Introduction to Isotope Fractionation

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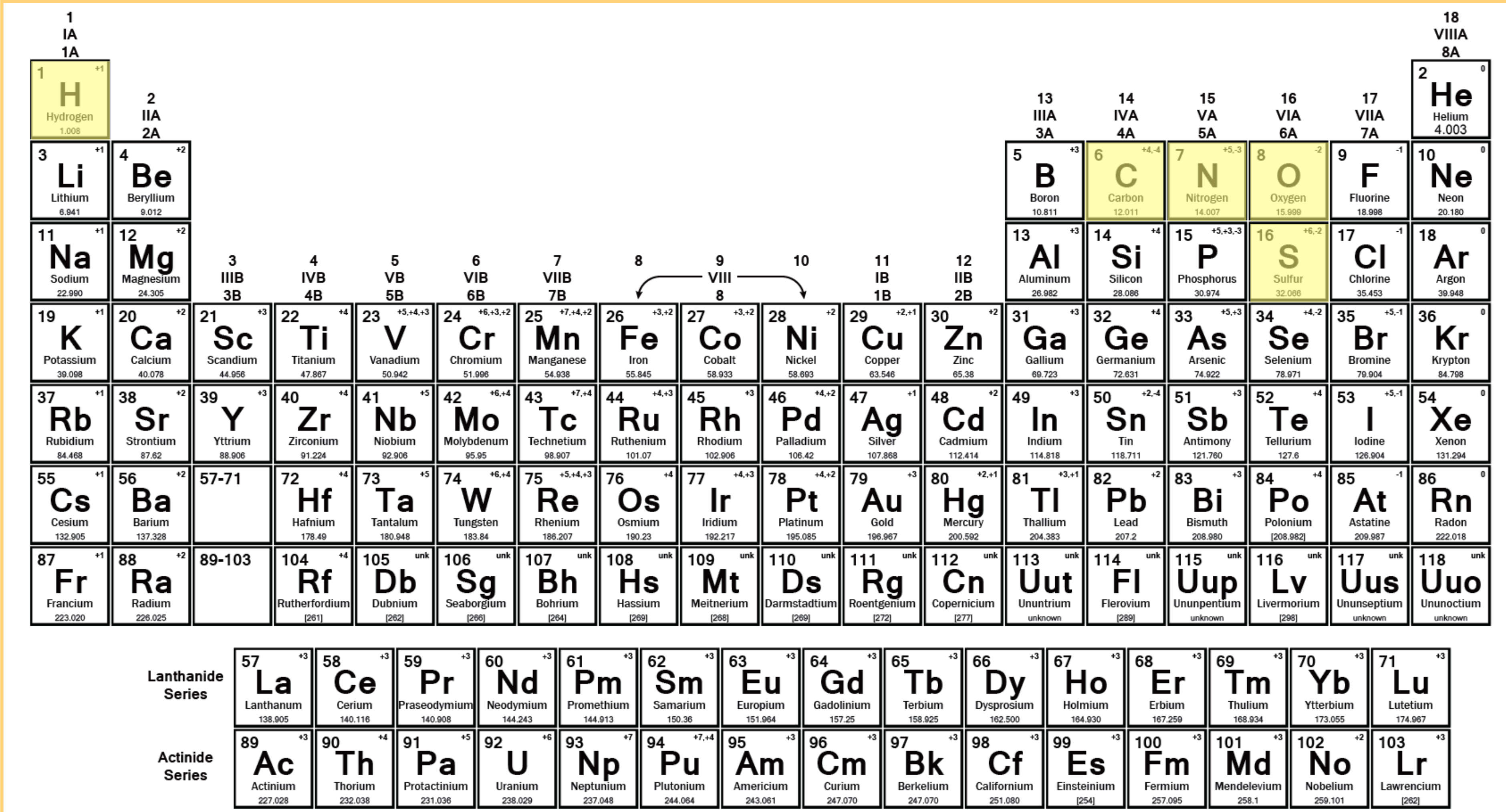
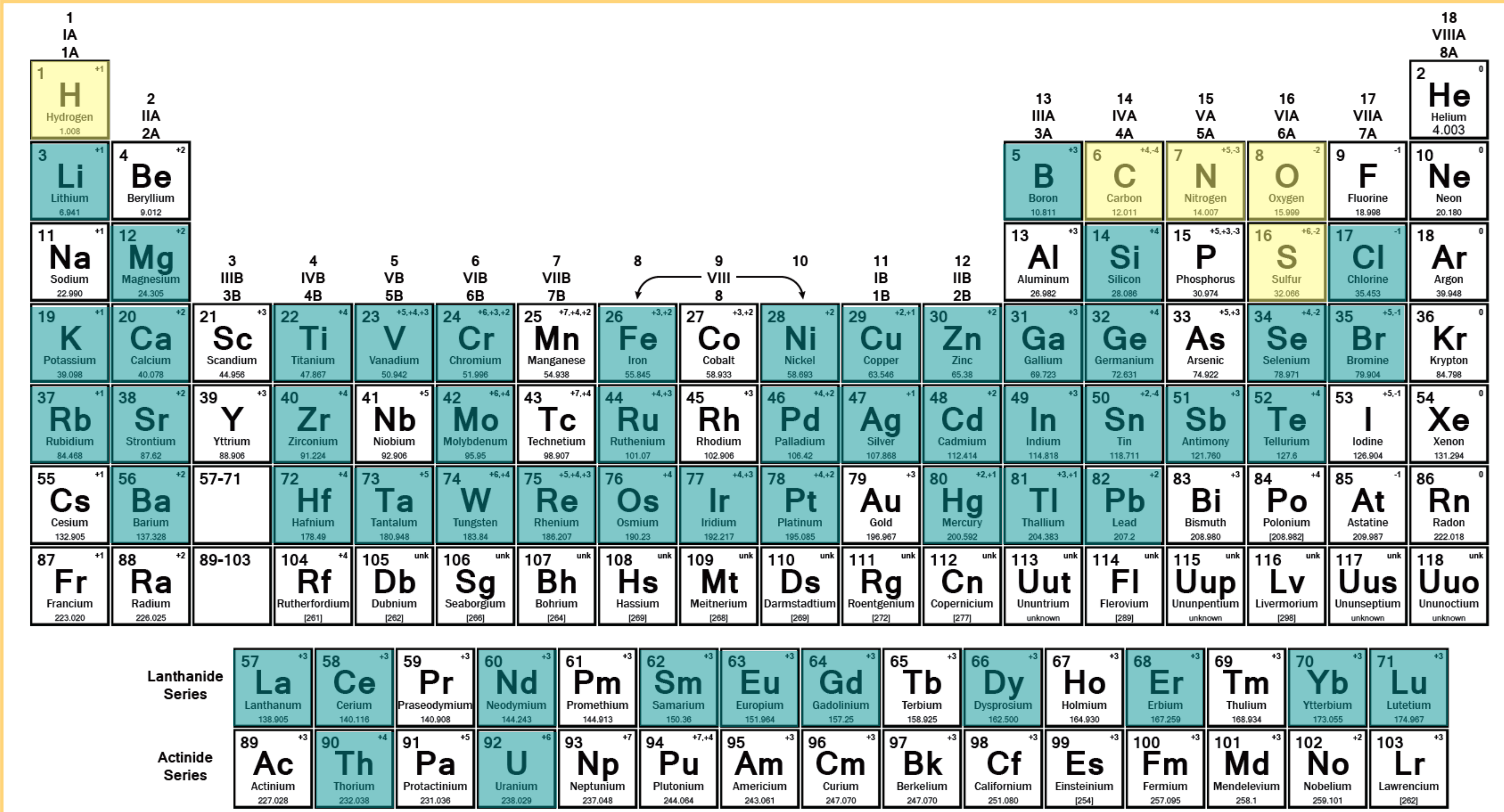


Look for elements that have more than one non-radiogenic isotope, for which the mass difference between isotopes is a significant fraction of the atomic mass (enough to measure)



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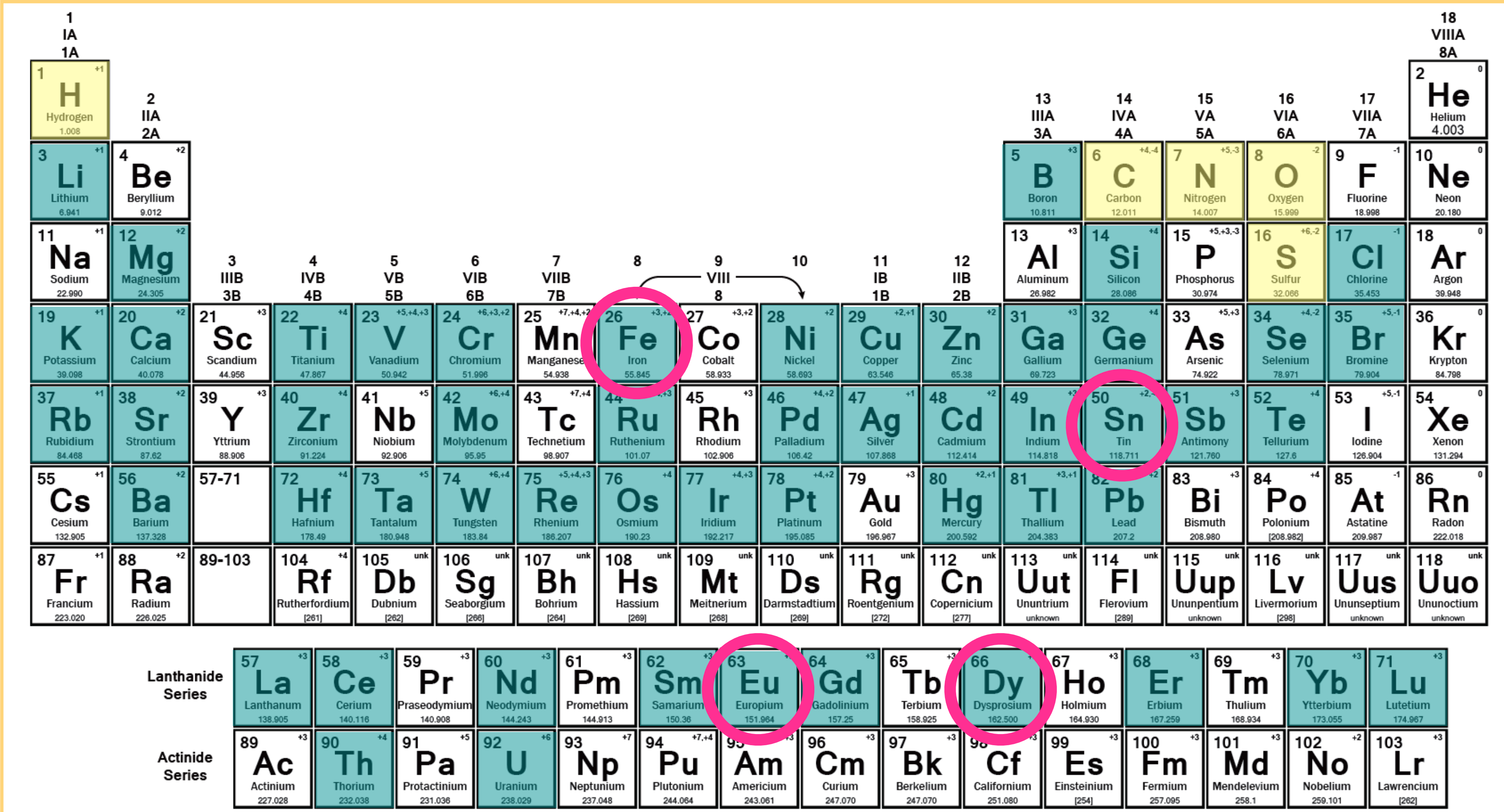
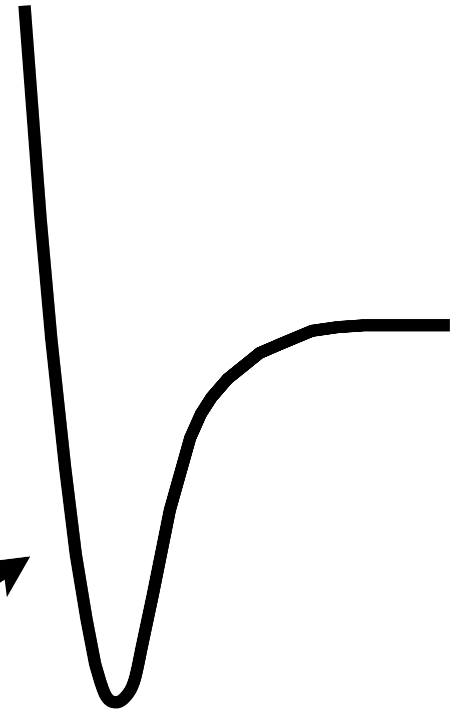


Look for elements that have a Mossbauer isotope

Fractionation refers to the partial separation of two isotopes of the same element, producing reservoirs with different ratios of the isotopes.

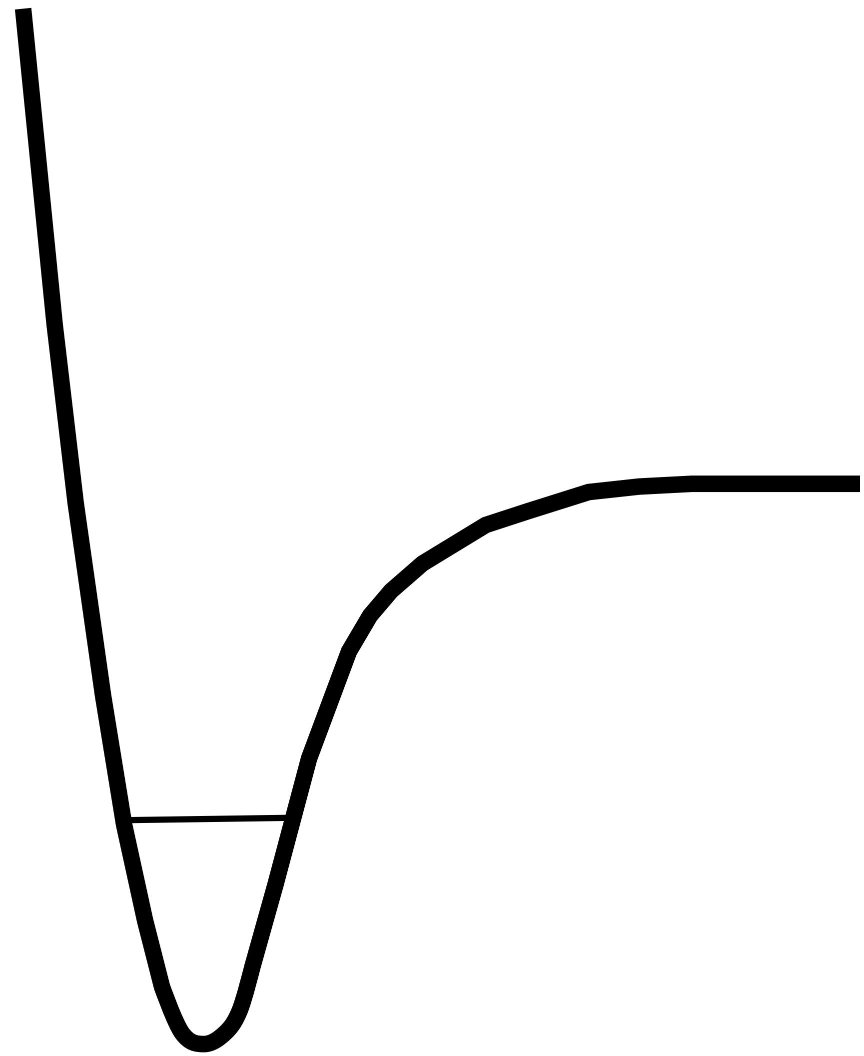
Isotopic fractionations occur due to:

