Geochemistry 2: Experimental and Stable Isotope Perspectives on the Deep Earth

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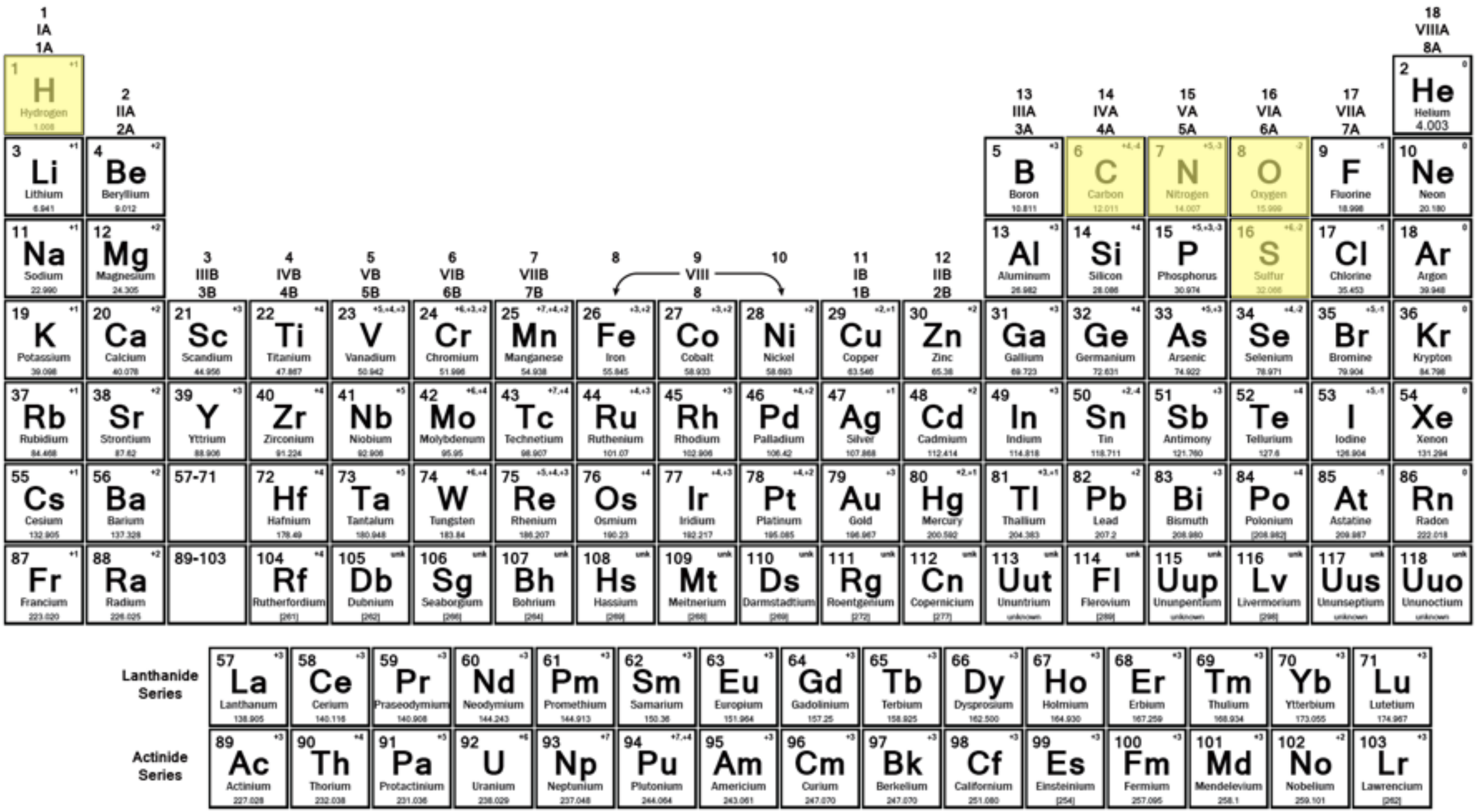
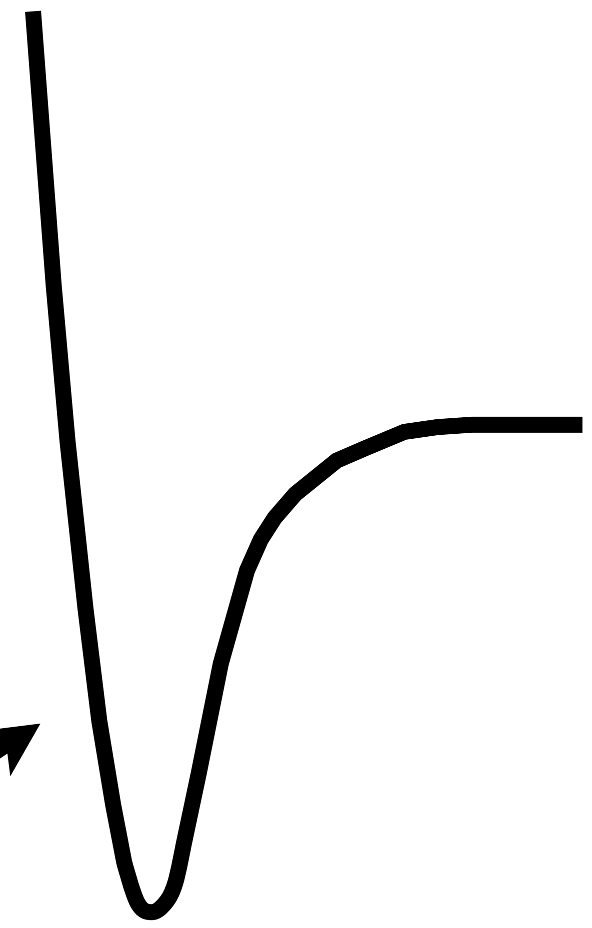


Look for elements that have more than one non-radiogenic isotope, for which the mass difference between isotopes is a significant fraction of the atomic mass (enough to measure)

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

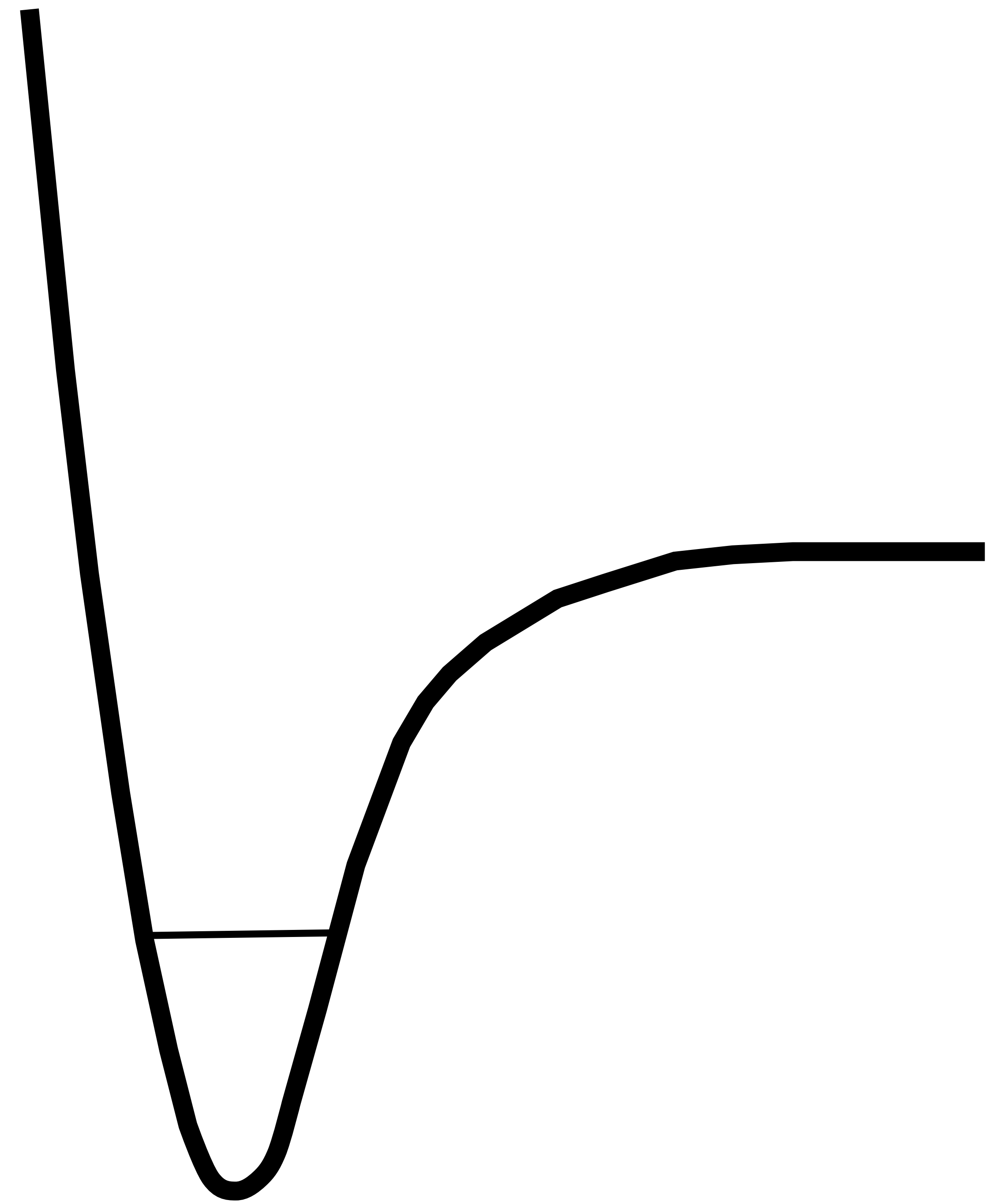
Isotopic fractionations occur due to:

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



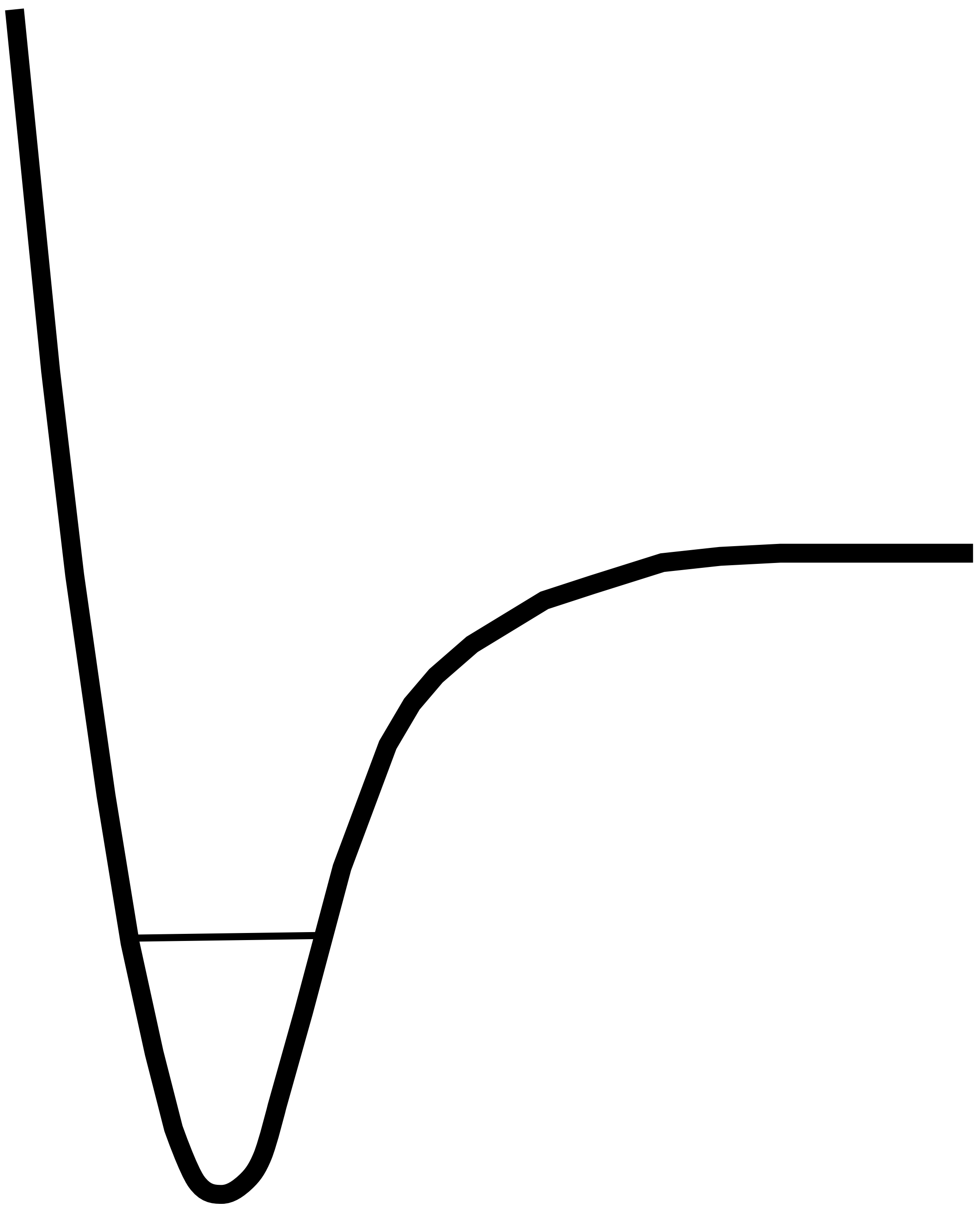
$$\frac{\langle v_1 \rangle}{\langle v_2 \rangle} = \sqrt{\frac{m_2}{m_1}}$$

$$E_n = h\nu(n+½)$$



$$E_n = h\nu(n + ½)$$

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



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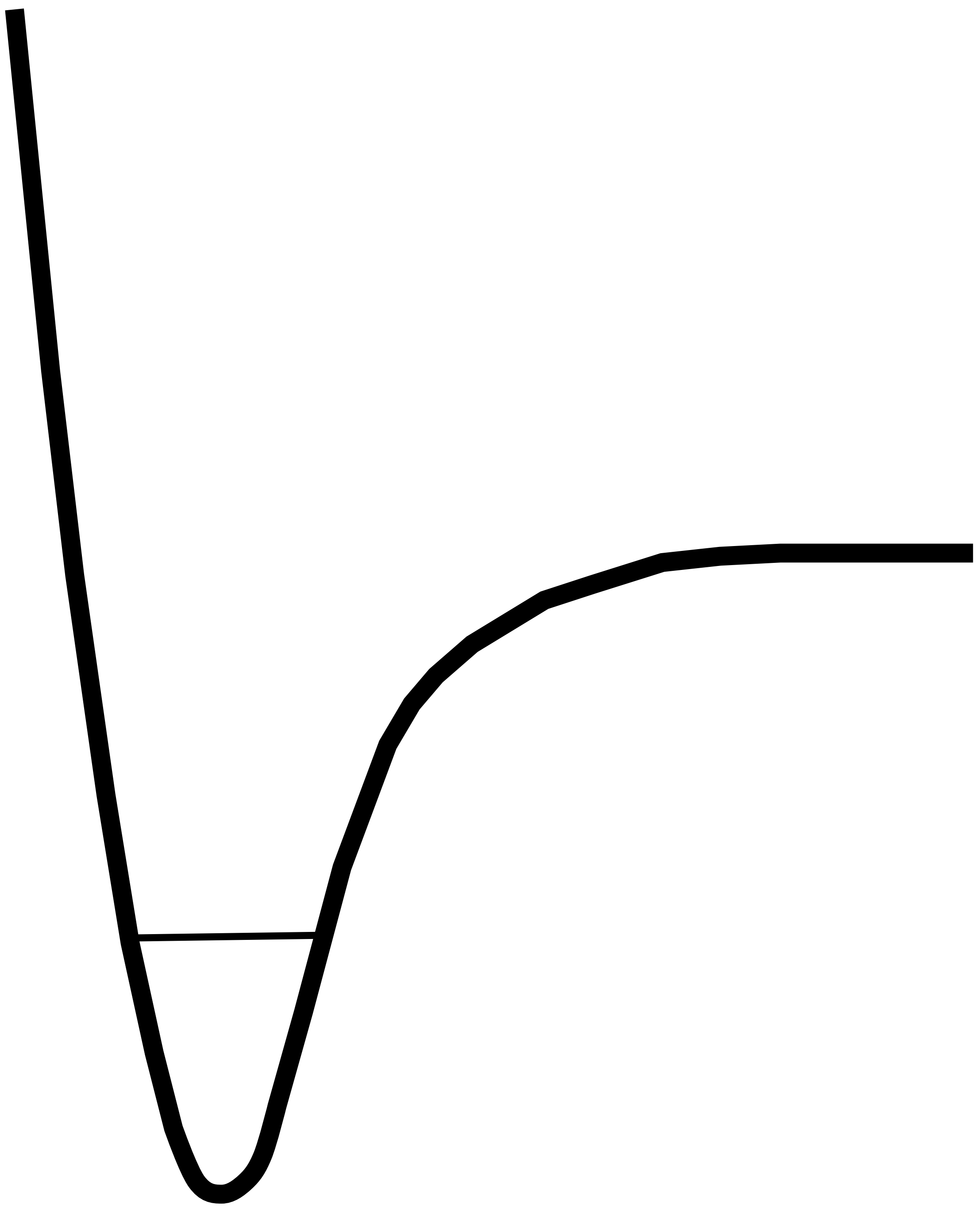
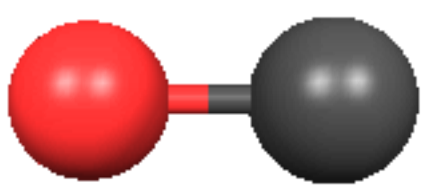
Zero-point energy differences drive typical equilibrium stable isotope fractionations.



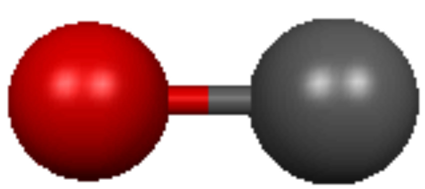
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Heavy isotopes have lower vibrational frequencies

