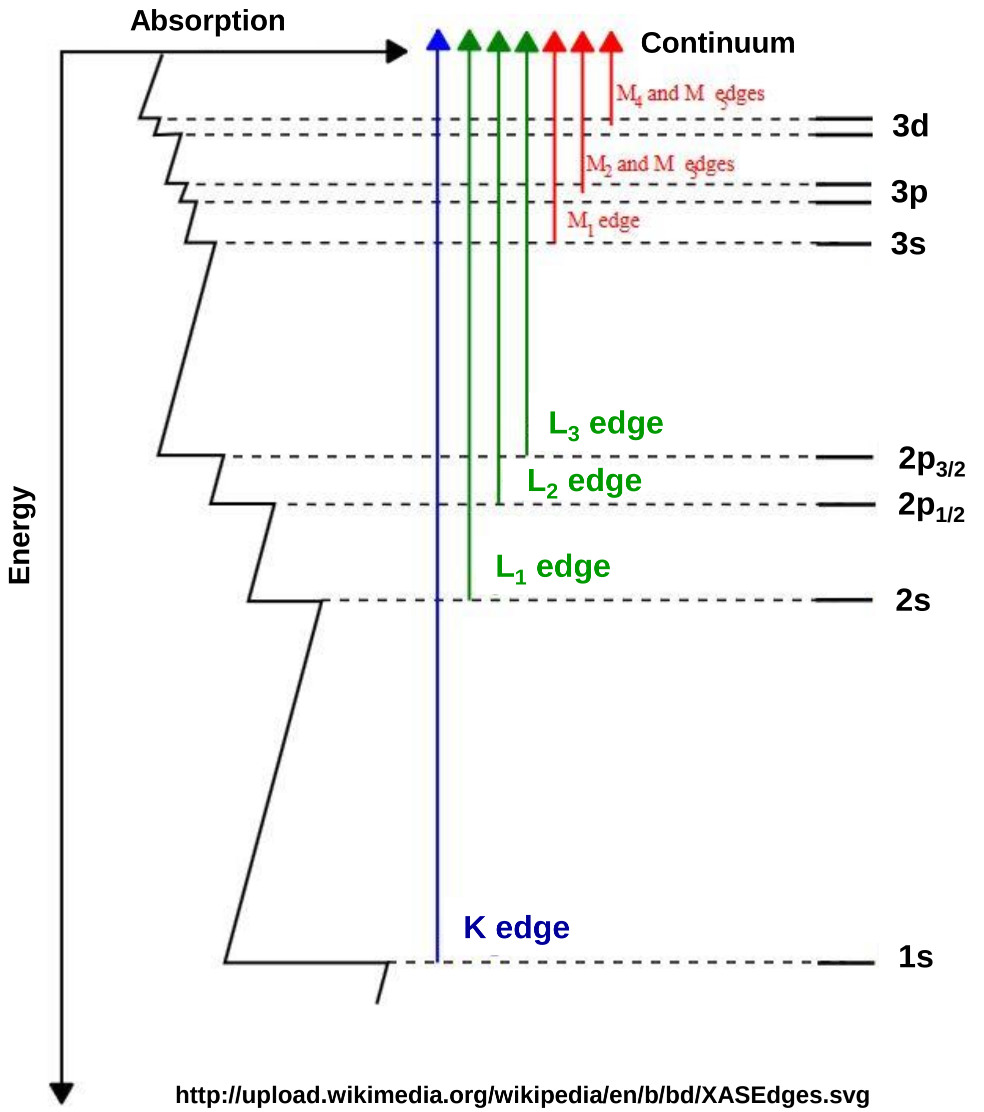
pH 8



Sorption is irreversible at pH 4

Partially reversible at pH 8

How can we use XANES and EXAFS to understand sorption mechanism?



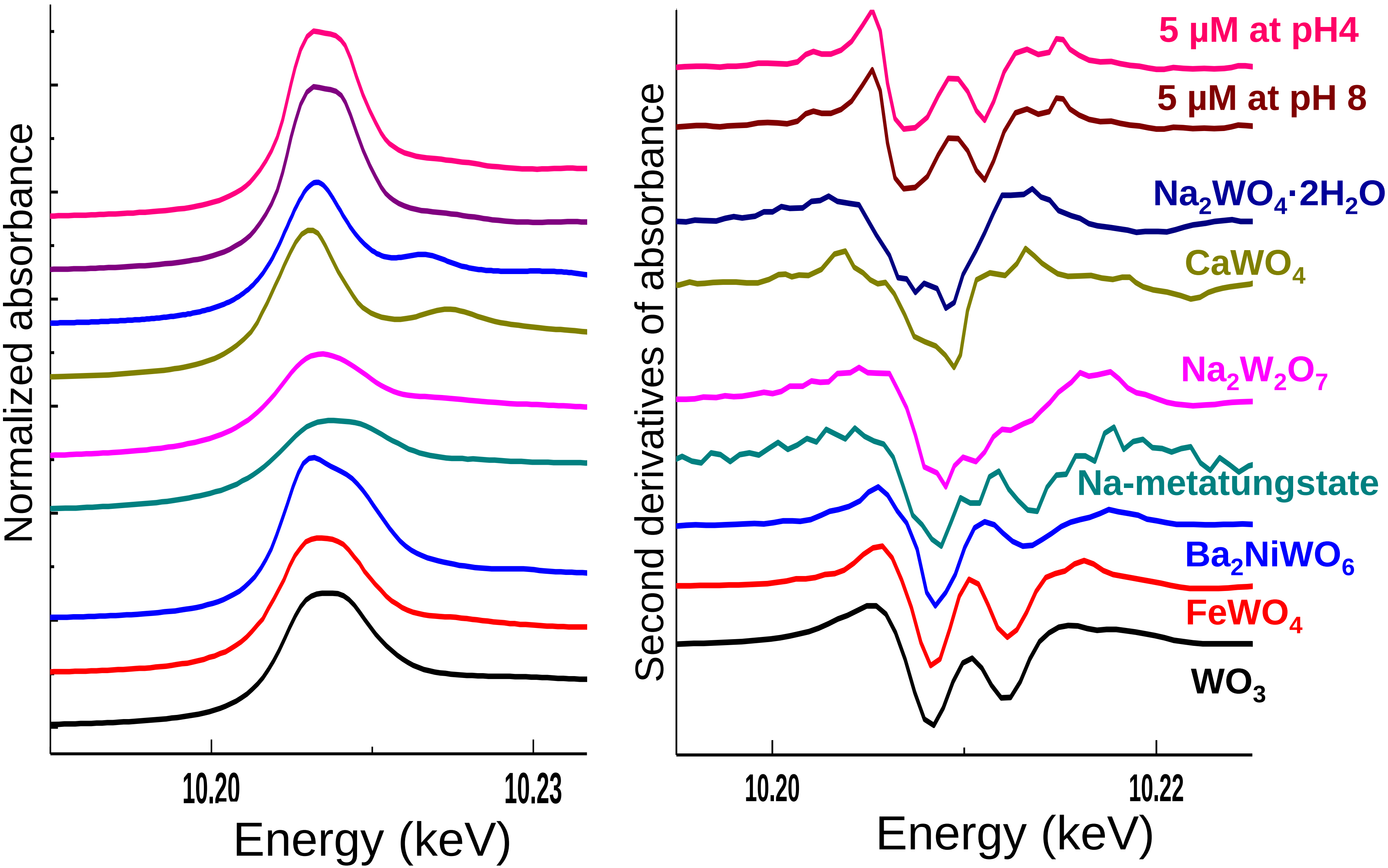
http://upload.wikimedia.org/wikipedia/en/b/bd/XASEdges.svg

Tungsten

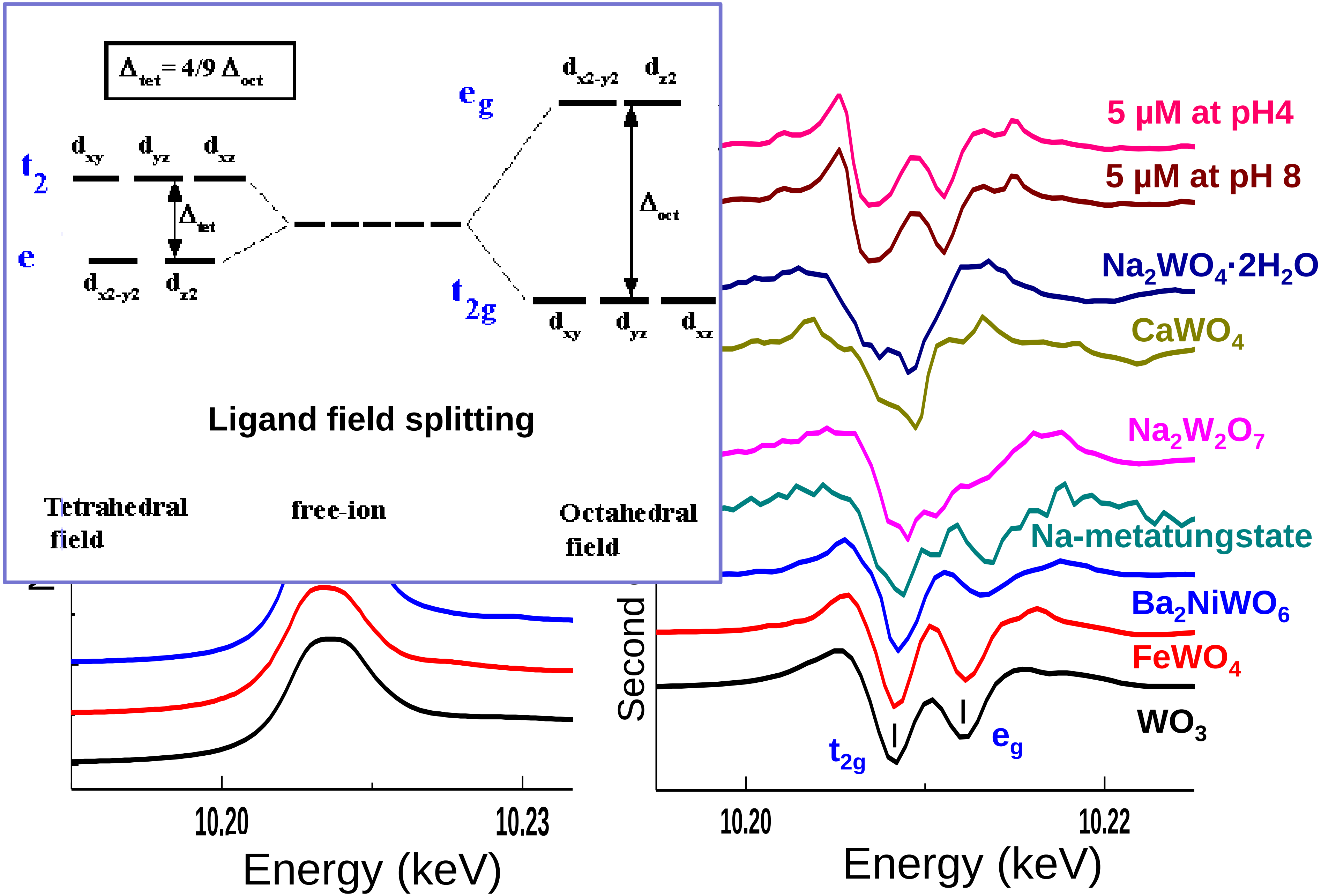
Edge	Energy (keV)
K	69.5
L_1	12.1
L_3	10.2