- Differences in bond energies (equilibrium)
- Reaction rates (kinetics)



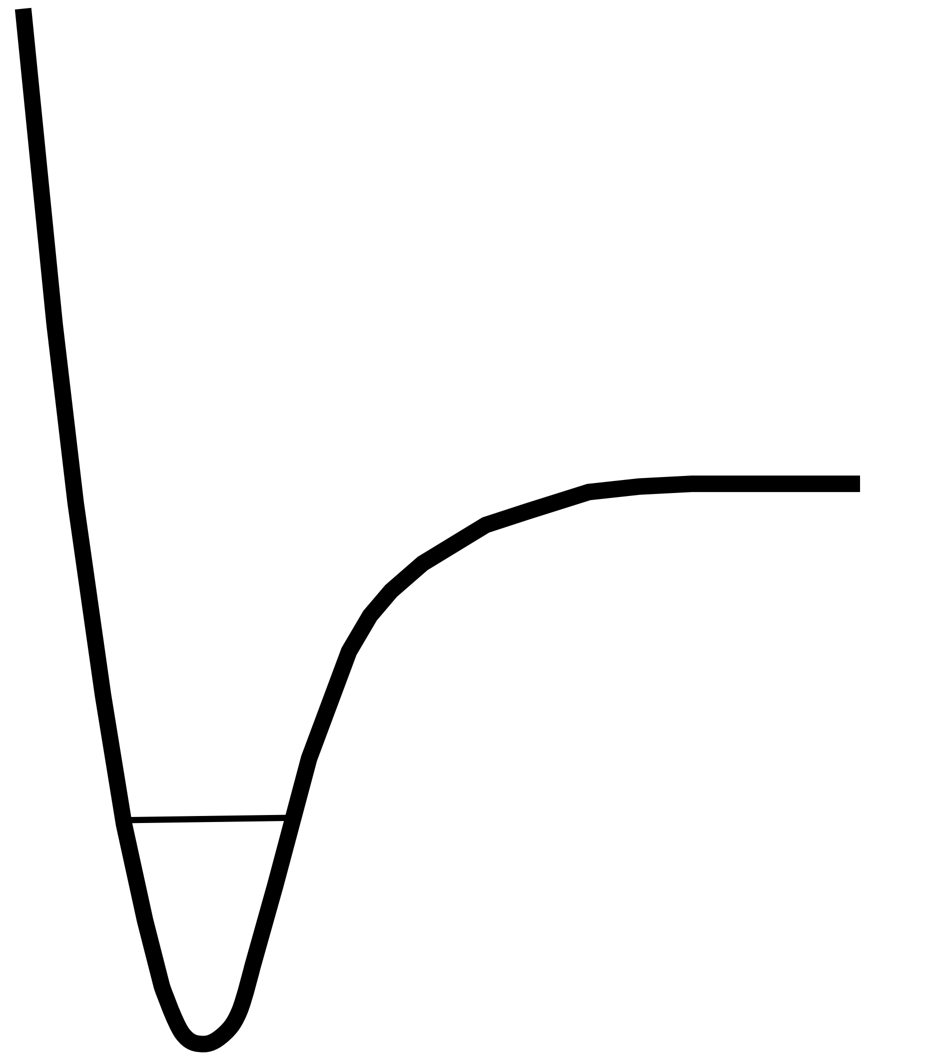
$$\frac{\langle v_1 \rangle}{\langle v_2 \rangle} = \sqrt{\frac{m_2}{m_1}}$$

$$E_n = h\nu(n + \tfrac{1}{2})$$



$$E_n = h\nu(n + ½)$$

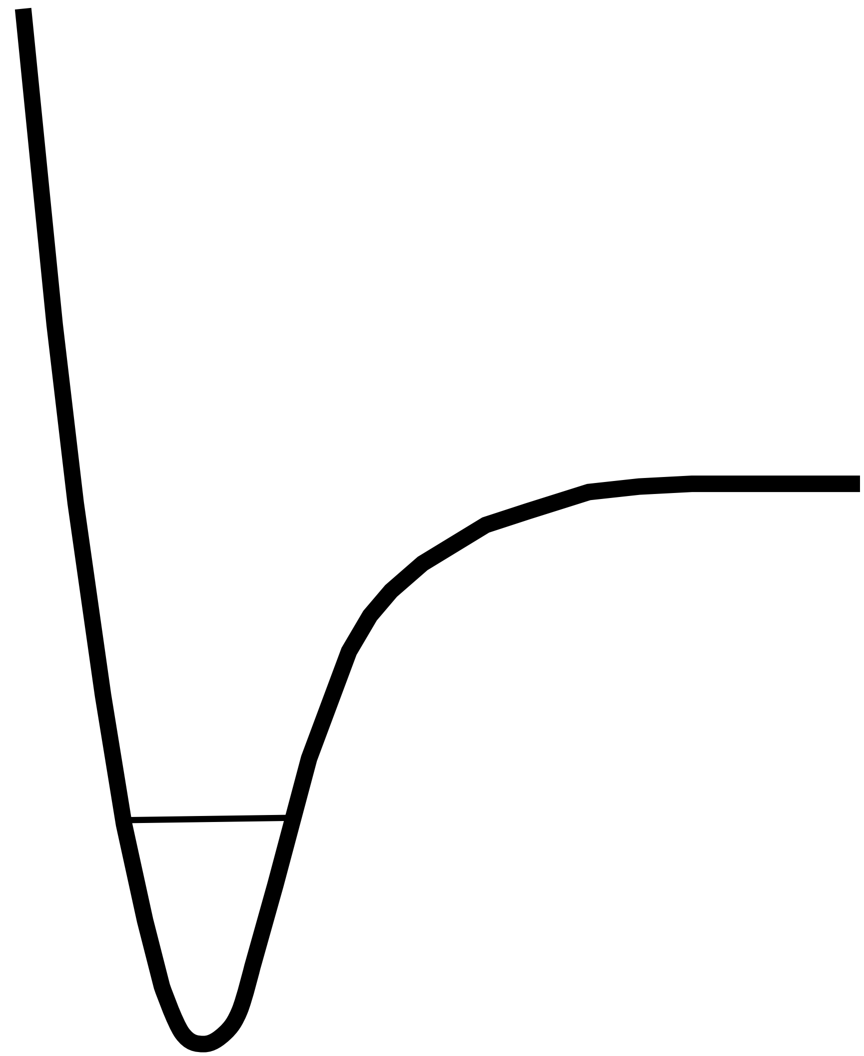
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$



$$E_n = h\nu(n + \tfrac{1}{2})$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

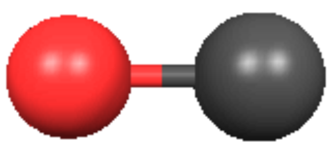
Zero-point energy differences drive typical equilibrium stable isotope fractionations.



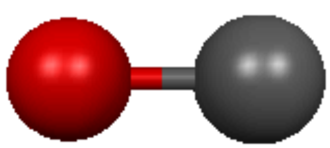
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Heavy isotopes have lower vibrational frequencies