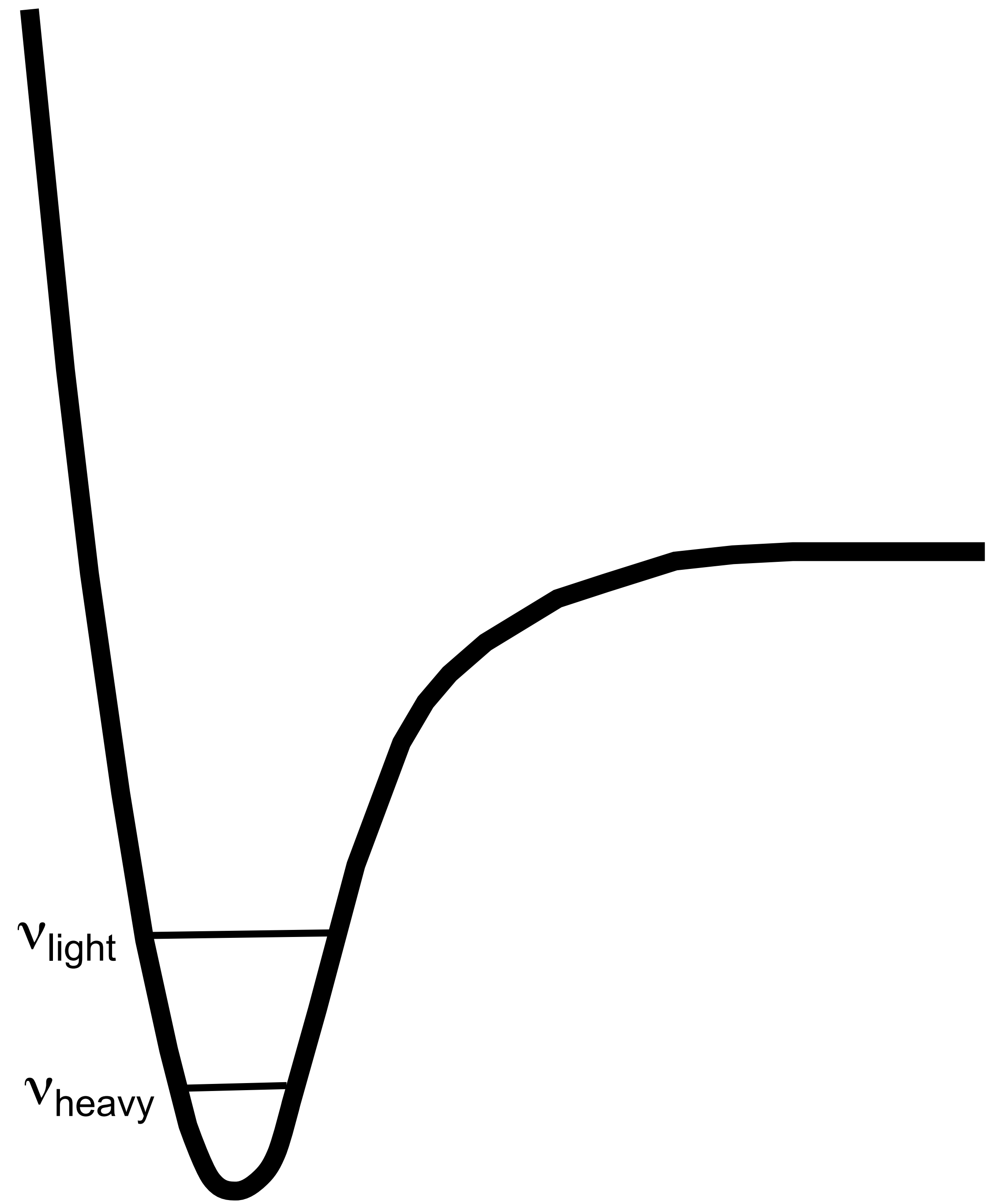
$^{12}C^{16}O$



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

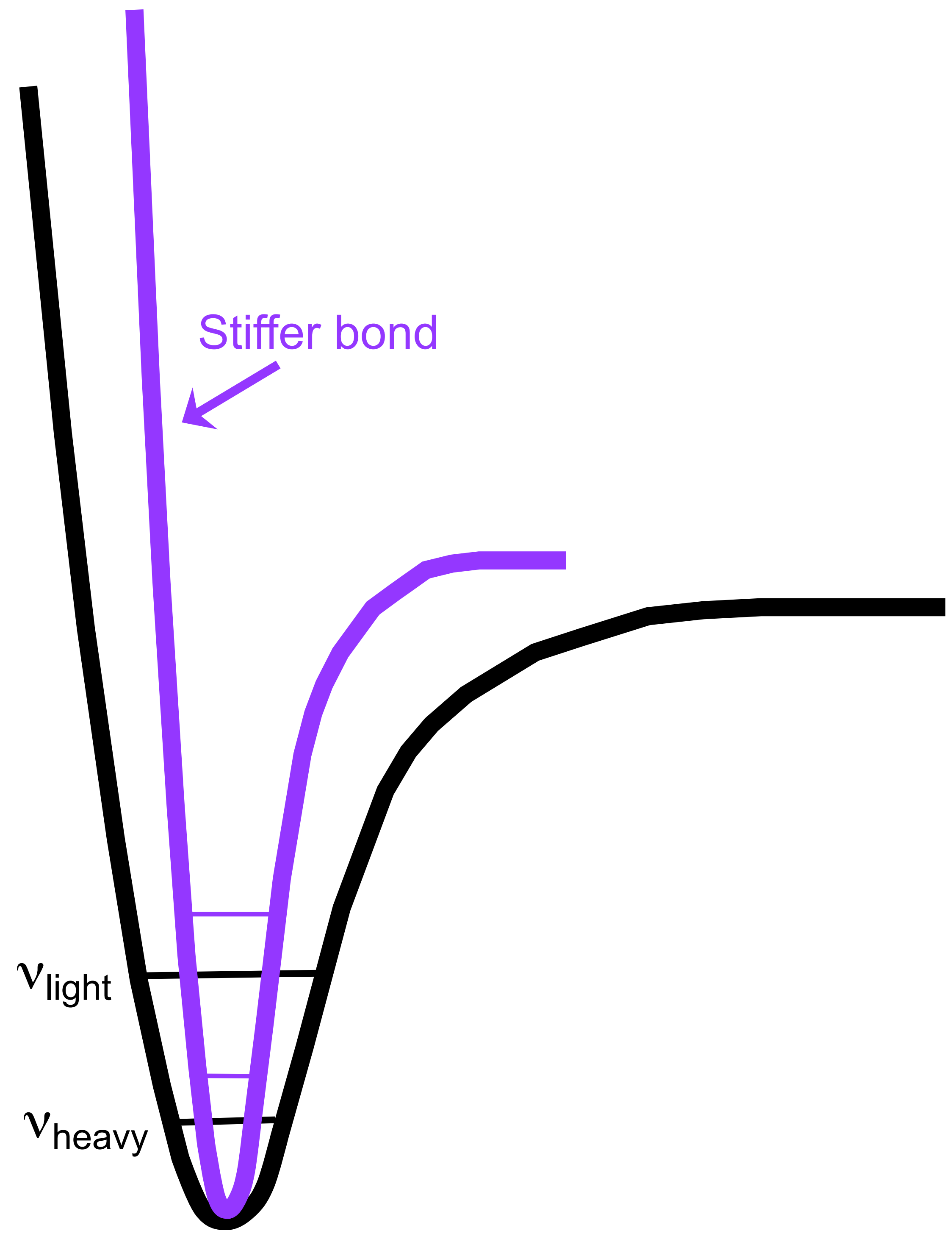


Credit: Edwin Schauble



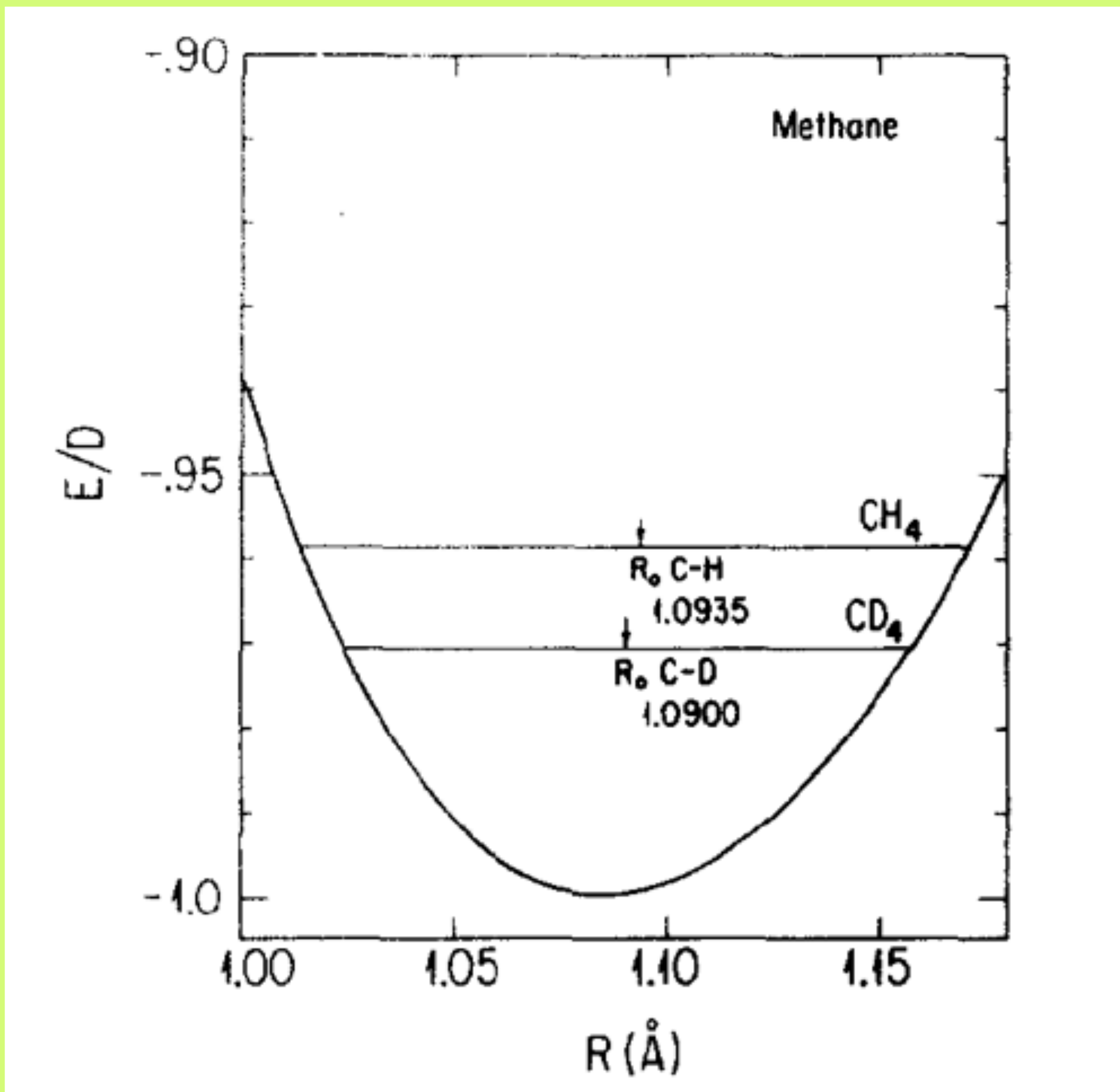
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

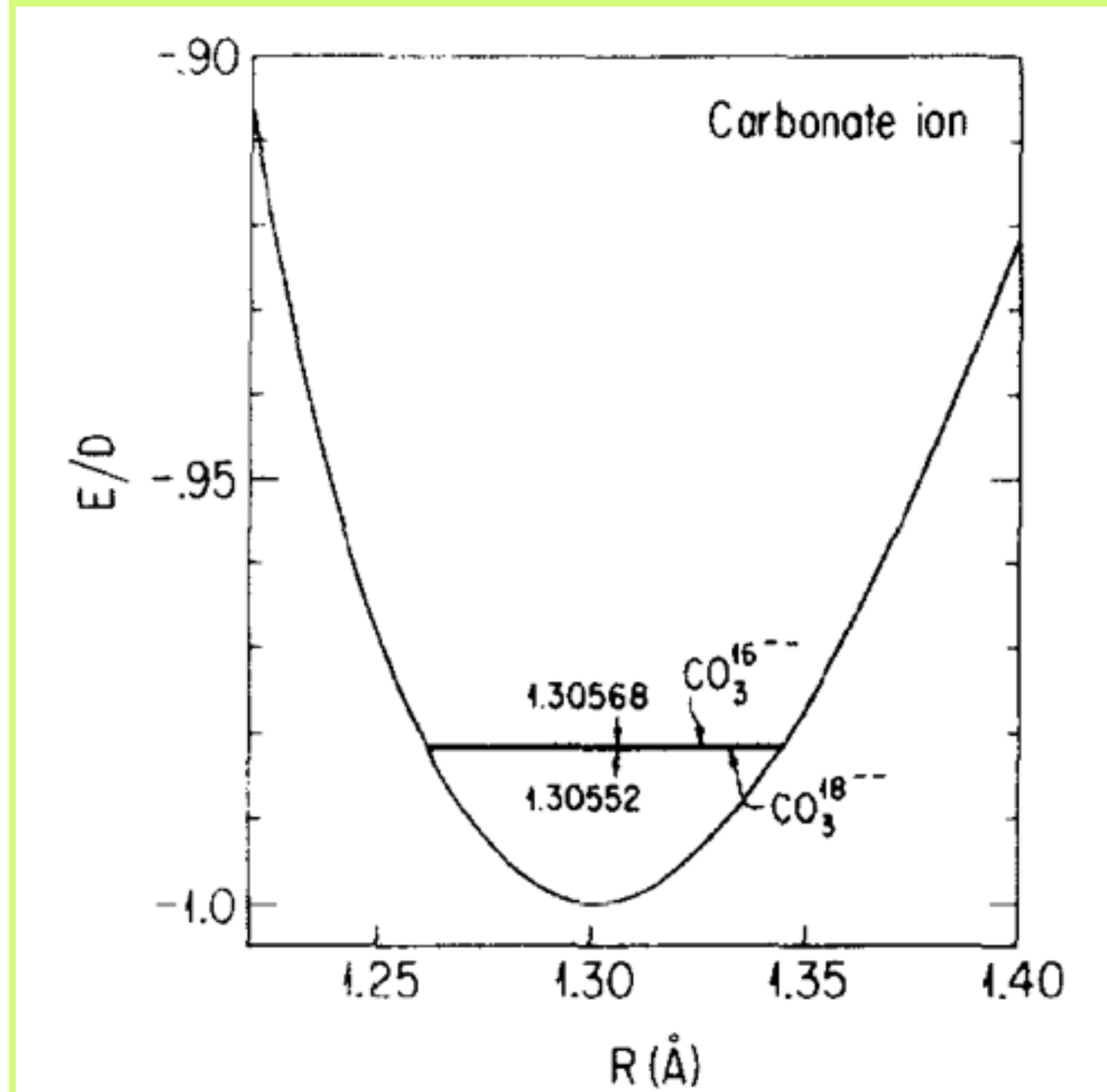
Stiffer bonds concentrate the heavy isotopes
- shorter bonds
- higher oxidation state
- low coordination number



O’Neil 1986 tabulated five common characteristics that are shared by elements that show large variations in isotopic compositions in nature:

- low atomic mass
- relative mass difference between isotopes is large
- tendency to form covalent bonds
- elements exist in more than one oxidation state
- abundances are high enough that we can measure them



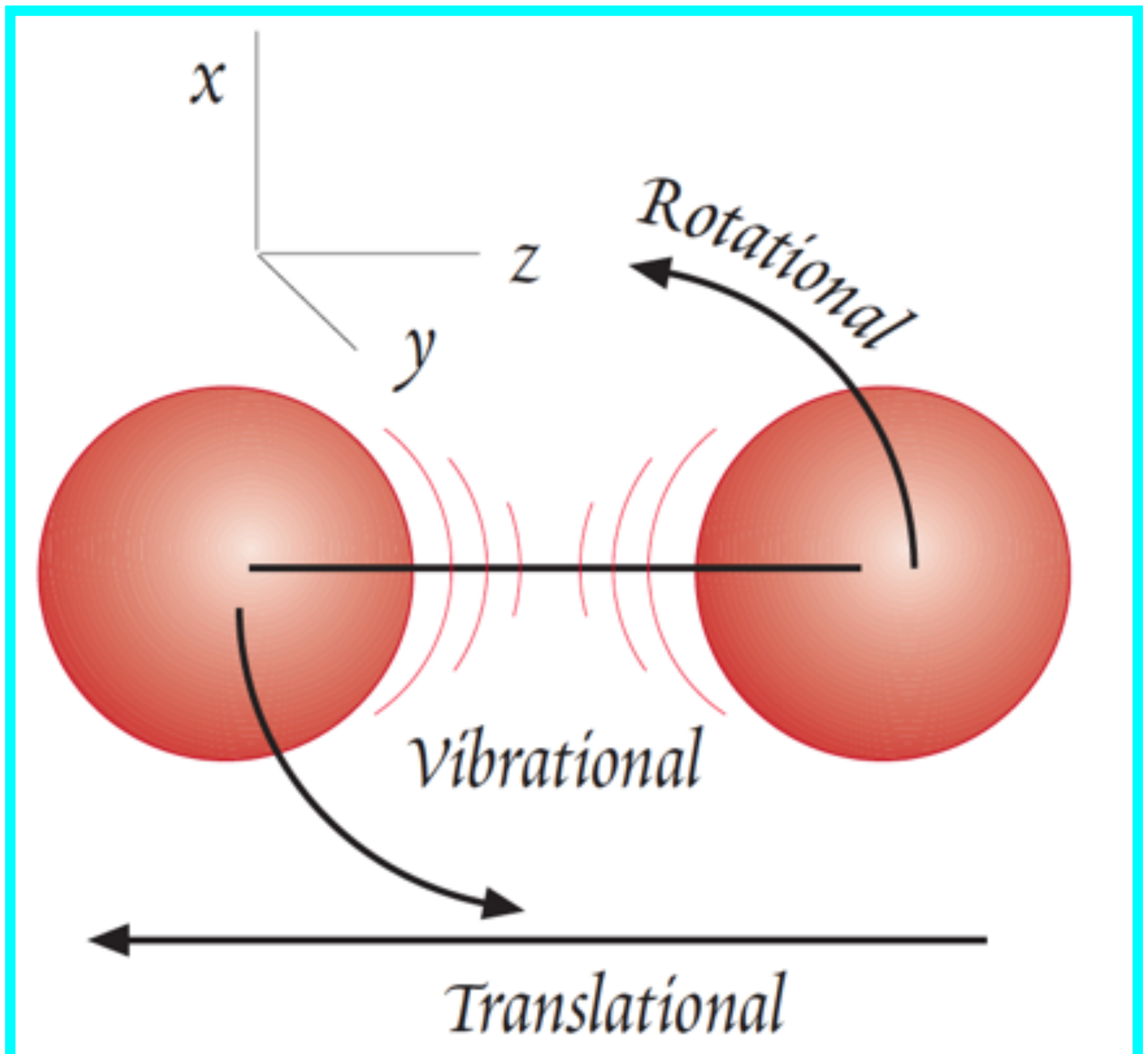


Clayton et al., 1975

$$\boxed{AX' + BX = AX + BX'}$$

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

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



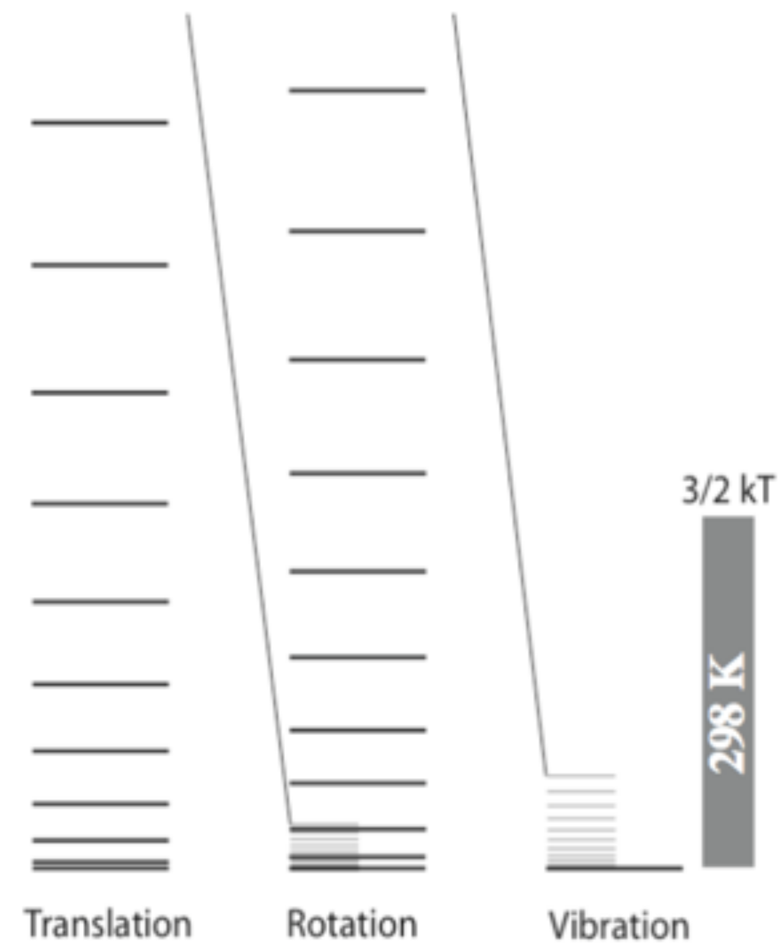
$$= \frac{\Pi_{\text{Products}}\left(Q_{\text{Trans}} \times Q_{\text{Rot}} \times Q_{\text{Vib}}\right)}{\Pi_{\text{Reactants}}\left(Q_{\text{Trans}} \times Q_{\text{Rot}} \times Q_{\text{Vib}}\right)}$$

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

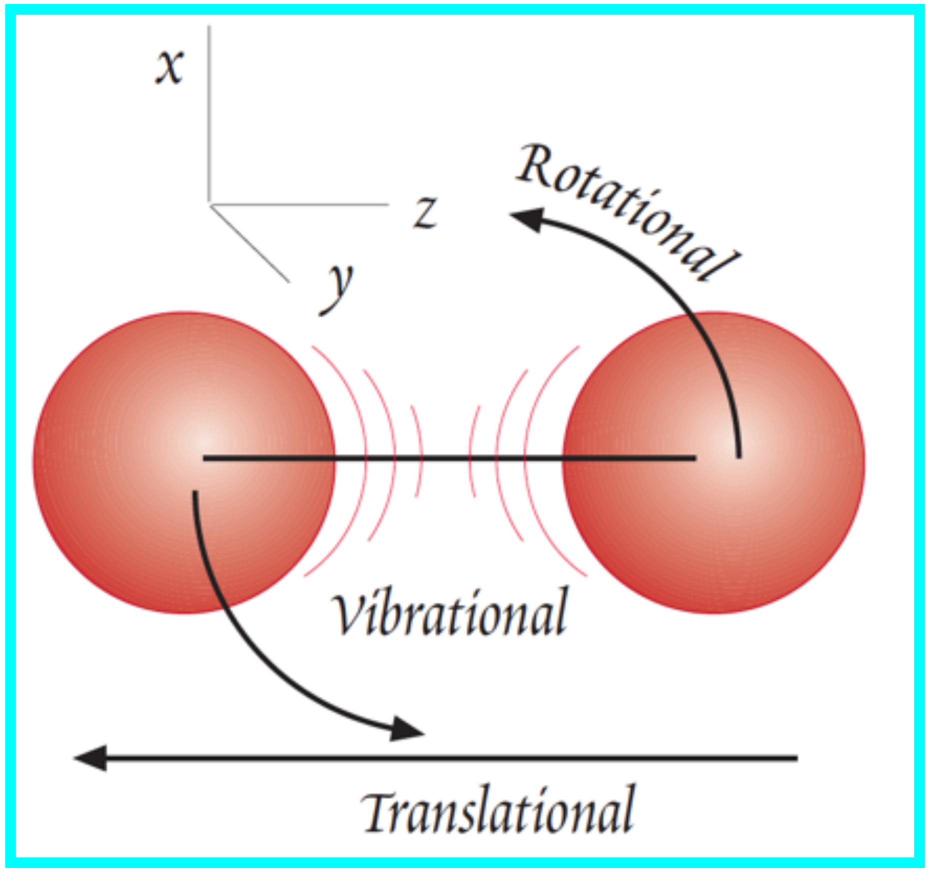
$$K_{eq} = Q(AX)Q(BX')/Q(AX')Q(BX)$$

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

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

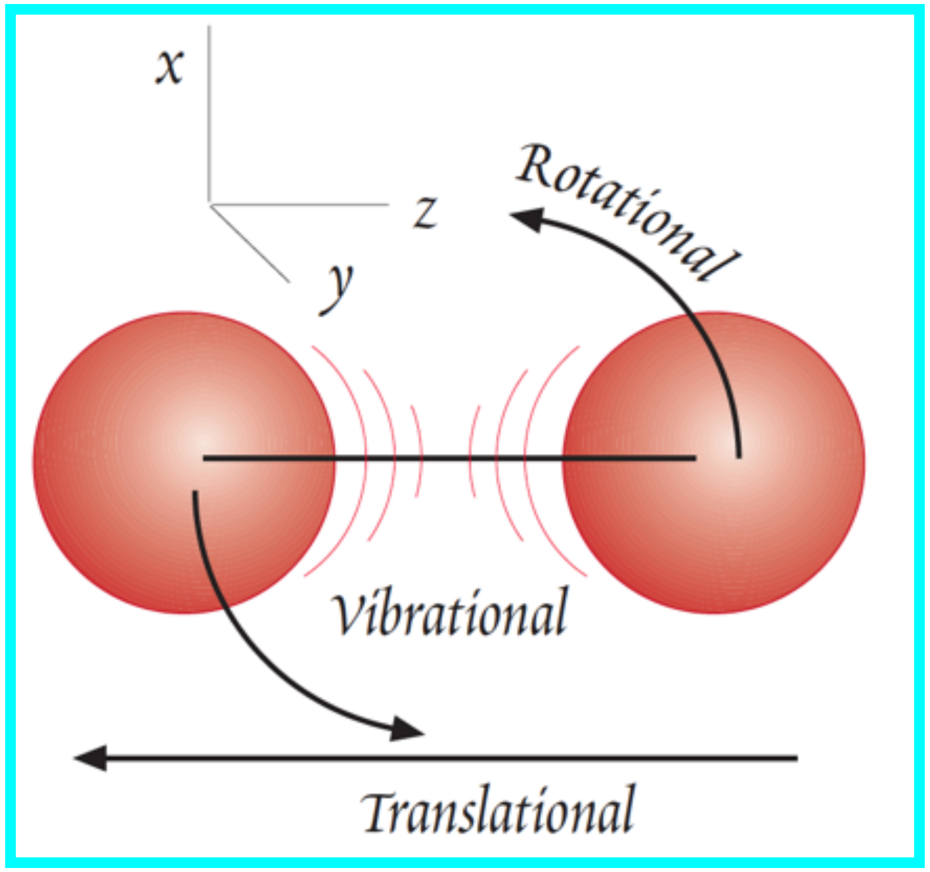


$$Q_{\text{trans}} = \frac{(2\pi m k T)^{3/2}}{h^3} V$$



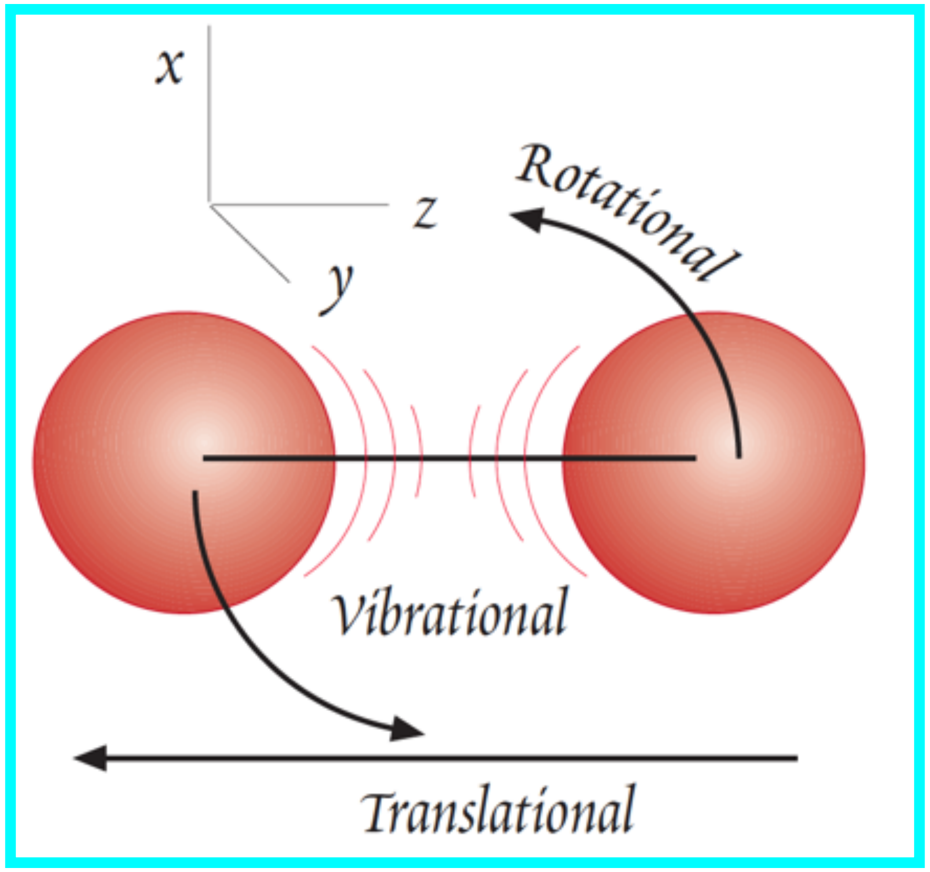
$$(Q/Q')_{tr} = (M'/M)^{3/2}$$

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



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

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



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

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

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

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

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

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

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

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

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

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

and

$$\delta^{i} = [R^{i/j}_{sample}/R^{i/j}_{standard} - 1]*1000$$

$$\delta_{A} - \delta_{B} = \Delta_{A\text{-}B} \approx 10^{3} \ln \alpha_{A\text{-}B}$$

$$\boxed{10^{3} \ln \alpha^{i/j}_{a-b} = \frac{10^{3}}{24}\left(\frac{h}{k_{b}T}\right)^{2}\left(\frac{1}{m_{j}} - \frac{1}{m_{i}}\right)\left[\sum_{x=1}\frac{K_{f,x,a}}{4\pi^{2}} - \sum_{x=1}\frac{K_{f,x,b}}{4\pi^{2}}\right]}$$

