

This set of handouts deals with issues that come up whenever a new isotope system is being developed.

“Non-traditional” Stable Isotope Systems

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	REE	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi			
La	Ce	Pr	Nd		Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
	Th		U														

Getting it right...

$$R_{\text{true}} = R_m * F$$

- Sample-standard bracketing
- Inter-element standardization
- Double or triple spiking
- Choice of fractionation “law”

ISOTOPE FRACTIONATION LAWS: A TEST USING CALCIUM

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ABSTRACT

A four-isotope equal atom mixture of ^{40}Ca , ^{42}Ca , ^{44}Ca and ^{48}Ca has been prepared and analyzed mass spectrometrically using a double-filament ionization mode. The maximum range of fractionation observed within a single run was 1.8‰ . Of the various isotope fractionation laws proposed, the exponential law provides the best fit to the data, with maximum deviations of about 0.01‰ over the total range of fractionation observed. However, the precision of the data is such that a fine structure can be observed with respect to deviations from an ideal exponential law, and we suggest that mixing effects from isotopically heterogeneous sample reservoirs are responsible for this fine structure. Because this effect is controlled by numerous free parameters, it will probably provide the ultimate limit of precision for multicollector analysis of strontium and neodymium.

Fractionation correction

The effects of mass fractionation can be corrected by applying semi-empirical “laws” to the measured ratios. The theoretical basis of these corrections is weak, but four different forms are widely used - linear law, power law, exponential law and Rayleigh law. All fractionation laws can be expressed as a power law according to

$$Y_m / Y_t = b (X_m / X_t)^a$$

where X and Y are ratios of the isotope masses m_1/m_2 and m_3/m_4 , respectively (Hart & Zindler, 1989). The subscripts t and m stand for the true (unfractionated) and the measured (fractionated) isotope ratios. The true ratio is the ratio of the natural abundance of the isotopes. The differences between the four laws is expressed by the constants a and b , which are functions of mass only. This formulation is true for the exponential and the Rayleigh law specifically if the ratios X and Y are written with the same mass in the denominator ($m_2 = m_4$). With this, the

Power law is defined as $a = (m_3 - m_4) / (m_1 - m_2)$ and $b = 1$

Exponential law is defined as $a = \ln(m_3/m_4) / \ln(m_1/m_2)$ and $b = 1$

Rayleigh law is defined as $a = (1 - (m_4/m_3)^{1/2}) / (1 - (m_2/m_1)^{1/2})$ and $b = (m_4/m_3)^{1/2} / [(m_2/m_1)^{1/2}]^a$

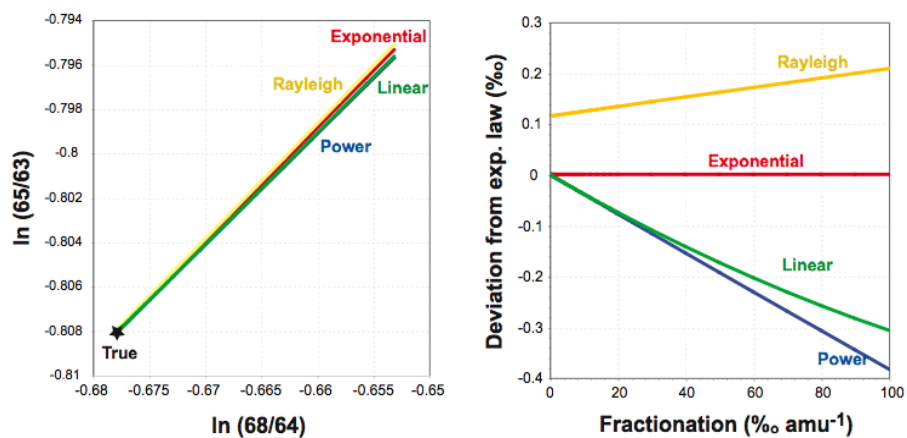
The linear law is derived by first-order Taylor-series expansion (for small fractional mass differences, i.e. small degree of fractionation) of the power law, i.e.

$$(Y_m - Y_t) / Y_t = a (X_m - X_t) / X_t \quad \text{with} \quad a = (m_3 - m_4) / (m_1 - m_2)$$

The choice of fractionation law becomes important if isotope ratios are measured at high precision. For less precise measurements (e.g., measurements on a single-collector mass spectrometer) the linear law serves as a good approximation.

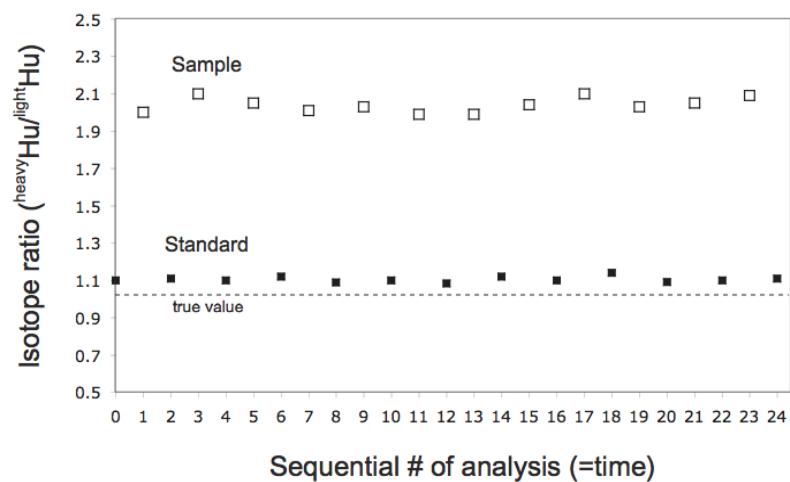
Isotope Fractionation “Laws”

(Hart & Zindler, 1989)



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Standard - Sample Bracketing



$$F_{\text{corr}} = (\text{Std}_{m,1} + \text{Std}_{m,2}) / (2 * \text{Std}_{\text{true}})$$

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Inter-Element Standardization

264

C.N. Maréchal et al. / Chemical Geology 156 (1999) 251–273

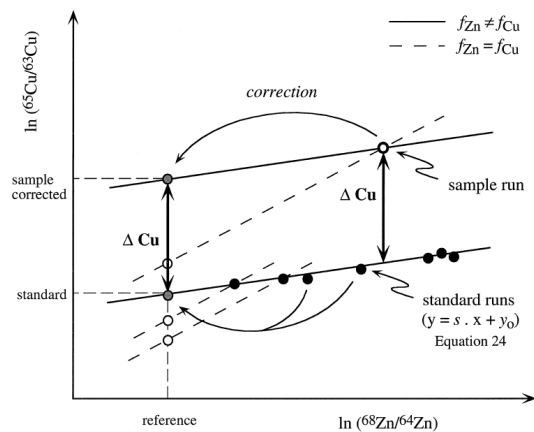
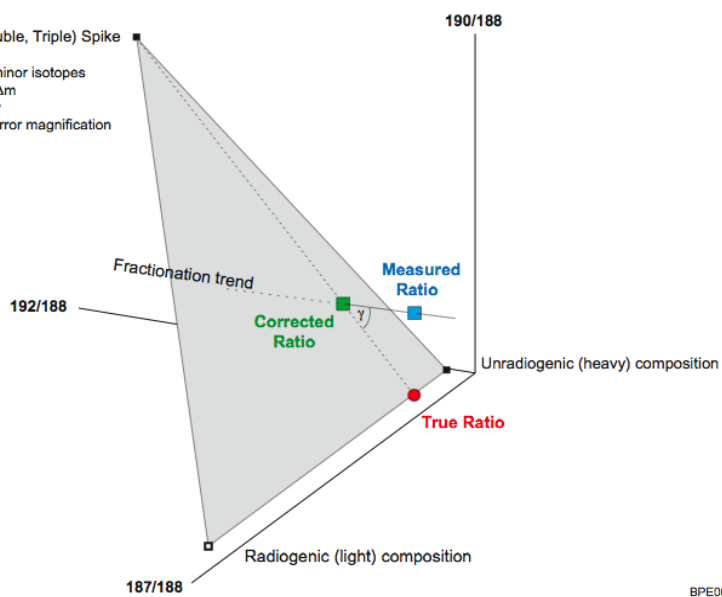