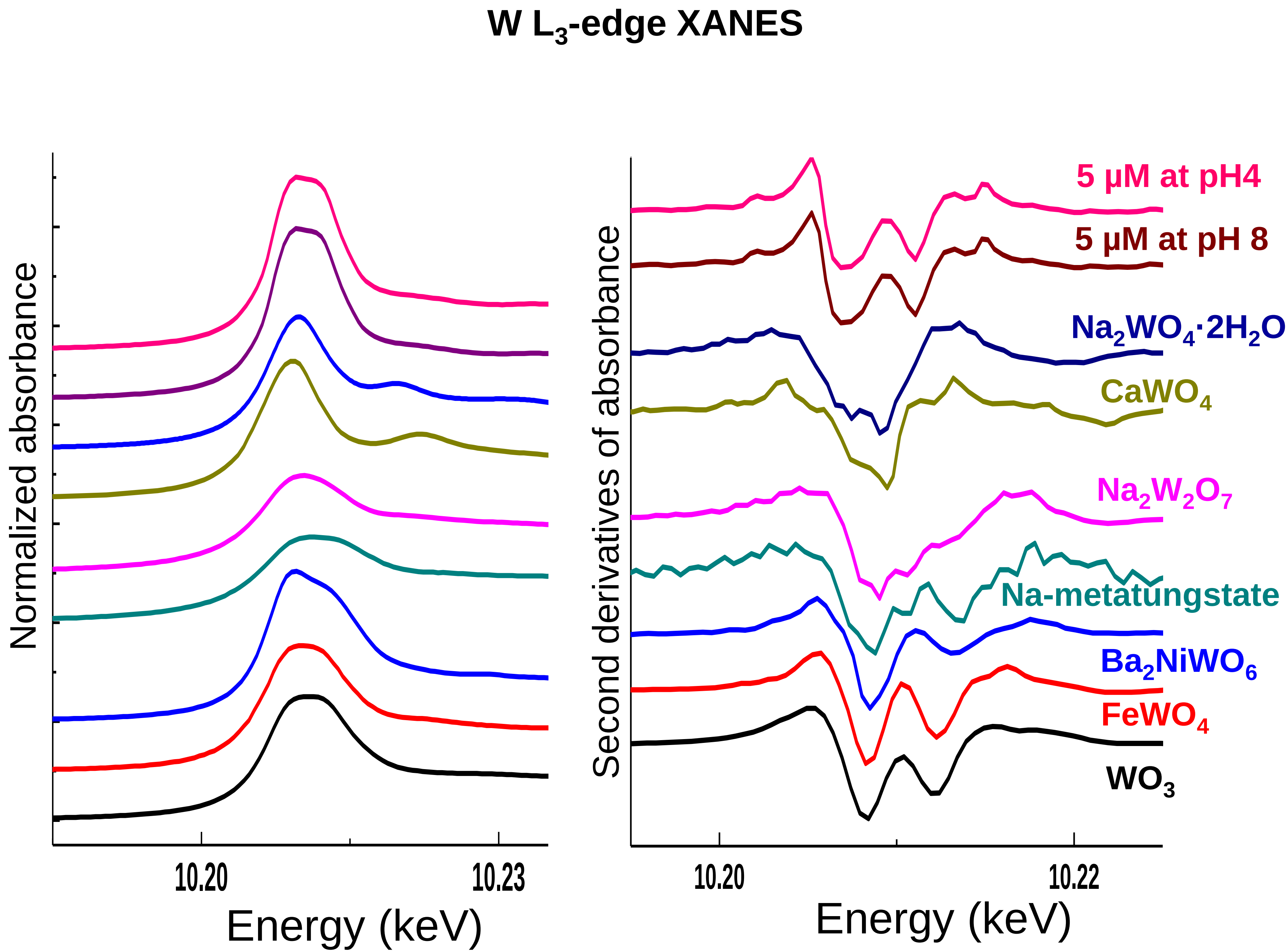
Tungsten L_1 and L_3 edges both useful

W L$_3$-edge XANES



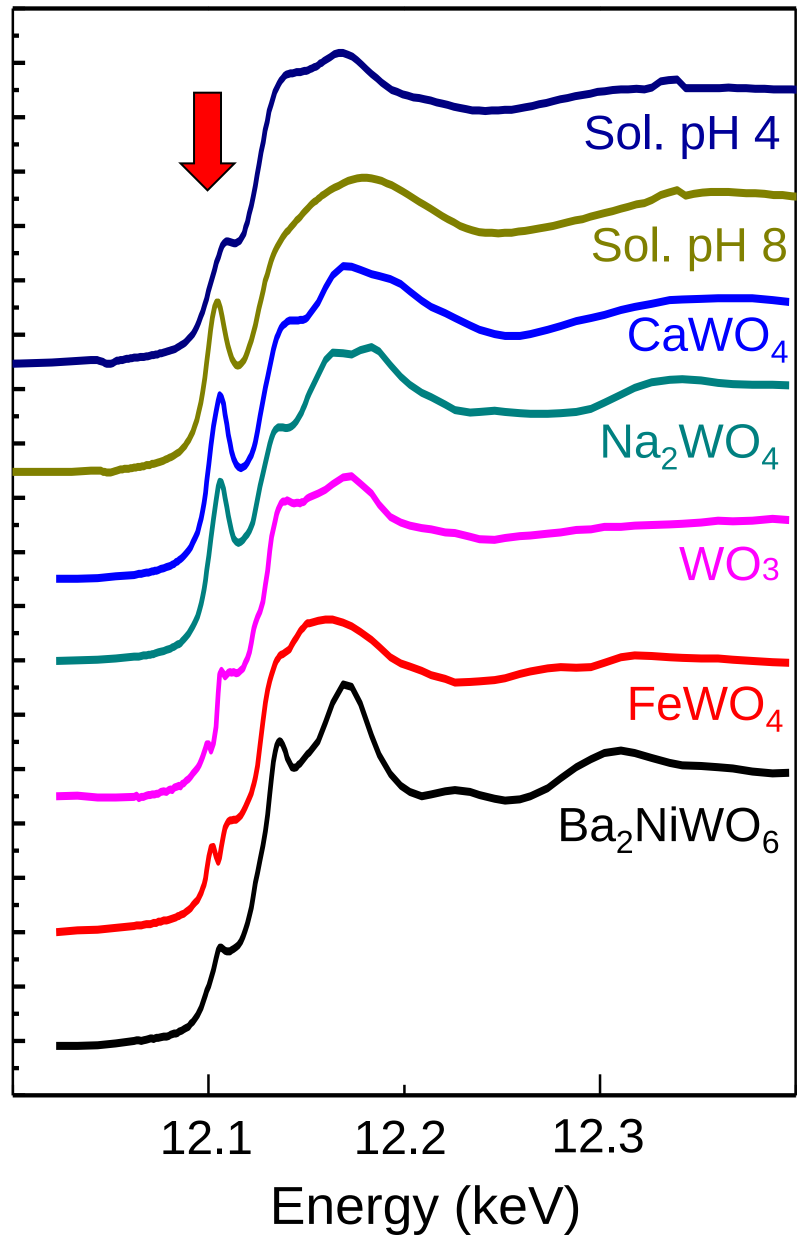
W L_3-edge XANES




W L3-edge XANES
Normalized absorbance
Energy (keV)
10.20
10.23
Second derivatives of absorbance
Energy (keV)
10.20
10.22
5 µM at pH4
5 µM at pH 8
Na2WO4·2H2O
CaWO4
Na2W2O7
Na-metatungstate
Ba2NiWO6
FeWO4
WO3

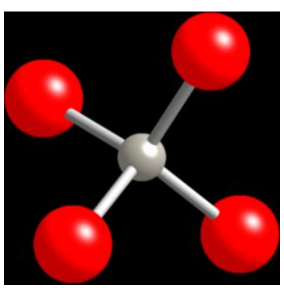
W L_1-edge XANES

- Pre-edge peak at 12.1 keV is attributed to 2s→5d transition
- Transition is dipole forbidden for regular octahedral symmetry
- Allowed for tetrahedral symmetry