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

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

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It is important to point out that these rules (particularly 3 and 4) are largely untested with respect to fractionations in the less-well studied elements (those other than H, C, N, O, and S) at the present time. Furthermore, within rule (3), it is not known which chemical properties

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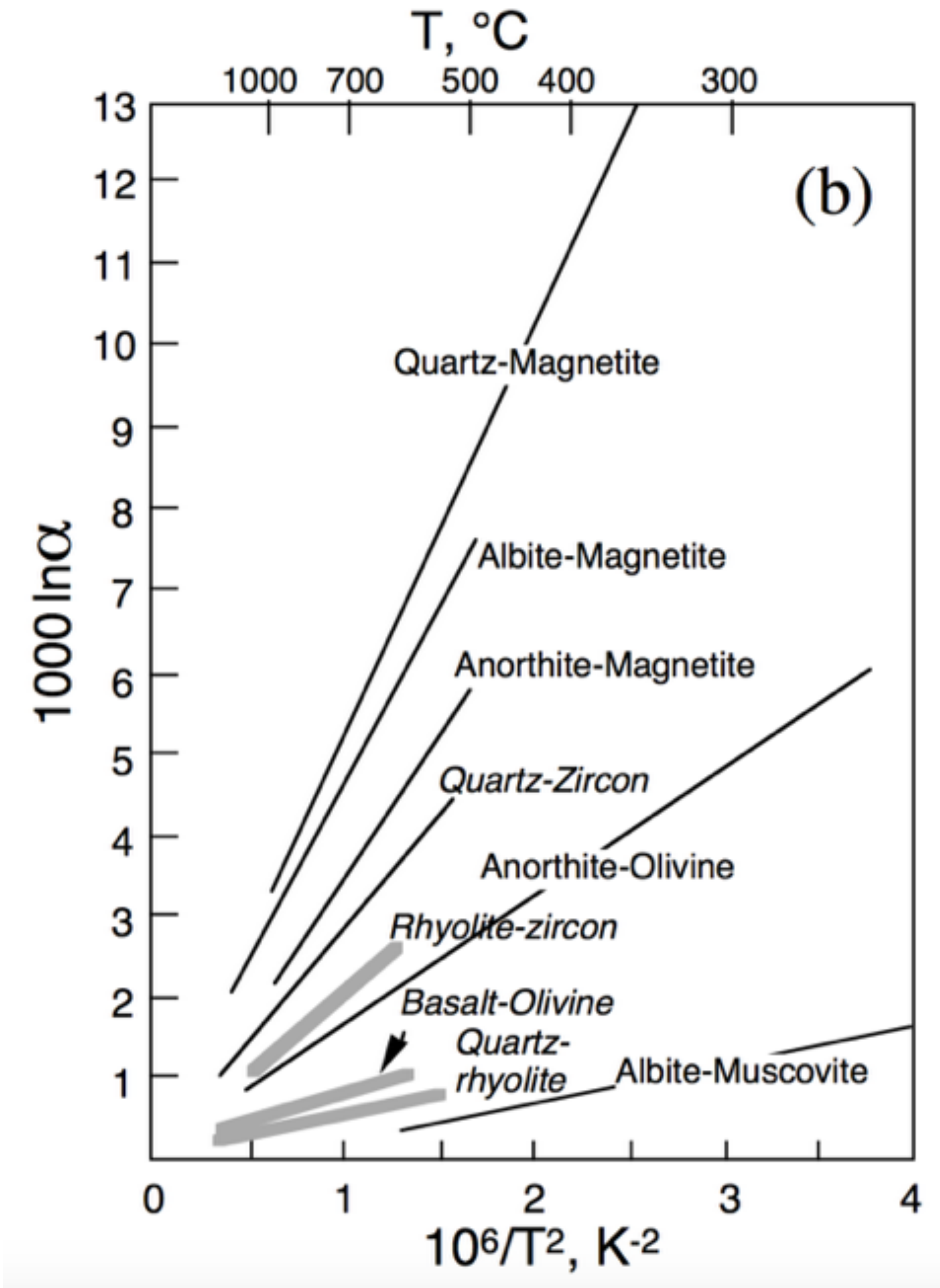
So what can we learn from stable isotopes about the deep earth? How do we use them?

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

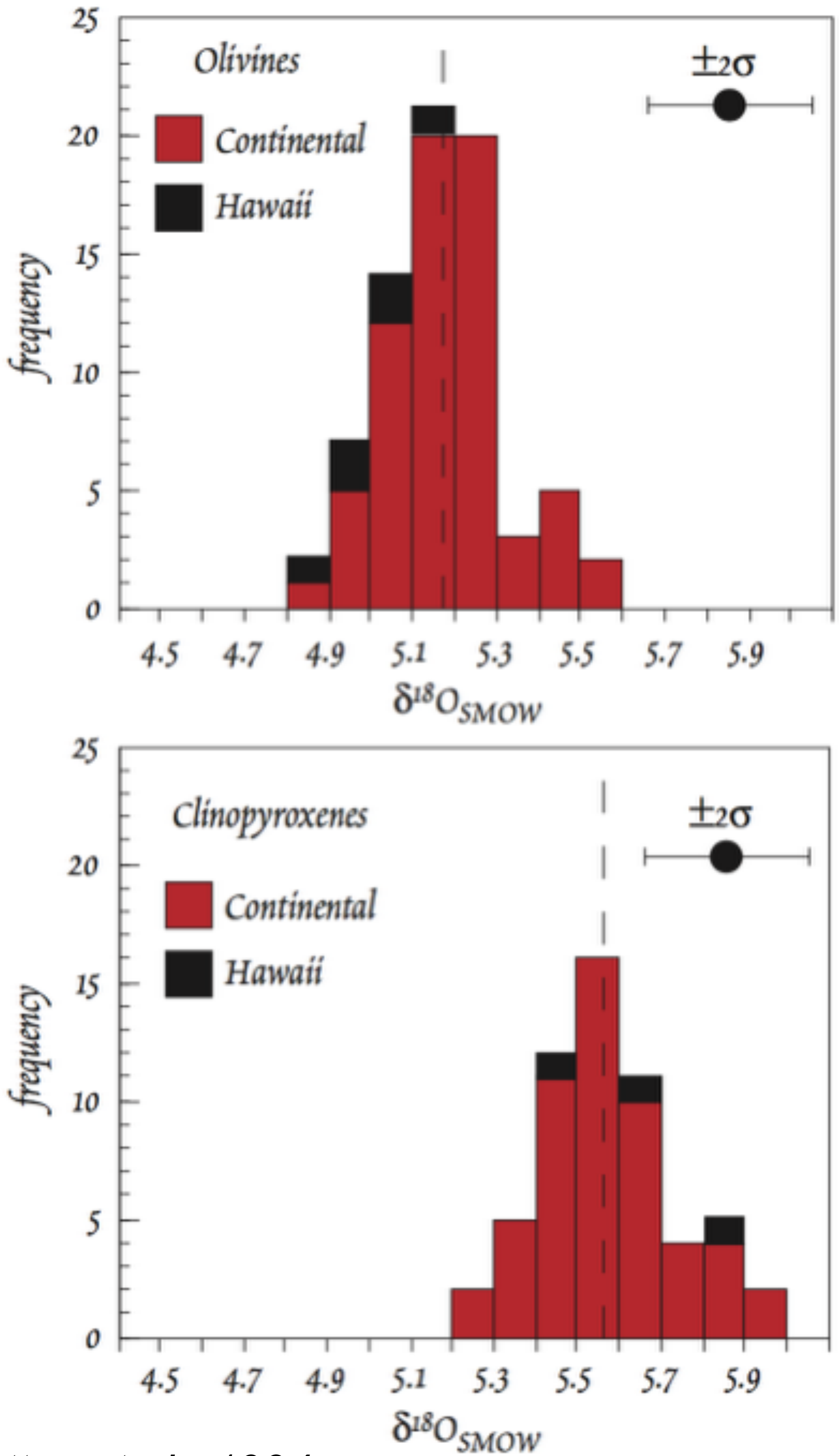
- From natural samples we can then determine which chemical reactions occurred in the samples and what temperature (etc.) the rocks equilibrated

Tracers!

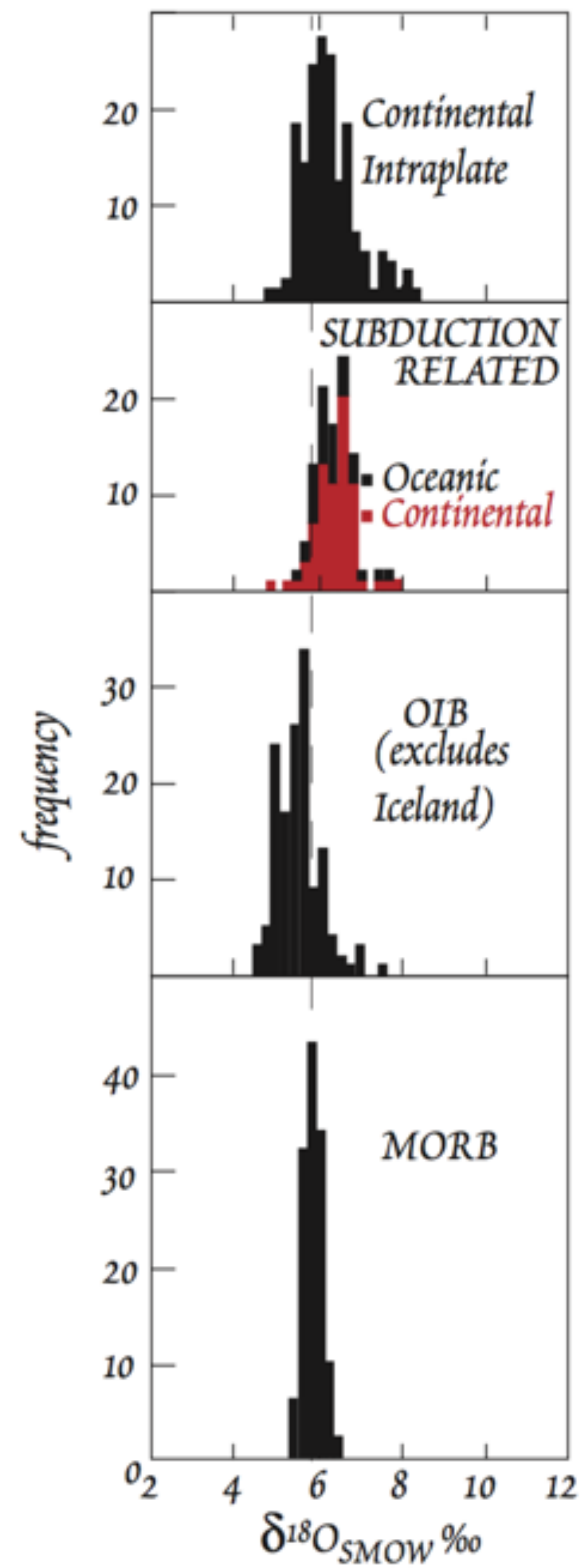
Example 1: Oxygen Isotopes for Thermometry



Bindeman, 2008, Data from Chiba et al. 1989

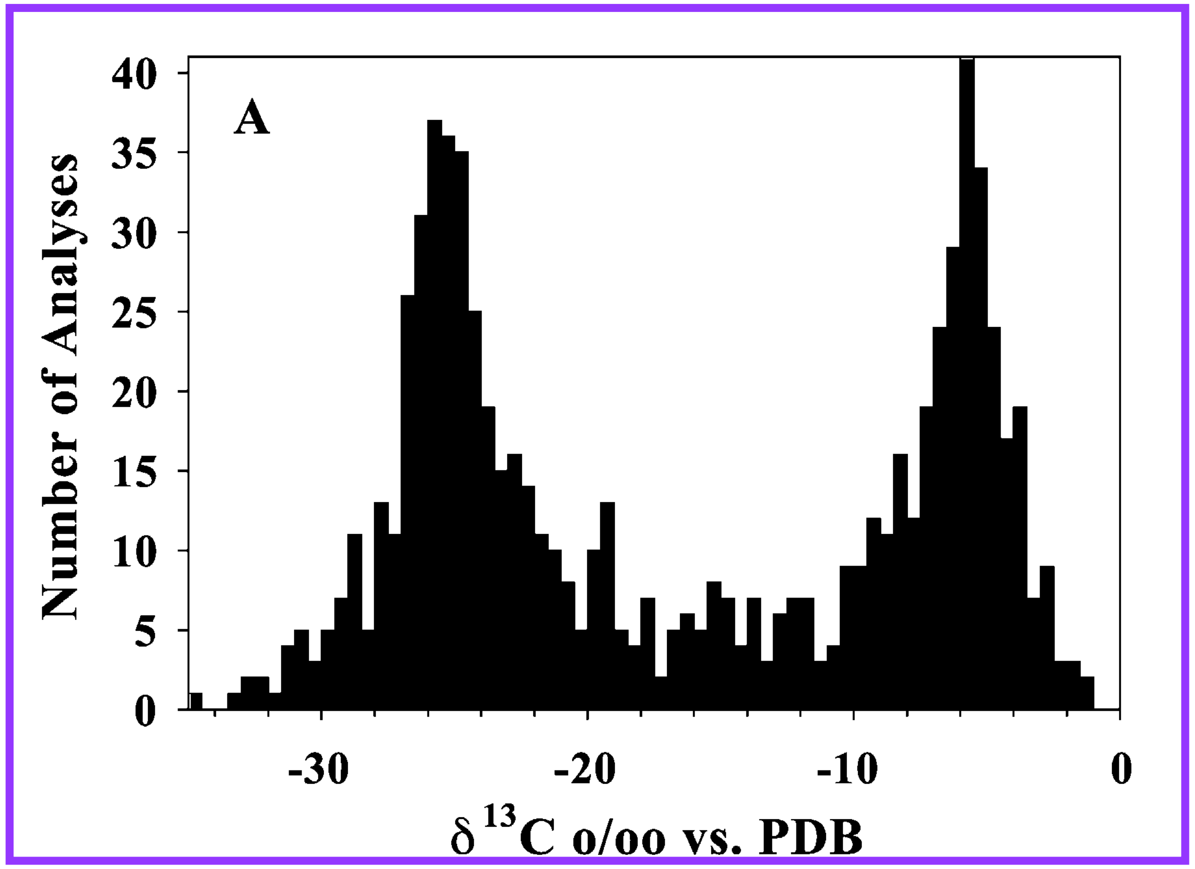


Mattey et al., 1994



Harmon and Hoefs, 1995

Example 2: Carbon Isotopes in Diamonds

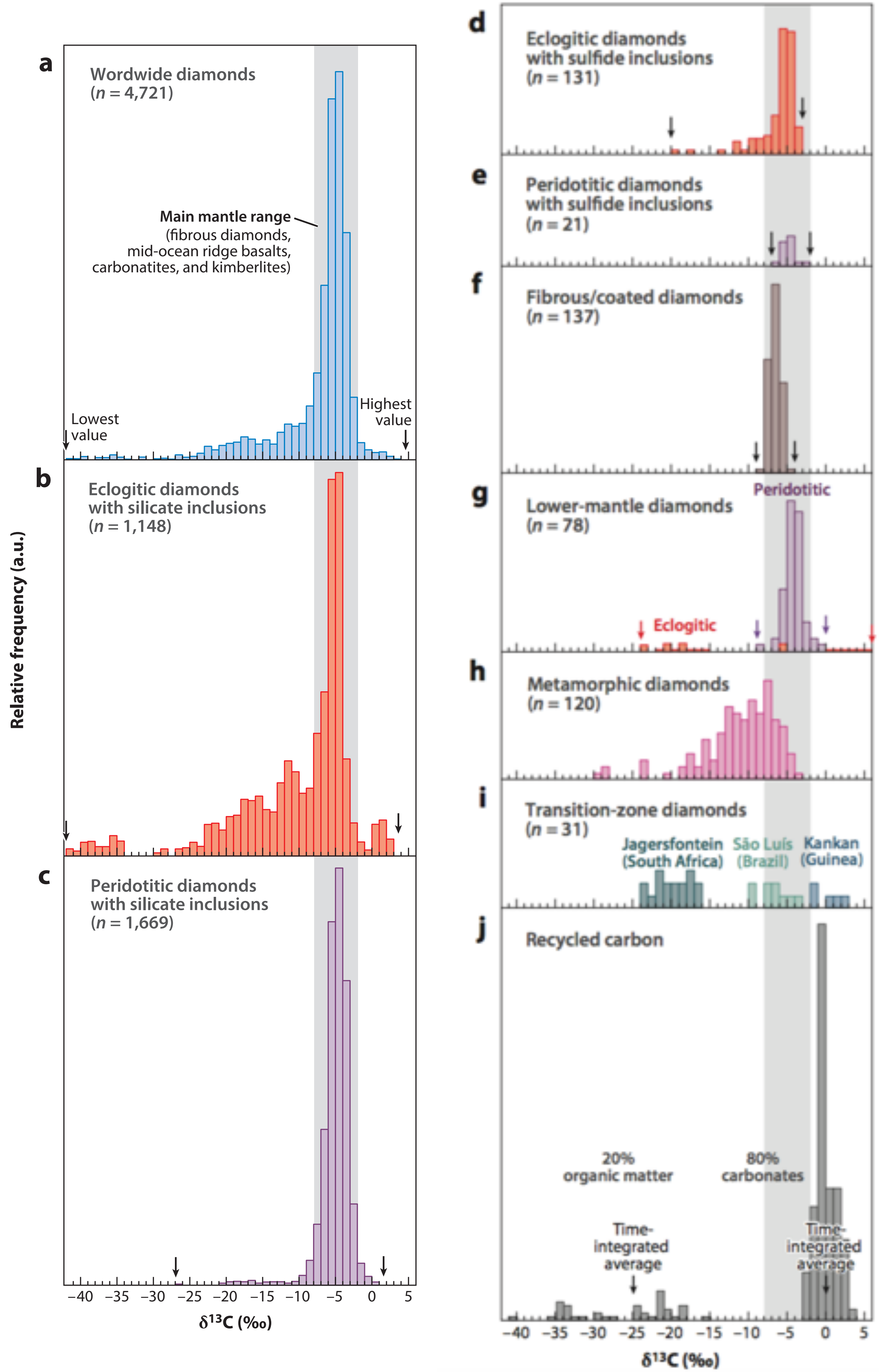


Deines, 2002

Whole rock mantle xenoliths and separated minerals

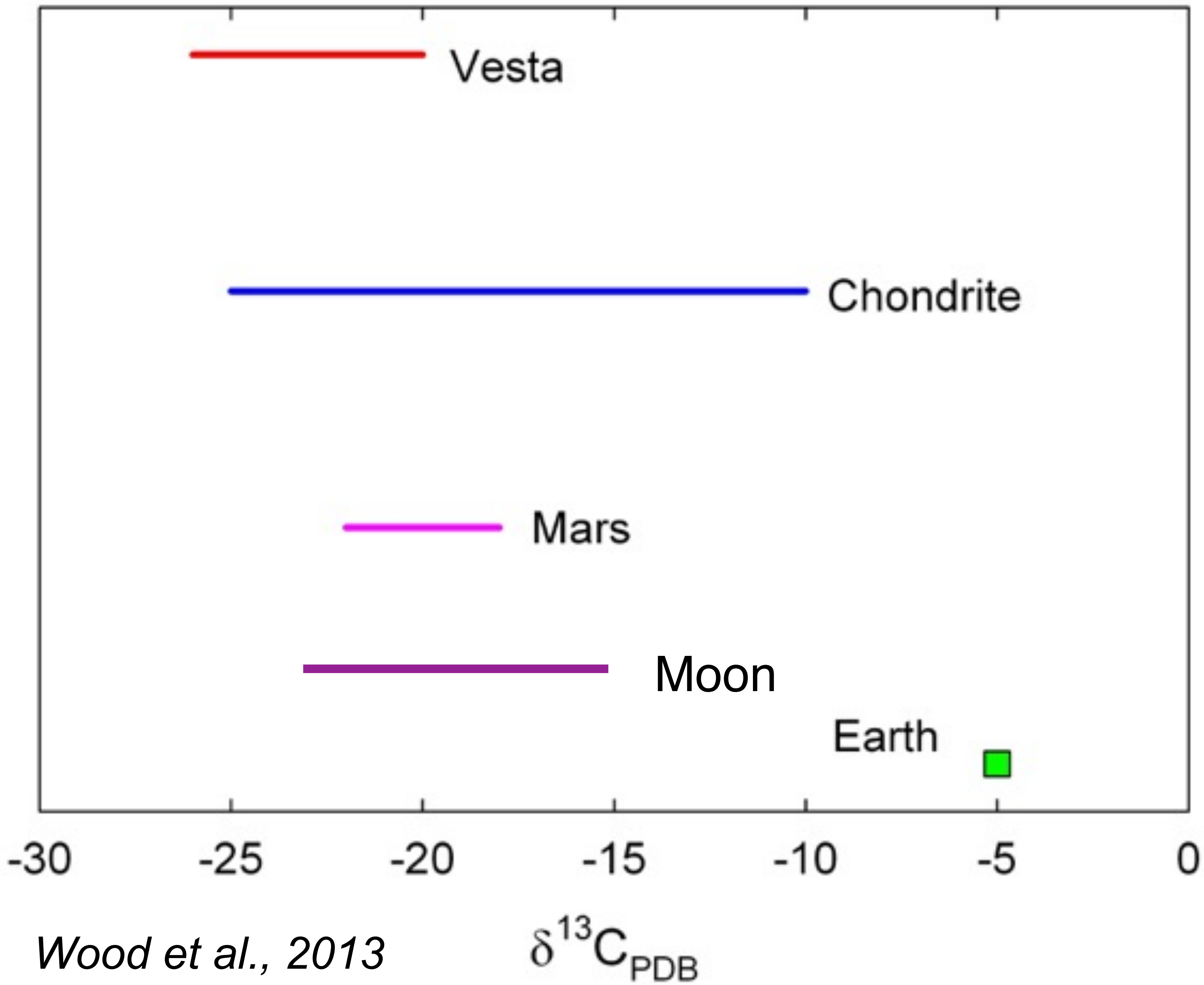
Bimodality of carbon isotope ratios - low T and high T?

Diamonds



Note: Eclogitic diamonds have a larger range of carbon isotope ratios

Cartigny et al., 2014



Wood et al., 2013

4. Although it would seem unlikely, perhaps the −5 ‰ signal observed on Earth is not representative of its primordial value. There appears to be a similarity in magmatic carbon isotopic composition (Fig. 3) between Mars (or at least Martian meteorites), Moon (Apollo samples) and Vesta (HED meteorites); if anything, it would seem that, in Solar System terms, it is the Earth that is unusual.

