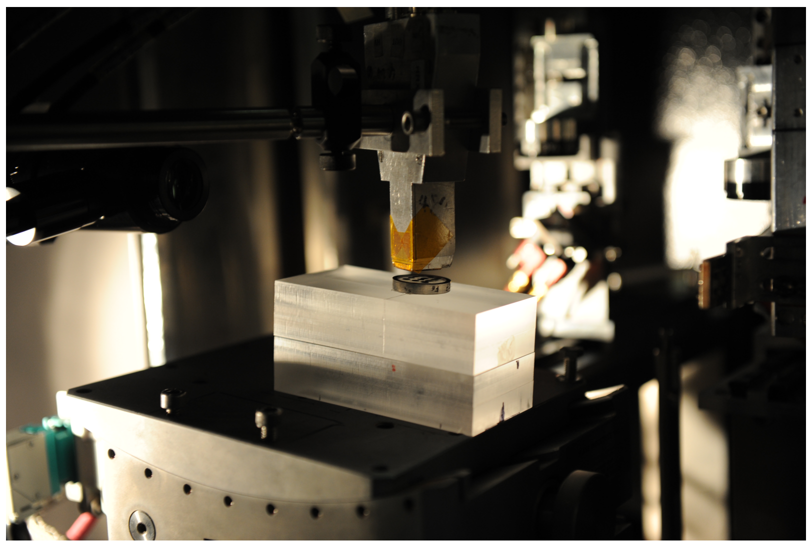
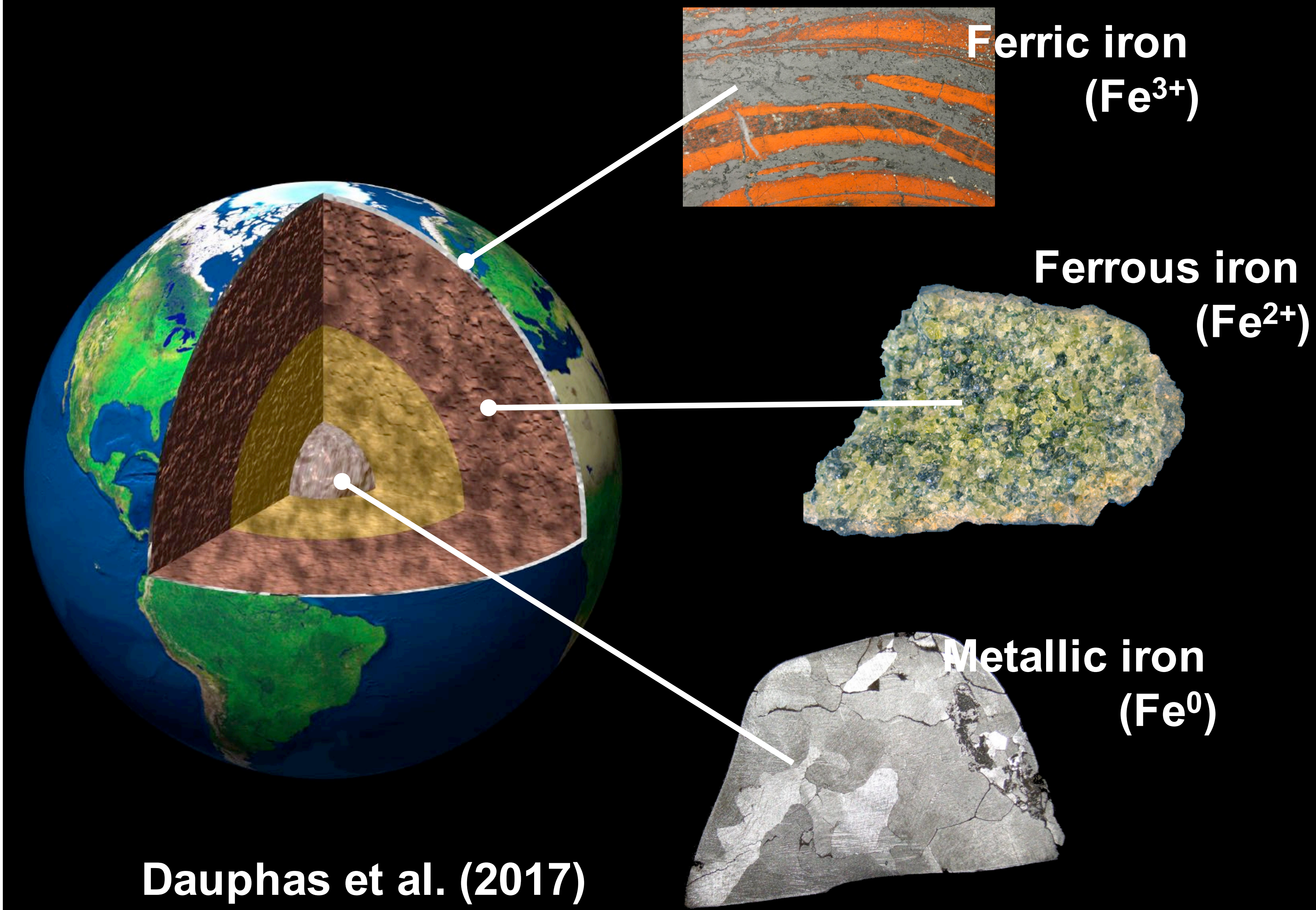
Introduction to isotope fractionation and SciPhon

Nicolas Dauphas
dauphas@uchicago.edu



Origins Laboratory
Department of the Geophysical Sciences and Enrico Fermi Institute
The University of Chicago



Dauphas et al. (2017)

Primer on isotopic fractionation

$$\delta^{56}\text{Fe} = \left[\frac{\left(^{56}\text{Fe}/^{54}\text{Fe}\right)_{\text{sample}}}{\left(^{56}\text{Fe}/^{54}\text{Fe}\right)_{\text{standard}}} - 1 \right] \times 1000$$

δ^{56}Fe is the deviation in part permil of the ^{56}Fe/^{54}Fe ratio of a sample relative to that of some reference material

Example:
15.6994 *vs*. 15.6979
=0.1‰ fractionation

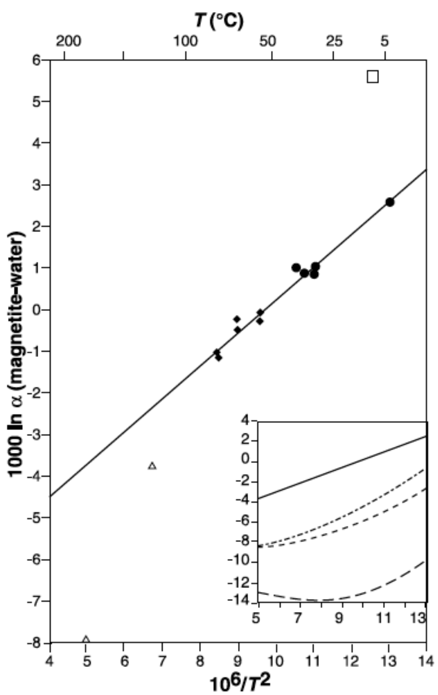
Dauphas & Rouxel (2006) Mass spectrometry and natural variations of iron isotopes. Mass Spectrom. Rev. 25, 515-550.

Uses of iron isotopes

Oxygen and Iron Isotope Studies of Magnetite Produced by Magnetotactic Bacteria

Kevin W. Mandernack,[1*] Dennis A. Bazylinski,[2]
Wayne C. Shanks III,[3] Thomas D. Bullen[4]

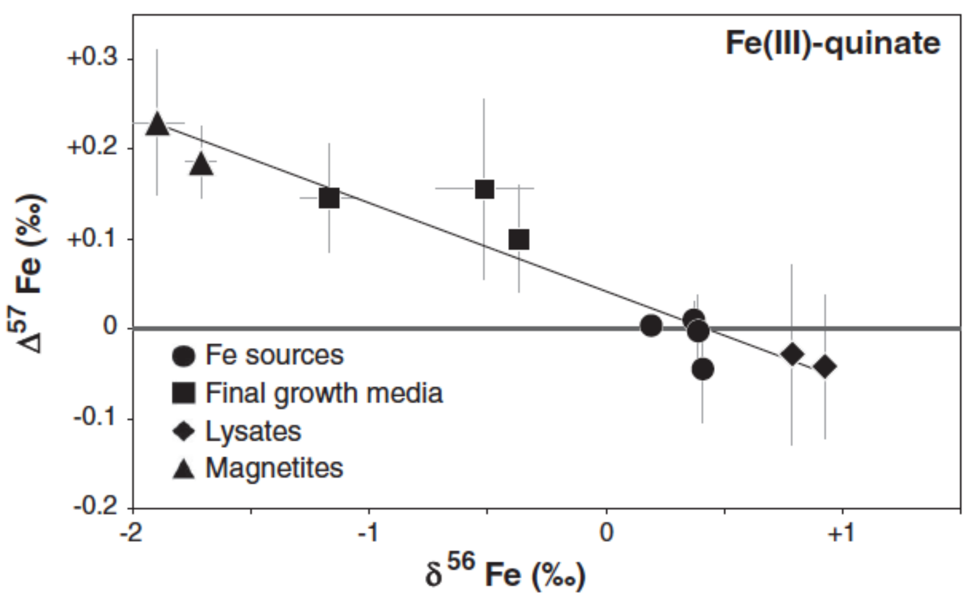
Science 1999



Mass-dependent and -independent signature of Fe isotopes in magnetotactic bacteria

Matthieu Amor,[1,2*] Vincent Busigny,[1*] Pascale Louvat,[1] Alexandre Gélabert,[1]
Pierre Cartigny,[1] Mickaël Durand-Dubief,[3] Georges Ona-Nguema,[2]
Edouard Alphandéry,[2,3] Imène Chebbi,[3] François Guyot[2]

Science 2016

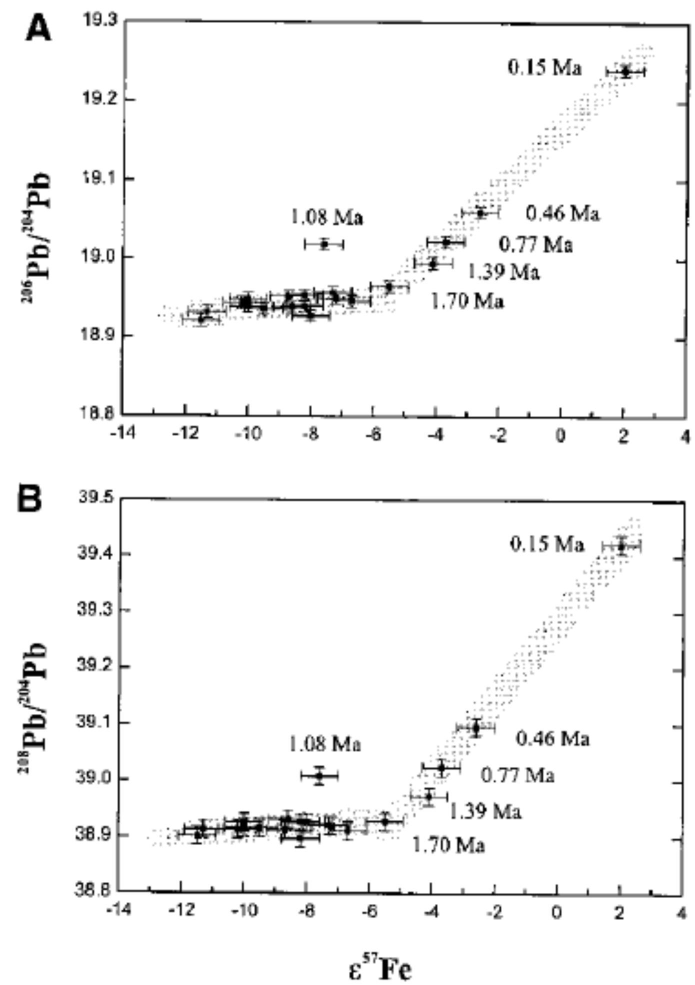


Uses of iron isotopes

Secular Variation of Iron Isotopes in North Atlantic Deep Water

Xiang-Kun Zhu,* R. Keith O'Nions, Yueling Guo, Ben C. Reynolds

Science 2000

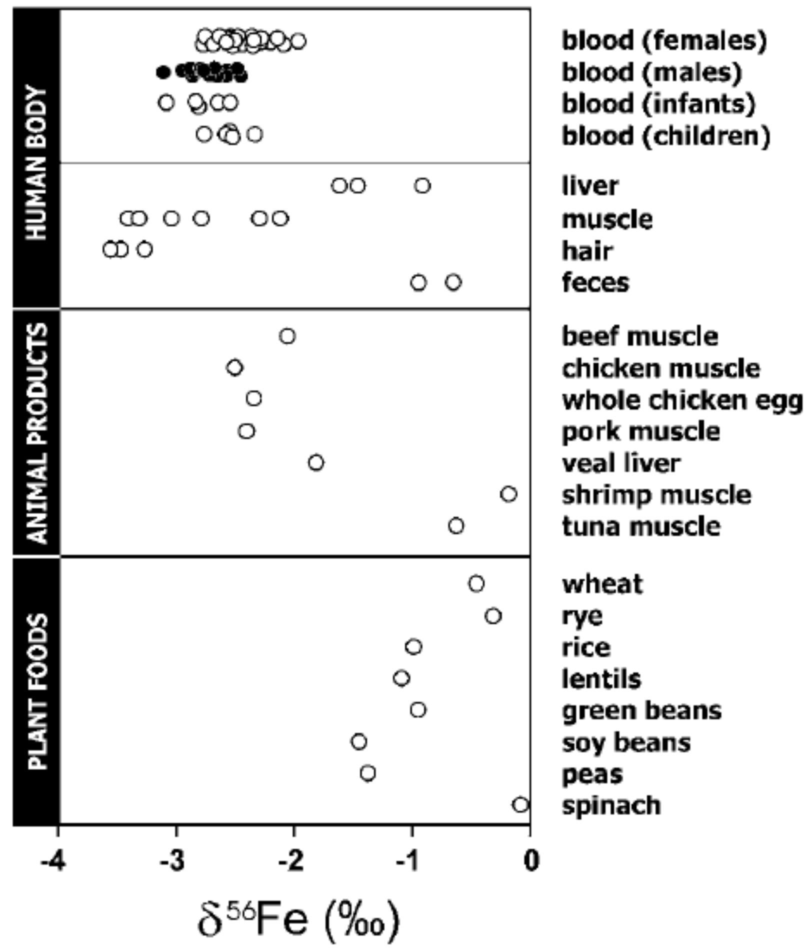


Uses of iron isotopes

Natural Iron Isotope Variations in Human Blood

Thomas Walczyk[1]* and Friedhelm von Blanckenburg[2]†

Science 2002

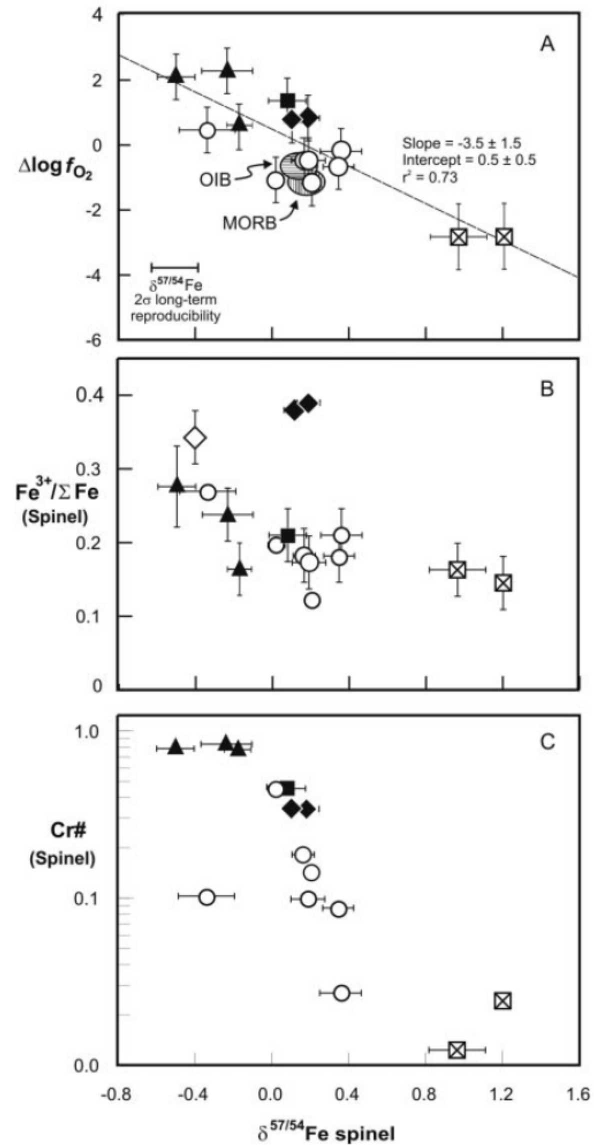


Uses of iron isotopes

Iron Isotope Fractionation and the Oxygen Fugacity of the Mantle

Helen M. Williams,[1]* Catherine A. McCammon,[2]
Anne H. Peslier,[3] Alex N. Halliday,[1] Nadya Teutsch,[1]
Sylvain Levasseur,[1] Jean-Pierre Burg[1]

Science 2004

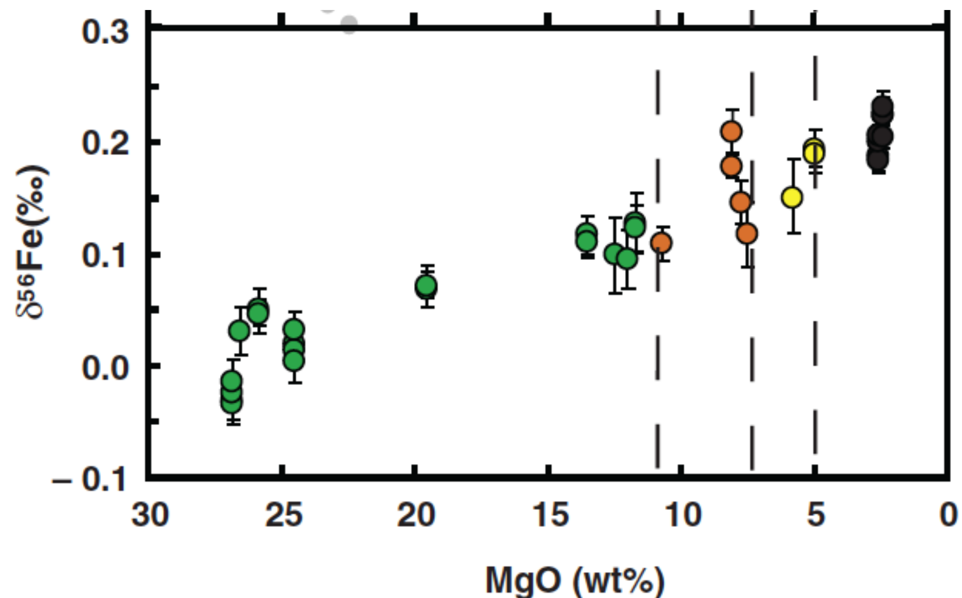


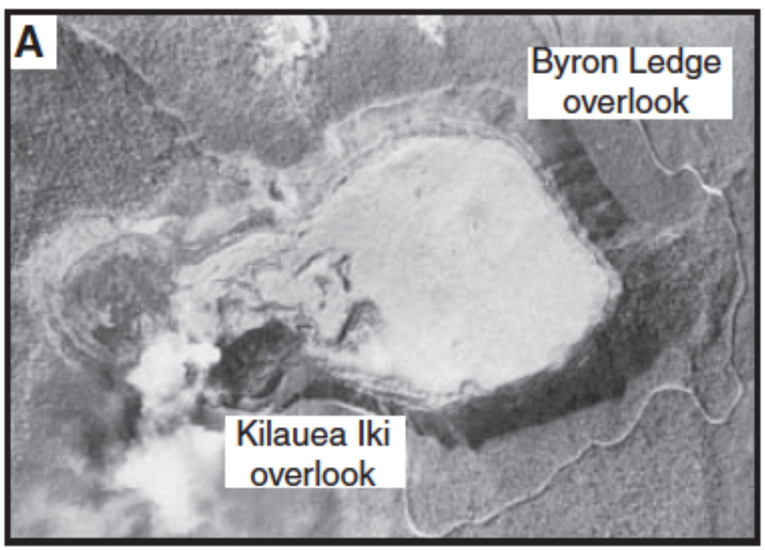
Uses of iron isotopes

Iron Isotope Fractionation During Magmatic Differentiation in Kilauea Iki Lava Lake