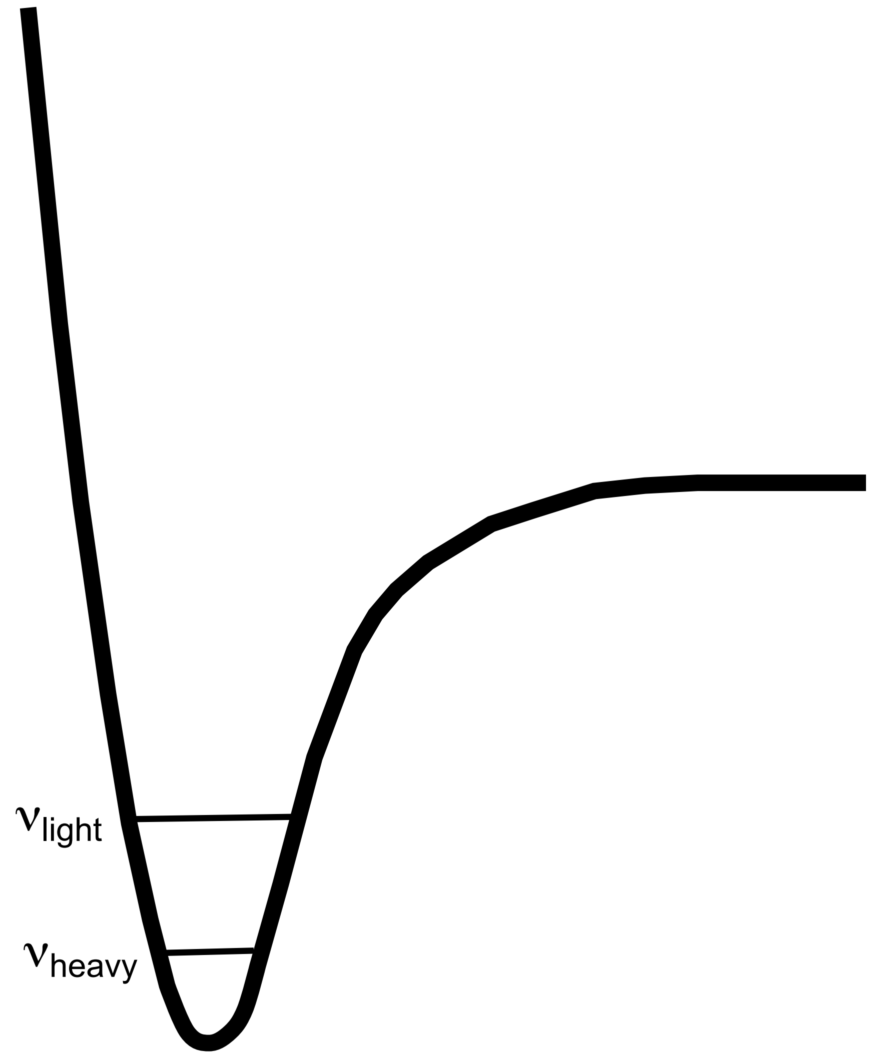
$^{12}C^{16}O$



$^{12}C^{18}O$



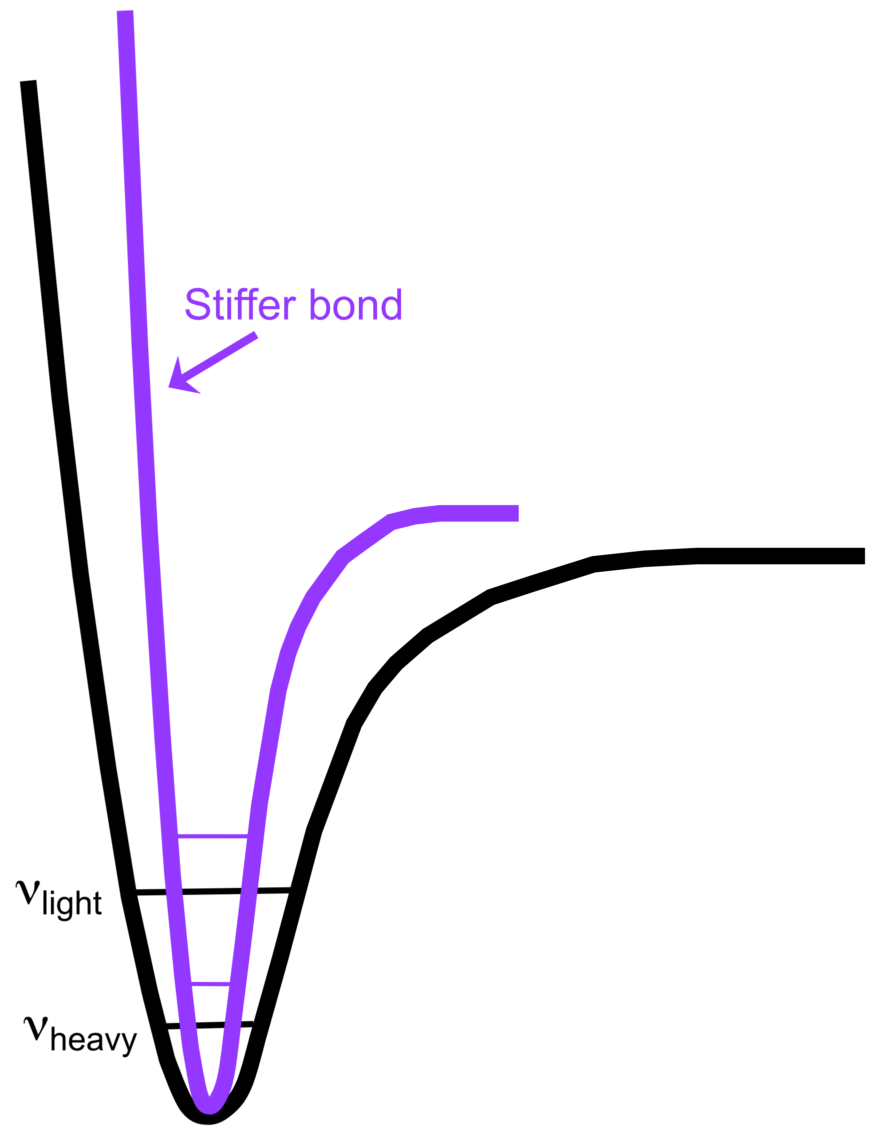
Credit: Edwin Schauble

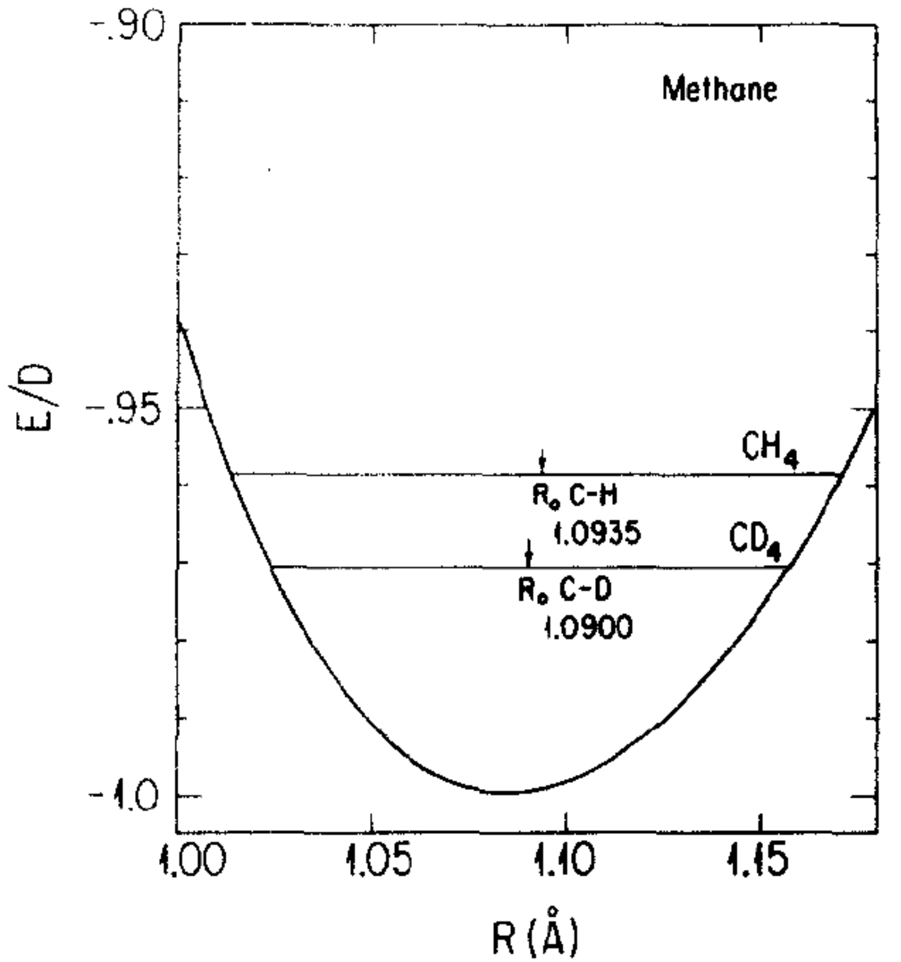


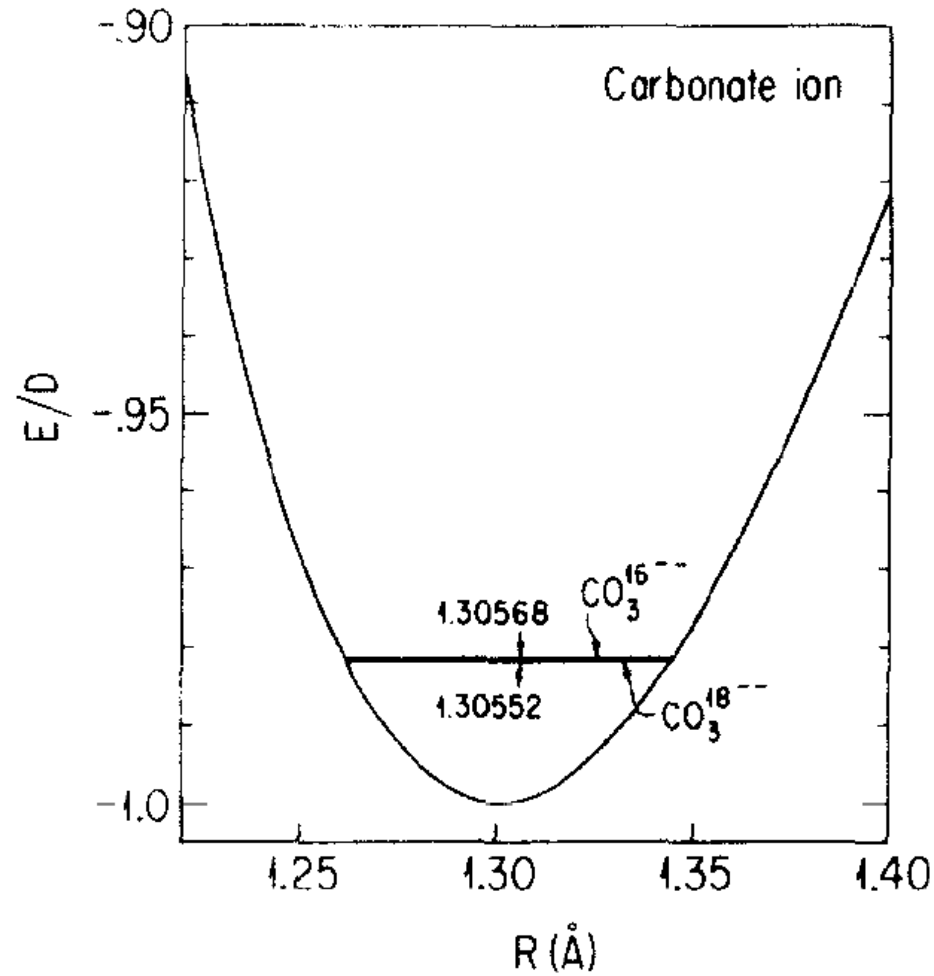
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Stiffer bonds concentrate the heavy isotopes

- shorter bonds
- higher oxidation state
- low coordination number





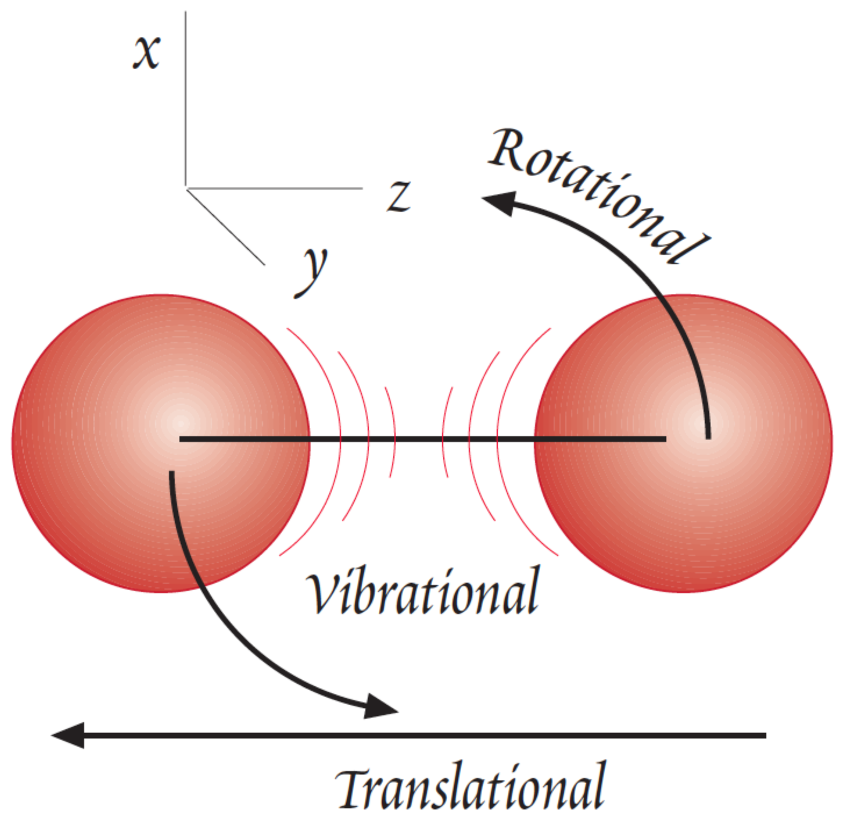


Clayton et al., 1975

$$AX' + BX = AX + BX'$$

$$K_{eq} = Q(AX)Q(BX')/Q(AX')Q(BX)$$

$$Q_{total} = Q_{translation}Q_{rotation}Q_{vibration}$$



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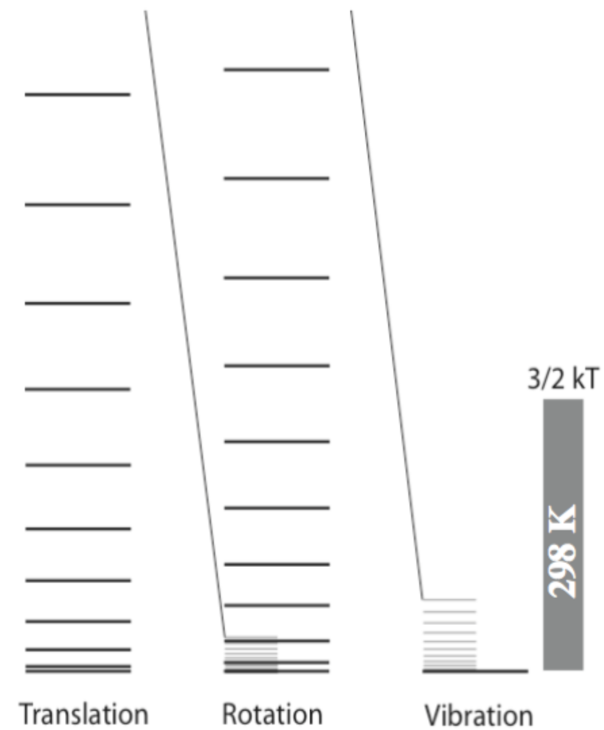
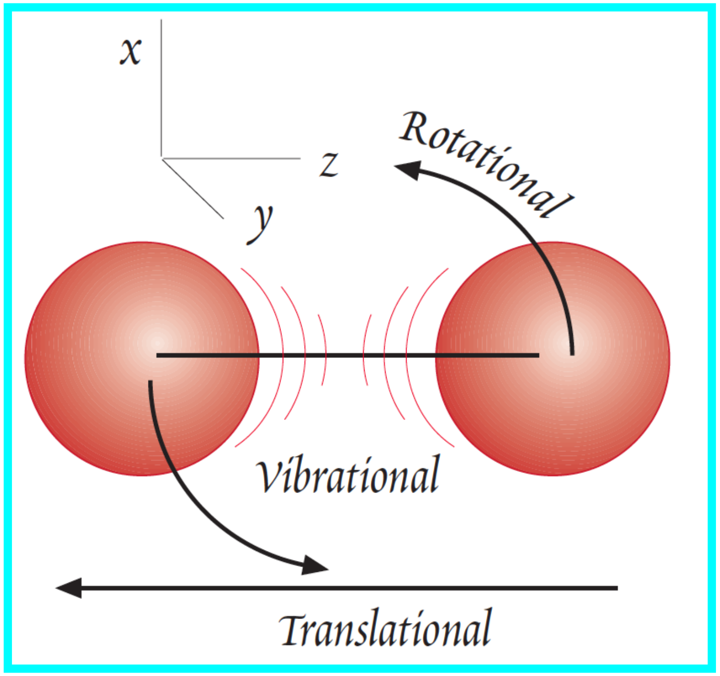
Energy quanta associated with molecular rotation and translation are so small that they can be treated approximately without an explicit sum over the quantum energies

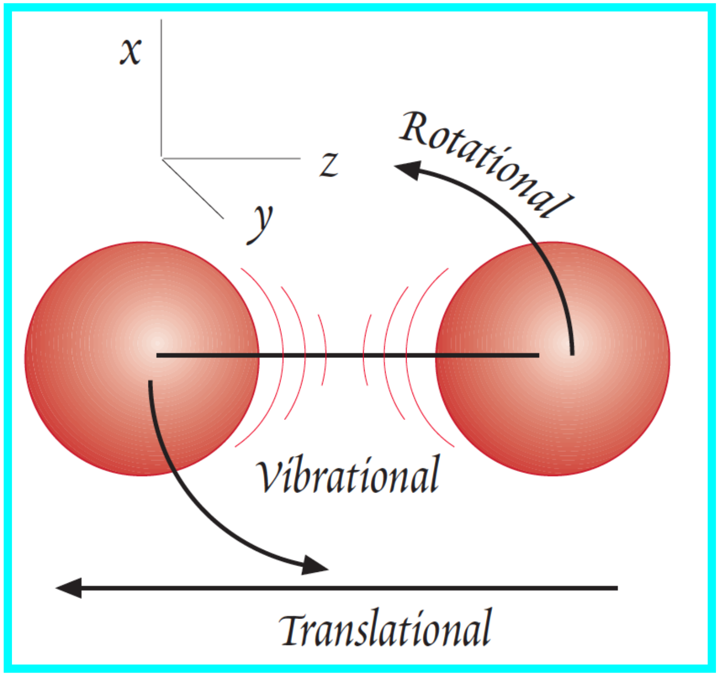


$$Q_{trans} = \frac{(2\pi mkT)^{3/2}}{h^3} V$$



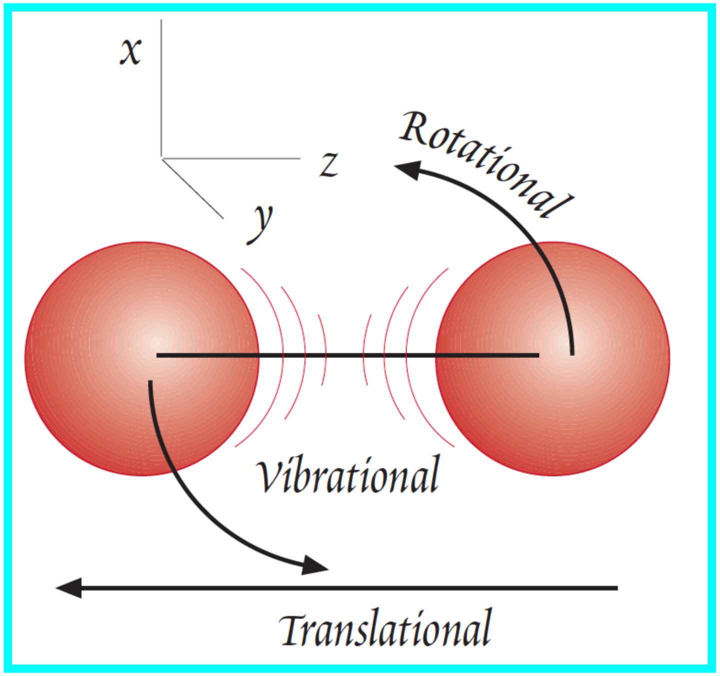
$$(Q/Q')_{tr} = (M'/M)^{3/2}$$

Translational energy is a function of the ratio of the molecular weights and is independent of temperature



$$Q_{rot} = \frac{8\pi^2 IkT}{h^2}$$

$$(Q/Q')_{rot} = \frac{s'I}{sI'}$$



$$Q_{vib} = \frac{e^{-h\nu/2kT}}{1-e^{-h\nu/kT}}$$

$$u_i = \frac{h\nu_i}{k_b T}$$

$$(Q/Q') = \prod_i \frac{e^{-u_i/2}}{e^{-u'_i/2}} \cdot \frac{1-e^{-u'_i}}{1-e^{-u_i}}$$

$$Q_{total} = Q_{vib} Q_{rot} Q_{trans} = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}} \frac{8\pi^2 IkT}{h^2} \frac{(2\pi mkT)^{3/2}}{h^3} V$$

$$(Q/Q') = \frac{s'}{s} \frac{I}{I'} \left(\frac{M}{M'}\right)^{3/2} \cdot \frac{e^{-u/2}}{e^{-u'/2}} \cdot \frac{1 - e^{-u'}}{1 - e^{-u}}$$

$$\left(\frac{m}{m'}\right)^{3/2} \frac{I'}{I} \left(\frac{M'}{M}\right)^{3/2} \frac{u}{u'} = 1$$

$$(Q/Q') = \frac{s'}{s} \left(\frac{m}{m'}\right)^{3/2} \frac{u}{u'} \cdot \frac{e^{-u'/2}}{e^{-u/2}} \cdot \frac{1 - e^{-u'}}{1 - e^{-u}}$$

$$10^3 \ln \alpha_{a-b}^{i/j} = \frac{10^3}{24}\left(\frac{h}{k_b T}\right)^2 \left(\frac{1}{m_j} - \frac{1}{m_i}\right)\left[\sum_{x=1} \frac{K_{f,x,a}}{4\pi^2} - \sum_{x=1} \frac{K_{f,x,b}}{4\pi^2}\right]$$

Schauble (2004) suggested the following rules governing equilibrium stable isotope fractionations:

- decrease as temperature increases
- fractionation scales with mass
- heavy isotopes of an element will tend to be concentrated in substances with stiffest bonds (high spring constants)
  - high oxidation state; highly covalent bonds; low coordination number; for anions high oxidation state to which the element of interest is bonded; bonds involving elements near the top of the periodic table; low-spin electronic configurations

