# X-ray Absorption Fine Structure Overview

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# **X-rays and Matter**

- Photoelectric effect (Einstein's 1921 Nobel Prize):
  - Dominates for X-rays with energies from 500 eV to 500 keV
  - X-ray photon is absorbed by an electron in a tightly bound quantum core level of an atom.
  - Binding energy of electron must be less than x-ray energy otherwise the electron does not interact with the X-ray.
  - The x-ray is destroyed (absorbed) and excess energy is given to the photelectron that is ejected from the atom.

**Electronic transitions due to X-ray** absorption must follow dipole selection rule requires conservation of angular momentum. Transitions are allow for  $\ell = +/-1$ 

Beer's Law: Absorption of X-rays by Matter

 $I_{f} = I_{0}e^{-\mu x}$ 



Absorption

X-Tay

photo-electron

 $\Lambda \Lambda \Lambda$ 

-0-0-0-0

Indedd ------



Relaxation

continuum



# **Hephaestus: Absorption Tools**



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Gold     Be     1.000     12.427     0.831       Iransitons     Iron     Iron     Iron     Iron       Iron     Kapton     Kindl     Kapton     Iron       Edge finder     Lead Titanate     Absorption length = 0.651 cm at 9000 eV.     A sample of 1 absorption length with area of 1 square       Line finder     Mca     No       Standards     Beylene-Ki     Paylene-Ki       Paylene-Ki     Paylene-Ki     Paylene-Ki       Paylene-Ki     Paylene-Ki     Paylene-Ki       Fand Fr     Polycaphonate     Paylome       Rutile     cna     Configure	11	Fluorite			
Iransmoss       Iransmoss         Iransmoss       Iransmoss         Kapton       Kapton         Komd       Absorption length = 0.651 cm at 9000 eV.         Lead Titante       Asample of 1 absorption length with area of 1 square om requires 1204.255 milligrams of sample at 9000.00 eV.         Nean       Nean         Nean       Nean         Standards       ParyleneC,         ParyleneC,       ParyleneC,         ParyleneC,       Used in the calculation.         F and F*       Polymode         Polymode       Polymode         Polymode       Polymode         Rutile          Configure       The		Gold	Be	1.000 12.427	0.831
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This calculation uses the Elam data resource and full cross sections.	This calculatio	n uses the Elam data resource and full cross se	ctions.		





## Measurement of X-ray Absorption Coefficient



Sample Transmission  $I_t$ **I**<sub>0</sub> log μ  $l_t$ If **Fluorescence** Pt Foil in energy 0.5 Pt Foil 0  $\mu \propto$ -0.5 WΛ xµ(E) -1 -1.5 -2 -2.5 -3 11400 11600 11800 12000 12200 Energy (eV) Demeter 0.9.9 @ Bruce Ravel 2006-2012

# **X-ray Absorption Process**





 #1: X-ray with energy below the binding energy of the core level does not interact with the atom

#### \*Presented by Matt Newville

# **X-ray Absorption Process**





 #2: X-ray with energy just above the binding energy of the core level has a probability of being adsorbed producing a low energy photoelectron

\*Presented by Matt Newville

# **X-ray Absorption Process**





 #3) X-ray with higher energy have a probability of being adsorbed and producing higher energy photo-electron



# $\mu(E) \propto |\langle i | \mathcal{H} | f \rangle|^2$

- Transition between two quantum states
- Initial state is well localized at the absorbing atom
- Final state is not, but can be written in terms of two parts  $|f\rangle = |f_0\rangle + |\Delta f\rangle_{\text{neighboring atoms}}$

 $\mu(E) = \mu_0(E)[1 + \chi(E)]$ 

 Probability for adsorption is the probability for an isolated atom multiplied by a perturbation due to neighboring atoms

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta \mu(E)}$$



 Interference between outgoing and scattered photoelectron at the absorbing atom causes modulations in the probability for absorption.

# **EXAFS Equation and Signal**





 EXAFS signal can be expressed as a sum of sine waves

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X-ray Absorption Near Edge Structure



### Analysis of XANES spectra

- Assigning absorption edge energies to oxidation states
- Linear combination fitting (LCF) using standard to reproduce the measured spectrum to determine the relative amount of each standard in the measured spectrum
- Theoretical Calculations (FEFF8) using atomic clusters to calculate the absorption edge spectrum to reproduce key features and assign those features to specific atomic configurations

# **Edge Position and Valence State**





- For some materials the edge position can be calibrated to determine the average valence state
- As an element becomes more positively charged the x-ray energy needed to remove an additional electron is increased causing the edge to shift.