Fang-Zhen Teng,[1]*† Nicolas Dauphas,[1] Rosalind T. Helz[2]

Science 2008



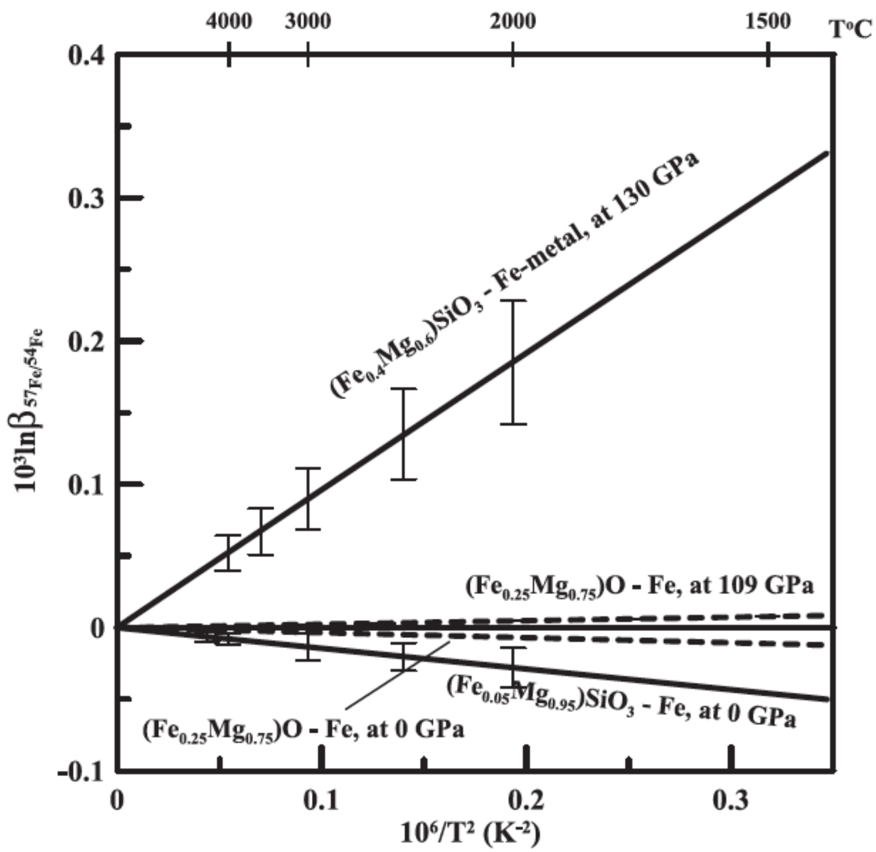


Uses of iron isotopes

Equilibrium Iron Isotope Fractionation at Core-Mantle Boundary Conditions

Veniamin B. Polyakov

Science 2009

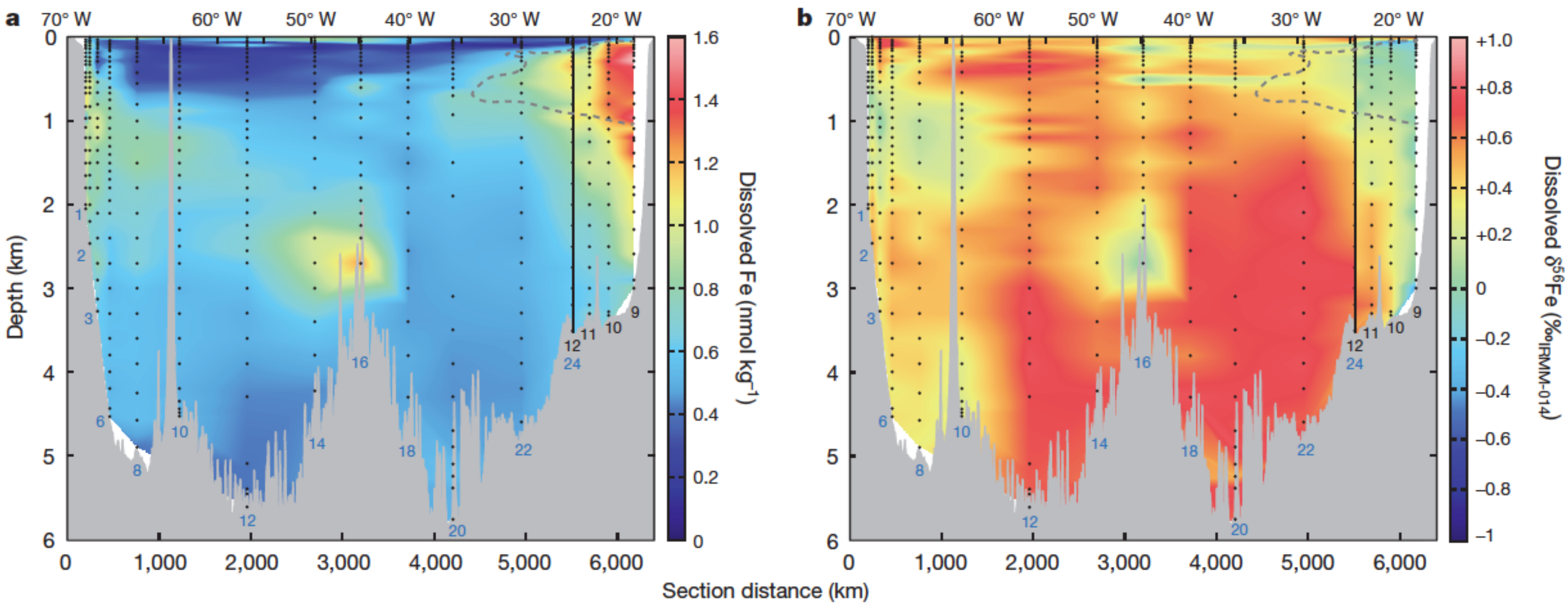


Uses of iron isotopes

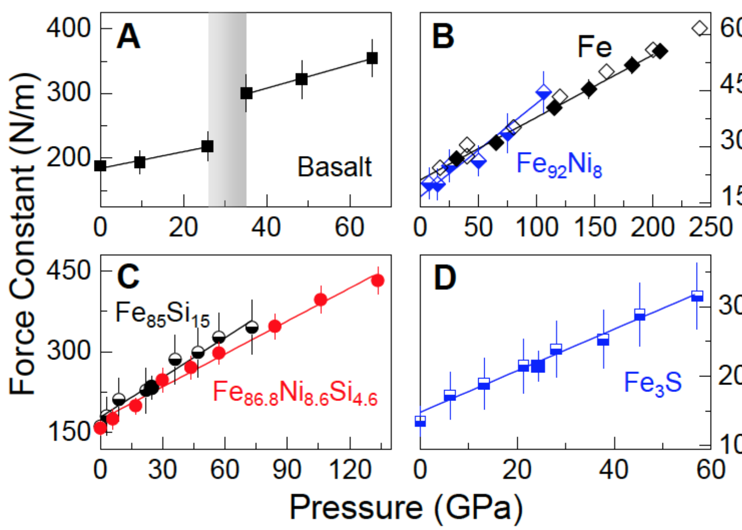
Quantification of dissolved iron sources to the North Atlantic Ocean

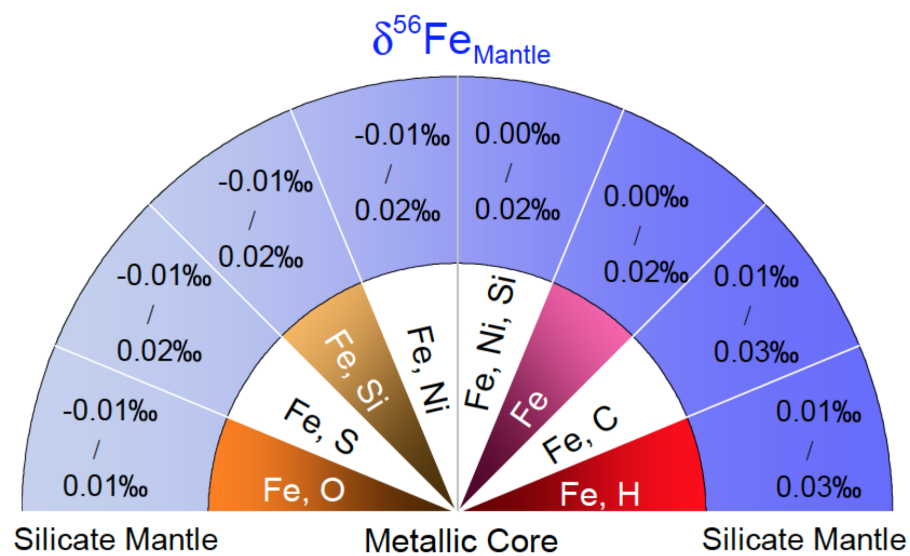
Tim M. Conway[1]† & Seth G. John[1]

Nature 2014



Uses of iron isotopes





Science 2016

Pressure-dependent isotopic composition of iron alloys

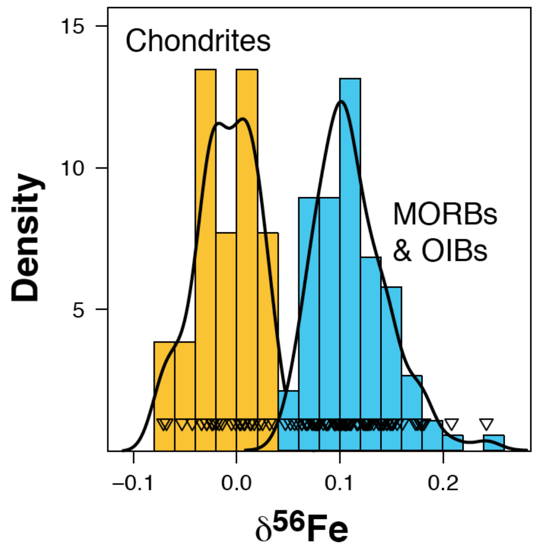
A. Shahar,[1]* E. A. Schauble,[2] R. Caracas,[3] A. E. Gleason,[4] M. M. Reagan,[5] Y. Xiao,[6] J. Shu,[1] W. Mao[5]

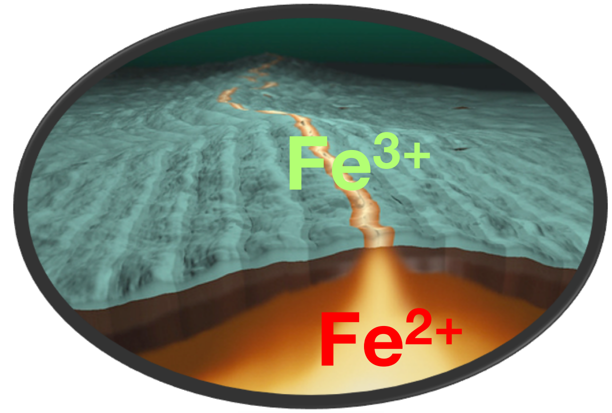
Nature Communications 2016

Liu et al. (in revision)

Motivation

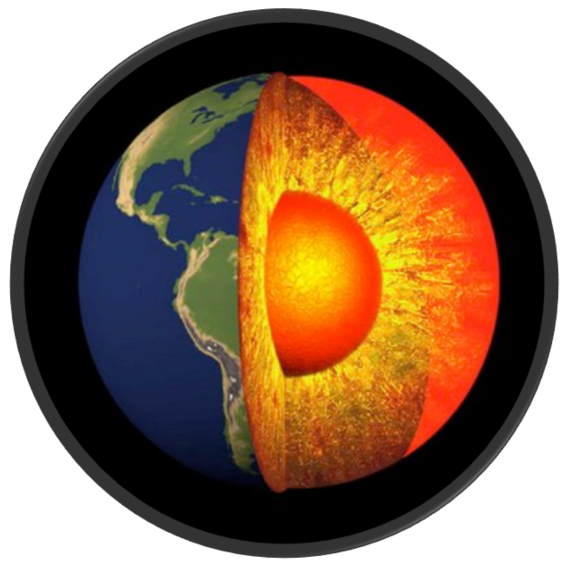
Teng *et al.* 13





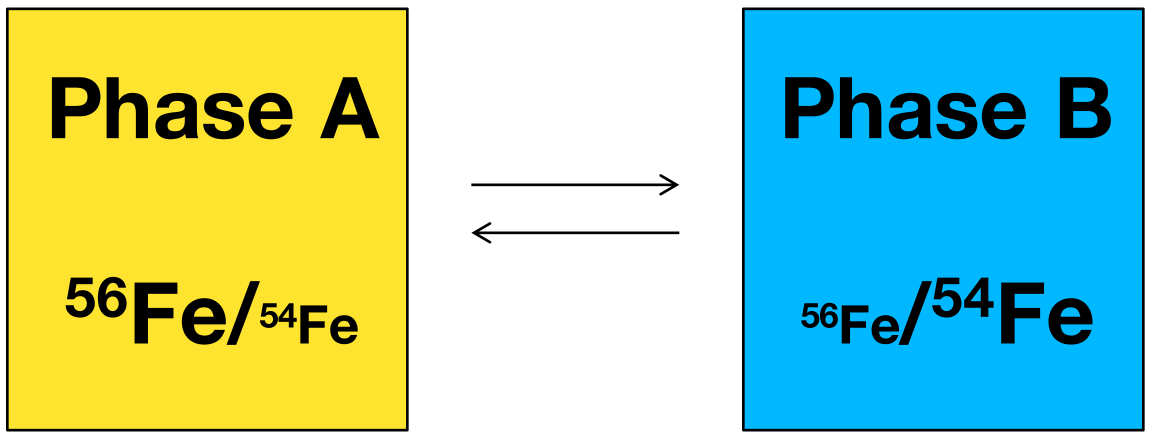
Mantle melting
(Williams *et al.* 05, Weyer & Ionov 07, Dauphas *et al.* 09)

Evaporation
(Poitrasson *et al.* 04)



Metal-silicate partitioning
(Polyakov 09)

Equilibrium isotopic fractionation



How do iron isotopes partition between coexisting phases at equilibrium?

Equilibrium isotopic fractionation

FeX *vs*. Fe_g

$$^{56}Fe_g + ^{54}FeX \rightleftharpoons ^{54}Fe_g + ^{56}FeX$$

$$K_{eq} = \frac{[^{54}Fe_g][^{56}FeX]}{[^{56}Fe_g][^{54}FeX]} = \frac{[^{56}FeX]/[^{54}FeX]}{[^{56}Fe_g]/[^{54}Fe_g]} = \frac{(^{56}Fe/^{54}Fe)_{FeX}}{(^{56}Fe/^{54}Fe)_{Fe_g}}$$

$$K_{eq} = e^{\frac{-\Delta_R G}{RT}}$$

$$K_{eq} = e^{\frac{-\Delta F}{RT}}$$

$$F = -RT \ln(Q_{trans} \times Q_{rot} \times Q_{vib})$$

$$K_{eq} = e^{\sum_{products}(Q_{trans} \times Q_{rot} \times Q_{vib}) - \sum_{reactants}(Q_{trans} \times Q_{rot} \times Q_{vib})}$$

$$K_{eq} = \frac{\prod_{products} Q_{trans} \times Q_{rot} \times Q_{vib}}{\prod_{reactants} Q_{trans} \times Q_{rot} \times Q_{vib}}$$

Urey (1947); Bigeleisen and Mayer (1947)

Equilibrium isotopic fractionation

$$Q_{\mathrm{vib},i} = \frac{e^{-\frac{h\upsilon_i}{2kT}}}{1 - e^{-\frac{h\upsilon_i}{kT}}}$$

$$\mathrm{K_{eq}} = \prod_i \frac{u_i'}{u_i} \frac{e^{-u_i'/2}}{1 - e^{-u_i'}} \frac{1 - e^{-u_i}}{e^{-u_i/2}}$$

$$u_i = \frac{h\upsilon_i}{kT}$$

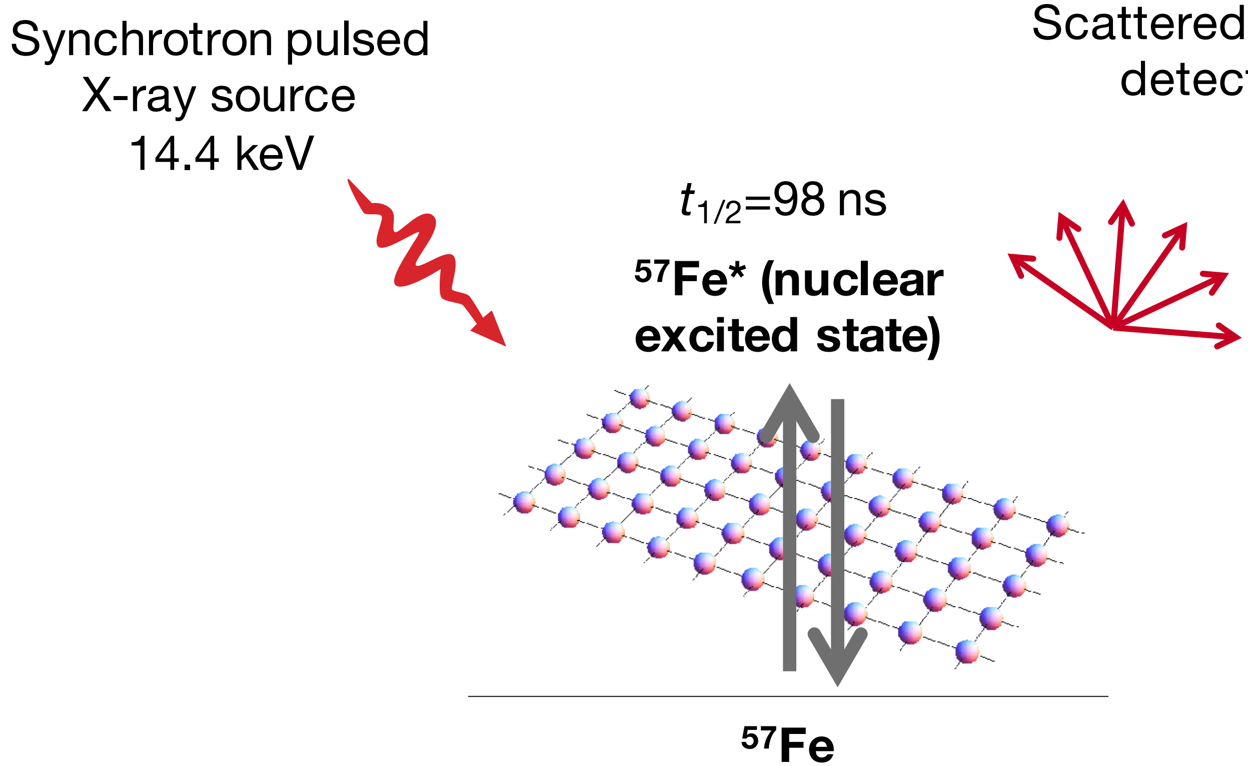
Equilibrium isotopic fractionation between a chemical compound and monoatomic gas is called the reduced partition function ratio and can be calculated from the vibration energies of the isotopic species

Reduced partition function ratio = β

Urey (1947); Bigeleisen and Mayer (1947)

NRIXS=Nuclear Resonant Inelastic X-ray Scattering

Sturhahn *et al.* 95
Seto *et al.* 95



β-factors in solids
(for harmonic potential)

Ratio of the masses of the isotopes involved (e.g., 56/54)