The extent of isotope separation in a particular reaction is the α

$$\alpha_{A\text{-}B} = R^{i/j}_A / R^{i/j}_B$$

where $R^{i/j}_A$ is the ratio of isotopes i and j in material A

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$$\alpha_{A\text{-}B} = R^{i/j}_{A}/R^{i/j}_{B}$$

where $R^{i/j}_{A}$ is the ratio of isotopes i and j in material A

and

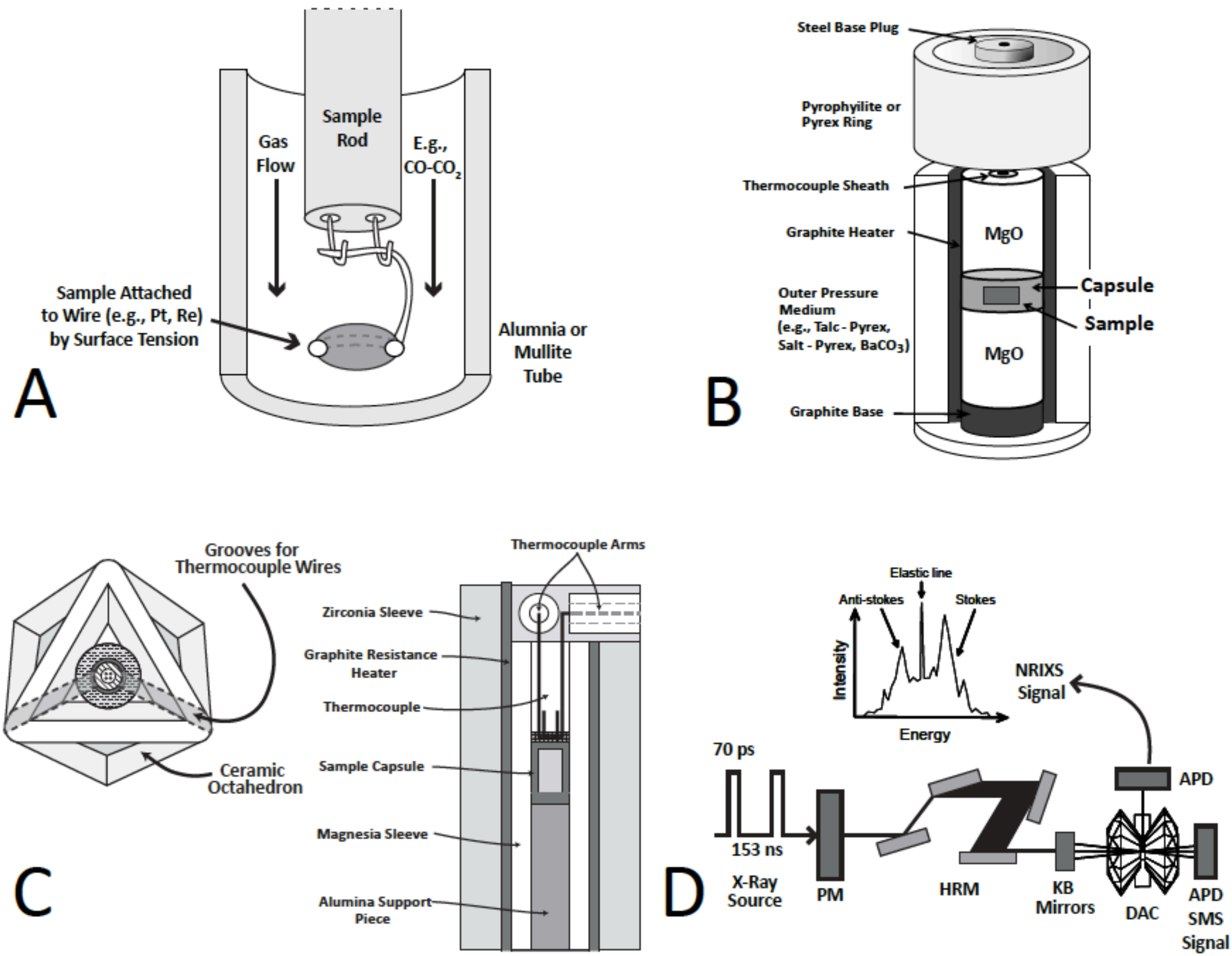
$$\ln \alpha_{A-B} = \ln \beta_A - \ln \beta_B$$

Equilibrium Fractionation Factor

Beta Factor

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

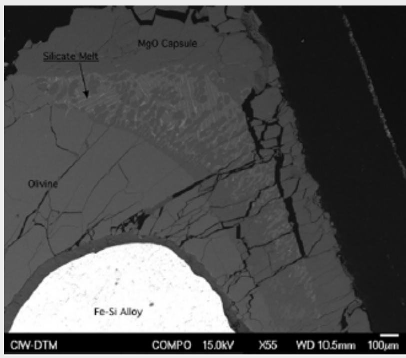
Force Constant



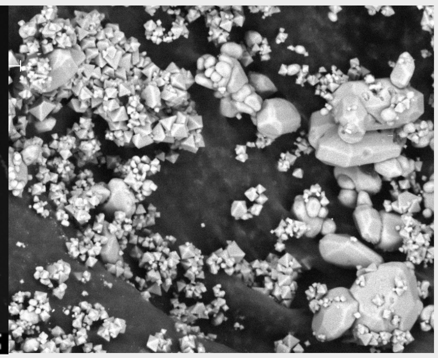
Shahar et al., 2017

Planning an equilibrium fractionation experiment: Challenges

sample size

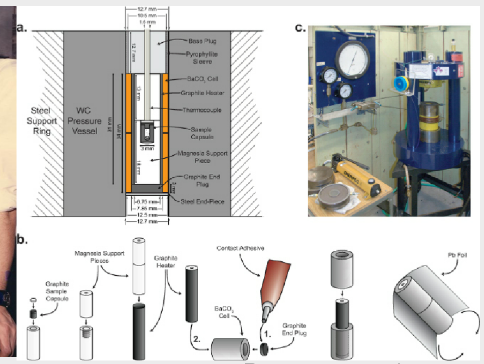


Shahar et al. 2011



Macris et al. 2013

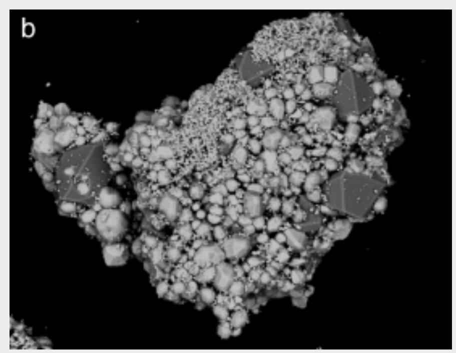
limits of experimental apparati



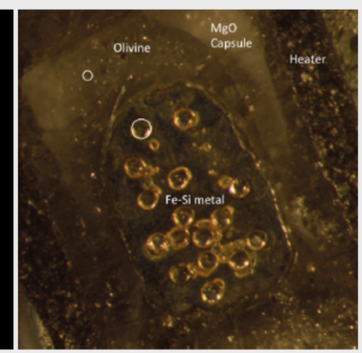
Bennett et al. 2015

starting materials, buffers, and containers

separate phases vs. *in situ*



Shahar et al. 2008



Shahar et al. 2011

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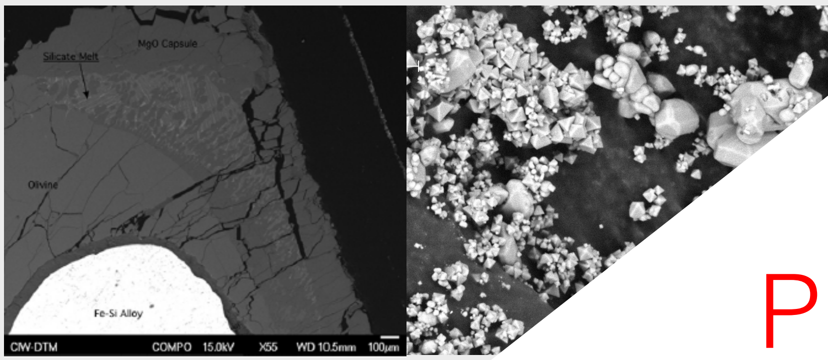

Shahar et al. 2011

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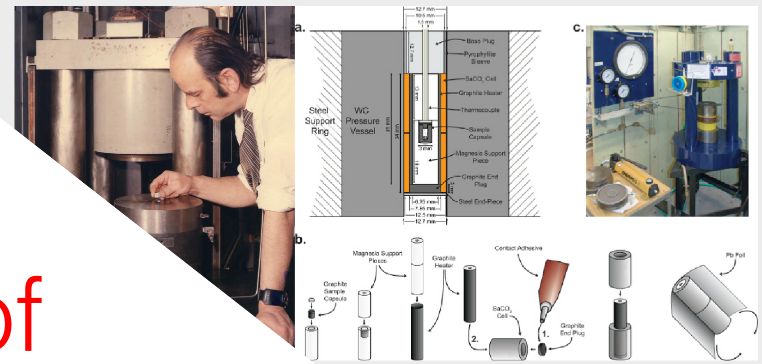
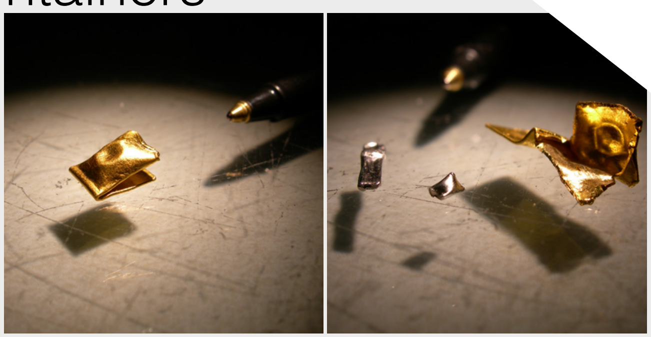
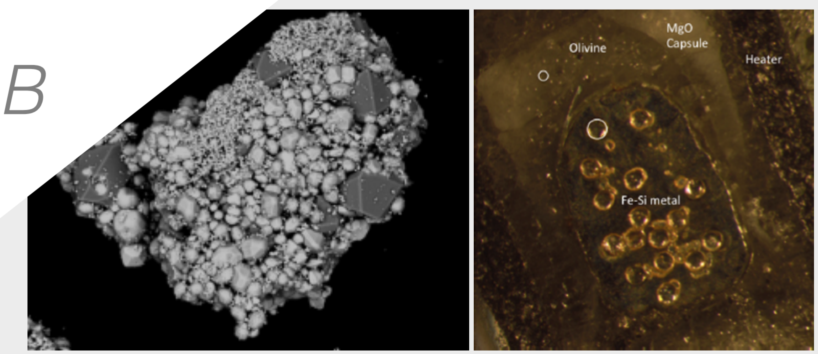


Bennett et al. 2015

starting materials, b
containers



hases vs. *in situ*



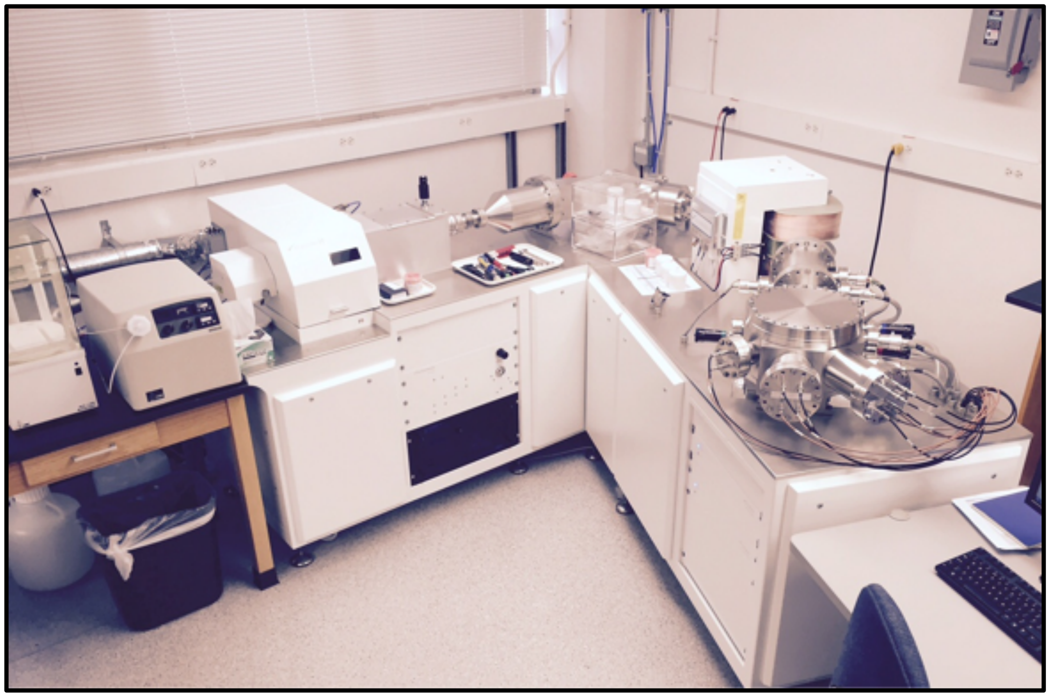
Shahar et al. 2008

Shahar et al. 2011

Proof of equilibrium

$\alpha_{A\text{-}B}$

Post-experiment analysis



Usually by solution MC-ICP-MS → requires quantitative separation of phases, acid digestion, and purification by column chemistry

Less often *in situ* LA-ICP-MS or SIMS → cut and polish experimental charge; usually associated with larger errors

So what can we learn from stable isotopes about the deep earth? How do we use them?

- From experiments we can determine what the fractionation factors are for certain reactions as a function of temperature, pressure and composition

- From natural samples we can then determine which chemical reactions and/or physical processes occurred in the samples

Tracers!

Geochimica et Cosmochimica Acta, Vol. 69, No. 23, pp. 5531–5536, 2005

0016-7037/05 $30.00 + .00

doi:10.1016/j.gca.2005.07.010

Determination of tin equilibrium isotope fractionation factors from synchrotron radiation experiments

V. B. Polyakov,[1,*] S. D. Mineev,[1] R. N. Clayton,[2] G. Hu,[3] and K. S. Mineev[4]

Available online at www.sciencedirect.com
ScienceDirect
Geochimica et Cosmochimica Acta 71 (2007) 3833–3846
Geochimica et Cosmochimica Acta
www.elsevier.com/locate/gca

Equilibrium iron isotope fractionation factors of minerals: Reevaluation from the data of nuclear inelastic resonant X-ray scattering and Mössbauer spectroscopy

V.B. Polyakov [a,b,*], R.N. Clayton [c], J. Horita [b], S.D. Mineev [d]

ARTICLE
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Iron isotopic fractionation between silicate mantle and metallic core at high pressure

Jin Liu[1,†], Nicolas Dauphas[2], Mathieu Roskosz[3], Michael Y. Hu[4], Hong Yang[5], Wenli Bi[4,6], Jiyong Zhao[4], Esen E. Alp[4], Justin Y. Hu[2] & Jung-Fu Lin[1,5]

Spinel–olivine–pyroxene equilibrium iron isotopic fractionation and applications to natural peridotites

Mathieu Roskosz [a,*], Corliss K.I. Sio [b,1], Nicolas Dauphas [b], Wenli Bi [c], François L.H. Tissot [b], Michael Y. Hu [c], Jiyong Zhao [c], Esen E. Alp [c]

Experimentally determined effects of olivine crystallization and melt titanium content on iron isotopic fractionation in planetary basalts

Kelsey B. Prissel [a,*], Michael J. Krawczynski [a], Nicole X. Nie [b], Nicolas Dauphas [b], Hélène Couvy [a], Michael Y. Hu [c], E. Ercan Alp [c], Mathieu Roskosz [d]

Equilibrium Iron Isotope Fractionation at Core-Mantle Boundary Conditions

Veniamin B. Polyakov

Experimental constraints on the thermodynamics and sound velocities of hcp-Fe to core pressures

Caitlin A. Murphy,[1] Jennifer M. Jackson,[1] and Wolfgang Sturhahn[1]

Received 27 November 2012; revised 7 March 2013; accepted 19 March 2013; published 20 May 2013.