Grady et al., 2004

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- elements exist in more than one oxidation state
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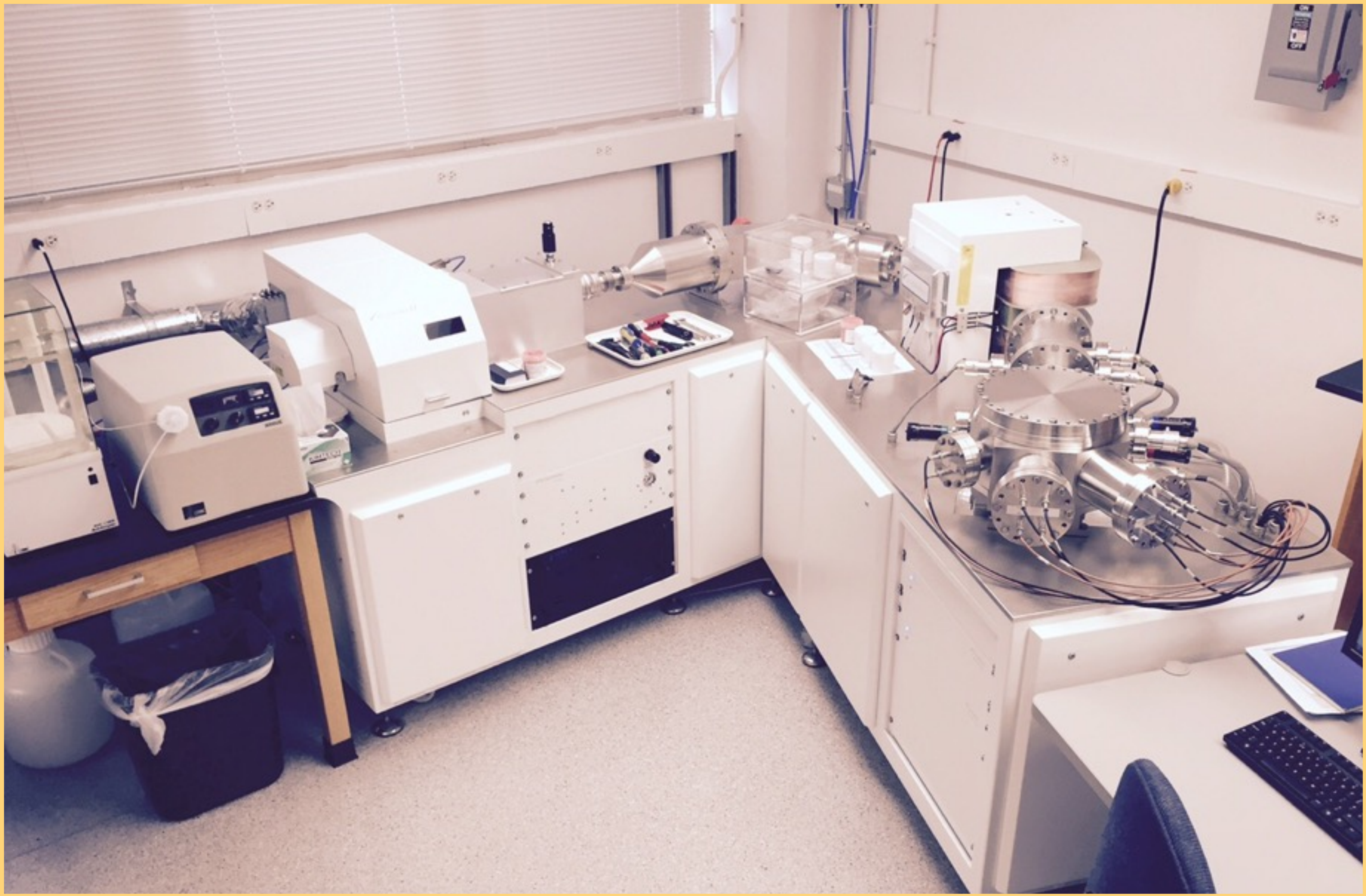
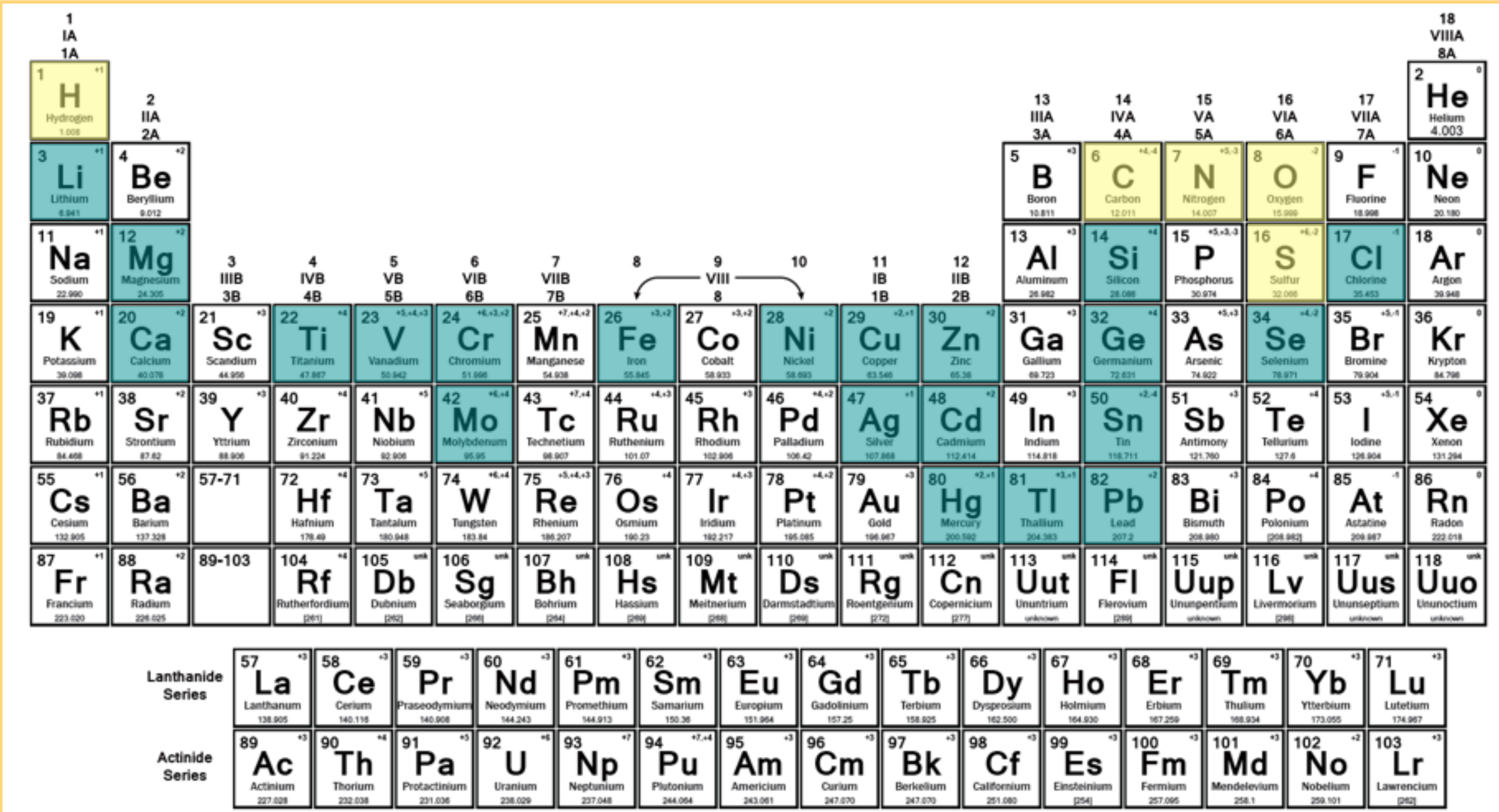
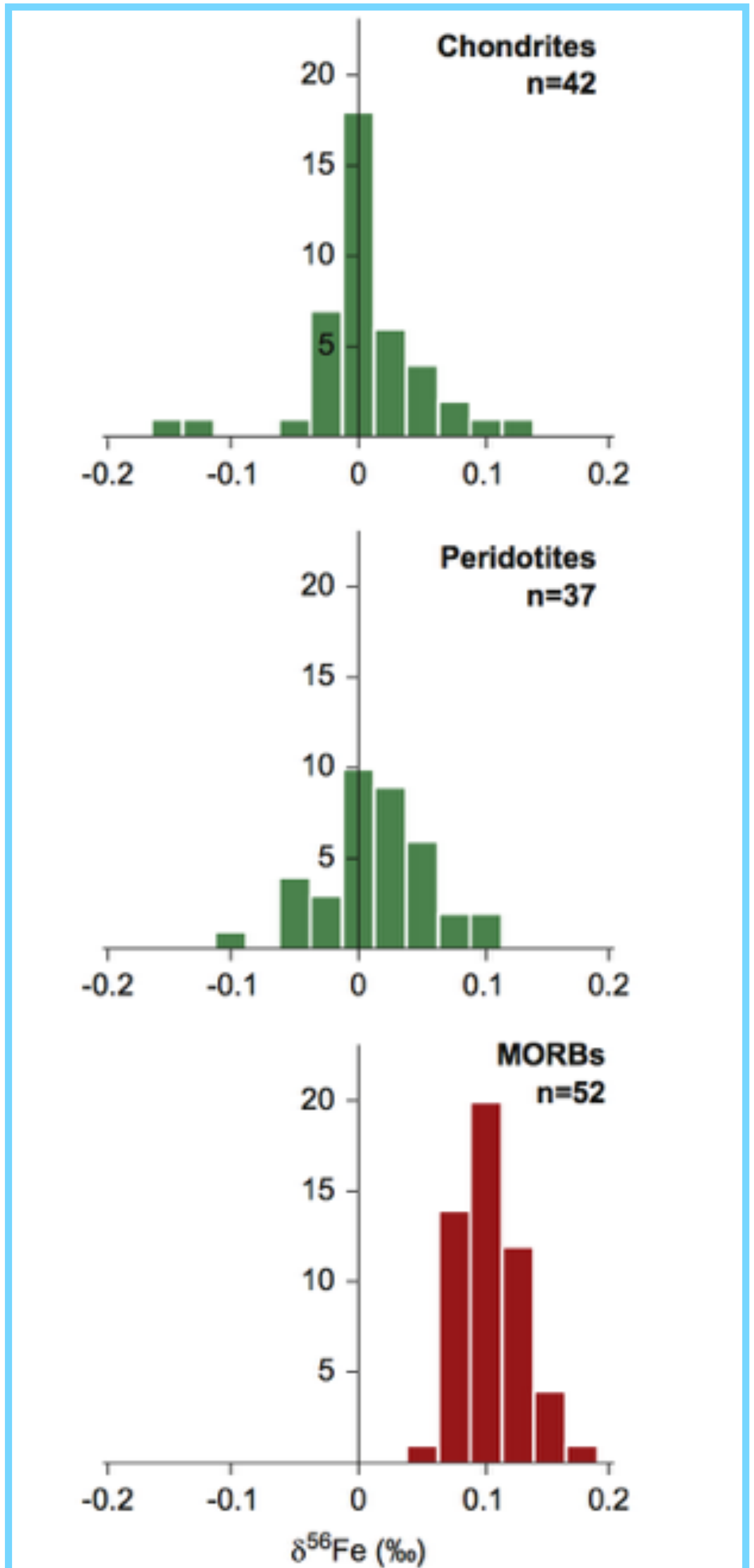
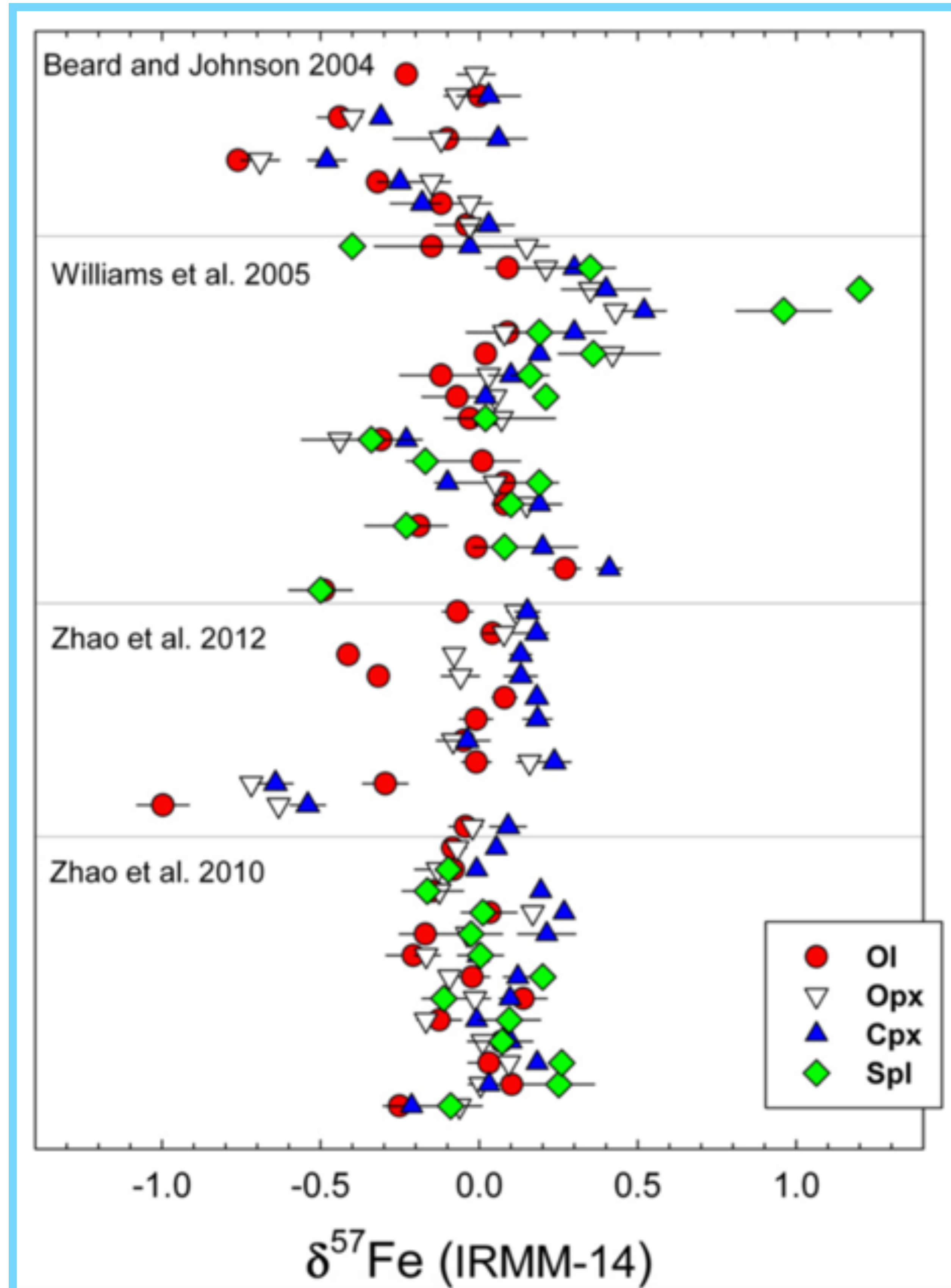


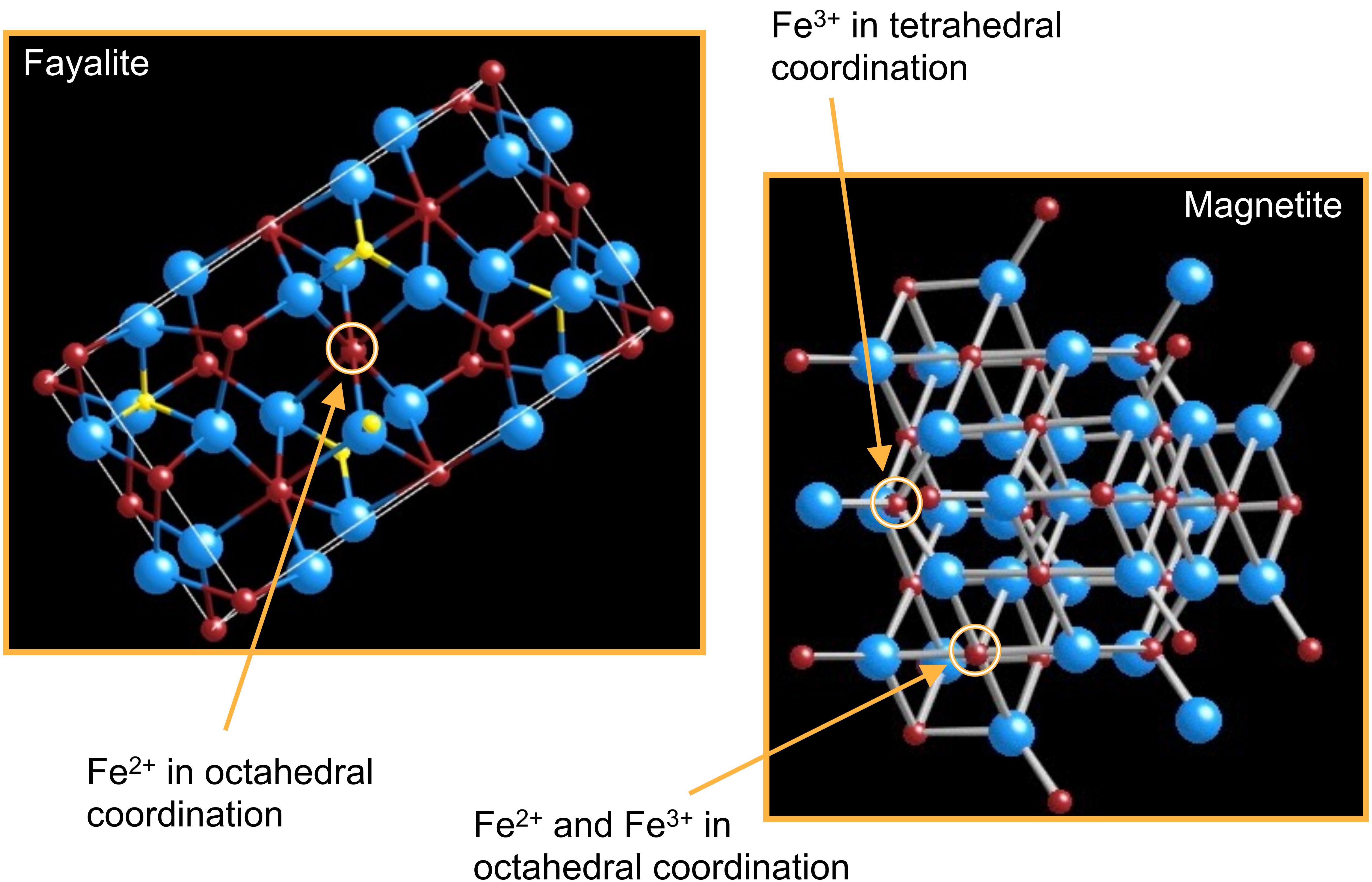


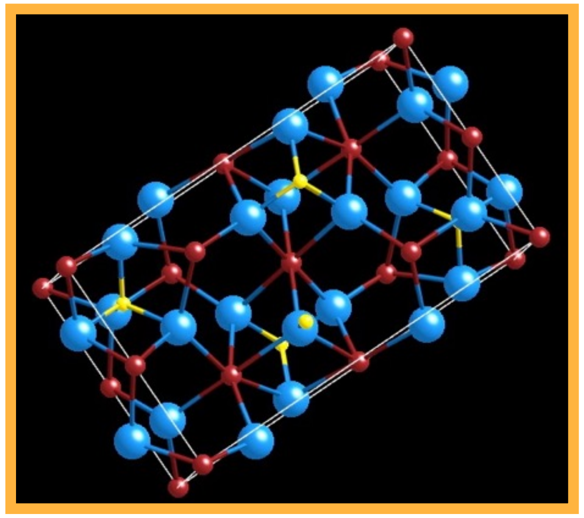
Look for elements that have more than one non-radiogenic isotope, for which the mass difference between isotopes is a significant fraction of the atomic mass (enough to measure)

Example 3: Iron Isotopes in Rocks

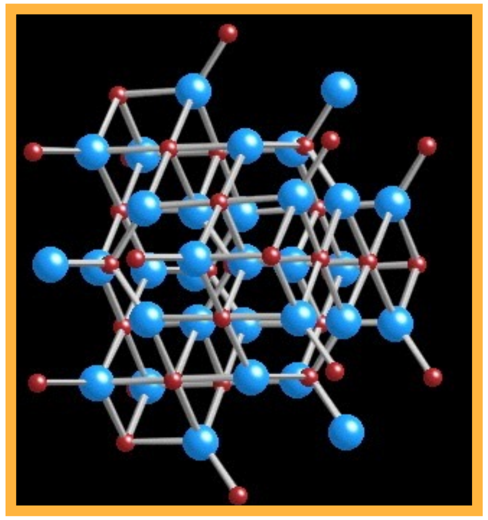





Fayalite
Magnetite
Fe^{3+} in tetrahedral coordination
Fe^{2+} in octahedral coordination
Fe^{2+} and Fe^{3+} in octahedral coordination



vs.



Fe^{2+} Only

Octahedral Coordination only

(1/3) Fe^{2+} and (2/3) Fe^{3+}

Octahedral and Tetrahedral Coordination

The heavier isotope will be concentrated in stiffer bonds, which are associated with (among others):

- higher oxidation state
- low coordination number

Therefore, magnetite should be more enriched in ^{57}Fe than fayalite.