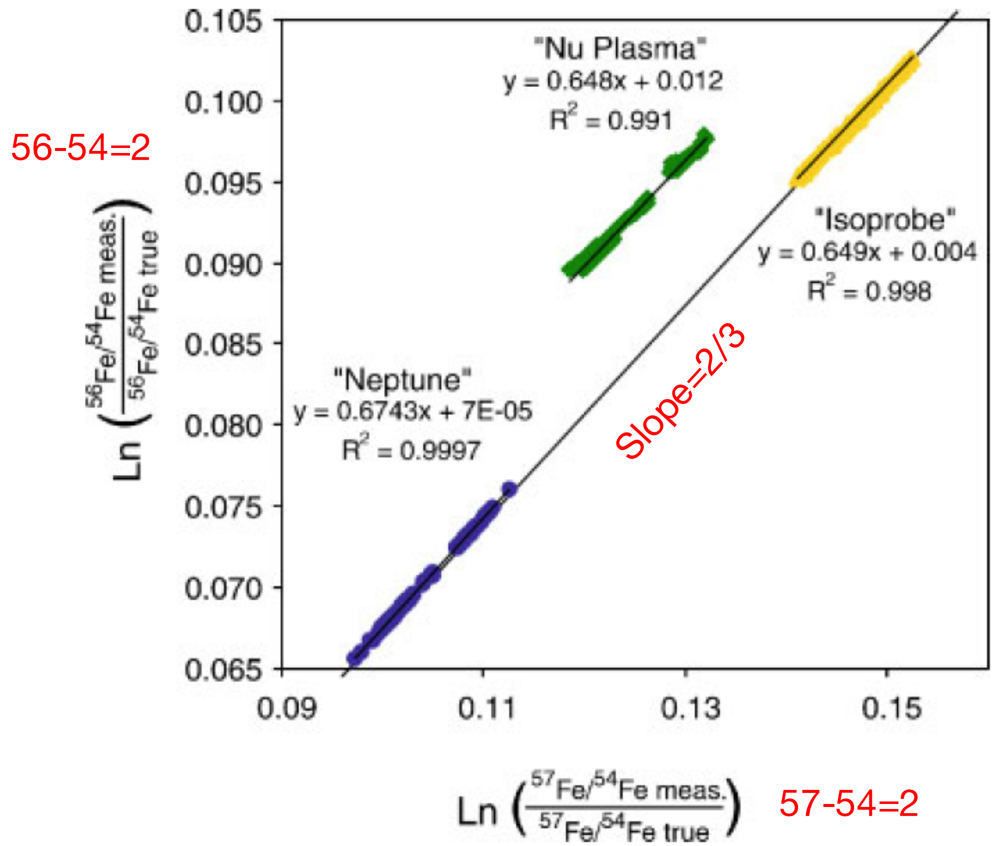
Iron partial phonon density of states (PDOS)

$$\ln \beta_{I/I^*} = \frac{3}{2}\left(\frac{M}{M^*} - 1\right)\int_0^{E_{\max}} \left(\frac{E}{2kT} + \frac{E/kT}{e^{E/kT} - 1} - 1\right) g(E)\, dE$$

Temperature at which one wants to calculate β

Polyakov et al. (2005)
Dauphas et al. (2012)

Mass-dependent fractionation



Dauphas and Rouxel (2006)

β-factors in solids

$$\ln \beta_{I/I^*} = \frac{3}{2}\left(\frac{M}{M^*} - 1\right)\int_0^{E_{\max}} \left(\frac{E}{2kT} + \frac{E/kT}{e^{E/kT} - 1} - 1\right) g(E)\, dE$$

To a very good approximation:

$$1000 \ln \beta_{I/I^*} \simeq 1000\left(\frac{M}{M^*} - 1\right)\left(\frac{m_2^g}{8k^2T^2} - \frac{m_4^g}{480k^4T^4} + \frac{m_6^g}{20{,}160k^6T^6}\right)$$

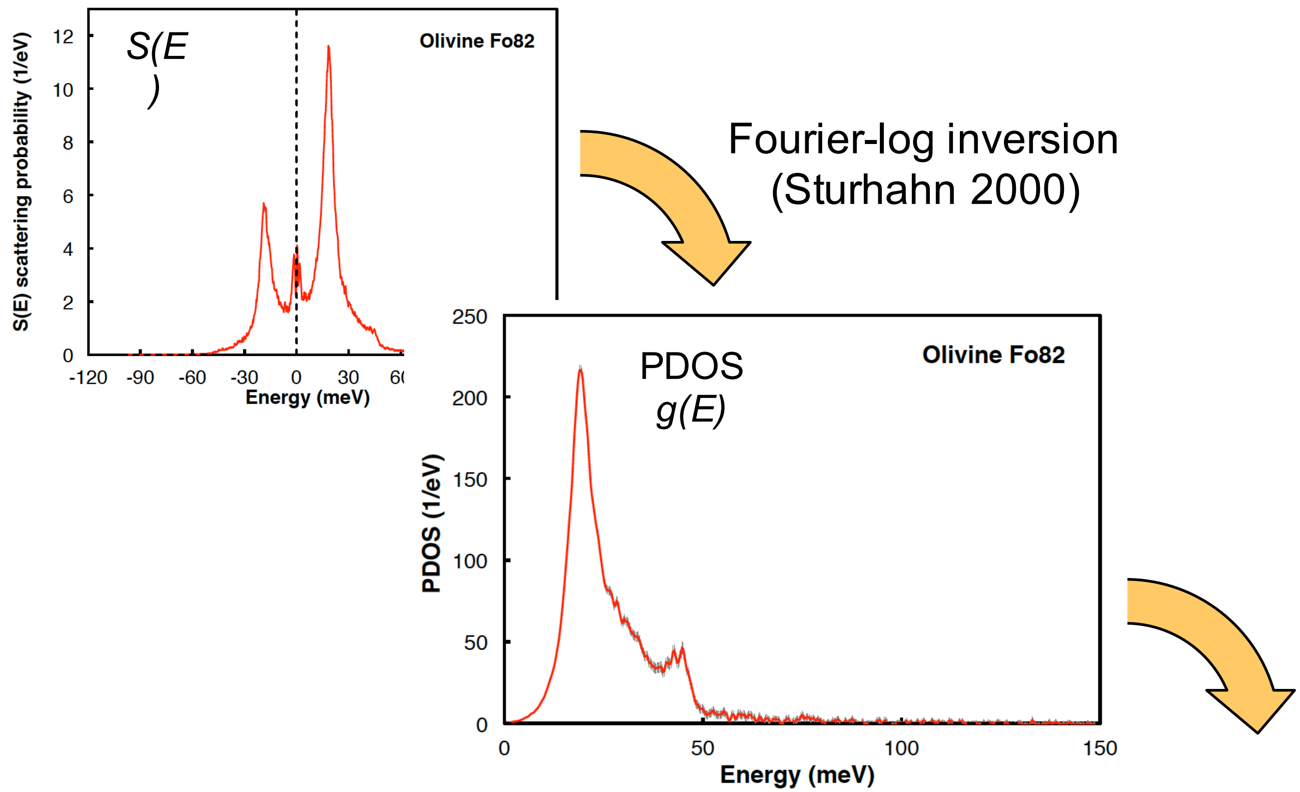
with

$$m_j^g = \int_0^{E_{\max}} E^j g(E)\, dE$$

j^{th} moment of g

Polyakov (2009)
Dauphas et al. (2012)

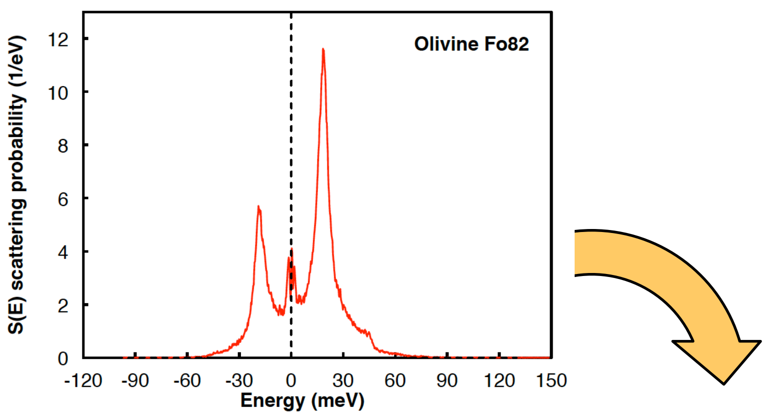
β-factors in solids



$$1000 \times \ln \beta_{I/I^*} \simeq 1000\left(\frac{M}{M^*}-1\right)\left(\frac{m_2^g}{8k^2T^2}-\frac{m_4^g}{480k^4T^4}+\frac{m_6^g}{20,160k^6T^6}\right)$$

β-factors in solids

Dauphas et al. (2012) and Hu et al. (2013) established relationships between the moments of S and g



$$1000 \times \ln \beta_{I/I^*} = 1000\left(\frac{M}{M^*} - 1\right) \times \frac{1}{E_r}\left[\frac{R_3^S}{8k^2T^2} - \frac{R_5^S - 10R_2^S R_3^S}{480k^4T^4} + \frac{R_7^S + 210(R_2^S)^2 R_3^S - 35R_3^S R_4^S - 21R_2^S R_5^S}{20,160k^6T^6}\right]$$

$$R_j^S = \int_{-\infty}^{+\infty} S(E)(E - E_R)^j \mathrm{d}E$$

High temperature approximation

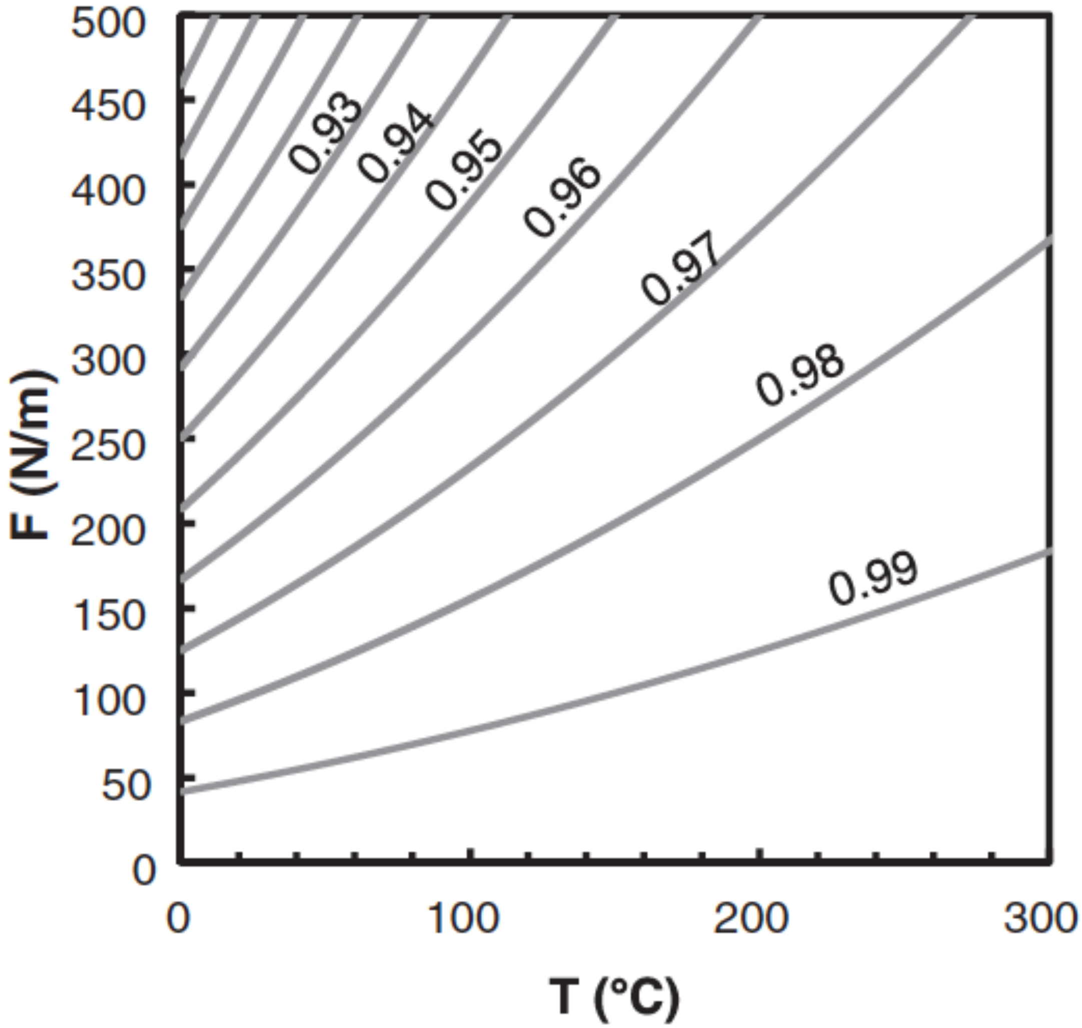
The sum rules of Lipkin (1995, 1999) identify the first terms with the mean force constant of iron bonds

$$1000 \times \ln\ \beta_{I/I^*} = 1000\left(\frac{1}{M^*} - \frac{1}{M}\right)\frac{\hbar^2}{8k^2T^2}\langle F\rangle$$

$$\langle F\rangle = \frac{M}{\hbar^2}\int_0^{+\infty} E^2 g(E)\mathrm{d}E = \frac{M}{E_R\hbar^2}\int_{-\infty}^{+\infty}(E - E_R)^3 S(E)\mathrm{d}E$$

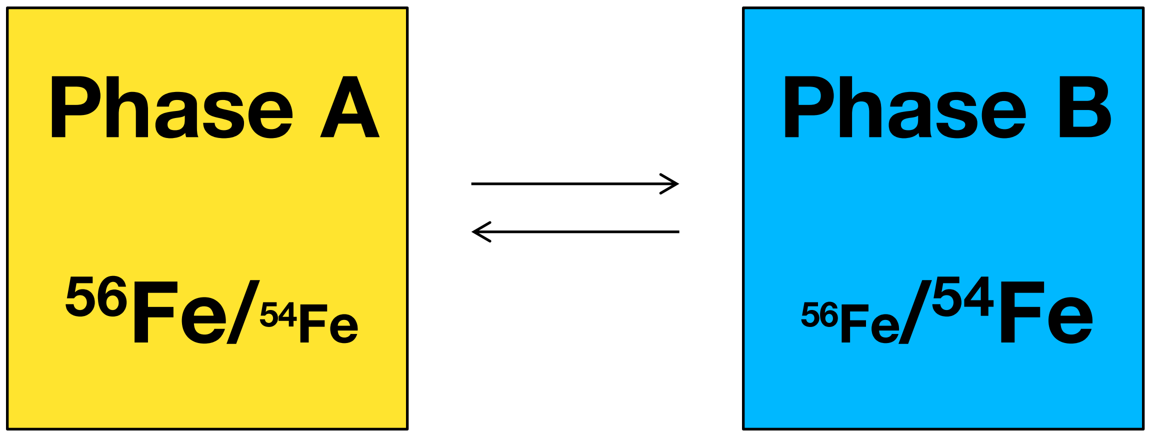
… a familiar formula in isotope geochemistry (Herzfeld and Teller, 1938; Bigeleisen and Mayer, 1947)

High temperature approximation



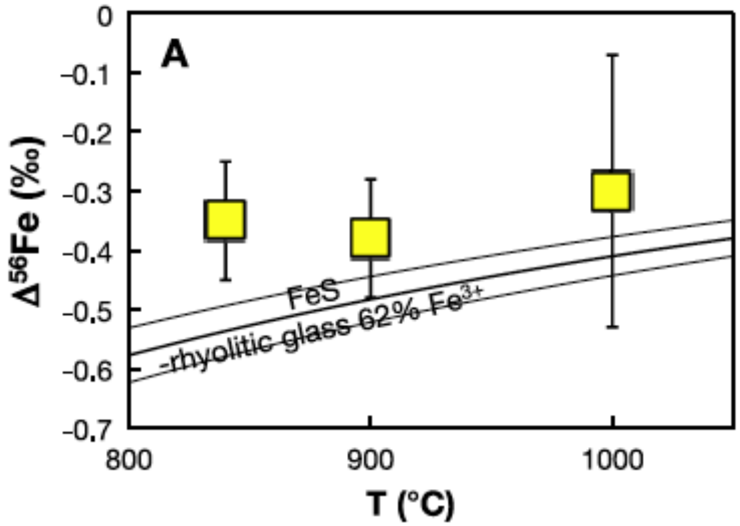
A good approximation for iron

Equilibration experiments

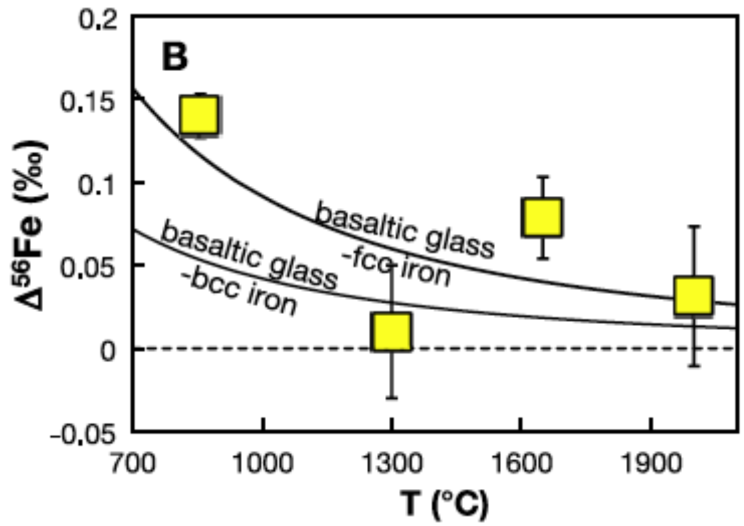


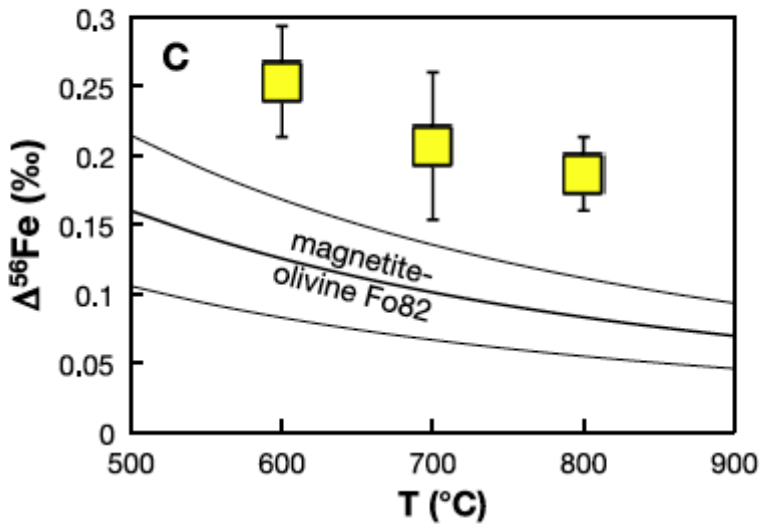
Method comparison

Data: Schuessler et al. (2007)
FC: Krawczynski et al. (2014), Dauphas et al. (2014)

