

Introduction to Isotope Fractionation



Anat Shahar
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1 H Hydrogen 1.008	2 IIA 2A													5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180								
3 Li Lithium 6.941	4 Be Beryllium 9.012	3 IIIB 3B			4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948								
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798										
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294										
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [209,982]	85 At Astatine 209.987	86 Rn Radon 222.018										
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [293]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown										
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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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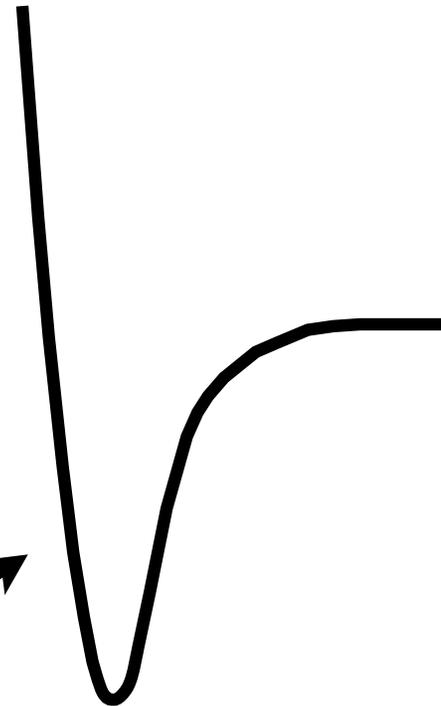
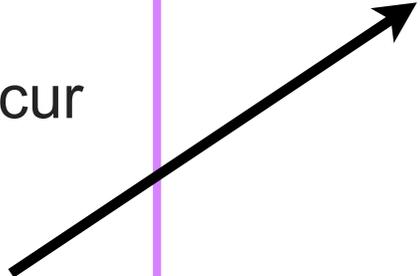
Look for elements that have a Mossbauer isotope

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:

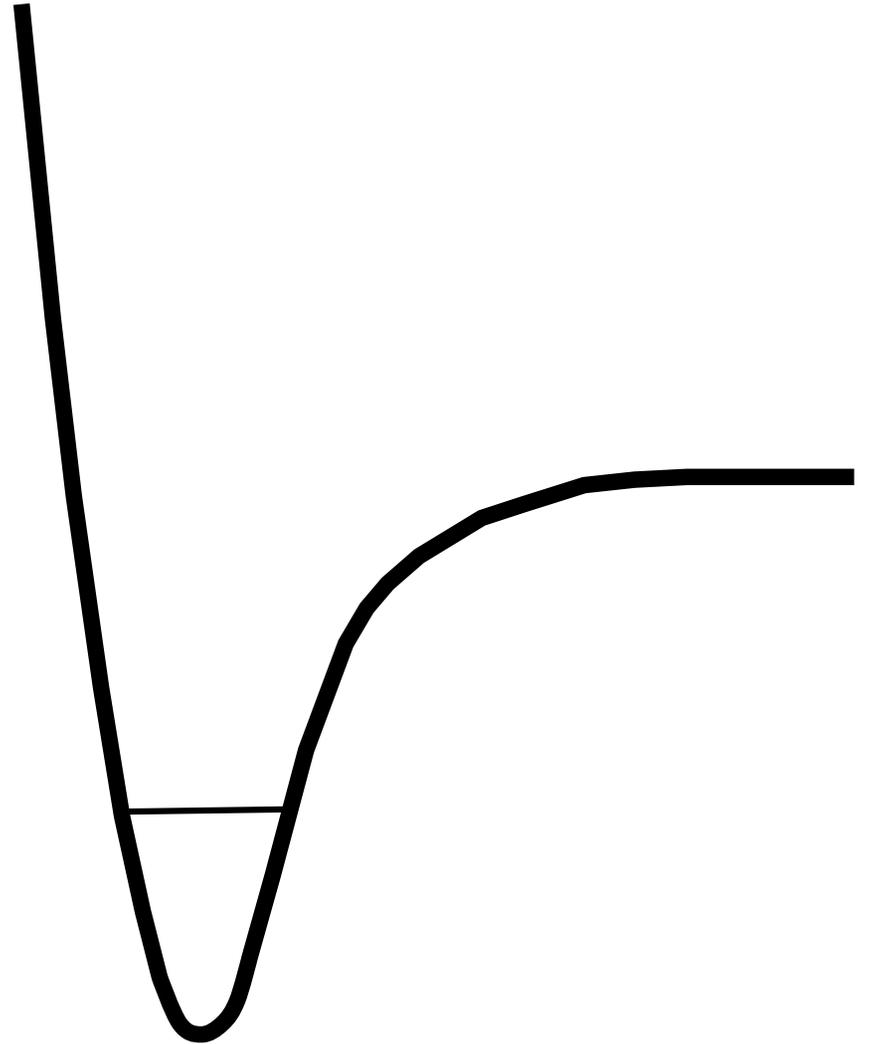
Differences in bond energies (*equilibrium*)

Reaction rates (*kinetics*)



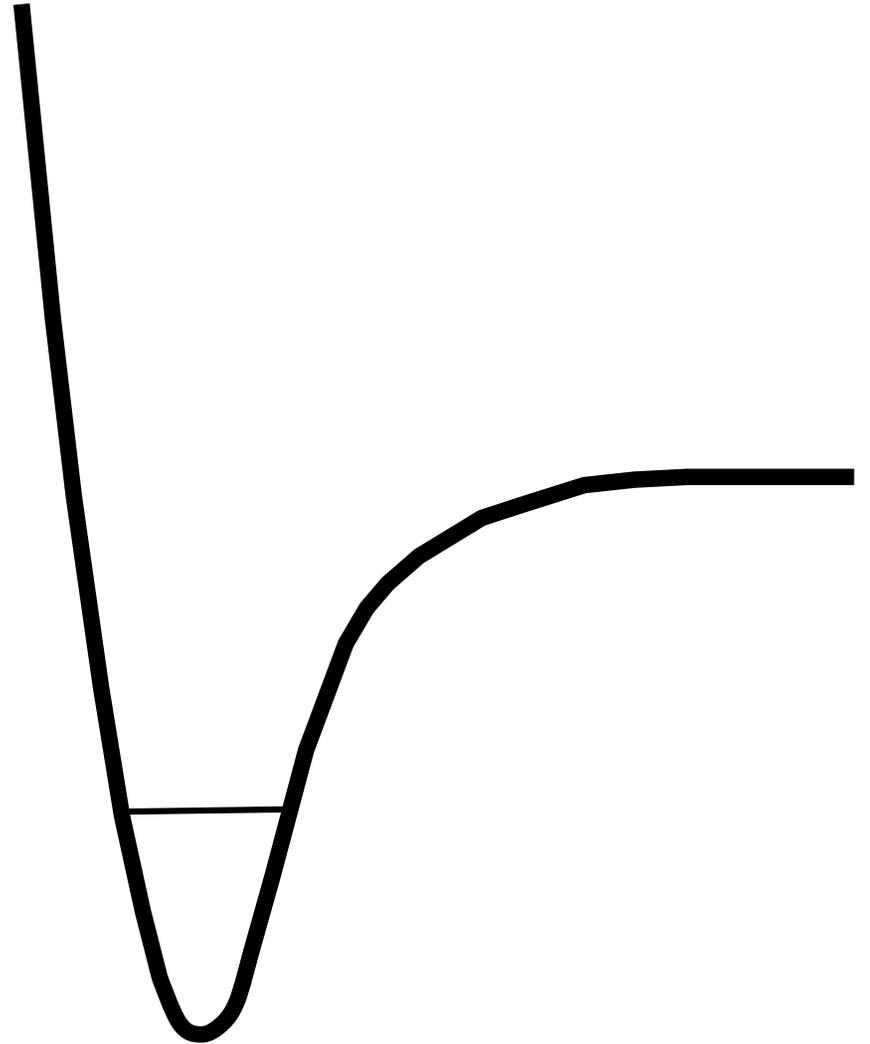
$$\frac{\langle v_1 \rangle}{\langle v_2 \rangle} = \sqrt{\frac{m_2}{m_1}}$$

$$E_n = h\nu(n + 1/2)$$



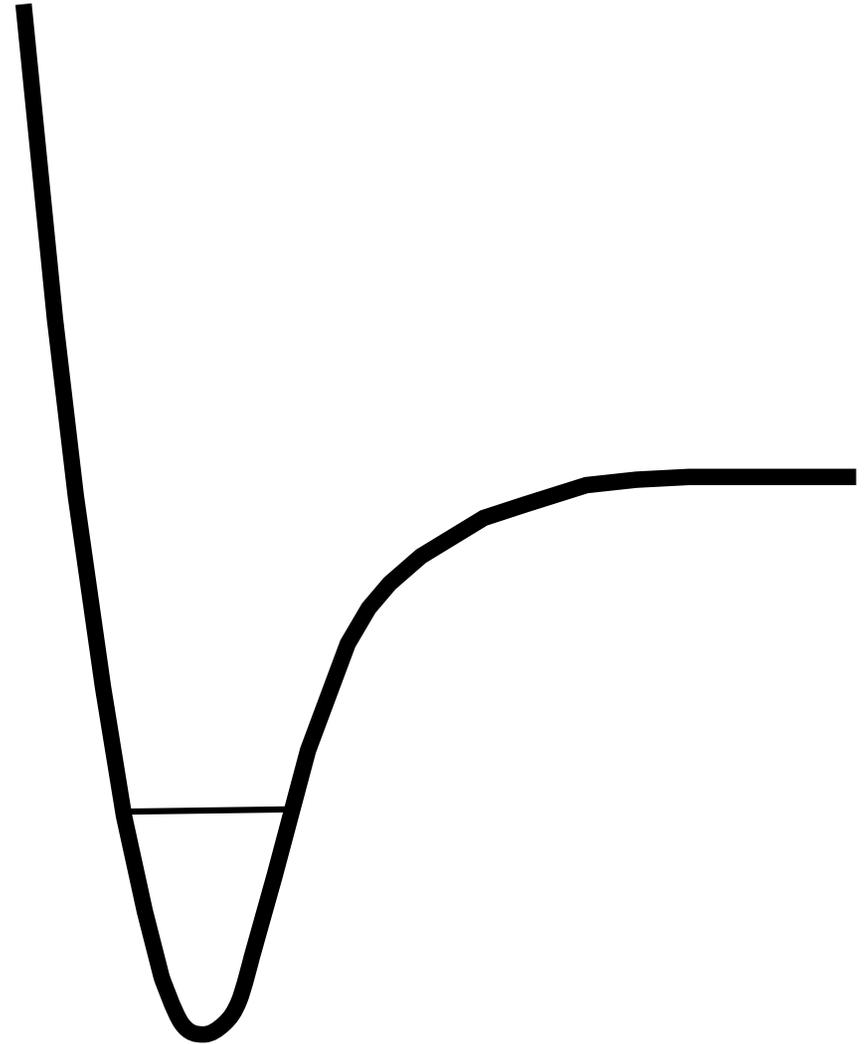
$$E_n = h\nu(n + 1/2)$$


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



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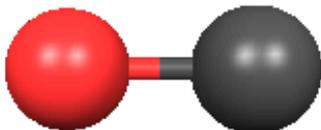


Zero-point energy differences drive typical equilibrium stable isotope fractionations.

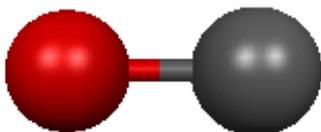
$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Heavy isotopes have lower vibrational frequencies