 Example were the edge position does not track cleanly with oxidation state

# **Pt Data Series**





- Data Series were Pt is being reduced in situ.
- Look for Isosbestic points in normalized XANES spectra

# **Interpretation of XANES**





- Plot white line height with temperature to determine the rate of Pt reduction
- White line height: White line height is a measured of the unoccupied d-electrons

# **Linear Combination Fitting #1**





 Fit 149°C data with combination of 29°C data and 150°C data.

# Comparison of LCF and white line height





- Similar results for both methods of interpretation
- LCF: Assume speciation of Pt evolves from the initial species to the final species. No intermediate species present.
- White line height: Assume white line height the available delectrons.





 Linear combination fitting using PtO<sub>2</sub> and Pt foil as a standards

# **Comparison of Fitting Results**





White line height scaled to 100% and 0% from Initial and final spectrum

# LCF using initial and final spectrum

LCF using PtO2 and Ptfoil

- All three methods give similar results.
- Largest source of error comes from incomplete knowledge of chemical speciation before, during and after in situ measurement.
- LCF using standards assumes that these standards are a good representation of Pt speciation in sample.



- Introduction to Athena (Background removal)
- Introduction to Artemis (EXAFS Modeling)
  - Modeling Cu foil
  - Modeling U to determine neighboring atom type
  - Multiple data set modeling

- M Newville. "IFEFFIT: interactive EXAFS analysis and FEFF fitting." <u>J. Synch. Rad.</u> 8: pp 322-324, 2001. http://cars9.uchicago.edu/ifeffit/
- J J Rehr."Ab initio multiple scattering X-ray absorption fine structure and X-ray absorption near edge structure code", University of Washington: pp, 1995. http://leonardo.phys.washington.edu/feff/
- E A Stern, M Newville, B Ravel, Y Yacoby and D Haskel. "The UWXAFS analysis package: Philosophy and details." <u>Physica B</u> 208 & 209: pp 117-120, 1995.

# **Athena: Background Removal**



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- Number of independent points is proportional to the data range used in FT and the fitting range.
- Cannot have more variables determined in a fit than the number of independent points

# **Comparison of Models**



 $\chi^2$ : sum of the difference between the data and the theory

$$\chi^{2} = \frac{N_{idp}}{\epsilon N_{data}} \sum_{i=min}^{max} [Re(\chi_{d}(r_{i}) - \chi_{t}(r_{i}))^{2}] + Im(\chi_{d}(r_{i}) - \chi_{t}(r_{i}))^{2}]$$
  

$$\epsilon = measurement uncertainty$$



Reduced  $\chi^2$ : sum of the difference between the data and the theory, scaled by the number of independent points.  $\nu = N_{idp} - N_{var}$ Useful for comparing models with different number of variables

**R-factor: fractional misfit** 

$$\mathcal{R} = \frac{\sum_{i=min}^{max} [Re(\chi_d(r_i) - \chi_t(r_i))^2 + Im(\chi_d(r_i) - \chi_t(r_i))^2]}{\sum_{i=min}^{max} [Re(\chi_d(r_i))^2 + Im(\chi_d(r_i))^2]}$$

- FEFFIT uses Levenberg-Marquardt non-linear least-squares minimization
- $\chi_{\nu}^2$  are used to compare between two different models.  $\chi_{\nu}^2$  values are poorly scaled and often 100 1000.  $\chi_{\nu}^2$  need to change by more than a factor of 2 to be significant.

be significant. • Error bars are scaled by  $\sqrt{\chi^2_{\nu}}$ , assuming that the model is good.

# Building Theoretical Model: Atoms page



#### File: open file: F:\lfeffit\examples\Artemis\Cu\atoms.inp

Artemis [EXAFS data analysis] * <untitled>************************************</untitled>	Artemis [Feff] Atoms and Feff
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Unit cell of Copper Absorption edge	Titles       Structural         Cu 222       Information         Name atoms       Lattice Constants         Space Group fcc       A 3.61       B 3.61       C 3.61         idge       K       ✓       90       β 90       Y 90         Style       Feff6 - elements ▼       Radial distances       Cluster size       7.0       Longest path       5.0         Add a site       Shift vector       0       0       0       0       0
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# **Feff Scattering Paths**



- **Degen:** Degeneracy of the path (number of identical scattering paths)
- **Reff:** Inital half path length (bond length for single scattering path)
- **Rank:** Estimate of amplitude of path relative to first path.
- **Type:** Description of the scattering path.
- **Scattering path:** atoms scattering photoelectron, [@] symbol represents core atom.