Reaction Sequence -

Fa + Hem + Qtz

$$\downarrow$$

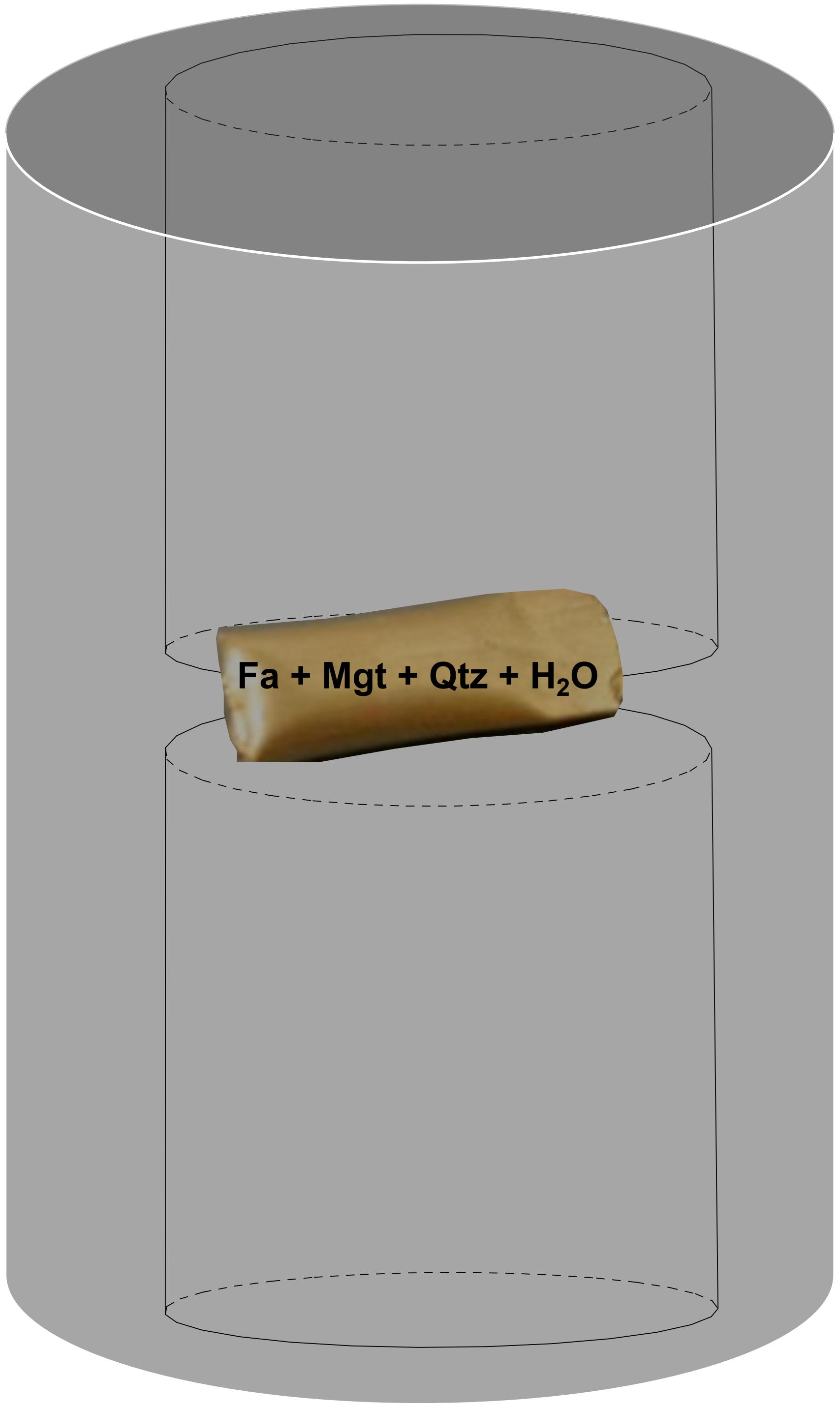
Fa + Hem $\rightarrow$ Mgt + Qtz

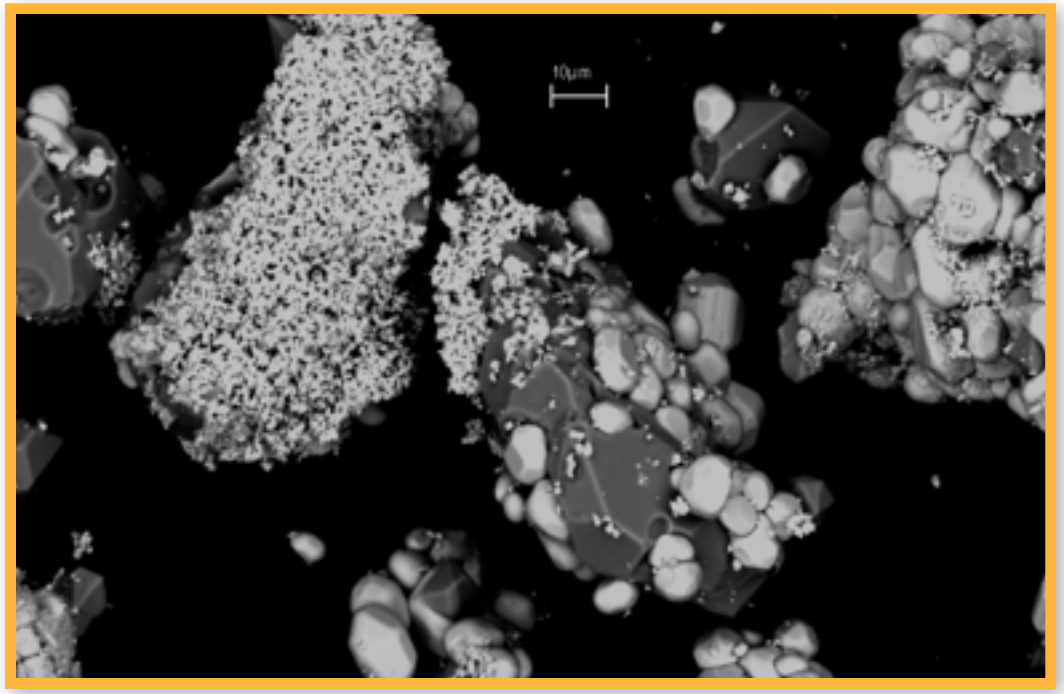
$$\downarrow$$

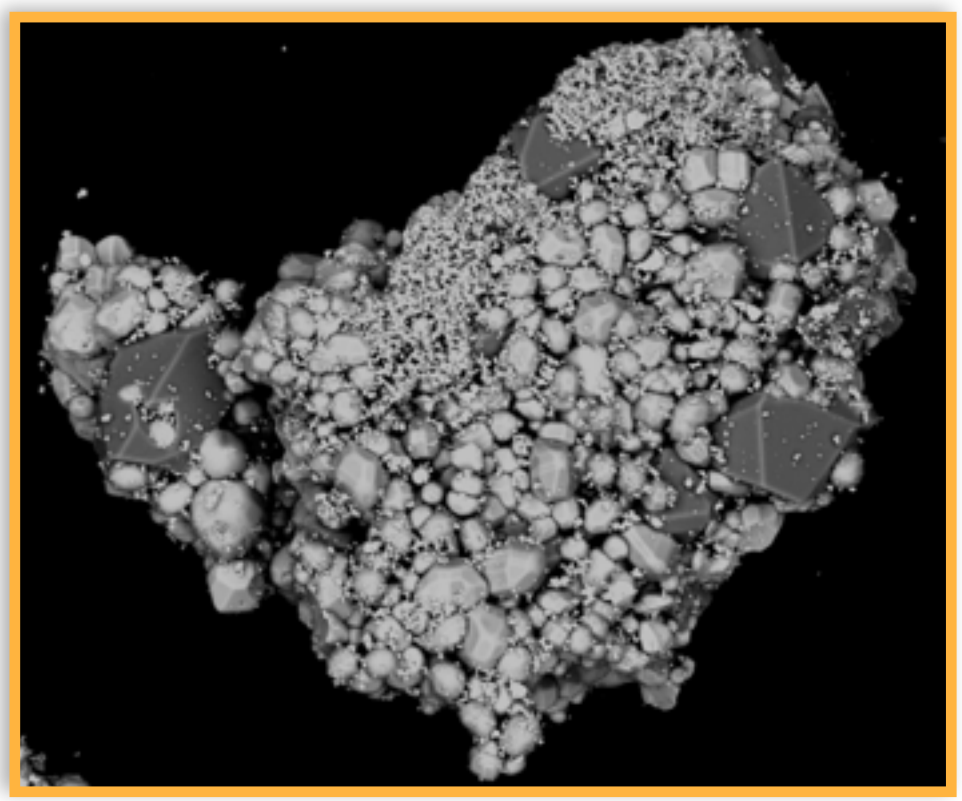
Fa + H_2O $\leftrightarrow$ Mgt + Qtz + H_2

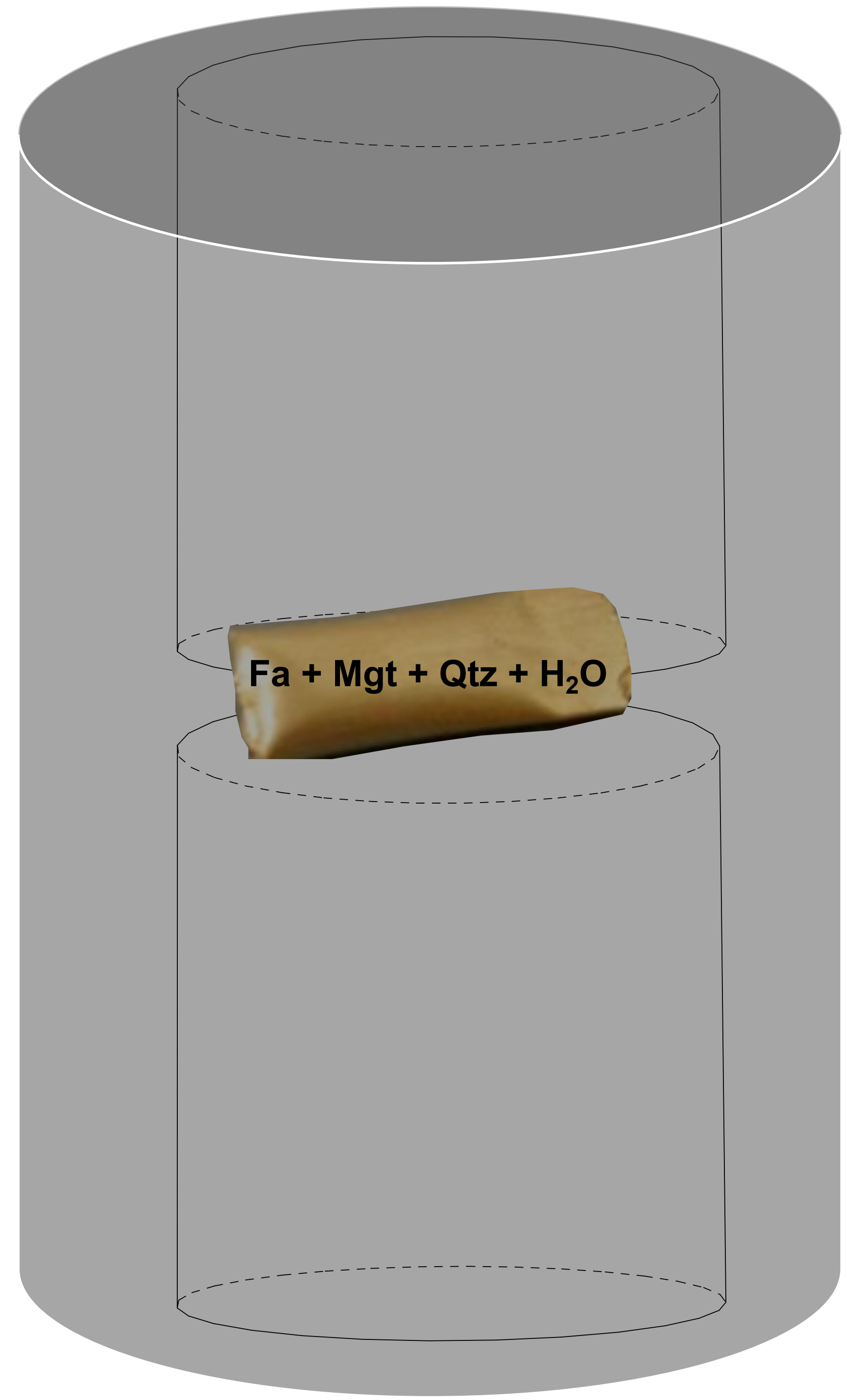
OR

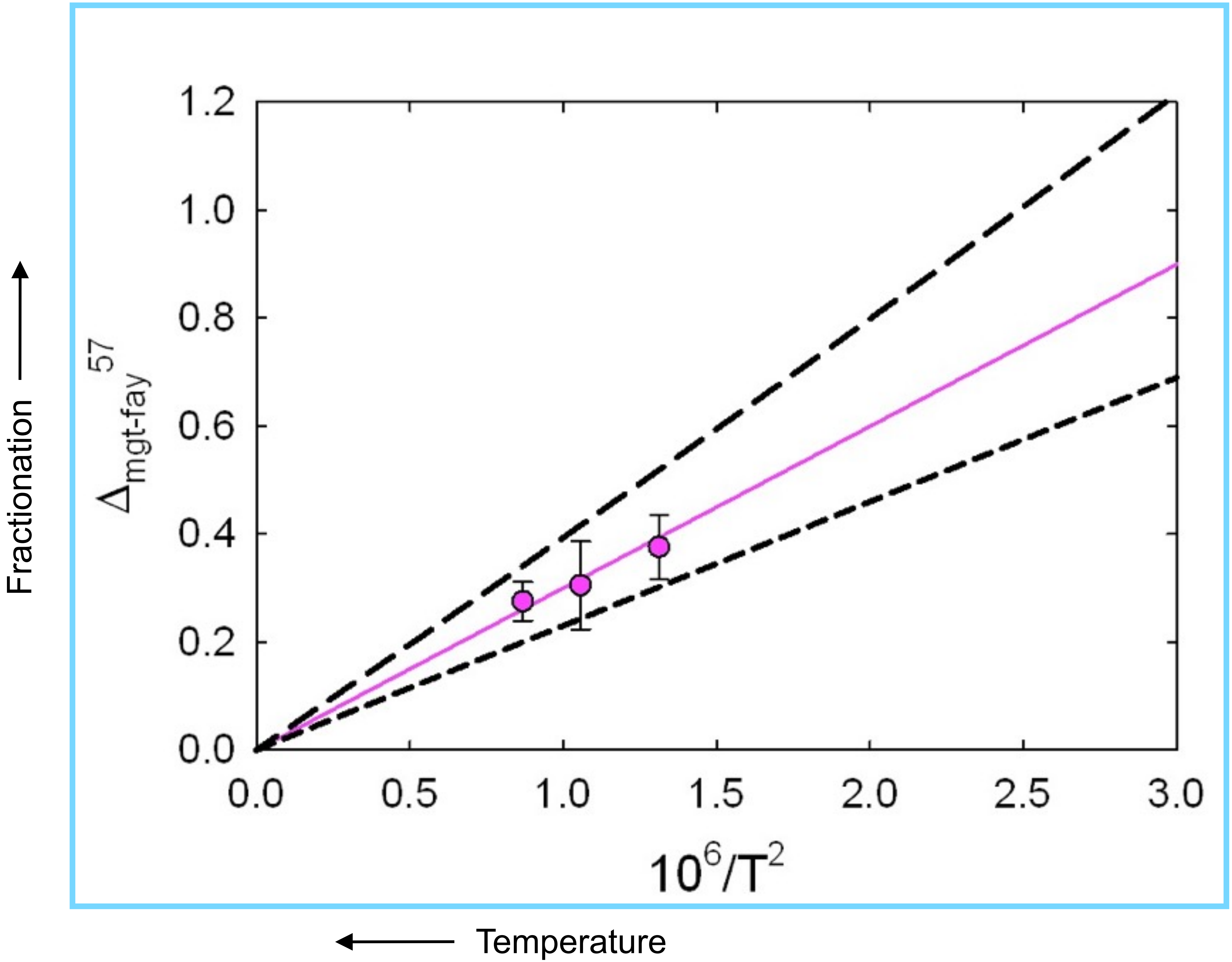
Fa + O_2 $\leftrightarrow$ Mgt + Qtz




10µm

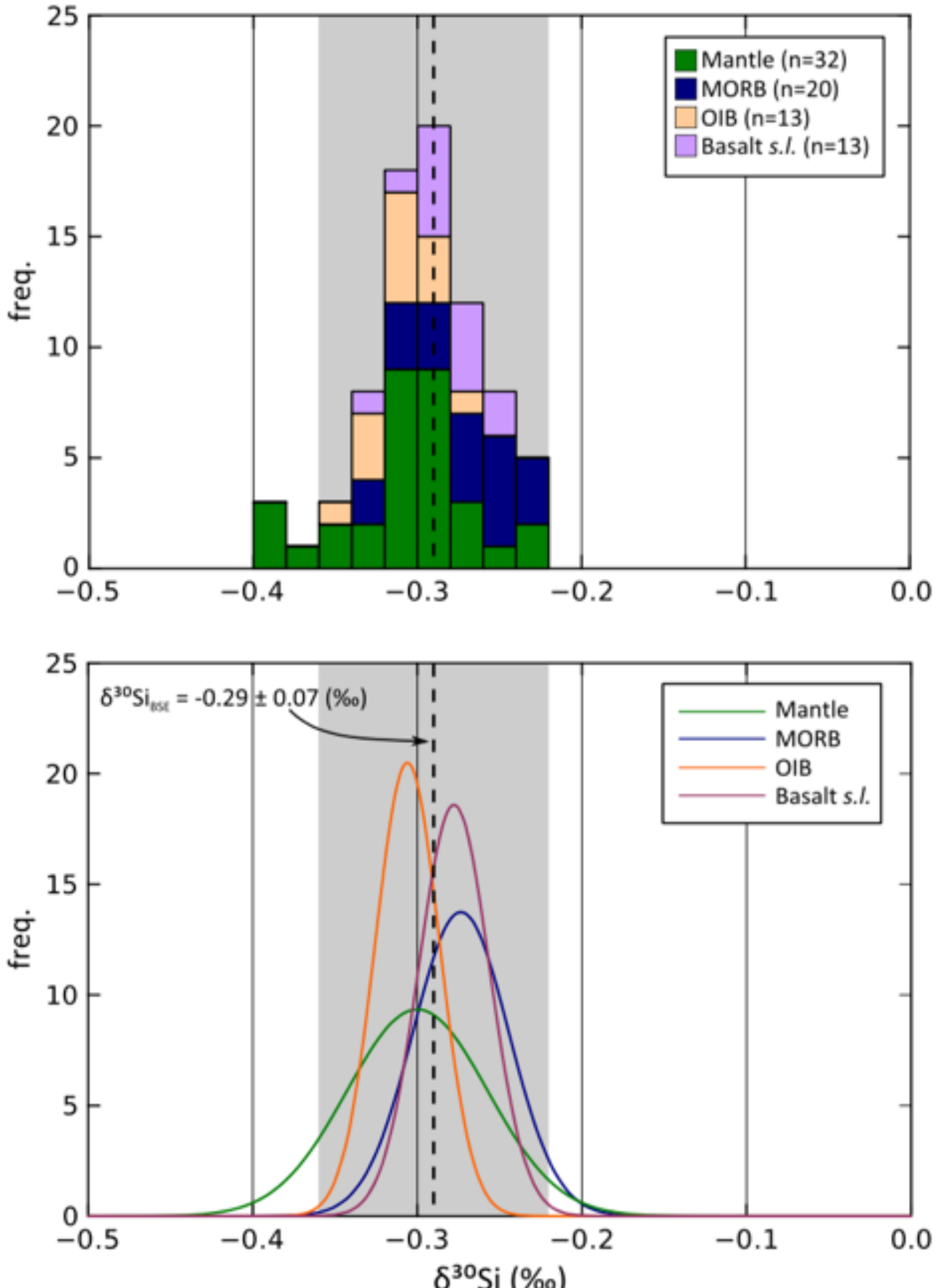



Fa + Mgt + Qtz + H_2O



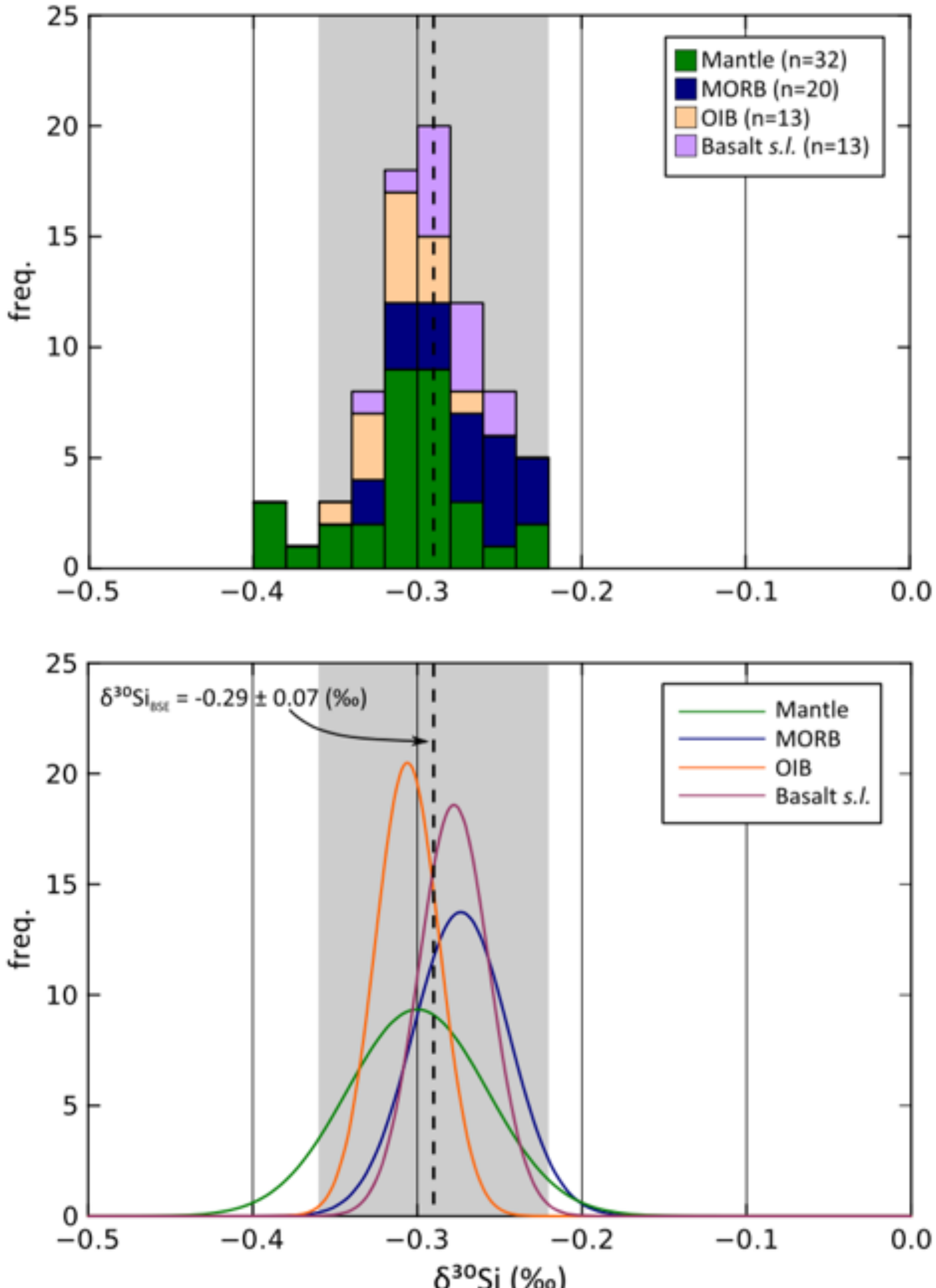
Fractionation
$\Delta^{57}_{mgt\text{-}fay}$
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
$10^6/T^2$
Temperature