Magma redox and structural controls on iron isotope variations in Earth's mantle and crust

N. Dauphas [a,*], M. Roskosz [b], E.E. Alp [c], D.R. Neuville [d], M.Y. Hu [c], C.K. Sio [a], F.L.H. Tissot [a], J. Zhao [c], L. Tissandier [e], E. Médard [f], C. Cordier [b]

GEOCHEMISTRY

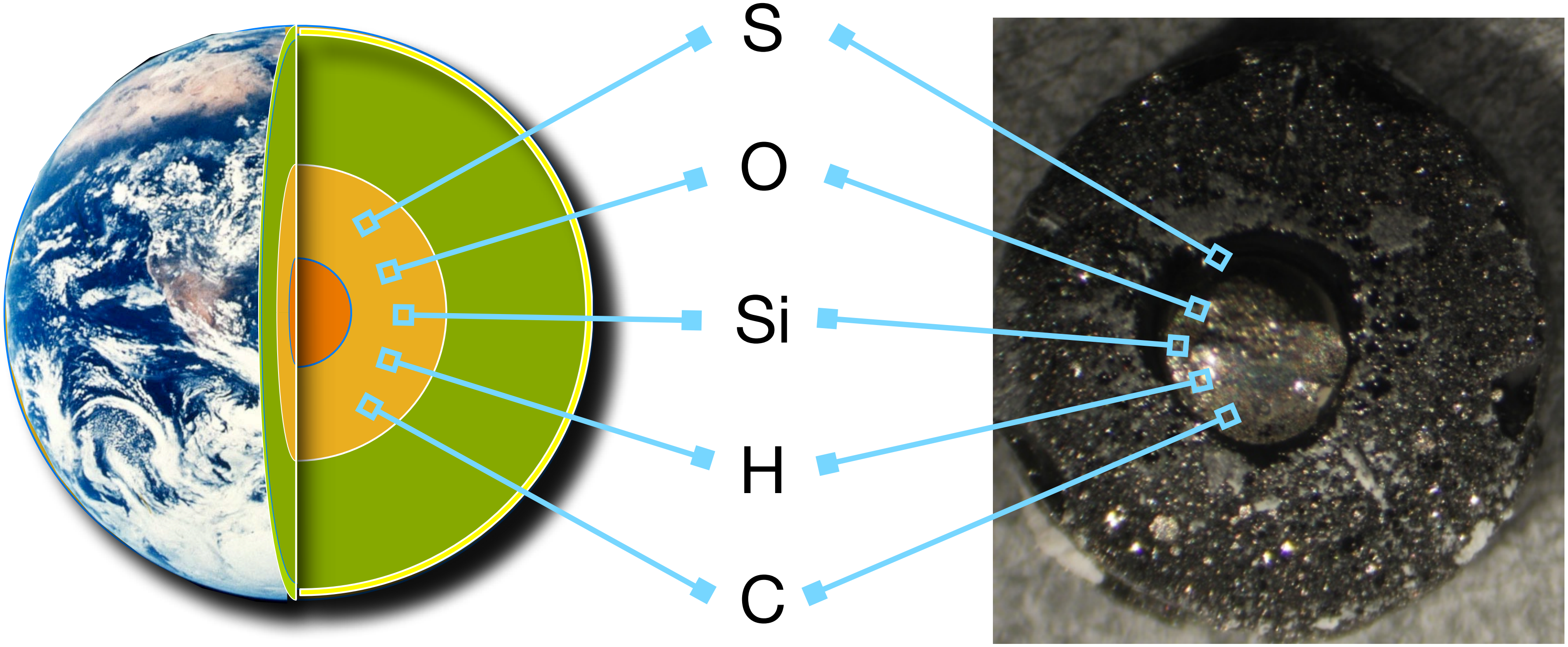
Pressure-dependent isotopic composition of iron alloys

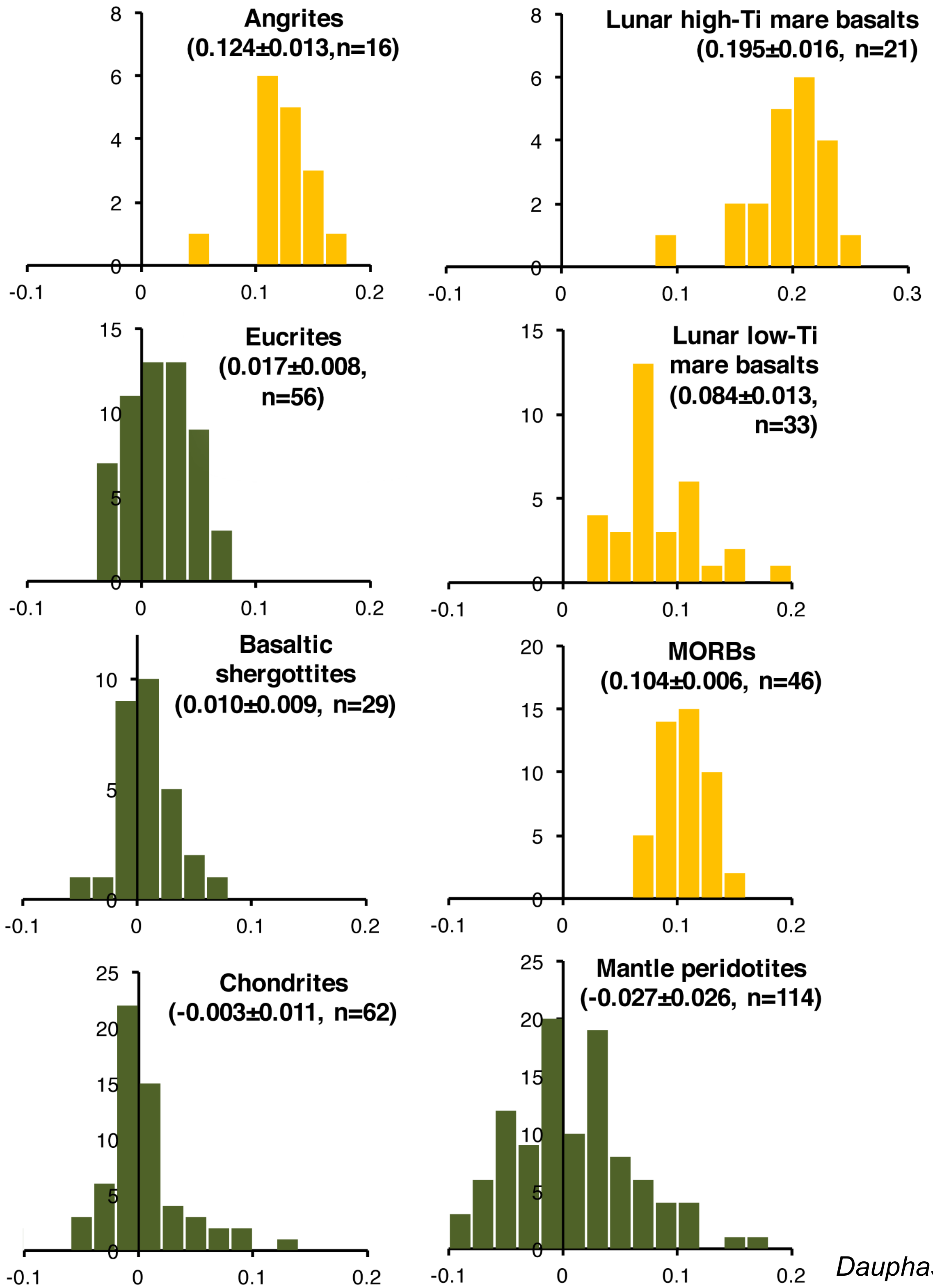
A. Shahar,[1*] E. A. Schauble,[2] R. Caracas,[3] A. E. Gleason,[4] M. M. Reagan,[5] Y. Xiao,[6] J. Shu,[1] W. Mao[5]

A *general moment* NRIXS approach to the determination of equilibrium Fe isotopic fractionation factors: Application to goethite and jarosite

N. Dauphas [a,*], M. Roskosz [b], E.E. Alp [c], D.C. Golden [d], C.K. Sio [a], F.L.H. Tissot [a], M.Y. Hu [c], J. Zhao [c], L. Gao [c], R.V. Morris [e]

Example: Iron Isotopic Fractionation During Earth's Differentiation and Evolution

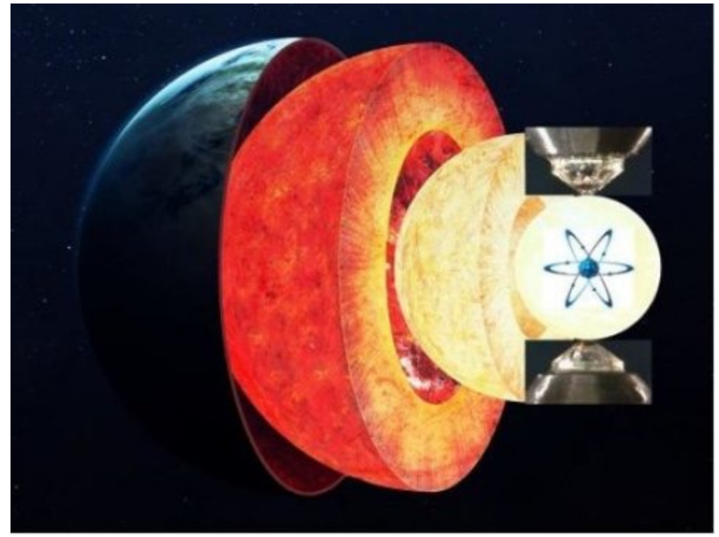




Iron isotopic compositions of planetary samples - trying to understand why MORBs, for example, are not the same as mantle peridotite and chondrites.

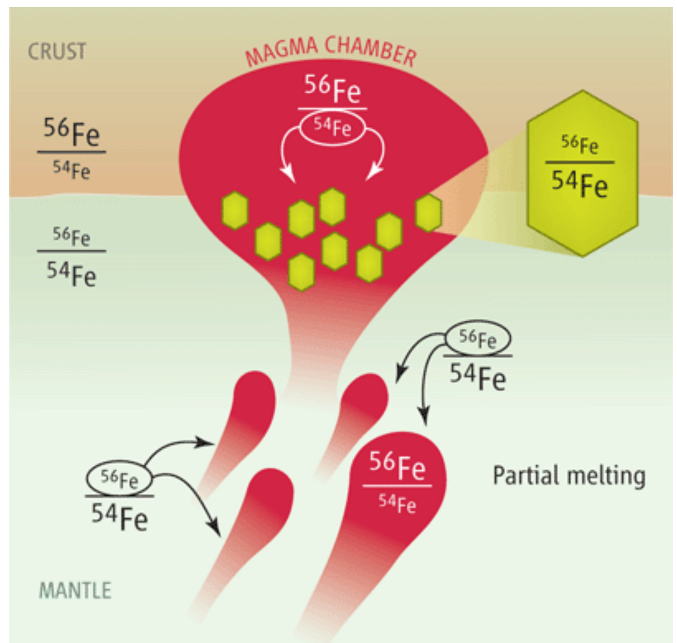
Dauphas et al., 2017

Suggestions for mechanisms causing iron isotope fractionation that cause the natural sample variation.



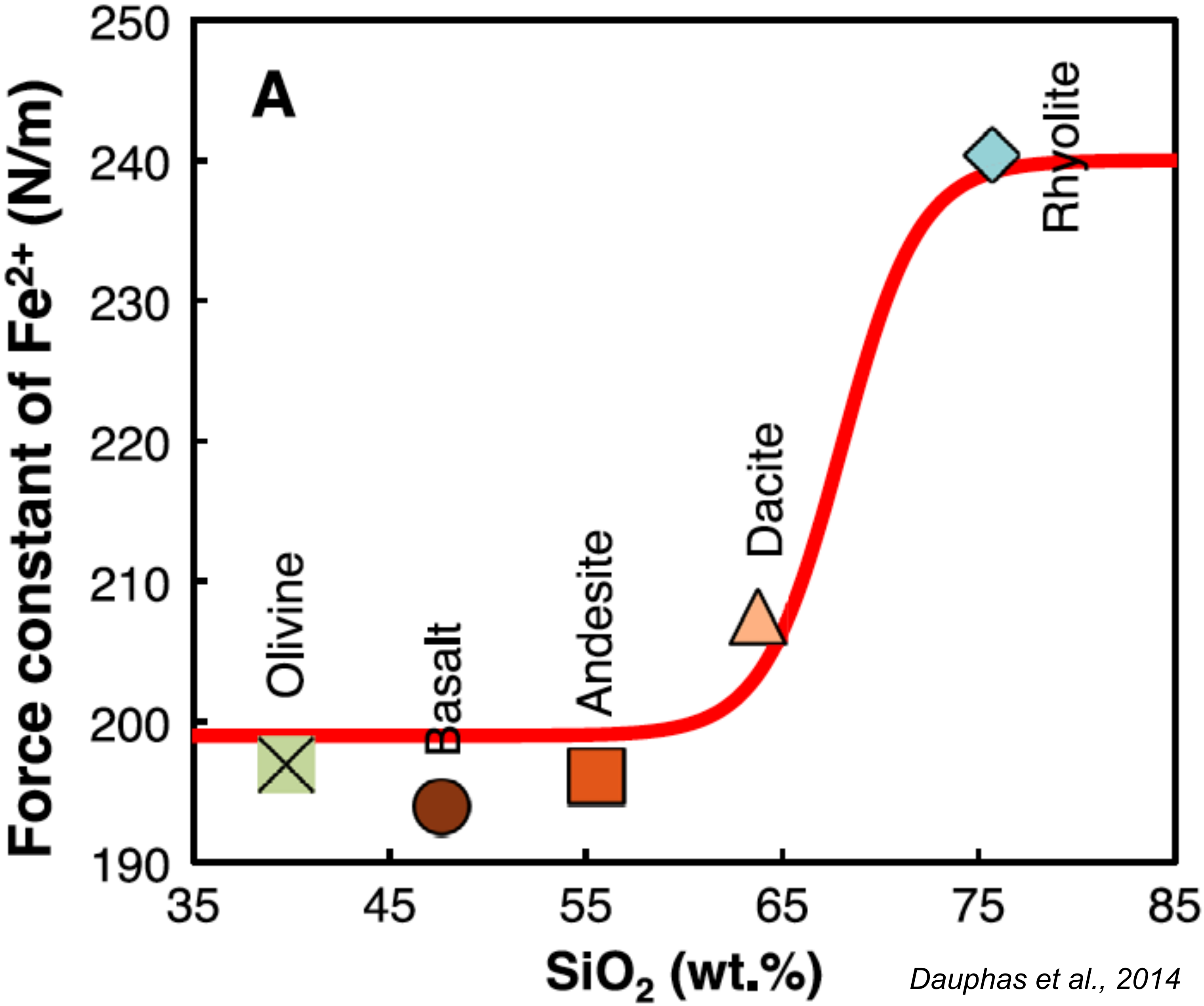
Differentiation (e.g. Polyakov 2009)