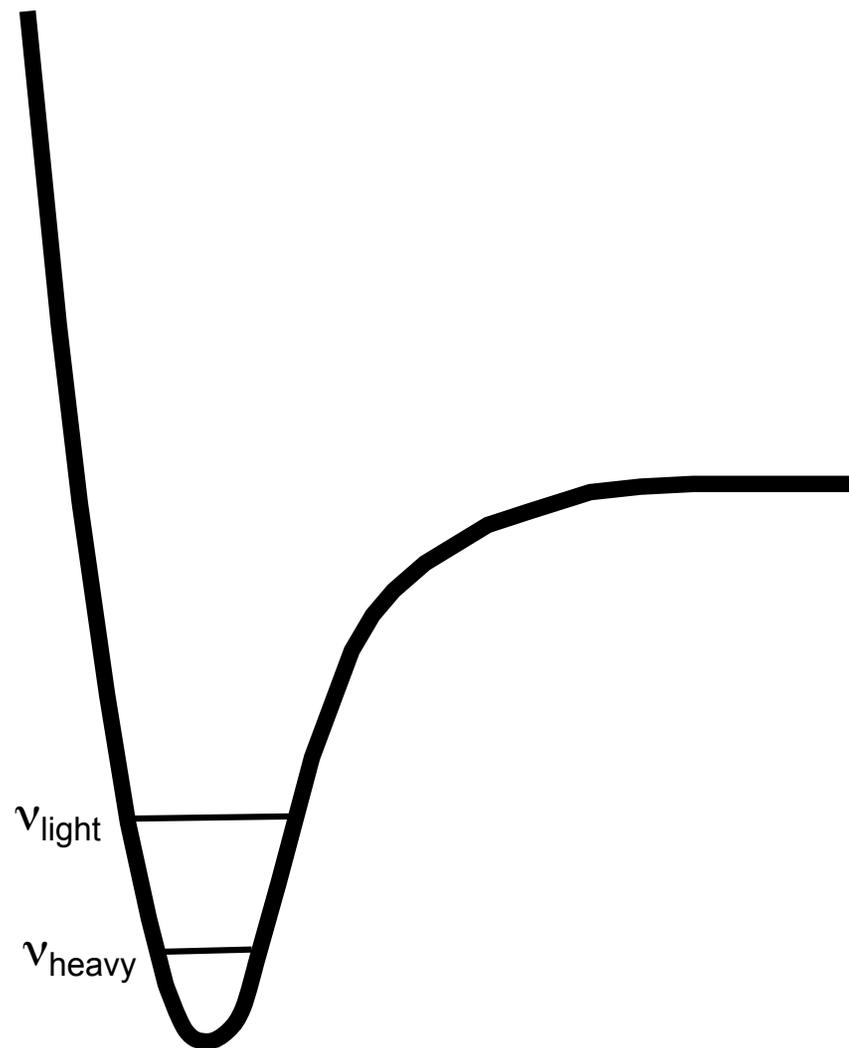
$^{12}\text{C}^{16}\text{O}$



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



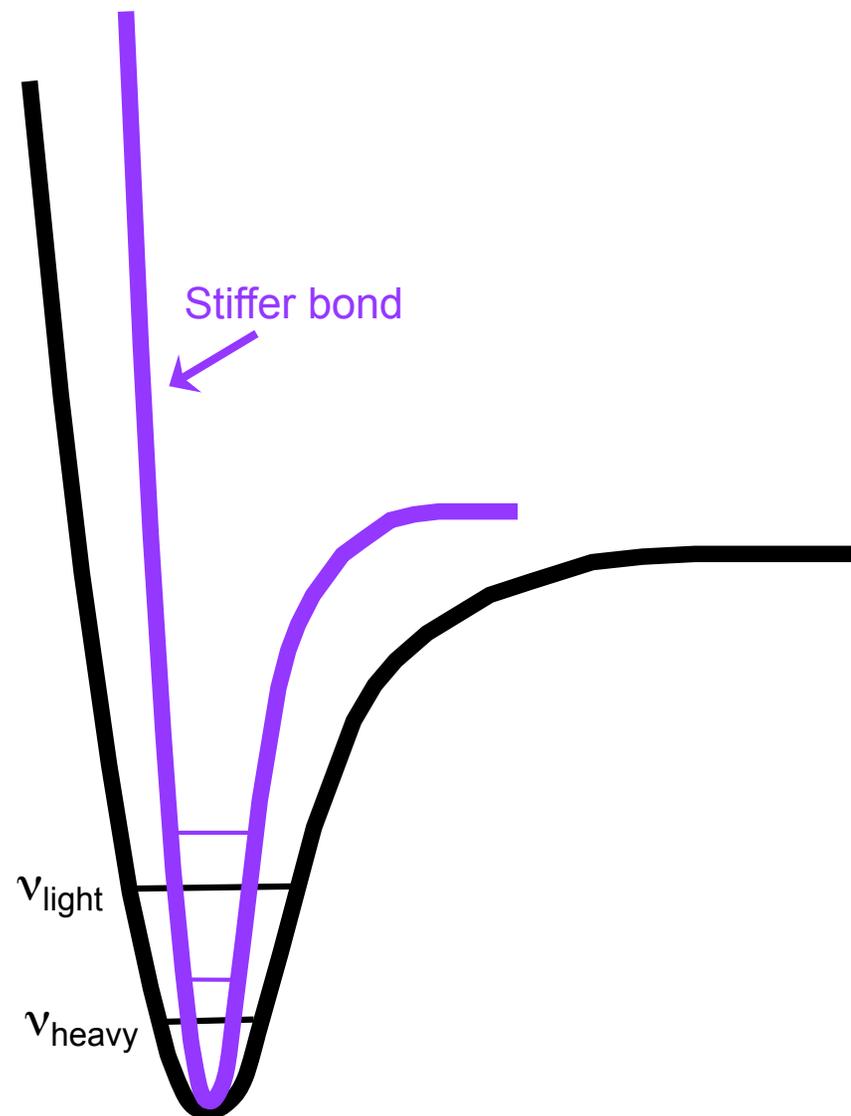
Credit: Edwin Schauble

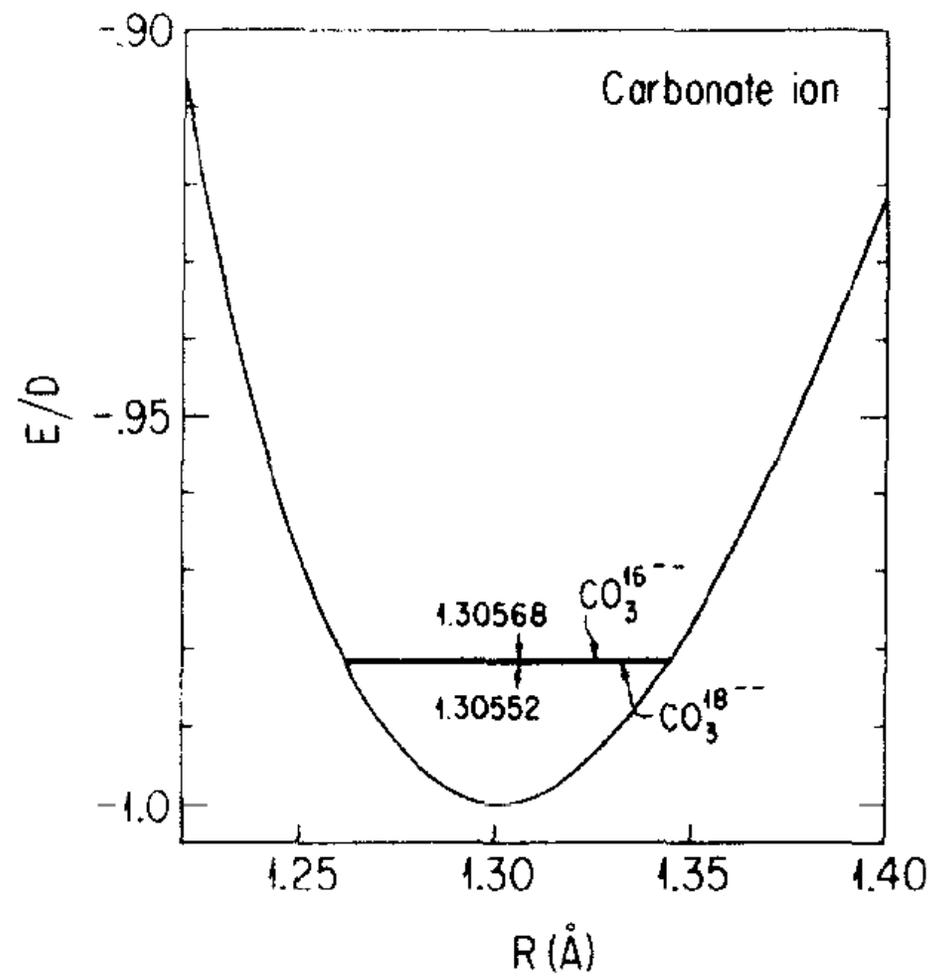
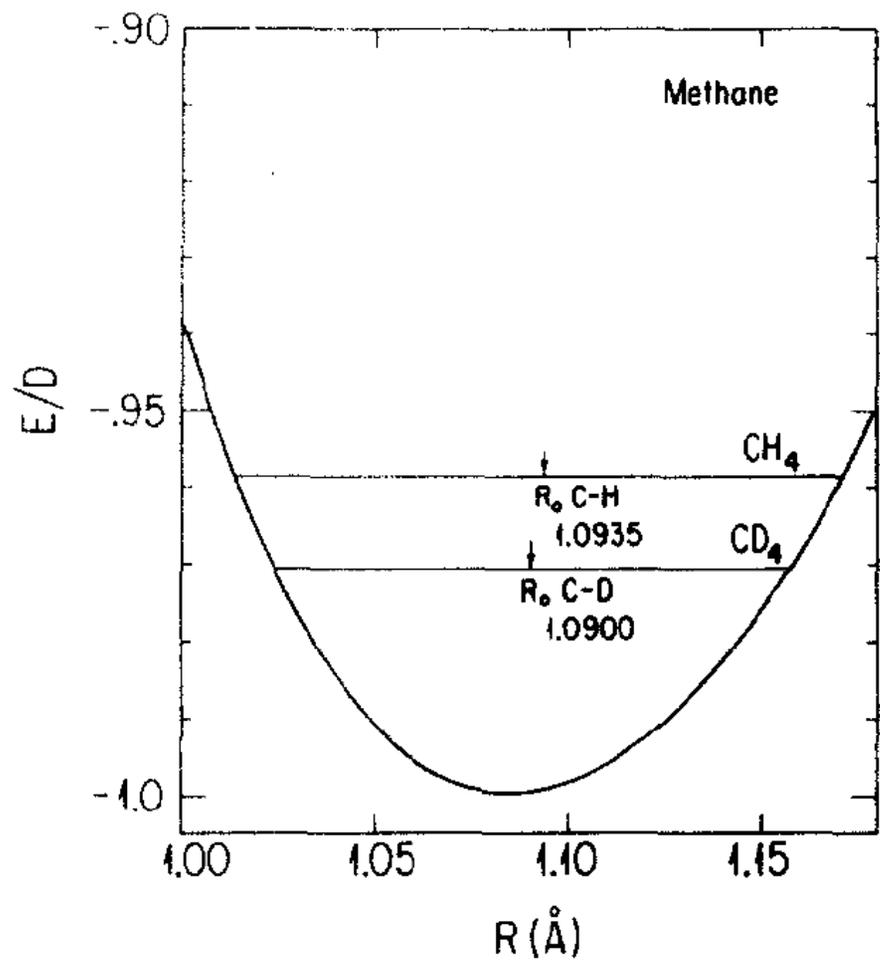


$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Stiffer bonds concentrate the heavy isotopes

- shorter bonds
- higher oxidation state
- low coordination number

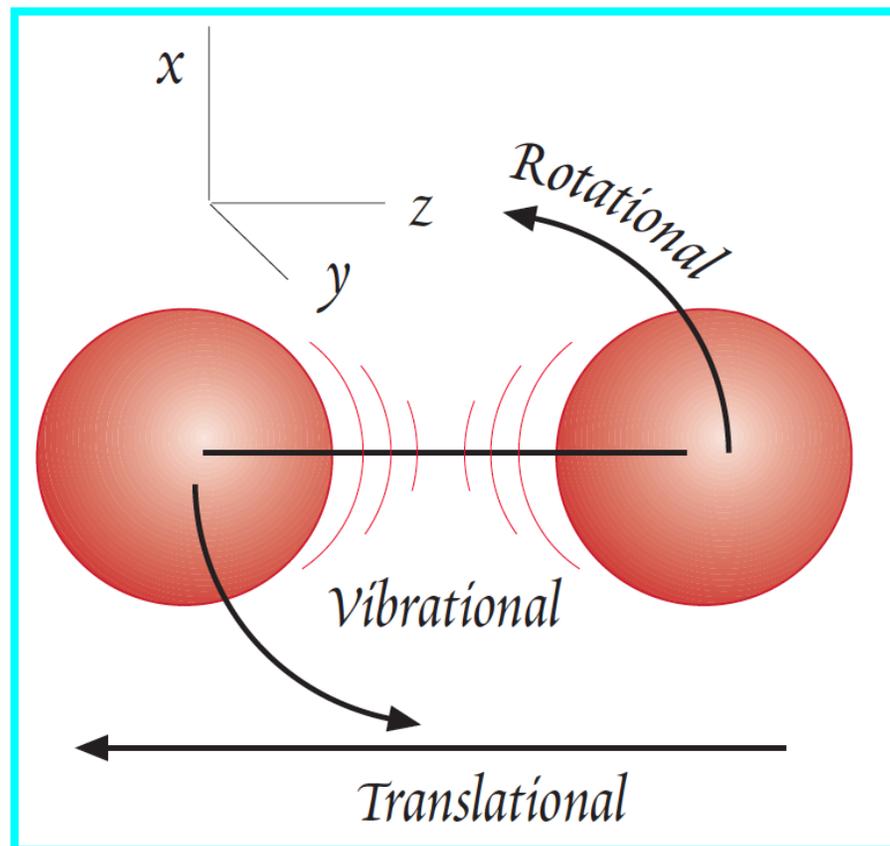


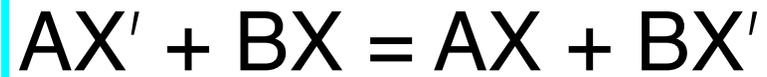


$$AX' + BX = AX + BX'$$

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

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

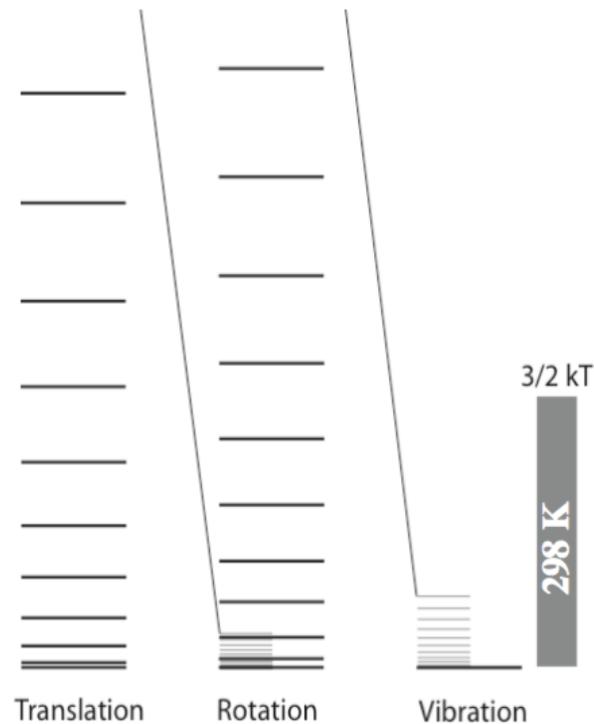


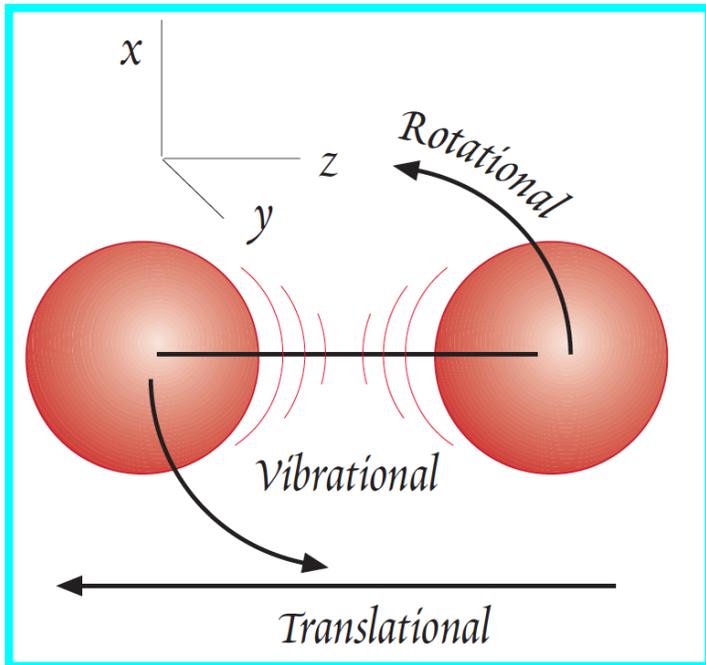


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Energy quanta associated with molecular rotation and translation are so small that they can be treated approximately without an explicit sum over the quantum energies