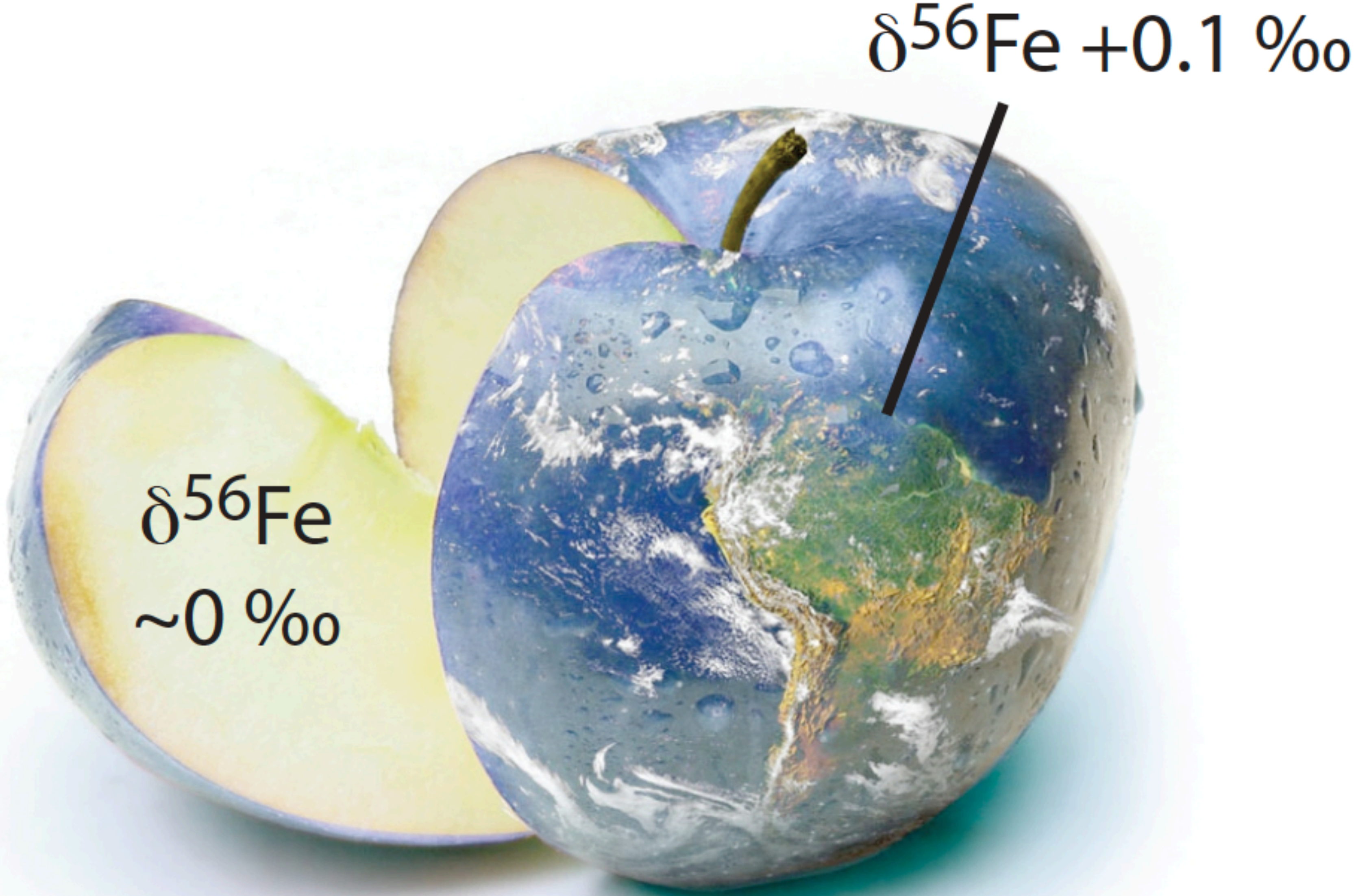


Data: Poitrasson et al. (2009), Hin et al. (2012),
Jordan and Young (2014), Shahar et al. (2013)
FC: Krawczynski et al. (2014), Dauphas et al. (2012)



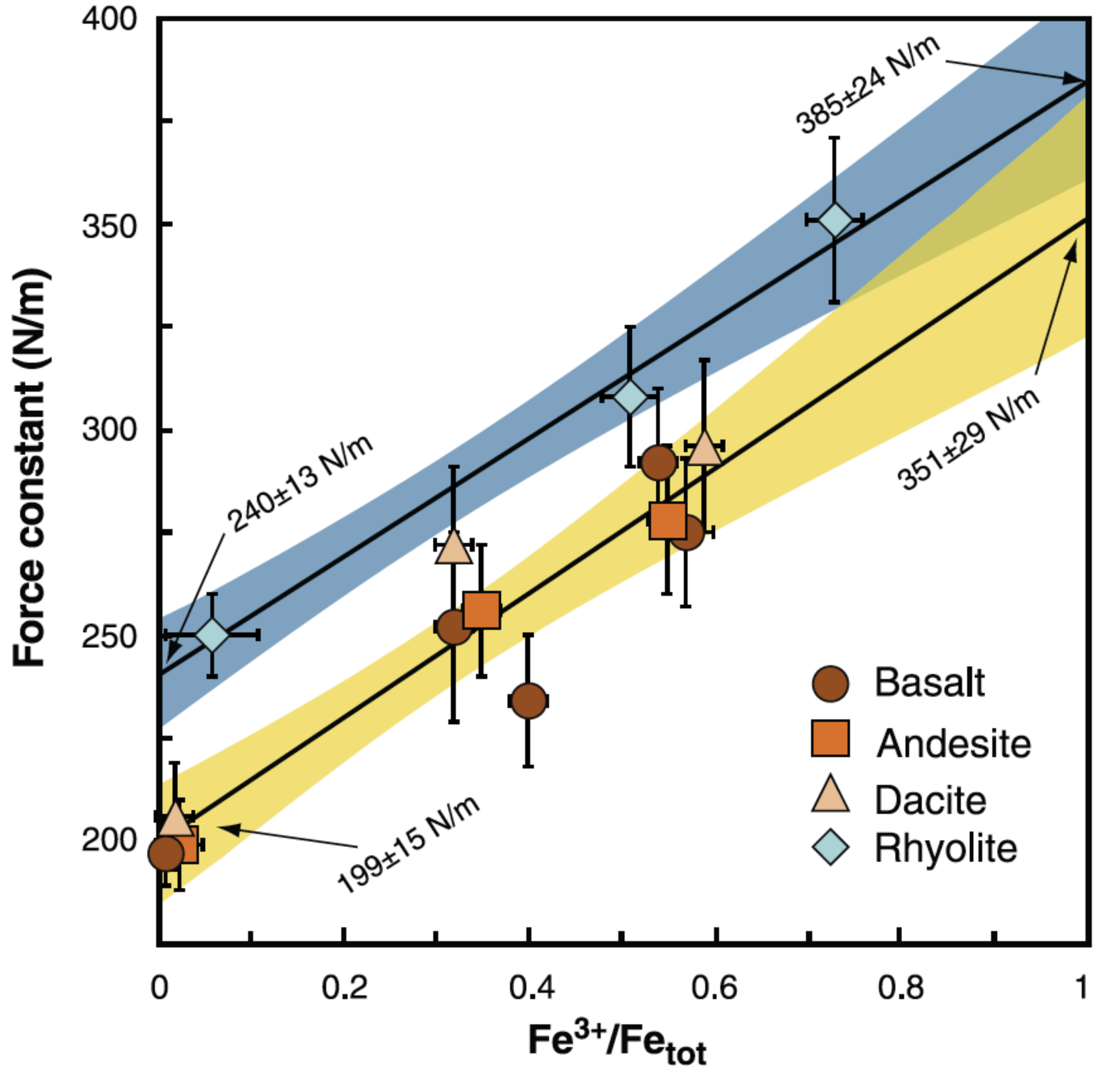


Data: Shahar et al. (2008)
FC: Polyakov et al. (2007), Dauphas et al. (2012, 2014)



Why does Earth's crust have different iron isotopic composition than the mantle, other planetary crusts, and chondrites?

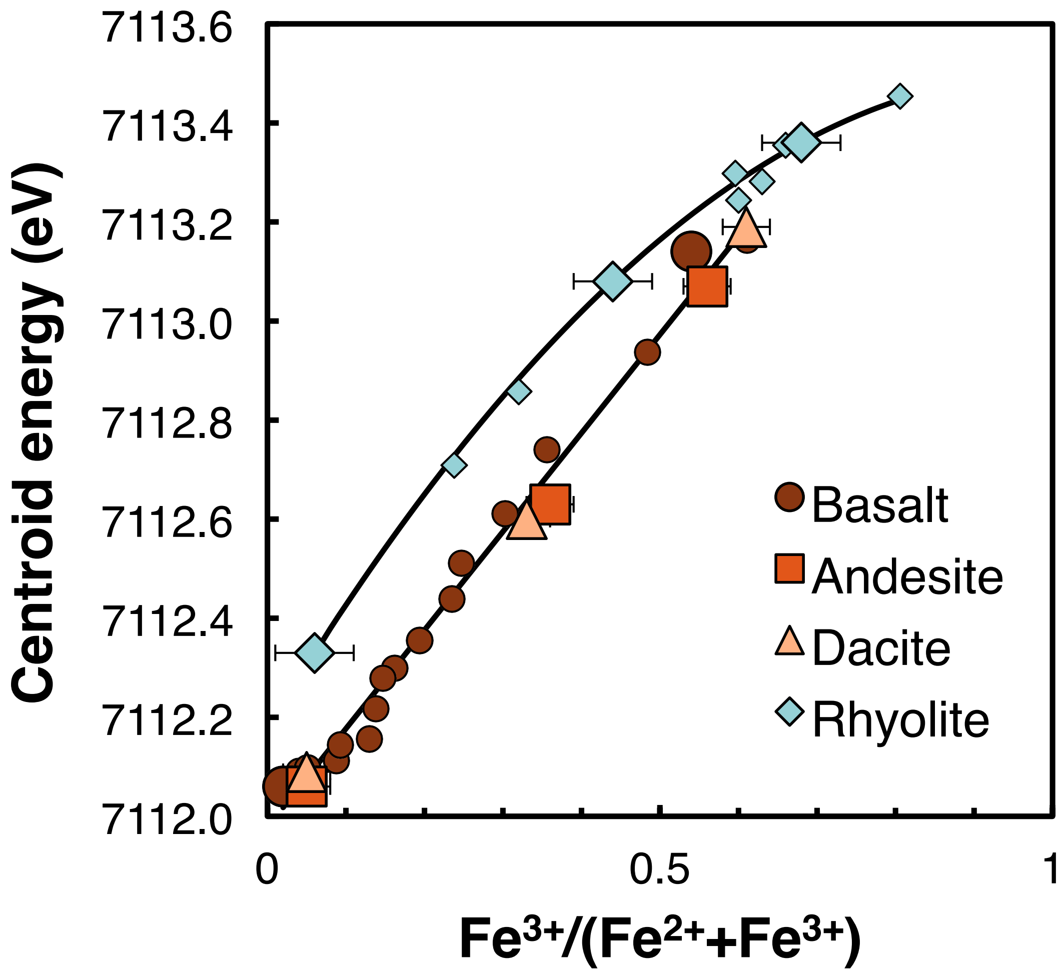
Force constant results



Dauphas et al. (2014)

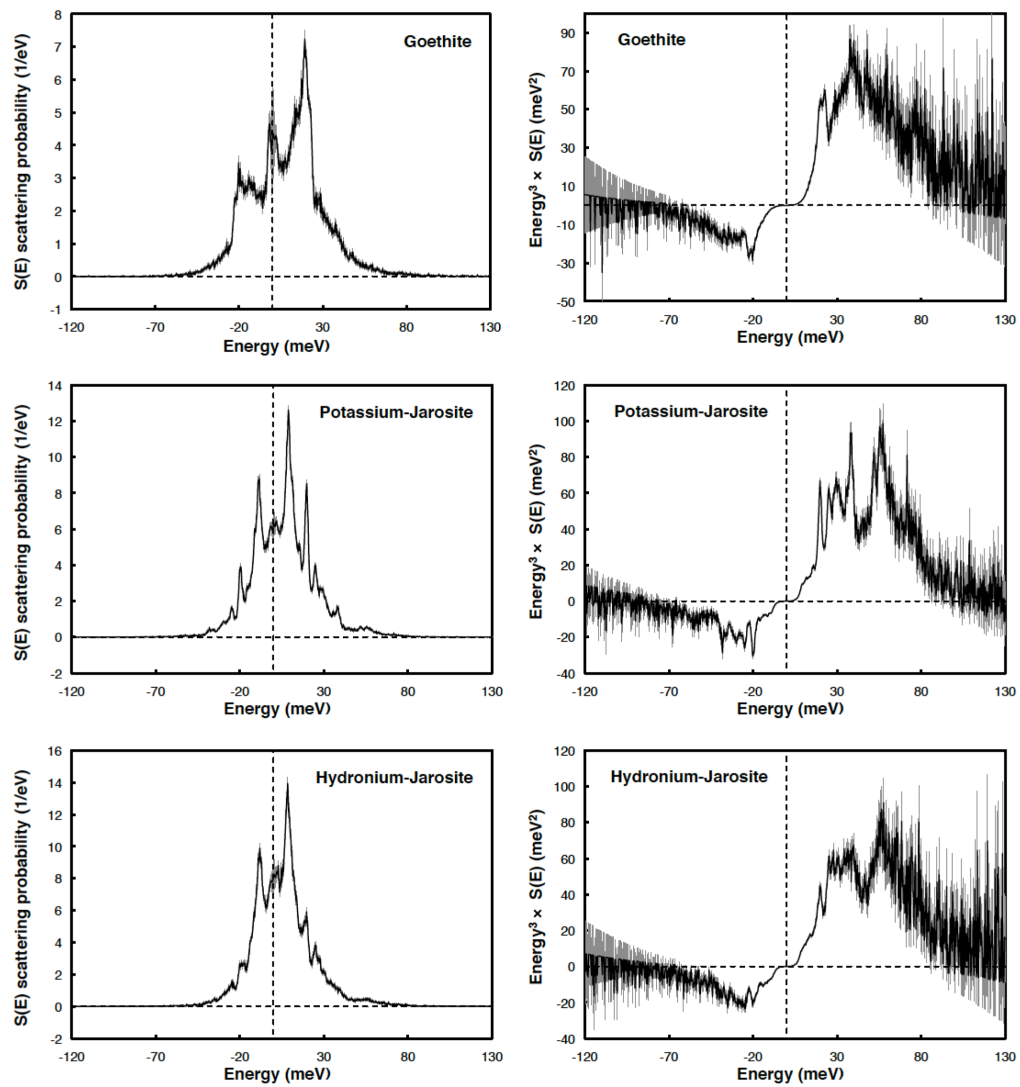
Redox and structural controls in glasses

XANES



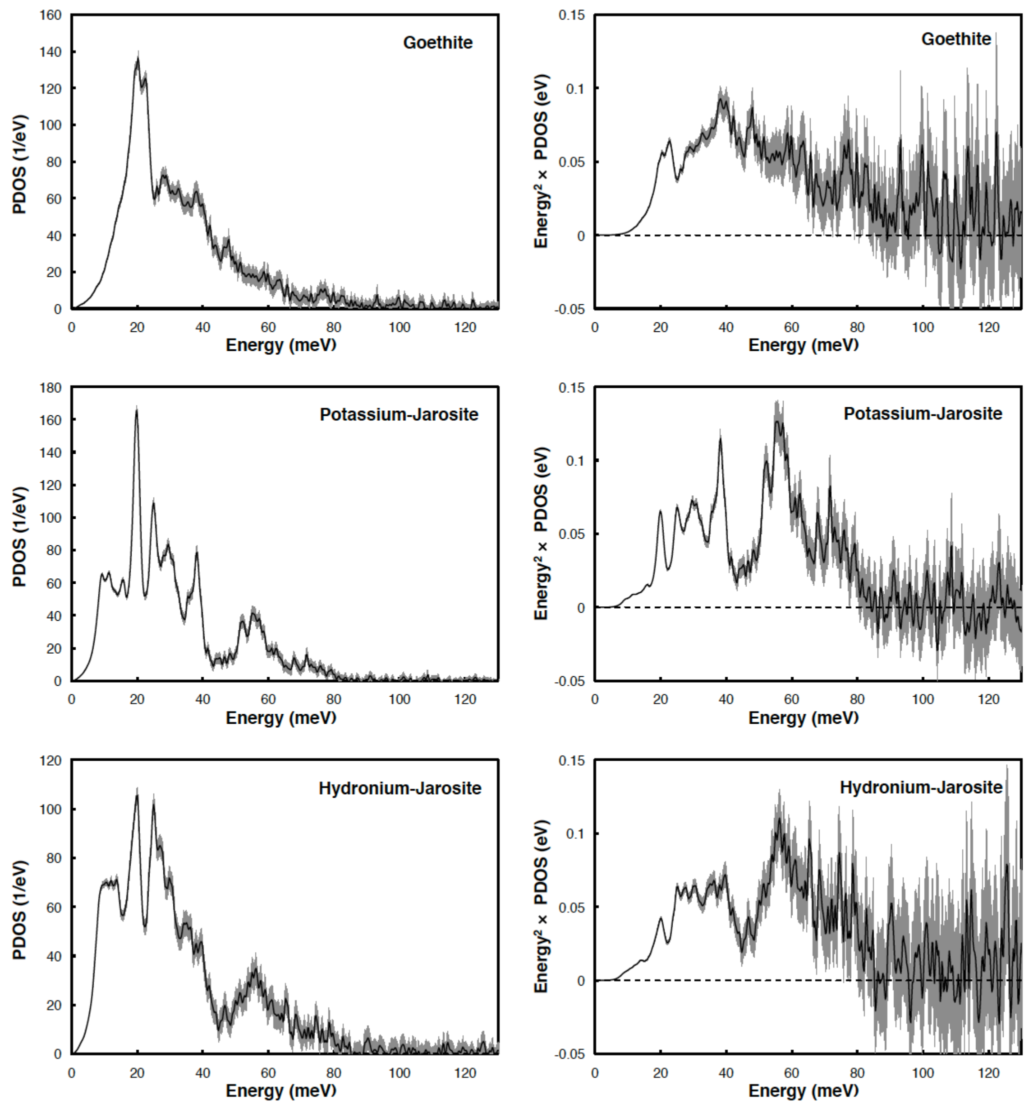
Cottrell *et al.* 09, Dauphas *et al.* (2014)