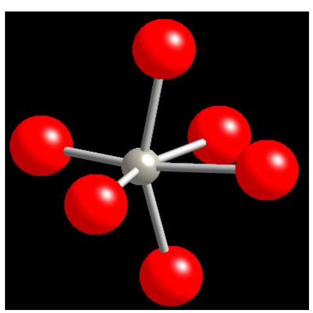


Tetrahedral

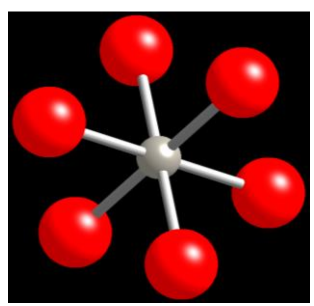
Octahedral



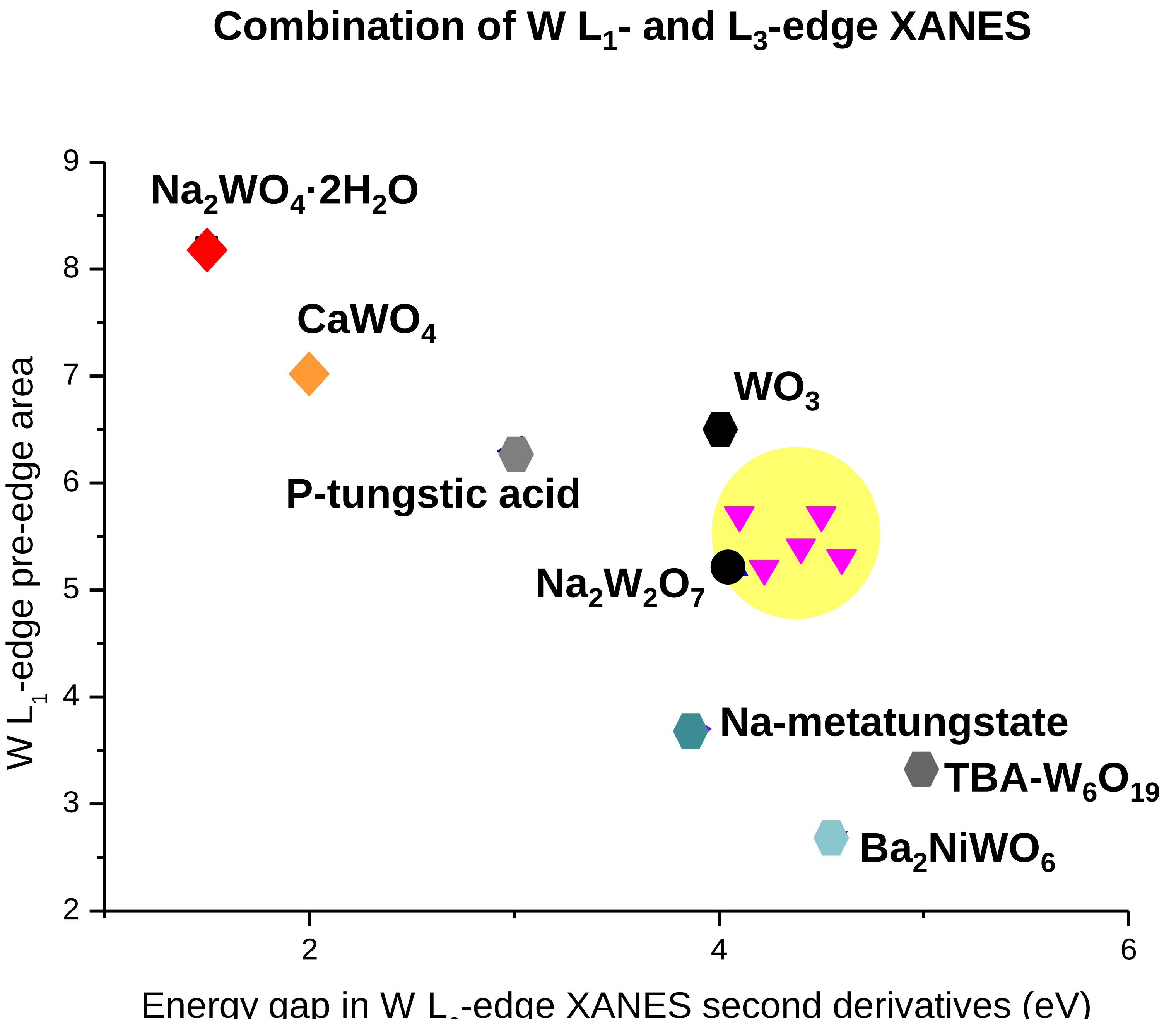
$CaWO_4$
Na_2WO_4



$FeWO_4$
WO_3

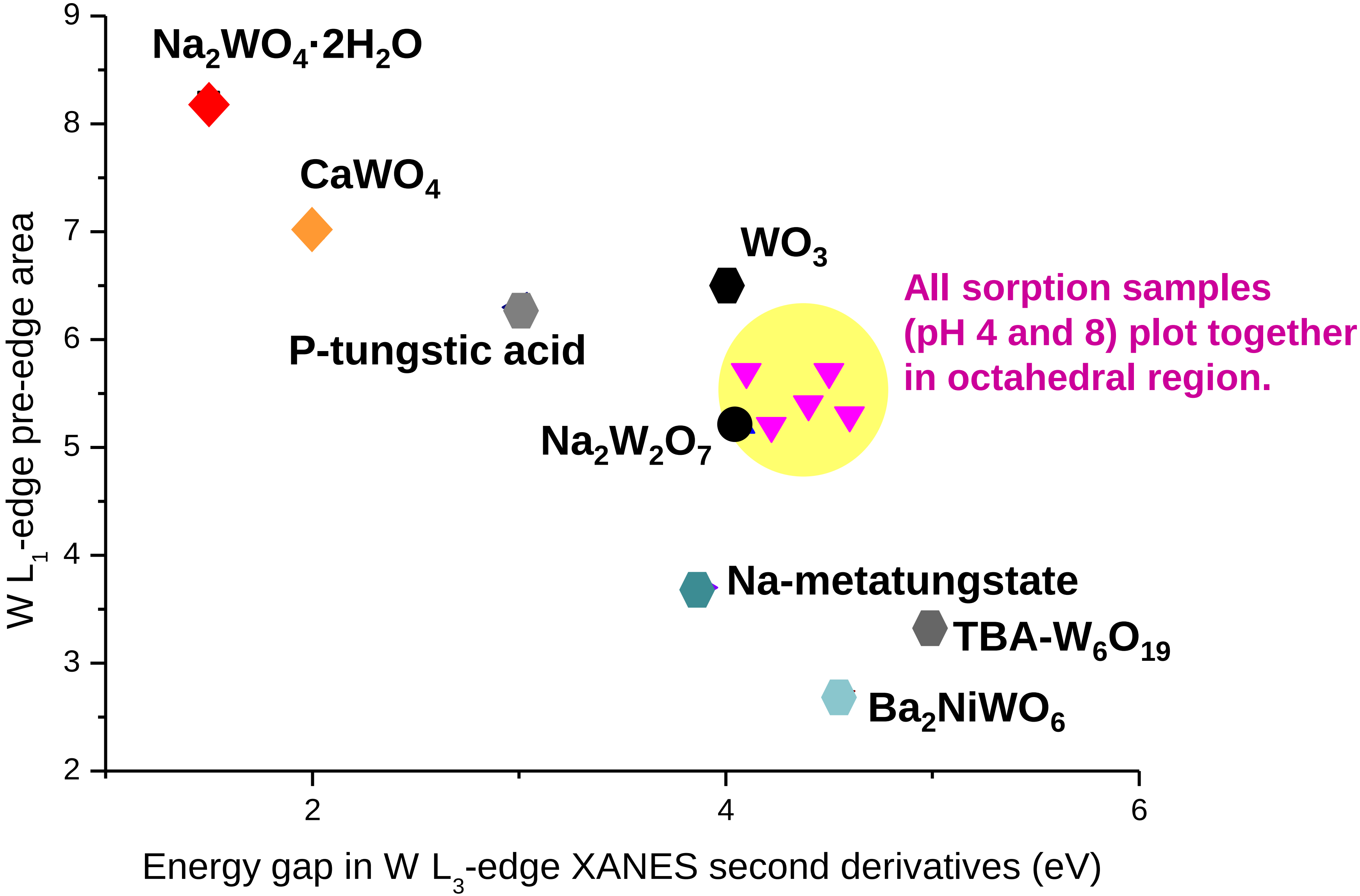


Ba_2NiWO_6

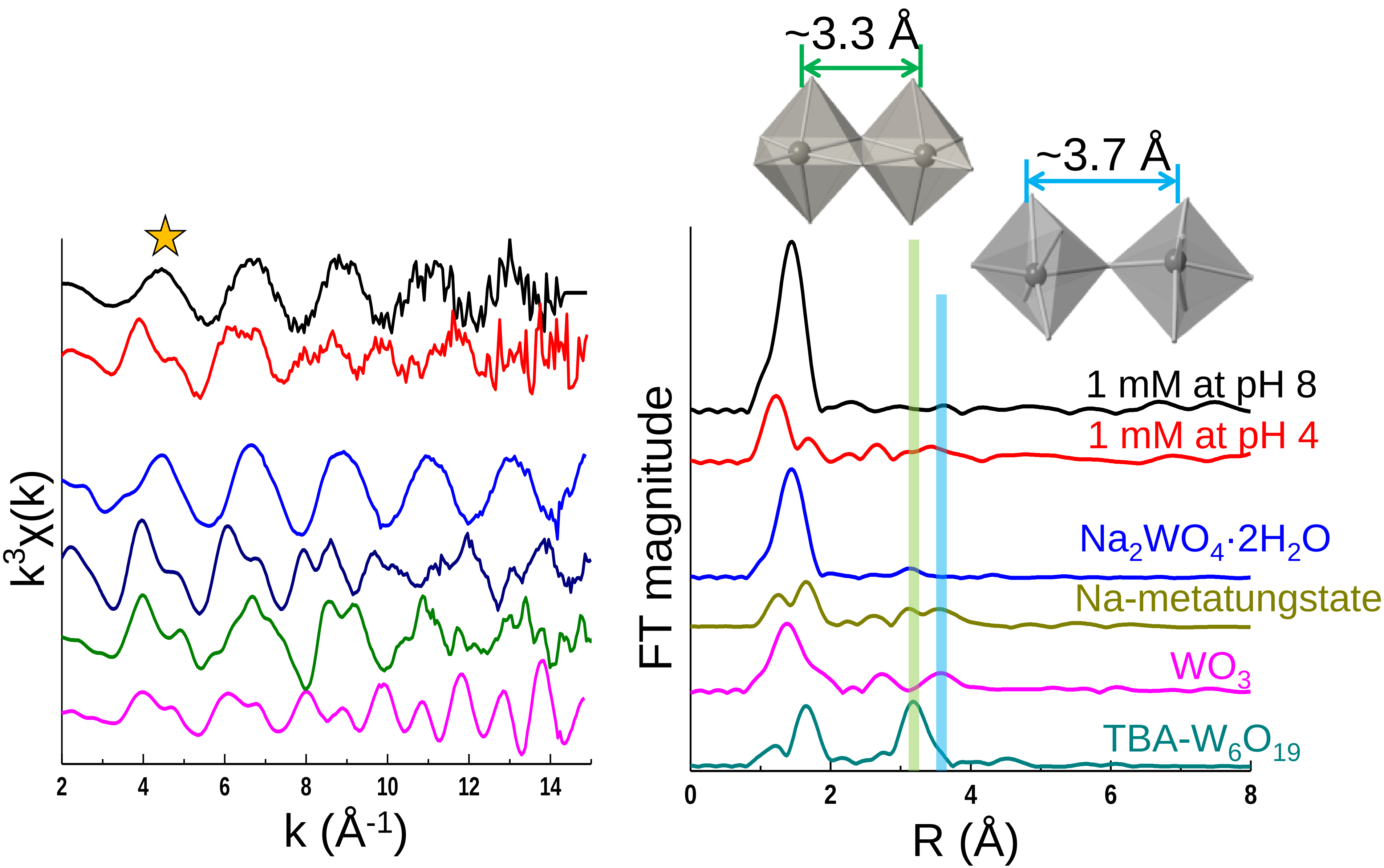


Combination of W L1- and L3-edge XANES
Na2WO4·2H2O
CaWO4
WO3
P-tungstic acid
Na2W2O7
Na-metatungstate
TBA-W6O19
Ba2NiWO6
W L1-edge pre-edge area
Energy gap in W L3-edge XANES second derivatives (eV)
9
8
7
6
5
4
3
2
2
4
6