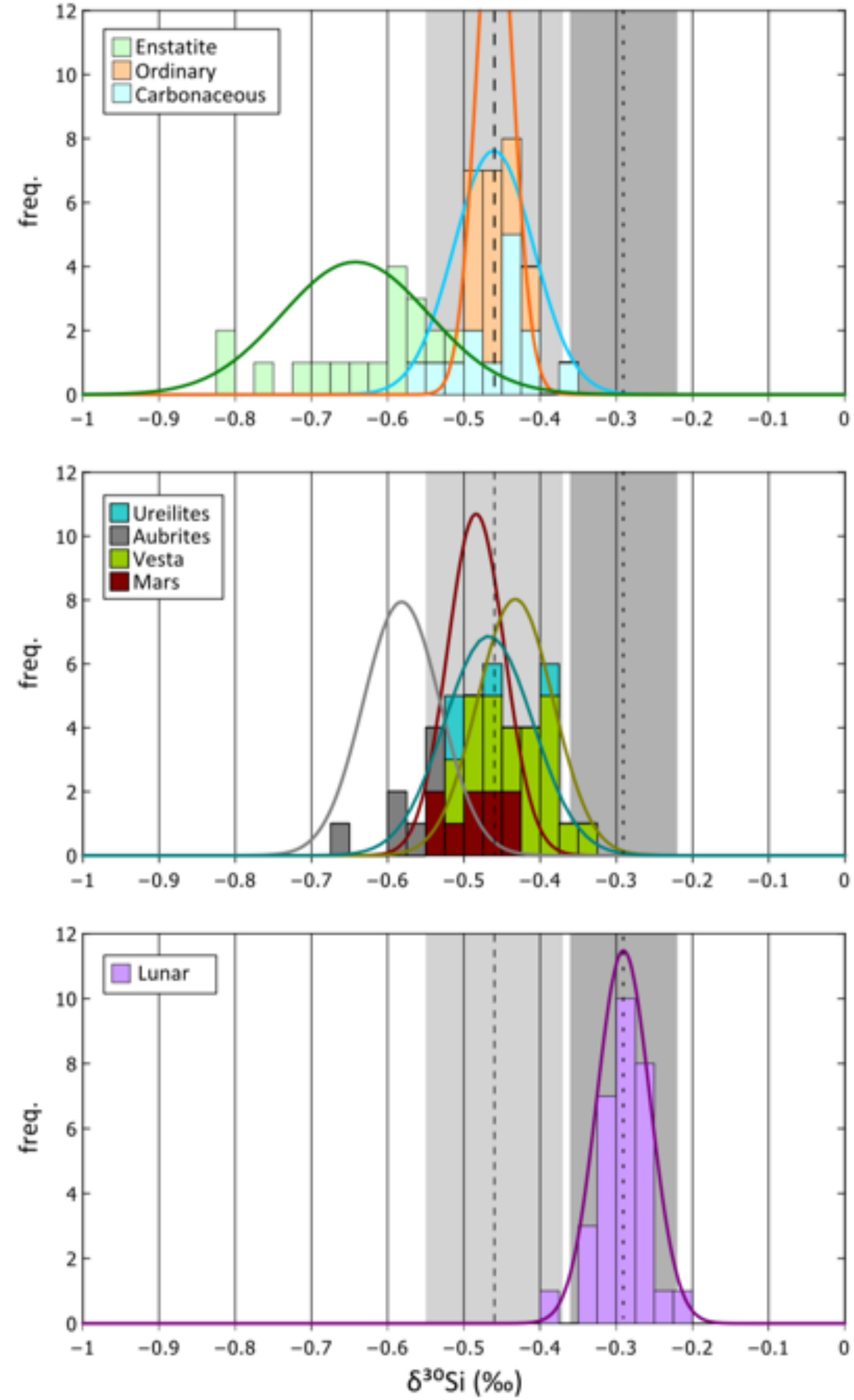
Example 4: Silicon Isotopes in Rocks



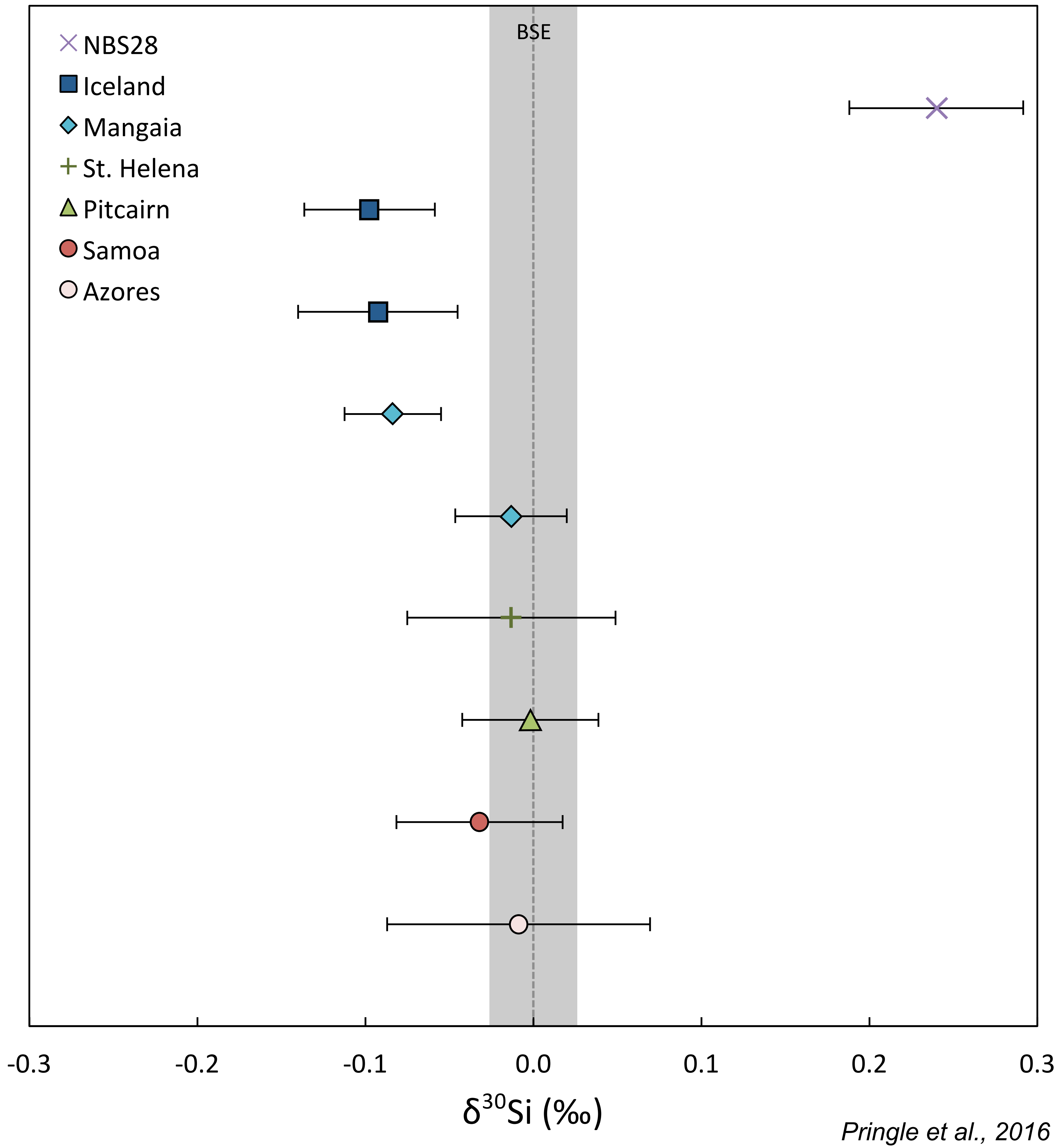
Savage et al., 2014

Example 4: Silicon Isotopes in Rocks



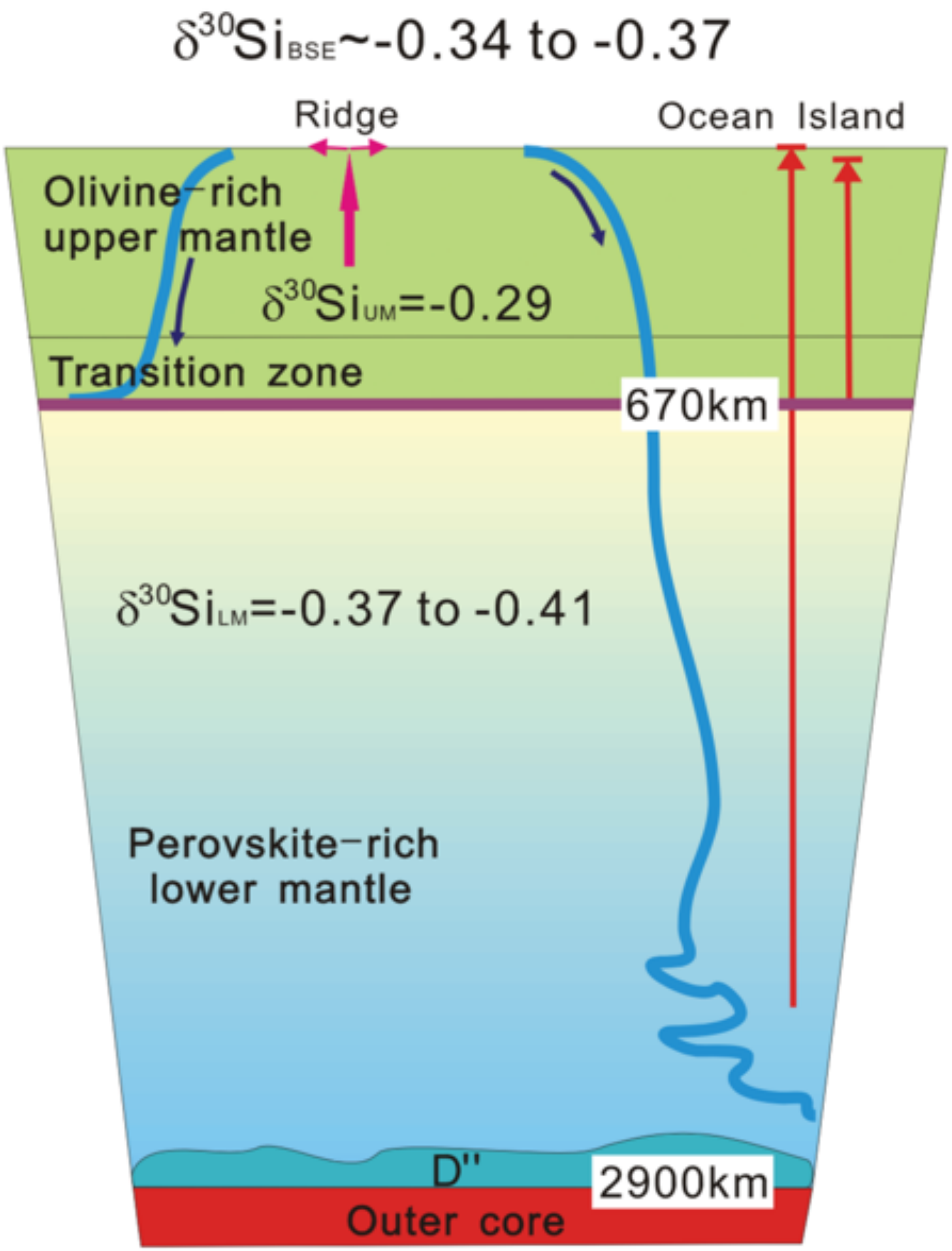


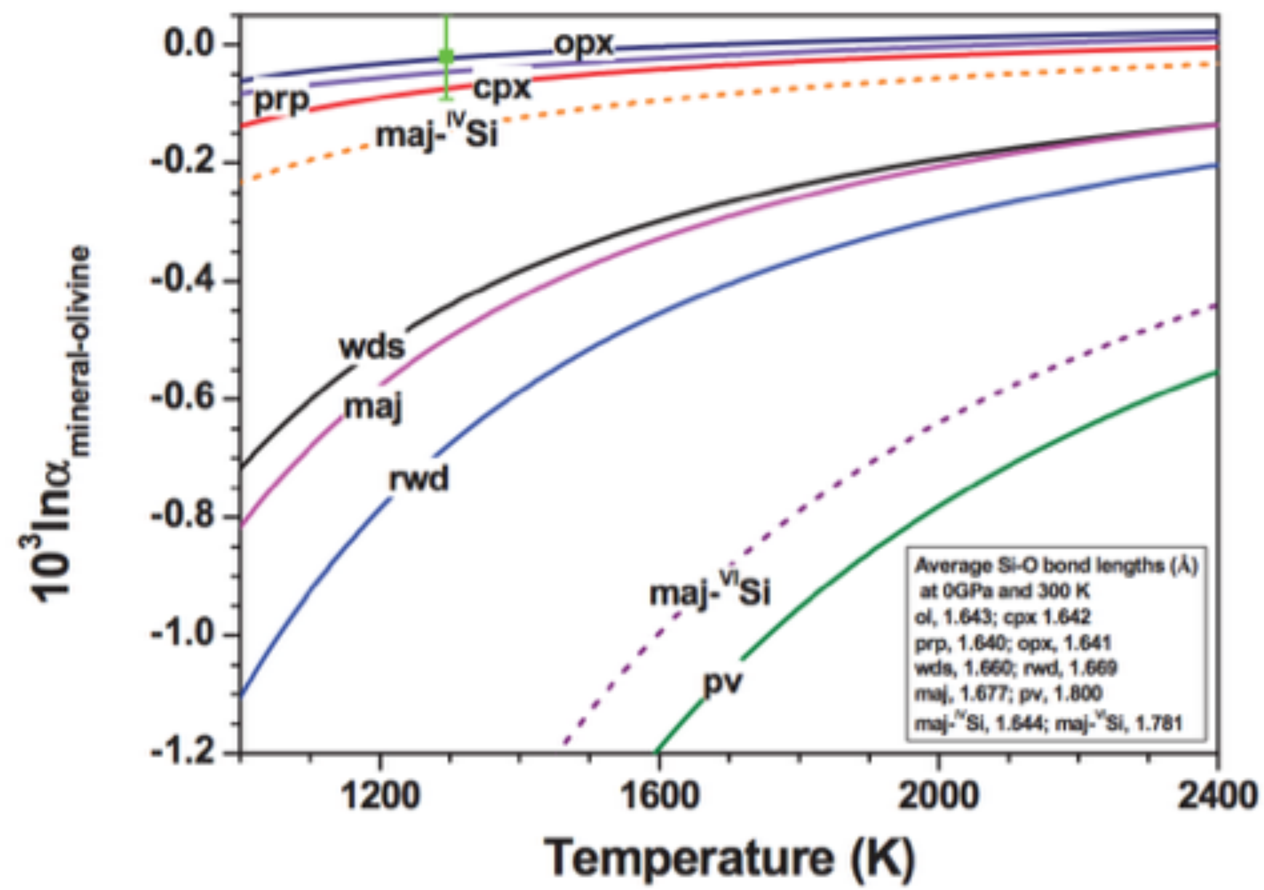
Savage et al., 2014



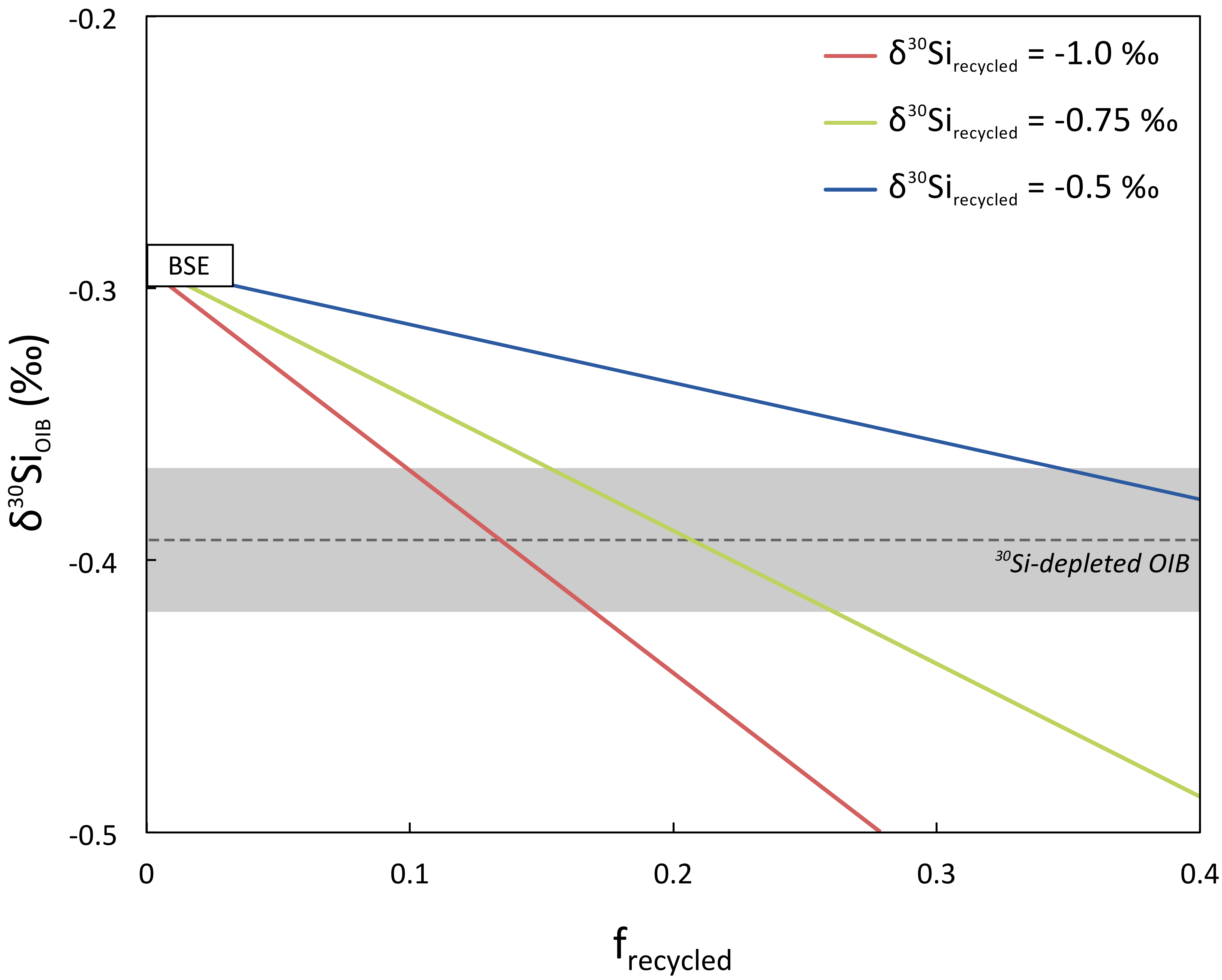
NBS28
Iceland
Mangaia
St. Helena
Pitcairn
Samoa
Azores
BSE
-0.3
-0.2
-0.1
0.0
0.1
0.2
0.3
$\delta^{30}Si$ (‰)
Pringle et al., 2016

(b): δ^{30}Si of the mantle



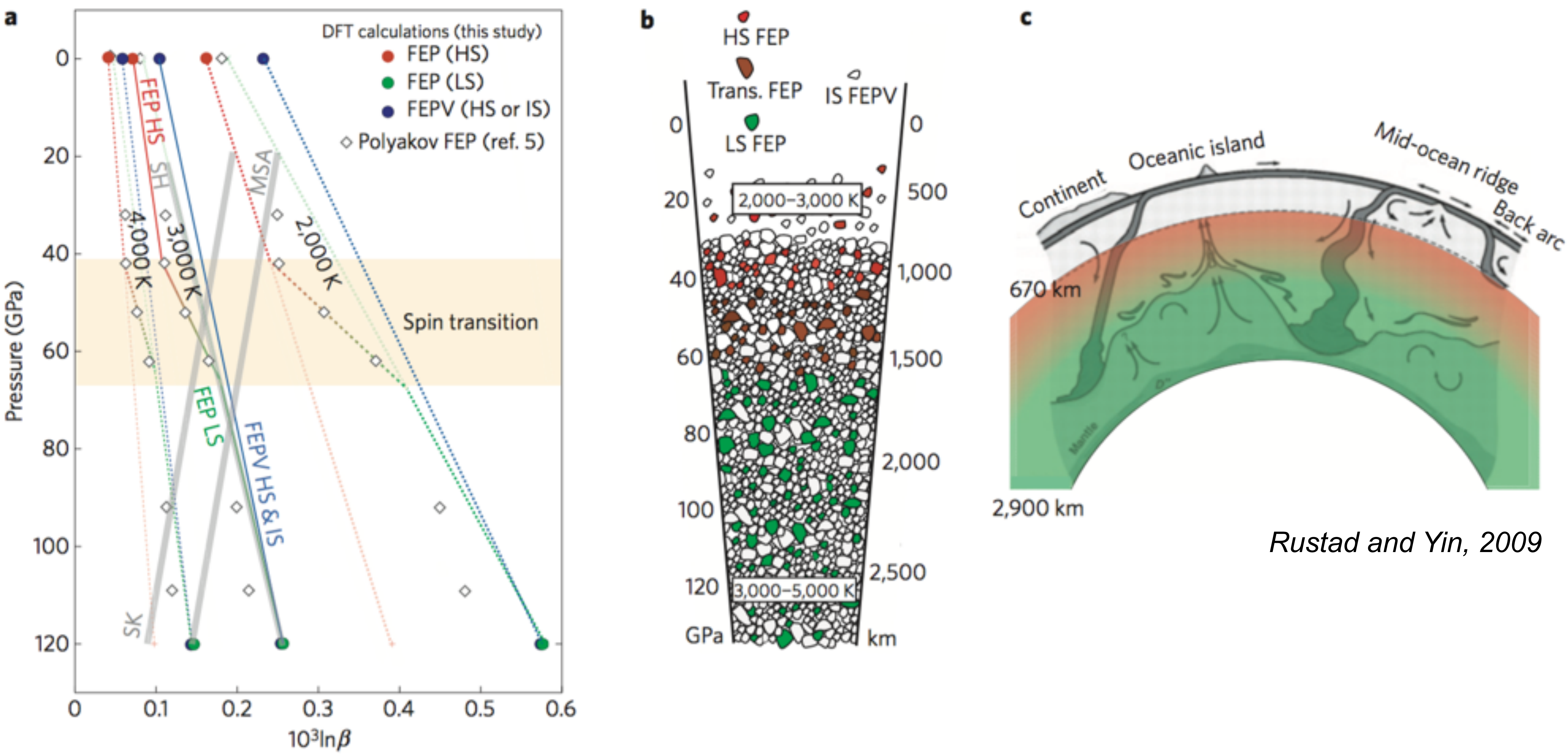


Huang et al., 2014

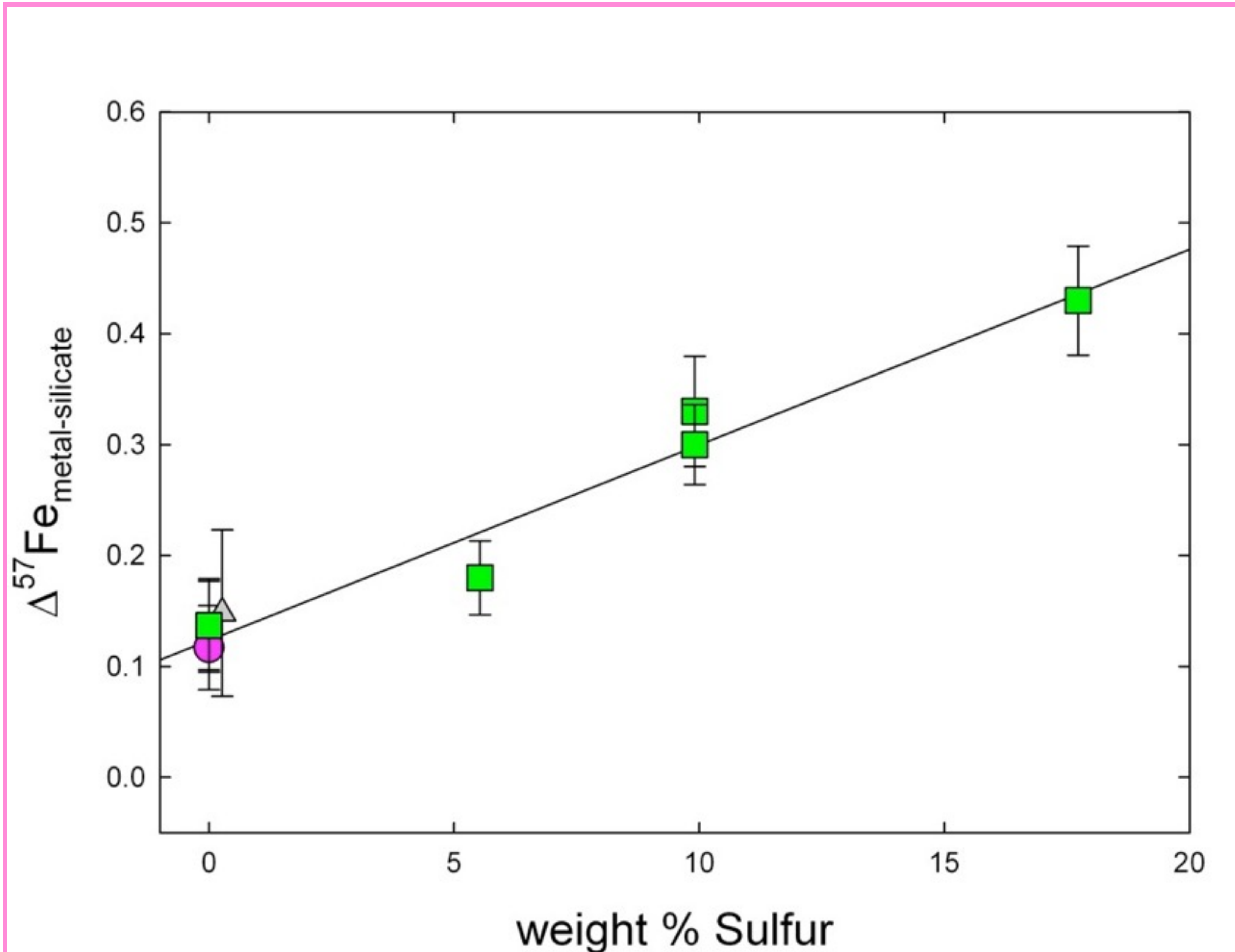


Pringle et al., 2016

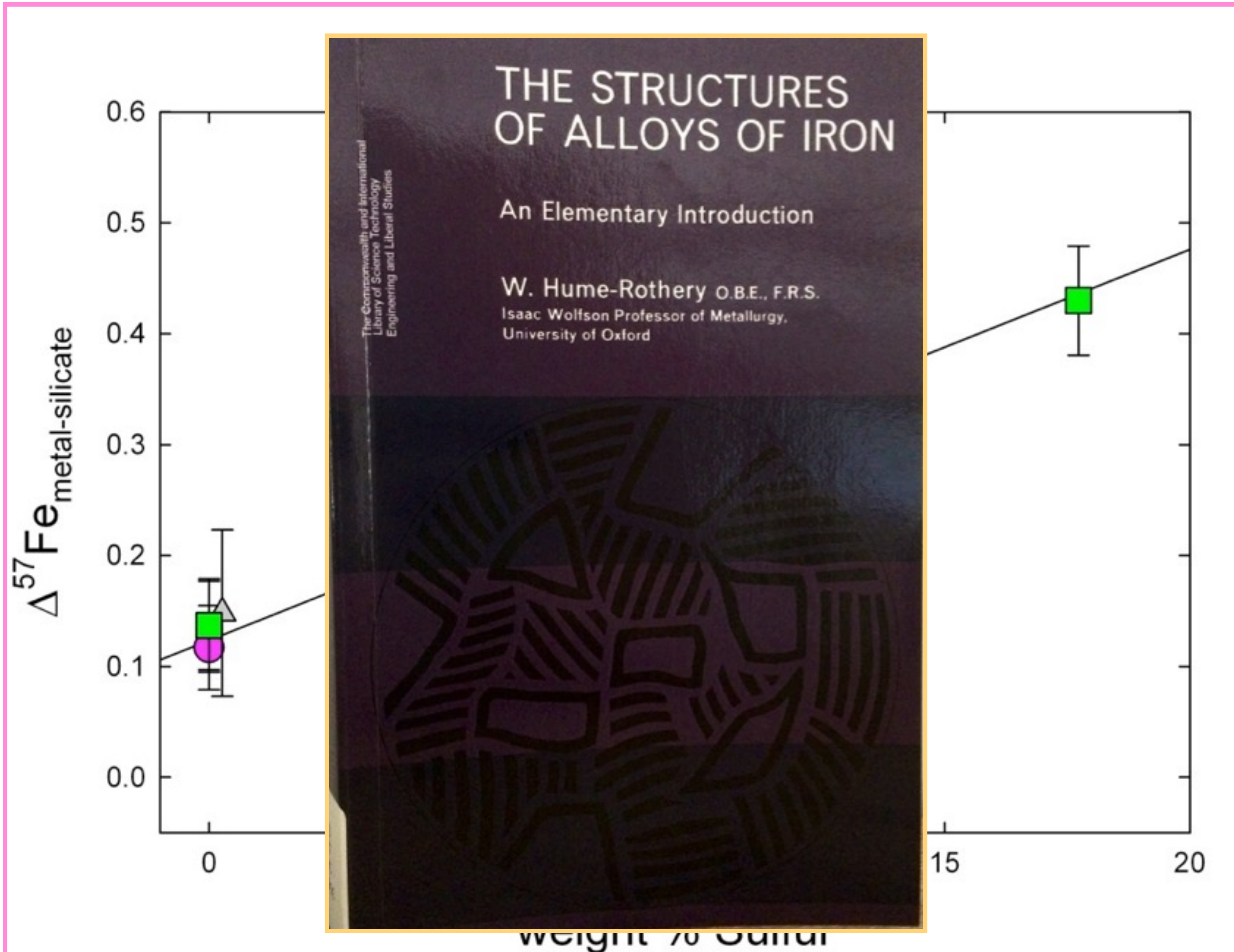
Example 5: Composition and Structure of Melts