Difficulties with force constant measurements



$$\langle F \rangle \propto R_3^S$$

Difficulties with force constant measurements



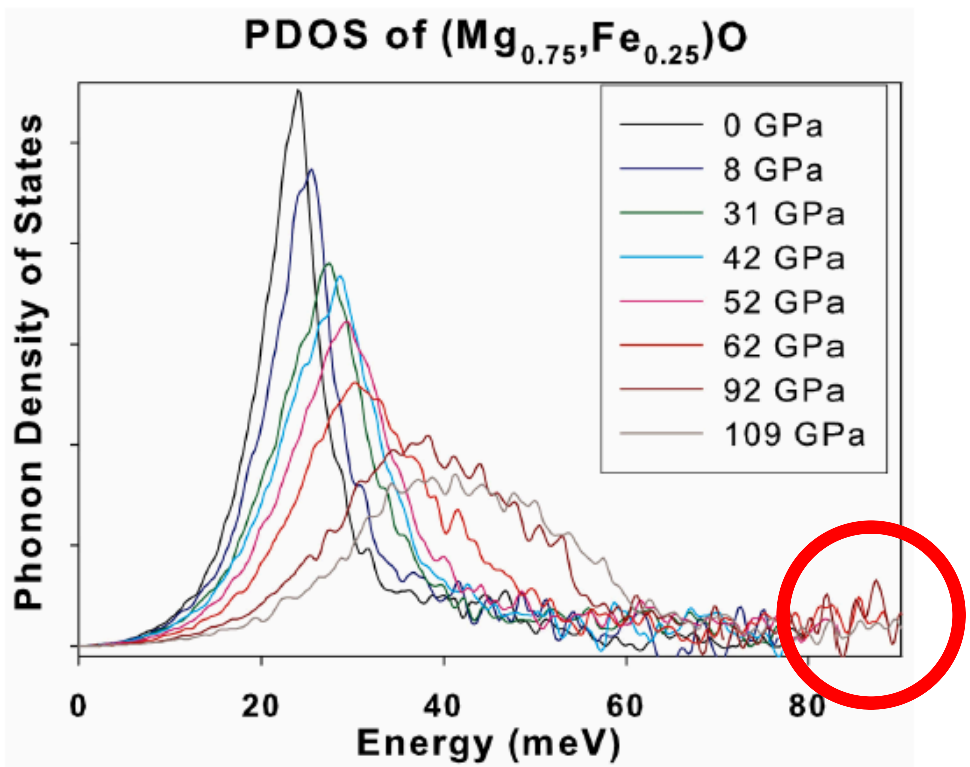
$$\langle F \rangle \propto m_2^g$$

A word of caution with published data

Equilibrium Iron Isotope Fractionation at Core-Mantle Boundary Conditions

Veniamin B. Polyakov

13 FEBRUARY 2009 VOL 323 SCIENCE www.sciencemag.org

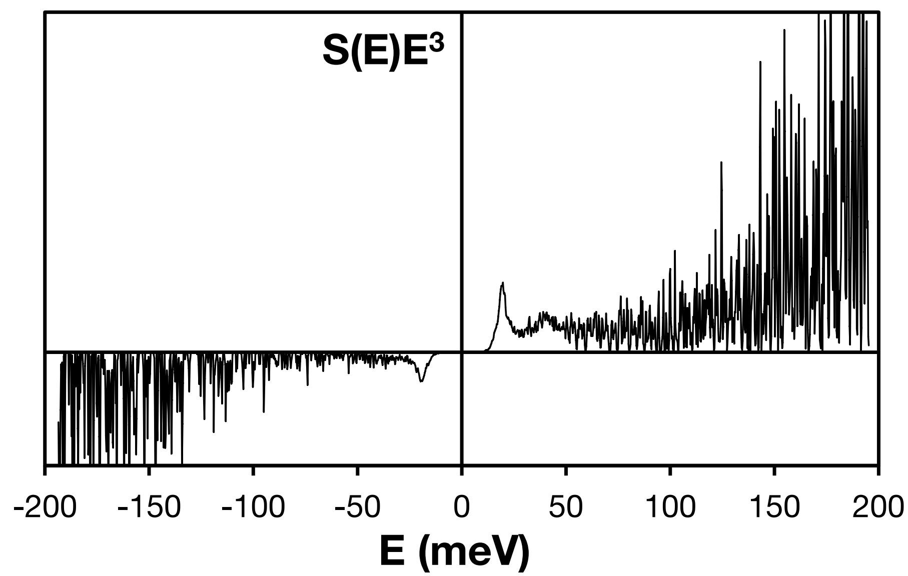


Lin et al. (2006)

Unaccounted baseline in NRIXS

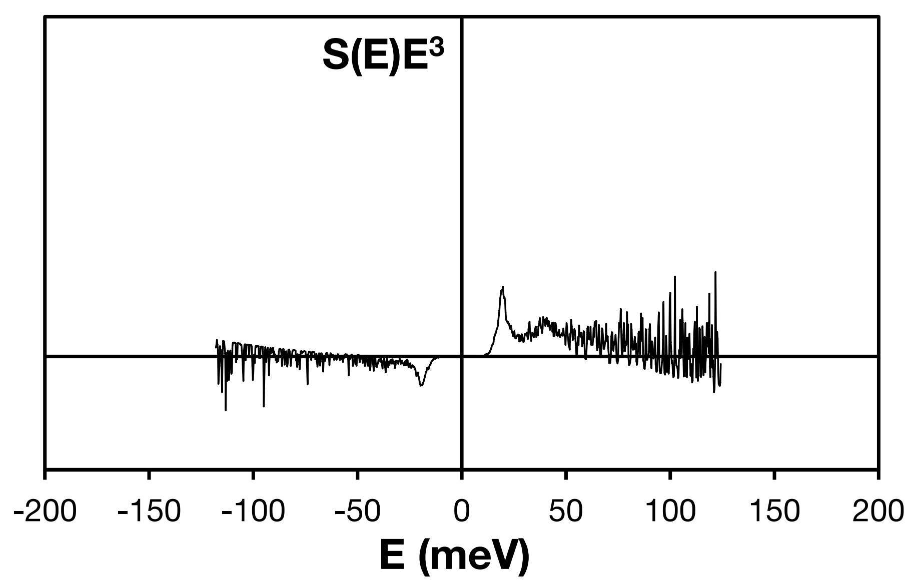
No baseline subtraction

<F> = 968±128 N/m

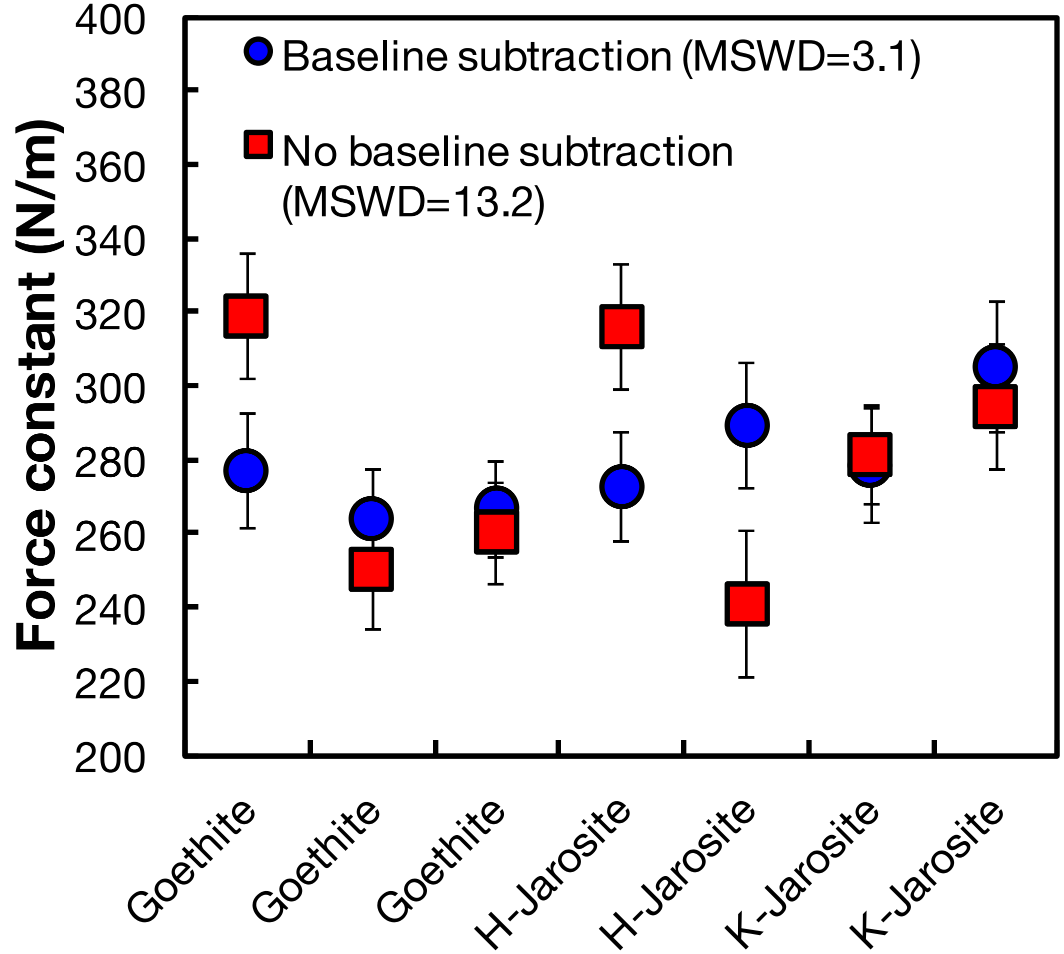


Baseline subtraction with SciPhon

<F> = 213±36 N/m



Baseline subtraction



Improves the session-to-session long term reproducibility

Error propagation in derived quantities

- Counting statistics

- Parameters of the baseline $(a \pm \sigma a)x+(b \pm \sigma b)$
- Zero energy bin
- Energy scaling
- Bin-to-bin energy variations

Hu et al. (2013); Dauphas et al. (2014)

Motivations for SciPhon

1. Have a GUI interface

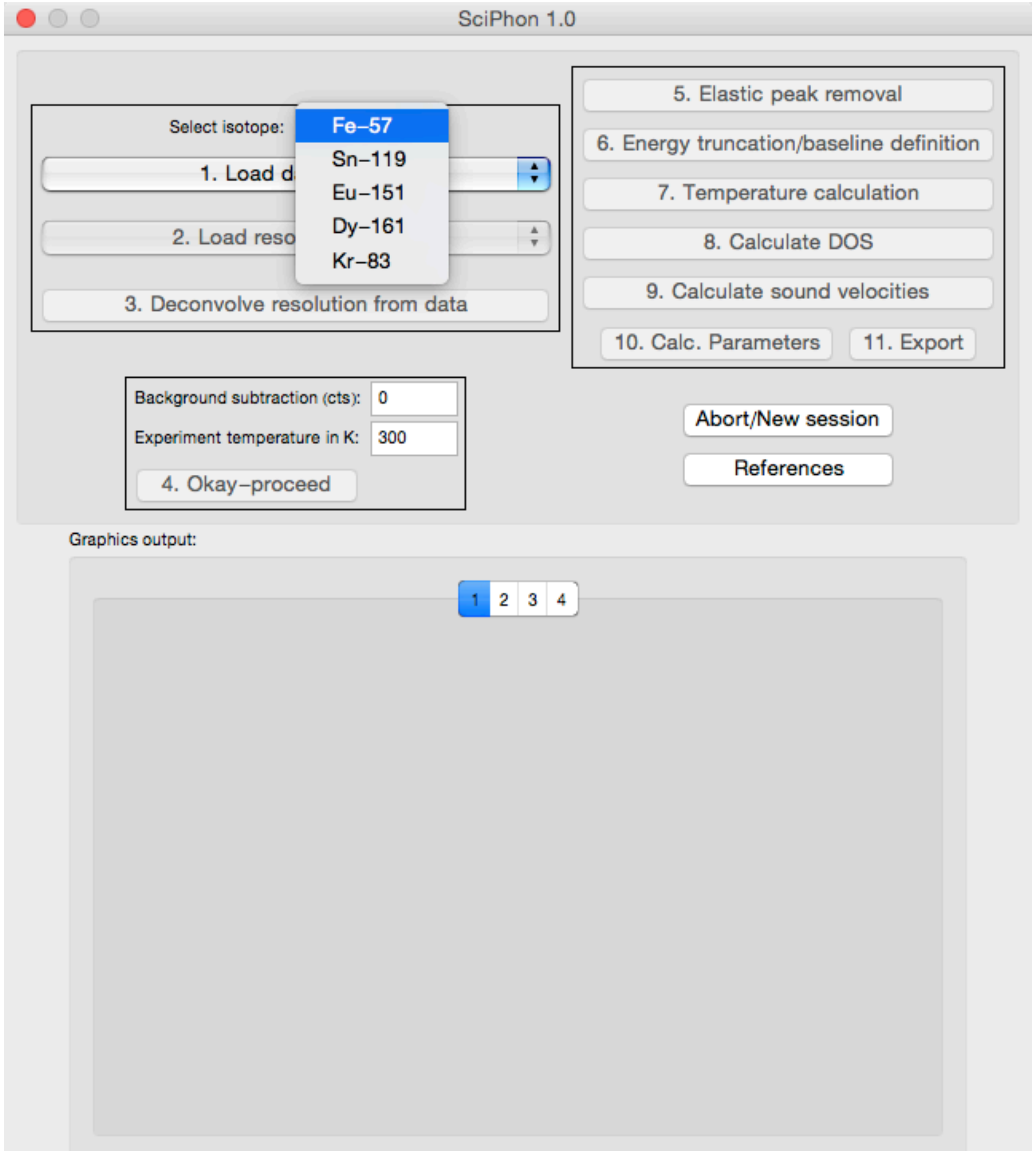
1. Streamline the baseline subtraction procedure

1. Propagate sources of uncertainties other than counting statistics

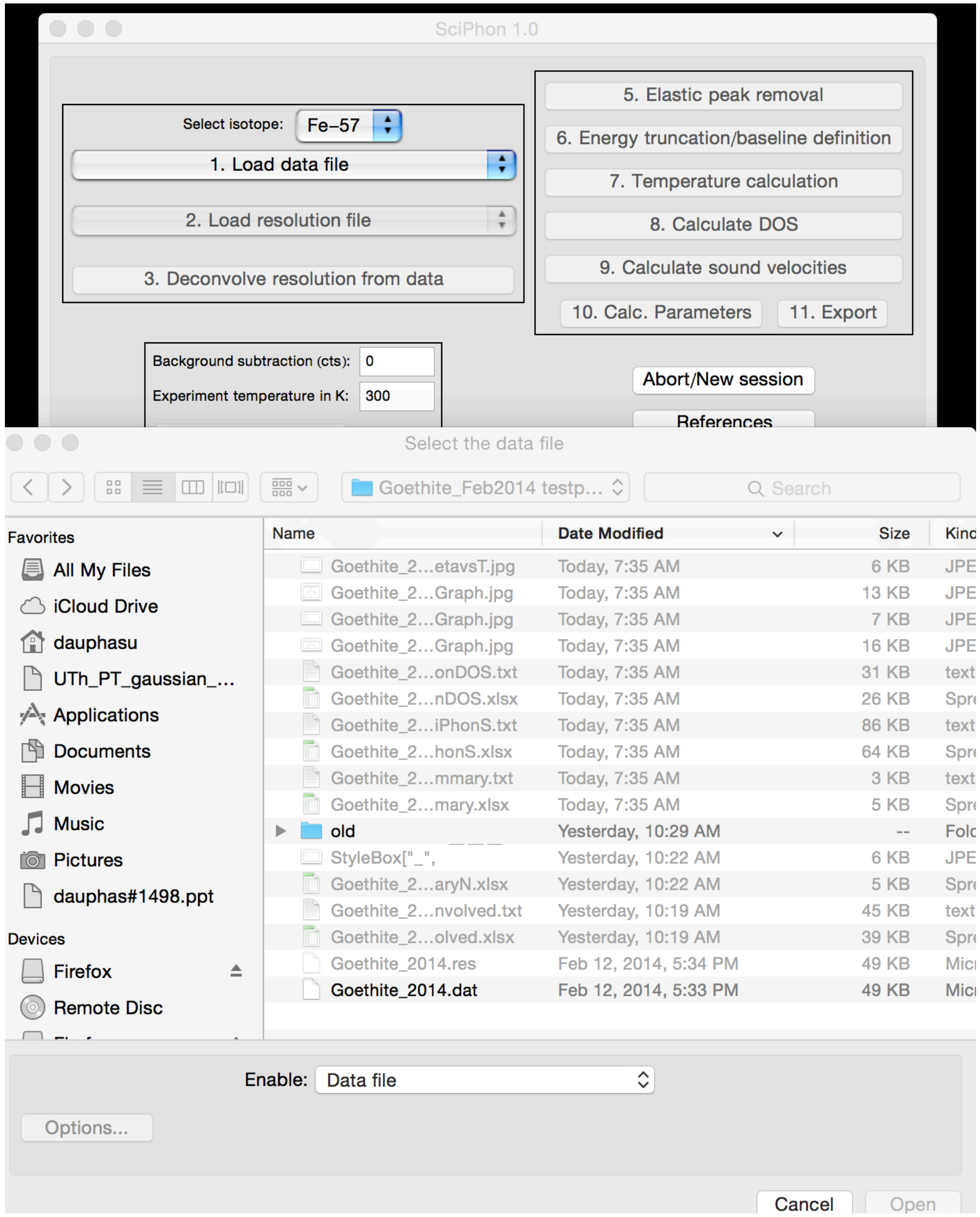
2. Output quantities directly usable in isotope geochemistry

SciPhon

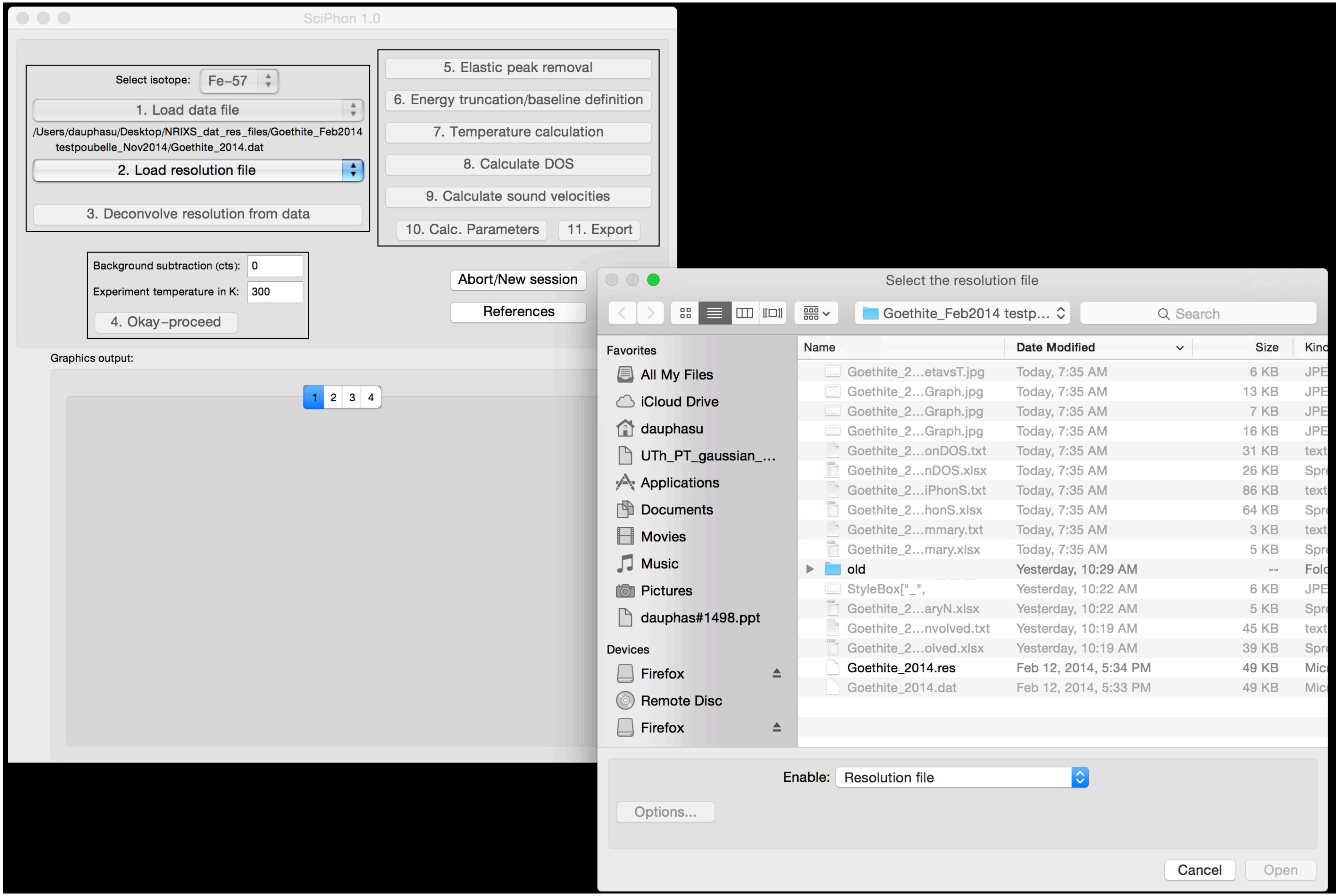
Select a Mossbauer isotope (^{57}Fe default choice)