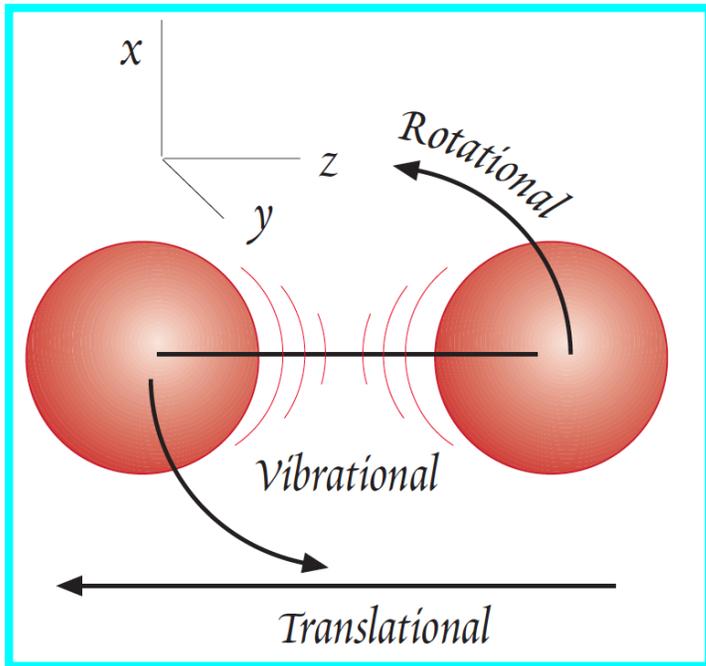




$$Q_{\text{trans}} = \frac{(2\pi mkT)^{3/2}}{h^3} V$$

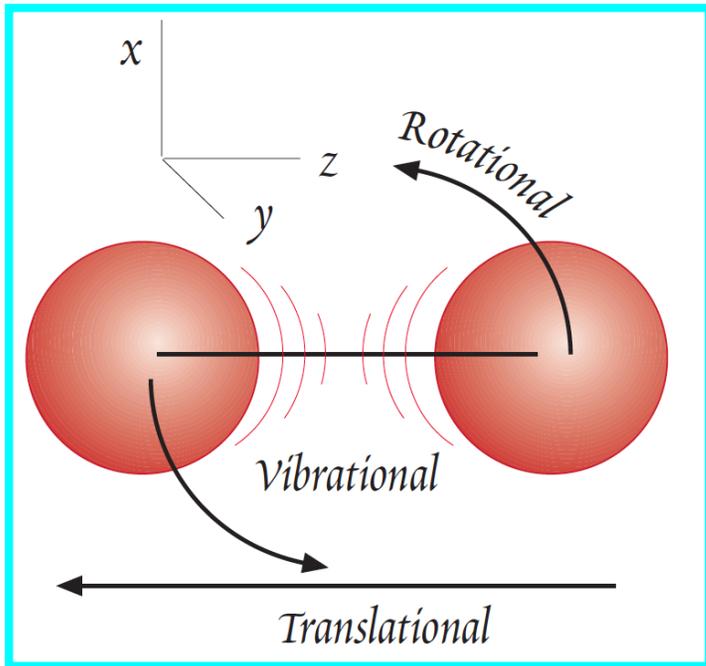
$$(Q/Q')_{tr} = (M'/M)^{3/2}$$

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



$$Q_{\text{rot}} = \frac{8\pi^2 I k T}{h^2}$$

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



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

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

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

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

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

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

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

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

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

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

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



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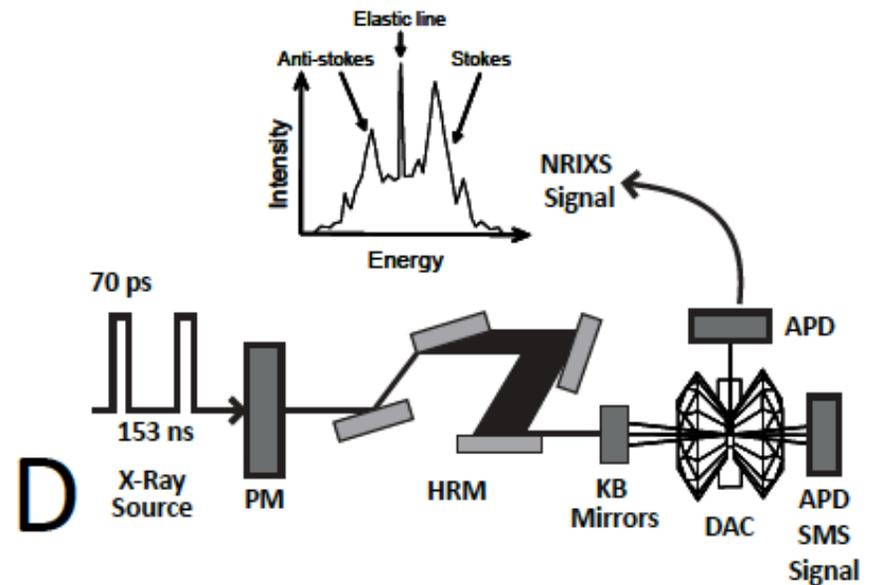
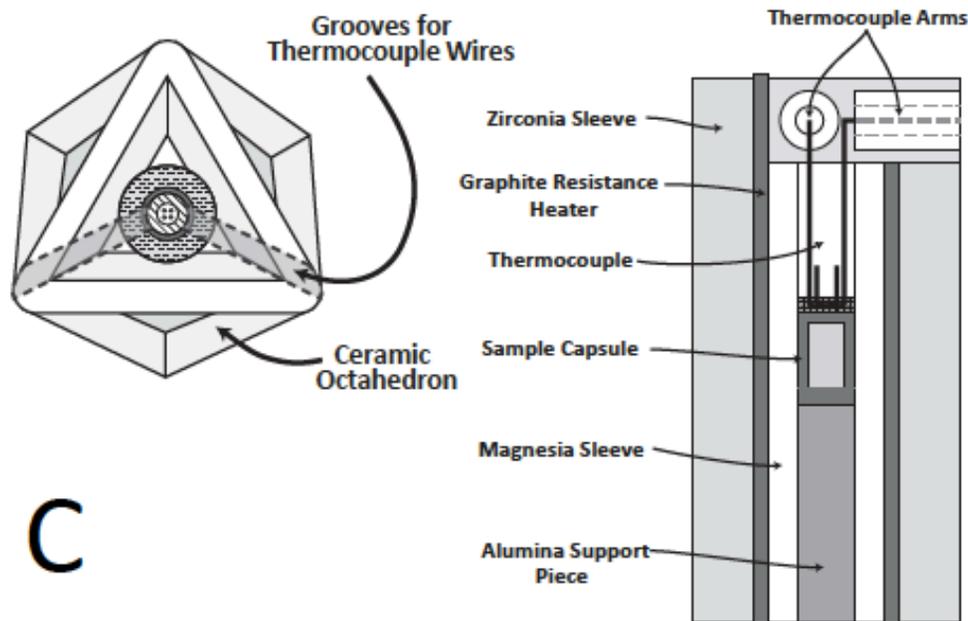
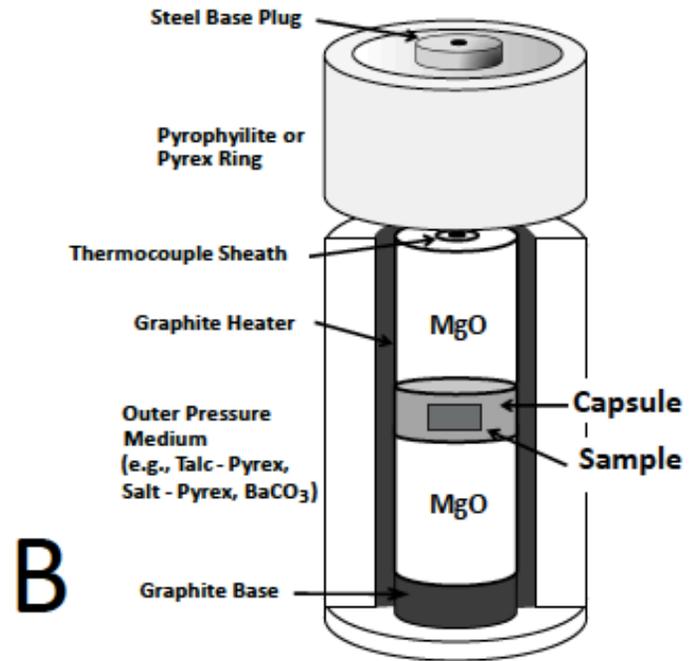
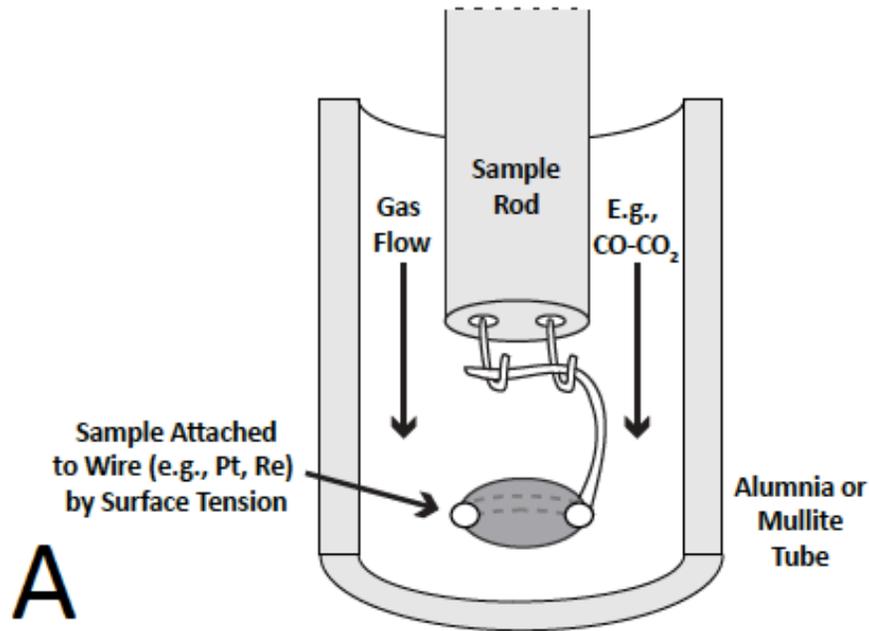
$$\ln \alpha_{A-B} = \ln \beta_A - \ln \beta_B$$

Equilibrium Fractionation Factor

Beta Factor

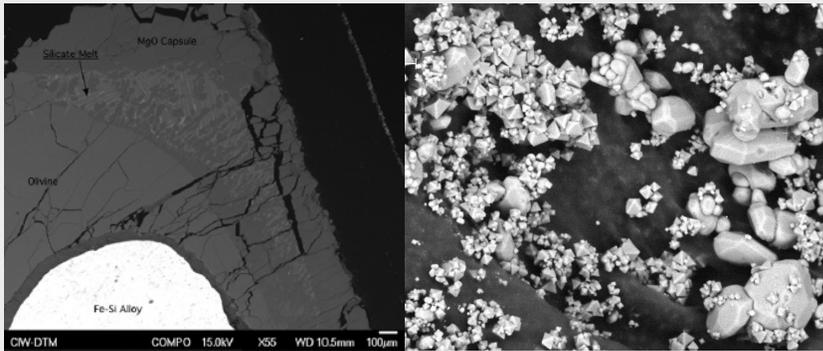
$$1000 \times \ln \beta_{I/I^*} = 1000 \left(\frac{1}{M^*} - \frac{1}{M} \right) \frac{\hbar^2}{8k^2 T^2} \langle F \rangle$$