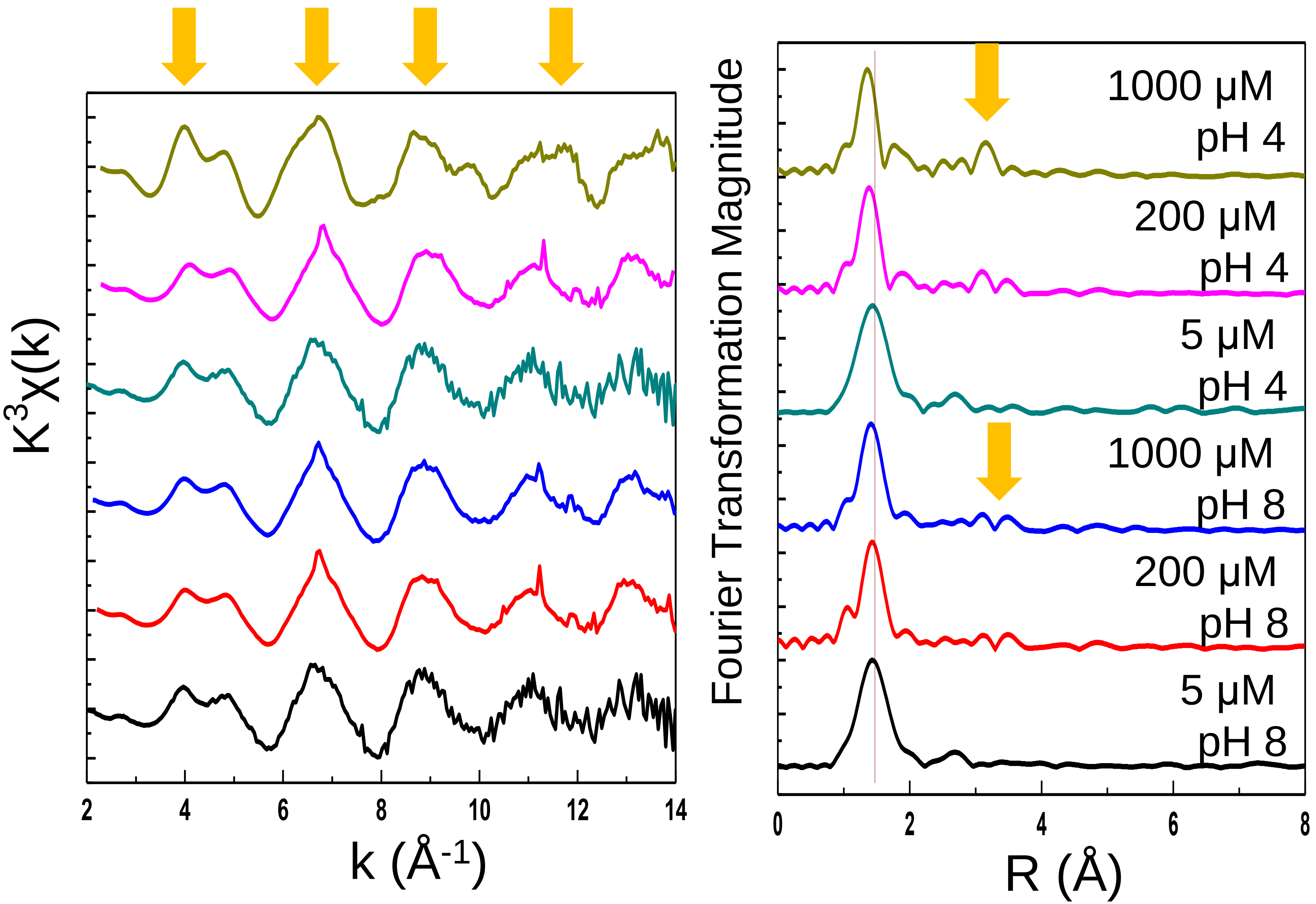
Combination of W L_1- and L_3-edge XANES