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S I Zabinsky, J J Rehr, A Ankudinov, R C Albers and M J Eller. "Multiple-scattering calculations of X-ray-absorption spectra." Phys. Rev. B **52**(4): pp 2995-3009, 1995.

# The EXAFS Equation



- E. A. Stern and S M Heald Basic principles and applications of EXAFS. Handbook of Synchrotron Radiaction. E. E. Koch. New York, North-Holland. 10: pp 995-1014, 1983.
- E. A. Stern. "Theory of the extended x-ray-absorption fine structure." Phys Rev B 10(8): pp 3027-3037, Oct 1974.
- E A Stern, "Structural determination by X-ray Absorption," Contemp. Phys 19(4): pp 239-310, 1978.

$$\chi(\mathbf{k}) = \Sigma_{i} \chi_{i}(\mathbf{k})$$

with each path written as:



$$\begin{split} \chi_{i}(k) &= \begin{pmatrix} (\underline{N_{i}S_{0}}^{2})\underline{F_{i}(k)} & \sin(2kR_{i} + \varphi_{i}(k)) \exp(-2\sigma_{i}^{2}k^{2}) \exp(-2R_{i}/\lambda(k)) \\ kR_{i}^{2} & R_{i} = R_{0} + \Delta R \\ k^{2} &= 2 m_{e}(E-E_{0})/\hbar \end{split}$$

#### Theoretically calculated values

- $F_i(k)$  effective scattering amplitude
- $\phi_i(\mathbf{k})$  effective scattering phase shift
- $\lambda(k)$  mean free path
- $R_0$ initial path length

Feff calculates the theoretical scattering amplitude F(k) effective, hence the name Feff. **26** 

#### Parameters often determined from a fit

- **N**<sub>i</sub> degeneracy of path
- $S_0^2$  passive electron reduction factor
- E<sub>0</sub> energy shift
- $\Delta \mathbf{R}$  change in half-path length
- $\sigma_i^2$  mean squared displacement

## Models to consider:



#### • ∆**r**:

- Symmetric expansion term: Alpha \* reff.
- Grouped depending on distance and atom types
- Related to unit cell dimensions
- **ΔE**:
  - Energy shifts that depend on atom type
  - One energy shift for all paths
  - Two energy shifts, one for first shell and another for all other shells
- σ<sup>2</sup>:
  - Grouped depending on distance and atom types.
  - Use a Debye or Einstien model, with one or more characteristic temperatures.
  - Each shell with independent value.
  - Separate structural disorder from thermal disorder components.
- S02:
  - One S02 for all paths.
  - Approximate S02 from standards.
- N:
  - Determined by the crystal structure.
  - Fit a data series were N is expected to change.

# **EXAFS** parameters



Artemis [Data] cu010k.dat		-	-	
Data Path Marks Actions Debug Help				
💽 cu010k.dat	CV 1	[atoms] Cu. 1	💽 [ate	oms] Cu.1
Data source C:\Users\E446095\Documents\Conferences\EXAFS School\?	2013 Thailand \Cu		Include pair Use this pair Q Cu.1 Q	th Dot after fit after fit of phase corrected plotting.
Plot this data set as       k123     R123     Rmr     Rk	kq		single sc x 1.80 0.00	attering, high (100.00) Y Z ipc 1.805000 0.000000 00000 0.000000 0.000000
Title lines				4 <u>m</u>
			Label N	Reff= 2.553 nleg=2 degen=12
Fourier transform parameters kmin 3.000 (a) kmax 23.019 (b) dk	1		S0 <sup>2</sup> ΔΕ0	s02 E0
rmin 1 irmax 3 i rmax 3	0.0		ΔR σ²	delcu1 sigcu1
Fitting k weights       I			Ei 3rd	Name of parameters
Other parameters Include in fit Plot after fit Fit background $\epsilon(k)$ 0 Plot with phase correction			4th	that YOU have creat
Created "sigcu1" as guess				values for each path