Force Constant



Planning an equilibrium fractionation experiment: Challenges

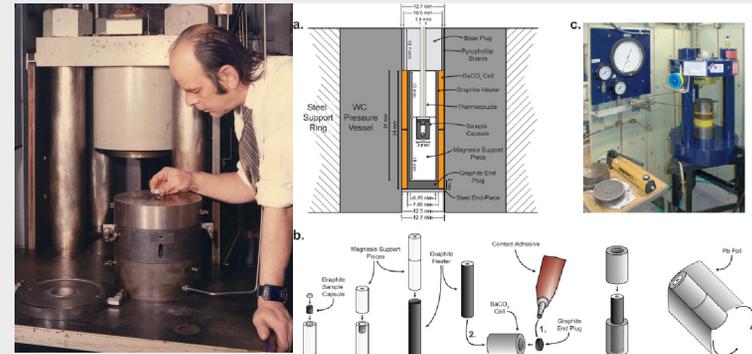
sample size



Shahar et al. 2011

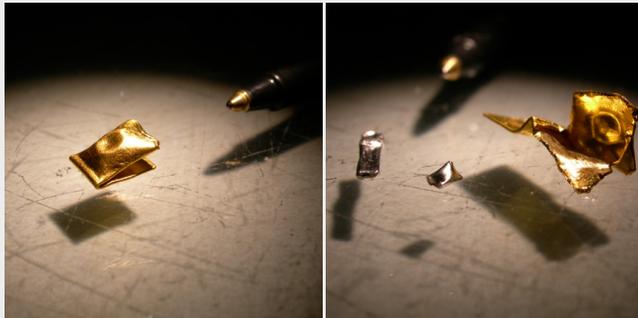
Macris et al. 2013

limits of experimental apparatus

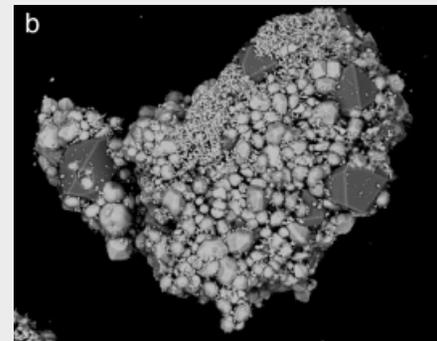


Bennett et al. 2015

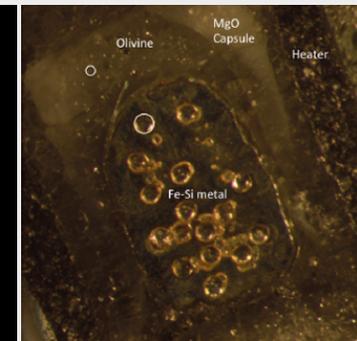
starting materials, buffers, and containers



separate phases vs. *in situ*



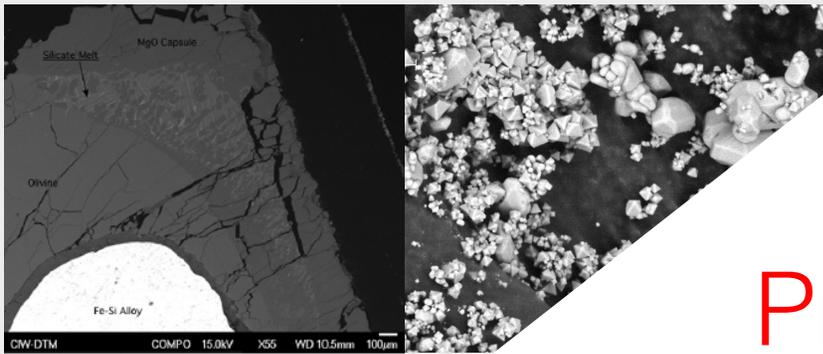
Shahar et al. 2008



Shahar et al. 2011

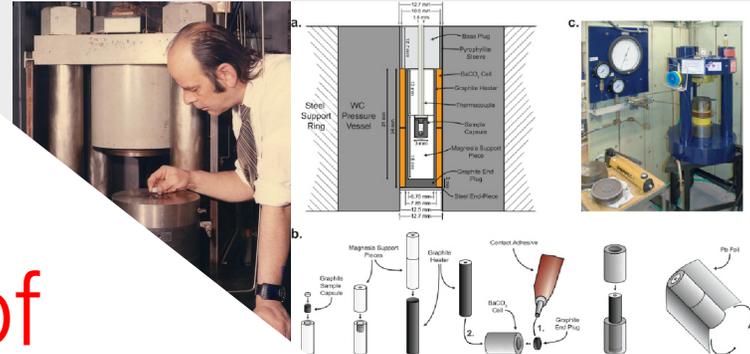
Planning an equilibrium fractionation experiment: Challenges

sample size



Shahar et al. 2011

limits of experimental apparatus

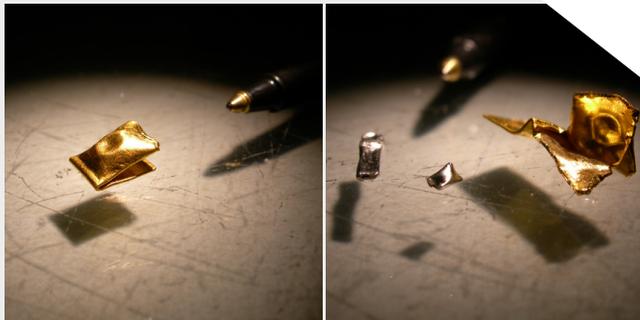


Bennett et al. 2015

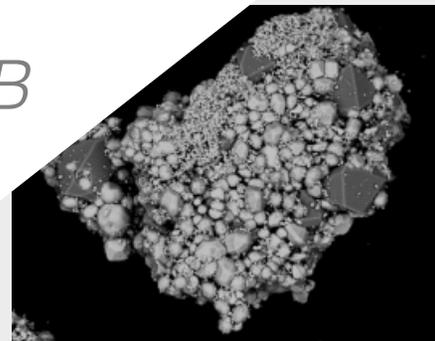
Proof
of equilibrium

$$\alpha_{A-B}$$

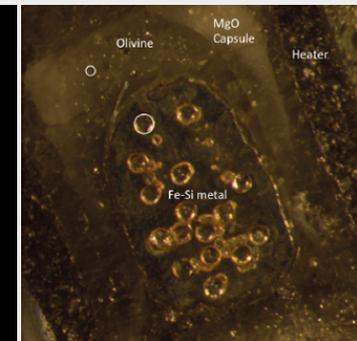
starting materials, b
containers



phases vs. *in situ*



Shahar et al. 2008



Shahar et al. 2011

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!



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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. MINEEV⁴



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

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ARTICLE

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

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

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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

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

Caitlin A. Murphy,¹ Jennifer M. Jackson,¹ and Wolfgang Sturhahn¹

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

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GEOCHEMISTRY

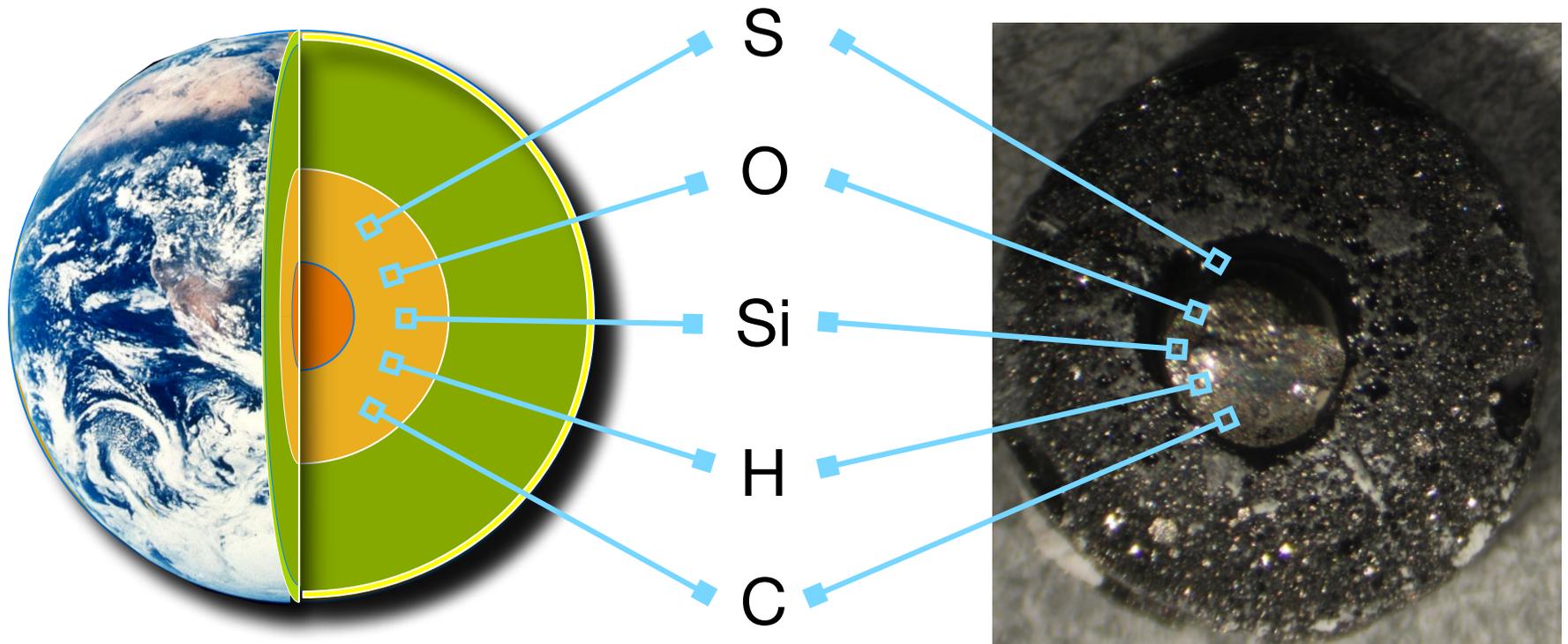
Pressure-dependent isotopic composition of iron alloys

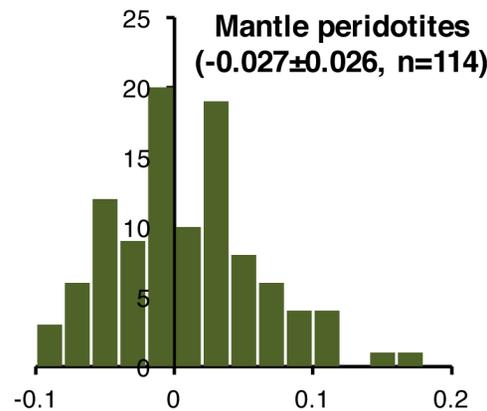
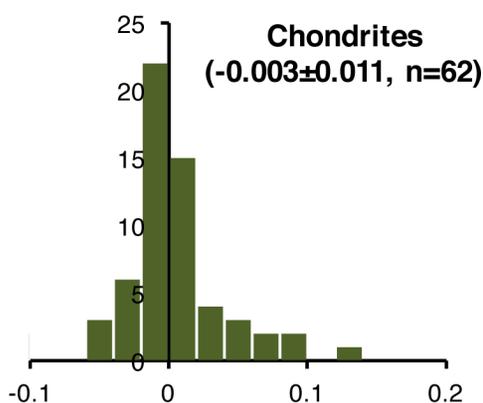
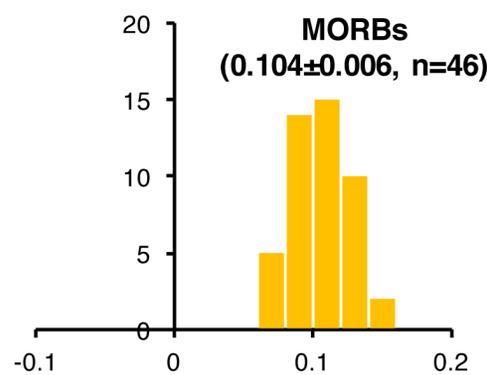
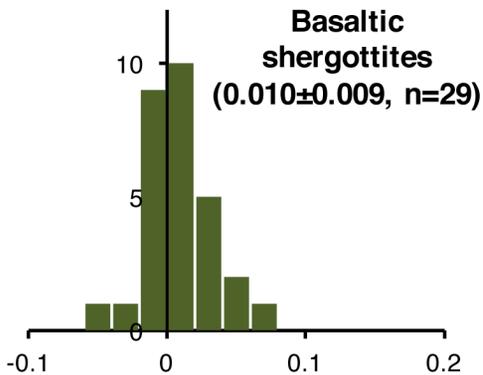
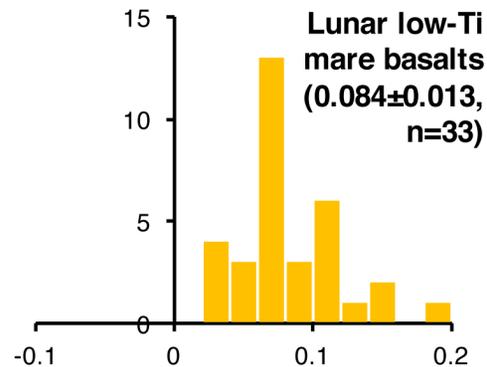
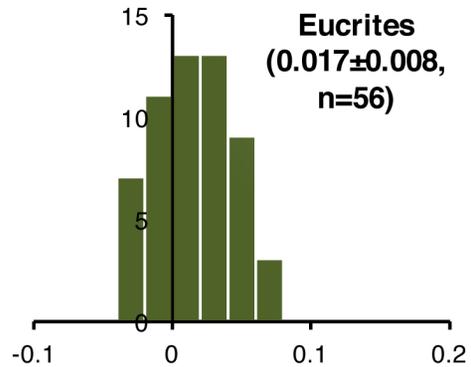
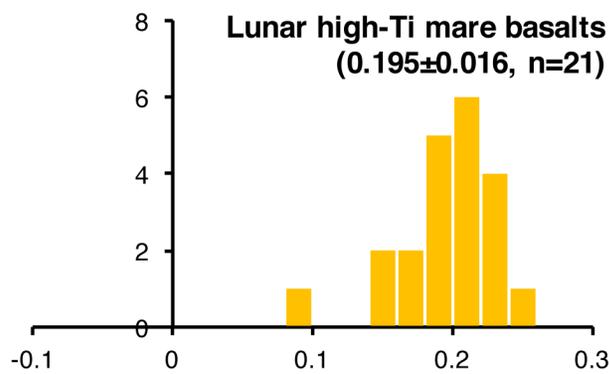
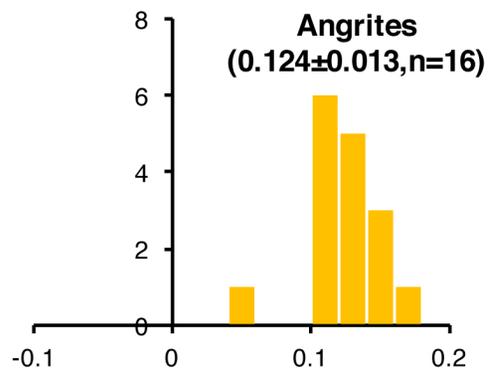
A. Shahar,^{1,*} E. A. Schauble,² R. Caracas,³ A. E. Gleason,⁴ M. M. Reagan,⁵ Y. Xiao,⁶ J. Shu,¹ W. Mao⁵

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

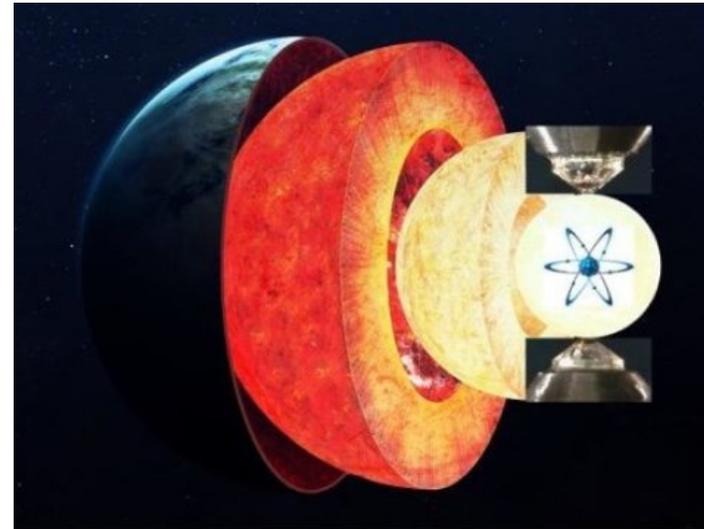
Example: Iron Isotopic Fractionation During Earth's Differentiation and Evolution





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

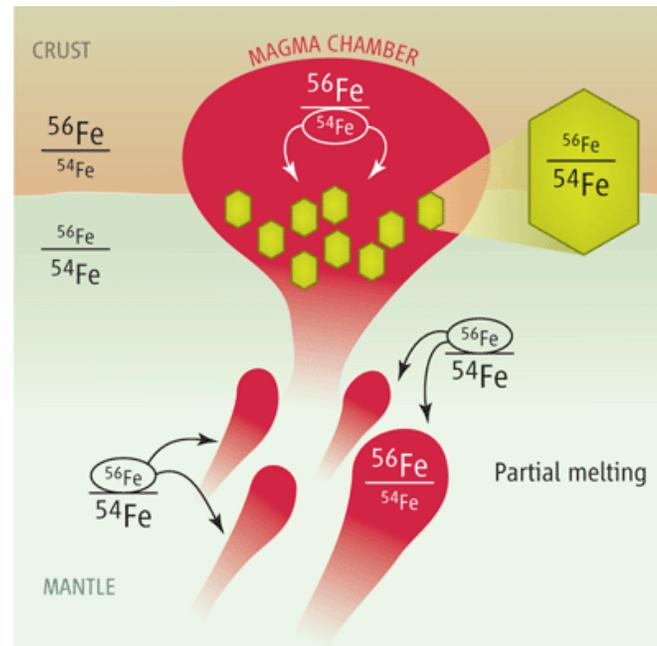
Suggestions for mechanisms causing iron isotope fractionation that cause the natural sample variation.