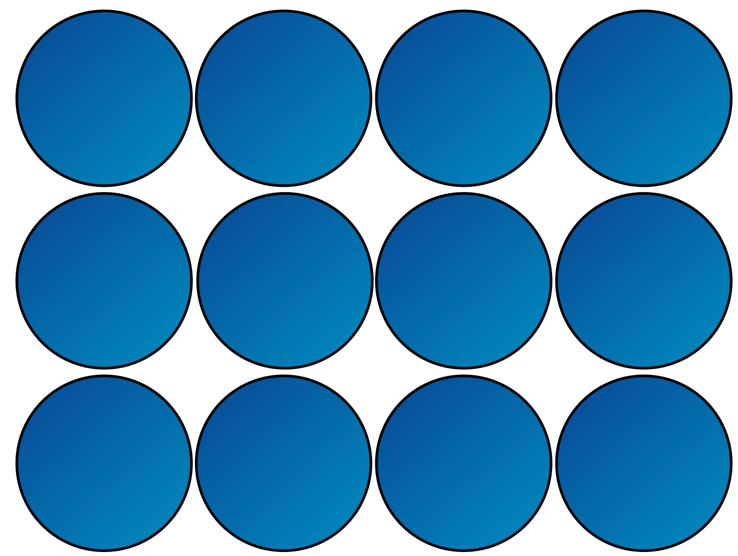
Rustad and Yin, 2009



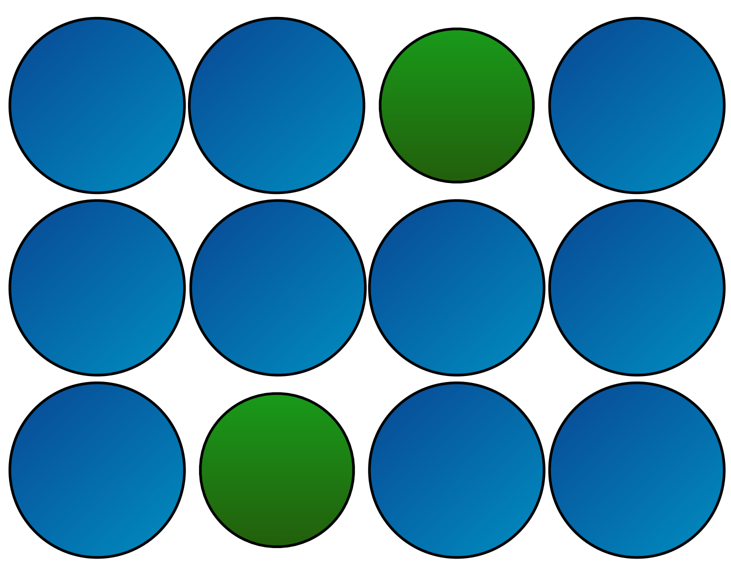
0.6
0.5
0.4
0.3
0.2
0.1
0.0
$\Delta^{57}Fe_{metal-silicate}$
0
5
10
15
20
weight % Sulfur


0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
15
20
$\Delta^{57}Fe_{metal-silicate}$
THE STRUCTURES OF ALLOYS OF IRON
An Elementary Introduction
W. Hume-Rothery O.B.E., F.R.S.
Isaac Wolfson Professor of Metallurgy, University of Oxford
The Commonwealth and International Library of Science Technology Engineering and Liberal Studies

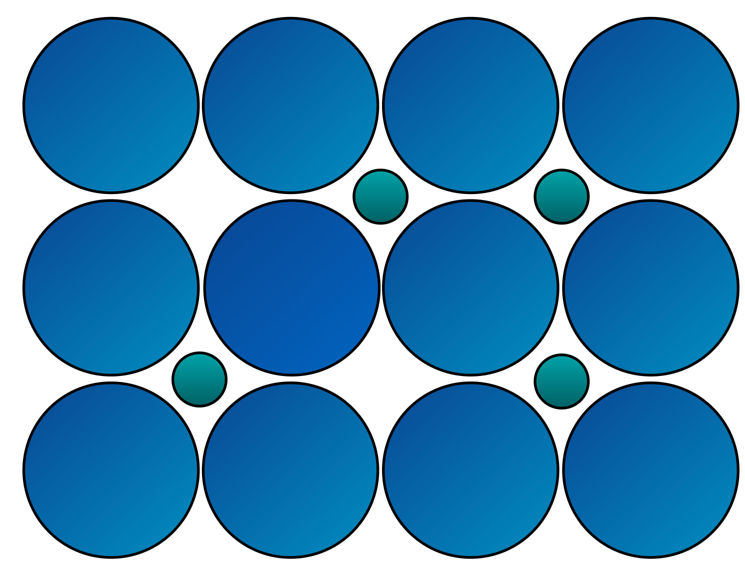
Structure of Alloys



Substitutional



Interstitial



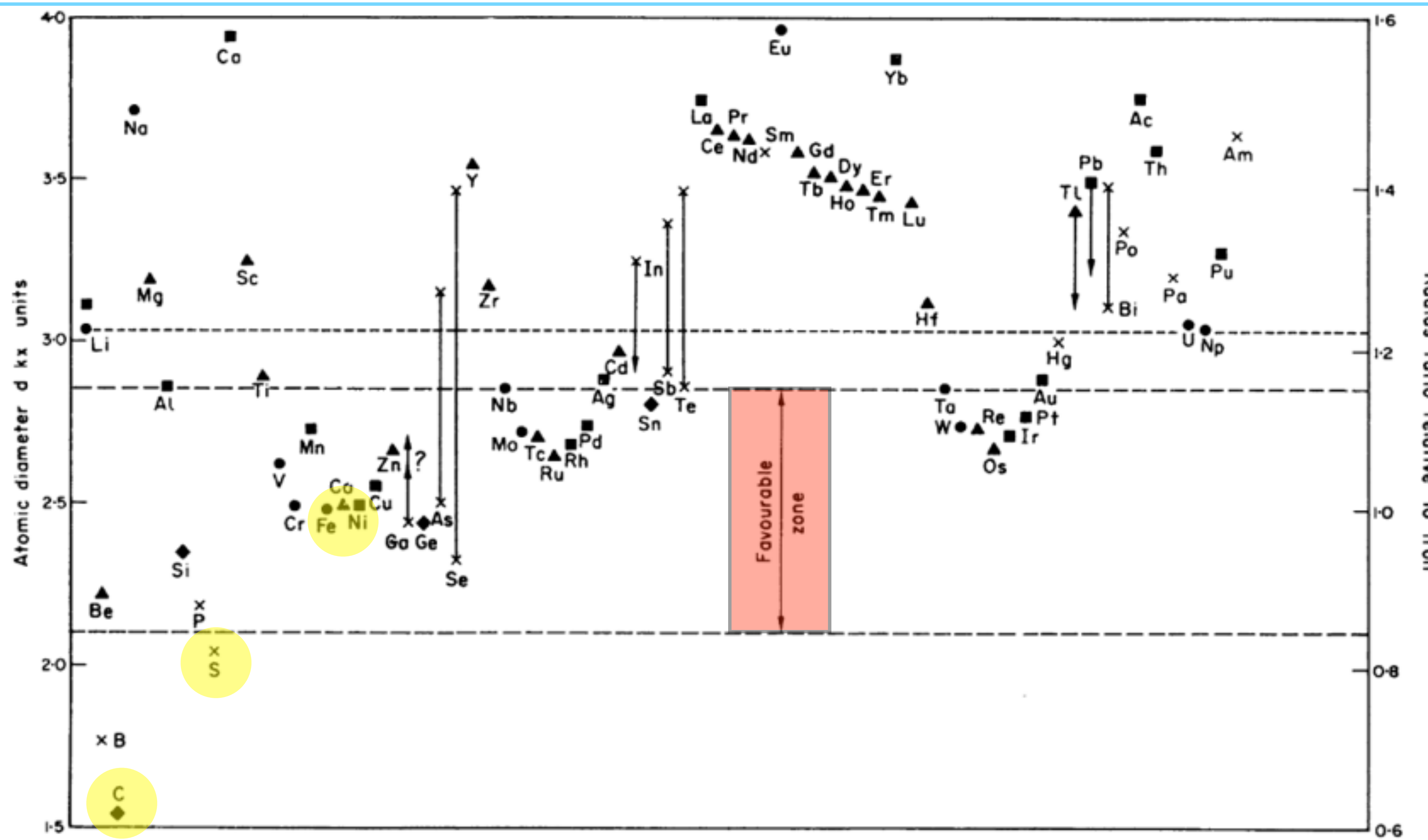
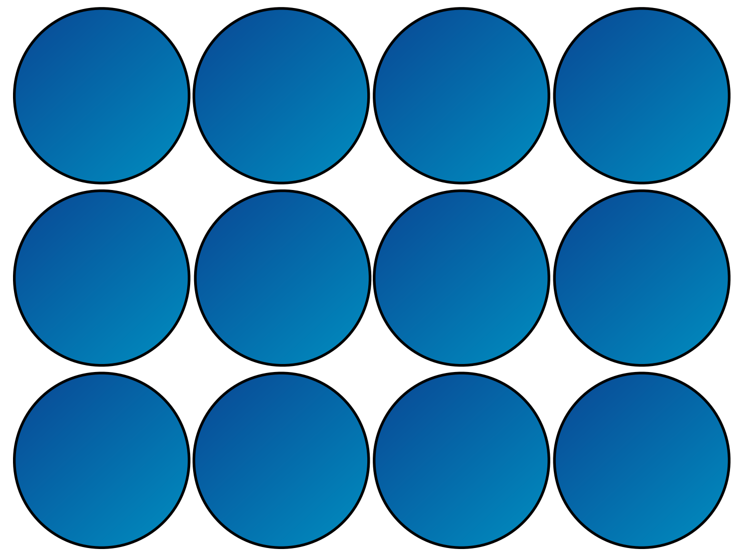


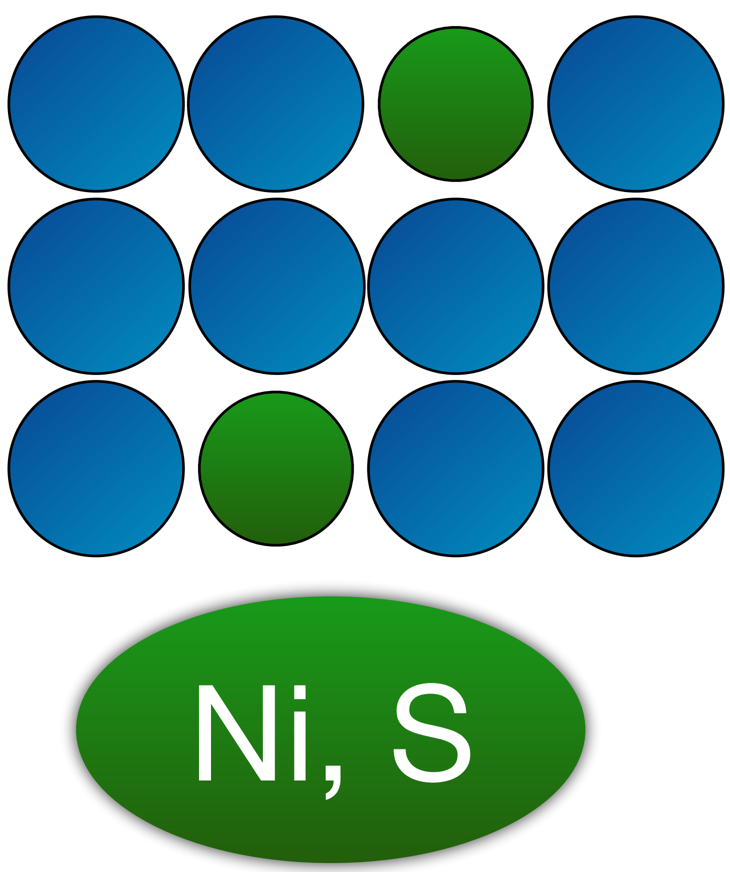
FIG. 5.1. The atomic diameters of the elements, as defined by the closest distances of approach of the atoms in the crystals of the elements.

● Body-centred cube. ▲ Close-packed hexagonal.
■ Face-centred cube. × Complex structures.

