

Introduction to X-ray Absorption Spectroscopy

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&

Beamline for Materials Measurements

National Synchrotron Light Source II

XAS 2023: Fundamentals of XAS Data Analysis: A Hands-on Tutorial

10 October, 2023

Part 1

The basic physics and chemistry of X-ray Absorption

This Talk

This talk is an introduction to the inner-shell spectroscopies, XAS and XRF.

Outline

- An overview of the basic physics of inner shell spectroscopies
- An introduction to XAS and XRF beamline instrumentation
- A flavor of the sorts of science that can be accomplished with XAS and XRF, including examples from my own research and my beamline.

My hope is that you will leave with a sense of how XAS and XRF might be applied to **your** research.

XAS and XRF

X-ray Absorption Spectroscopy and X-Ray Fluorescence spectroscopy

These are inner shell spectroscopies.

Inner shell means that an x-ray interacts primarily with a deep-core electron rather than with a valence electron.

Spectroscopy means that some aspect of the interaction changes as a function of photon energy.

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XAS and XRF

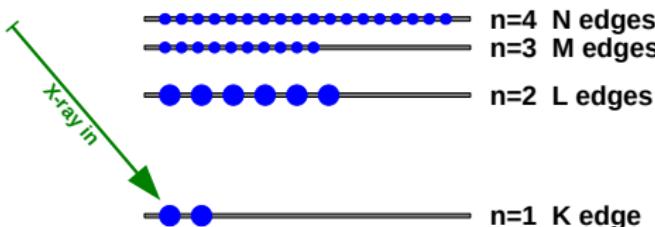
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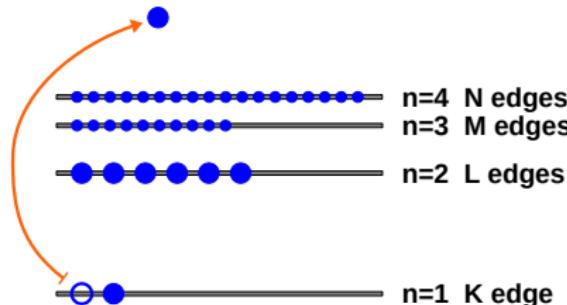
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The basic physical process in XAS and XRF



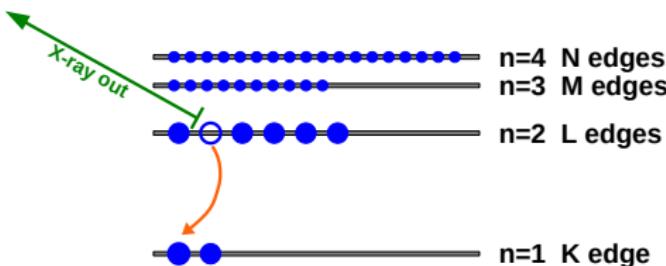
- ① An incoming photon interacts with a deep-core electron. Shown here, a 1s electron is excited for a K-edge spectrum.
- ② The deep-core electron is promoted to some unoccupied state above the Fermi energy, propagates away, and leaves behind a core-hole.
- ③ A short time later (1 or 2 femtoseconds), a higher-lying electron decays into the core-hole and emits a photon. Shown here, a $2p^{3/2}$ or $2p^{1/2}$ electron fills the 1s hole.
- ④ Alternately, the energy from the higher-lying electron can be used to emit an Auger electron.

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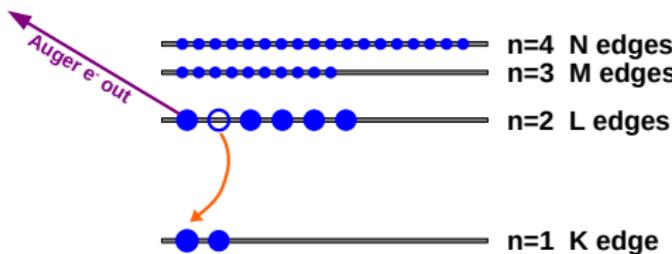
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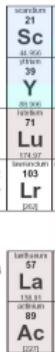


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Elements and Beamlines

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sodium 11 Na 22.990	magnesium 12 Mg 24.305	silicon 13 Al 26.982	phosphorus 14 Si 30.986	sulfur 15 P 32.065	chlorine 16 S 35.452	aristane 17 Cl 36.945	chlorine 18 Ar 39.948																																																																																																																																																																																																																																																																																																																																																																																								
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.960	thorium 22 Th 264.967	vanadium 23 V 50.942	chromium 24 Cr 51.961	manganese 25 Mn 54.938	iron 26 Fe 55.847	cobalt 27 Co 58.931	nickel 28 Ni 58.931	copper 29 Cu 63.546	zinc 30 Zn 65.402	gallium 31 Ga 69.713	indium 32 In 113.41	tin 33 Ge 114.82	tin 34 As 117.402	antimony 35 Br 119.84	antimony 36 Kr 83.80																																																																																																																																																																																																																																																																																																																																																																														
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	tantalum 42 Mo 95.941	rhenium 43 Tc 95.941	osmium 44 Ru 95.941	rhodium 45 Rh 95.941	palladium 46 Pd 95.942	silver 47 Ag 107.87	cadmium 48 Cd 112.41	tin 49 In 113.41	tin 50 Sn 113.71	tin 51 Sb 121.20	tin 52 Te 127.40	tin 53 I 126.90	tin 54 Xe 132.29																																																																																																																																																																																																																																																																																																																																																																														
cesium 55 Cs 132.01	boron 56 B 137.35	lanthanides 57 La 138.91	cerium 71 Ce 140.91	europium 72 Pr 141.91	neodymium 73 Nd 142.91	promethium 74 Pm 143.91	samarium 75 Sm 146.91	gadolinium 76 Gd 150.91	thulium 77 Tb 151.91	ytterbium 78 Dy 158.91	erbium 79 Ho 160.91	thulium 80 Er 161.91	ytterbium 81 Tm 168.91	ytterbium 82 Yb 173.91	ytterbium 83 Lu 174.91	ytterbium 84 Hf 176.91	ytterbium 85 Ta 177.91	ytterbium 86 W 178.91	ytterbium 87 Re 179.91	ytterbium 88 Os 180.91	ytterbium 89 Rb 181.91	ytterbium 90 Sr 182.91	ytterbium 91 Ba 183.91	ytterbium 92 Ra 184.91																																																																																																																																																																																																																																																																																																																																																																							
francium 87 Fr 223.01		actinides 93 Ac 222.01	lanthanides 94 Th 223.01	cerium 95 Pa 224.01	europium 96 Np 225.01	neodymium 97 Pu 226.01	promethium 98 Am 227.01	samarium 99 Gd 228.01	gadolinium 100 Tb 229.01	thulium 101 Dy 230.01	ytterbium 102 Ho 231.01	ytterbium 103 Er 232.01	ytterbium 104 Tm 233.01	ytterbium 105 Yb 234.01	ytterbium 106 Lu 235.01	ytterbium 107 Hf 236.01	ytterbium 108 Os 237.01	ytterbium 109 Tb 238.01	ytterbium 110 Dy 239.01	ytterbium 111 Ho 240.01	ytterbium 112 Er 241.01	ytterbium 113 Tm 242.01	ytterbium 114 Yb 243.01	ytterbium 115 Lu 244.01	ytterbium 116 Hf 245.01	ytterbium 117 Os 246.01	ytterbium 118 Tb 247.01	ytterbium 119 Dy 248.01	ytterbium 120 Ho 249.01	ytterbium 121 Er 250.01	ytterbium 122 Tm 251.01	ytterbium 123 Yb 252.01	ytterbium 124 Lu 253.01	ytterbium 125 Hf 254.01	ytterbium 126 Os 255.01	ytterbium 127 Tb 256.01	ytterbium 128 Dy 257.01	ytterbium 129 Ho 258.01	ytterbium 130 Er 259.01	ytterbium 131 Tm 260.01	ytterbium 132 Yb 261.01	ytterbium 133 Lu 262.01	ytterbium 134 Hf 263.01	ytterbium 135 Os 264.01	ytterbium 136 Tb 265.01	ytterbium 137 Dy 266.01	ytterbium 138 Ho 267.01	ytterbium 139 Er 268.01	ytterbium 140 Tm 269.01	ytterbium 141 Yb 270.01	ytterbium 142 Lu 271.01	ytterbium 143 Hf 272.01	ytterbium 144 Os 273.01	ytterbium 145 Tb 274.01	ytterbium 146 Dy 275.01	ytterbium 147 Ho 276.01	ytterbium 148 Er 277.01	ytterbium 149 Tm 278.01	ytterbium 150 Yb 279.01	ytterbium 151 Lu 280.01	ytterbium 152 Hf 281.01	ytterbium 153 Os 282.01	ytterbium 154 Tb 283.01	ytterbium 155 Dy 284.01	ytterbium 156 Ho 285.01	ytterbium 157 Er 286.01	ytterbium 158 Tm 287.01	ytterbium 159 Yb 288.01	ytterbium 160 Lu 289.01	ytterbium 161 Hf 290.01	ytterbium 162 Os 291.01	ytterbium 163 Tb 292.01	ytterbium 164 Dy 293.01	ytterbium 165 Ho 294.01	ytterbium 166 Er 295.01	ytterbium 167 Tm 296.01	ytterbium 168 Yb 297.01	ytterbium 169 Lu 298.01	ytterbium 170 Hf 299.01	ytterbium 171 Os 300.01	ytterbium 172 Tb 301.01	ytterbium 173 Dy 302.01	ytterbium 174 Ho 303.01	ytterbium 175 Er 304.01	ytterbium 176 Tm 305.01	ytterbium 177 Yb 306.01	ytterbium 178 Lu 307.01	ytterbium 179 Hf 308.01	ytterbium 180 Os 309.01	ytterbium 181 Tb 310.01	ytterbium 182 Dy 311.01	ytterbium 183 Ho 312.01	ytterbium 184 Er 313.01	ytterbium 185 Tm 314.01	ytterbium 186 Yb 315.01	ytterbium 187 Lu 316.01	ytterbium 188 Hf 317.01	ytterbium 189 Os 318.01	ytterbium 190 Tb 319.01	ytterbium 191 Dy 320.01	ytterbium 192 Ho 321.01	ytterbium 193 Er 322.01	ytterbium 194 Tm 323.01	ytterbium 195 Yb 324.01	ytterbium 196 Lu 325.01	ytterbium 197 Hf 326.01	ytterbium 198 Os 327.01	ytterbium 199 Tb 328.01	ytterbium 200 Dy 329.01	ytterbium 201 Ho 330.01	ytterbium 202 Er 331.01	ytterbium 203 Tm 332.01	ytterbium 204 Yb 333.01	ytterbium 205 Lu 334.01	ytterbium 206 Hf 335.01	ytterbium 207 Os 336.01	ytterbium 208 Tb 337.01	ytterbium 209 Dy 338.01	ytterbium 210 Ho 339.01	ytterbium 211 Er 340.01	ytterbium 212 Tm 341.01	ytterbium 213 Yb 342.01	ytterbium 214 Lu 343.01	ytterbium 215 Hf 344.01	ytterbium 216 Os 345.01	ytterbium 217 Tb 346.01	ytterbium 218 Dy 347.01	ytterbium 219 Ho 348.01	ytterbium 220 Er 349.01	ytterbium 221 Tm 350.01	ytterbium 222 Yb 351.01	ytterbium 223 Lu 352.01	ytterbium 224 Hf 353.01	ytterbium 225 Os 354.01	ytterbium 226 Tb 355.01	ytterbium 227 Dy 356.01	ytterbium 228 Ho 357.01	ytterbium 229 Er 358.01	ytterbium 230 Tm 359.01	ytterbium 231 Yb 360.01	ytterbium 232 Lu 361.01	ytterbium 233 Hf 362.01	ytterbium 234 Os 363.01	ytterbium 235 Tb 364.01	ytterbium 236 Dy 365.01	ytterbium 237 Ho 366.01	ytterbium 238 Er 367.01	ytterbium 239 Tm 368.01	ytterbium 240 Yb 369.01	ytterbium 241 Lu 370.01	ytterbium 242 Hf 371.01	ytterbium 243 Os 372.01	ytterbium 244 Tb 373.01	ytterbium 245 Dy 374.01	ytterbium 246 Ho 375.01	ytterbium 247 Er 376.01	ytterbium 248 Tm 377.01	ytterbium 249 Yb 378.01	ytterbium 250 Lu 379.01	ytterbium 251 Hf 380.01	ytterbium 252 Os 381.01	ytterbium 253 Tb 382.01	ytterbium 254 Dy 383.01	ytterbium 255 Ho 384.01	ytterbium 256 Er 385.01	ytterbium 257 Tm 386.01	ytterbium 258 Yb 387.01	ytterbium 259 Lu 388.01	ytterbium 260 Hf 389.01	ytterbium 261 Os 390.01	ytterbium 262 Tb 391.01	ytterbium 263 Dy 392.01	ytterbium 264 Ho 393.01	ytterbium 265 Er 394.01	ytterbium 266 Tm 395.01	ytterbium 267 Yb 396.01	ytterbium 268 Lu 397.01	ytterbium 269 Hf 398.01	ytterbium 270 Os 399.01	ytterbium 271 Tb 400.01	ytterbium 272 Dy 401.01	ytterbium 273 Ho 402.01	ytterbium 274 Er 403.01	ytterbium 275 Tm 404.01	ytterbium 276 Yb 405.01	ytterbium 277 Lu 406.01	ytterbium 278 Hf 407.01	ytterbium 279 Os 408.01	ytterbium 280 Tb 409.01	ytterbium 281 Dy 410.01	ytterbium 282 Ho 411.01	ytterbium 283 Er 412.01	ytterbium 284 Tm 413.01	ytterbium 285 Yb 414.01	ytterbium 286 Lu 415.01	ytterbium 287 Hf 416.01	ytterbium 288 Os 417.01	ytterbium 289 Tb 418.01	ytterbium 290 Dy 419.01	ytterbium 291 Ho 420.01	ytterbium 292 Er 421.01	ytterbium 293 Tm 422.01	ytterbium 294 Yb 423.01	ytterbium 295 Lu 424.01	ytterbium 296 Hf 425.01	ytterbium 297 Os 426.01	ytterbium 298 Tb 427.01	ytterbium 299 Dy 428.01	ytterbium 300 Ho 429.01	ytterbium 301 Er 430.01	ytterbium 302 Tm 431.01	ytterbium 303 Yb 432.01	ytterbium 304 Lu 433.01	ytterbium 305 Hf 434.01	ytterbium 306 Os 435.01	ytterbium 307 Tb 436.01	ytterbium 308 Dy 437.01	ytterbium 309 Ho 438.01	ytterbium 310 Er 439.01	ytterbium 311 Tm 440.01	ytterbium 312 Yb 441.01	ytterbium 313 Lu 442.01	ytterbium 314 Hf 443.01	ytterbium 315 Os 444.01	ytterbium 316 Tb 445.01	ytterbium 317 Dy 446.01	ytterbium 318 Ho 447.01	ytterbium 319 Er 448.01	ytterbium 320 Tm 449.01	ytterbium 321 Yb 450.01	ytterbium 322 Lu 451.01	ytterbium 323 Hf 452.01	ytterbium 324 Os 453.01	ytterbium 325 Tb 454.01	ytterbium 326 Dy 455.01	ytterbium 327 Ho 456.01	ytterbium 328 Er 457.01	ytterbium 329 Tm 458.01	ytterbium 330 Yb 459.01	ytterbium 331 Lu 460.01	ytterbium 332 Hf 461.01	ytterbium 333 Os 462.01	ytterbium 334 Tb 463.01	ytterbium 335 Dy 464.01	ytterbium 336 Ho 465.01	ytterbium 337 Er 466.01	ytterbium 338 Tm 467.01	ytterbium 339 Yb 468.01	ytterbium 340 Lu 469.01	ytterbium 341 Hf 470.01	ytterbium 342 Os 471.01	ytterbium 343 Tb 472.01	ytterbium 344 Dy 473.01	ytterbium 345 Ho 474.01	ytterbium 346 Er 475.01	ytterbium 347 Tm 476.01	ytterbium 348 Yb 477.01	ytterbium 349 Lu 478.01	ytterbium 350 Hf 479.01	ytterbium 351 Os 480.01	ytterbium 352 Tb 481.01	ytterbium 353 Dy 482.01	ytterbium 354 Ho 483.01	ytterbium 355 Er 484.01	ytterbium 356 Tm 485.01	ytterbium 357 Yb 486.01	ytterbium 358 Lu 487.01	ytterbium 359 Hf 488.01	ytterbium 360 Os 489.01	ytterbium 361 Tb 490.01	ytterbium 362 Dy 491.01	ytterbium 363 Ho 492.01	ytterbium 364 Er 493.01	ytterbium 365 Tm 494.01	ytterbium 366 Yb 495.01	ytterbium 367 Lu 496.01	ytterbium 368 Hf 497.01	ytterbium 369 Os 498.01	ytterbium 370 Tb 499.01	ytterbium 371 Dy 500.01	ytterbium 372 Ho 501.01	ytterbium 373 Er 502.01	ytterbium 374 Tm 503.01	ytterbium 375 Yb 504.01	ytterbium 376 Lu 505.01	ytterbium 377 Hf 506.01	ytterbium 378 Os 507.01	ytterbium 379 Tb 508.01	ytterbium 380 Dy 509.01	ytterbium 381 Ho 510.01	ytterbium 382 Er 511.01	ytterbium 383 Tm 512.01	ytterbium 384 Yb 513.01	ytterbium 385 Lu 514.01	ytterbium 386 Hf 515.01	ytterbium 387 Os 516.01	ytterbium 388 Tb 517.01	ytterbium 389 Dy 518.01	ytterbium 390 Ho 519.01	ytterbium 391 Er 520.01	ytterbium 392 Tm 521.01	ytterbium 393 Yb 522.01	ytterbium 394 Lu 523.01	ytterbium 395 Hf 524.01	ytterbium 396 Os 525.01	ytterbium 397 Tb 526.01	ytterbium 398 Dy 527.01	ytterbium 399 Ho 528.01	ytterbium 400 Er 529.01	ytterbium 401 Tm 530.01	ytterbium 402 Yb 531.01	ytterbium 403 Lu 532.01	ytterbium 404 Hf 533.01	ytterbium 405 Os 534.01	ytterbium 406 Tb 535.01	ytterbium 407 Dy 536.01	ytterbium 408 Ho 537.01	ytterbium 409 Er 538.01	ytterbium 410 Tm 539.01	ytterbium 411 Yb 540.01	ytterbium 412 Lu 541.01	ytterbium 413 Hf 542.01	ytterbium 414 Os 543.01	ytterbium 415 Tb 544.01	ytterbium 416 Dy 545.01	ytterbium 417 Ho 546.01	ytterbium 418 Er 547.01	ytterbium 419 Tm 548.01	ytterbium 420 Yb 549.01	ytterbium 421 Lu 550.01	ytterbium 422 Hf 551.01	ytterbium 423 Os 552.01	ytterbium 424 Tb 553.01	ytterbium 425 Dy 554.01	ytterbium 426 Ho 555.01	ytterbium 427 Er 556.01	ytterbium 428 Tm 557.01	ytterbium 429 Yb 558.01	ytterbium 430 Lu 559.01	ytterbium 431 Hf 560.01	ytterbium 432 Os 561.01	ytterbium 433 Tb 562.01	ytterbium 434 Dy 563.01	ytterbium 435 Ho 564.01	ytterbium 436 Er 565.01	ytterbium 437 Tm 566.01	ytterbium 438 Yb 567.01	ytterbium 439 Lu 568.01	ytterbium 440 Hf 569.01	ytterbium 441 Os 570.01	ytterbium 442 Tb 571.01	ytterbium 443 Dy 572.01	ytterbium 444 Ho 573.01	ytterbium 445 Er 574.01	ytterbium 446 Tm 575.01	ytterbium 447 Yb 576.01	ytterbium 448 Lu 577.01	ytterbium 449 Hf 578.01	ytterbium 450 Os 579.01	ytterbium 451 Tb 580.01	ytterbium 452 Dy 581.01	ytterbium 453 Ho 582.01	ytterbium 454 Er 583.01	ytterbium 455 Tm 584.01	ytterbium 456 Yb 585.01	ytterbium 457 Lu 586.01	ytterbium 458 Hf 587.01	ytterbium 459 Os 588.01	ytterbium 460 Tb 589.01	ytterbium 461 Dy 590.01	ytterbium 462 Ho 591.01	ytterbium 463 Er 592.01	ytterbium 464 Tm 593.01	ytterbium 465 Yb 594.01	ytterbium 466 Lu 595.01	ytterbium 467 Hf 596.01	ytterbium 468 Os 597.01	ytterbium 469 Tb 598.01	ytterbium 470 Dy 599.01	ytterbium 471 Ho 600.01	ytterbium 472 Er 601.01	ytterbium 473 Tm 602.01	ytterbium 474 Yb 603.01