# **Check Model**



Arter	mis [GDS] Gue	ss, Def, Set param	neters						
	Туре	Name		Math expressio	n	Evaluated	^ 🧡	Use best fit	
	set	s02	1.00000		Artemis[Plot.1]		-		
	set	delE	0			<u>ه د</u>			
:	set	delcu1	0			<b>≫</b> ≝			
	set	sigcu1	0.00300			cu010k.da	in R spac	е	
-	guess				100		1	-	
	guess							cu010k	.dat ——
	guess				50	ii _/ _/			fit
-	guess				50			$\wedge$	
-	guess				-4		$\sim$		<u> </u>
)	guess				₹ 0			٨	
	guess							$\wedge$	
2	guess				-50			$H \rightarrow H$	$\sim$
					<u> </u>	Ť		V V V	
					-100		 		
						V			
					150	V			
					-150	1 2	3	4 5	; ;
					_	Radial di	stance (A)	- Demeter 0.9.17 @ E	iruce Ravel 2006
					2.13746, 142.858		. /		

 Good practice: Set all parameters to a reasonable value and run a "fit" to see if the model is close to the data.

# **Fit Results**





# Cu: Three Shell Model





- Use alpha to define path lengths
- Use Debye temperature to define  $\sigma^2$  values
- Each single scattering path fits into a specific signal in the data
- Check model by adding up all set parameters

## **GSD** Info

emis [GDS] Gu	ess, Def, Set param	neters	
Туре	Name		Math expression
set	s02	1.00000	
set	delE	5.46772	
set	sigcu1	0.00300	
set	temp	10	
set	thetad	500.00000	
set	alpha	0	
guess			
	emis [GDS] Gu Type set set set set set set guess	Type     Name       set     s02       set     delE       set     sigcu1       set     temp       set     alpha       guess     guess	Type     Name       Type     Name       set     s02     1.00000       set     delE     5.46772       set     sigcu1     0.00300       set     temp     10       set     thetad     500.00000       set     alpha     0

# Fitting results for three shell fit to Cu





#### There is more to this example on your computer. Modeling more shells and modeling temperature dependent spectra series

### **Results Info**

<pre>Name : Fit 10 (hzpnp) Description : fit to cu010k.dat Figure of merit : 10 Time of fit : 2013-07-07T04:19:14 Environment : Demeter 0.9.17 with perl 5.012003 and using Ifeffit 1.2 Interface : Artemis (Wx 0.99) Prepared by : Contact :</pre>	.11d or
Independent points: 32.7304688Number of variables: 4Chi-square: 854.6011128Reduced chi-square: 29.7454636R-factor: 0.0032286Measurement uncertainty (k): 0.0007153Measurement uncertainty (R): 0.0040642Number of data sets: 1	
Happiness = 100.00/100 color = #D8E796 ***** Note: happiness is a semantic parameter and should ***** ***** NEVER be reported in a publication NEVER! ***** <u>quess parameters:</u> s02 = 0.92090854 # +/- 0.01835249 [1.00000] dollar = 5.74010405 # +/- 0.24545150 [5.46772]	
delt       =       5.74919405       # +/-       0.24545150       [5.46772]         thetad       =       279.86684625       # +/-       9.09200248       [500.00000]         alpha       =       -0.00134933       # +/-       0.00046635       [0]         .       .       .       .       .       .         .       .       .       .       .       .         .       .       .       .       .       .       .         .       .       .       .       .       .       .       .         .       .       .       .       .       .       .       .       .         .       .       .       .       .       .       .       .       .         .       .       .       .       .       .       .       .       .         .       .       .       .       .       .       .       .       .       .         .       .       .       .       .       .       .       .       .       .       .       .       .       .       .       .       .       .       . <th></th>	