W L_3-edge EXAFS – reference compounds and solutions

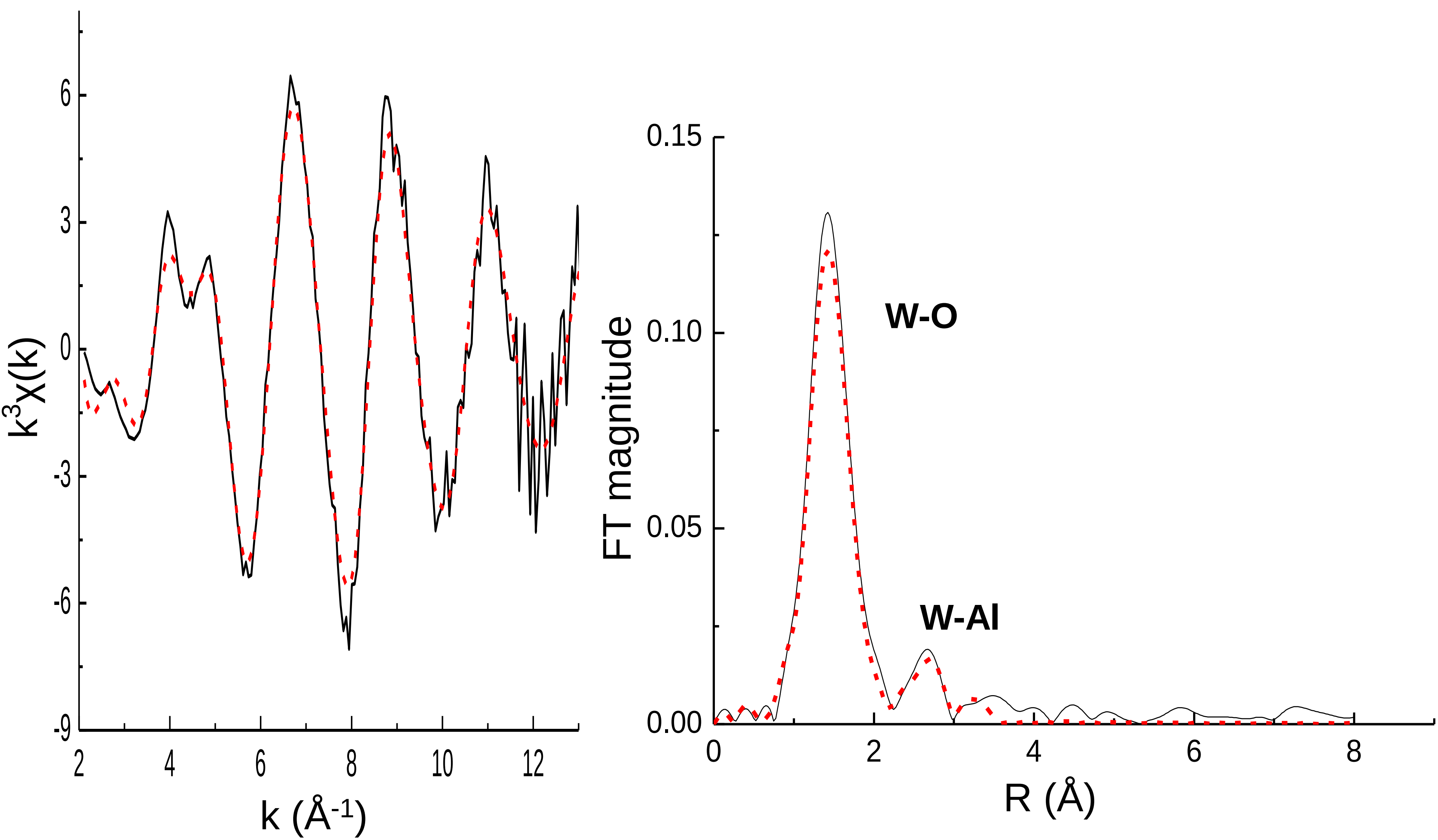


W L_3-edge EXAFS for tungstate sorbed onto boehmite



W L_3-edge EXAFS fits for tungstate sorbed on boehmite

5 µM sorption sample

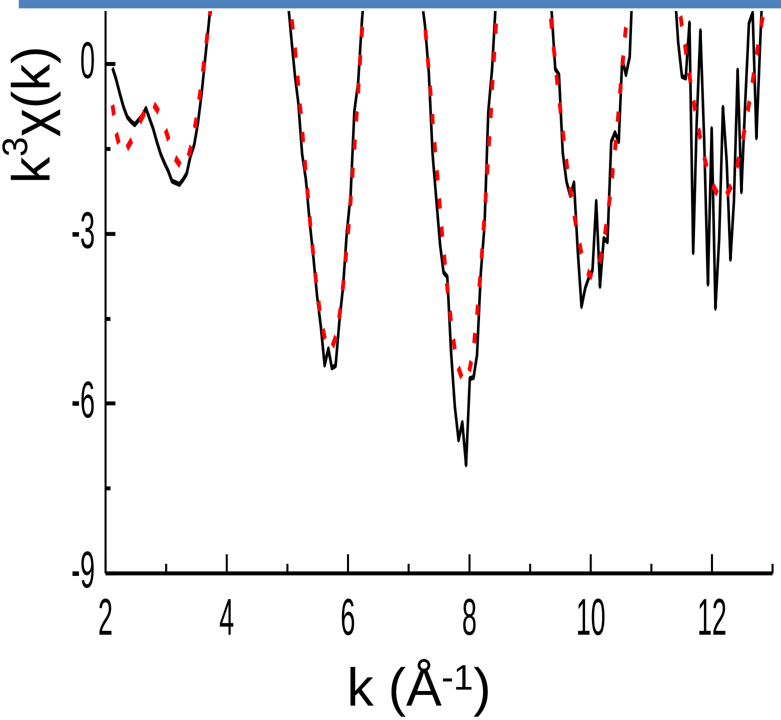


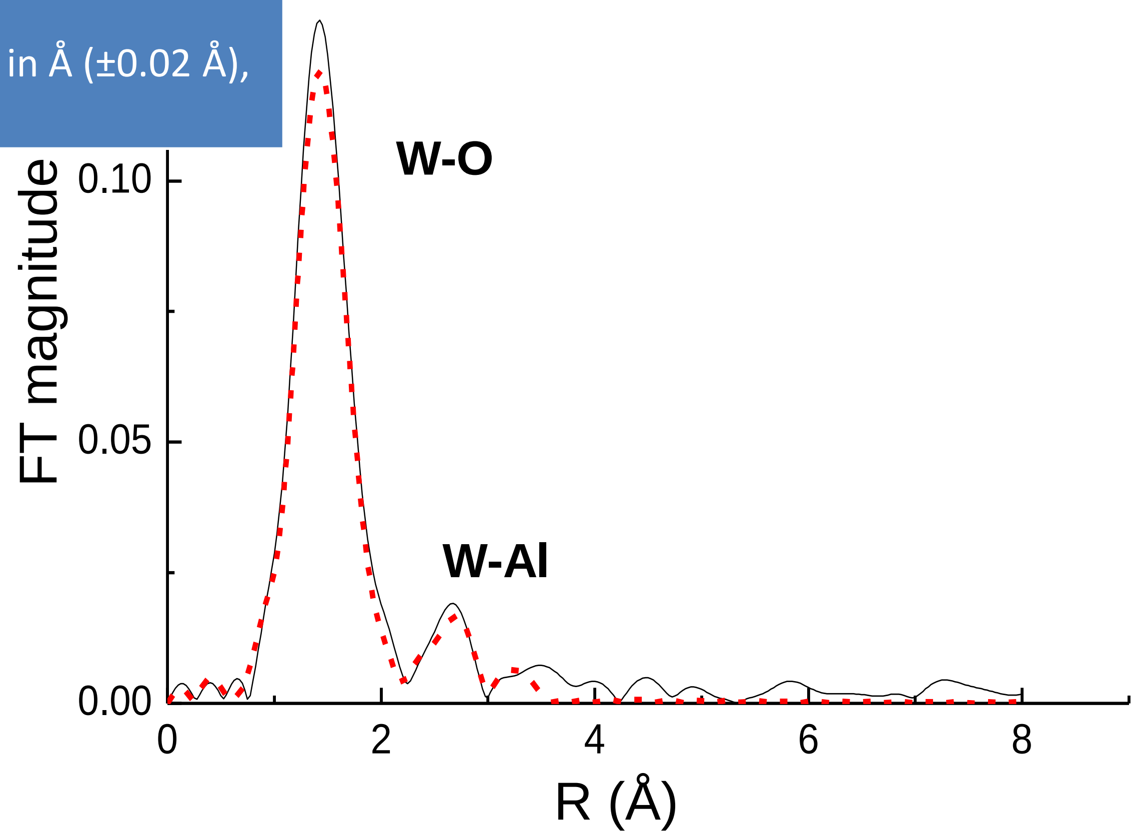
W L_3-edge EXAFS fits for tungstate sorbed on boehmite

5 µM sorption sample

Sample	Path	CN[a]	R (Å)[b]	σ^2 (Å^2)[c]	ΔE_0 (eV)
5 µM	W-O1	3.1	1.75	0.002	3.4
	W-O2	3.2	2.14	0.009	
	W-Al	2.2	3.14	0.01	

*: fixed in the fitting,
a : coordination number (±20%), b: distance in Å (±0.02 Å),
c : Debye-Waller factor





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*: fixed in the fitting,
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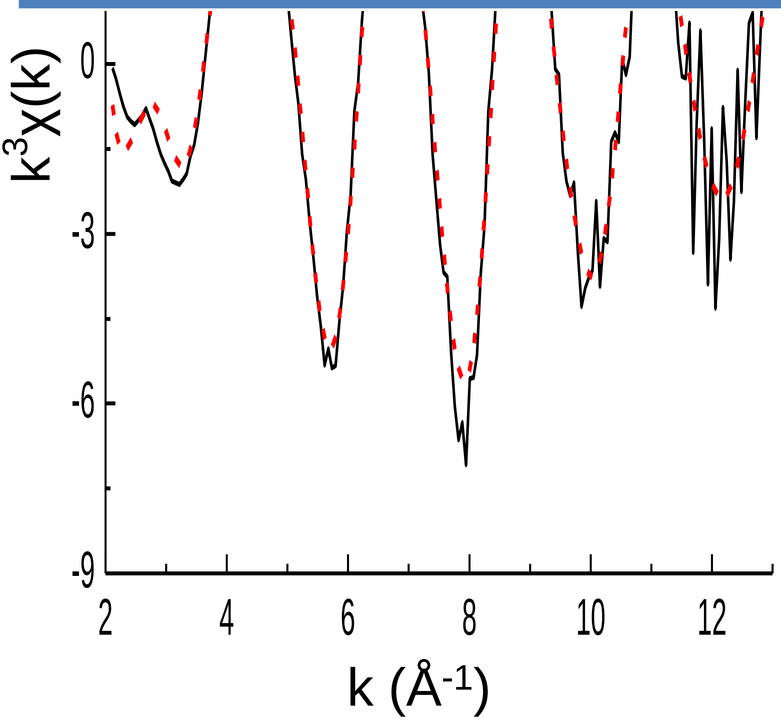
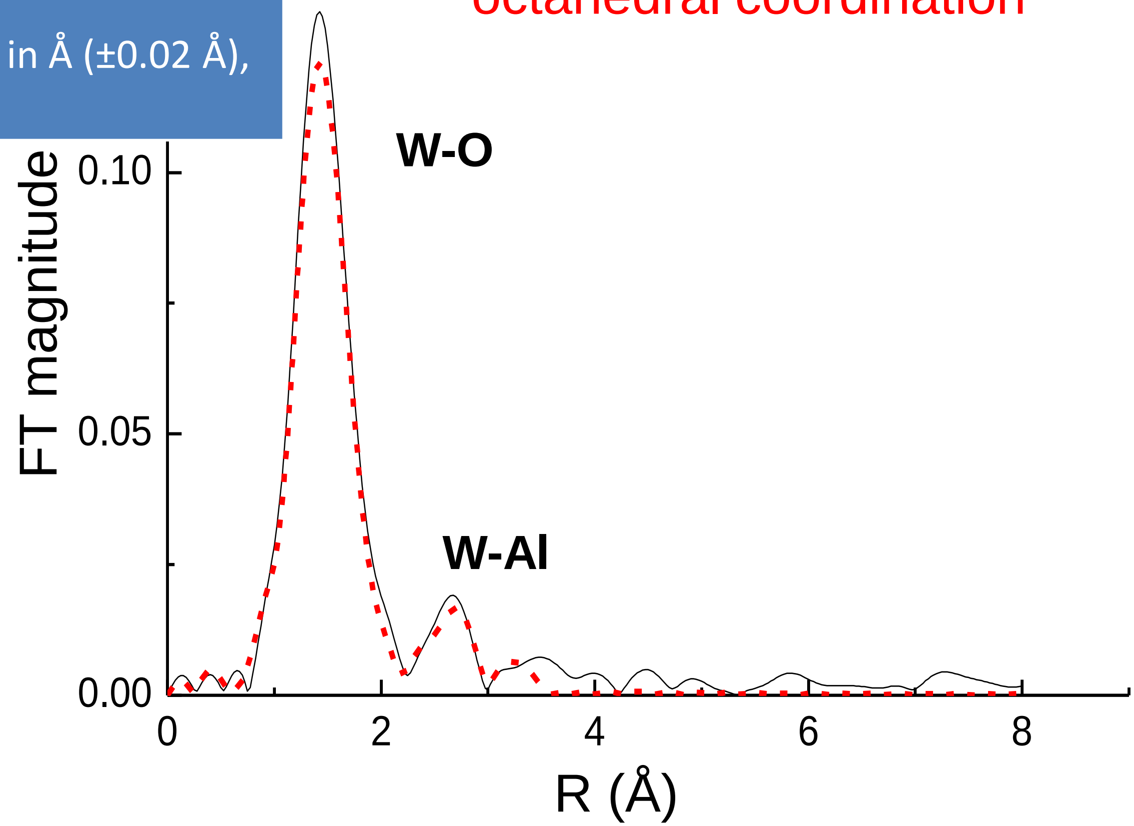
c : Debye-Waller factor