Elements and Beamlines

hydrogen 1 H 1.0079	beryllium 3 Li 6.941	boron 5 B 10.811	helium 2 He 4.003
lithium 3 Li 6.941	beryllium 4 Be 9.0122	carbon 6 C 12.011	nitrogen 7 N 14.007
sodium 11 Na 22.990	magnesium 12 Mg 24.305	phosphorus 15 P 30.974	oxygen 8 O 15.999
potassium 19 K 39.098	silicon 14 Si 28.086	sulfur 16 S 32.065	fluorine 9 F 18.998
calcium 20 Ca 40.080	chromium 21 Cr 51.996	chlorine 17 Cl 35.453	neon 10 Ne 20.180
rubidium 37 Rb 85.468	nickel 24 Ni 58.696	aristoteles 18 Ar 36.947	
strontium 38 Sr 87.62	iron 26 Fe 55.845		
cesium 55 Cs 132.91	cobalt 27 Co 58.937		
barium 56 Ba 137.35	nickel 28 Ni 58.693		
francium 87 Fr 223.024	copper 29 Cu 63.546		
	zinc 30 Zn 65.409		
	gallium 31 Ga 69.721		
	germanium 32 Ge 72.61		
	arsenic 33 As 74.933		
	sele-nium 34 Se 78.96		
	bronze 35 Br 79.947		
	krayon 36 Kr 83.901		
↑ Vanadium			
K: 5465 eV Kα_1 (K-L3): 4953 eV L₁: 627 eV Kα_2 (K-L2): 4945 eV L₂: 520 eV K$\beta_{1,3}$ (K-M3/M2): 5428 eV L₃: 512 eV Kβ_5 (K-M4,5): 5463 eV			
* Lanthanide series ** Actinide series			
			

K- or L-edges measured at a soft-X-ray beamline

K-edges measured at a hard-X-ray beamline

L-edges measured at a hard-X-ray beamline

Elements and Beamlines

hydrogen 1 H 1.0000	beryllium 3 Li 6.941	boron 5 B 10.811	helium 2 He 1.0000
lithium 3 Li 6.941	beryllium 4 Be 9.0322	carbon 6 C 12.011	nitrogen 7 N 14.007
sodium 11 Na 22.990	magnesium 12 Mg 24.305	phosphorus 15 P 30.974	oxygen 8 O 15.999
potassium 19 K 39.098	aluminum 21 Al 26.982	sulfur 16 S 32.065	fluorine 9 F 18.998
rubidium 37 Rb 85.468	titanium 22 Ti 47.867	chlorine 17 Cl 35.453	neon 10 Ne 20.180
strontium 38 Sr 87.62	vanadium 23 V 50.947	nitrogen 14 N 14.007	oxygen 10 O 16.999
barium 56 Ba 137.321	chromium 24 Cr 51.996	phosphorus 15 P 30.974	fluorine 10 F 18.998
cesium 55 Cs 132.904	manganese 25 Mn 54.938	sulfur 16 S 32.065	oxygen 10 O 16.999
francium 87 Fr 223.024	iron 26 Fe 55.845	chlorine 17 Cl 35.453	oxygen 10 O 16.999
lanthanide series	nickel 27 Ni 58.697	nickel 27 Ni 58.697	oxygen 10 O 16.999
actinide series	cobalt 28 Co 58.937	copper 29 Cu 63.546	oxygen 10 O 16.999
actinide series	zinc 30 Zn 65.409	zinc 30 Zn 65.409	oxygen 10 O 16.999
actinide series	gallium 31 Ga 69.721	gallium 31 Ga 69.721	oxygen 10 O 16.999
actinide series	germanium 32 Ge 72.611	germanium 32 Ge 72.611	oxygen 10 O 16.999
actinide series	arsenic 33 As 74.961	arsenic 33 As 74.961	oxygen 10 O 16.999
actinide series	sele-nium 34 Se 78.961	sele-nium 34 Se 78.961	oxygen 10 O 16.999
actinide series	bronze 35 Br 80.947	bronze 35 Br 80.947	oxygen 10 O 16.999
actinide series	krone 36 Kr 83.900	krone 36 Kr 83.900	oxygen 10 O 16.999
lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.92	oxygen 10 O 16.999
actinide series	europium 63 Eu 152.94	europium 63 Eu 152.94	oxygen 10 O 16.999
actinide series	thorium 90 Th 232.04	thorium 90 Th 232.04	oxygen 10 O 16.999

↑ Chromium

K: 5989 eV $\text{K}\alpha_1$ (K-L3): 5415 eV
L₁: 696 eV $\text{K}\alpha_2$ (K-L2): 5405 eV
L₂: 584 eV $\text{K}\beta_{1,3}$ (K-M3/M2): 5947 eV
L₃: 574 eV $\text{K}\beta_5$ (K-M4,5): 5987 eV

K- or L-edges measured at a soft-X-ray beamline

K-edges measured at a hard-X-ray beamline

L-edges measured at a hard-X-ray beamline

Elements and Beamlines

hydrogen 1 H 1.0079	beryllium 3 Li 6.941	boron 5 B 10.811	helium 2 He 1.0083
lithium 3 Li 6.941	beryllium 4 Be 9.0122	carbon 6 C 12.011	nitrogen 7 N 14.0071
sodium 11 Na 22.990	magnesium 12 Mg 24.305	phosphorus 13 P 30.9731	oxygen 8 O 15.999
potassium 19 K 39.098	calcium 20 Ca 40.078	sulfur 14 S 32.065	fluorine 9 F 18.998
rubidium 37 Rb 85.468	strontium 21 Sc 44.966	chlorine 15 Cl 35.453	neon 10 Ne 20.180
cesium 55 Cs 132.91	titanium 22 Ti 47.867	manganese 25 Cr 54.938	argon 18 Ar 36.947
francium 87 Fr 223.02	vanadium 23 V 50.942	iron 26 Fe 55.845	silicon 14 Si 28.086
* Lanthanide series		nickel 27 Co 58.937	phosphorus 15 P 30.9731
** Actinide series		cobalt 28 Ni 58.693	oxygen 8 O 15.999
* Lanthanide series		copper 29 Cu 63.546	fluorine 9 F 18.998
** Actinide series		zinc 30 Zn 65.409	neon 10 Ne 20.180
* Lanthanide series		gallium 31 Ga 69.721	silicon 14 Si 28.086
** Actinide series		germanium 32 Ge 71.997	phosphorus 15 P 30.9731
* Lanthanide series		arsenic 33 As 74.933	oxygen 8 O 15.999
** Actinide series		sele-nium 34 Se 78.96	fluorine 9 F 18.998
* Lanthanide series		bronze 35 Br 79.947	silicon 14 Si 28.086
** Actinide series		krone 36 Kr 83.813	phosphorus 15 P 30.9731

↑ Manganese

- K: 6539 eV $\text{K}\alpha_1$ (K-L3): 5900 eV
 L₁: 769 eV $\text{K}\alpha_2$ (K-L2): 5889 eV
 L₂: 650 eV $\text{K}\beta_{1,3}$ (K-M3/M2): 6492 eV
 L₃: 639 eV $\text{K}\beta_5$ (K-M4,5): 6537 eV

K- or L-edges measured at a soft-X-ray beamline

K-edges measured at a hard-X-ray beamline

L-edges measured at a hard-X-ray beamline

Elements and Beamlines

hydrogen 1 H 1.0079	beryllium 3 Li 6.941	boron 5 B 10.811	helium 2 He 1.003
lithium 3 Li 6.941	beryllium 4 Be 9.0122	carbon 6 C 12.011	nitrogen 7 N 14.007
sodium 11 Na 22.990	magnesium 12 Mg 24.305	nitrogen 7 N 14.007	oxygen 8 O 15.999
potassium 19 K 39.098	aluminum 13 Al 26.982	oxygen 8 O 15.999	fluorine 9 F 18.998
calcium 20 Ca 40.078	silicon 14 Si 28.086	phosphorus 15 P 30.974	neon 10 Ne 20.180
rubidium 37 Rb 85.468	phosphorus 15 P 30.974	phosphorus 15 P 30.974	argon 18 Ar 36.961
strontium 21 Sc 44.960	chromium 22 Ti 47.867	silicon 14 Si 28.086	hydrogen 1 H 1.003
barium 56 Ba 137.35	vanadium 23 V 50.942	silicon 14 Si 28.086	helium 2 He 1.003
cesium 55 Cs 132.91	chromium 24 Cr 51.961	chromium 25 Mn 54.938	hydrogen 1 H 1.003
lanthanum 57 La 138.91	nickel 26 Fe 55.845	nickel 27 Co 58.933	hydrogen 1 H 1.003
cerium 58 Ce 140.91	nickel 28 Ni 58.693	nickel 29 Cu 63.934	hydrogen 1 H 1.003
praseodymium 59 Pr 144.91	nickel 30 Zn 65.390	nickel 31 Ga 69.713	hydrogen 1 H 1.003
neodymium 60 Nd 144.24	nickel 32 Ge 71.023	nickel 33 As 74.032	hydrogen 1 H 1.003
promethium 61 Pm 147.94	nickel 34 Br 77.905	nickel 35 Br 79.905	hydrogen 1 H 1.003
samarium 62 Sm 151.90	nickel 36 Kr 84.770	nickel 36 Kr 84.770	hydrogen 1 H 1.003
europium 63 Eu 151.96	nickel 37 Cd 112.47	nickel 37 Cd 112.47	hydrogen 1 H 1.003
gadolinium 64 Gd 157.93	nickel 38 In 115.82	nickel 38 In 115.82	hydrogen 1 H 1.003
thulium 65 Tb 158.93	nickel 39 Sn 119.71	nickel 39 Sn 119.71	hydrogen 1 H 1.003
dysprosium 66 Dy 162.50	nickel 40 Sb 121.26	nickel 40 Sb 121.26	hydrogen 1 H 1.003
holmium 67 Ho 164.93	nickel 41 Te 127.40	nickel 41 Te 127.40	hydrogen 1 H 1.003
erbium 68 Er 167.26	nickel 42 Po 128.90	nickel 42 Po 128.90	hydrogen 1 H 1.003
thulium 69 Tm 173.05	nickel 43 At 129.22	nickel 43 At 129.22	hydrogen 1 H 1.003
ytterbium 70 Yb 173.04	nickel 44 Rn 132.29	nickel 44 Rn 132.29	hydrogen 1 H 1.003
lanthanide series	lanthanide series	lanthanide series	lanthanide series
actinium series	actinium series	actinium series	actinium series