Fig. 10. Procedure for mass fractionation correction on $^{65}\text{Cu}/^{63}\text{Cu}$ using $^{68}\text{Zn}/^{64}\text{Zn}$ as an external isotopic standard. The slope derived from the data on Cu + Zn standard mixtures is used to correct the data on the Cu sample + Zn standard mixtures. The difference in ordinates between the two lines (ΔCu) defines the difference in $^{65}\text{Cu}/^{63}\text{Cu}$ ratios between the Cu standard and the Cu sample. As this difference clearly depends on the slope, the results obtained in this way are expected to be different from those (dashed line) derived from the assumption of identical f for Zn and Cu (Longerich et al., 1987). The protocol to correct Zn isotopic ratios using Cu as an external standard is identical.

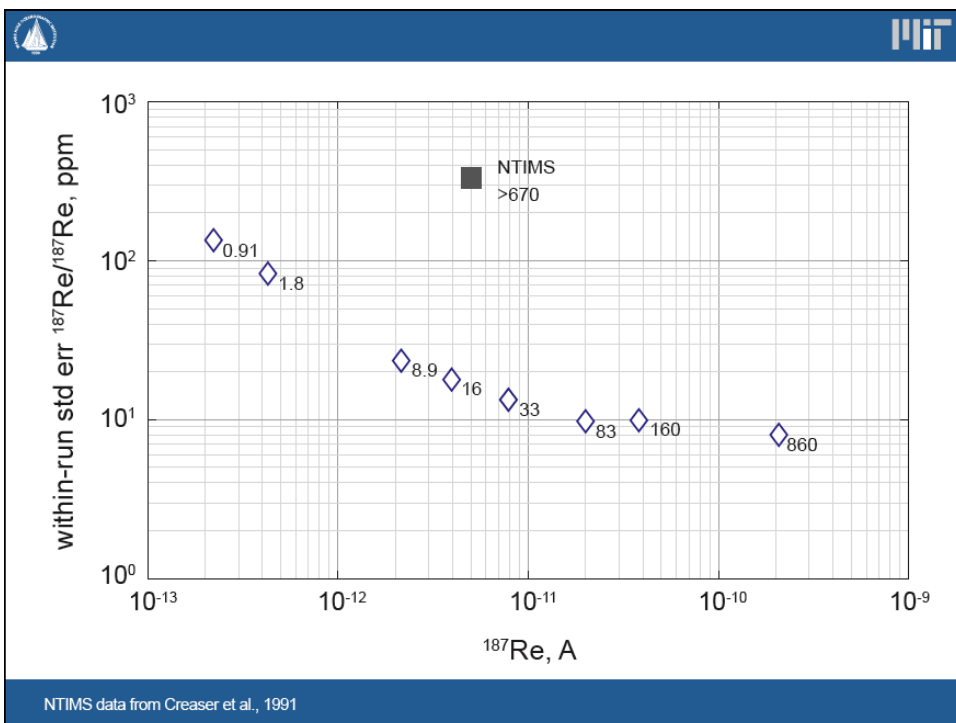
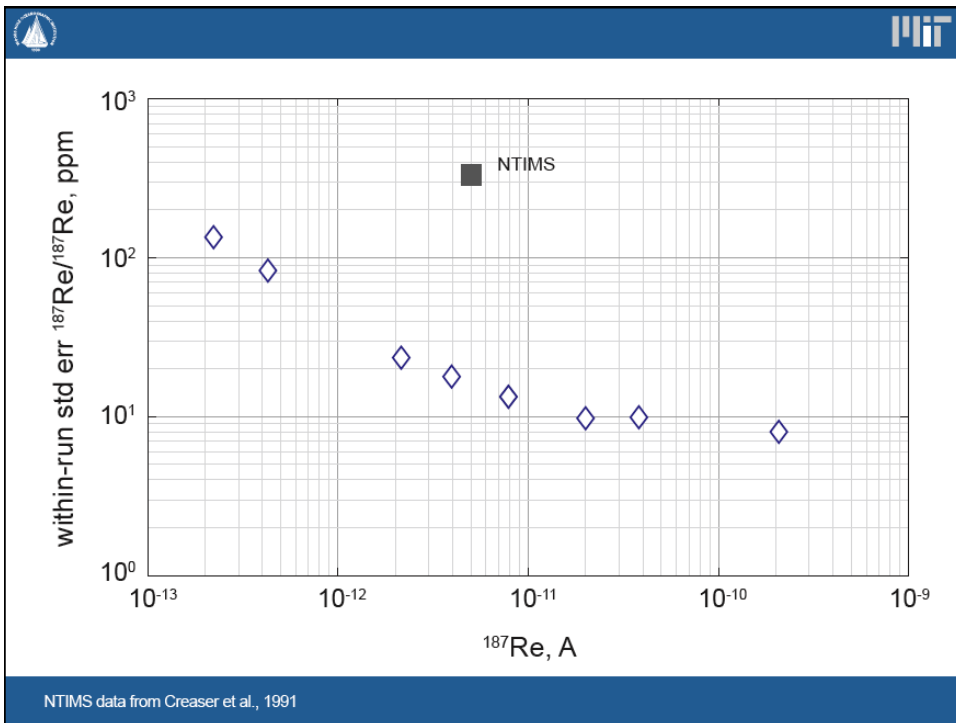
Spiking - Unspiking