Evaporation (e.g. Poitrasson et al. 2004)



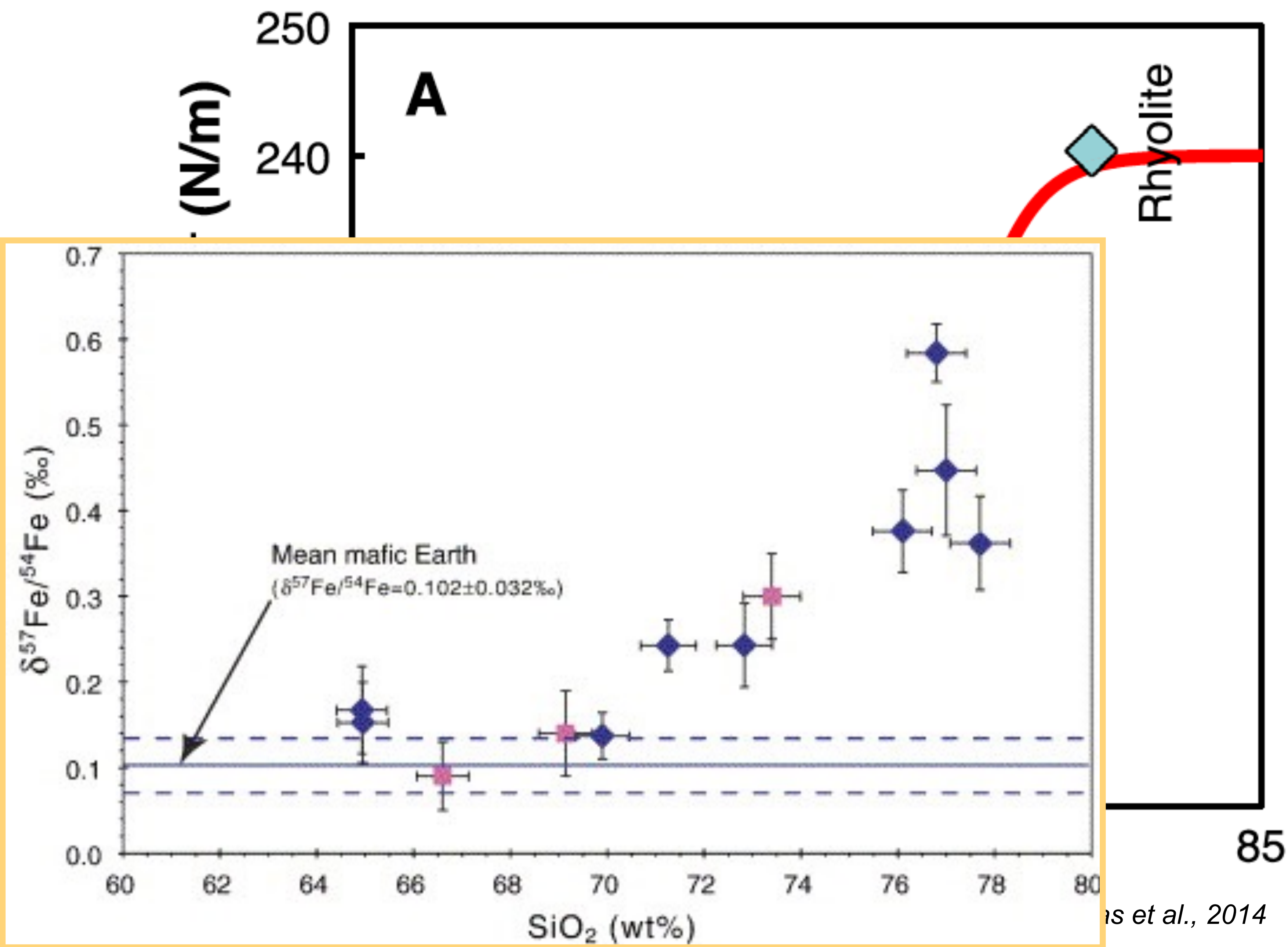
Magmatic Processes (e.g. Williams et al. 2005, Teng et al. 2008)