* Lanthanide series

** Actinide series

lanthanum 57 La 138.91	cerium 58 Ce 140.91	praseodymium 59 Pr 144.91	neodymium 60 Nd 144.24	promethium 61 Pm 147.94	samarium 62 Sm 151.90	europium 63 Eu 151.96	gadolinium 64 Gd 157.93	thulium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 173.05	ytterbium 70 Yb 173.04
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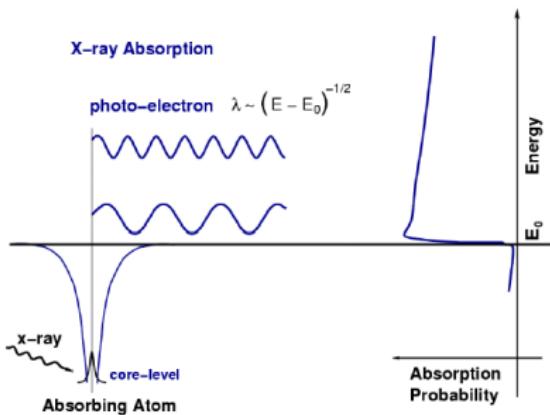
K- or L-edges measured
 K-edges measured
 L-edges measured

← Uranium

- K: 115606 eV La_1 (L3-M5), 13614 eV
 L₁: 21757 eV La_2 (L3-M4), 13438 eV
 L₂: 20948 eV $\text{L}\beta_2$ (L3-N4,5), 16388 eV
 L₃: 17166 eV $\text{L}\beta_5$ (L3-O4,5), 17063 eV
 L₆ (L3-N1): 15727 eV
 L_ℓ (L3-M1): 11618 eV

A simple picture of X-ray absorption

An incident x-ray of energy E is absorbed, destroying a core electron of binding energy E_0 and emitting a photo-electron with kinetic energy $(E - E_0)$. The core state is eventually filled, ejecting a fluorescent x-ray or an Auger electron.



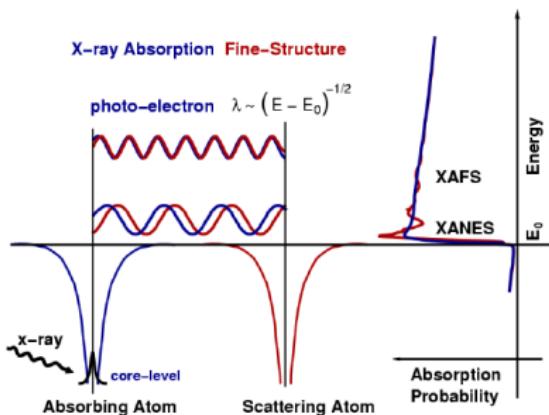
An empty final state is required.
**No available state,
no absorption!**

When the incident x-ray energy is larger than the binding energy, there is a sharp increase in absorption.

For an isolated atom, $\mu(E)$ has a sharp step at the core-level binding energy and is a smooth function of energy above the edge.

X-ray absorption in condensed matter

The ejected photo-electron can scatter from neighboring atoms. R has some relationship to λ and there is a phase shift associated with the scattering event. Thus the outgoing and scattered waves interfere.

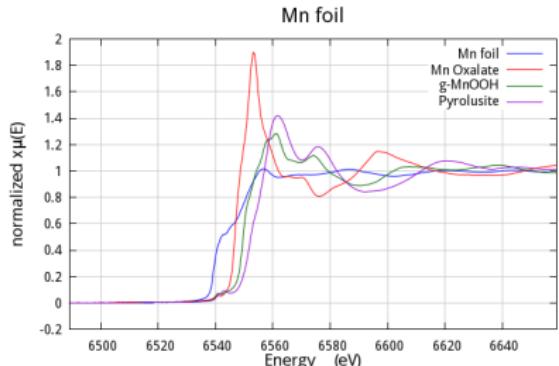


The scattering of the photo-electron wave function interferes with itself.

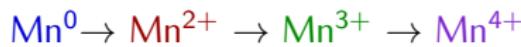
$\mu(E)$ depends on the density of states with energy $(E - E_0)$ at the absorbing atom.

This interference **at the absorbing atom** will vary with energy, causing the oscillations in $\mu(E)$.

XAS and Valence State



As the valence increases

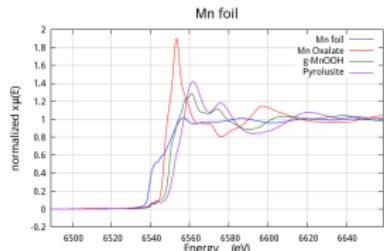


the edge position shifts to higher energy.

XAS is a direct measure of valence state

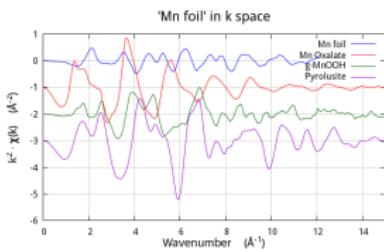
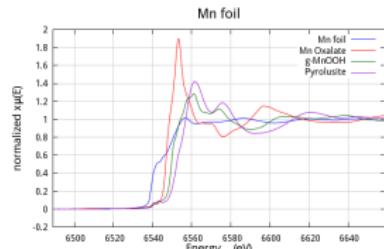
- Since each element has its own edge energy, an element's valence can be measured even in a heterogeneous sample
- Since x-rays are deeply penetrating into matter, samples often require only preparation
- No assumption of symmetry or periodicity is made, so the sample can be crystalline, amorphous, thin film, in solution, surface sorbed, . . . , whatever

XAS and Local Atomic Structure



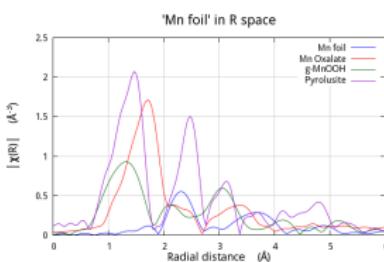
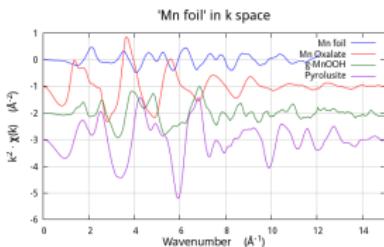
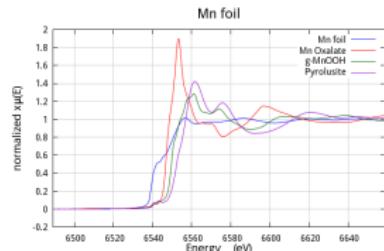
- The different Mn species display big differences in the fine structure beyond the edge as the valence increases (Mn^0 , Mn^{2+} , Mn^{3+} , Mn^{4+}). The white line and subsequent oscillations are quite different.
- The oscillatory portion of the spectrum can be isolated and ...
- ... Fourier transformed. This FT function can be interpreted to yield partial pair distribution functions of atoms about the absorber. The Mn-O distances are different for the Mn^{2+} , Mn^{3+} , and Mn^{4+} and clearly different from the Mn-Mn distance in Mn metal.

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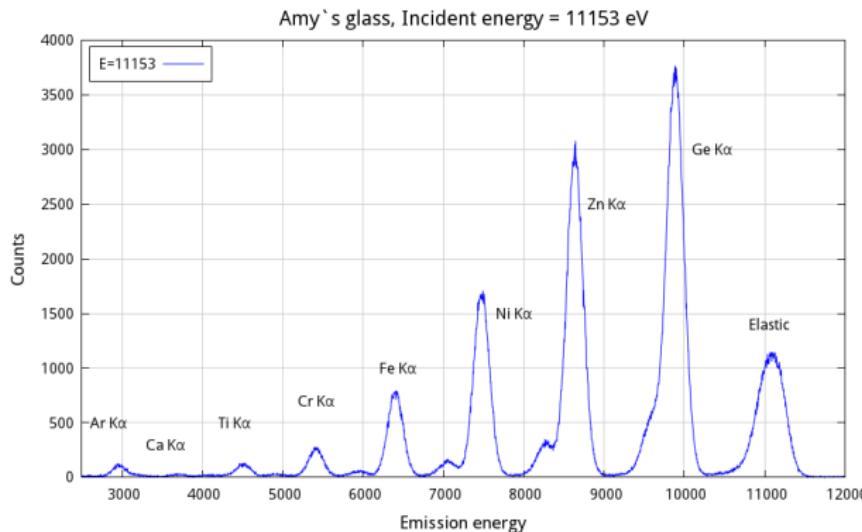
- ... Fourier transformed. This FT function can be interpreted to yield partial pair distribution functions of atoms about the absorber. The Mn-O distances are different for the Mn^{2+} , Mn^{3+} , and Mn^{4+} and clearly different from the Mn-Mn distance in Mn metal.

Fluorescence from Many Elements

X-ray fluorescence is a **spectroscopy** in which the incident energy is fixed and the energy dependence of the secondary photons is measured.

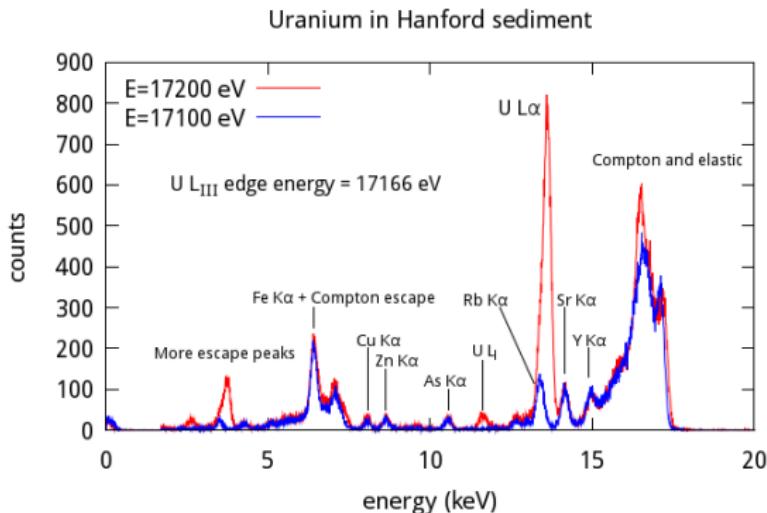
Every element with an edge **below** the incident energy will fluoresce.

Glass with every 2nd element Ca–Ge, incident energy = 11153 eV



Fluorescence from A Sediment Sample

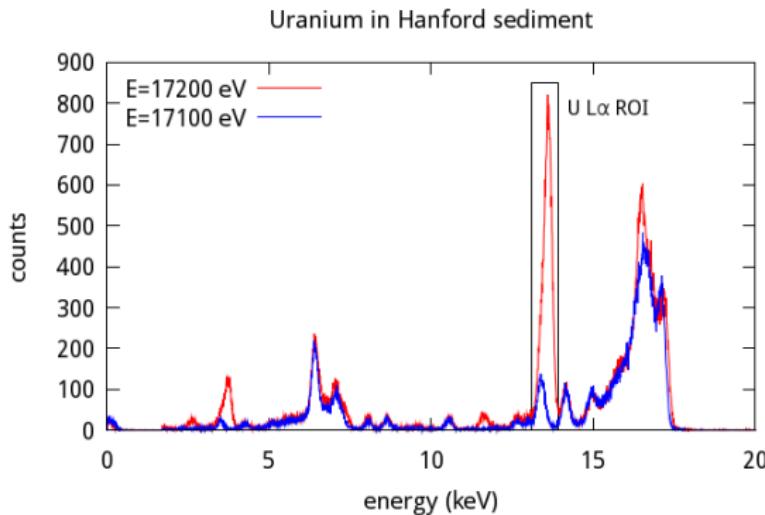
Here are the XRF spectra with incident beams **above** and **below** the U L_{III} edge for a sediment heavily contaminated with uranium.



When combined with a standard measured under identical conditions, element concentrations can be *quantified*.

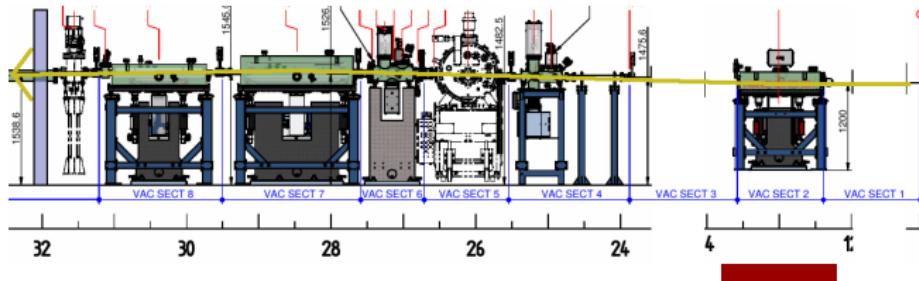
Using the Fluorescence Spectrum for XAS

We can place a **region of interest** (ROI) around the U L α peak and measure its variation as a function of incident energy.



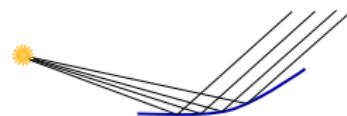
In this way, we measure signal only from the absorber and reject all other photons entering the detector.