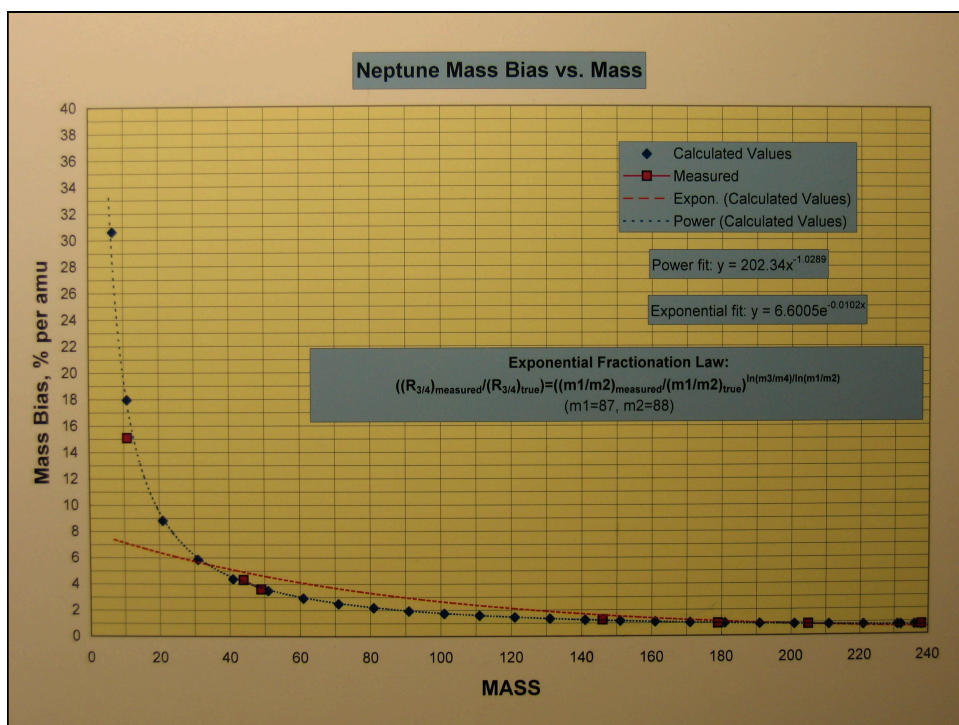
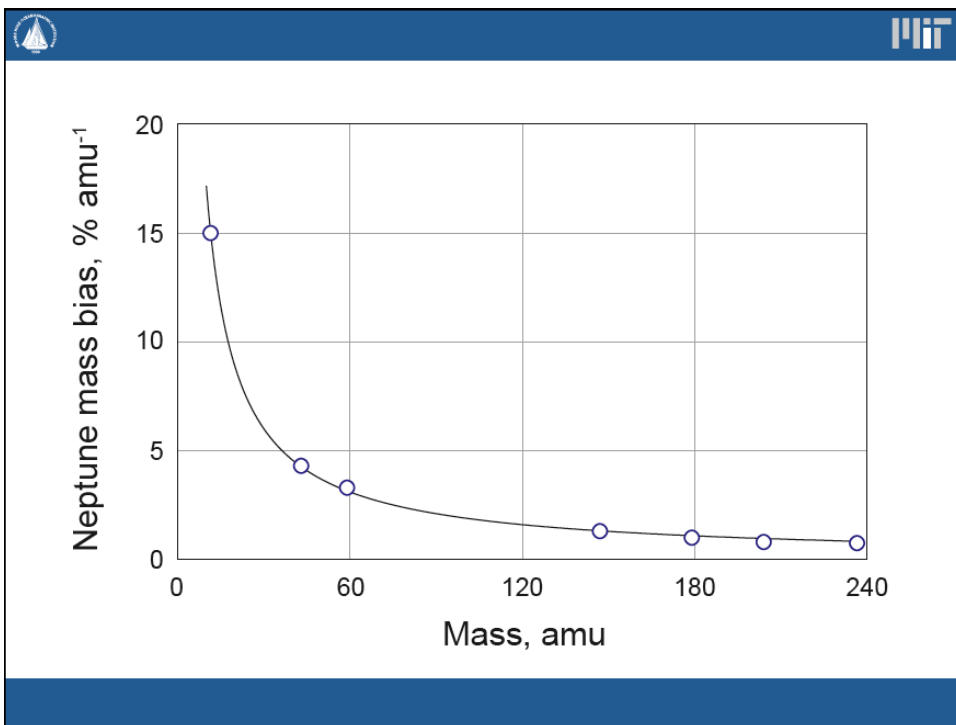
(Single, Double, Triple) Spike

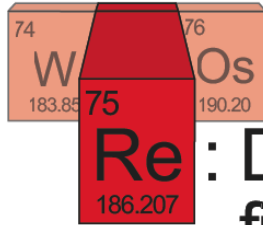
- best with minor isotopes
- maximize Δm
- maximize γ
- minimize error magnification



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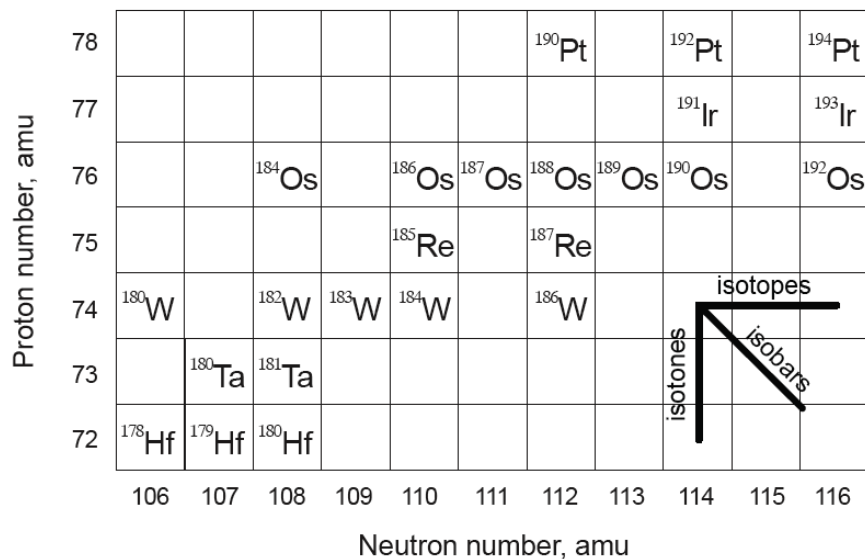