<W-O>$_{ave}$ = 1.95 Å

Typical distance for octahedral coordination



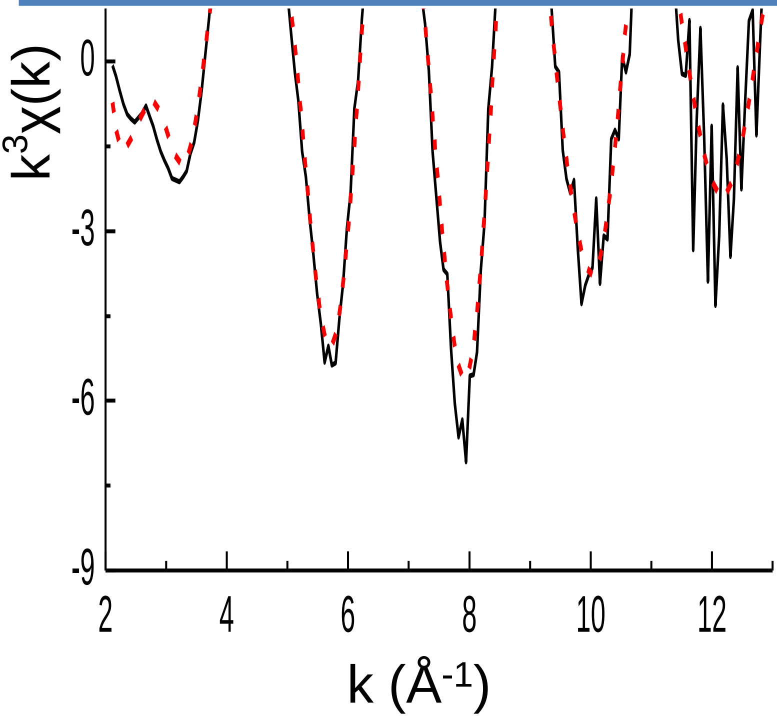


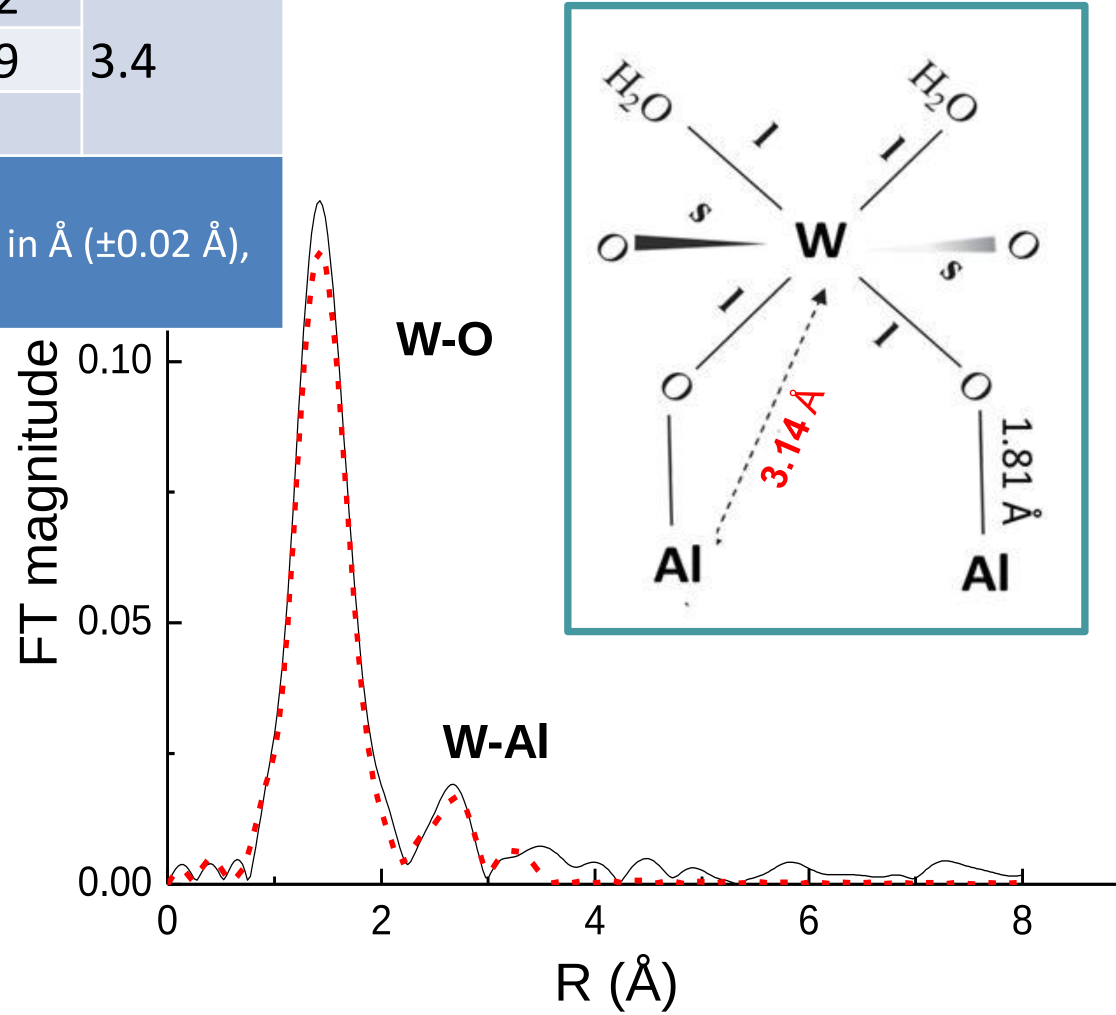
W L_3-edge EXAFS fits for tungstate sorbed on boehmite

5 µM sorption sample

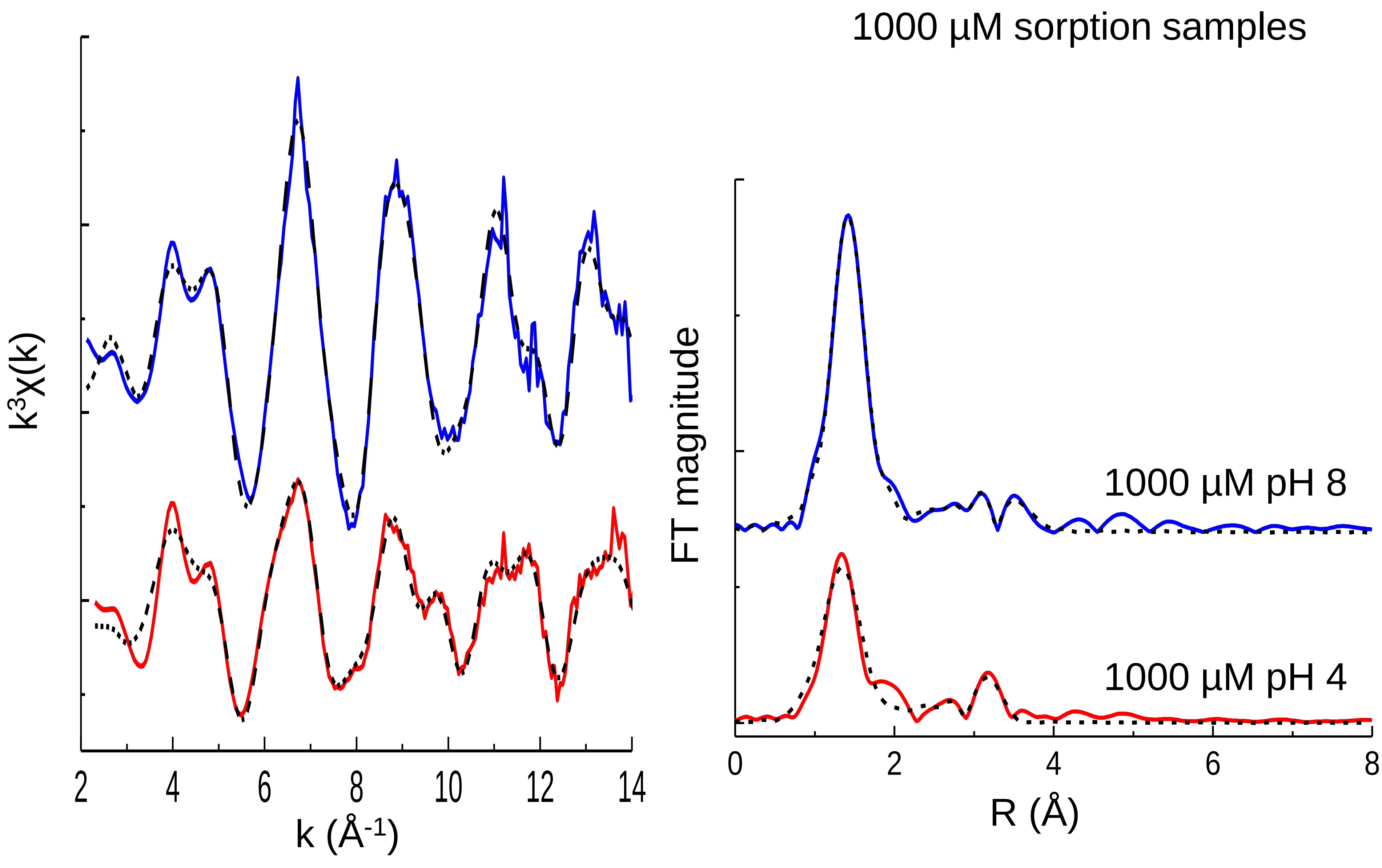
Sample	Path	CN[a]	R (Å)[b]	σ^2 ($Å^2$)[c]	ΔE_0 (eV)
5 µM	W-O1	3.1	1.75	0.002	3.4
	W-O2	3.2	2.14	0.009	
	W-Al	2.2	3.14	0.01	

*: fixed in the fitting,
a : coordination number (±20%), b: distance in Å (±0.02 Å),
c : Debye-Waller factor





W L$_3$-edge EXAFS fits for tungstate sorbed on boehmite

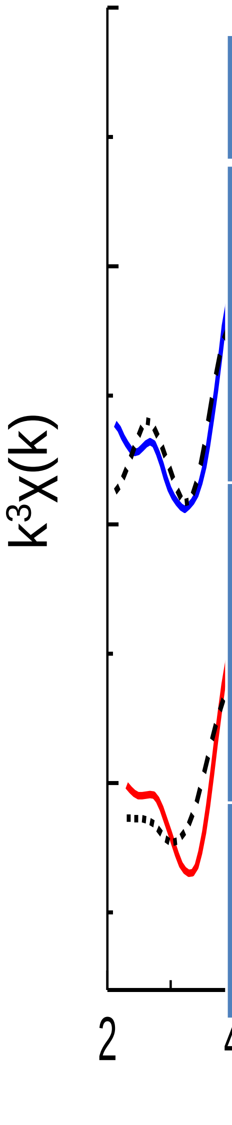


W L_3-edge EXAFS fits for tungstate sorbed on boehmite

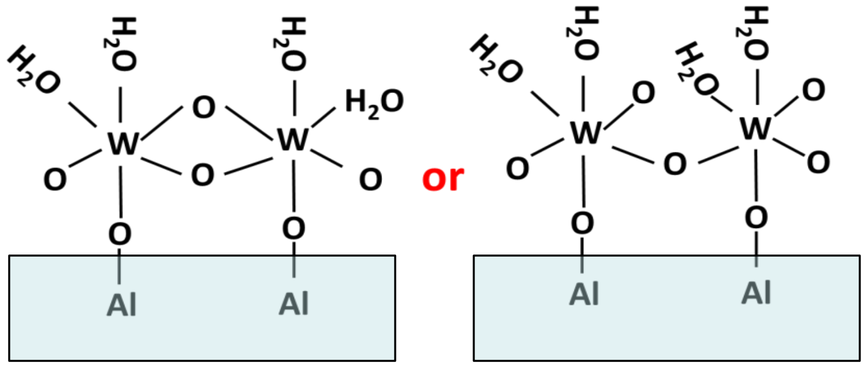
1000 µM sorption samples

Sample	Path	CN[a]	R (Å)[b]	σ^2 ($Å^2$)[c]	ΔE0 (eV)
1000 µM pH 8	W-O1	3.0	1.75	0.003	-0.4
	W-O2	4.0	2.14	0.009	
	W-Al	2*	3.14	0.012	
	W-W1	0.6	3.23	0.004	
	W-W2	1.6	3.73	0.007	
1000 µM pH 4	W-O1	2*	1.74	0.003	-1.2
	W-O2	2*	1.98	0.019	
	W-O3	2*	2.21	0.006	
	W-Al	2*	3.15	0.015	
	W-W	3.4	3.25	0.008	