Typical optics for an XAS beamline

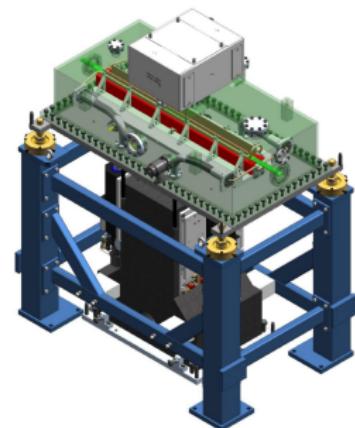


Collimating mirror

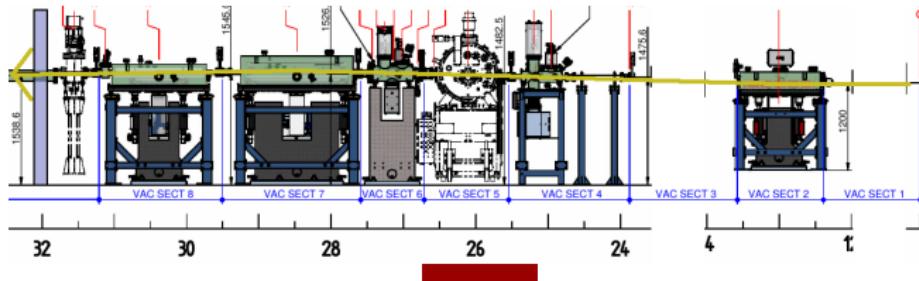
Makes the divergent rays from the source parallel, setting the beam size (8 mm × 1 mm at BMM)



Total external reflection from a paraboloid surface

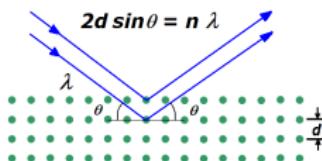


Typical optics for an XAS beamline

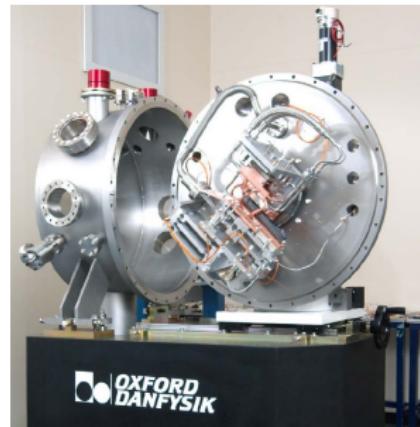


Monochromator

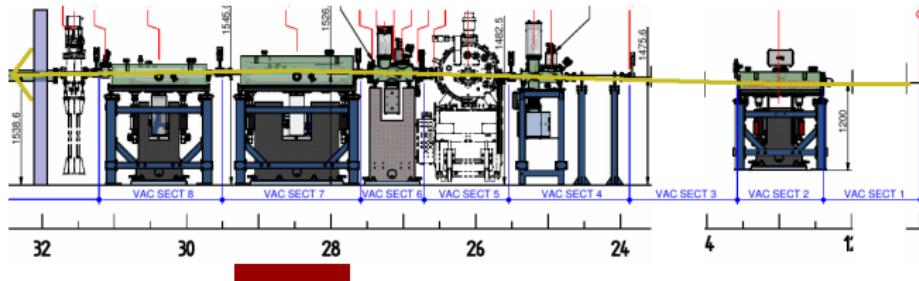
Bragg diffraction from a Si crystal to pass a narrow bandwidth from the pink beam



Change energy by changing angle

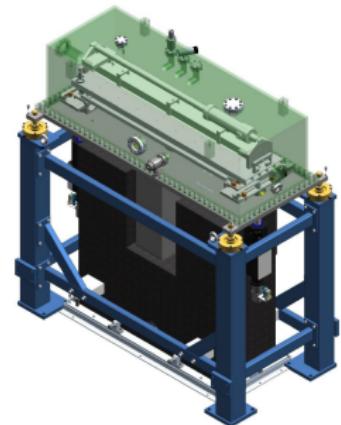


Typical optics for an XAS beamline



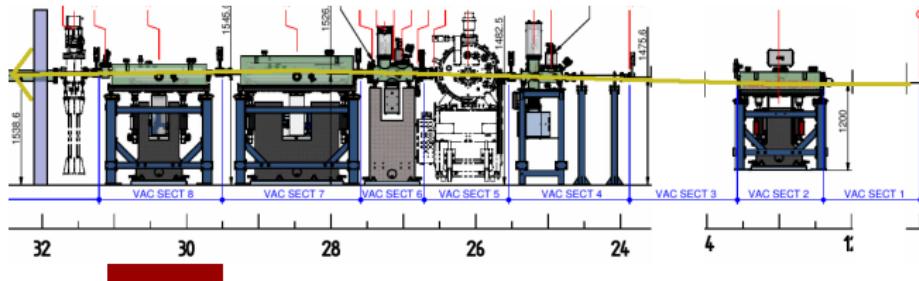
Focusing mirror

Total external reflection from a torroid surface, bent such that rays focus to a spot



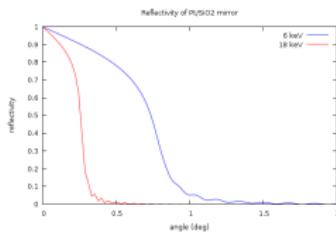
All instrumentation images are from FMB Oxford Beamlines Ltd.
Photo of mirror is from ESRF ID09B

Typical optics for an XAS beamline

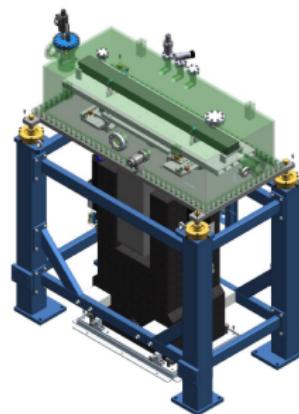


Harmonic rejection mirror

Flat mirror redirects beam from mono and M2

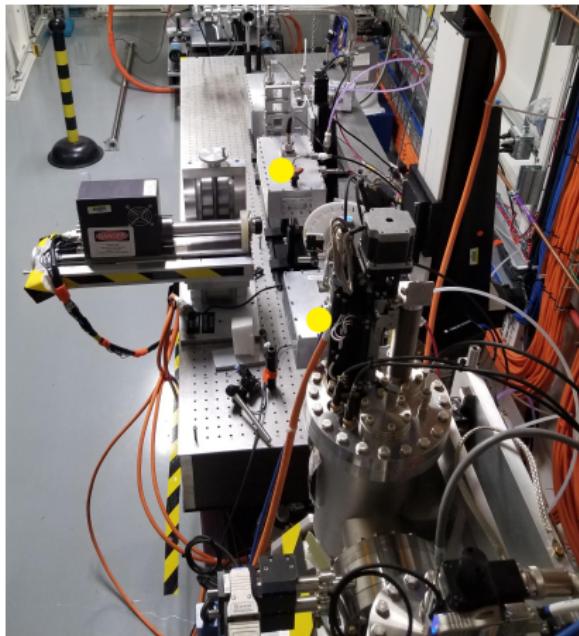


Choose an angle to pass the fundamental but absorb harmonics

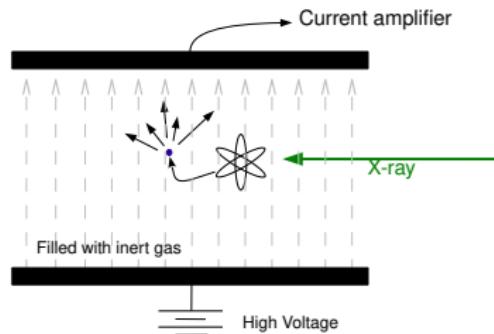


All instrumentation images are from FMB Oxford Beamlines Ltd.

A typical XAS hutch (BMM at NSLS-II)



Ionization chambers



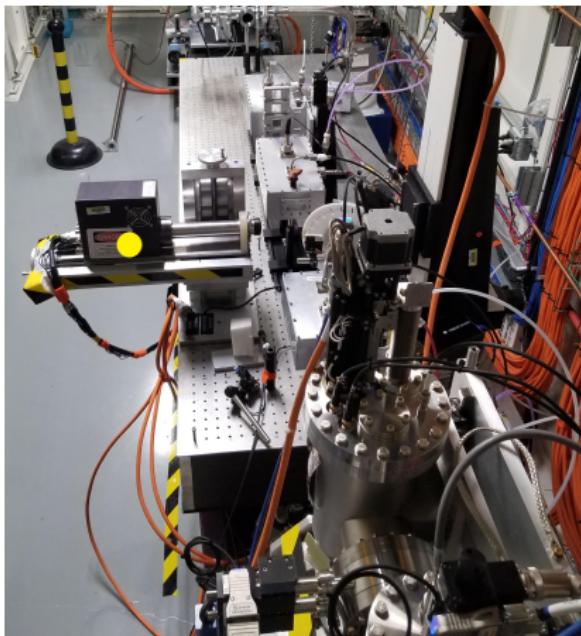
Gas-filled capacitors. Incoming photon ionizes a gas molecule. The electron cascade produces a measurable current.

Transmission XAS

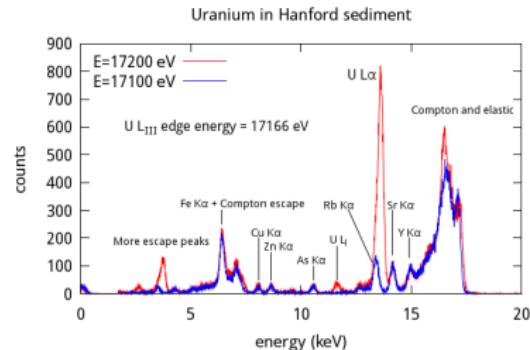
$$\mu(E) = \ln(I_0/I_t)$$

i.e. Beers' Law for X-rays

A typical XAS hutch (BMM at NSLS-II)



Energy discriminating fluorescence detector

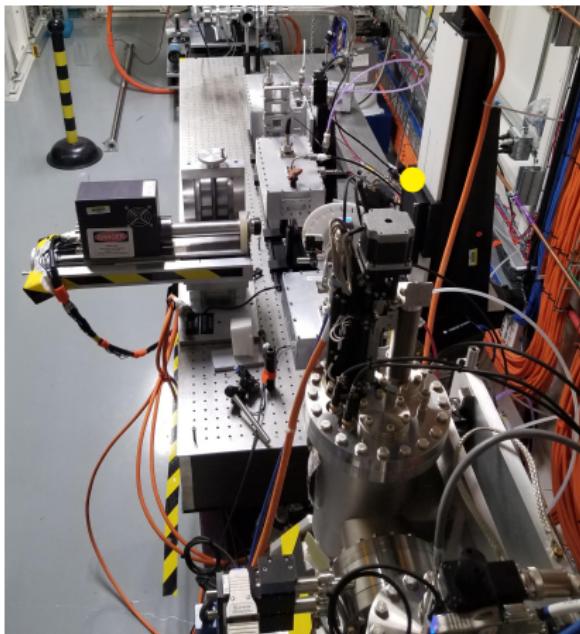


Silicon drift diode measures energy of each photon deposited

Fluorescence XAS

$$\mu(E) \propto I_f / I_0$$

A typical XAS hutch (BMM at NSLS-II)



Sample stage

Hard X-rays are deeply penetrating into matter, so the stage could be:

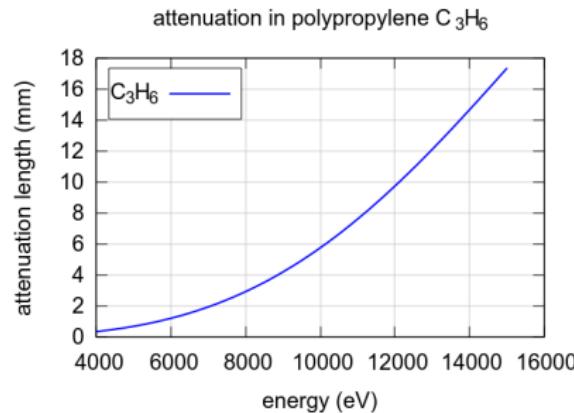
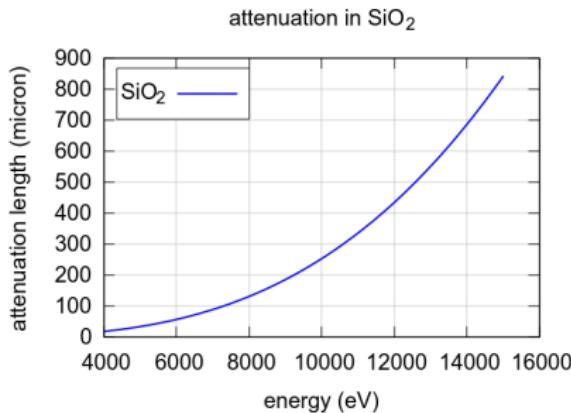
- Cryostat
- Furnace
- Pressure cell
- Electrochemistry cell
- Stop-flow cell
- Gas flow reactor
- Controlled atmosphere

etc. etc. etc.

Real samples under real conditions

What is meant by “deeply penetrating”?

The ↗ [Center for X-ray Optics](#) provides a tool for estimating the attenuation of X-rays as they pass through matter.
↗ http://henke.lbl.gov/optical_constants/atten2.html



So, windows made of low-Z materials can be quite thick and still pass hard X-rays. This allows deployment of specialized sample environments for use in XAS experiments.

Acronyms

XANES X-ray Absorption Near-Edge Structure

NEXAFS Near-Edge X-ray Absorption Fine Structure

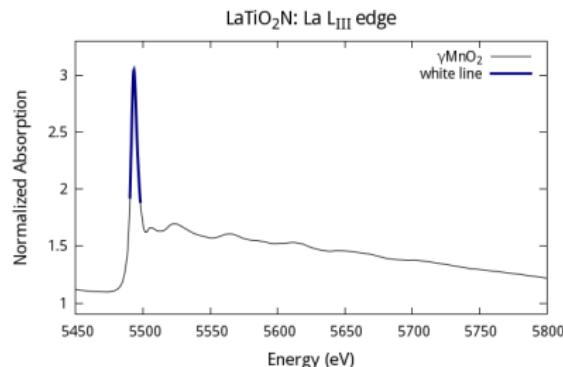
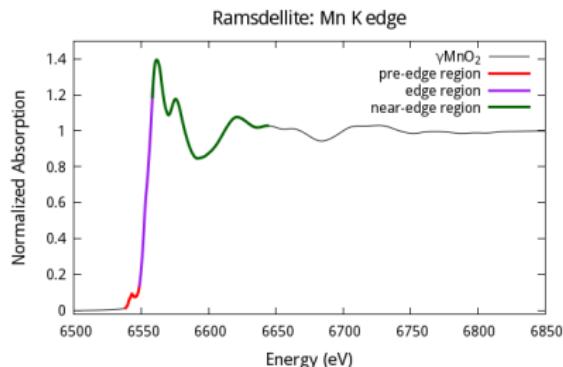
XANES and NEXAFS are exactly the same thing. Historically, the soft X-ray community says “NEXAFS” while the hard X-ray community says “XANES”.

Both acronyms refer to the portion of the XAS (X-ray Absorption Spectroscopy) measurement in the vicinity of the absorption edge.

The Extended X-ray Absorption Fine Structure is oscillatory data extending hundreds of volts above the edge.

Some vocabulary

Words commonly used to describe specific parts of the XANES spectrum.



pre-edge Small (or large, certainly meaningful!) features between the Fermi energy and the threshold

edge The main rising part of XAS spectrum

near-edge Characteristic features above the edge

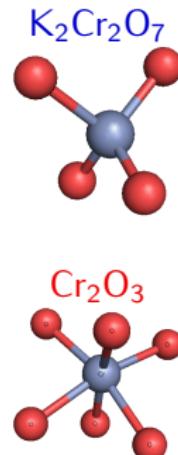
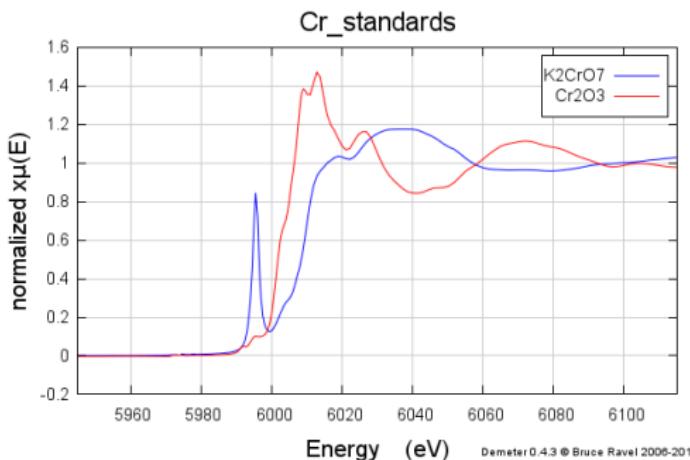
white line Large, prominent peak just above the edge, particularly in L or M edge spectra

Part 2

Understanding XANES

Speciation at a glance: Coordination

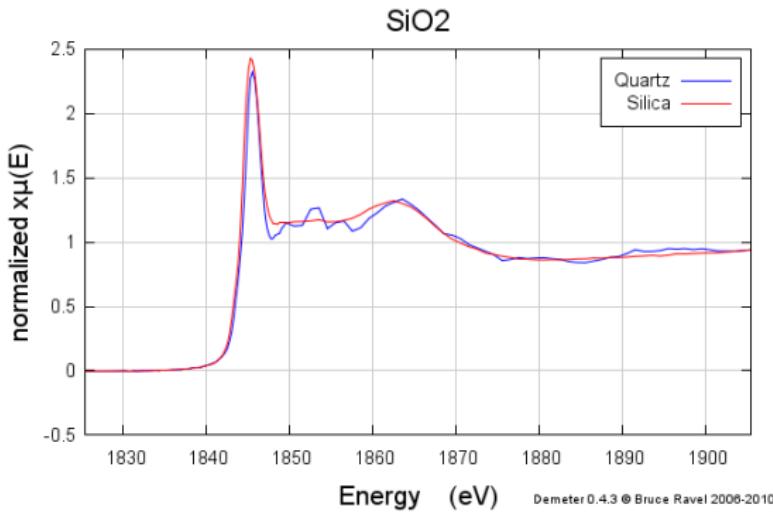
Here is Cr K edge data for tetragonally coordinated, hexavalent $K_2Cr_2O_7$ and hexagonally coordinated, trivalent Cr_2O_3 . Trivalent Cr is insoluble and non-toxic. Hexavalent Cr is readily soluble and highly toxic.