# Some EXAFS references



- Multiple edges, structural information: B Ravel, E. Cockayne, M. Newville and K. M. Rabe. "Combined EXAFS and firstprinciples theory study of Pb1-xGexTe." <u>Phys. Rev. B</u> 60(21): pp 14632–14642, Dec 1999
- Structural information, bond angles: A. I. Frenkel, E A Stern, A. Voronel, M. Qian and M Newville. "Solving the structure of disordered mixed salts." <u>Phys. Rev. B</u> 49(17 – 1): pp 11662–11674, May 1994.
- Model two phases, then combined to model a mixture: S. Kelly, R. Ingalls, F. Wang, B. Ravel and D. Haskel. "X-rayabsorption fine-structure study of the B1-to-B2 phase transition in RbCl." <u>Phys. Rev. B</u> 57(13): pp 7543–7550, April 1998
- Determine neighbor atom types and number using standards: S. D. Kelly, K. M. Kemner, J. B. Fein, D. A. Fowle, M. I. Boyanov, B. A. Bunker and N. Yee. "X-ray absorption fine-structure determination of pH dependent U-bacterial cell wall interactions." <u>Geochem. Cosmo. acta.</u> 66(22): pp 3855-3871, Nov 2002.
- Multiple techniques: P G Allen, J J Bucher, D L Clark, N M Edelstein, S A Ekberg, J W Gohdes, E A Hudson, N Kaltsoyannis, W W Lukens, M P Neu, P D Palmer, T Reich, D K Shuh, C D Tait and B D Zwick. "Multinuclear NMR, Raman, EXAFS, and X-ray diffraction studies of uranyl carbonate complexes in near-neutral aqueous solution. X-ray structure of [C(NH2)3]6[(UO2)3(CO3)6] 6.5H20." Inorg. Chem. 34: pp 4797-4807, 1995.
- Pressure dependent data: A. I. Frenkel, F. M. Wang, S. Kelly, R. Ingalls, D. Haskel, E. A. Stern and Y. Yacoby, "Local structural changes in KNbO3 under high pressure", *Physical Review B* 56, 10869, 1997.
- Temperature dependent data: D. Haskel, E.A. Stern, D.G. Hinks, A.W. Mitchell, J.D. Jorgensen, J.I. Budnick, "Dopant and Temperature Induced Structural Phase Transitions in La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub>" Physical Review Letters, 76 (3) pg 439
- Multiple edges, structural disorder: S. Calvin, E. E. Carpenter, B. Ravel, V. G. Harris and S. A. Morrison. "Multiedge refinement of extended x-ray-absorption fine structure of manganese zinc ferrite nanoparticles." <u>Phys. Rev. B</u> 66: pp 224405, 2002.
- Structural information from XANES and EXAFS: B. Ravel, E. A. Stern, R. I. Vedrinskii and V. Kraizman. "Local structure and the phase transitions of BaTiO3." <u>FERROELECTRICS</u> 206(1-4): pp 407-430, 1998.
- Temperature dependence and nanoparticles: A. I. Frenkel, C. W. Hills and R. G. Nuzzo. "A view from the inside: Complexity in the atomic scale ordering of supported metal nanoparticles." <u>JOURNAL OF PHYSICAL CHEMISTRY B</u> 105(51): pp 12689-12703, 2001.
- Kelly, S. D.; Hesterberg, D.; Ravel, B. Analysis of soils and minerals using X-ray absorption spectroscopy. In Methods of soil analysis, Part 5 -Mineralogical methods; Ulery, A. L., Drees, L. R., Eds.; Soil Science Society of America: Madison, WI, USA, 2008; pp 367-463.

## **Determining 2<sup>nd</sup> shell atom type and number**



- Uranyl in equilibrium with a mixture of Fe-oxides and different microbial components.
- Possible second shell atoms, O, C, P, Fe, U.
- 30-50 combinations of these atoms were tested.
- Three of these tests are shown here:
  - C and Fe,
  - P and Fe,
  - Fe and Fe



# Setting up a Uranyl Model



Artemis [Data] Fe1M1.xmu	
Data Path Marks Actions Debug Help	
Fe1M1.xmu CV 1	U-Oax U-Oeq [Uranium monophosphate atom:
Data source C:\Users\E446095\Documents\Conferences\EXAFS School\2013 Thailand\Ur Plot this data set as k123 R123 Rmr Rk kq Title lines Athena data file Athena version 0.8.059 Saving Fe 1M1 as mu(E) . Element=U Edge=L3 Background parameters . E0=17189.150 Eshift=0.000 Rbkg=1.000 . Standard=0: None . Kweight=1.0 Edge step=1.004 Fourier transform parameters kmin 3  kmax 10  k 1 min 1  rmax 3.5  kmax 10 Fitting k weights V 1 V 2 V 3 other 0.5	U-Oeq ((([Sodium Uranyl tria U-Oax1-U-Oax1 U-Oax1-U-Oax2 U-Oax1-U-Oax2 U-Oax1-U-Oax2 U-P at 3.0 U-P at 3.0
Other parameters       ✓ Include in fit       ✓ Plot after fit       ε(k)       0   Plot with phase correction	4th
Transfered path "U-P at 3.0" to the plotting list.	