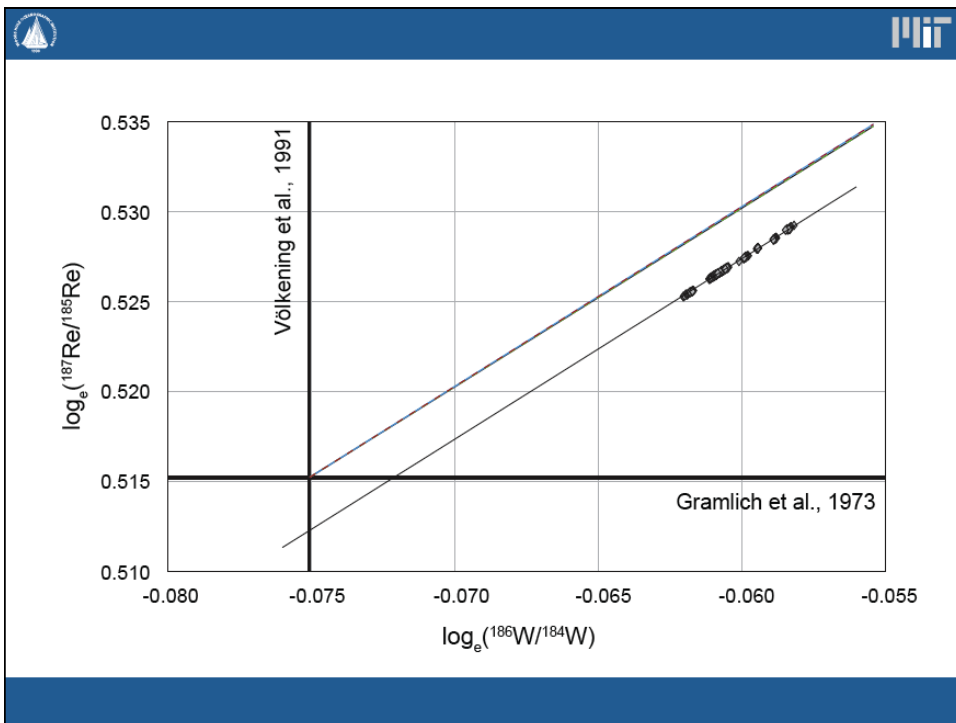
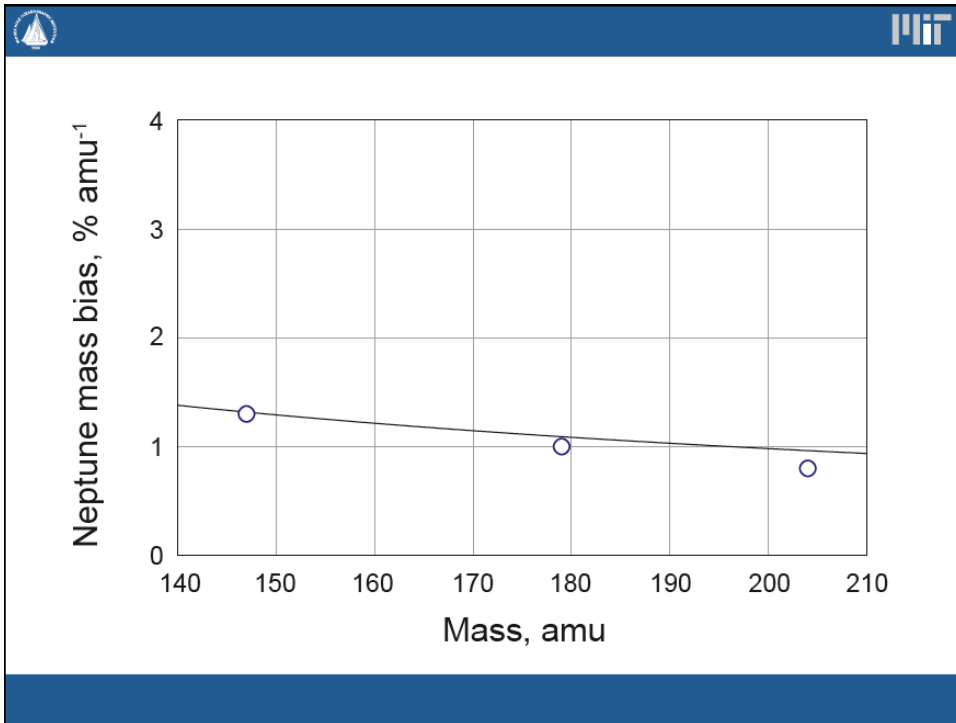
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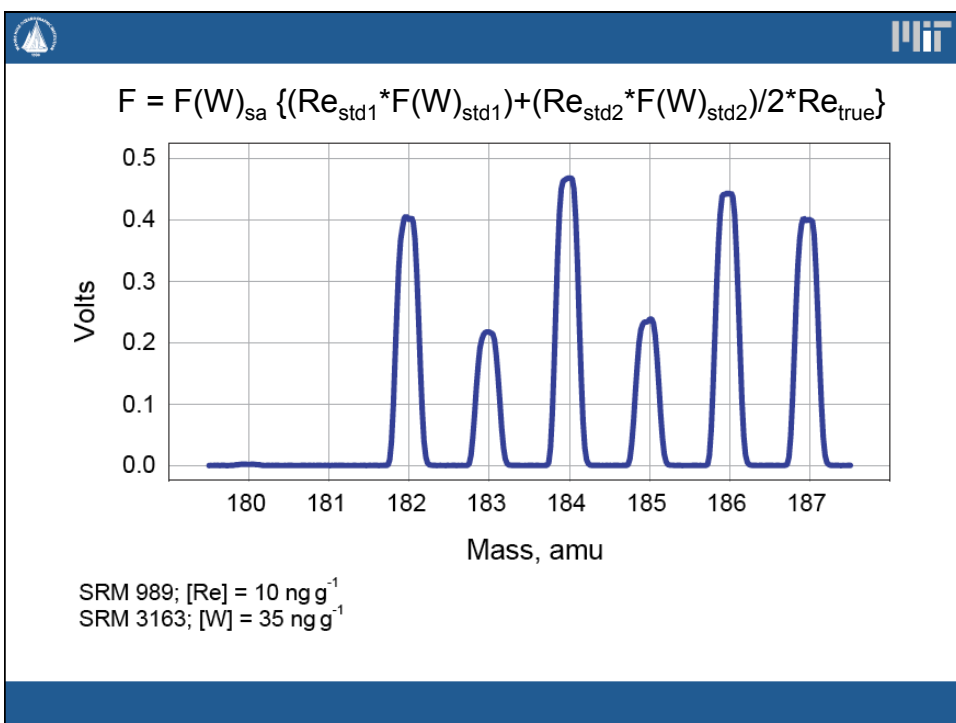
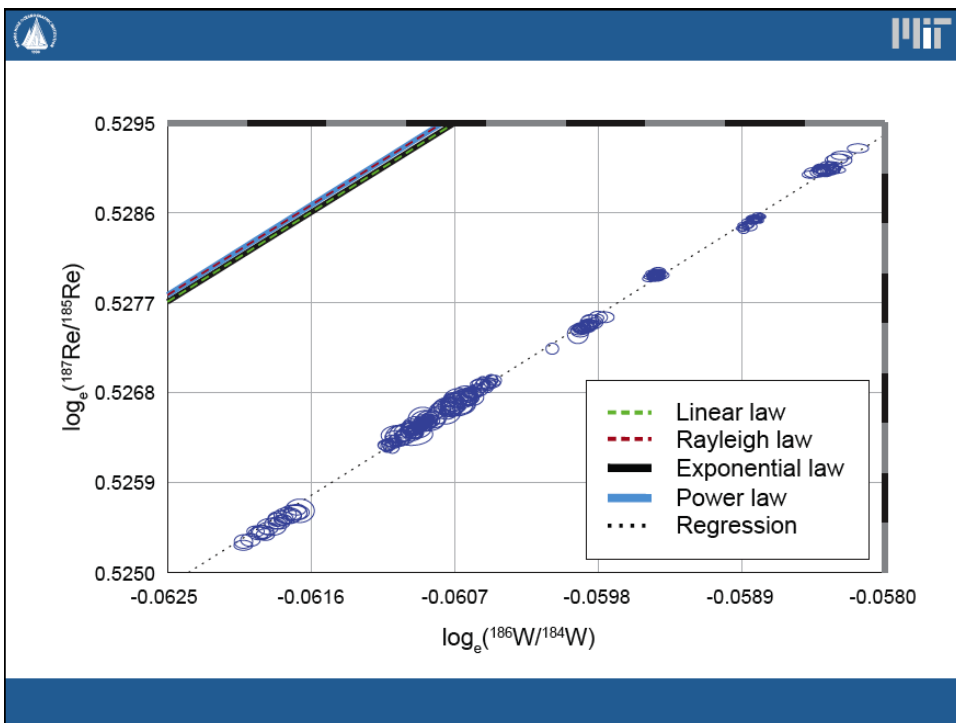
Christian Miller^{MC&G, EAPS}