Differentiation (e.g. Polyakov 2009)

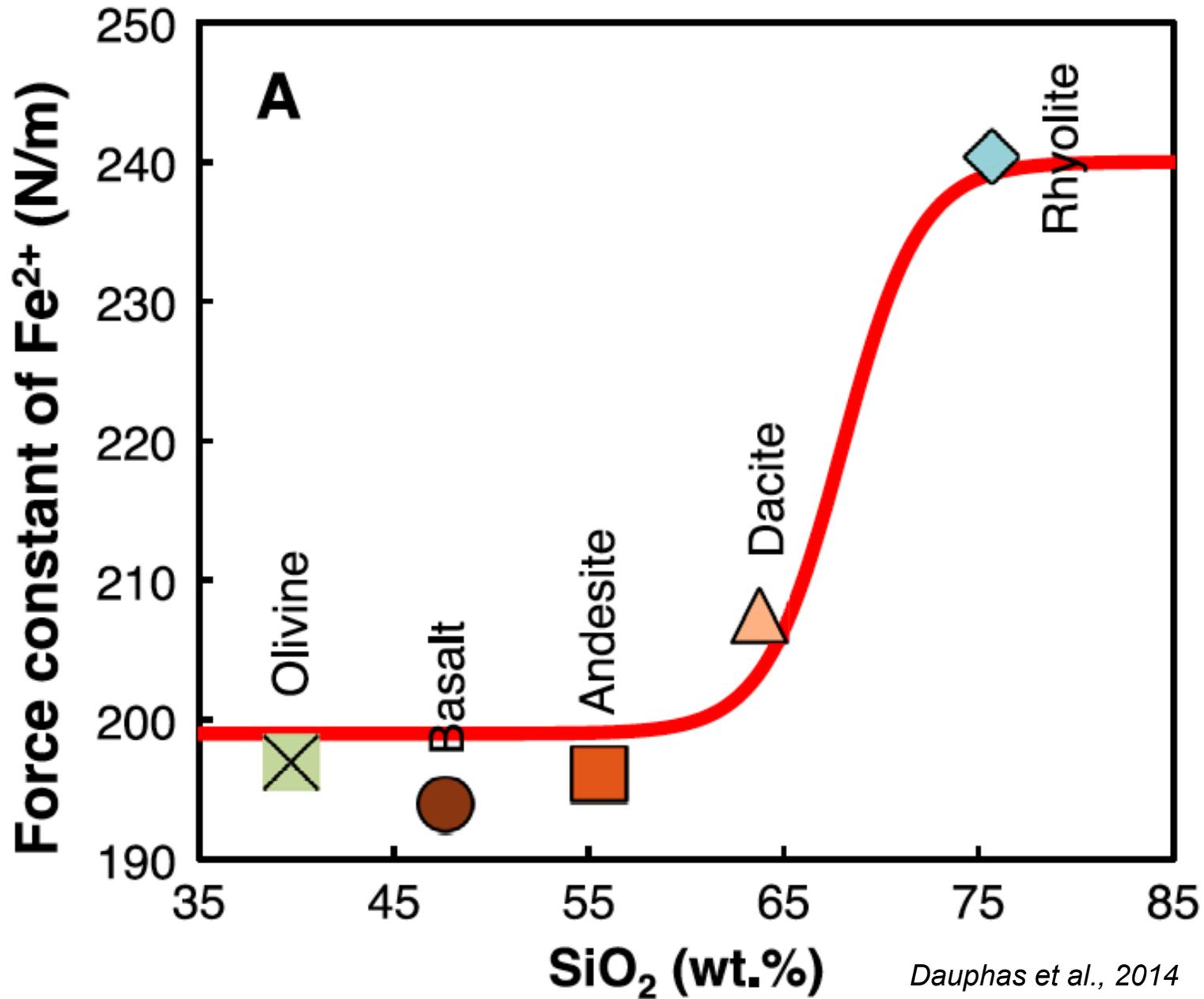


Evaporation (e.g. Poitrasson et al. 2004)

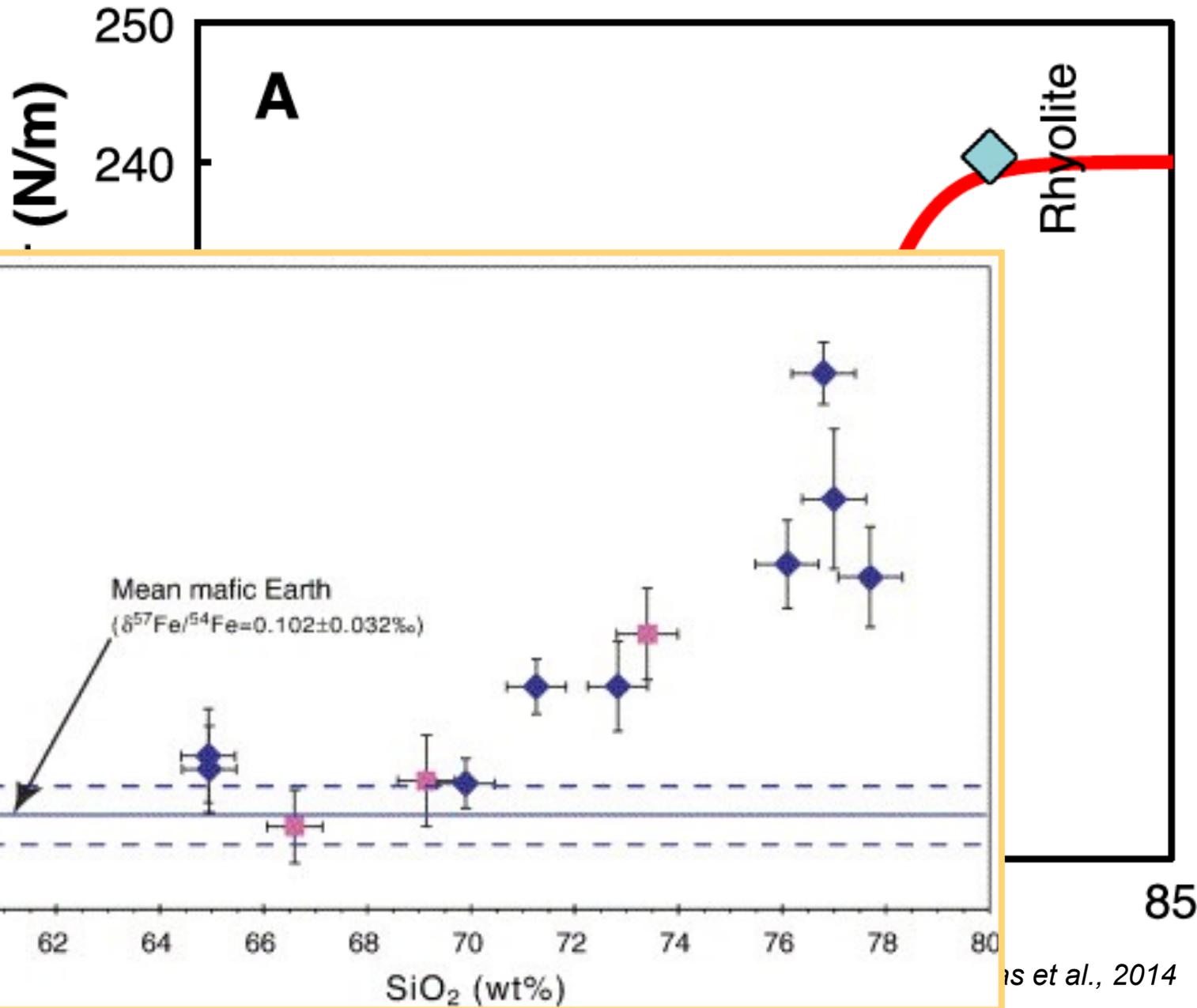


Magmatic Processes (e.g. Williams et al. 2005, Teng et al. 2008)