Composition



Dauphas et al., 2014

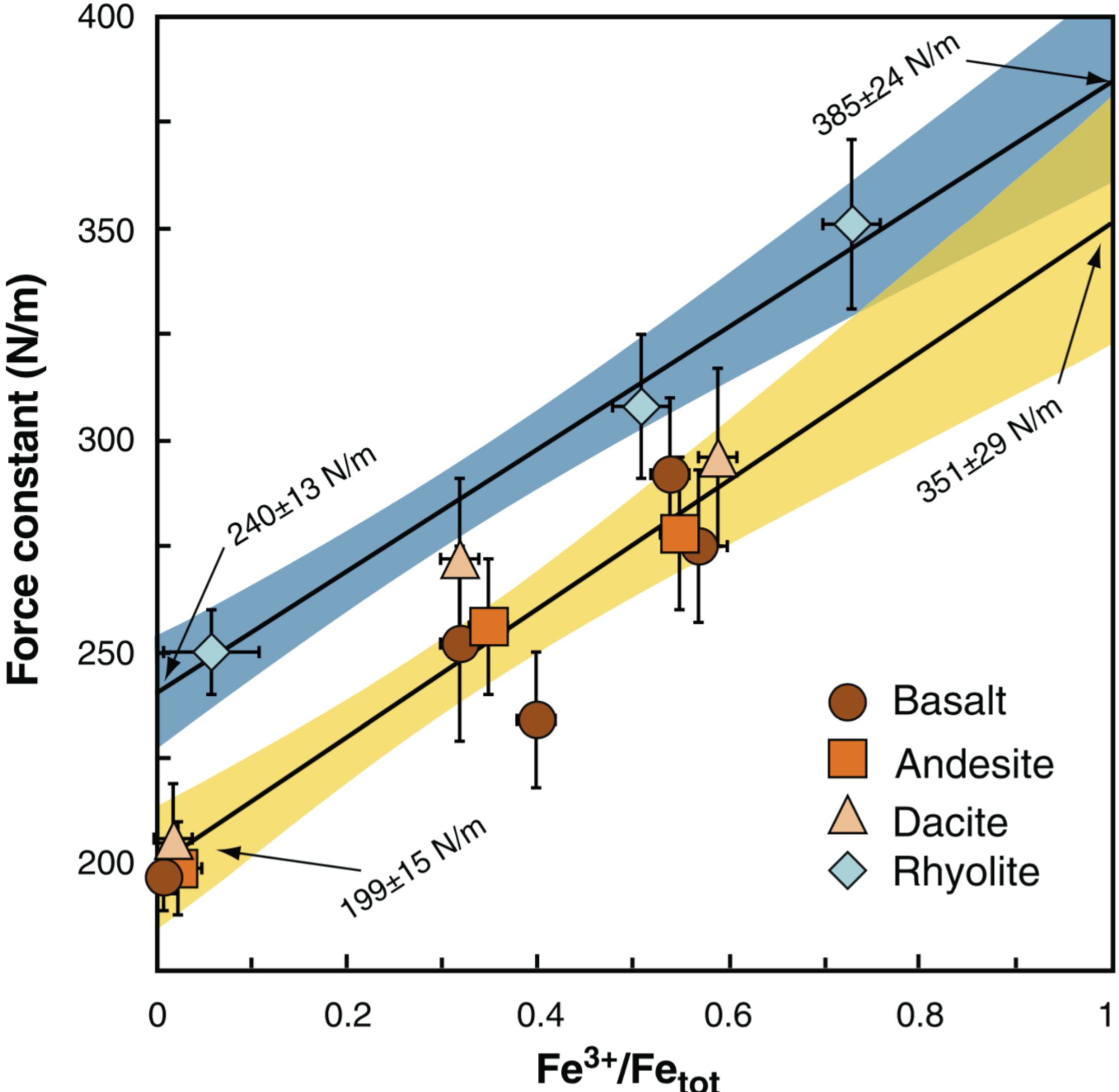
Composition



as et al., 2014

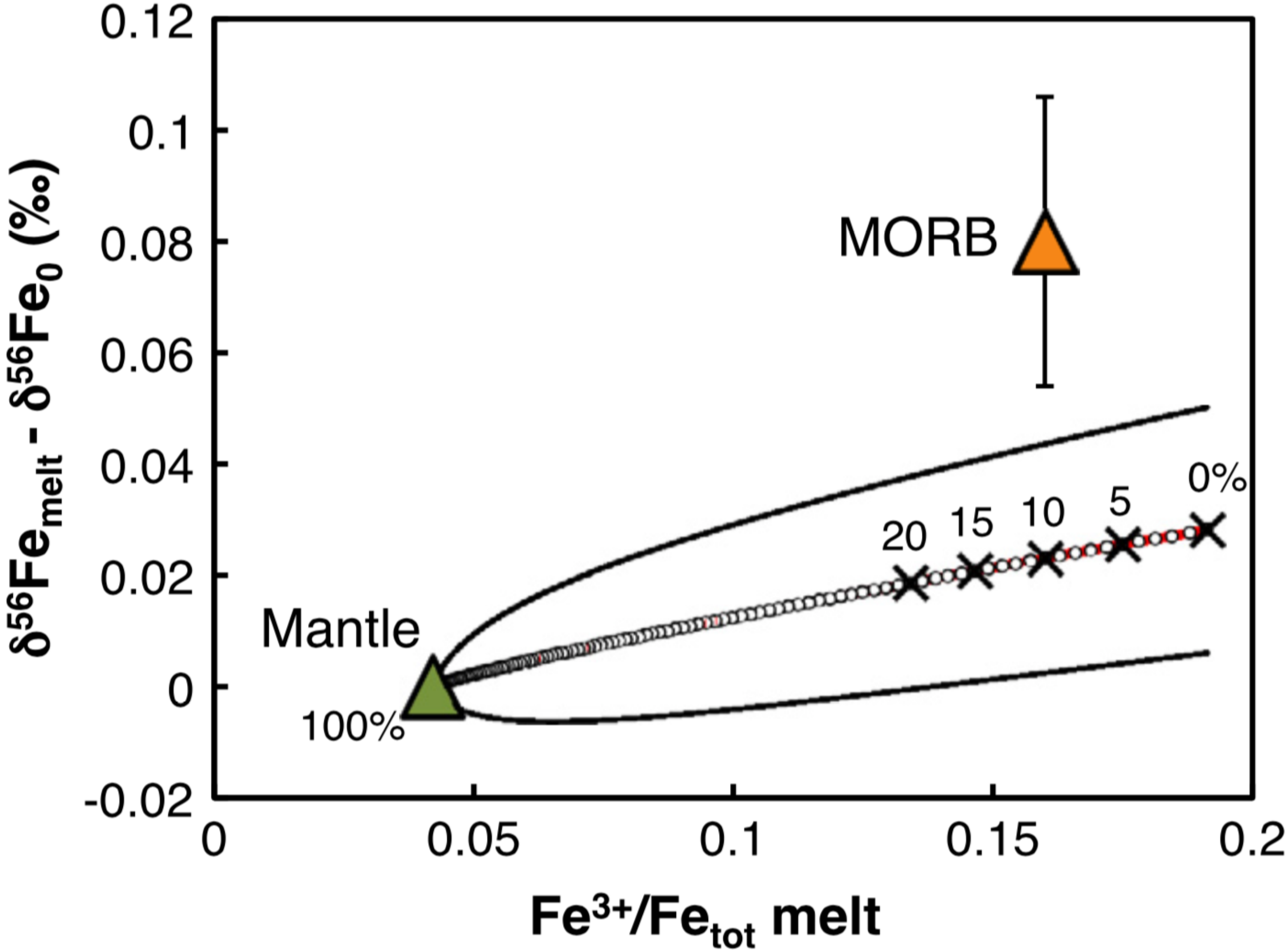
Poitrasson et al., 2005

Oxidation State



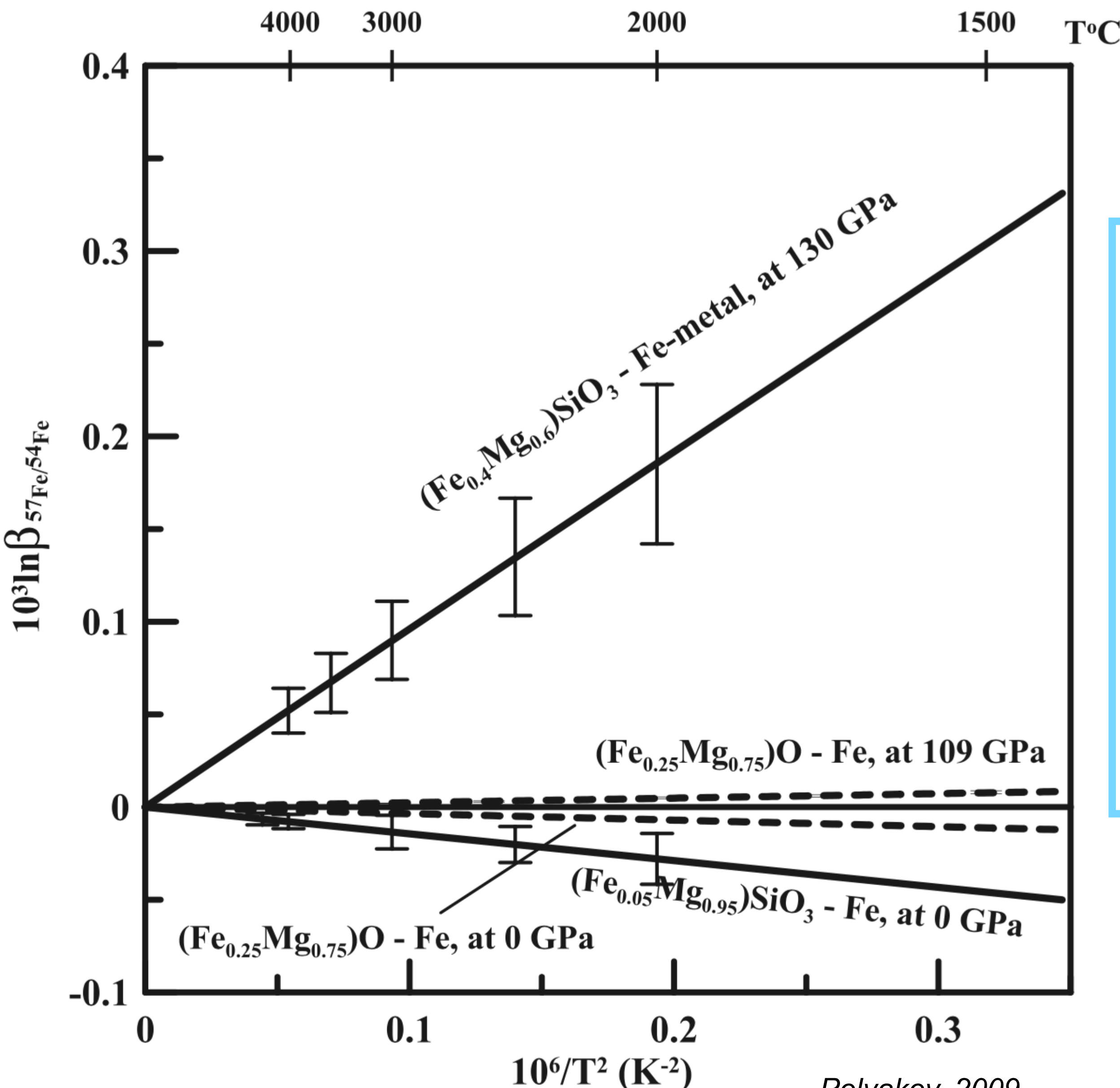
Dauphas et al., 2014

Partial Melting



Dauphas et al., 2014

Differentiation



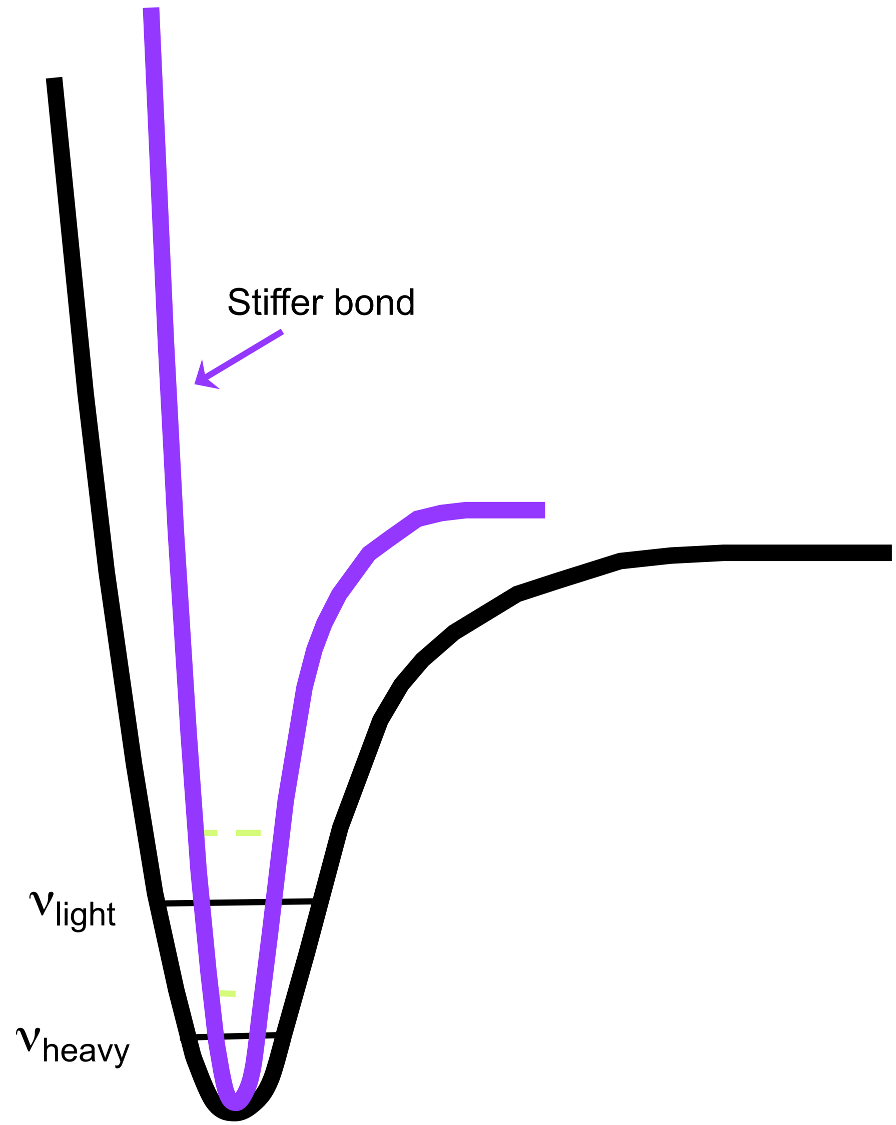
Polyakov, 2009

First suggestion that pressure might have an effect on isotope fractionation and that there is a fractionation during core formation.

Molar Volume Isotope Effect

Bond Stiffening

$$\left(\frac{\partial \ln\beta}{\partial P}\right)_T = -\frac{\Delta V}{nRT}$$



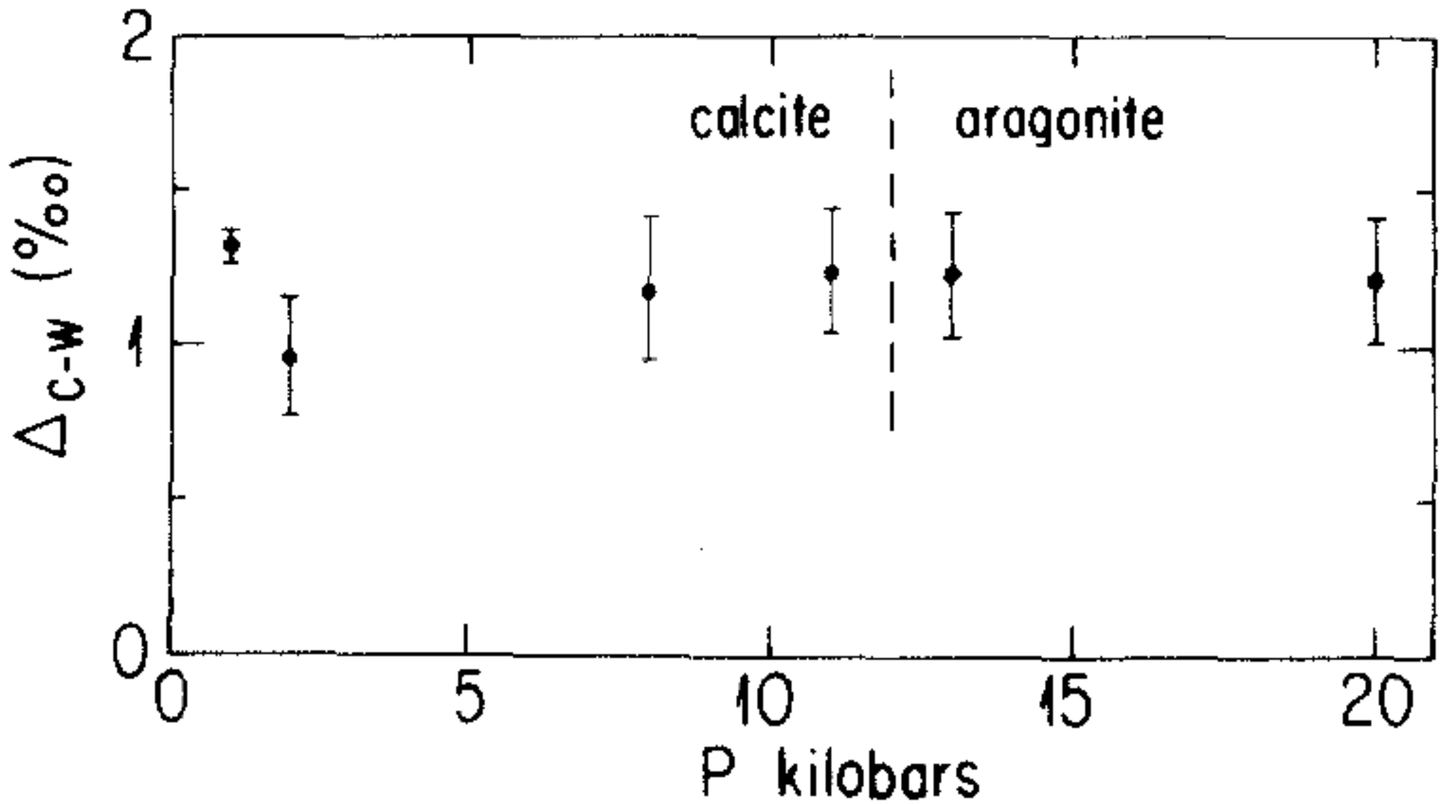
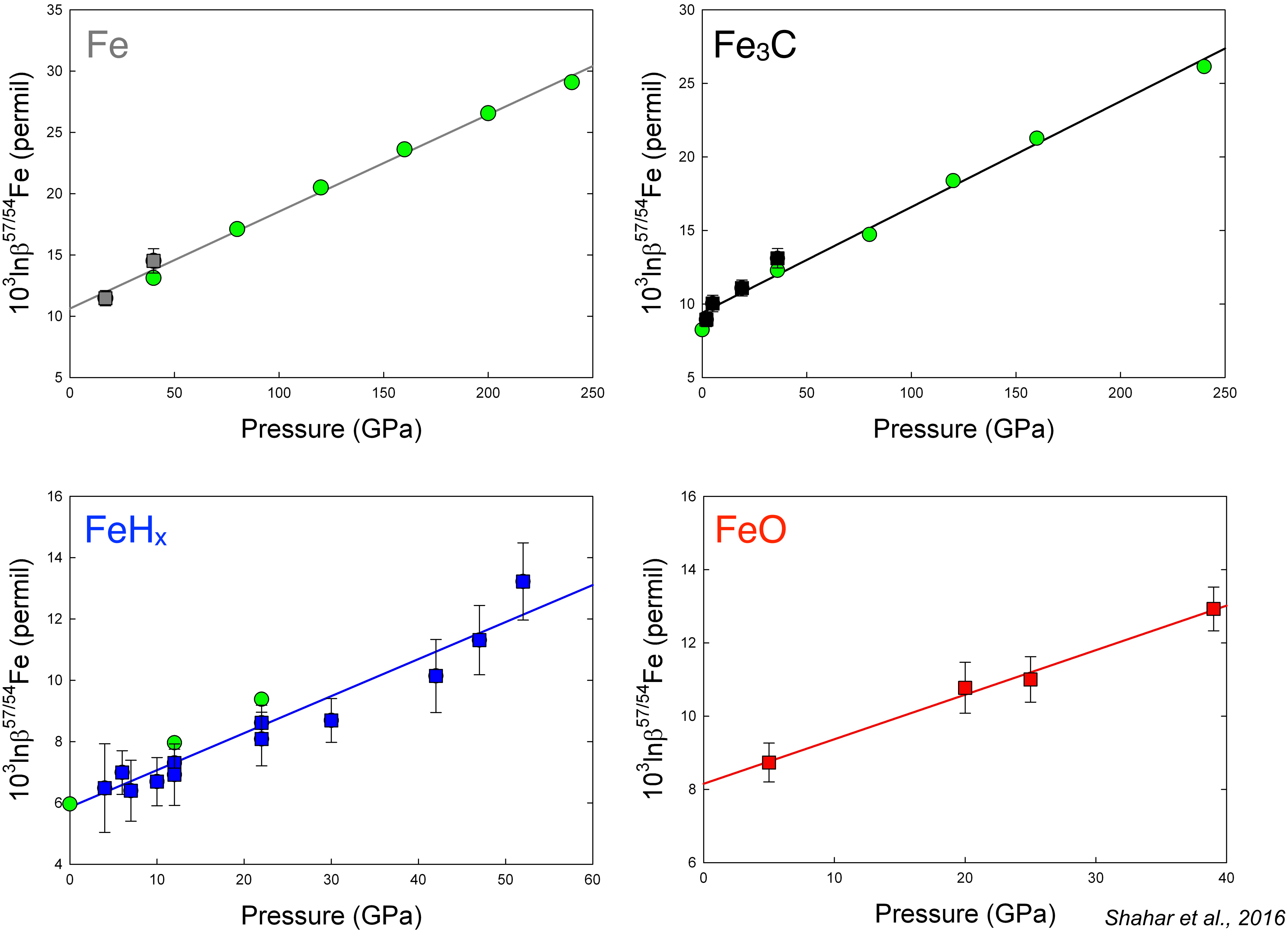
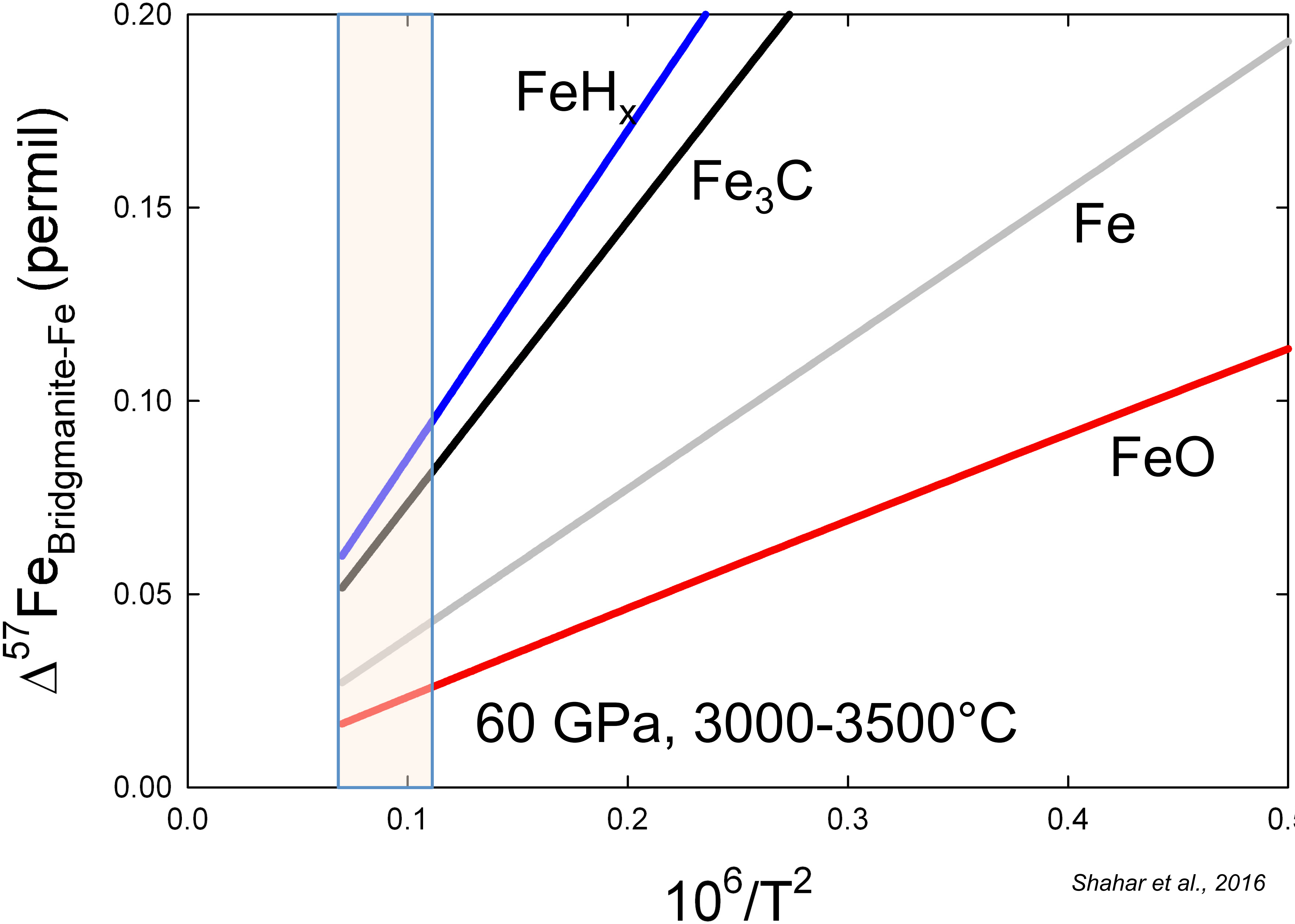