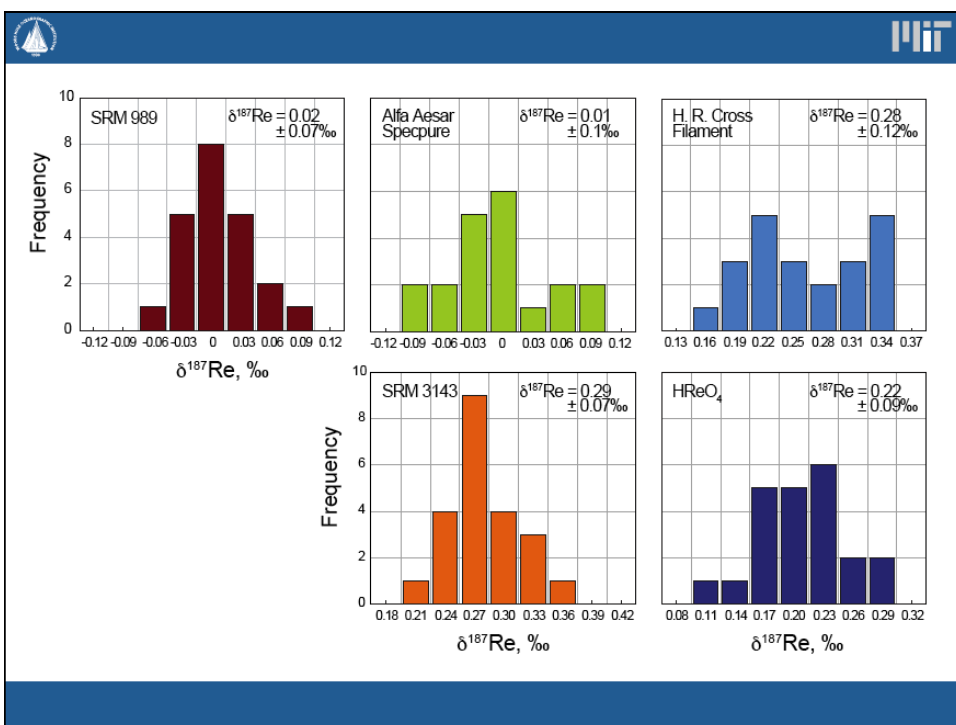
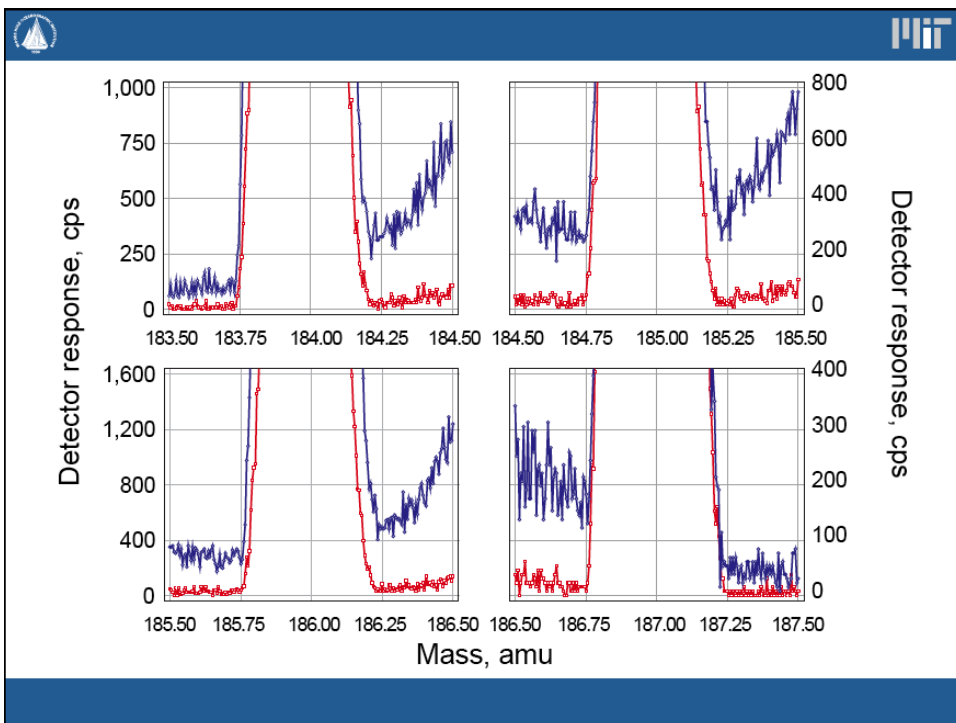
Bernhard Peucker-Ehrenbrink^{MC&G}

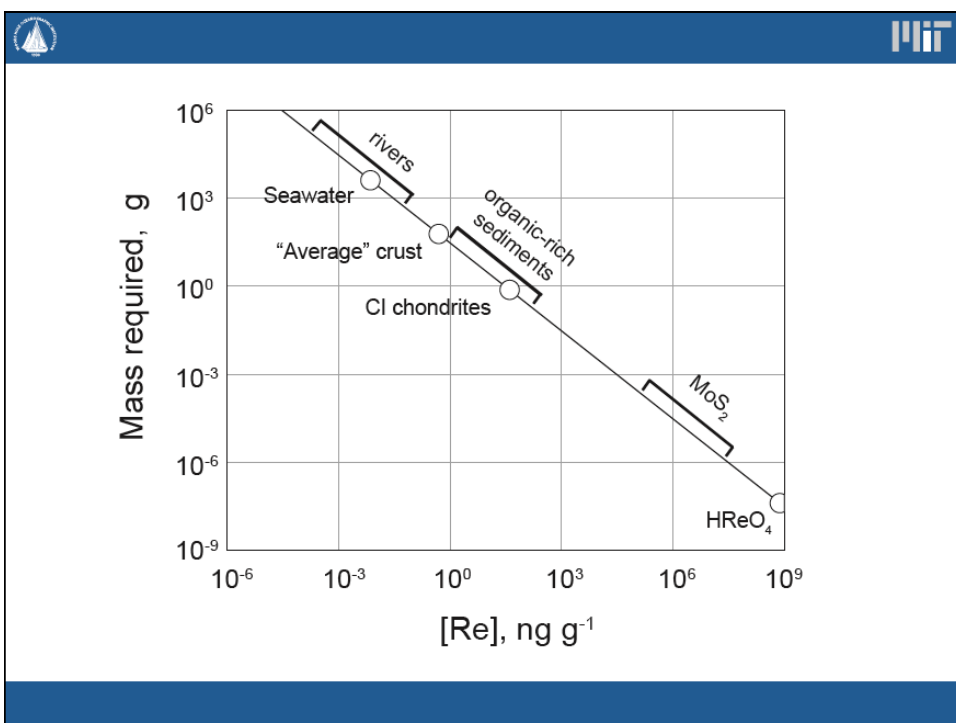
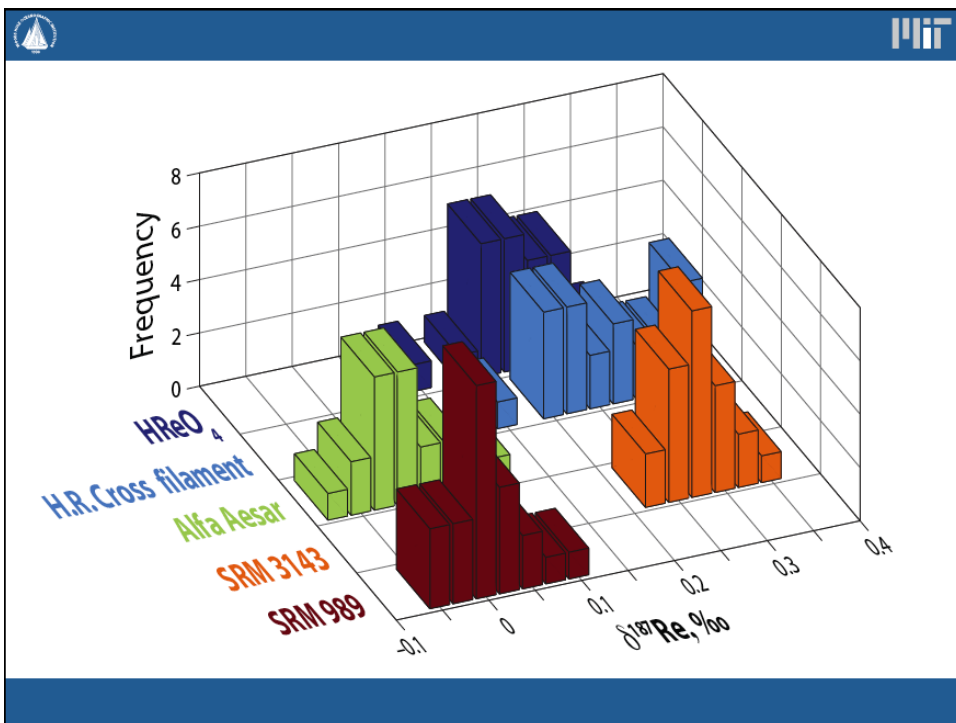
Lary Ball^{MC&G, Thermo Fisher Scientific}