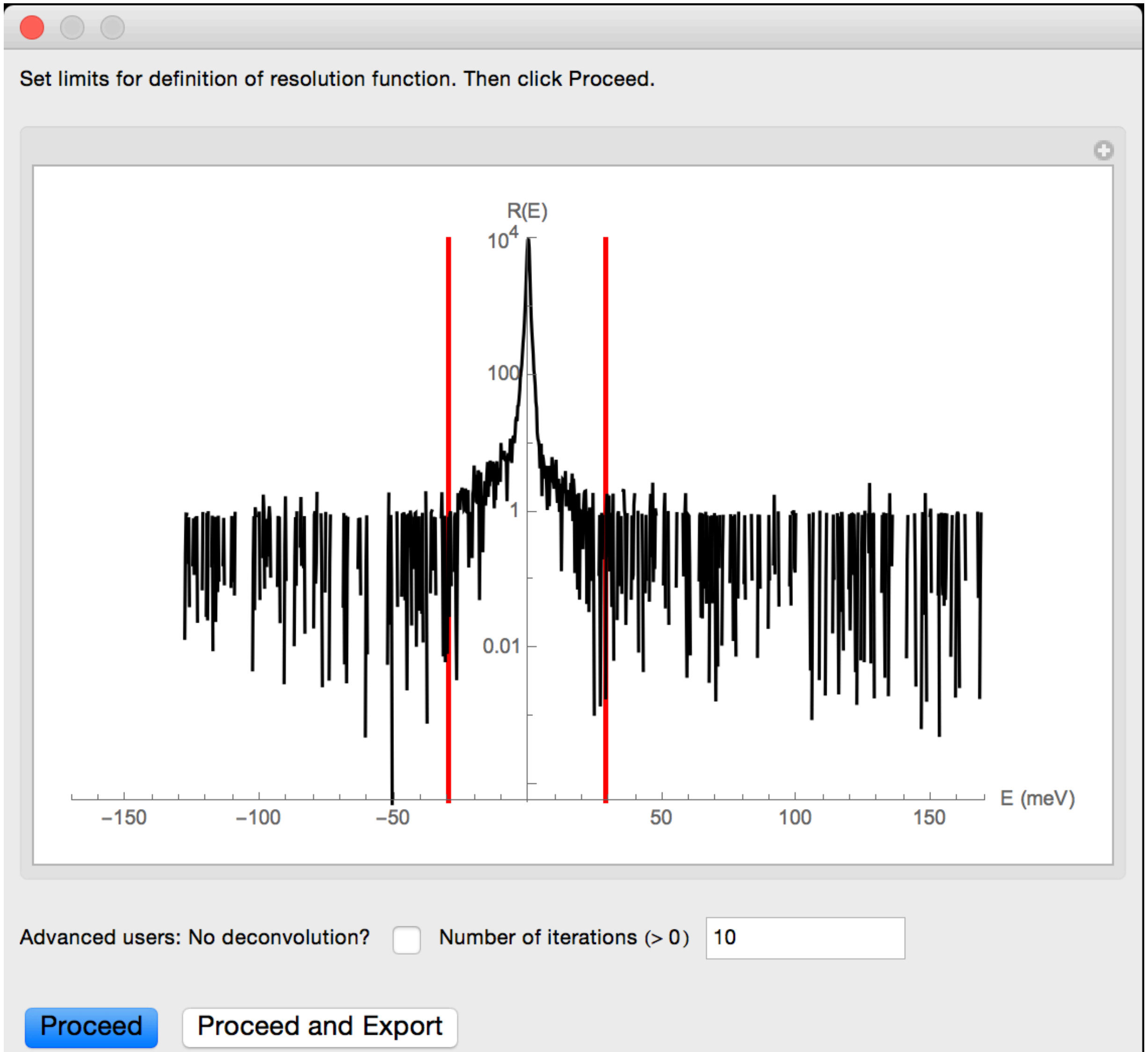
Load a ".dat" file (you need padd from Phoenix to make such a file)



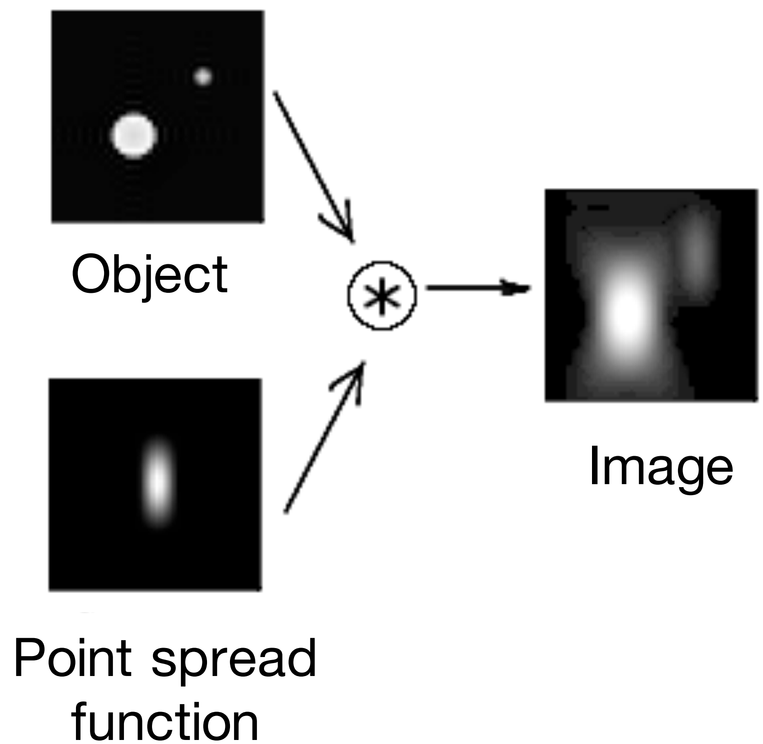
Load a ".res" file (you need padd from Phoenix to make such a file)



Deconvolution of the resolution from the data using the steepest descent algorithm



Deconvolution



Deconvolution

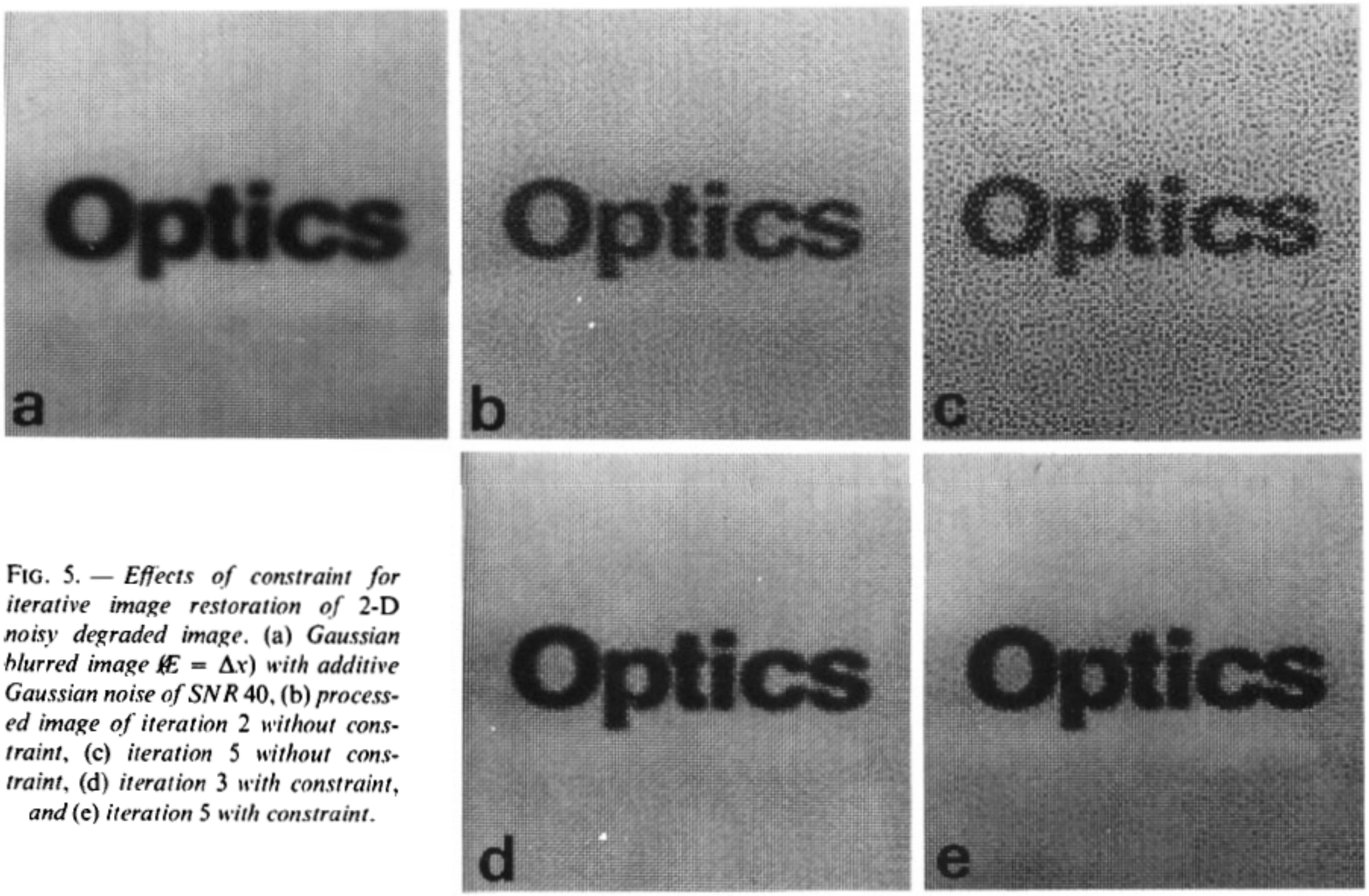
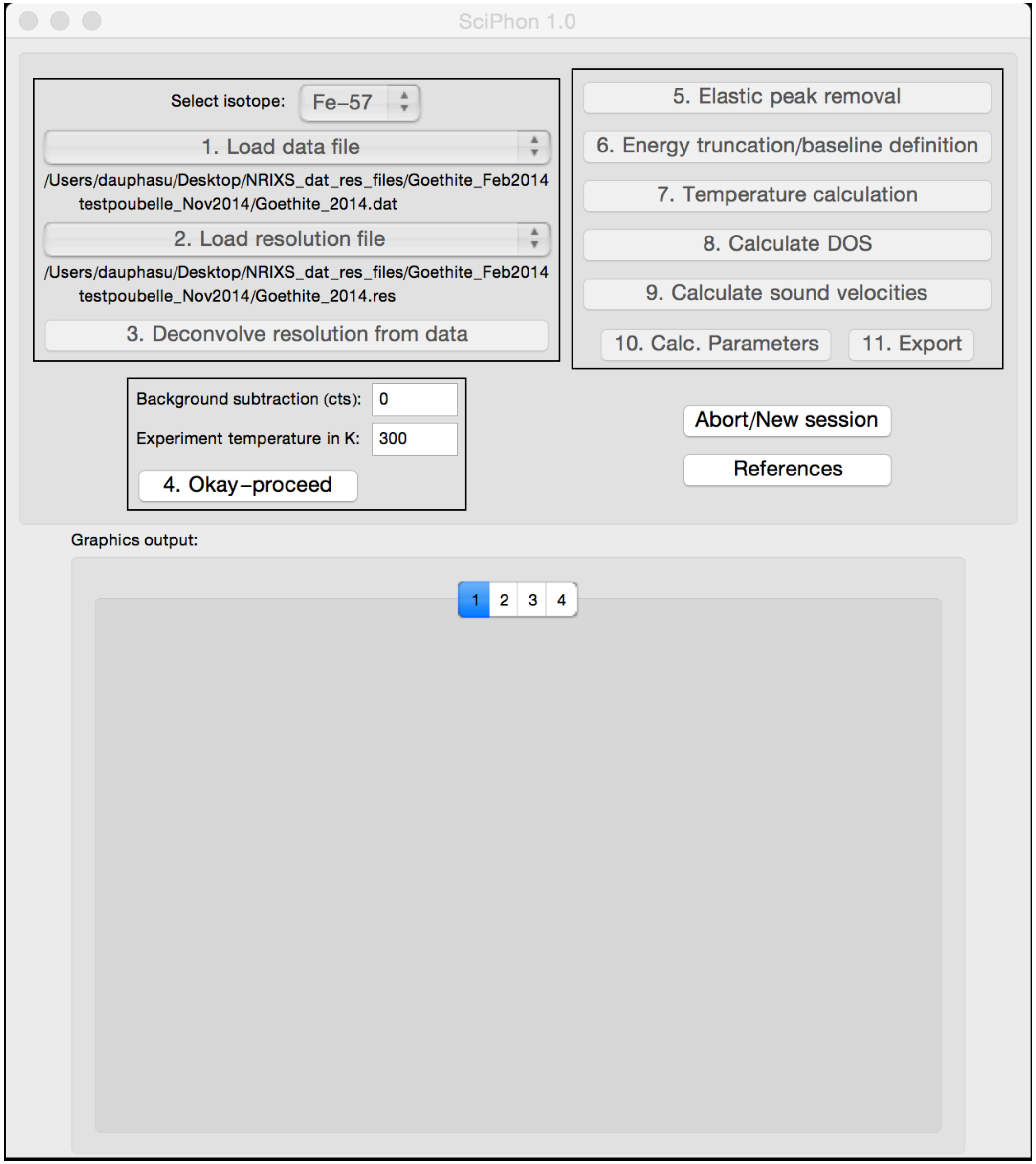


FIG. 5. — *Effects of constraint for iterative image restoration of* 2-D *noisy degraded image.* (a) *Gaussian blurred image* (Æ = Δx) *with additive Gaussian noise of SNR* 40, (b) *processed image of iteration* 2 *without constraint,* (c) *iteration* 5 *without constraint,* (d) *iteration* 3 *with constraint, and* (e) *iteration* 5 *with constraint.*

In the steepest descent algorithm, the restoration vector is manipulated so as to only return positive values and reduce oscillations (Ichioka et al., 1981)

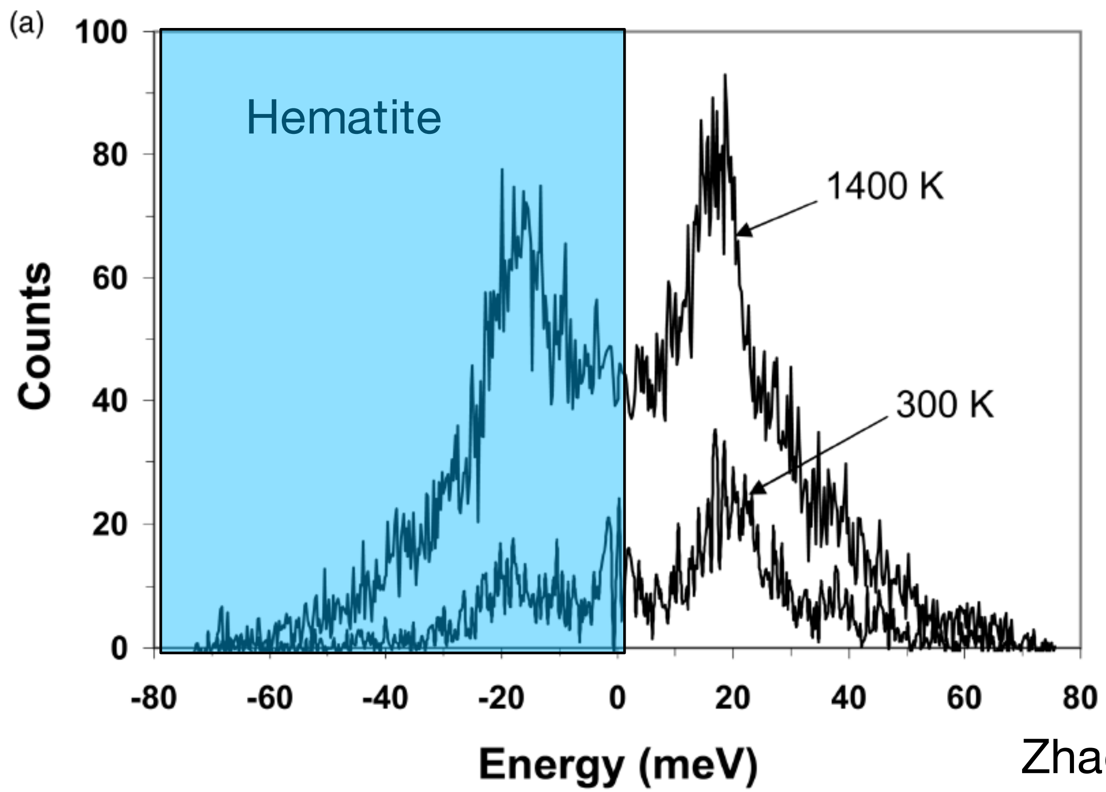
Noise amplification can be limited by terminating the algorithm after a finite number of iterations

Input the experiment temperature and background



Detailed balance

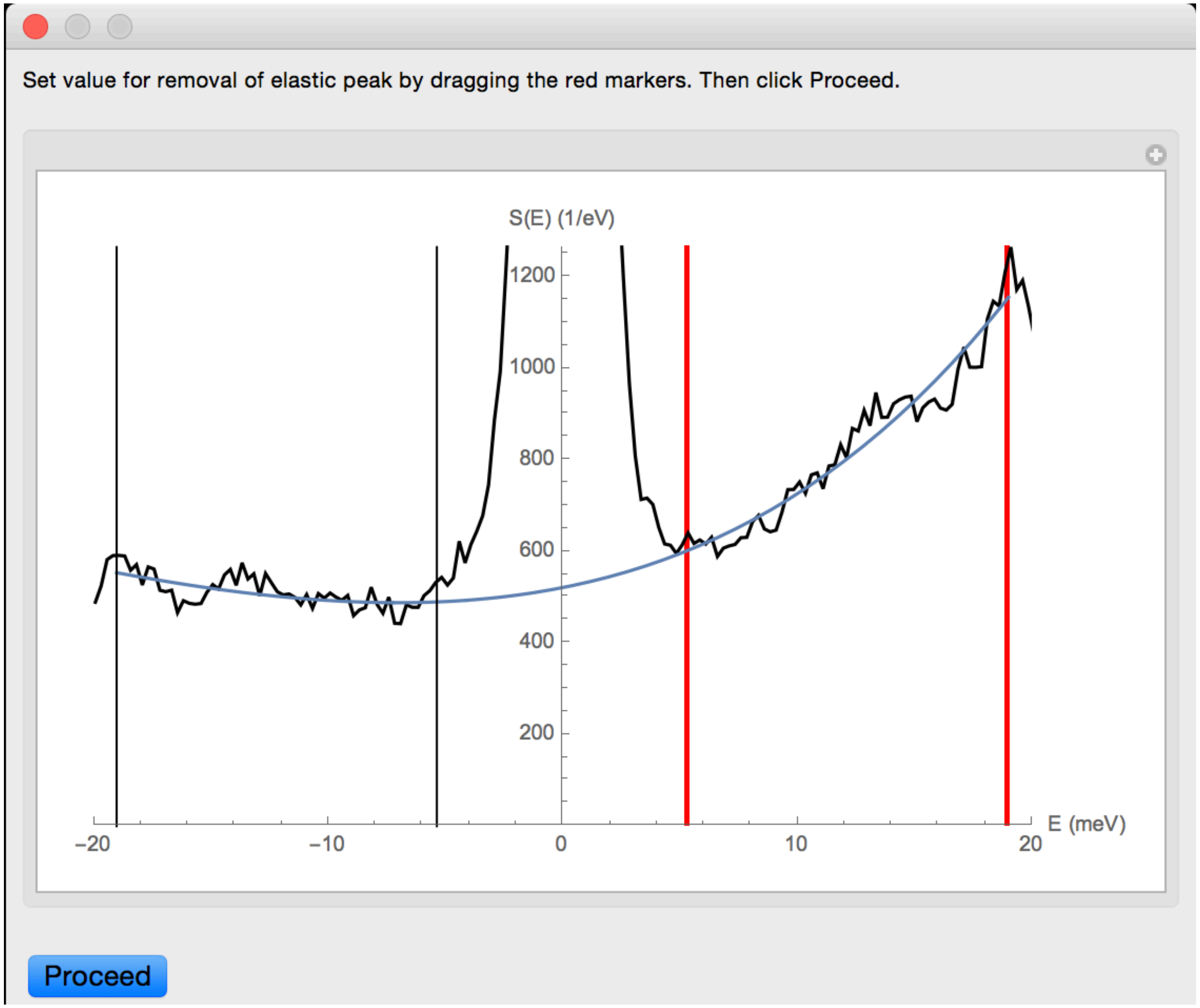
$$\frac{I(E)}{I(-E)} = e^{E/kT}$$



Zhao et al. (2004)