Composition



Composition

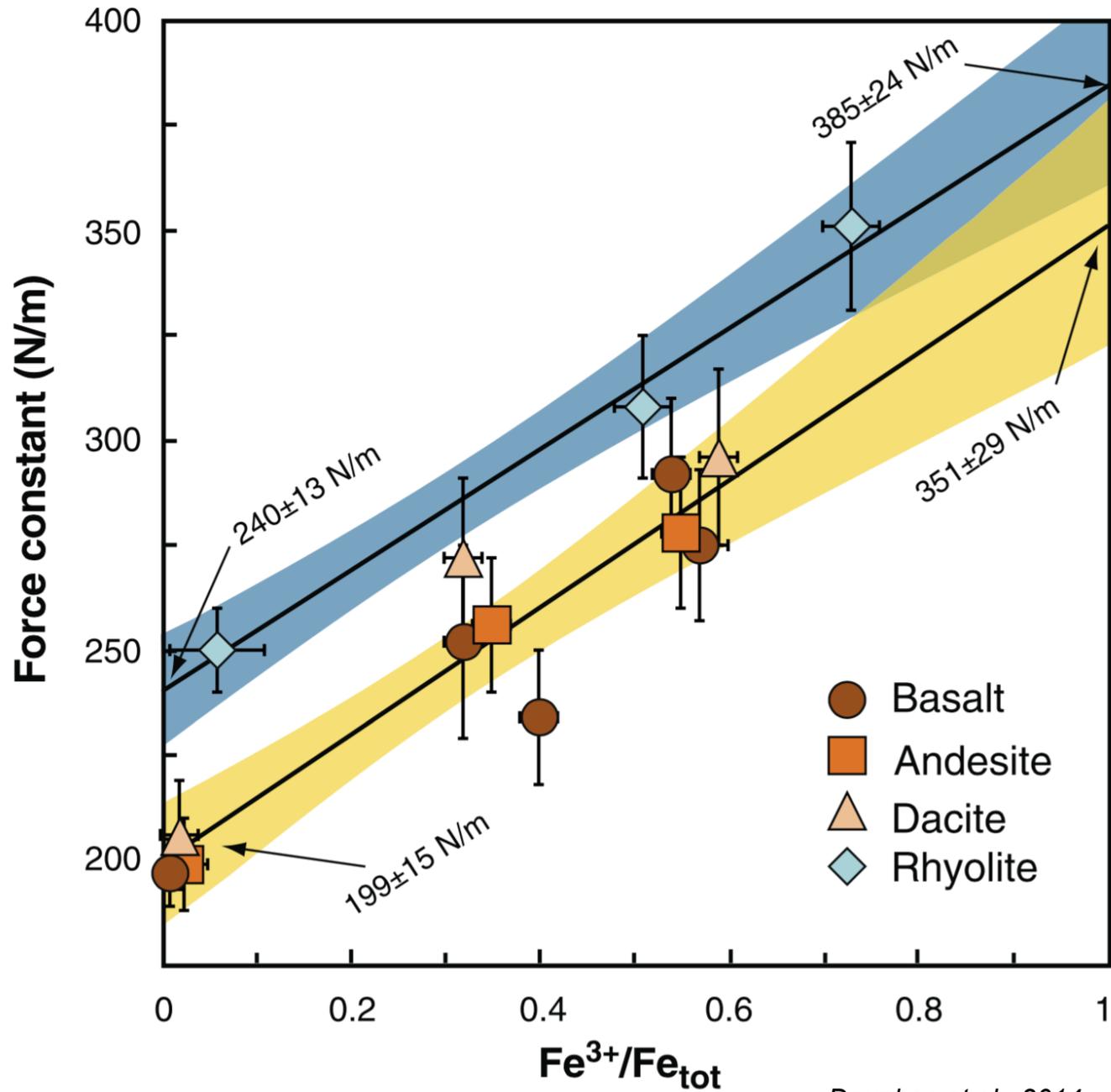


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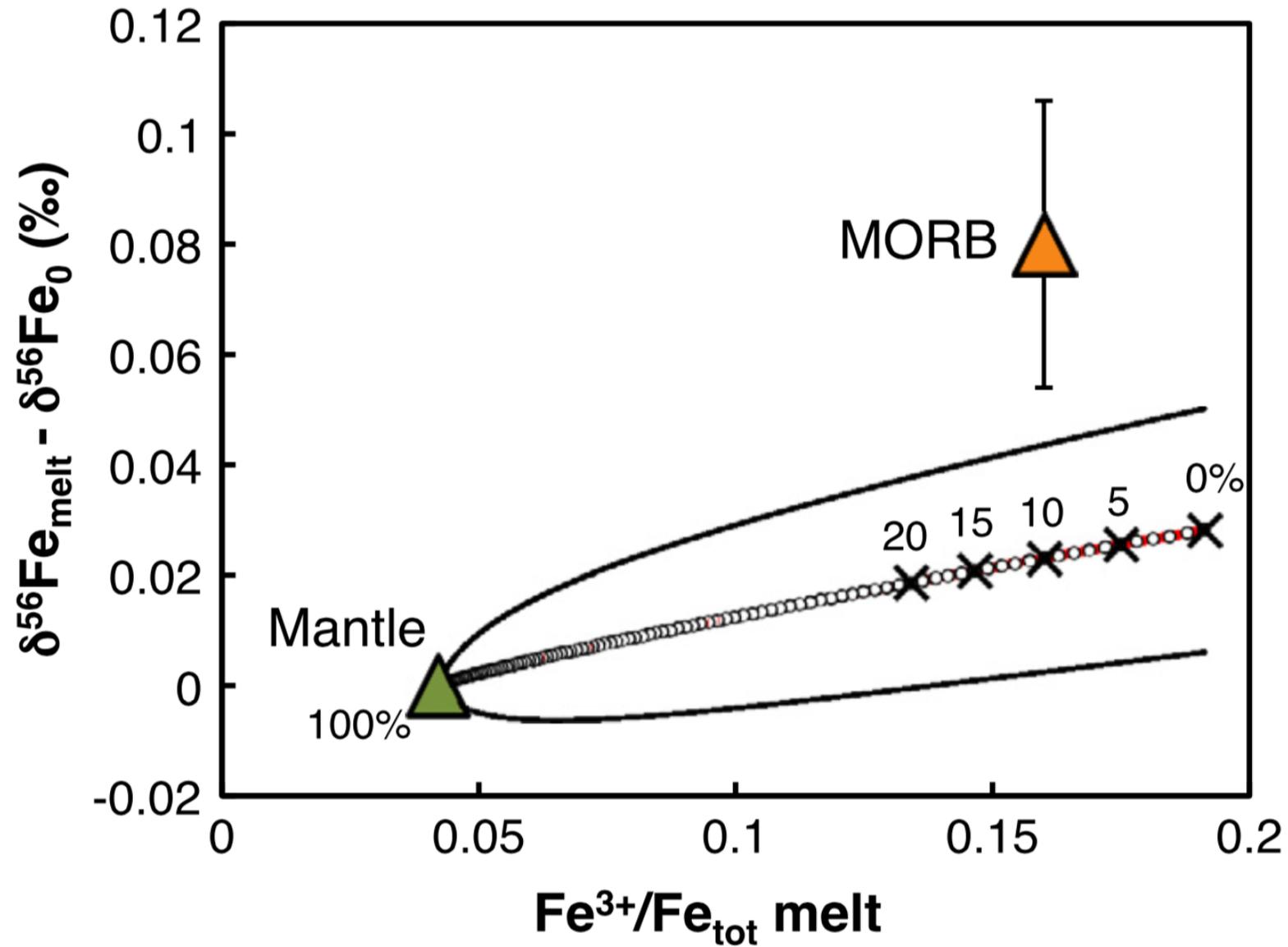
ns et al., 2014

Poitrasson et al., 2005

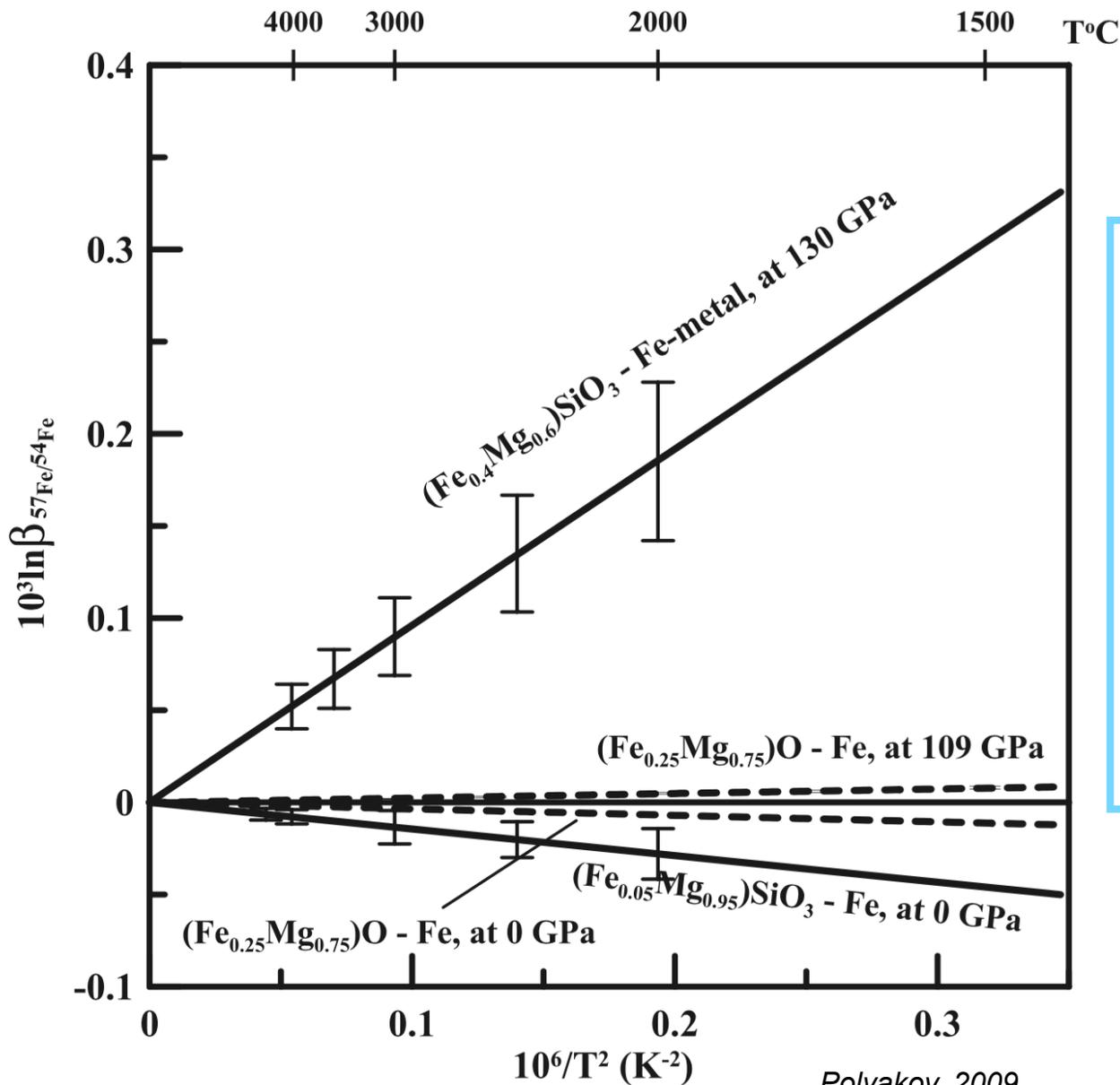
Oxidation State



Partial Melting



Differentiation

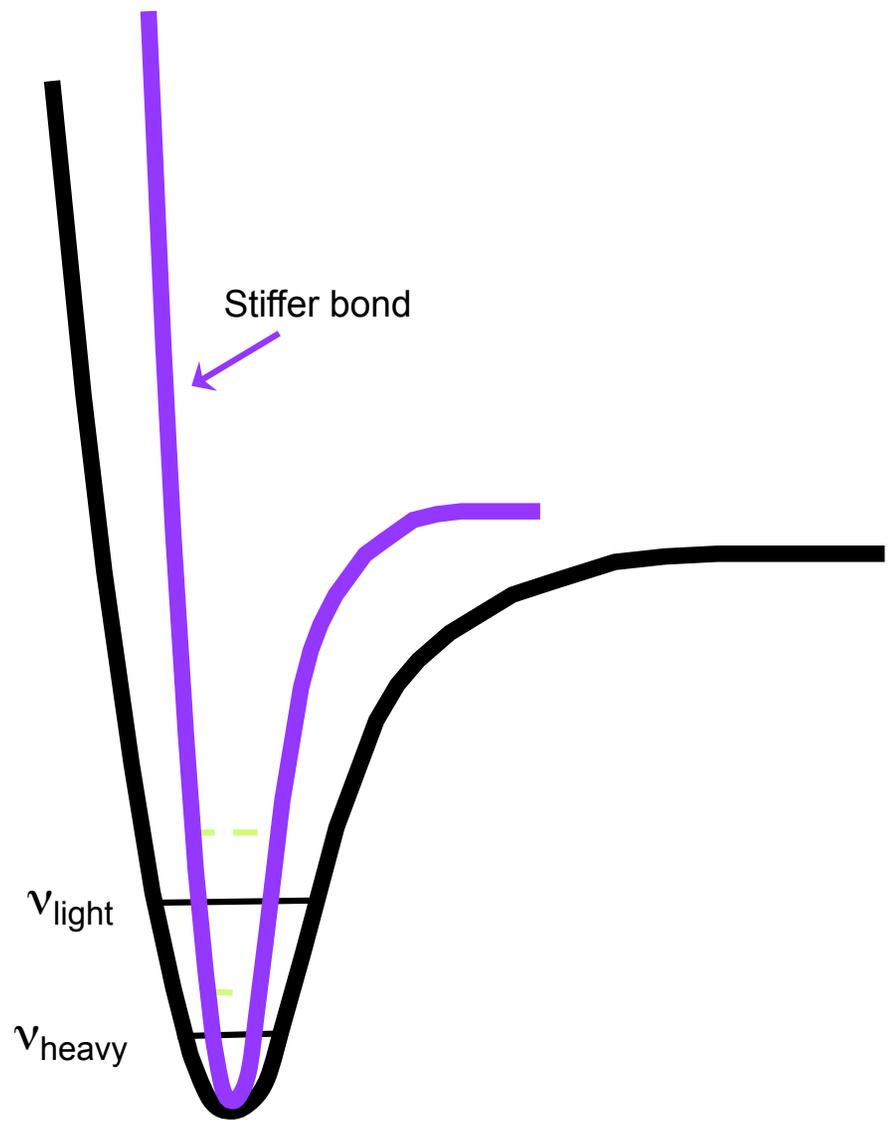


First suggestion that pressure might have an effect on isotope fractionation and that there is a fractionation during core formation.