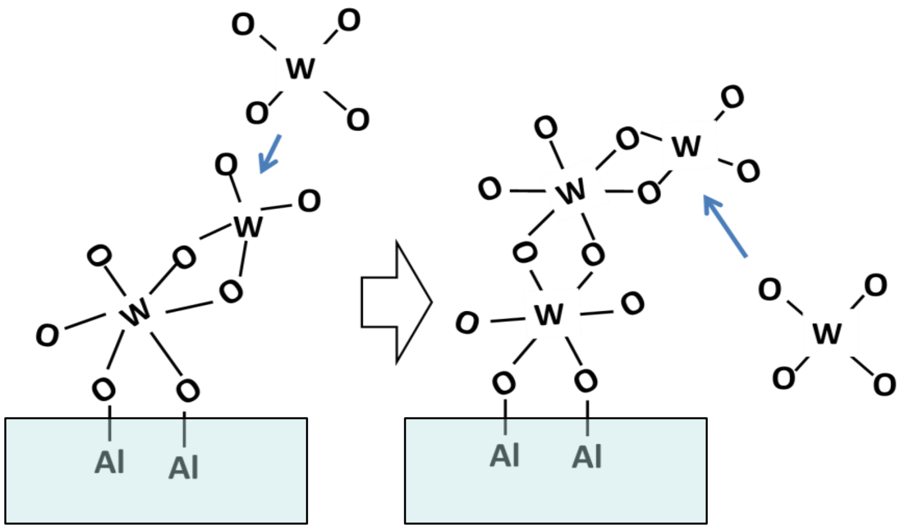
*: fixed in the fitting,
a : coordination number (±20%), b: distance in Å (±0.02 Å),
c : Debye-Waller factor



Surface-induced tungstate polymerization



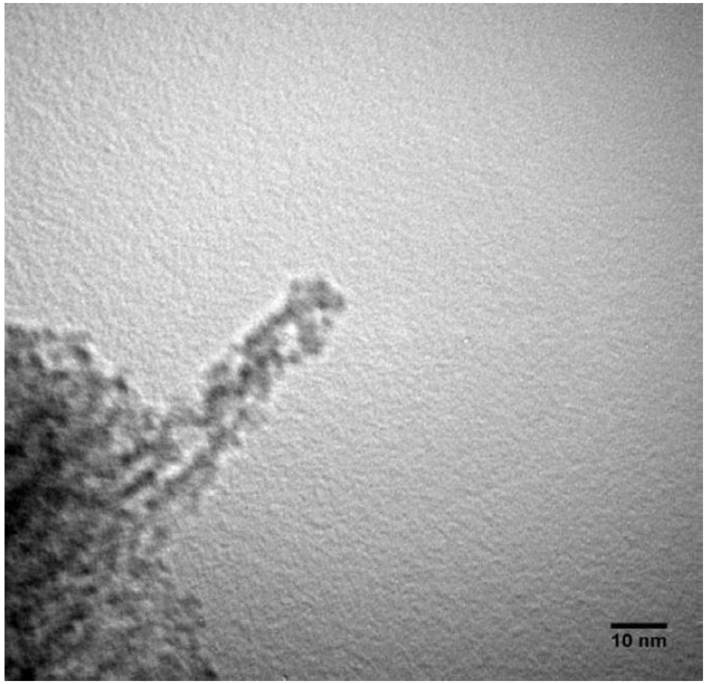
Co-location polymerization



Open chain polymerization

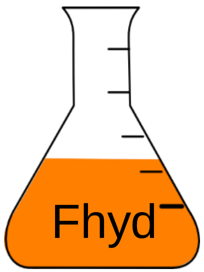
Coupled Redox Transformation of Chromate and Arsenite on Ferrihydrite

- Chromium and arsenic commonly coexist at contaminated sites
- Cr(VI) is soluble, mobile, toxic (carcinogenic), and bioavailable
- Cr(III) is generally insoluble, micro-nutrient
- As(III) is generally more mobile and toxic than As(V)
- Coupled redox involving As(III) and Cr(VI) at ferrihydrite surface



2-line ferrihydrite

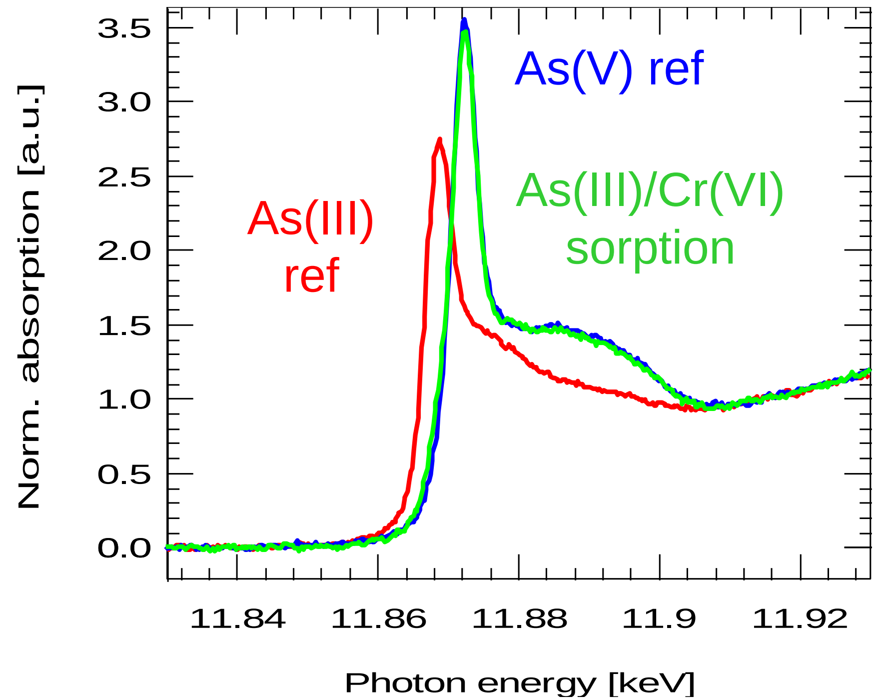
As(III)-Cr(VI) co-sorption on Ferrihydrite

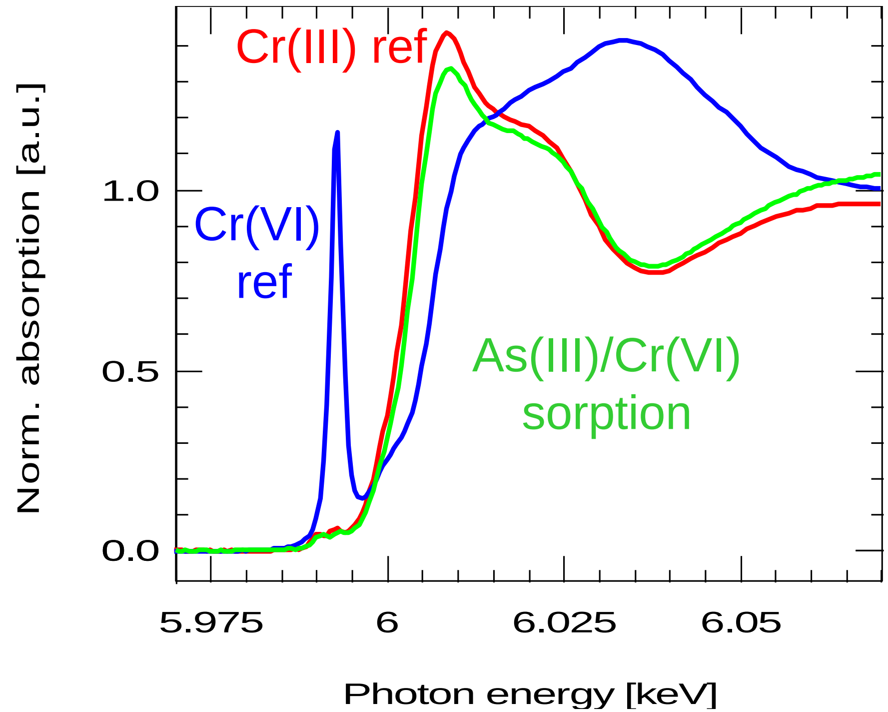


As and/or Cr reacted with Fhyd suspension for 12 hr at pH 5

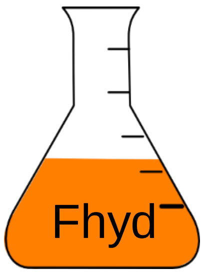
Sorbed species	**Rxn product**
As(III)	----
As(V)	----
Cr(III)	----
Cr(VI)	----
As(III) + C(VI)	As(V) + Cr(III)