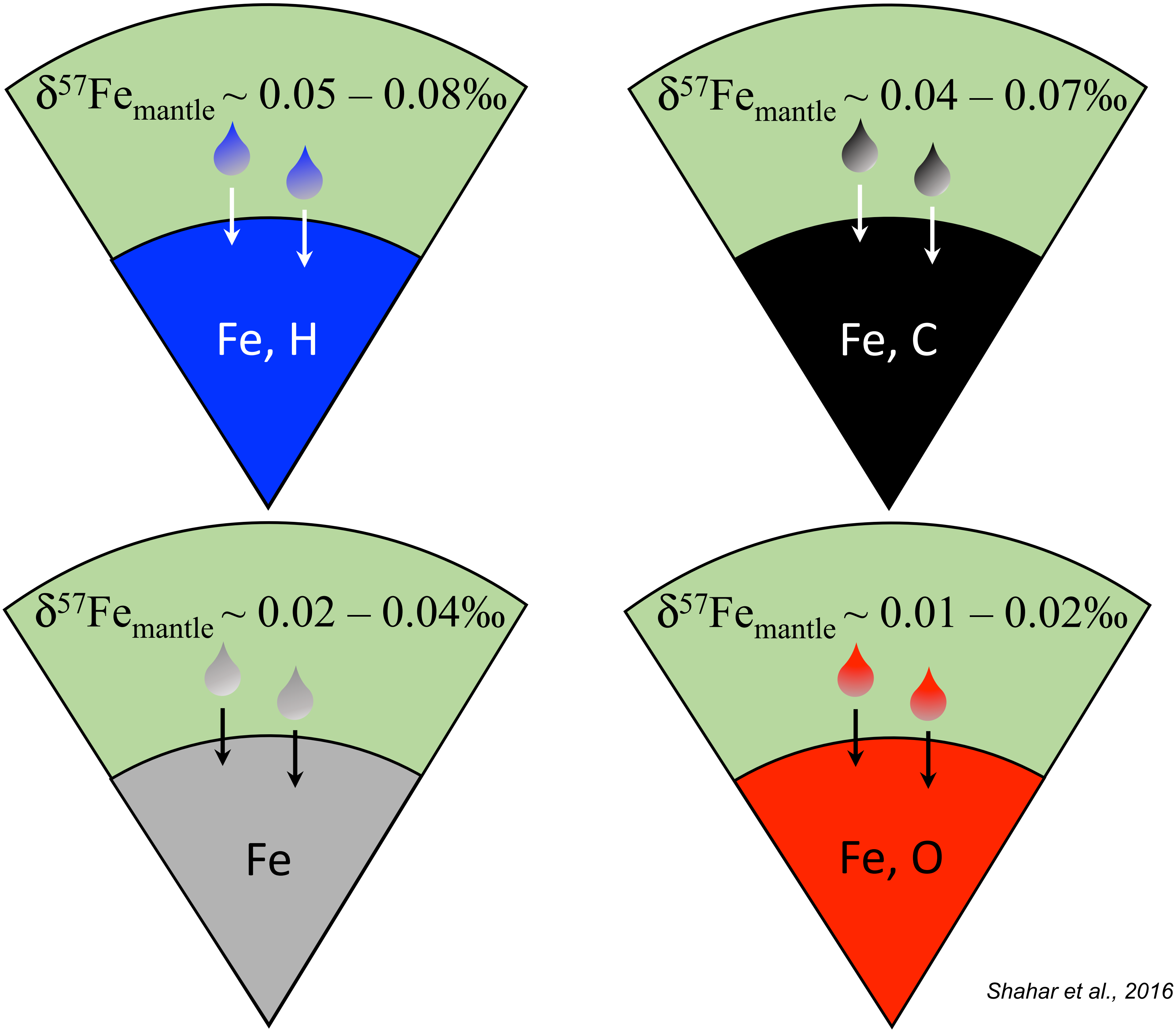
Fig. 2. Isotopic fractionation between $CaCO_3$ and water at 500°C as a function of pressure. Below 12 kbar, calcite is stable; above 12 kbar, aragonite is stable. Error bars show mean deviations from mean at each pressure.

Clayton et al., 1975

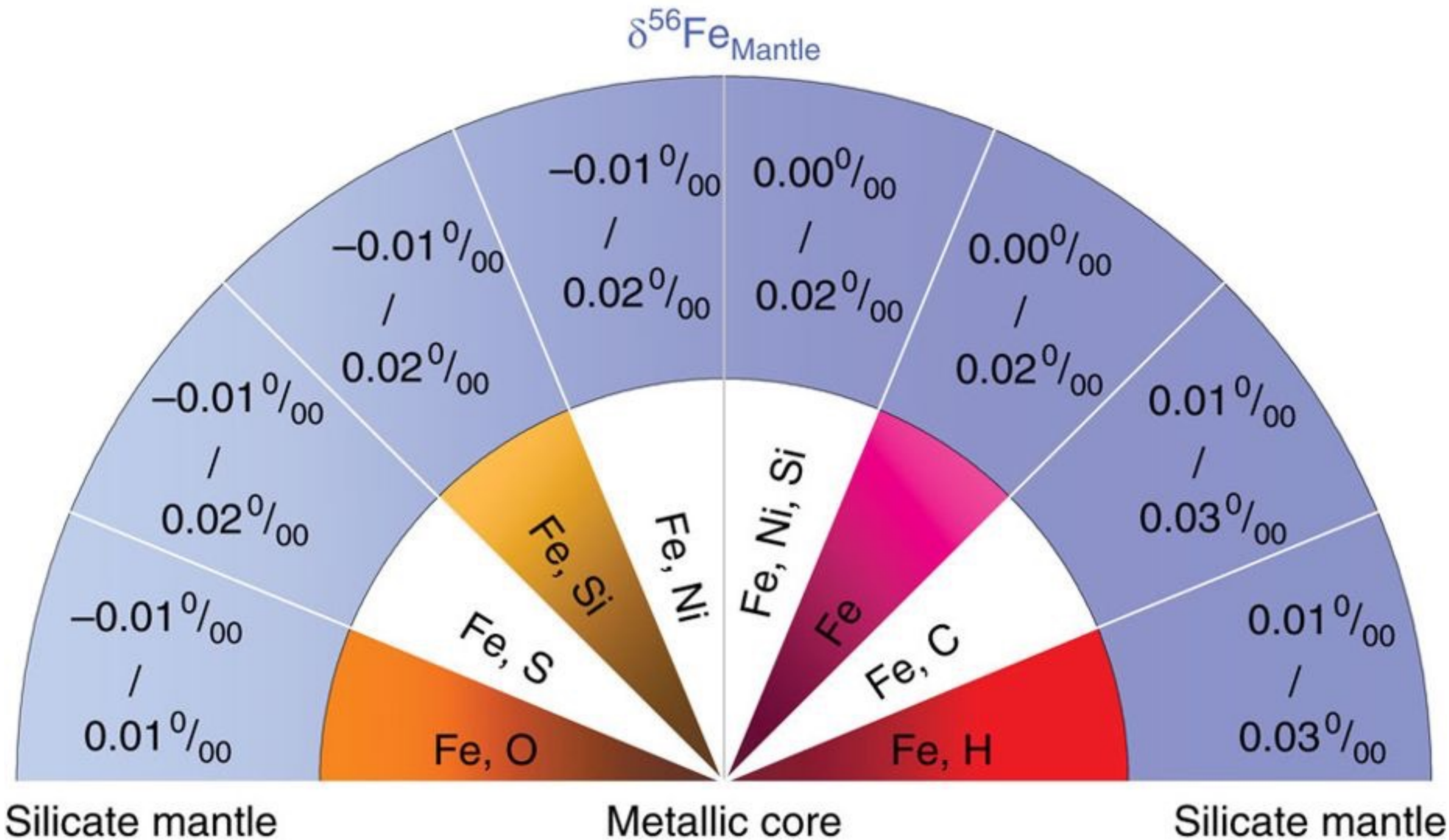

Fe
Fe3C
FeHx
FeO
10^3 lnβ^57/54 Fe (permil)
Pressure (GPa)
35 30 25 20 15 10 5
30 25 20 15 10 5
16 14 12 10 8 6 4
16 14 12 10 8 6
0 50 100 150 200 250
0 10 20 30 40 50 60
0 10 20 30 40
Shahar et al., 2016



FeHx
Fe3C
Fe
FeO
60 GPa, 3000-3500°C
Δ57Fe Bridgmanite-Fe (permil)
0.00
0.05
0.10
0.15
0.20
0.0
0.1
0.2
0.3
0.4
0.5
10^6/T^2
Shahar et al., 2016

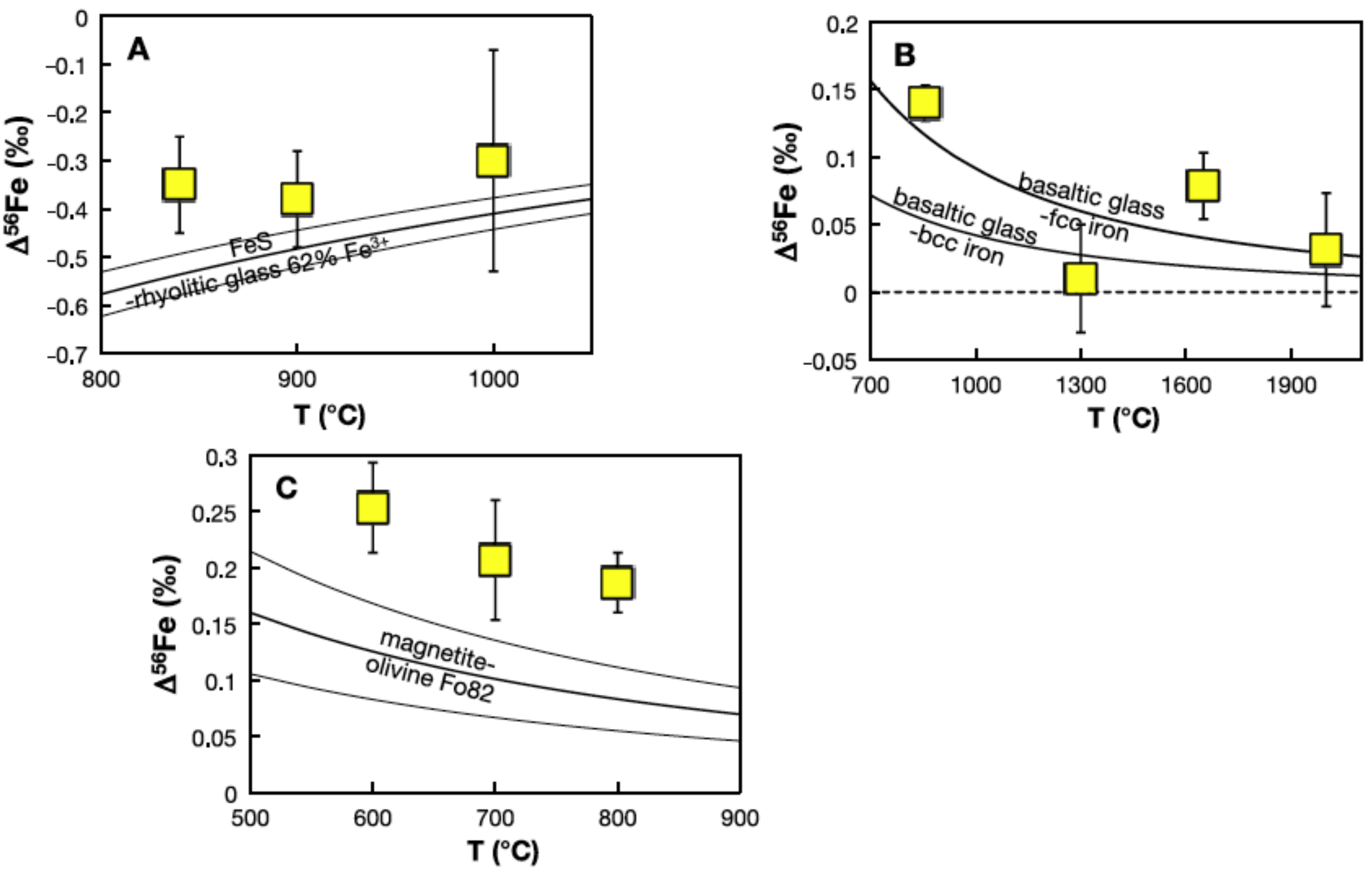


$\delta^{57}Fe_{mantle} \sim 0.05 - 0.08‰$
Fe, H
$\delta^{57}Fe_{mantle} \sim 0.04 - 0.07‰$
Fe, C
$\delta^{57}Fe_{mantle} \sim 0.02 - 0.04‰$
Fe
$\delta^{57}Fe_{mantle} \sim 0.01 - 0.02‰$
Fe, O
Shahar et al., 2016



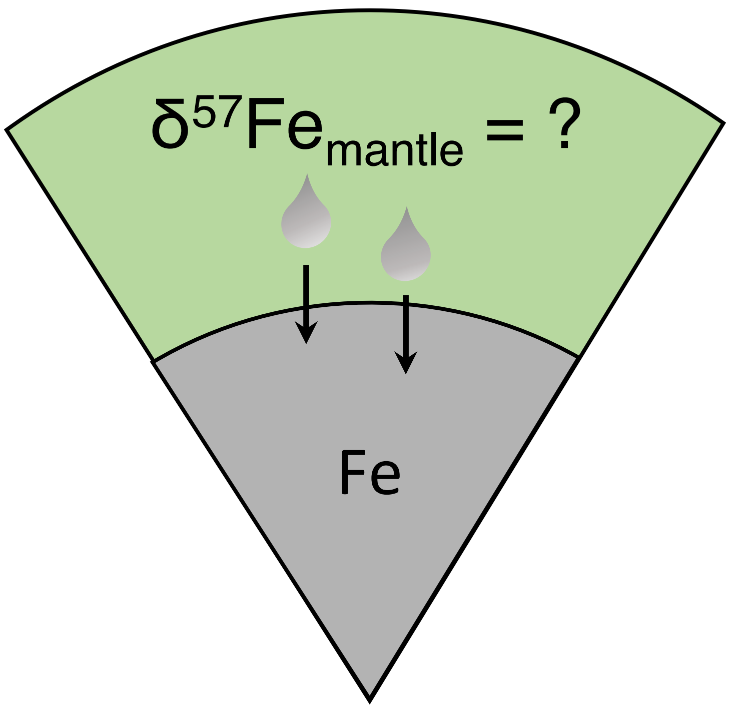
Lin et al., 2017

As a result, the fractionation values that they calculated were systematically heavier than ours by ~0.01–0.02‰ at approximately 40–60 GPa and 3,500 K. Although we agree with Shahar *et al*. that FeHx and Fe3C would lead to the largest shifts in δ56Fe values, we find that the shift would be smaller than what they predicted by 0.01–0.02‰.



Dauphas et al., 2012

NRIXS is a powerful and unique tool for determining isotopic fractionation factors at a range of conditions. However, it is still a new tool for this field and systematic studies need to be done to validate the technique relative to the more traditional techniques.



Temperature

Fractional Crystallization

Diffusion

Oxygen Fugacity

Pressure

Evaporation

Differentiation

Partial Melting

Composition