It is very easy to tell "good" Cr from "bad" Cr in a XANES measurement.

Speciation at a glance: Crystallinity

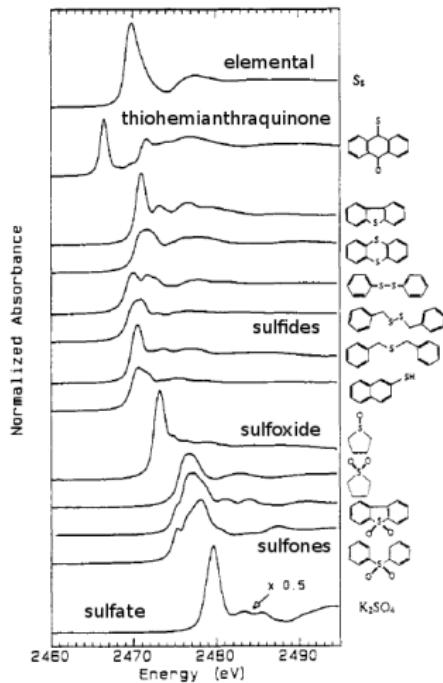
SiO_2 is found in two forms* under standard conditions: **crystalline (the mineral quartz)** and **amorphous (common glass)**.



Again, these are readily distinguished by a XANES measurement.

* Wikipedia identifies 14 other metastable, high-T, or high-P forms of SiO_2 .

Speciation at a glance: Oxidation



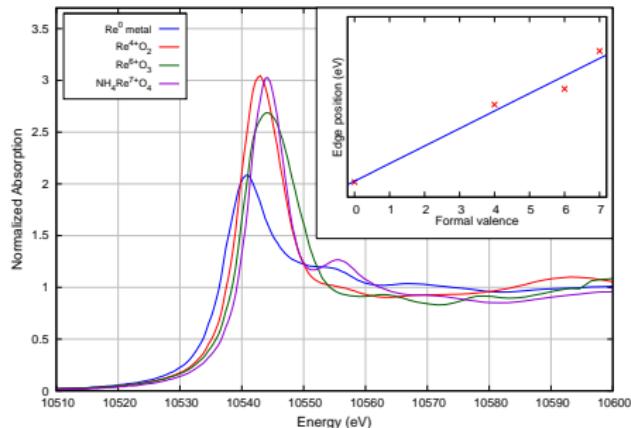
- There is an 11 eV shift from S^{2-} to S^{6+} with lots of variation among species.
- S speciation is of importance across a broad range of disciplines, including life science, catalysis, petroleum science, photovoltaics, environmental science and more.
- P and Cl are similarly rich in their XAS.

Sulfur K-edge x-ray absorption spectroscopy of petroleum asphaltenes and model compounds, G.N. George, M.L. Gorbaty, J. Am. Chem. Soc. (1989) 111:9,
3182 ▲ DOI: 10.1021/ja00191a012

Oxidation and edge position

There is a relationship between formal valence of a metal and the position of the edge in the XANES spectrum. Here is Re metal along with 4+, 6+, and 7+ oxides of Re.

The shift to higher energy is, to first order, a Coulomb effect. Less charge on the atom means less screening of the core.



Some more examples:

Mo S.P. Cramer et al. J. Am. Chem. Soc., **98**:5, pp 1287 (1976)

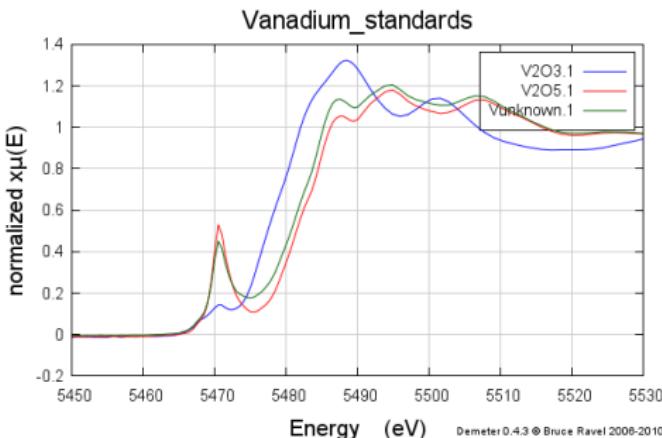
DOI: [10.1021/ja00421a053](https://doi.org/10.1021/ja00421a053)

V J. Wong et al. Phys. Rev. B**30**, 5596–5610 (1984) DOI: [10.1103/PhysRevB.30.5596](https://doi.org/10.1103/PhysRevB.30.5596)

Simultaneous XAFS measurements of multiple samples, B. Ravel, C. Scorzato, D.P. Siddons, S.D. Kelly and S.R. Bare, J. Synchrotron Rad. (2010) 17, 380–385
DOI: [10.1107/S0909049510006230](https://doi.org/10.1107/S0909049510006230)

Mixed phases

Here we see trivalent V_2O_3 , pentavalent V_2O_5 and an unknown Vanadium compound plotted together.



Like in the Cr example, we see a distinct difference between 6-coordinated and 4-coordinated V.

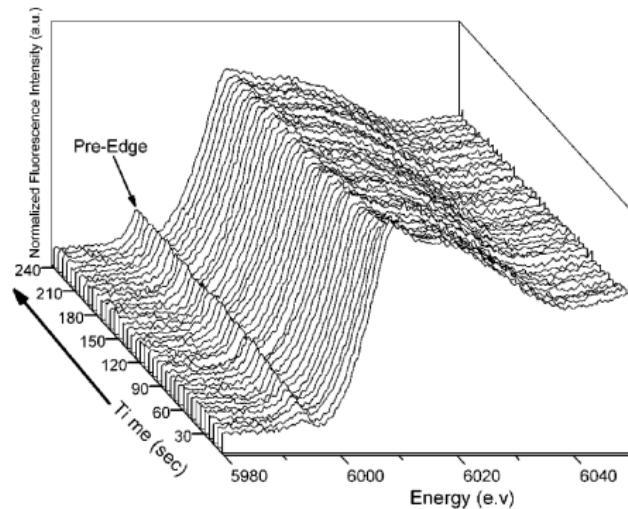
Our unknown is partially reduced, as can be seen by the reduction in pre-edge peak and the left-ward shift of the main edge.

Later we will discuss ways of determining the content of the unknown.

Evolution of redox state

The edge features are often large enough that their evolution can be measured in an *in situ* experiment.

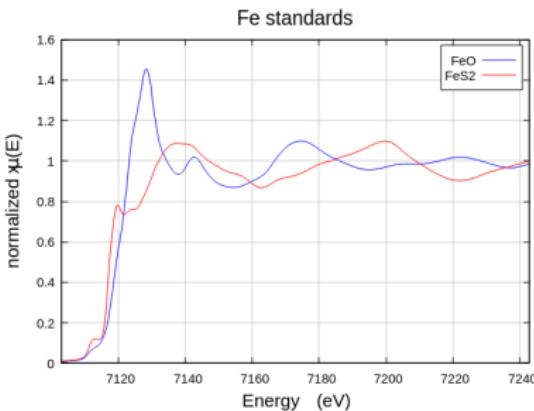
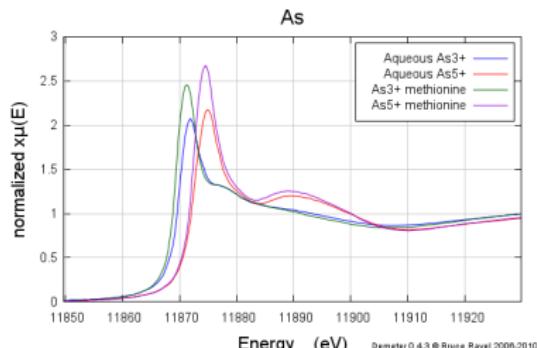
Here we see the kinetics of $\text{Cr}^{III} \rightarrow \text{Cr}^{VI}$ oxidation by Mn oxide over the course of four minutes of reaction time. Each scan was measured in 3 second.



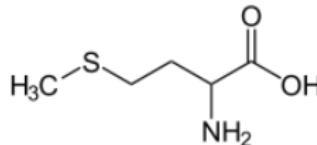
The *in situ* experiment could involve a chemical reaction, a change in temperature, electrochemical cycling, and so on.

Kinetics of Chromium(III) Oxidation by Manganese(IV) Oxides Using Quick Scanning X-ray Absorption Fine Structure Spectroscopy (Q-XAFS), G. Landrot, M. Ginder-Vogel, and D.L. Sparks, Environ. Sci. Technol., (2010) 44:1, pp 143-149
DOI: 10.1021/es901759w

Ligands



We see a significant edge shift between aqueous As³⁺ and aqueous As⁵⁺, as we expect. Note that the As³⁺ and As⁵⁺ methionine solutions are similar, but shifted to lower energy.



The same shift is seen between divalent wüstite (FeO) and divalent pyrite (FeS₂).

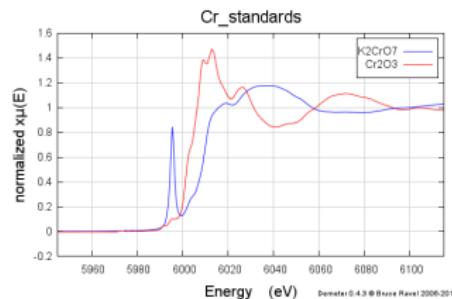
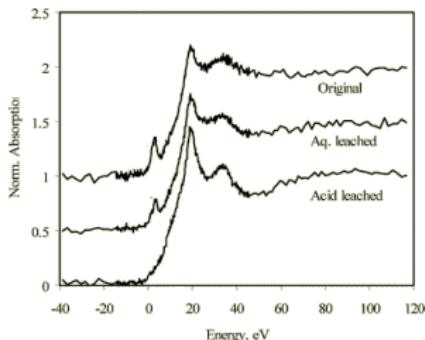
Fingerprinting

Fingerprint, tr.v.

To identify by means of a distinctive mark or characteristic.

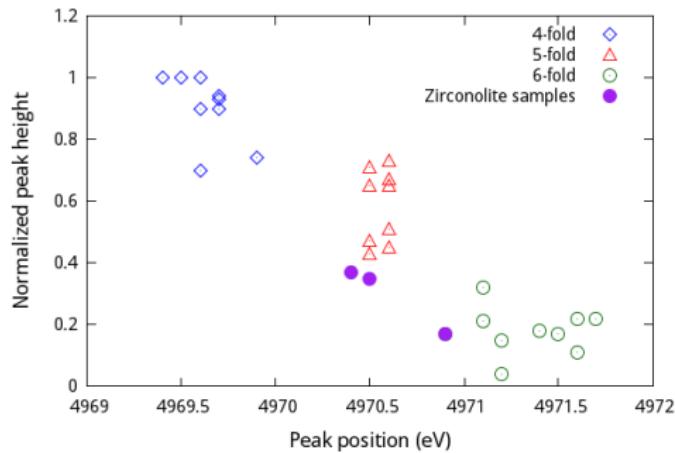
One of the most powerful uses of XANES data is to simply identify what is in front of the beam.

Looking back at the Cr^{III}/Cr^{VI} example, what might you say about the valence of the chromium contained in coal combustion residue?



Categorizing spectra

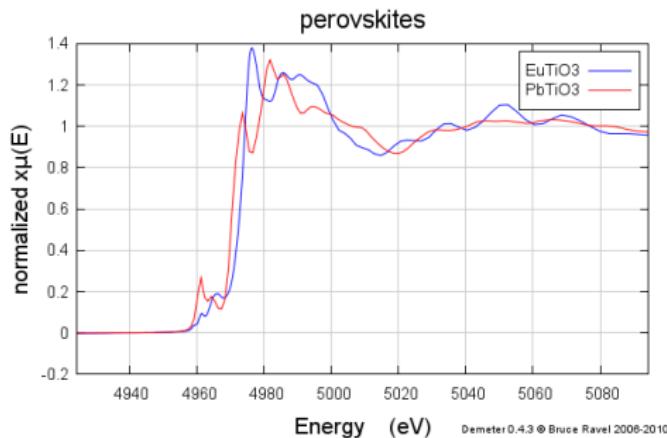
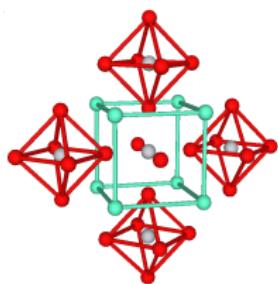
In a study of Ti-containing standard materials, the different coordination environments were found to aggregate when plotting pre-edge peak height v. peak position.



Here we see the data from the reference below along with Ti K-edge data from various Zirconolite ($\text{CaZrTi}_2\text{O}_7$) samples.

XANES and disorder

The details of the XANES can often give information about structural disorder about the absorbing atom.



EuTiO_3 is a true cubic perovskite. PbTiO_3 is a tetragonally distorted perovskite with substantial disorder in the oxygen octahedron. Consequently, the pre-edge peak is much larger for PbTiO_3 .

Why are local disorder and the pre-edge peak related?

- XAS is a dipole transition. The photoelectron changes angular momentum by 1: $\ell \pm 1$.
- For a K-edge spectrum, the initial state is s : $\ell = 0$. Thus the final state must be $\ell = 1$.
- Ti has a filled p shell but a completely empty d shell.
- With centro-symmetry, as in a true perovskite, the p and d states cannot hybridize. Broken symmetry leads to mixing of p and d states around the Fermi level.
- Disorder-driven admixture of d character results in an enhanced pre-edge peak.