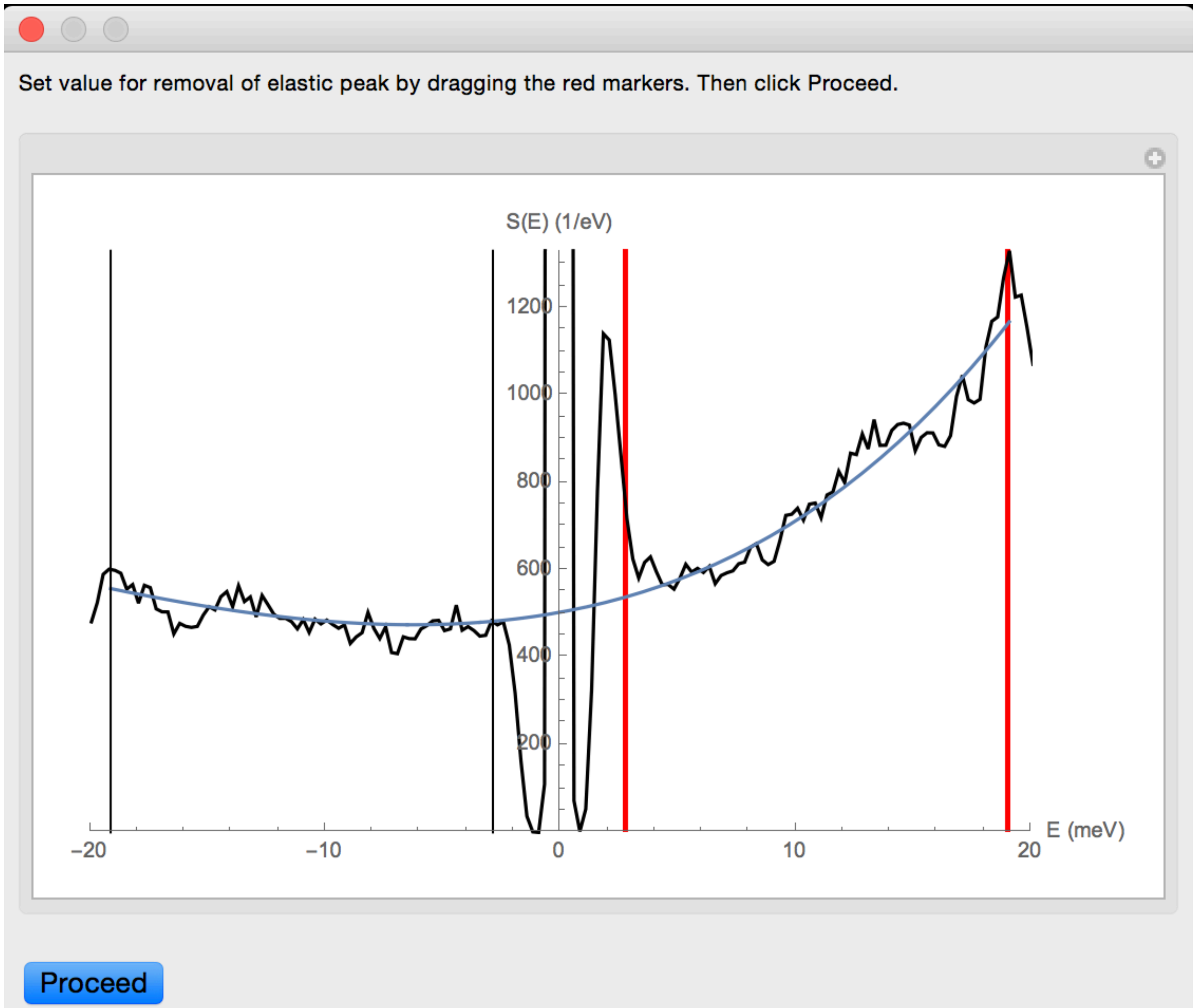
The phonon annihilation part is used. It added to the phonon creation part by applying the proper weights and using the experimental temperature