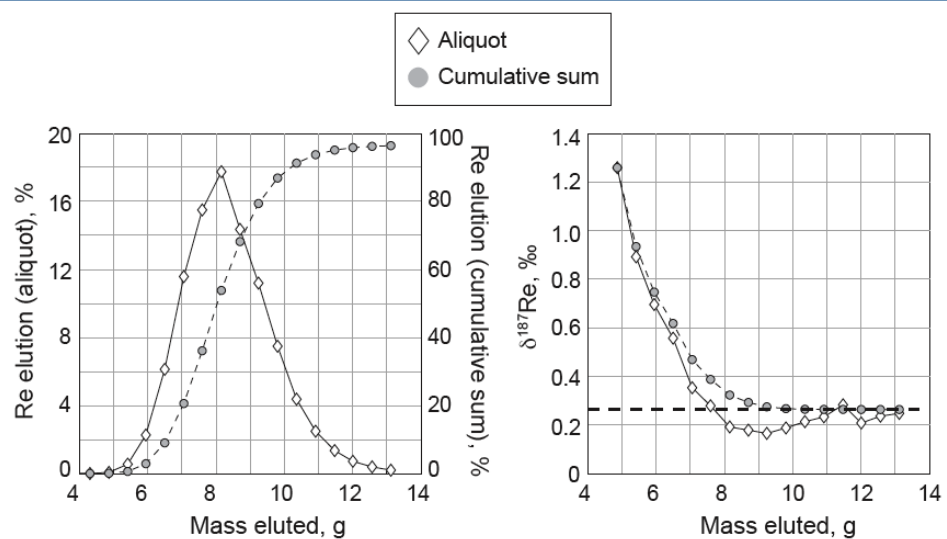
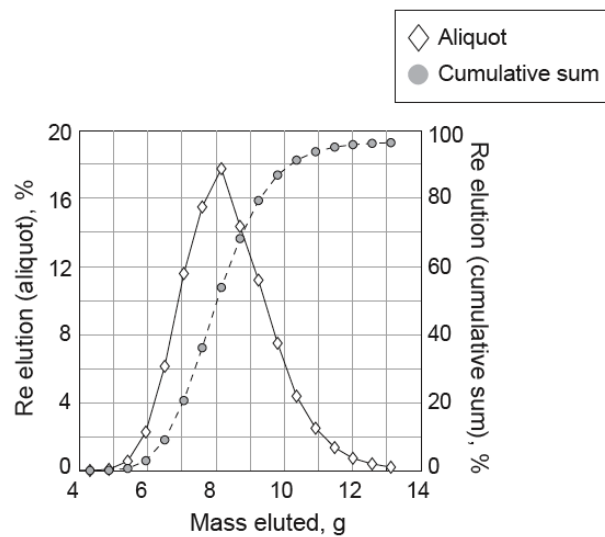


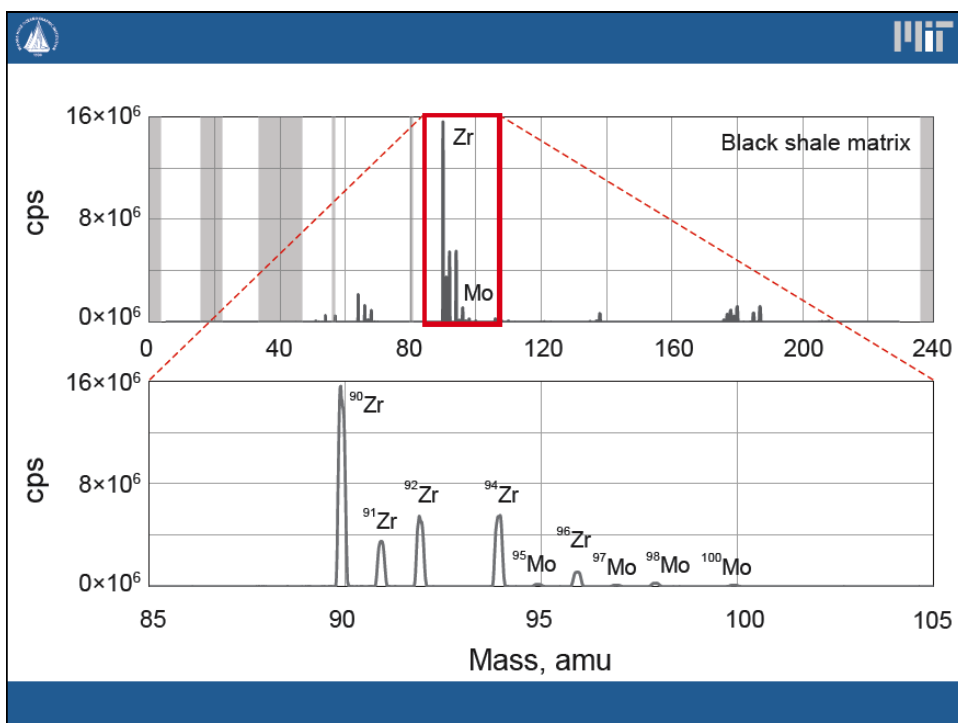
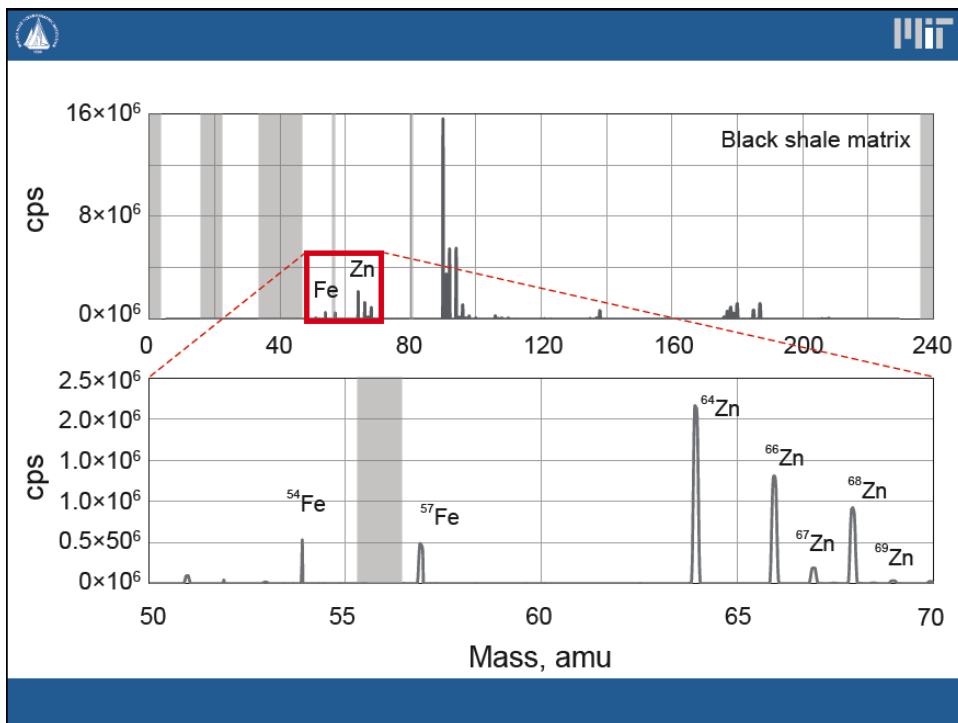