Analysis

There are a number of ways to get quantitative results from XANES spectra. Here's an incomplete list:

Linear Combination Fitting

Interpret data by comparison with standards

Peak Fitting

Fit peak-like and step-like line-shapes to the XANES data

Principle Components Analysis

Decompose an ensemble of data into a mathematical basis

Difference Spectra

Subtract one normalized spectrum from another

LCF

The working assumption of LCF

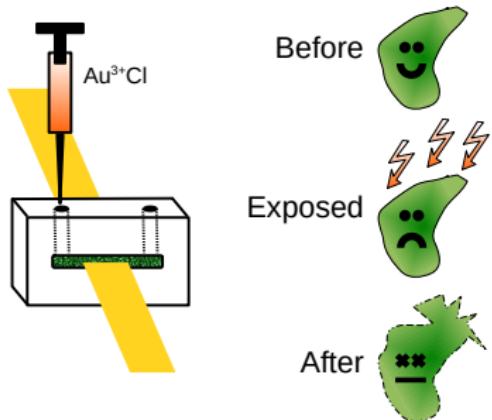
The spectrum from an unknown sample can be understood as a linear superposition of the spectra of two or more known samples.

That is:



Economic geology (I)

One way that gold deposits form is by having Au chloride fluids rise from the deep earth, wash over cyanobacteria colonies, and reduce to metallic gold.



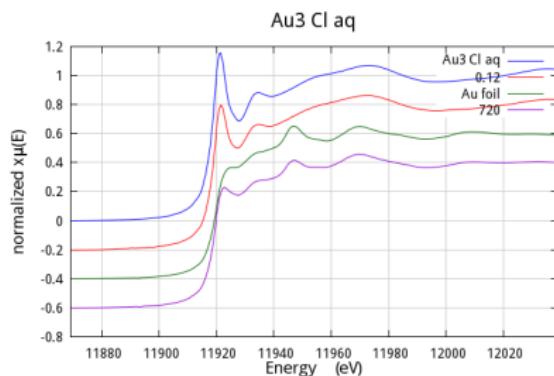
We simulated this process at the beamline by exposing cyanobacteria to an Au^{3+} solution and “watching” the evolution of the Au XAS from Au^{3+} to Au^0 .

Questions

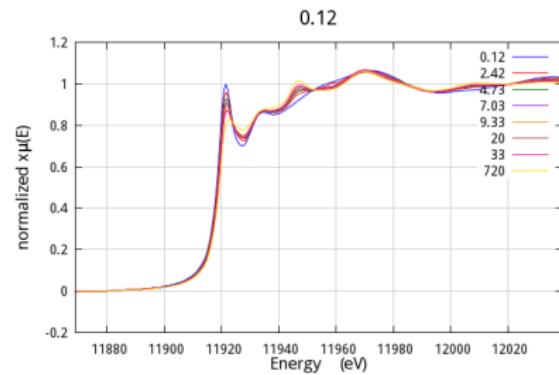
- What is the rate constant?
- Is there an intermediate species?

Economic geology (II)

We see that **7 minutes** after injection, the data strongly resemble the Au^{3+}Cl . After **one week**, the data resemble **Au metal**.

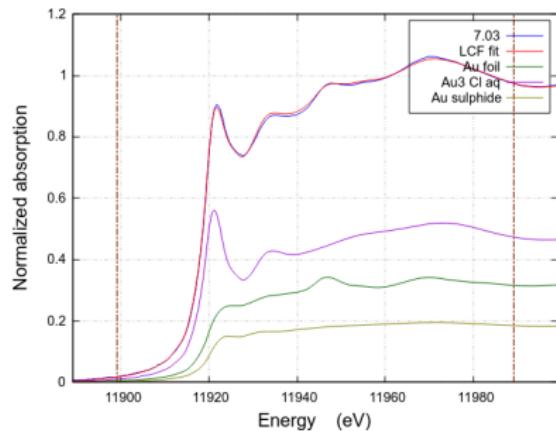


Over the course of the time series, the white line ~ 11921 shrinks while the bump ~ 11945 grows, suggesting the reduction to Au metal.

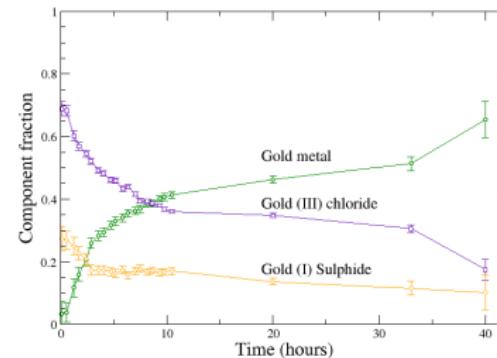


Economic geology (III)

We can analyze these data as a linear combination of species, including Au^{3+}Cl , Au metal, and Au^{1+} sulfide.



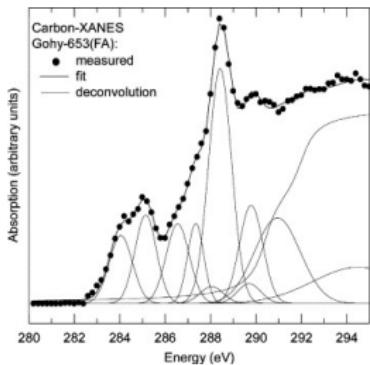
We can plot out the contributions from these species as a function of time to get a sense of reaction rates.



Peak fitting

The working assumption of peak fitting

A spectrum can be meaningfully deconstructed into a set of step-like (atan or erfc) and peak (Gaussian, Lorentzian, Voight) functions.

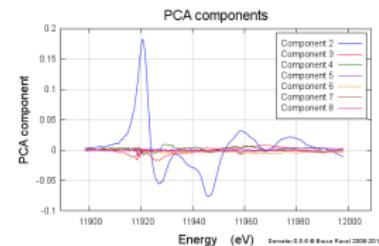
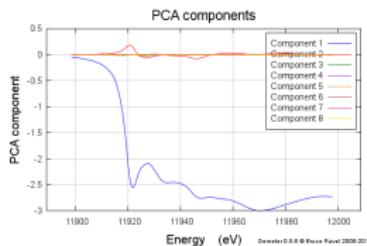
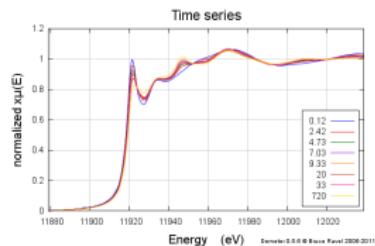


In this case, various Gaussians are interpreted as the main $1s-\pi^*$ or Rydberg/mixed valence transitions and two higher energy ($1s-2\pi^*$) transition in the C K-edge XANES of a sediment.

This sort of analysis is most meaningful when performed across an ensemble of related data. The drawback is that the physical significance of the line-shapes is sketchy, at best.

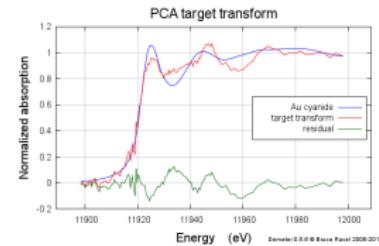
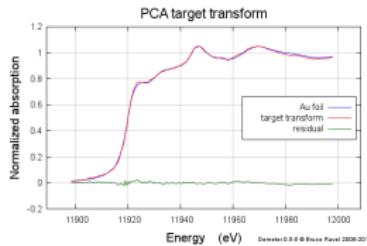
XANES: Principle Components Analysis

PCA is a bit of linear algebra which breaks down an ensemble of related data into abstract components.



The components can then be used to try to construct a standard as a test to see whether that standard is present in the ensemble.

The number of species represented in the ensemble is related to the number of statistically significant components.



S.R. Wasserman, J. Phys. IV France (1997) C2-203-C2-205; [DOI: 10.1051/jp4/1997163](https://doi.org/10.1051/jp4/1997163)

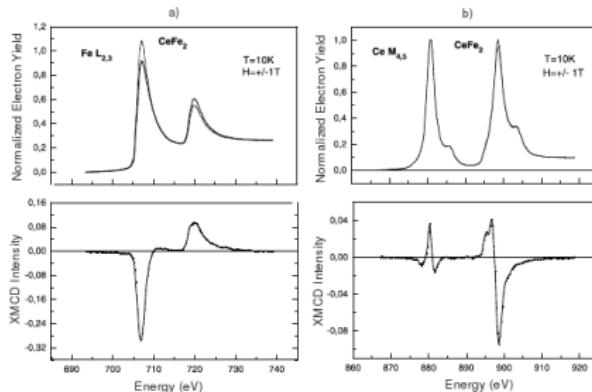
S.R. Wasserman et al., J. Synchrotron Rad. (1999) 6, 284-286; [DOI: 10.1107/S0909049599000965](https://doi.org/10.1107/S0909049599000965)
+ references therein

Difference Spectra

Difference spectra

Subtract one spectrum from another.

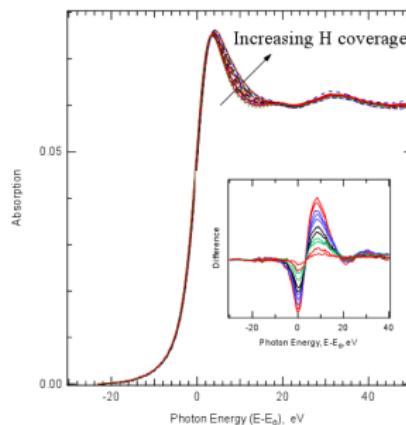
The most common use is for X-ray Magnetic Circular Dichroism (XMCD)



The areas under the difference spectra tell you about moment and magnetic ordering.

X-ray magnetic circular dichroism study on CeFe₂, A. Delobbe, et al., Europhys. Lett. 43 320 (1998), DOI: 10.1209/epl/i1998-00359-2
Pt data courtesy of Simon Bare

Difference spectra can also be used to highlight a subtle change in a data sequence.



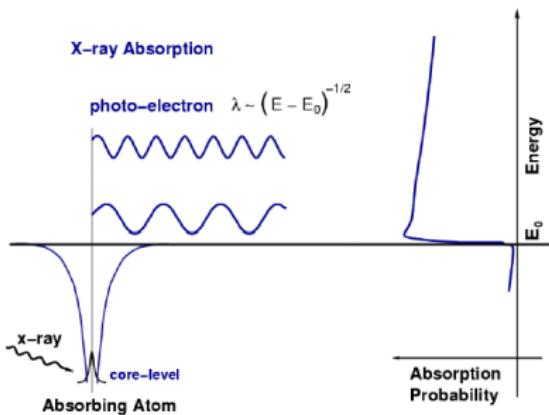
Here, hydrogenation of the Pt nanoparticles alters the Pt DOS

Part 3

Understanding EXAFS

A simple picture of X-ray absorption

An incident x-ray of energy E is absorbed, destroying a core electron of binding energy E_0 and emitting a photo-electron with kinetic energy $(E - E_0)$. The core state is eventually filled, ejecting a fluorescent x-ray or an Auger electron.



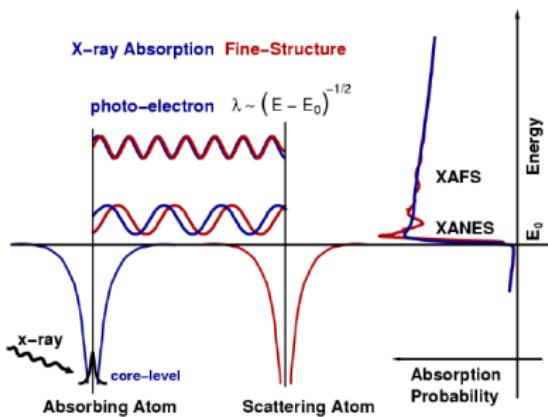
An empty final state is required.
**No available state,
no absorption!**

When the incident x-ray energy is larger than the binding energy, there is a sharp increase in absorption.

For an isolated atom, $\mu(E)$ has a sharp step at the core-level binding energy and is a smooth function of energy above the edge.

X-ray absorption in condensed matter

The ejected photo-electron can scatter from neighboring atoms. R has some relationship to λ and there is a phase shift associated with the scattering event. Thus the outgoing and scattered waves interfere.



The scattering of the photo-electron wave function interferes with itself.

$\mu(E)$ depends on the density of states with energy $(E - E_0)$ at the absorbing atom.

This interference **at the absorbing atom** will vary with energy, causing the oscillations in $\mu(E)$.

The EXAFS equation

For each kind of path, we evaluate the EXAFS equation:

$$\chi(k, \Gamma) = \frac{(N_\Gamma S_0^2) F_\Gamma(k) e^{-2\sigma_\Gamma^2 k^2} e^{-2R_\Gamma/\lambda(k)}}{2 k R_\Gamma^2} \sin(2kR_\Gamma + \Phi_\Gamma(k)) \quad (1)$$

$$\chi_{\text{theory}}(k) = \sum_{\Gamma} \chi(k, \Gamma) \quad (2)$$

$$R_\Gamma = R_{0,\Gamma} + \Delta R_\Gamma \quad (3)$$

$$k = \sqrt{2m_e(E_0 - \Delta E_0)/\hbar^2} \approx \sqrt{(E_0 - \Delta E_0)/3.81} \quad (4)$$

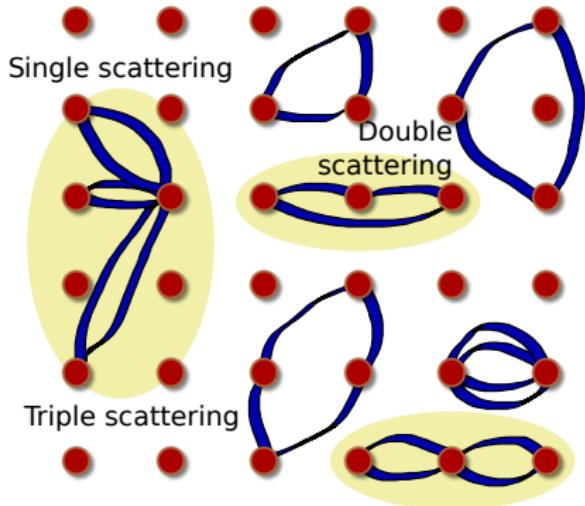
The terms in blue come from theory. (I use a thing called **FEFF**).

FEFF treats SS and MS paths equivalently. F_Γ and ϕ_Γ are the effective scattering amplitude and phase shift for the path.

The strategy of EXAFS analysis

In **FEFFIT** the terms in red are not themselves the fitting parameters. They are written in terms of the actual fitting parameters.

Real space multiple scattering in pictures



Here are some examples (in two dimensions) of single, double, and triple scattering paths.

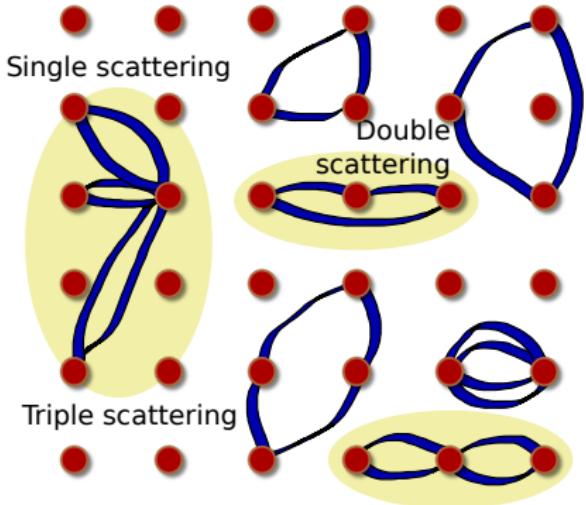
For SS, FEFF computes the three SS paths shown and all others (up to some maximum length).

SS and *collinear* MS paths tend to be the dominant contributions to the EXAFS.