Molar Volume Isotope Effect

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

Bond Stiffening



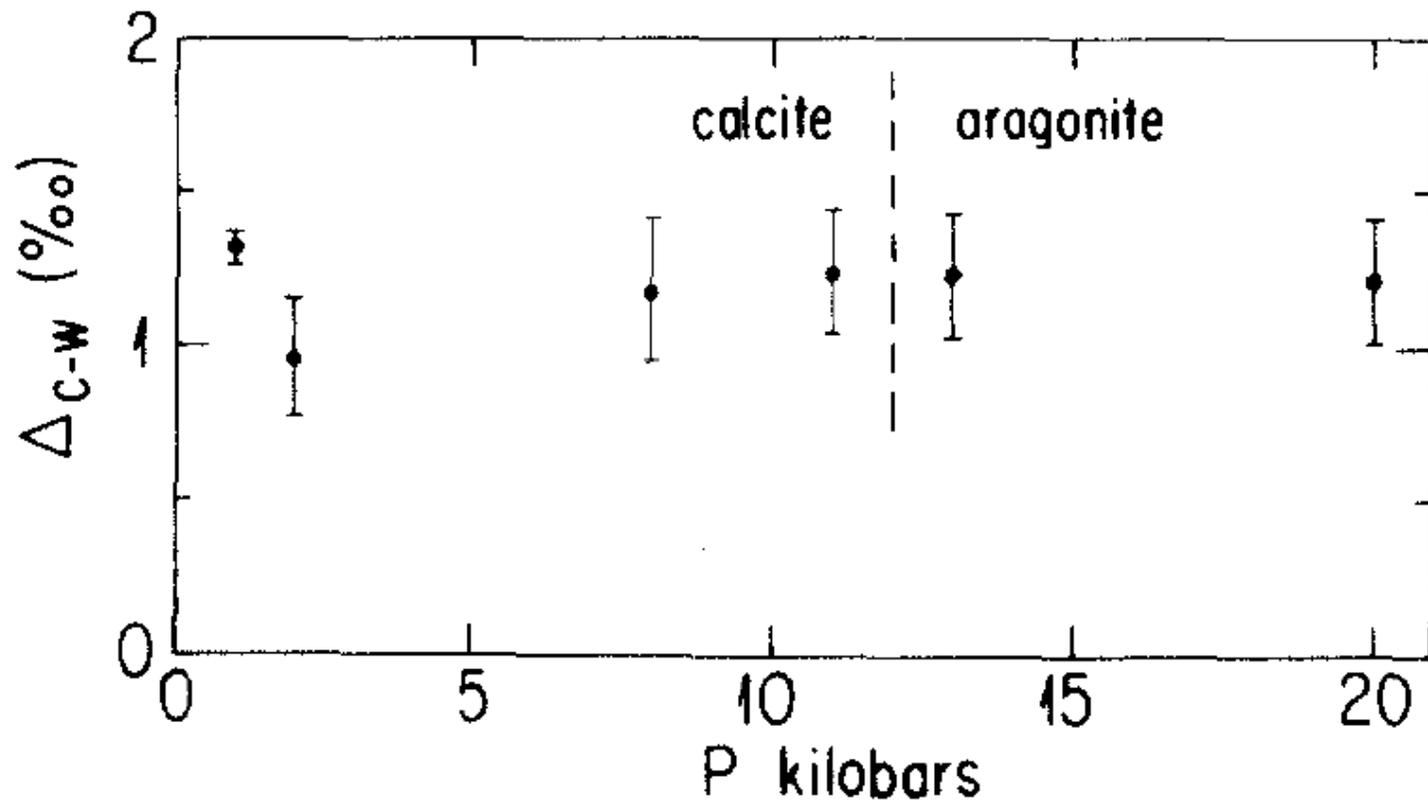
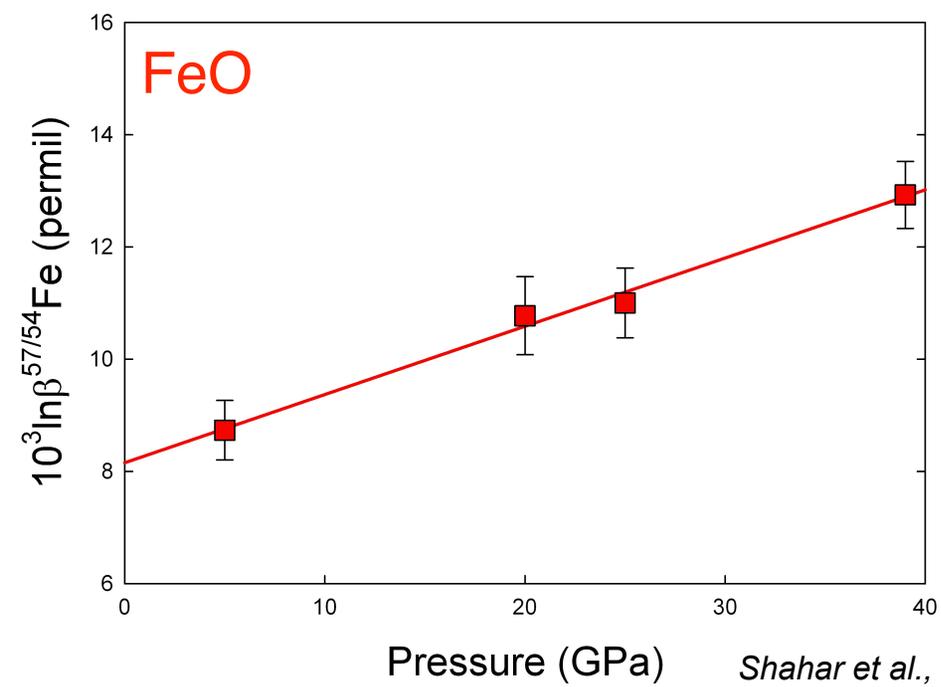
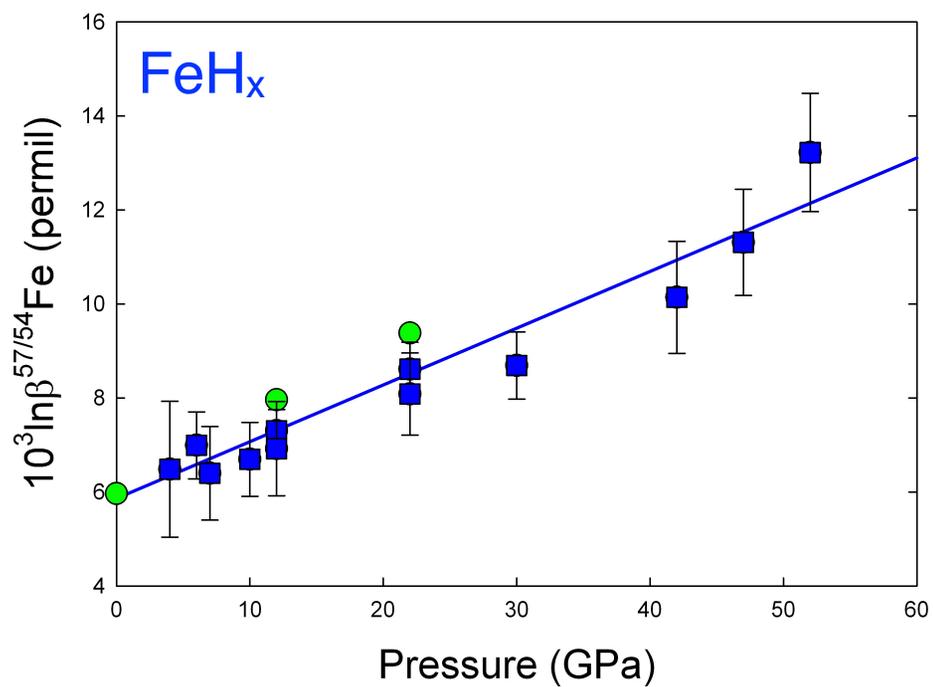
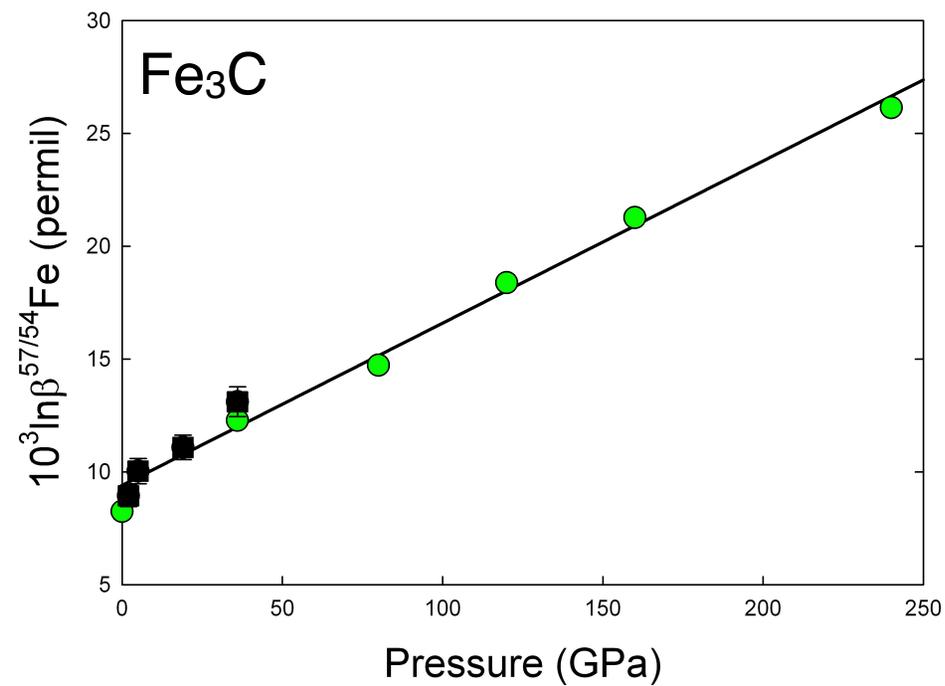
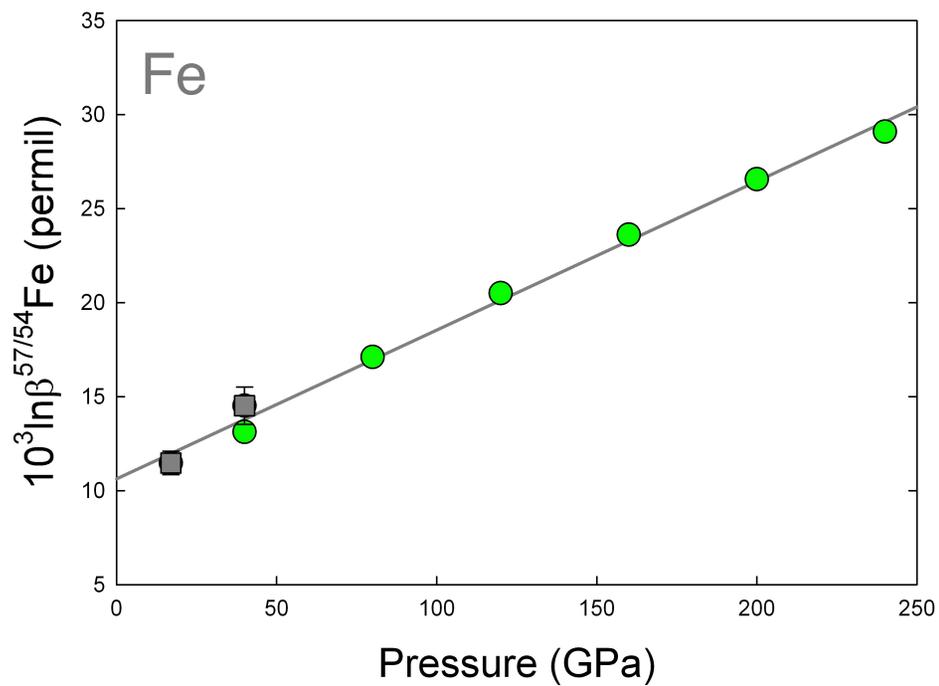
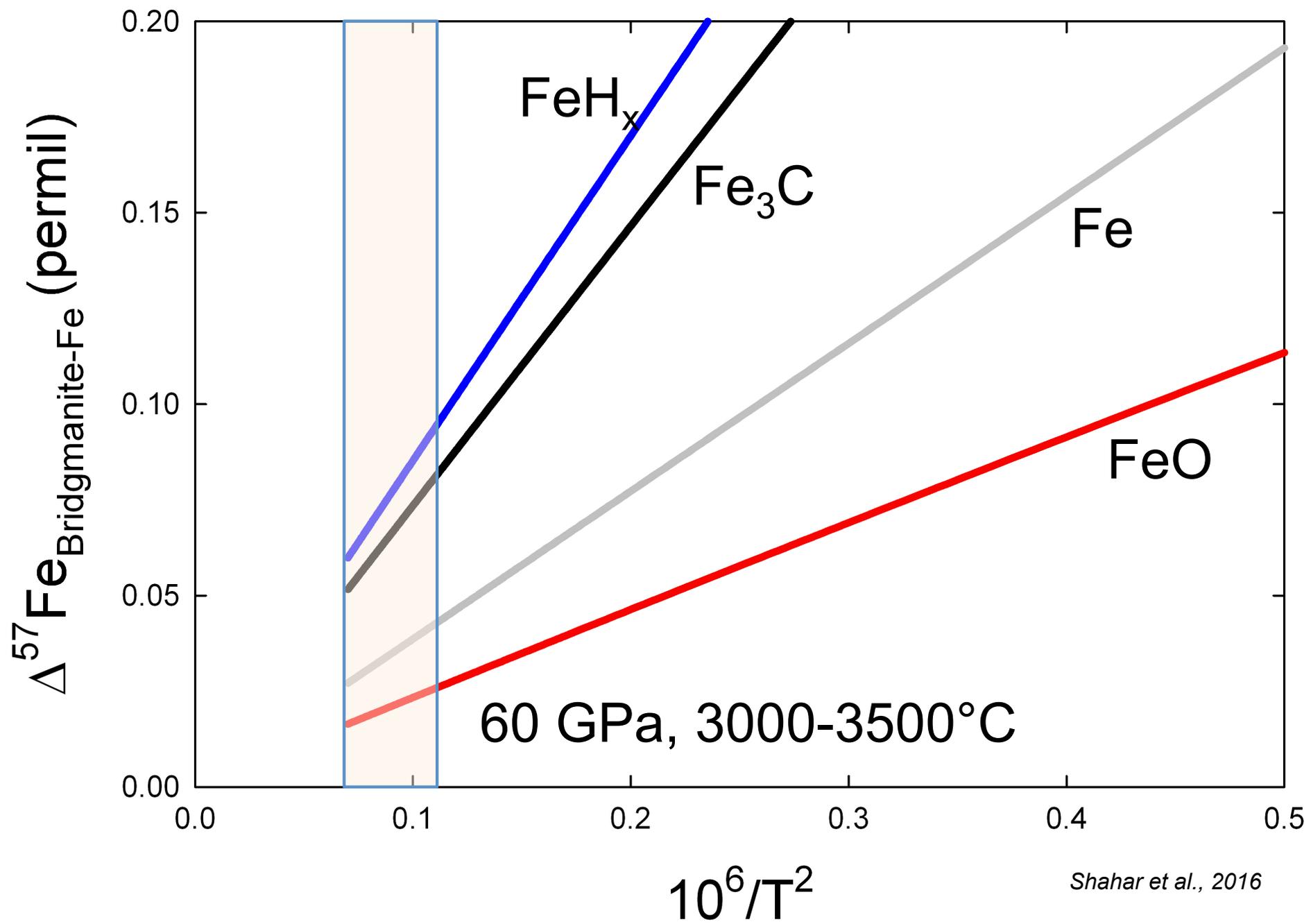
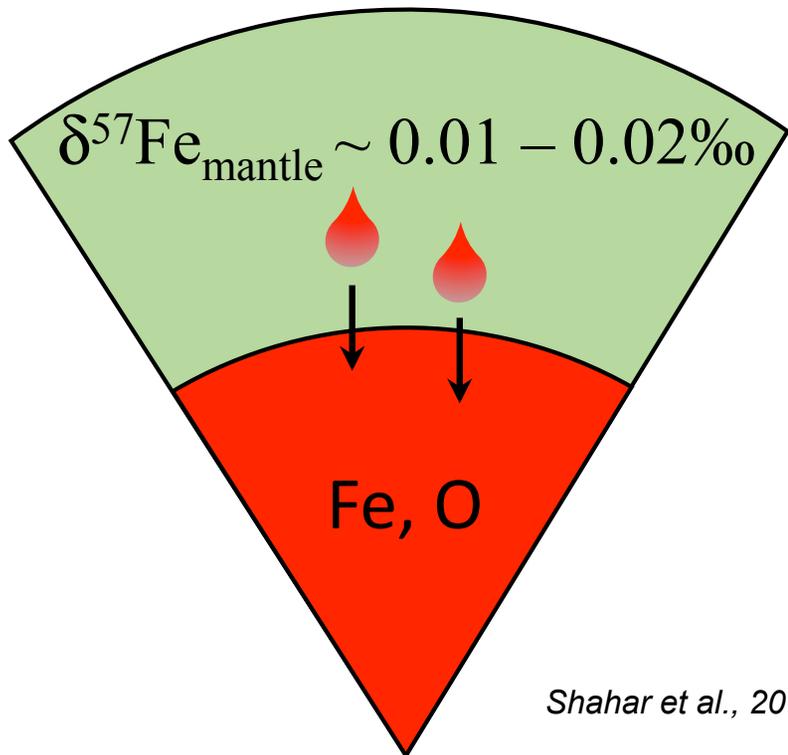
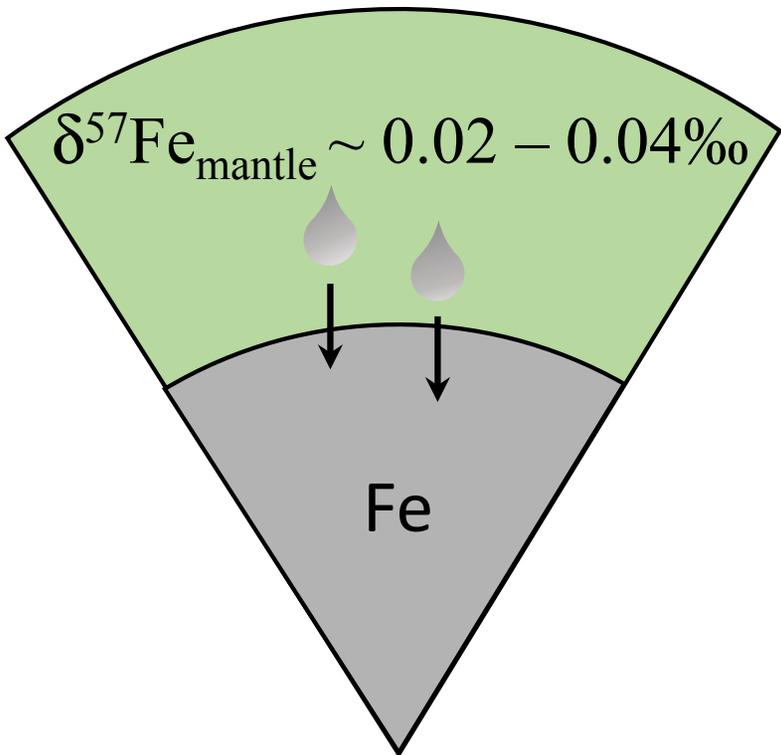
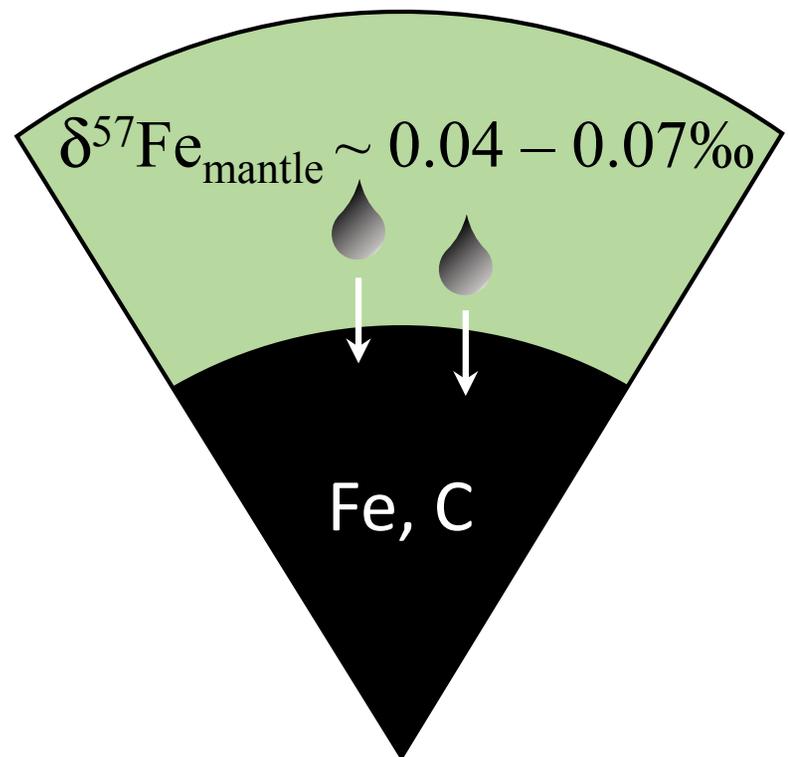
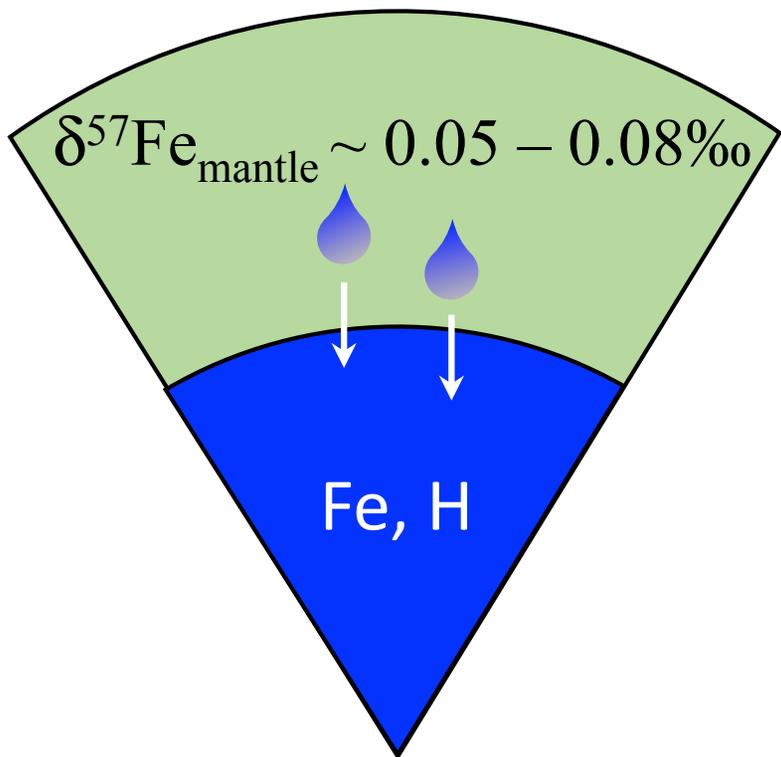
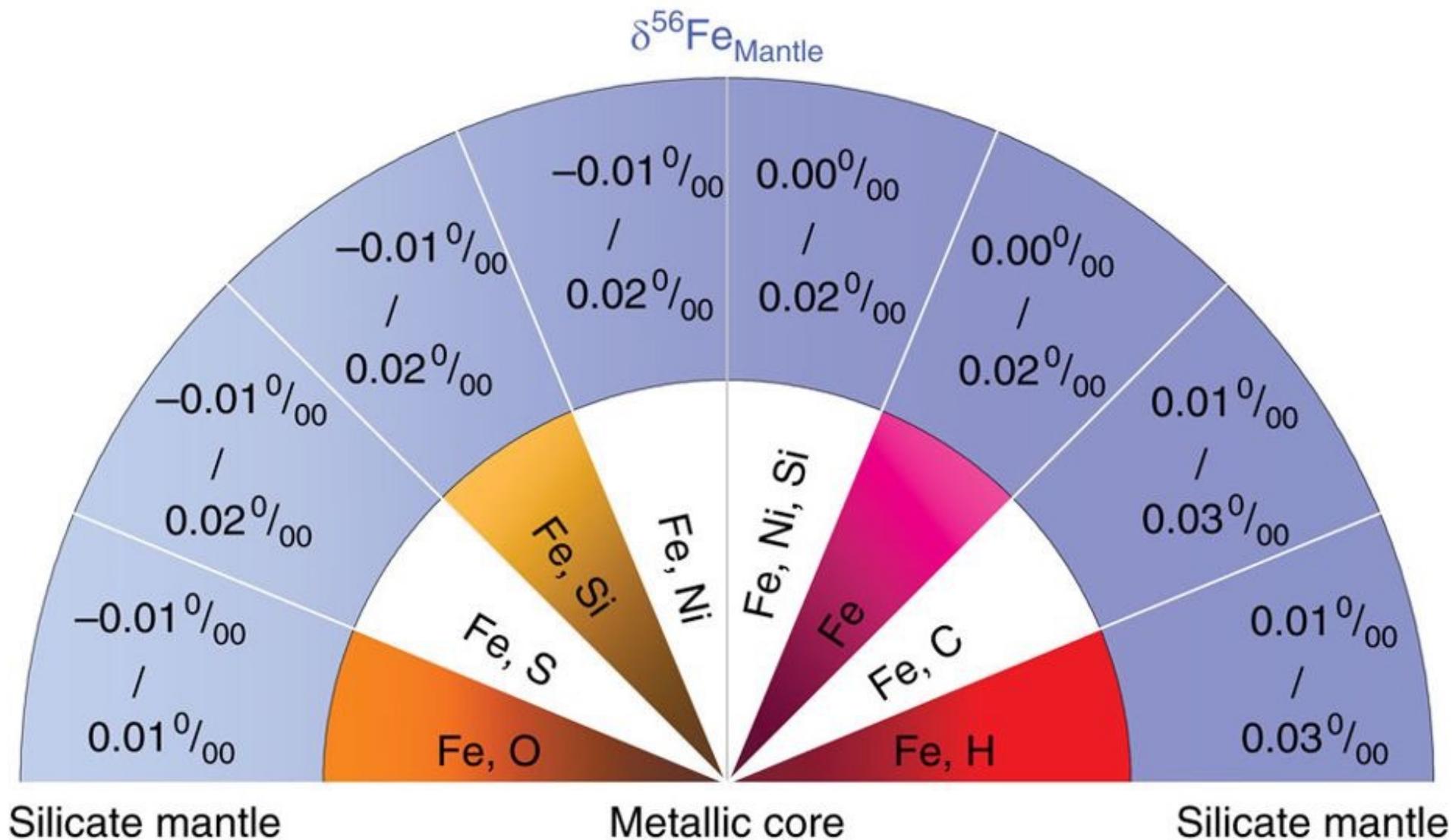