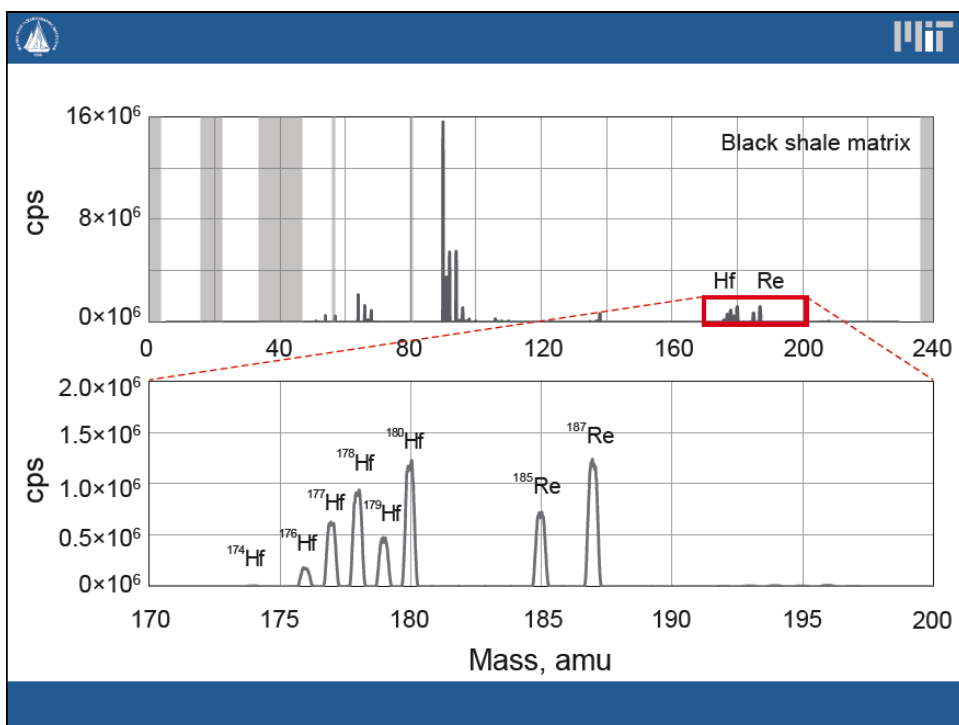
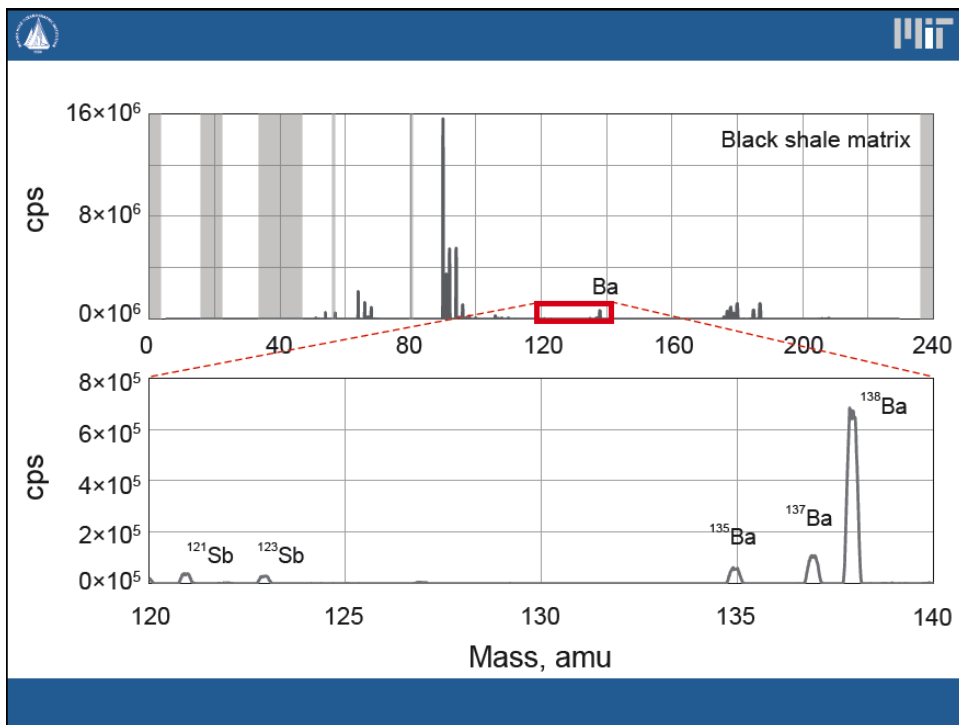


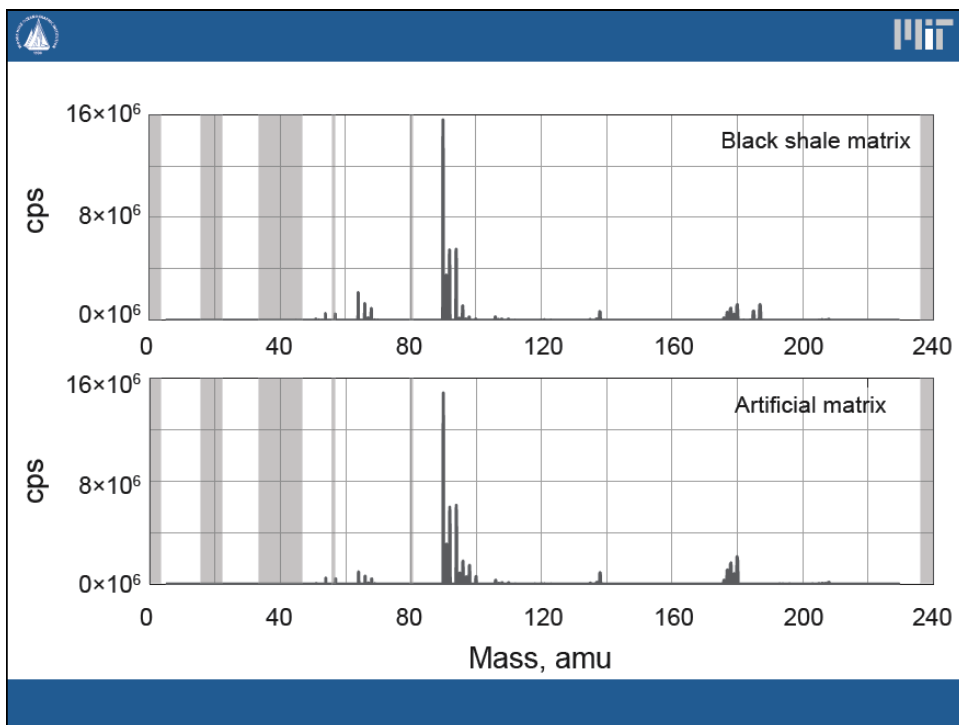
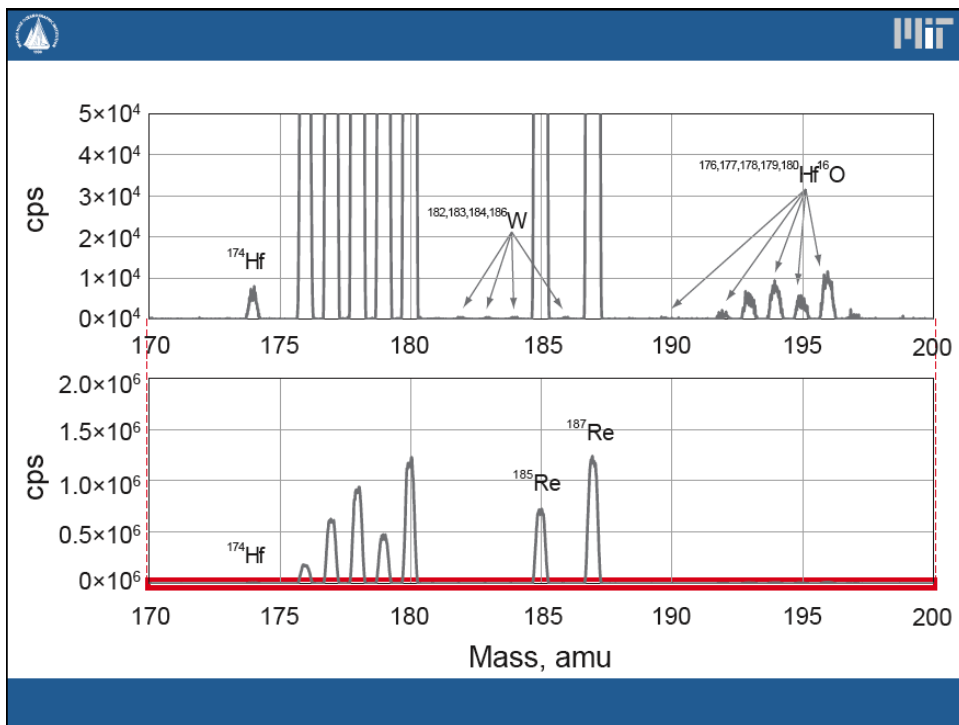