The trick to EXAFS analysis

Somehow evaluate each path and choose which ones to include in a fit.

Real space multiple scattering in pictures



Here are some examples (in two dimensions) of single, double, and triple scattering paths.

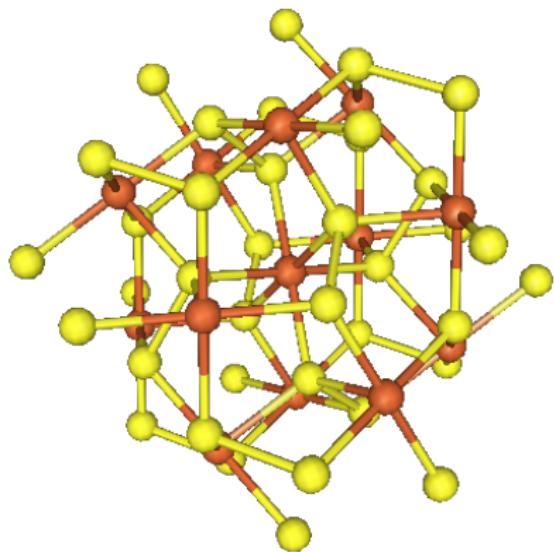
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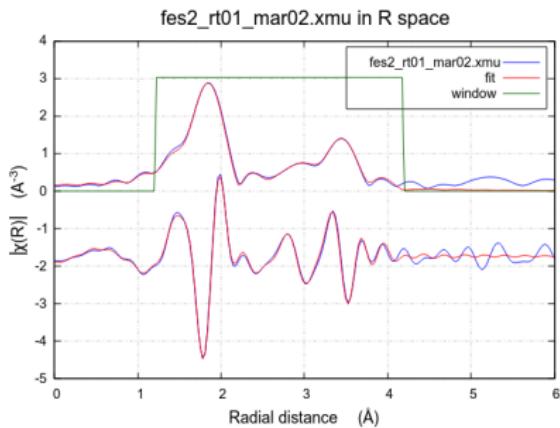
FeS₂ structure



Somehow add up the contributions from each of the scatterers **and** from all the MS paths involving those scatterers.

The **Fe atom** is surrounded by an octahedron of **S atoms**

- 6 **S nearest neighbors** at 2.257 Å
- 6 **S next nearest neighbors** at 3.445 Å
- 2 **S scatterers** at 3.594 Å
- 12 **Fe scatterers** at 4.167 Å



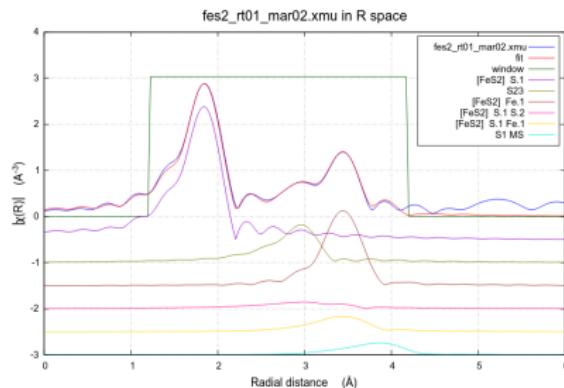
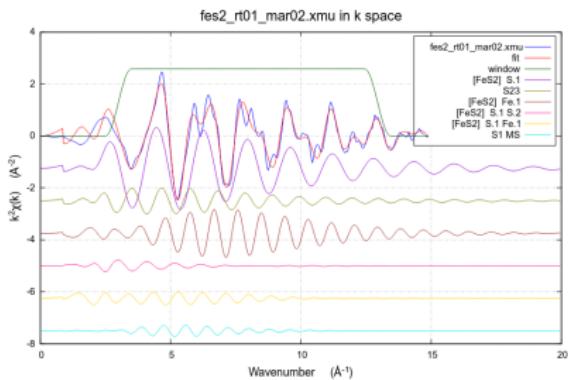
Path expansion

$$\chi(k, \Gamma) = \frac{(N_r S_0^2) F_\Gamma(k) e^{-2\sigma_\Gamma^2 k^2} e^{-2R_\Gamma/\lambda(k)}}{2 k R_\Gamma^2} \sin(2kR_\Gamma + \Phi_\Gamma(k)) \quad (1)$$

$$\chi_{\text{theory}}(k) = \sum_{\Gamma} \chi(k, \Gamma) \quad (2)$$

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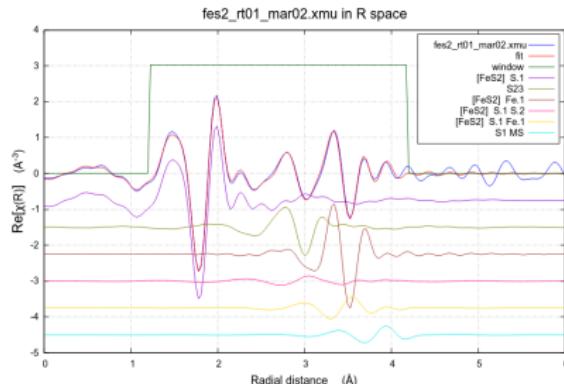
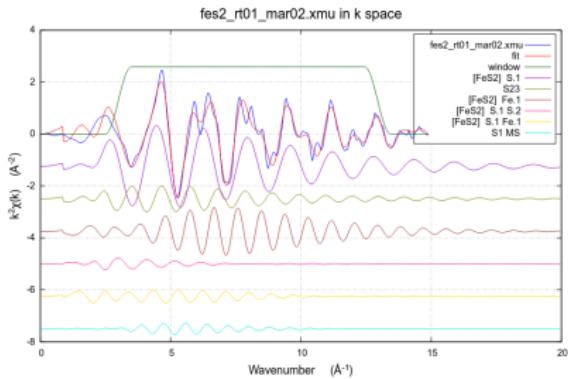
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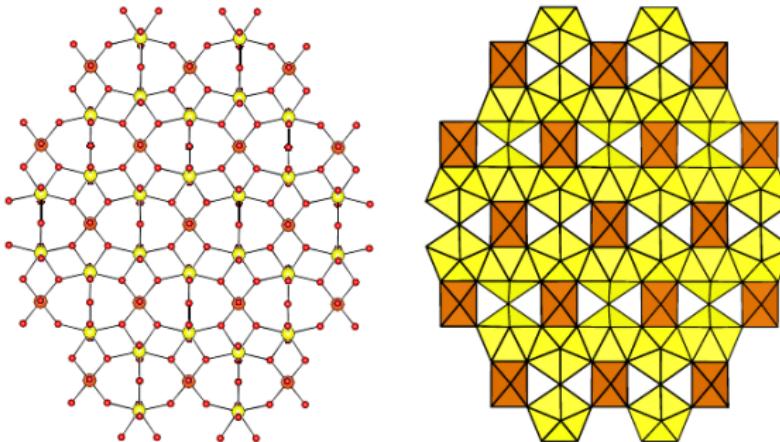
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$$k = \sqrt{2m_e(E_0 - \Delta E_0)/\hbar^2} \approx \sqrt{(E_0 - \Delta E_0)/3.81} \quad (4)$$



Minerology (I)

A deep understanding of the nuclear fuel cycle requires study of “exotic” pentavalent uranium minerals that can form under specific mine or storage facility conditions. One such mineral, $\text{U}^{\text{V}}(\text{H}_2\text{O})_2(\text{U}^{\text{VI}}\text{O}_2)_2\text{O}_4(\text{OH}) + 4 \cdot \text{H}_2\text{O}$, has recently been synthesized.



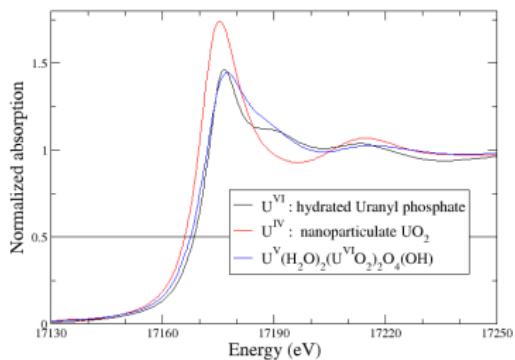
XRD is an indirect measure of valence — XAS is a direct measure!

N. Belai et al., *Pentavalent Uranium Oxide via Reduction of $[\text{UO}_2]^{2+}$ Under Hydrothermal Reaction Conditions*, Inorg. Chem., 2008, 47 (21), pp 10135–10140, DOI: 10.1021/ic801534m

Minerology (II)



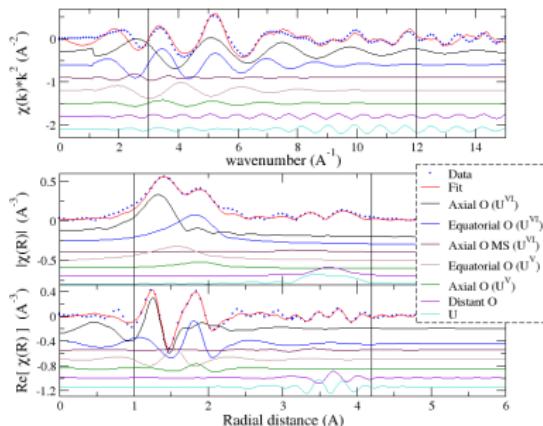
XANES data



We see evidence of U^{V} by the intermediate edge position between our U^{IV} and U^{VI} standards.

N. Belai et al., *Pentavalent Uranium Oxide via Reduction of $[\text{UO}_2]^{2+}$ Under Hydrothermal Reaction Conditions*, Inorg. Chem., 2008, 47 (21), pp 10135–10140, DOI: 10.1021/ic801534m

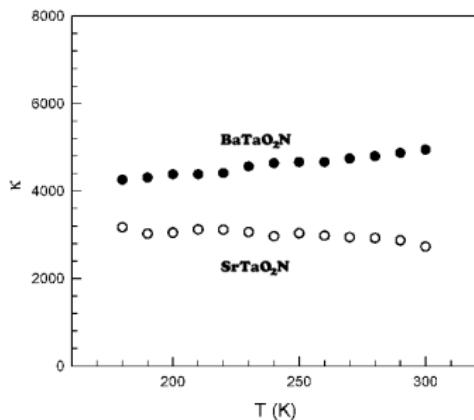
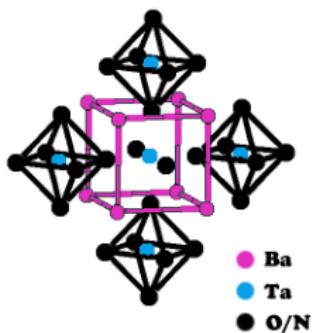
EXAFS analysis



The crystal structure refined from the XRD is consistent with the EXAFS data.

Dielectric materials (I)

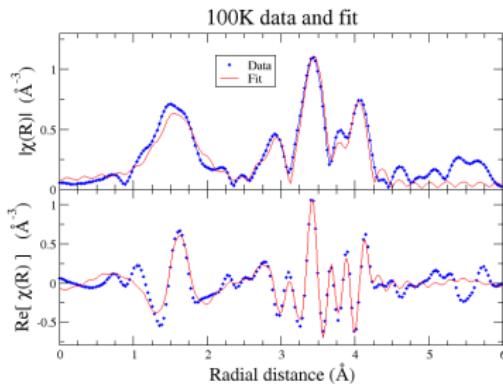
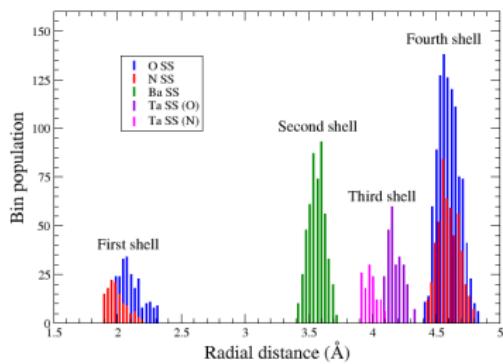
Tantalum oxynitrides are a class of dielectric materials with high K which is tunable by selection of the A cation. By mixing A cations, a temperature-constant dielectric is possible.



First principles DFT on BaTaO_2N suggests that the different ionic radii of O and N introduce substantial disorder around the Ta atom.

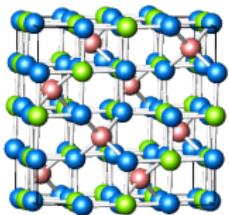
Dielectric materials (II)

The DFT results in a rather complex coordination environment about the Ta atom — much more complex than the simple perovskite structure.

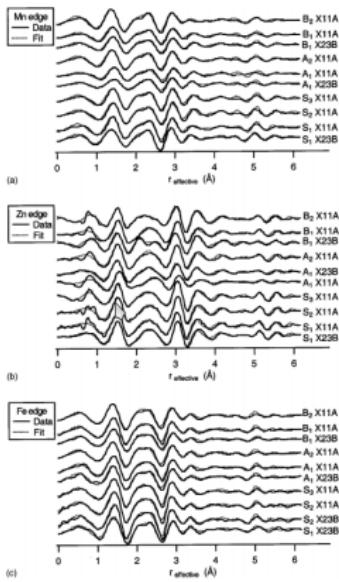


With some effort, this complexity can be incorporated into the data analysis. The EXAFS data are shown to be (mostly) consistent with the DFT results.

EXAFS analysis can be quite elaborate...



Oxygen
Octahedral site
Tetrahedral site



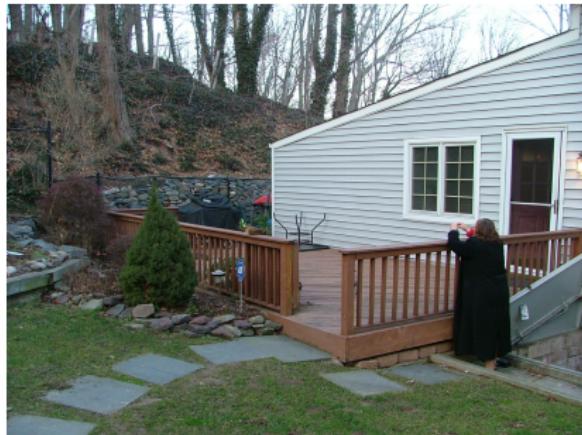
- Manganese zinc ferrite nanoparticles
- Each element can occupy each either metal site
- Oxygen vacancies can exist
- Data collected at 3 edges and on various sample preparations
- A fitting model was created using all the data simultaneously and considering occupancies of each metal on each site, oxygen vacancy, and nanoparticle undercoordination

Part 4

A real-world example

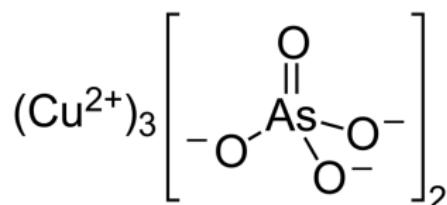
My vegetable garden

When I bought my house, there was a wooden deck off the dining room. I replaced this with a paving stone patio and converted the adjacent plot of ground into a vegetable garden.



Wood preservative

The wood used to make the deck was treated with the wood preservative chromated copper arsenate (CCA), which is chromium-bearing analogue of copper orthoarsenate, $\text{Cu}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$.