Fig. 2. Isotopic fractionation between CaCO_3 and water at 500°C as a function of pressure. Below 12 kbar, calcite is stable; above 12 kbar, aragonite is stable. Error bars show mean deviations from mean at each pressure.



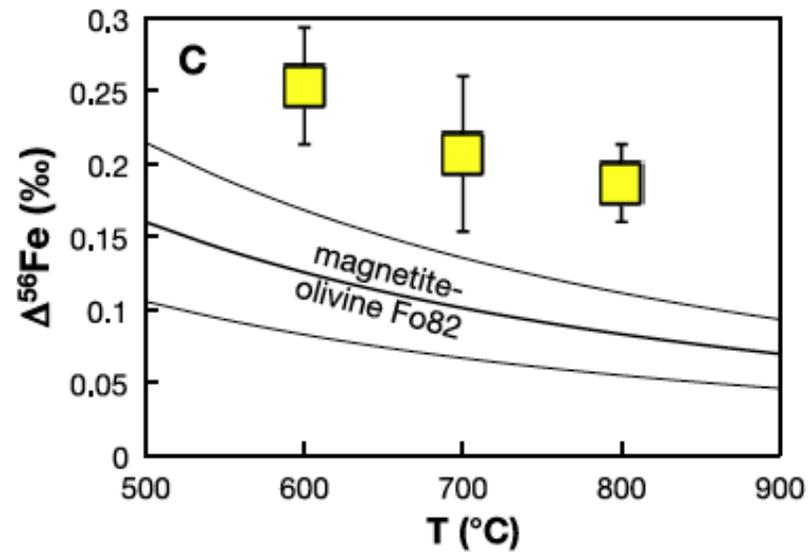
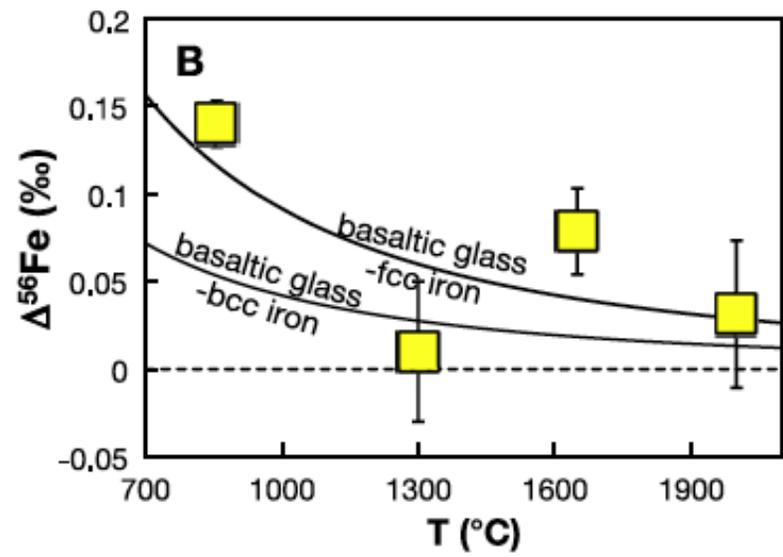
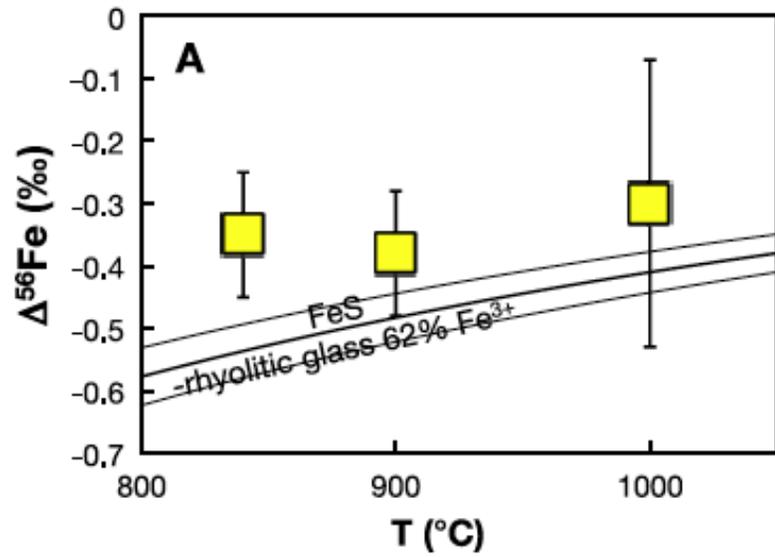






Lin et al., 2017

As a result, the fractionation values that they calculated were systematically heavier than ours by $\sim 0.01\text{--}0.02\text{‰}$ 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 $\delta^{56}\text{Fe}$ values, we find that the shift would be smaller than what they predicted by 0.01–0.02‰.



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.