- Place C and Fe shells in a "good" spot
  - set parameters no fitting
  - monitor results and fit spectra
  - Needs to be done using real or imaginary part of FT, can not always be done using magnitude of FT.

# Fit Results using C and Fe shells





#### Signals became broad and unrealistic





- Place P and Fe shells in a "good" spot
  - set parameters no fitting
  - monitor results and fit spectra

# Fit Results using P and Fe shells



	Fe1M1.xmu in R space	Fe1M1.xmu ii	n R space
	Fe1M1.xmu fit U-Oax U-Oeq Oax MS U-C at 2.85 U-Fe at 3.58 U-P at 3.0		Fe1M1.xmu fit U-Oax U-Oeq Oax MS U-C at 2.85 U-Fe at 3.58 U-P at 3.0
guess parameter	Z 3 4 5 Radial distance (Å) Demeter 0.9.17 @ Bruce Ravel 2006	Radial dista	nce (Å) Demeter 0.9.17 © Bruce Ravel 2006-2013
delE0	= 5.61401930 # +/-	27.80359821 [0.65657]	EXAFS Parameters
NO1	= 1.87756022 # +/-	5.01084021 [1.78168]	
NO2	= 4.69820412 # +/-	8.94502263 [4.50466]	
delo1	= 0.02593456 # +/-	0.16855444 [0.00291]	σ <sup>2</sup> -values -
delo2	= -0.15241235 # +/-	0.19664655 [-0.18795]	
sigo1	= 0.00000001 # +/-	0.02509008 [1.00742e-009]	Distances +
sigo2	= 0.00603437 # +/-	0.03047295 [0.00466]	
Nfe2	= 0.26864818 # +/-	7.34270113 [1.54468]	Coordination +
delfe2	= -0.05663159 # +/-	0.66187494 [-0.17012]	
sigfe2	= -0.00036128 # +/-	0.22371051 [0.01153]	numbers
delp1	= 0.07282056 # +/-	0.40898253 [0.06738]	∆E-value +
sigp1	= 0.00088094 # +/-	0.08136929 [0.00300]	
Np1	= 0.94722667 # +/-	7.57814884 [1.00000]	
MDT	- 0.54/2200/ # +/-		

#### Signals became unrealistically sharp





- Place Fe and Fe shells in a "good" spot
  - set parameters no fitting
  - monitor results and fit spectra

# Fit Results using Fe and Fe shells



Fe1M1.xmu in R sp	bace	Fe1M1.	xmu in R space	
1.5 1.5 0.5 -0.5 -1 0 1 2 3 Radial distance (	Fe1M1.xmu fit U-Oax U-Oeq Oax MS U-Fe at 3.58 U-Fe at 2.85 4 5 6 A) Demeter 0.9.17 @ Bruce Ravel 2008-2013	1.5 1.5 1.5 0 -0.5 -1 -1.5 0 1 2 Radia	Fe1M1.× U-( U-( Oax U-Fe at 2 U-Fe a	cmu fit Deq MS 3.58 2.85 56 Bruce Ravel 2008-2013
de1E0 = -0.52309493	# +/- 13.03833870	[5,57110]		
NO1 = 2.03134042	# +/- 1.61713414	[2.00000]	EXAFS Parame	eters
NO2 = 5.73627907	# +/- 4.82822216	[3.96132]		
delo1 = 0.00417472	# +/- 0.05467323	[0.02440]	$\sigma^2$ -values	
delo2 = -0.19840310	# +/- 0.07727996	[-0.15727]		Ŧ
sigo1 = -0.00170651	# +/- 0.00571344	[-0.00021]	Distances	Ŧ
sigo2 = 0.00755140	# +/- 0.00688098	[0.00439]		T
Nfe2 = 1.70423291	# +/- 6.96079514	[1.00000]	Coordination	<b>_</b>
delfe2 = -0.16643599	# +/- 0.18133249	[-0.10000]	numbers.	Т
sigfe2 = 0.01446017	# +/- 0.04156123	[0.00800]	numpers	
Nfe1 = 0.96716126	# +/- 0.84064342	[0.85186]	∧F-value	
delfe1 = -0.01339862	# +/- 0.11102923	[0.05000]		т