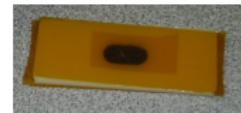


CCA-treated wood is known to leach all three elements into surrounding soils. I had some questions:

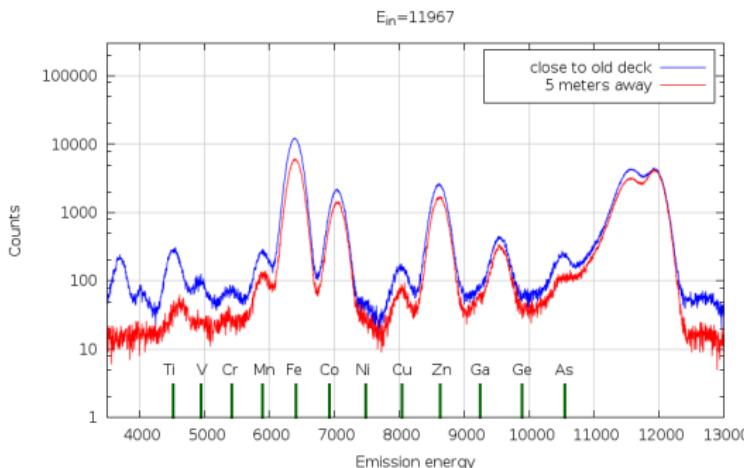
- ① How much As is in the soil? Is it higher near the patio than elsewhere in the garden? (Use XRF)
- ② What chemical species is the As in the soil? (Use XAS)

XRF spectra

I took soil samples from a few centimeters below the surface from a spot adjacent to the old deck and from a spot 5 meters away and slightly uphill.



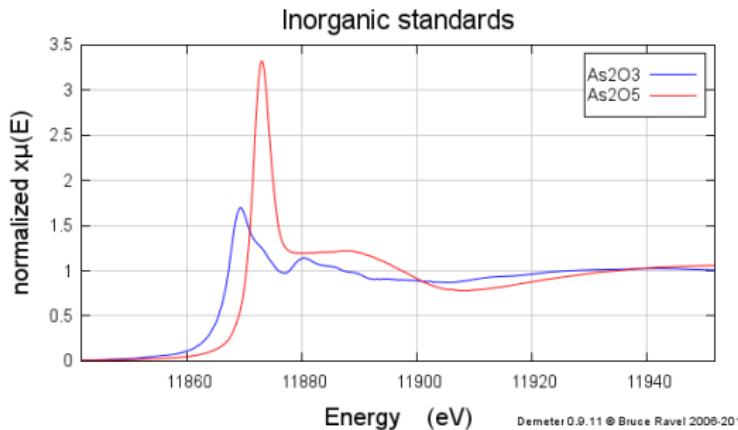
Here are the XRF spectra from those two spots:



There is a clear enhancement of both As and Cr in the soil adjacent to the old deck. The As is enhanced roughly two-fold.

As standards

As a point of reference, here are the XAS spectra from two inorganic As standards, $\text{As}_2^{3+}\text{O}_3$ and $\text{As}_2^{5+}\text{O}_5$.



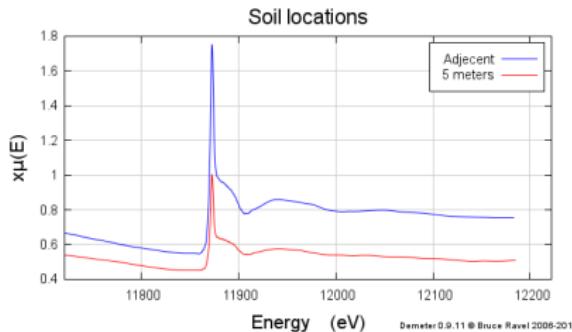
Note that the edge of As^{5+} standard is shifted substantially to higher energy and that the first peak is much enhanced.

As^{5+} is water soluble, thus more mobile than As^{3+} .

Also As^{5+} is quite toxic.

XAS from the soil samples

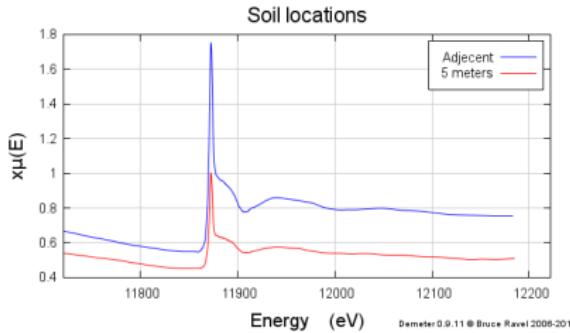
Here are the raw $\mu(E)$ data from the two soil locations. Sure enough, the signal from the site adjacent to the old deck is enhanced by about a factor of 2.



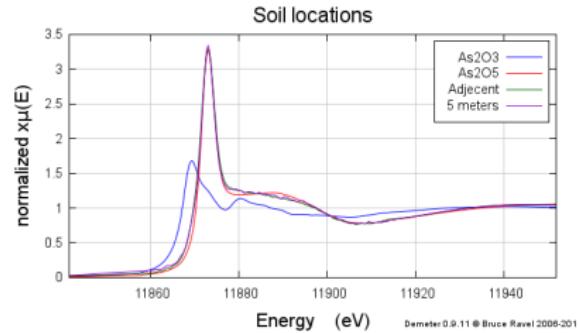
Should I be worried about eating produce from my garden?

XAS from the soil samples

Here are the raw $\mu(E)$ data from the two soil locations. Sure enough, the signal from the site adjacent to the old deck is enhanced by about a factor of 2.



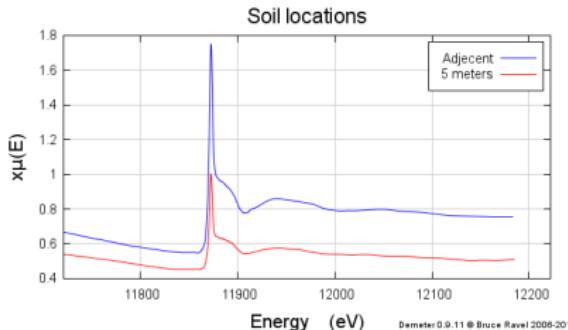
Here are the normalized data compared to standards. The As is slightly reduced, but predominantly As^{5+} . As in soil is well known to bind to soil particles as As^{5+} .



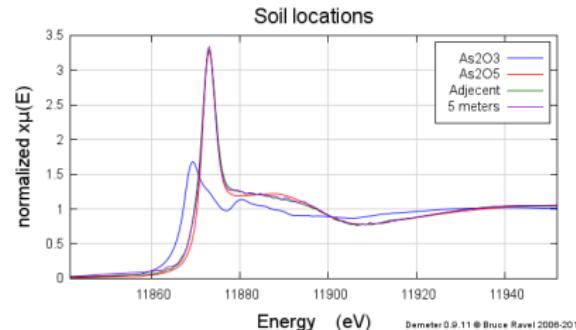
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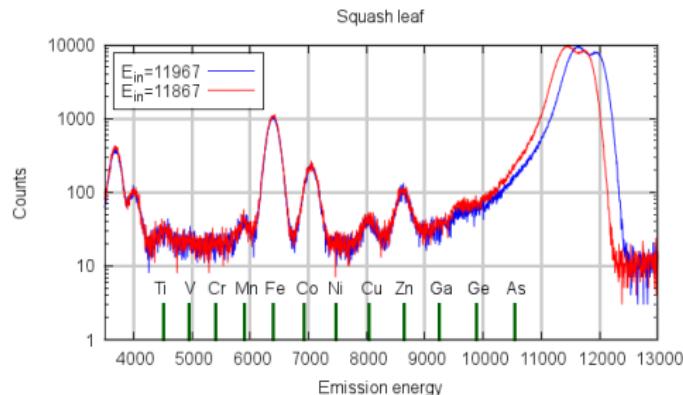
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Should I be worried about eating produce from my garden?

XRF spectra from plant leaves

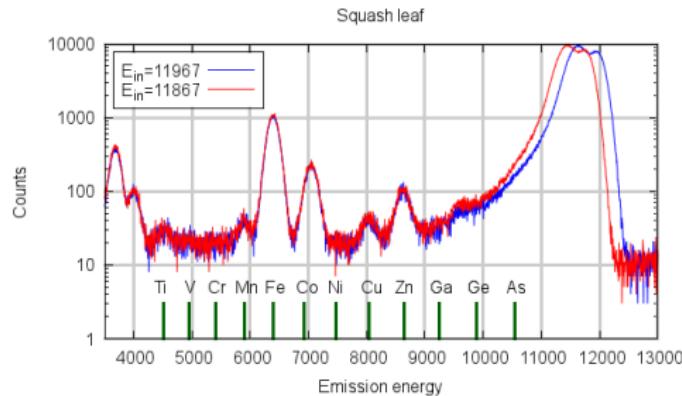
Here are XRF spectra from the leaf of a squash plant growing in the soil adjacent to the old deck.



Although toxic As^{5+} is present in the soil in elevated quantities, very little is taken up by the plants growing that soil.

XRF spectra from plant leaves

Here are XRF spectra from the leaf of a squash plant growing in the soil adjacent to the old deck.



Although toxic As^{5+} is present in the soil in elevated quantities, very little is taken up by the plants growing that soil.



The squash were delicious!

More information

About NSLS-II

↪ <http://www.bnl.gov/nsls2>

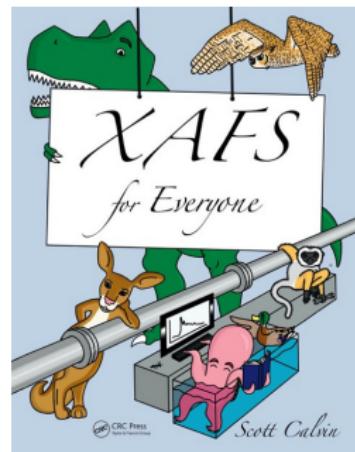
About synchrotron science

↪ <http://www.lightsources.org/>

About X-ray Absorption Spectroscopy

↪ <http://www.xrayabsorption.org/>

↪ XAFS for Everyone by Scott Calvin



Information about XAS

☞ <http://xrayabsorption.org/Tutorials>

The screenshot shows a Mozilla Firefox browser window displaying the IXAS (The International X-ray Absorption Society) website. The URL in the address bar is <https://xrayabsorption.org/tutorials/>. The page title is "IXAS: The International X-ray Absorption Society". The main navigation menu includes "IXAS", "Conferences", "Resources", "Data & Software", and "People". A "Tutorials" section is highlighted. Below it, a sub-section titled "Tutorials" contains text about X-ray absorption and related spectroscopies, mentioning external websites like <https://xafs.xrayabsorption.org/tutorials.html>. It also notes that many tutorial resources are available online. A list of external links follows, including "XAFS Tutorials" from Grant Bunker, "XAS Overview" from Iztok Arcon, "X-ray Spectroscopy mini Courses" from Jim Penner-Hahn, and "XAS Education" from Bruce Ravel. Another section lists "Some slides from oral presentations hosted here (PDF format except where noted)" with links to Matt Newville's XAFS overview, XAFS Fundamentals, EXAFS Processing by Shelly Kelly, and EXAFS Data Analysis by Shelly Kelly. To the right, there is a "NEWS AND EVENTS" calendar for May 2020, a "RELATED SITES" section with links to XAFS2021 Conference, IUCr XAFS Commission, and xafs.xrayabsorption.org, and a "SITE ACCESS" sidebar with links to Log In, Entries feed, Comments feed, and WordPress.org.

Tutorials - IXAS: The International X-ray Absorption Society - Mozilla Firefox

IXAS: The International X-ray Absorption Society

Search

Tutorials

Tutorials on X-ray absorption and related spectroscopies. See also <https://xafs.xrayabsorption.org/tutorials.html>.

There are many tutorial resources available on-line. Many of these may be from Training Workshops and Short Courses and so may change over time. A partial list of external websites with introductory and tutorial pages on XAFS

- XAFS Tutorials from Grant Bunker, Illinois Institute of Technology
- XAS Overview from Iztok Arcon, University of Nova Gorica, Jozef Stefan Institute, Slovenia
- X-ray Spectroscopy mini Courses from Jim Penner-Hahn, University of Michigan.
- XAS Education from Bruce Ravel, National Institute of Standards and Technology. See also: <https://speakerdeck.com/bruceravel>

Some slides from oral presentations hosted here (PDF format except where noted):

- XAFS Overview from Matt Newville, University of Chicago. Slides from an overview of XAFS.
- Fundamentals of XAFS from Matt Newville, University of Chicago. A longer (~40 page) writeup of notes and discussion of the basics of XAFS.
- Basics of EXAFS Processing from Shelly Kelly, UOP. Introducing the basics of processing $\chi(k)$ data in Athena.
- Basics of EXAFS Data Analysis from Shelly Kelly, UOP. Introducing the basics of modeling EXAFS

<https://xrayabsorption.org/feed/> in Artemis

May 2020

M	T	W	T	F	S	S
				1	2	3
4	5	6	7	8	9	10
11	12	13	14	15	16	17
18	19	20	21	22	23	24
25	26	27	28	29	30	31

RELATED SITES:

- XAFS2021 Conference
- IUCr XAFS Commission
- xafs.xrayabsorption.org

SITE ACCESS

Log In

Entries feed

Comments feed

WordPress.org

Free* XAS software

☞ <http://bruceravel.github.io/demeter/>

The screenshot shows a Mozilla Firefox browser window displaying the Demeter software website. The address bar shows the URL <http://bruceravel.github.io/demeter/>. The main content area features a sidebar on the left with a statue of Demeter, links for X-ray Absorption Spectroscopy Using Feff + Larch or Ieffit, and download links for Windows and Source code. The main content area has a heading "About Demeter" and describes Demeter as a comprehensive system for processing and analyzing X-ray Absorption Spectroscopy data. It lists several bullet points about Demeter's features, including being version 0.9.26, available for Linux, Windows, and Macintosh, and being a Perl module. A red annotation with three arrows points to the "Ieffit Mailing List" link. The bottom of the page includes sections for asking questions, reporting bugs, citing Demeter, and a Windows Installer & Updater.

Demeter

X-ray Absorption Spectroscopy Using Feff + Larch or Ieffit.

Windows download:

[Version 0.9.26](#)

Source code:

[View On GitHub](#)

Demeter © 2006-2018
Bruce Ravel

About Demeter

Demeter is a comprehensive system for processing and analyzing X-ray Absorption Spectroscopy data.

Demeter is:

- currently at version **0.9.26**
- available for **Linux**, **Windows**, and **Macintosh**
- a set of **perl** modules and related files
- a programming tool -- it is the thing from which applications are built
- **free software**, freely available from a **git server**
- actively developed and maintained
- in use by its author and users for real data analysis problems
- a front end to **Feff**, **Larch**, and **Ieffit** (and, soon, **Fefft**)
- the code base for **Athena** and **Artemis**
- named for the **Greek goddess of the harvest**

To ask questions or report bugs :

[Use the Ieffit Mailing List](#)

To cite Demeter in a publication, use

B. Ravel and M. Newville, **ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT**, *Journal of Synchrotron Radiation* **12**, 537-541 (2005) doi:[10.1107/S0909049505012719](https://doi.org/10.1107/S0909049505012719)

The new WebAtoms: reborn and updated!

Windows Installer & Updater

Download the **64 bit Installer package** and double-click to install the Demeter system

Have a question? ↗
Found a bug? ↗
[Ieffit Mailing List](#)

The **Ieffit Mailing List** is the best place to ask questions about the software and about XAFS. Please use the mailing list rather than contacting the author of Demeter directly.

* Free of cost, freely available source code, freely redistributable

Introduction to X-ray Absorption Spectroscopy