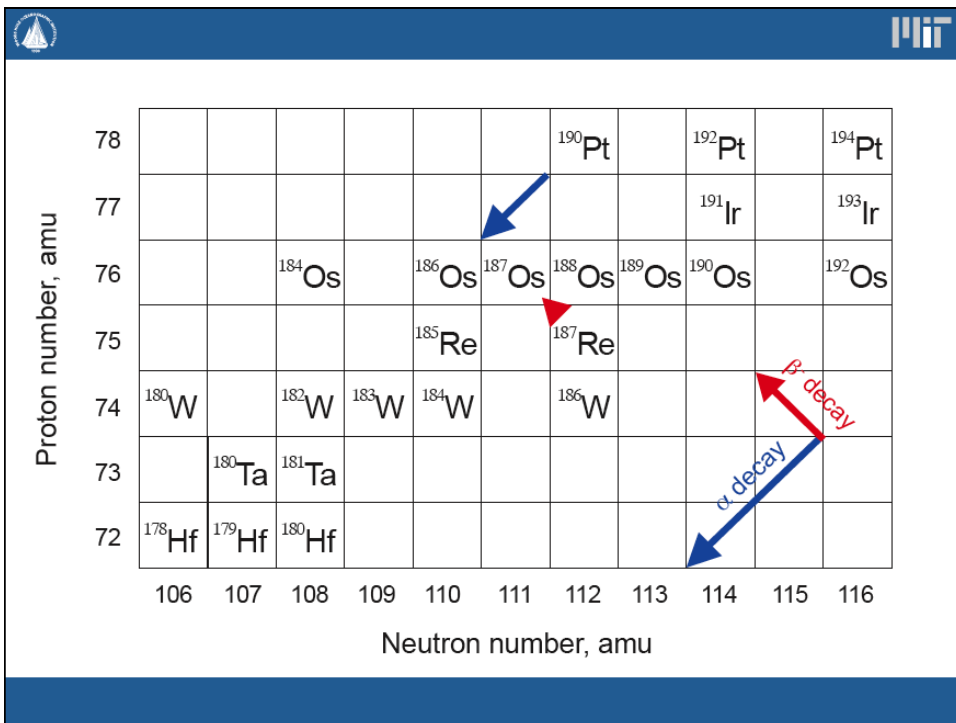
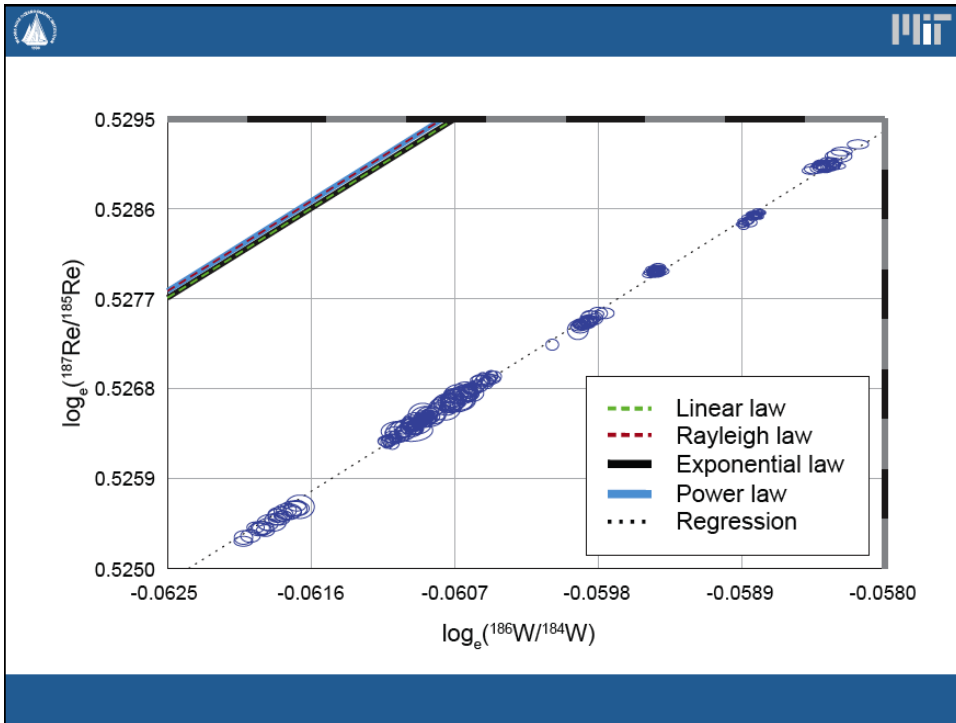














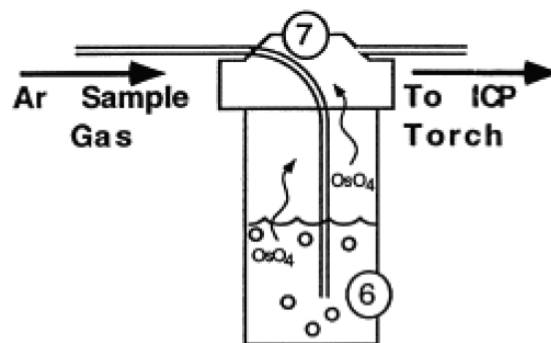
Aittojärvi:

MoS_2
 $2,809 \pm 11 \text{ Ma}$
 $[\text{Re}] = 0.118 \mu\text{mol g}^{-1}$

If we assume a modern $^{187}\text{Re}/^{185}\text{Re}$ of 0‰, we would measure a value of +47‰ due to ^{187}Os .



Sparging set-up:



Taken from Hassler et al., 2000