Elastic peak removal



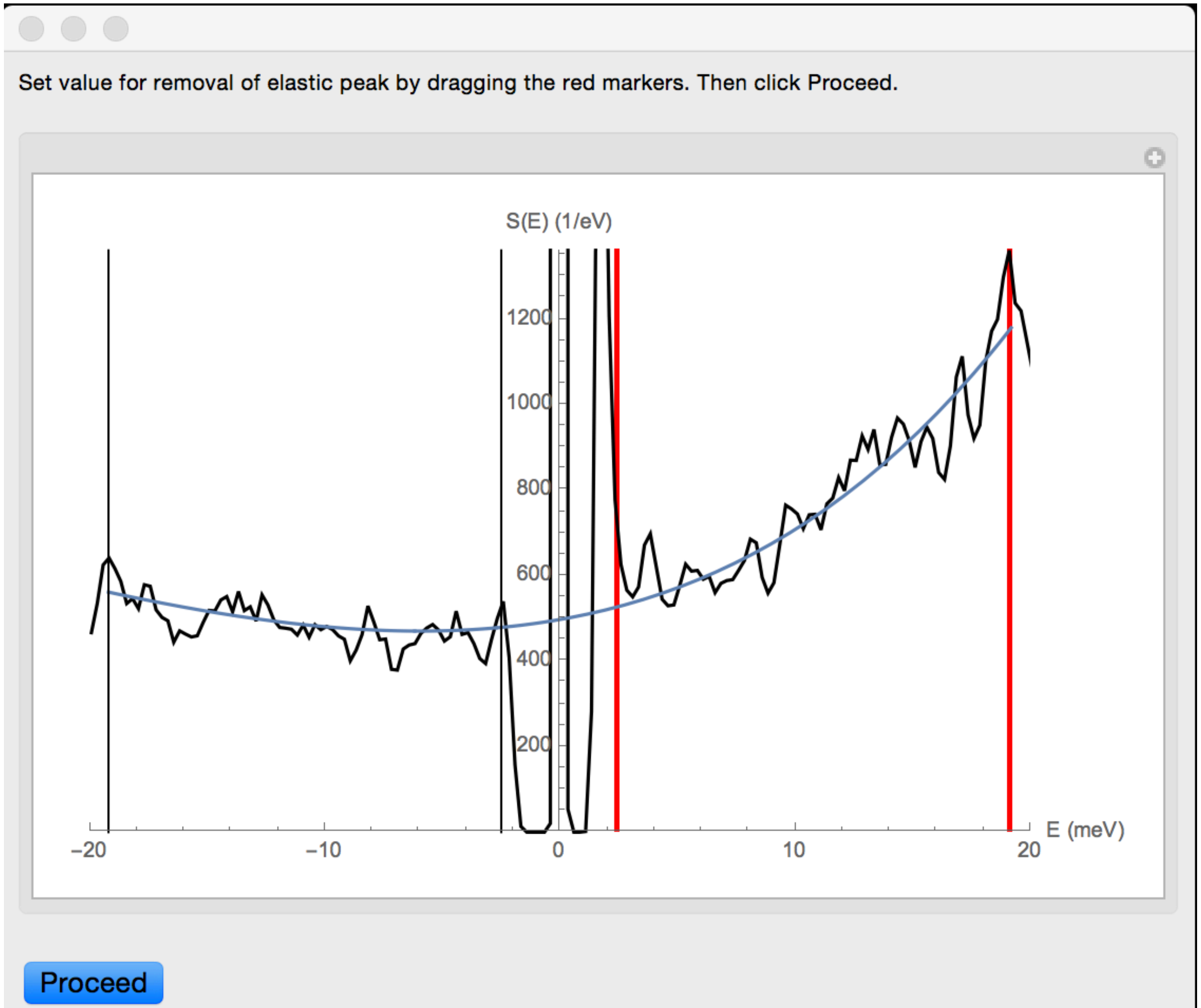
No peak deconvolution

Elastic peak removal



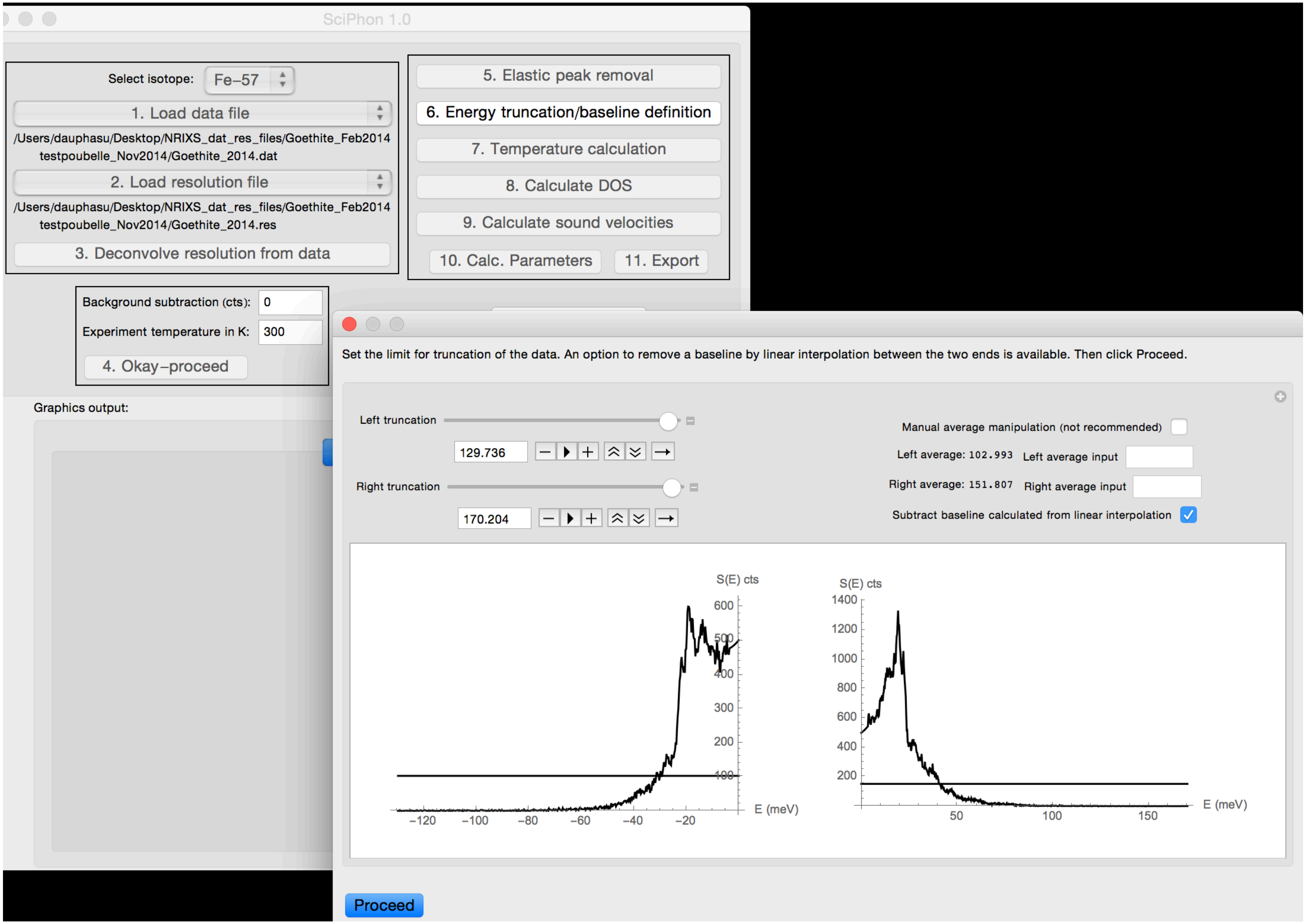
10 iterations

Elastic peak removal

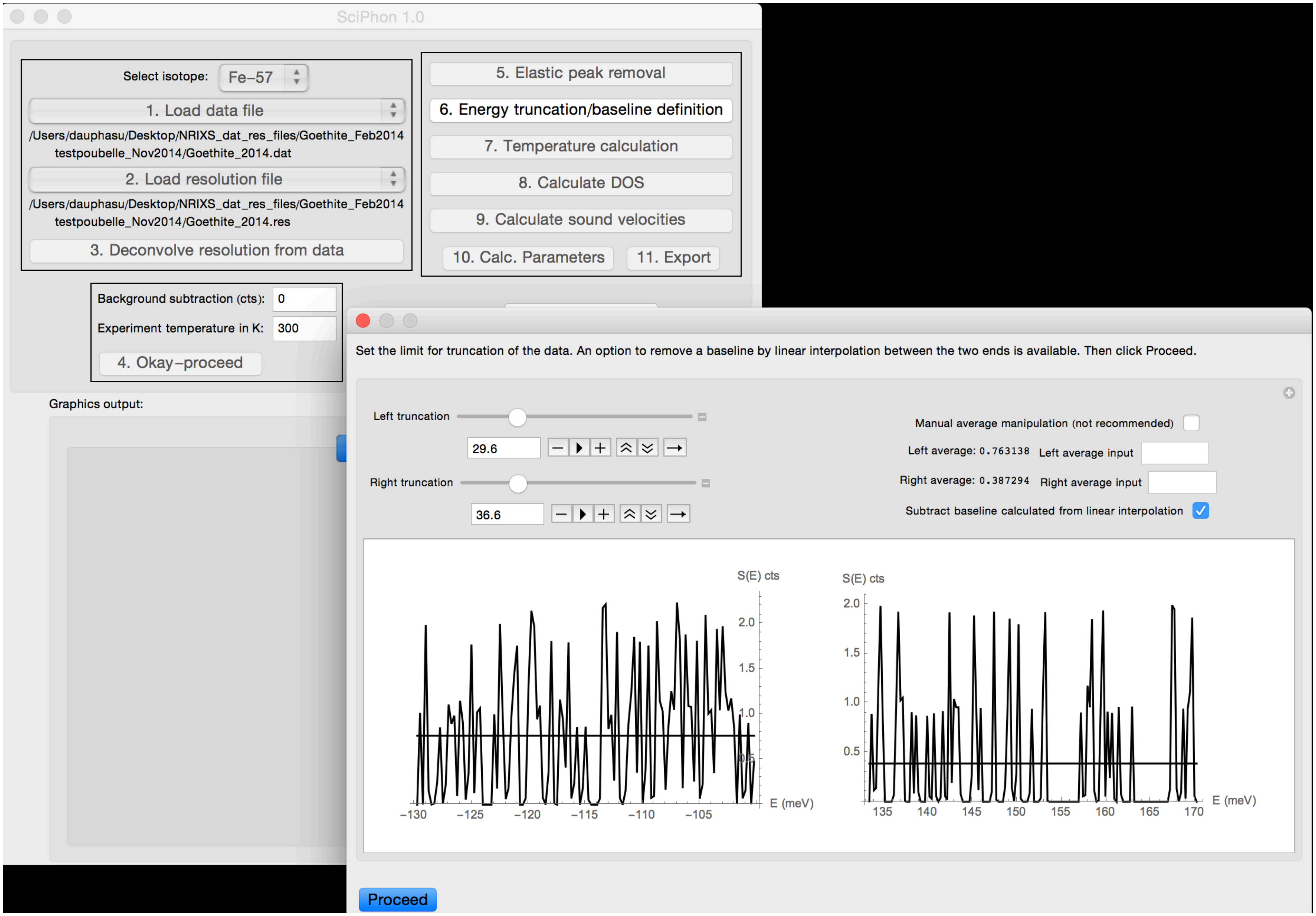


1000 iterations

Truncation and baseline definition

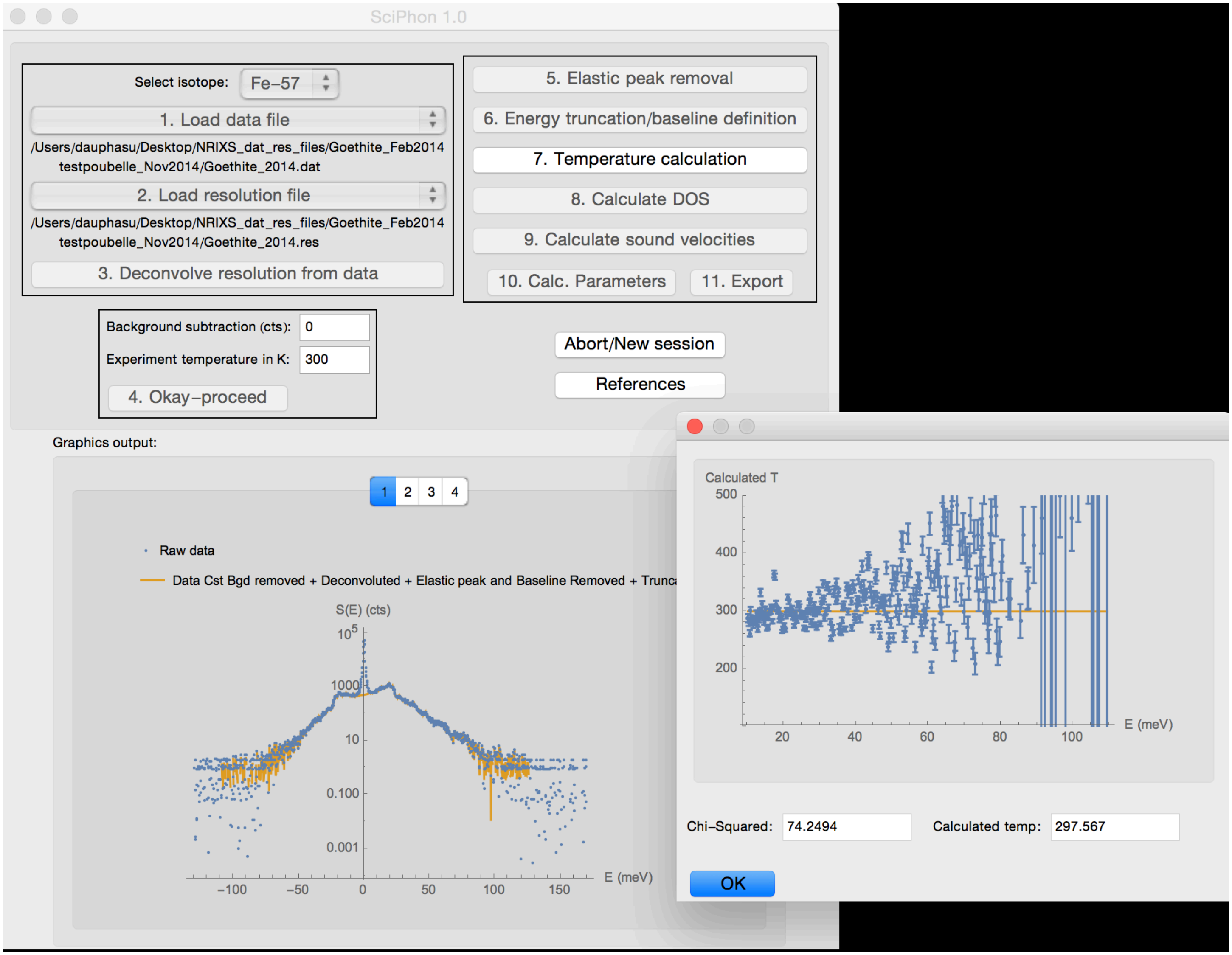


Truncation and baseline definition

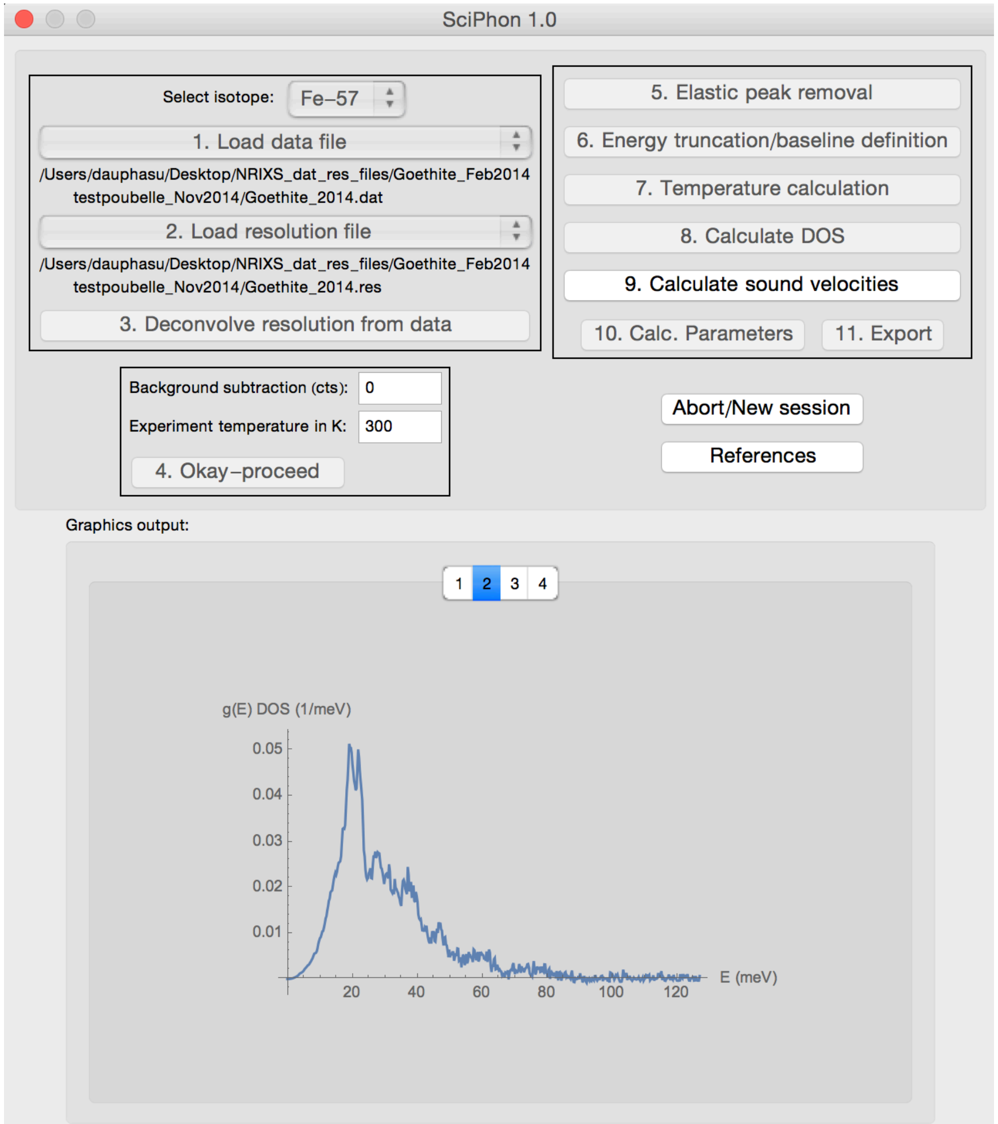


Temperature determination

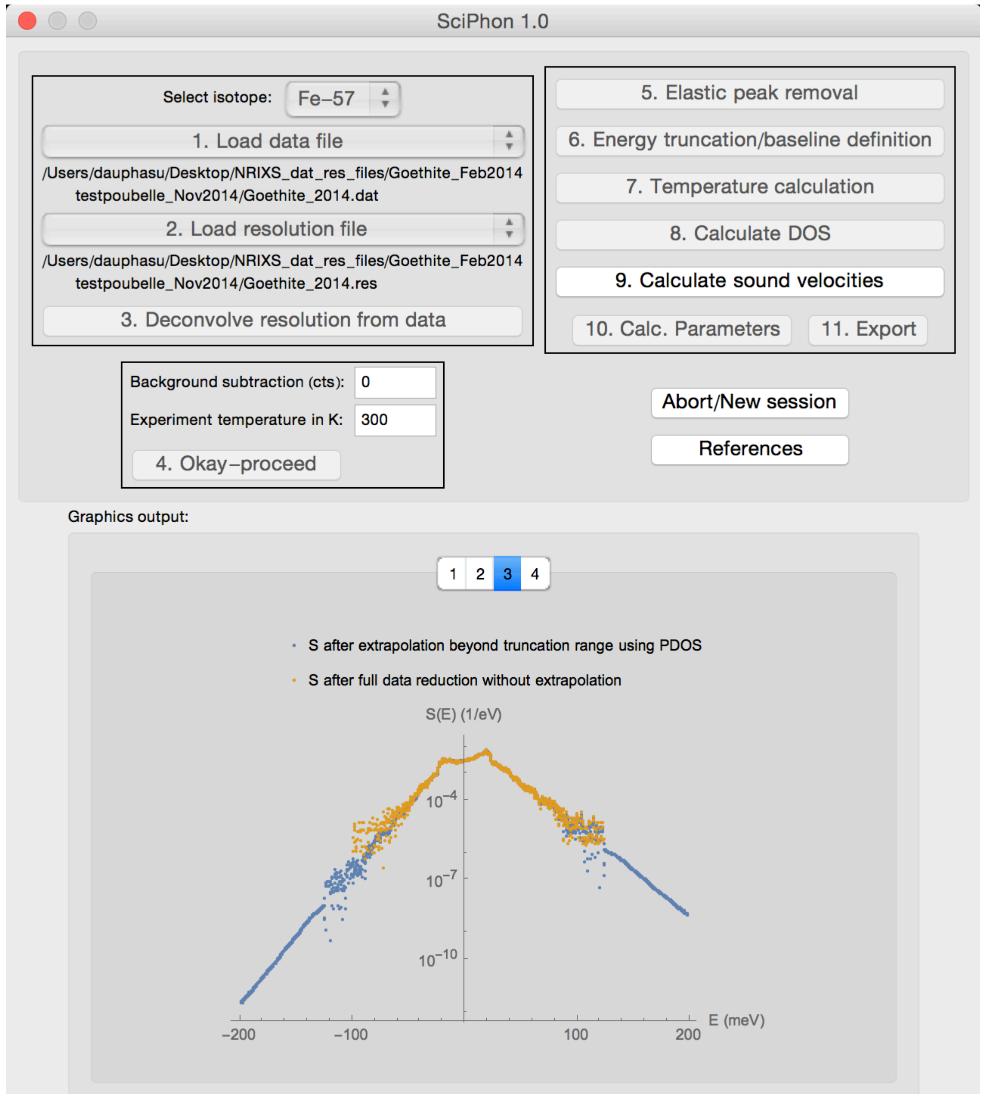
$$\frac{I(E)}{I(-E)} = e^{E/kT}$$



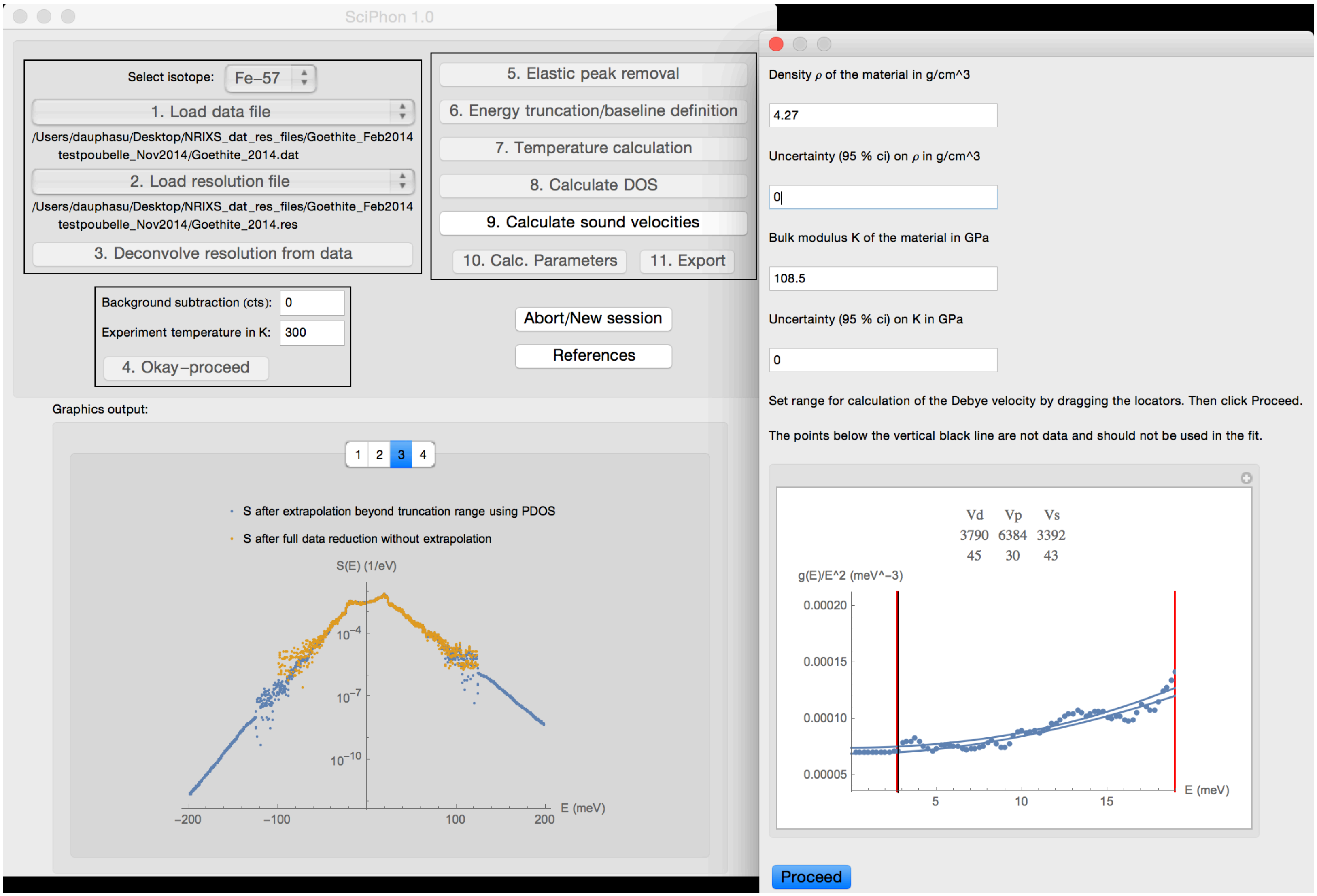
DOS calculation



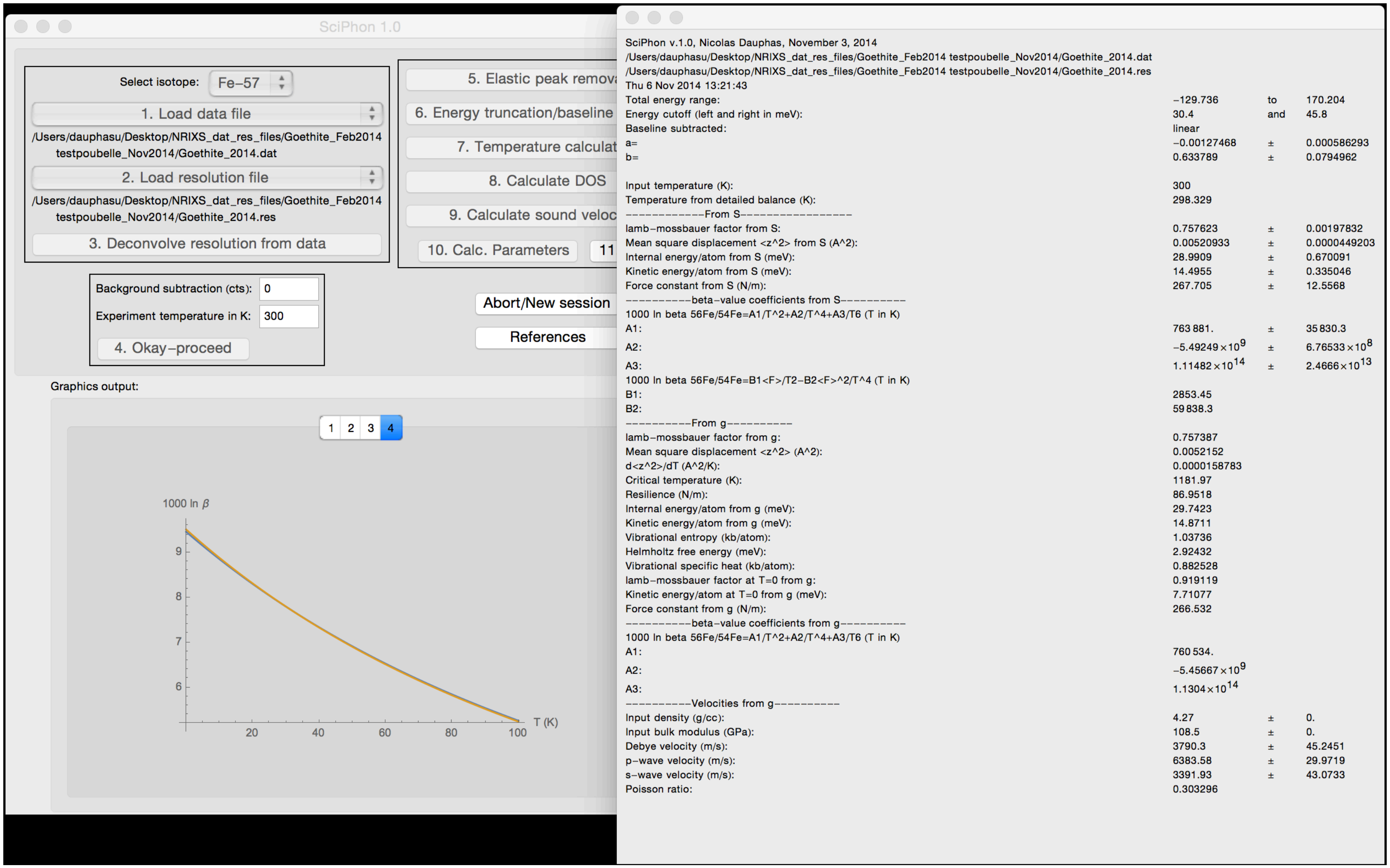
Extrapolation beyond the truncation range using the DOS



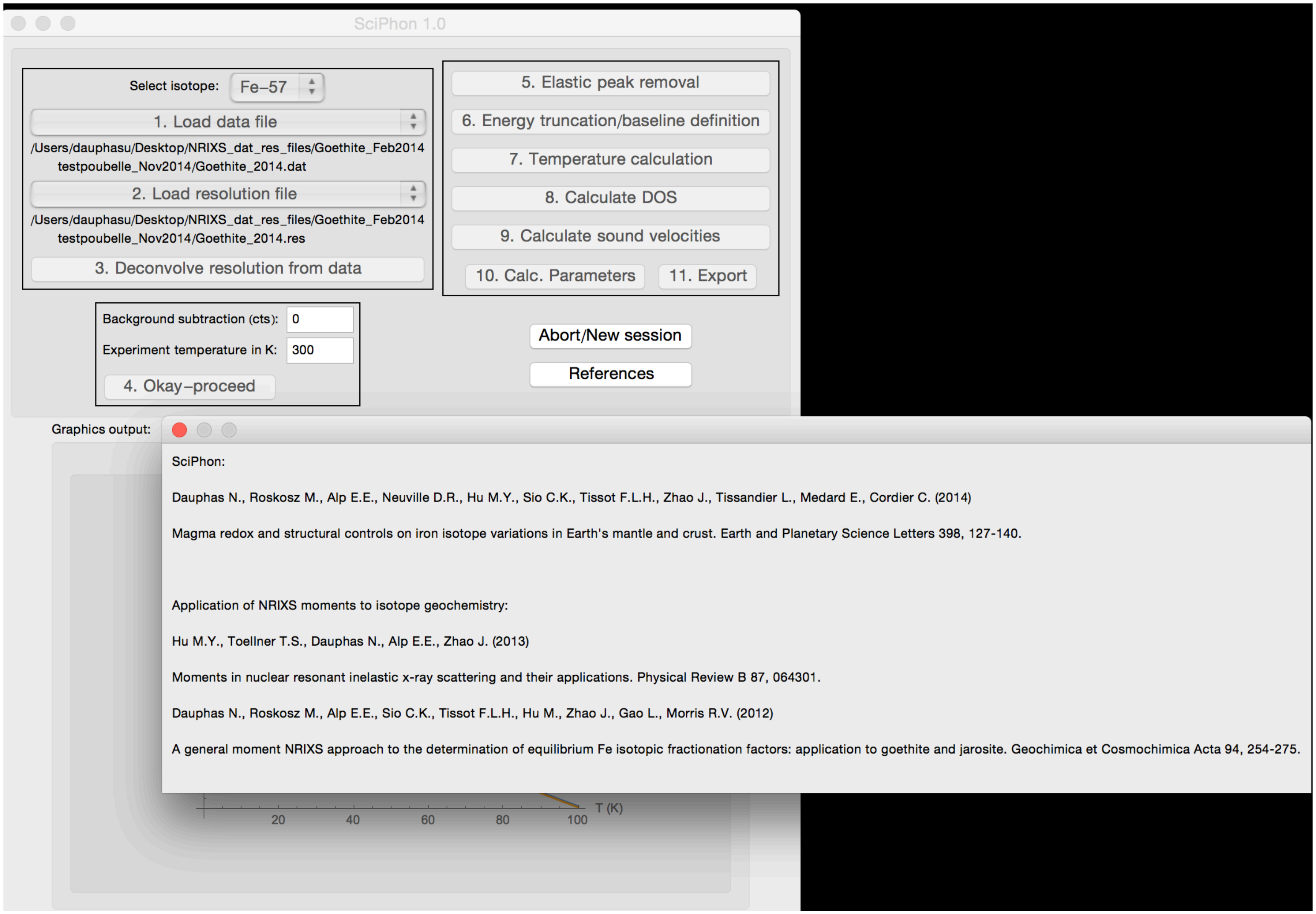
Calculate sound velocities



Calculated parameters



References


SciPhon 1.0
Select isotope:
Fe–57
1. Load data file
/Users/dauphasu/Desktop/NRIXS_dat_res_files/Goethite_Feb2014
testpoubelle_Nov2014/Goethite_2014.dat
2. Load resolution file
/Users/dauphasu/Desktop/NRIXS_dat_res_files/Goethite_Feb2014
testpoubelle_Nov2014/Goethite_2014.res
3. Deconvolve resolution from data
Background subtraction (cts):
0
Experiment temperature in K:
300
4. Okay–proceed
5. Elastic peak removal
6. Energy truncation/baseline definition
7. Temperature calculation
8. Calculate DOS
9. Calculate sound velocities
10. Calc. Parameters
11. Export
Abort/New session
References
Graphics output:
SciPhon:
Dauphas N., Roskosz M., Alp E.E., Neuville D.R., Hu M.Y., Sio C.K., Tissot F.L.H., Zhao J., Tissandier L., Medard E., Cordier C. (2014)
Magma redox and structural controls on iron isotope variations in Earth's mantle and crust. Earth and Planetary Science Letters 398, 127-140.
Application of NRIXS moments to isotope geochemistry:
Hu M.Y., Toellner T.S., Dauphas N., Alp E.E., Zhao J. (2013)
Moments in nuclear resonant inelastic x-ray scattering and their applications. Physical Review B 87, 064301.
Dauphas N., Roskosz M., Alp E.E., Sio C.K., Tissot F.L.H., Hu M., Zhao J., Gao L., Morris R.V. (2012)
A general moment NRIXS approach to the determination of equilibrium Fe isotopic fractionation factors: application to goethite and jarosite. Geochimica et Cosmochimica Acta 94, 254-275.
T (K)
20
40
60
80
100

Conclusions

NRIXS is a powerful tool in isotope geochemistry

Beware of the baseline in NRIXS

Use SciPhon and give us some feedback

SciPhon development team:
Nicolas Dauphas
Michael Hu
Erik Baker
François Tissot
Ercan Alp
Justin Hu

Collaborators:
Mathieu Roskosz
Daniel Neuville
Corliss Sio
Jiyong Zhao
Etienne Médard