Solution species	
As(III) + Cr(VI)	----



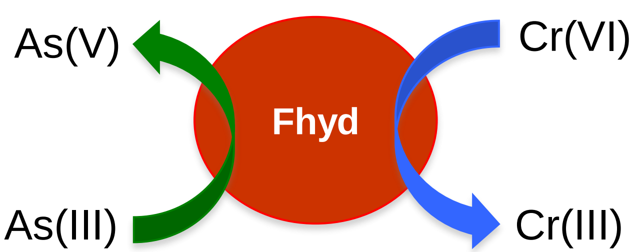


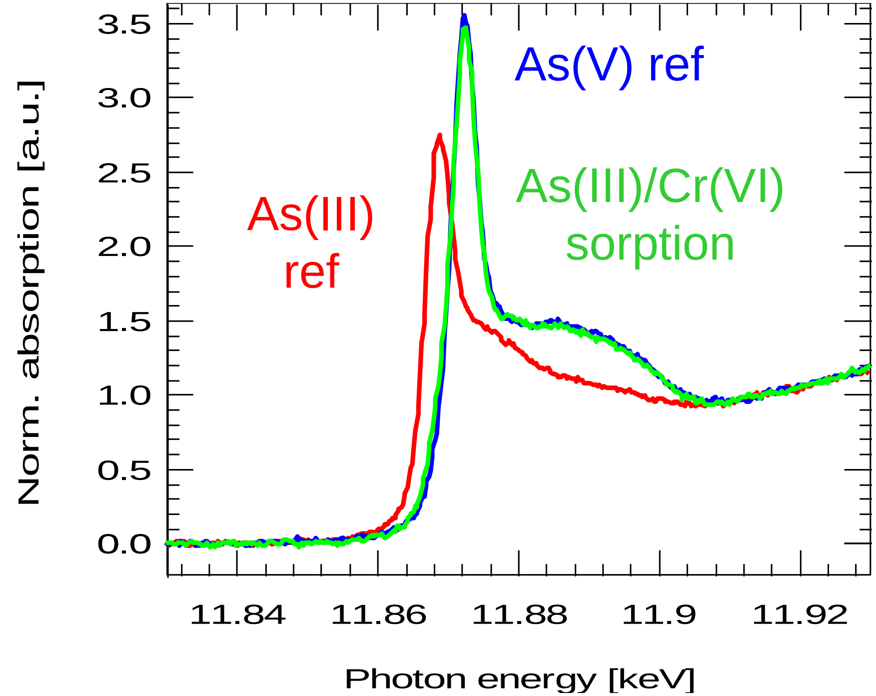
As(III)-Cr(VI) co-sorption on Ferrihydrite

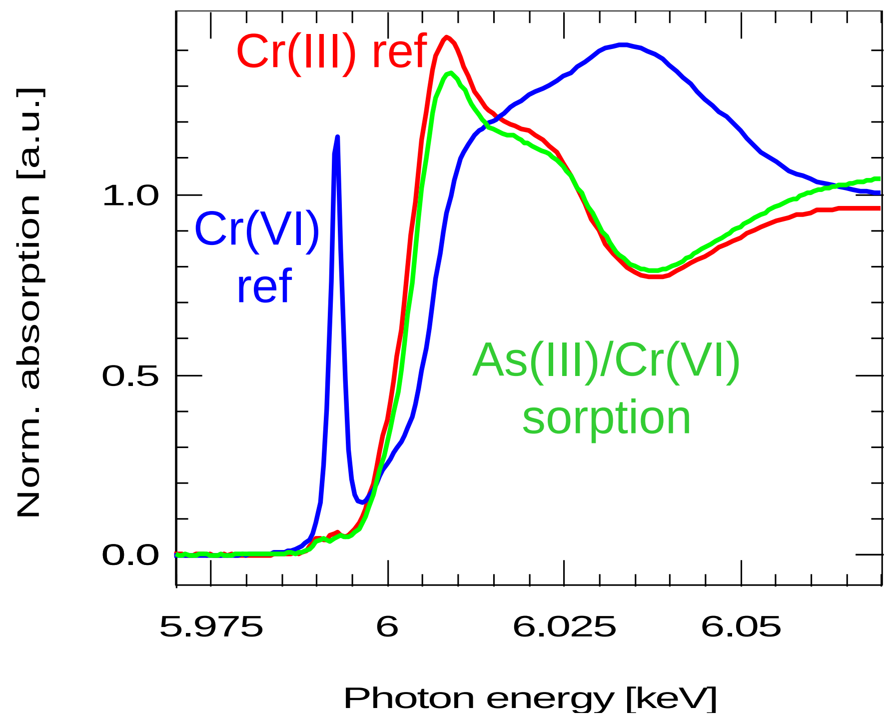


As and/or Cr reacted with Fhyd suspension for 12 hr at pH 5

Sorbed species	**Rxn product**
As(III)	----
As(V)	----
Cr(III)	----
Cr(VI)	----
As(III) + C(VI)	As(V) + Cr(III)
Solution species	
As(III) + Cr(VI)	----

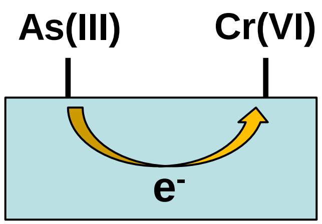


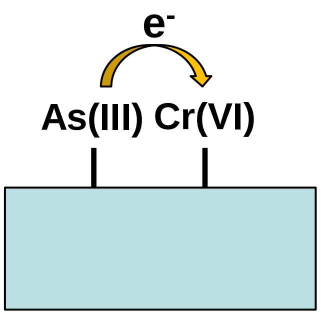




What role does the surface play?

Two mechanisms for e^- transfer:





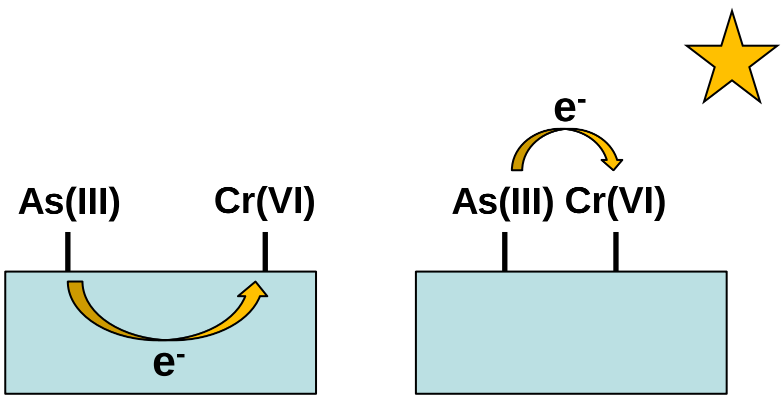
Long-range charge transfer in bulk semiconductor (or near surface)

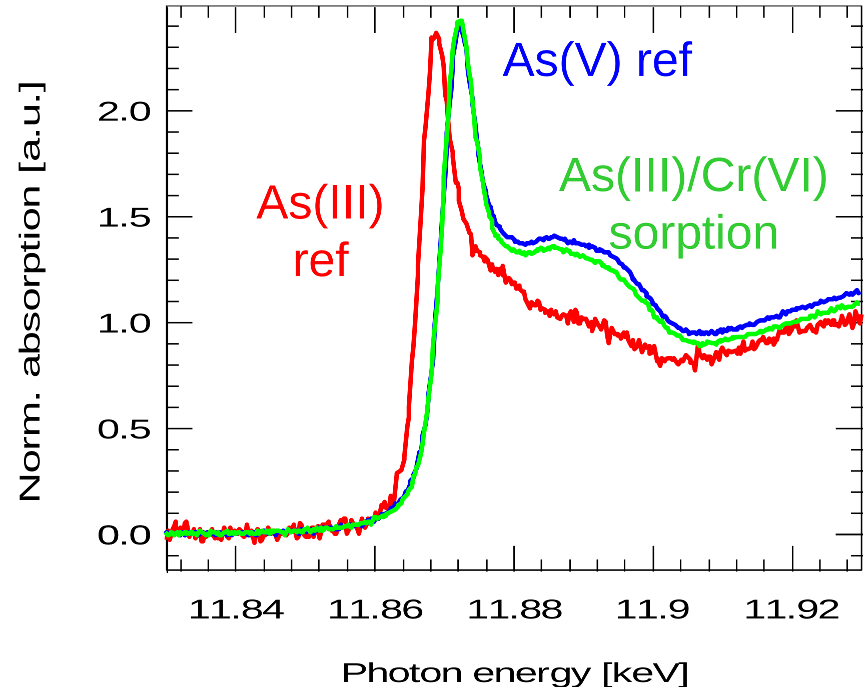
Co-localization at surface

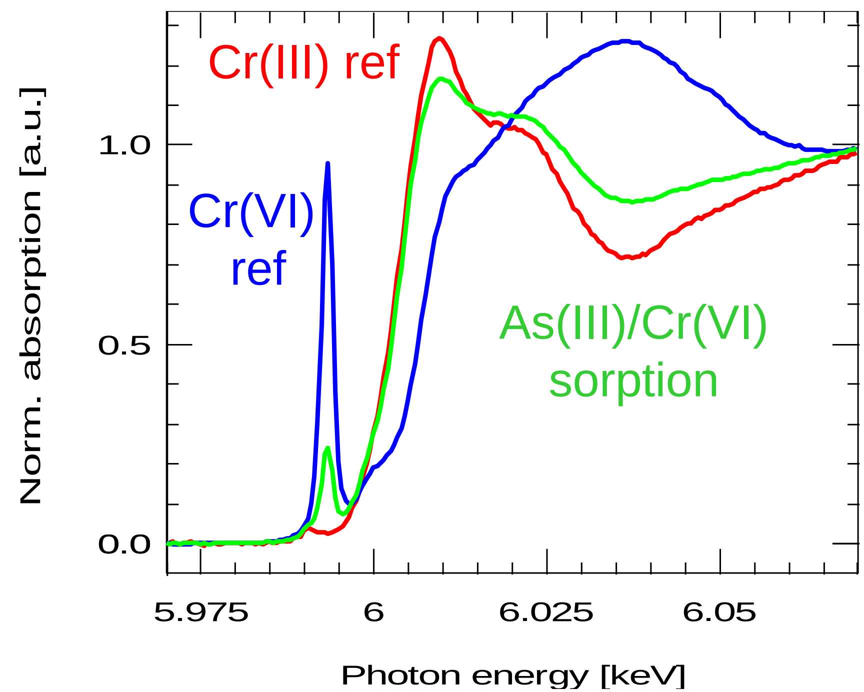
Duplicate experiment on insulator

As(III)-Cr(VI) co-sorption on $Al(OH)_3$

Nearly same results







Summary

- Synchrotron-based X-ray absorption spectroscopy offers a suite of techniques for characterization of metal speciation
- Complementary to other methods
- Element specific
- Local structure of species sorbed at mineral-water interface
- Can be used when metal/metalloid is very dilute
- Suitable for micro-spectroscopy applications to obtain spatial resolution (100 nm – 10 µm)

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