#### Values are realistic, but uncertainties are large

# Multiple data set fit



		Data sets	•		4 data	Feff calculations		
GDS Plot History				Add	- uata	Add		K
		Show "Fe1M1.xmu" Show "Fe1M2.xmu" Show "Fe2M1.xmu"			sets	Show "Sodium Uranyl triacetate atoms" Hide "Uranium monophosphate atoms.inp"		
<u>ه</u> الم	mai		3100 1	C2011.XIIIG		Show Sub Didentate Fe		
			Show "	Fe2M2.xmu"			_	
		_				4		
	Arten	nis [GDS] Gue	ss, Def, Set param	neters		,		
		Туре	Name		l or Feff in M	put files or to open an empty Atoms input fil	е.	
		-+	ciefe 1	cicfe 2				
	10 S	et	NO1 11	2				
	12 0	IUESS	NO1_11 NO2_11	5			1	
1	13 0	juess	Nfe2 11	1.00000	N value	S		
1	L4 g	juess	Nfe1_11	1.00000		- -		
1	L <b>5</b> s	et	NO1_22	2	that de	pend on		
1	<b>16</b> g	juess	NO2_22	5				
1	L7 g	juess	Nfe2_22	1.00000	Data se	et. All other		
1	<b>18</b> g	juess	Nfe1_22	1.00000	-			
<b>19</b> s		et	NO1_12	2	Parame	eters are the same		
2	20 g	juess	NO2_12	5			J	
2	21 9	juess	Nfe2_12	1.00000		• Fit / data sots		
2	2 <b>2</b> g	juess	Nfe1_12	1.00000		· 1 11 4 Uala 3013		
2	23 s	et	NO1_21	2		<ul> <li>Use K-weights of 1.2</li> </ul>	and 3	
24 guess NO2_21 5							· · · ·	
•						<ul> <li>Fit different N values</li> </ul>	tor each da	ta set
						<ul> <li>Data series is needed determine the number</li> </ul>	d to accurate er of Fe aton	ely ns in the

# **Modeling a Data Series**



Independent points	: 29.750000	)		Fe1M1.x	mu in R space
Chi-square	: 6548.03201	63		1.5	Fe1M1 xmu
Reduced chi-square R-factor Measurement uncertair Measurement uncertair	: 349.228374 : 0.0455832 aty (k) : 0.0002134	12			Fe1M2.xmu
<pre>Measurement uncertain Number of data sets Happiness = 74.42/100 An R-factor of 0.0 ***** Note: happiness ***** NEVER be rep guess parameters:</pre>	color 24558 gives a penalt 2558 semantic para 2558 in a publicat	= #FEC182 by of 25.58320. wmeter and should *** ion NEVER! ***	**		Fe2M2.xmu fit 3 4 5 6
delfe2	= -0.12831700 #	+/- 0.01601433	[-0.12072]	Radial	distance (Å) Demeter 0.9.17 © Bruce Ravel 2006-2013
sigfe1 Nfe2_11 Nfe2_12 Nfe1_12 Nfe1_21 Nfe2_21 Nfe2_22 Nfe1_22	= 0.00647446 = 0.66241492 = 0.88582314 = 0.53389948 = 0.98037888 = 1.17116425 = 0.32360733 = 0.67699484 = 0.99083810	<pre>+/- 0.00292661 +/- 0.23026024 +/- 0.34515786 +/- 0.27788274 +/- 0.38456367 +/- 0.43261640 +/- 0.29454535 +/- 0.34524740 +/- 0.39030744</pre>	[0.00611] [1.10762] [0.88654] [0.92843] [0.90765] [1.01045] [0.56411] [1.20824] [0.92682]	Fe1M1.x	mu in R space
				0 1 2	3 4 5 6
				Radia	distance (Å) Demeter 0.9.17 @ Bruce Ravel 2006-2013

#### **Reasonable modeling of data series**





- Athena and Artemis: a complete set of tools to process XAS spectra utilizing Ifeffit.
- Thank-you to the authors Bruce Ravel (A&A) and Matt Newville (Ifeffit).
- When you get stuck, check out the ifeffit mailing list for help from the experts:

http://cars9.uchicago.edu/mailman/listinfo/ifeffit/