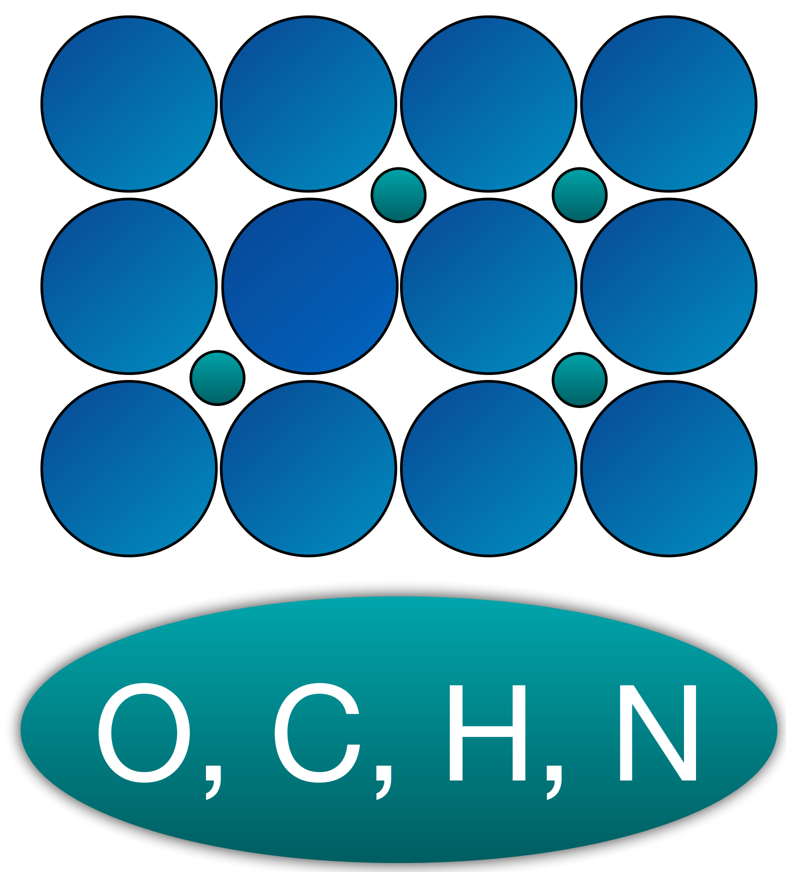
Structure of Alloys

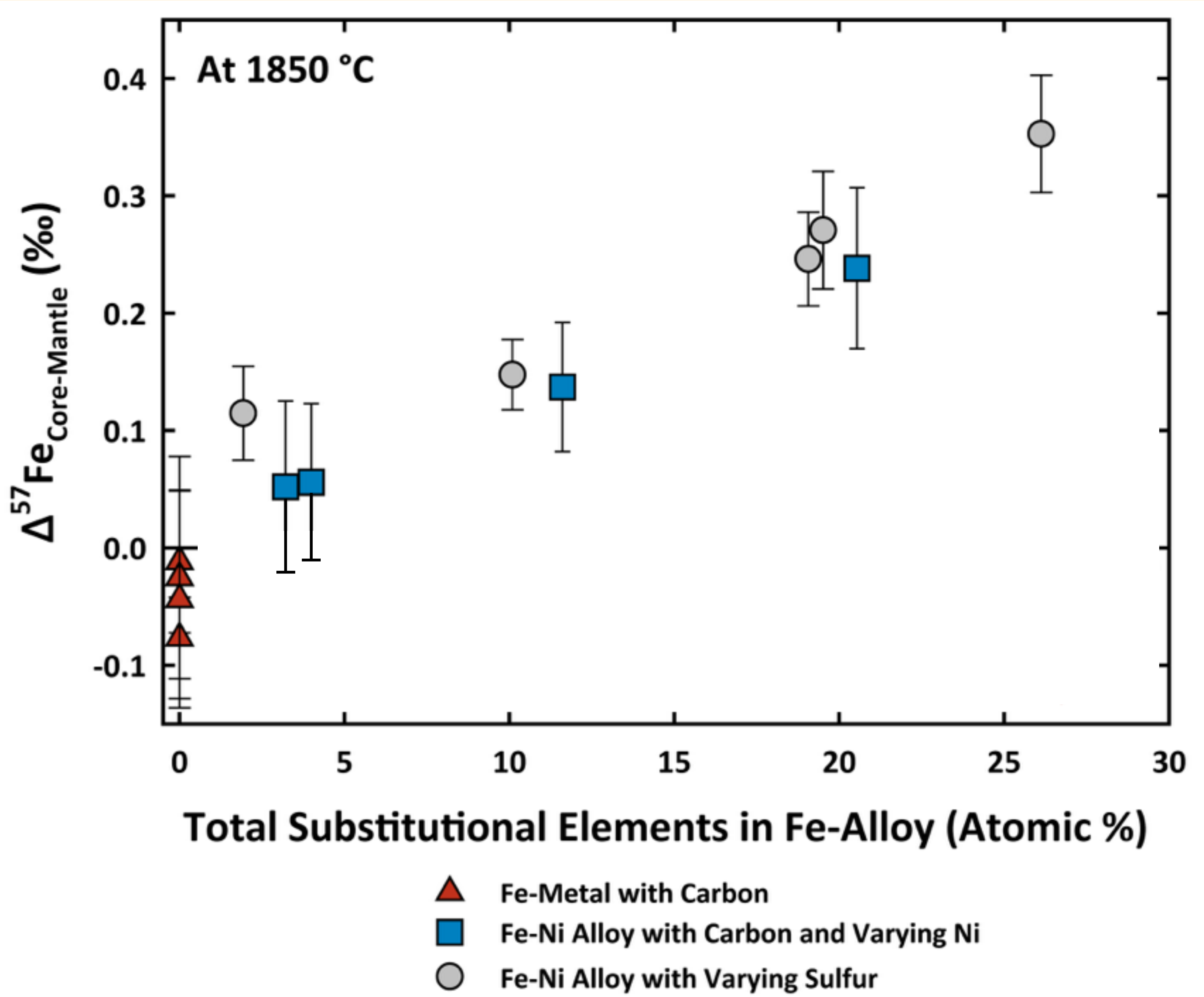


Substitutional

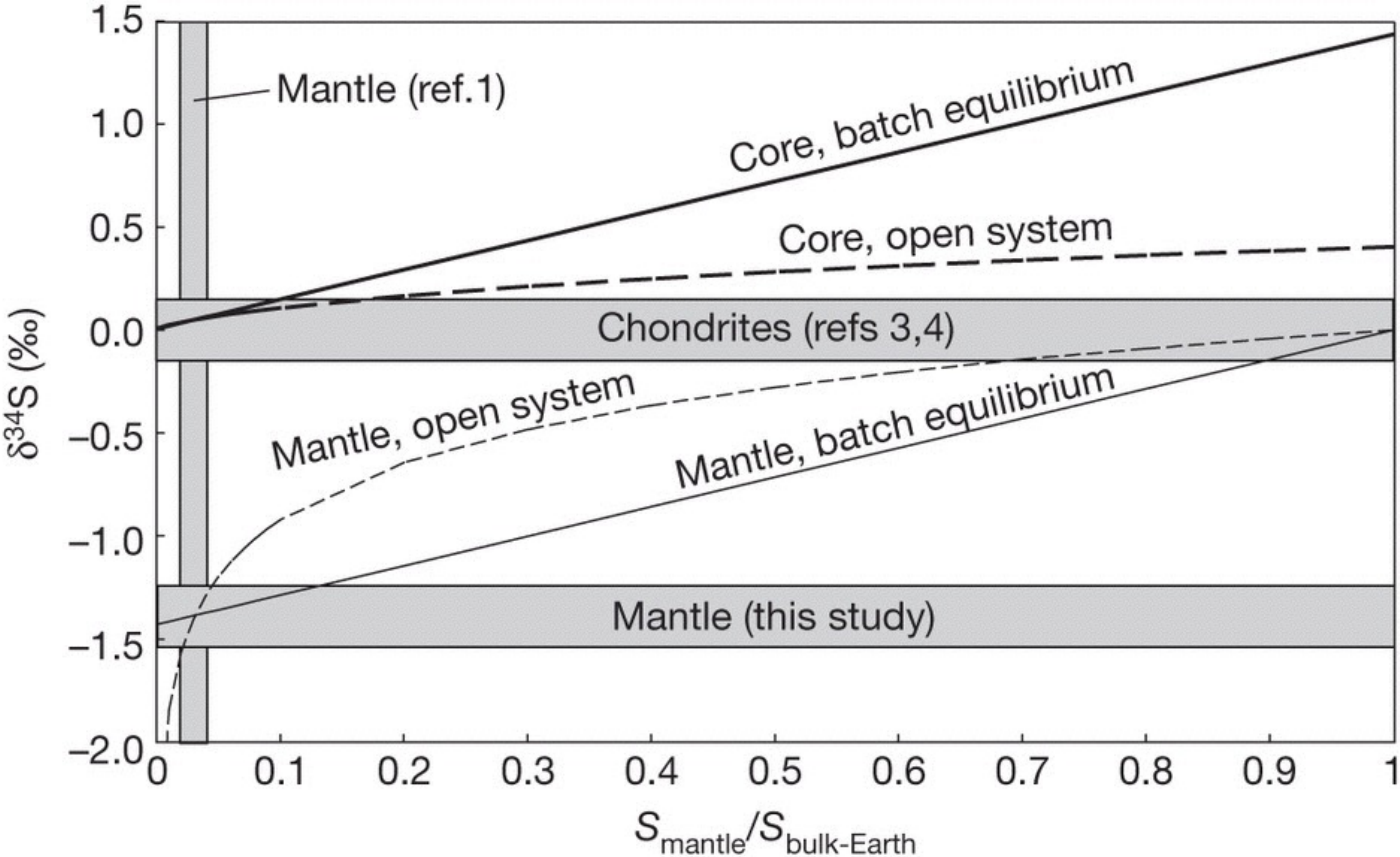


Interstitial

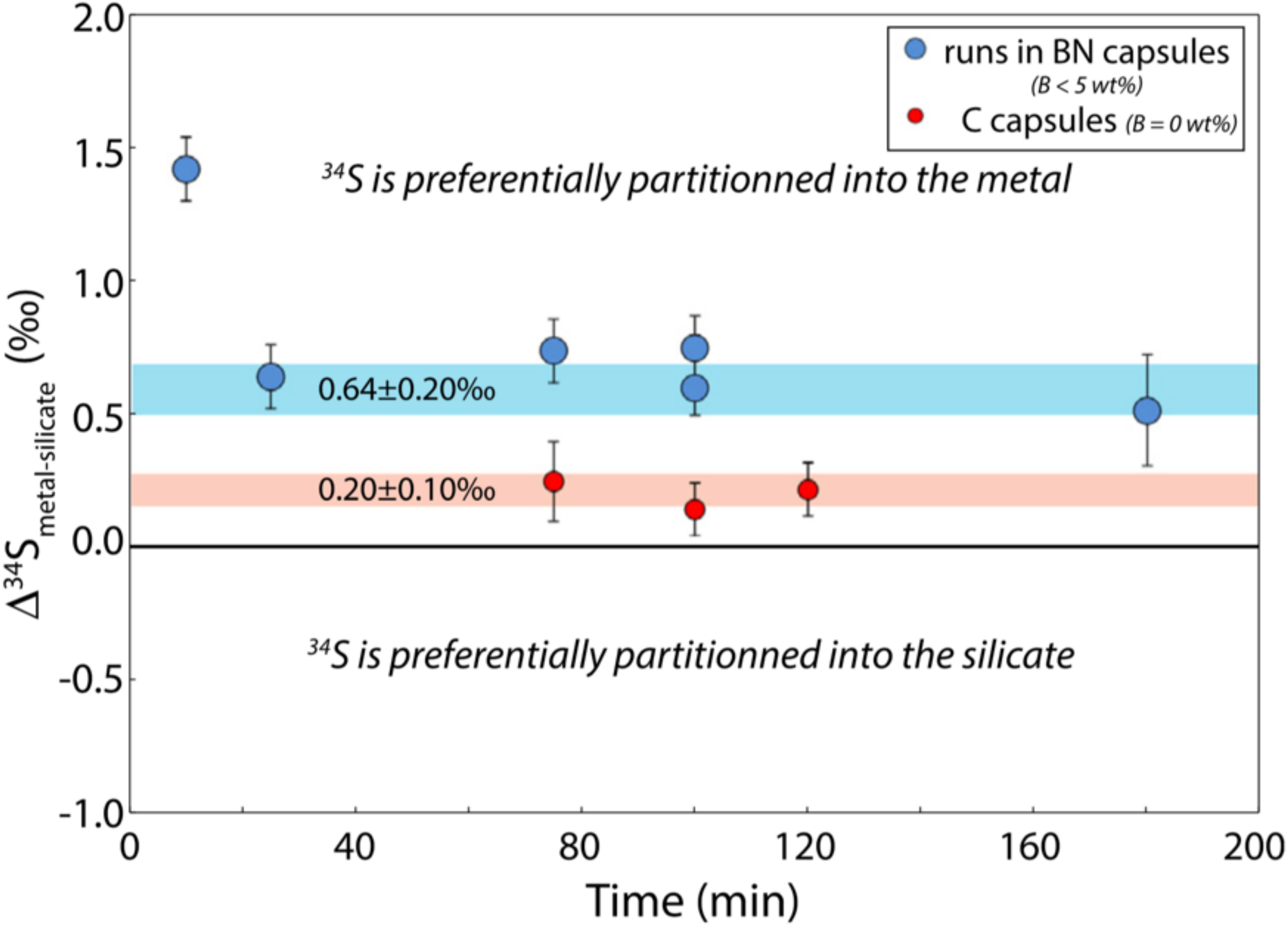




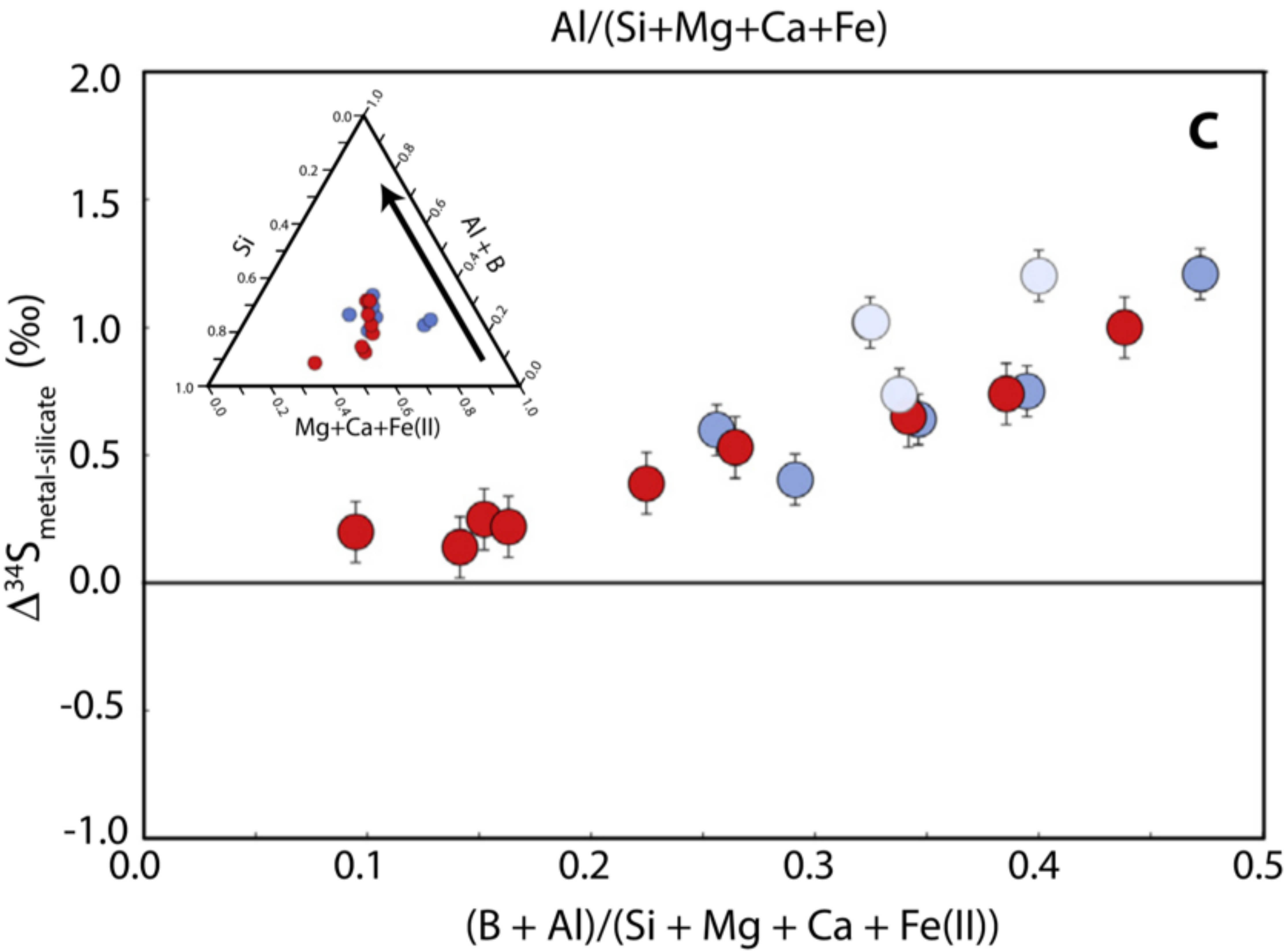
At 1850 °C
$\Delta^{57}Fe_{Core-Mantle}$ (‰)
0.4
0.3
0.2
0.1
0.0
-0.1
0
5
10
15
20
25
30
Total Substitutional Elements in Fe-Alloy (Atomic %)
Fe-Metal with Carbon
Fe-Ni Alloy with Carbon and Varying Ni
Fe-Ni Alloy with Varying Sulfur



Labidi et al., 2014

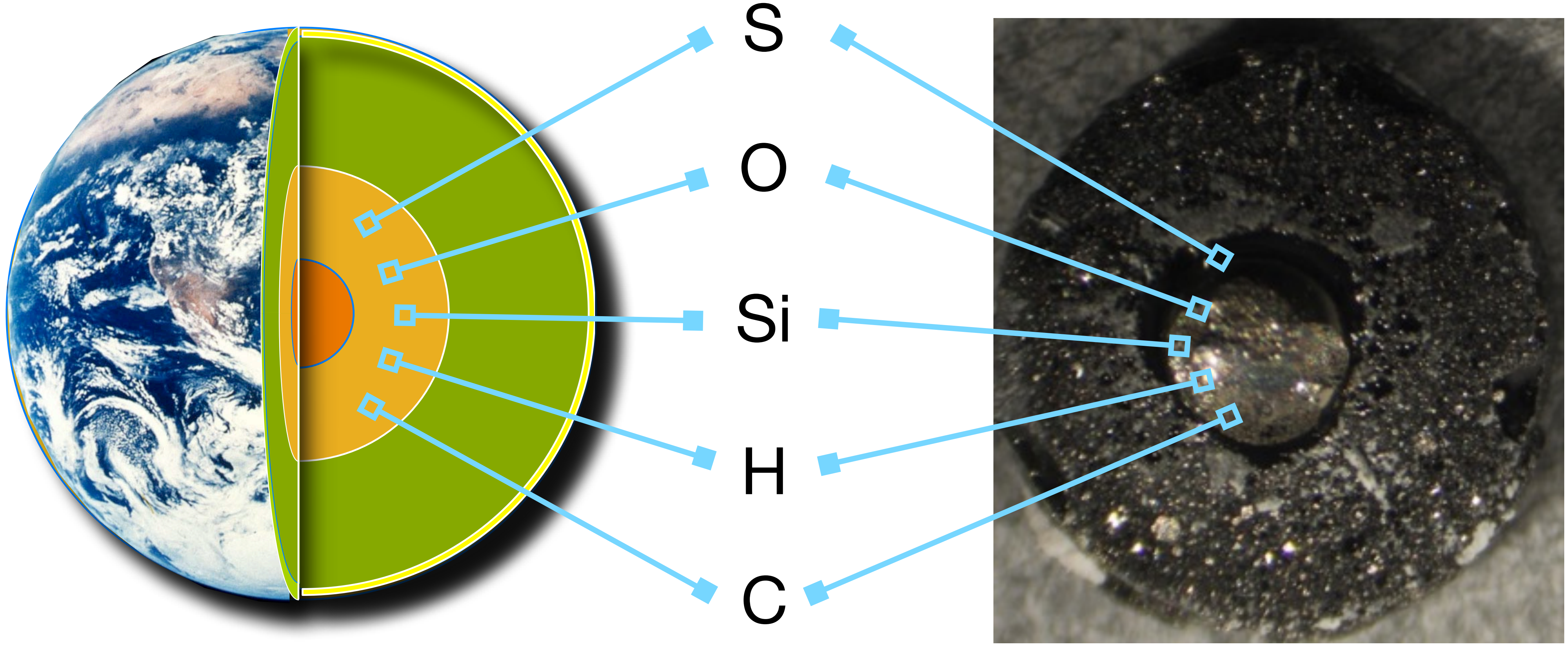


Labidi et al., 2016



Labidi et al., 2016

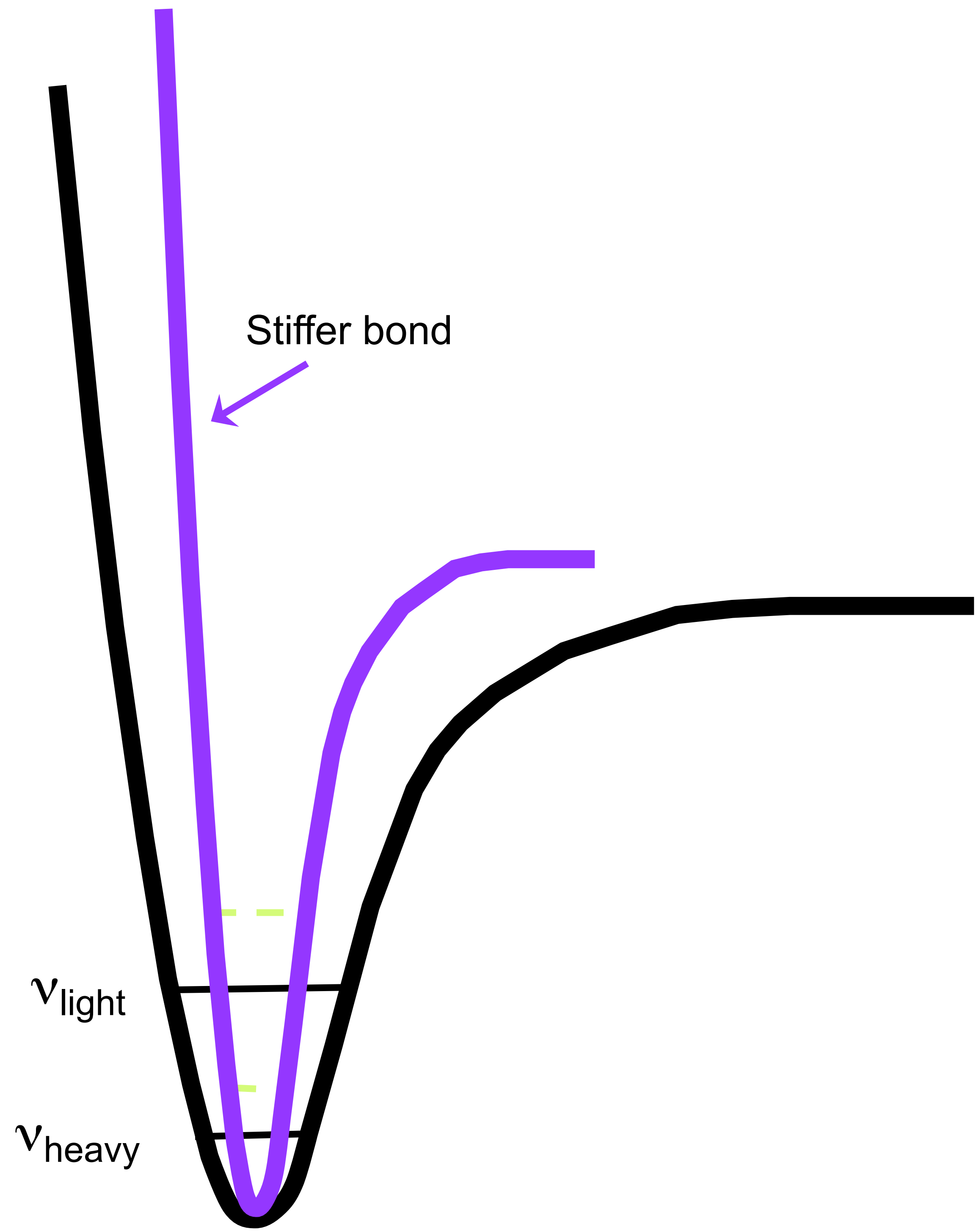
Example 6: Iron Isotopes and the Composition of the Core



Molar Volume Isotope Effect

Bond Stiffening

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



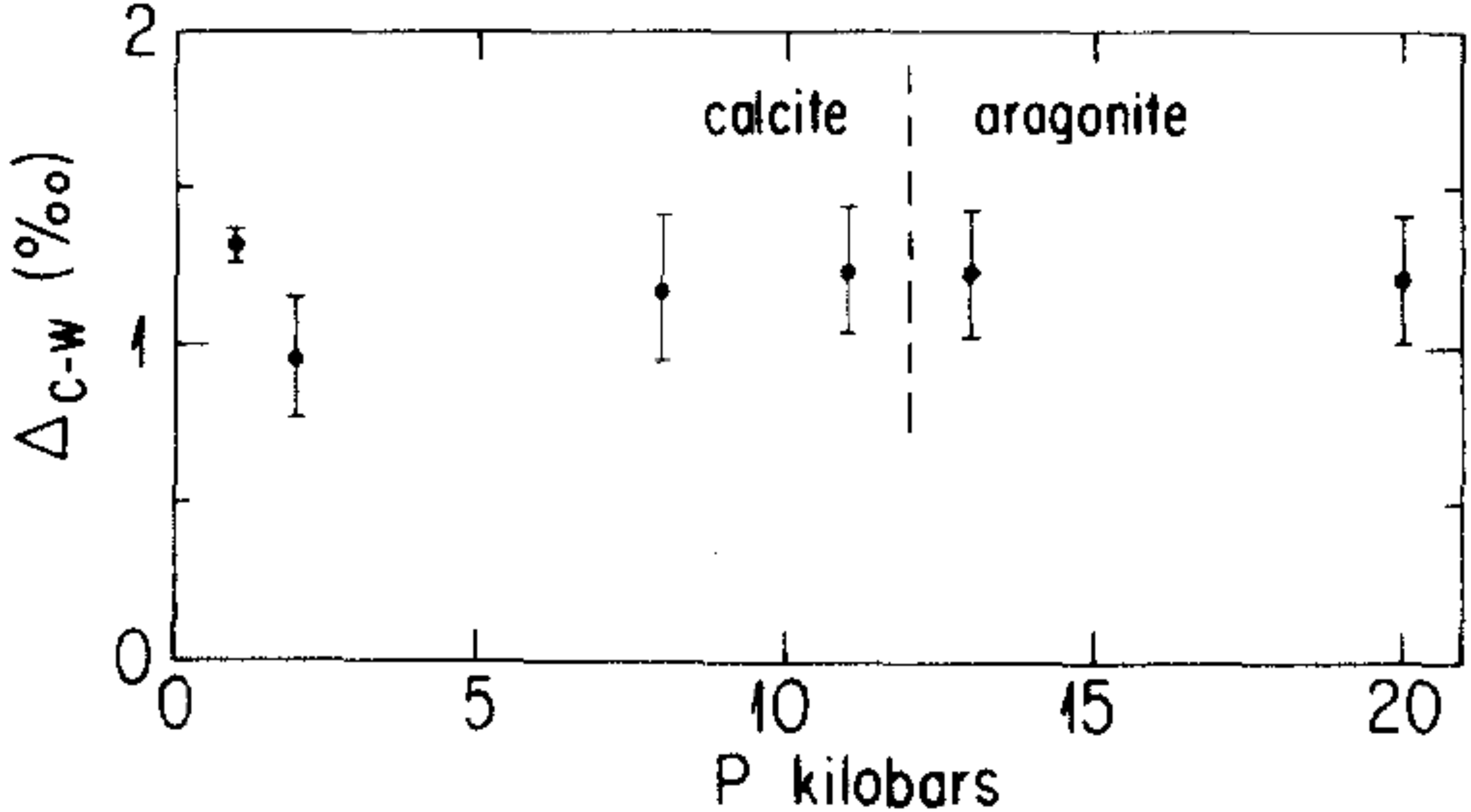


Fig. 2. Isotopic fractionation between $CaCO_3$ and water at 500°C as a function of pressure. Below 12 kbar, calcite is stable; above 12 kbar, aragonite is stable. Error bars show mean deviations from mean at each pressure.

Clayton et al., 1975

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

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

$$10^3 \ln\ \alpha_{\mathrm{A\text{-}B}} \cong \delta^{\mathrm{i}}\mathrm{E}_{\mathrm{A}} - \delta^{\mathrm{i}}\mathrm{E}_{\mathrm{B}} = \Delta_{\mathrm{A\text{-}B}}$$

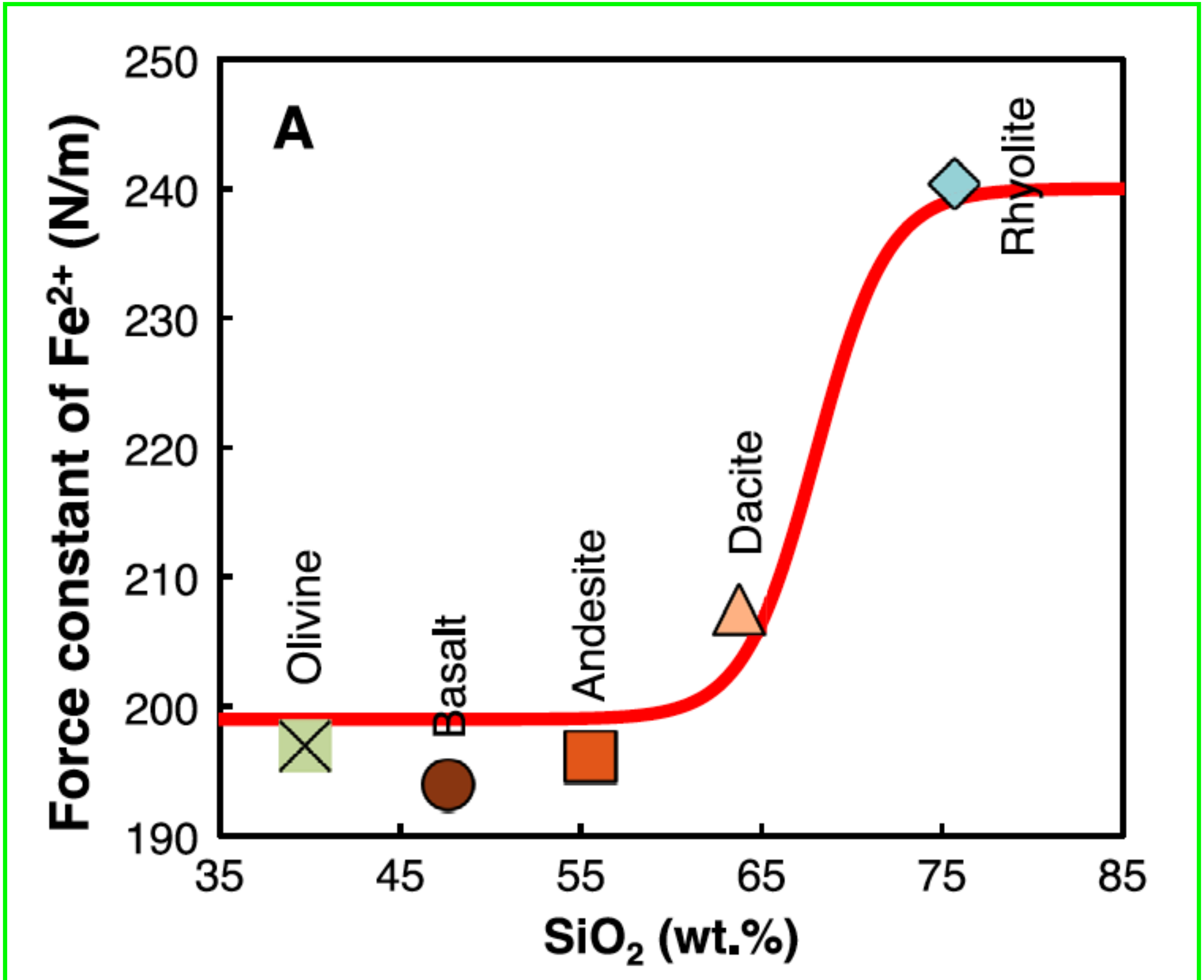
$$1000 \times \ln\ \beta_{I/I^*} = 1000\left(\frac{1}{M^*} - \frac{1}{M}\right)\frac{\hbar^2}{8k^2T^2}\boxed{\langle F \rangle}$$

Force Constant

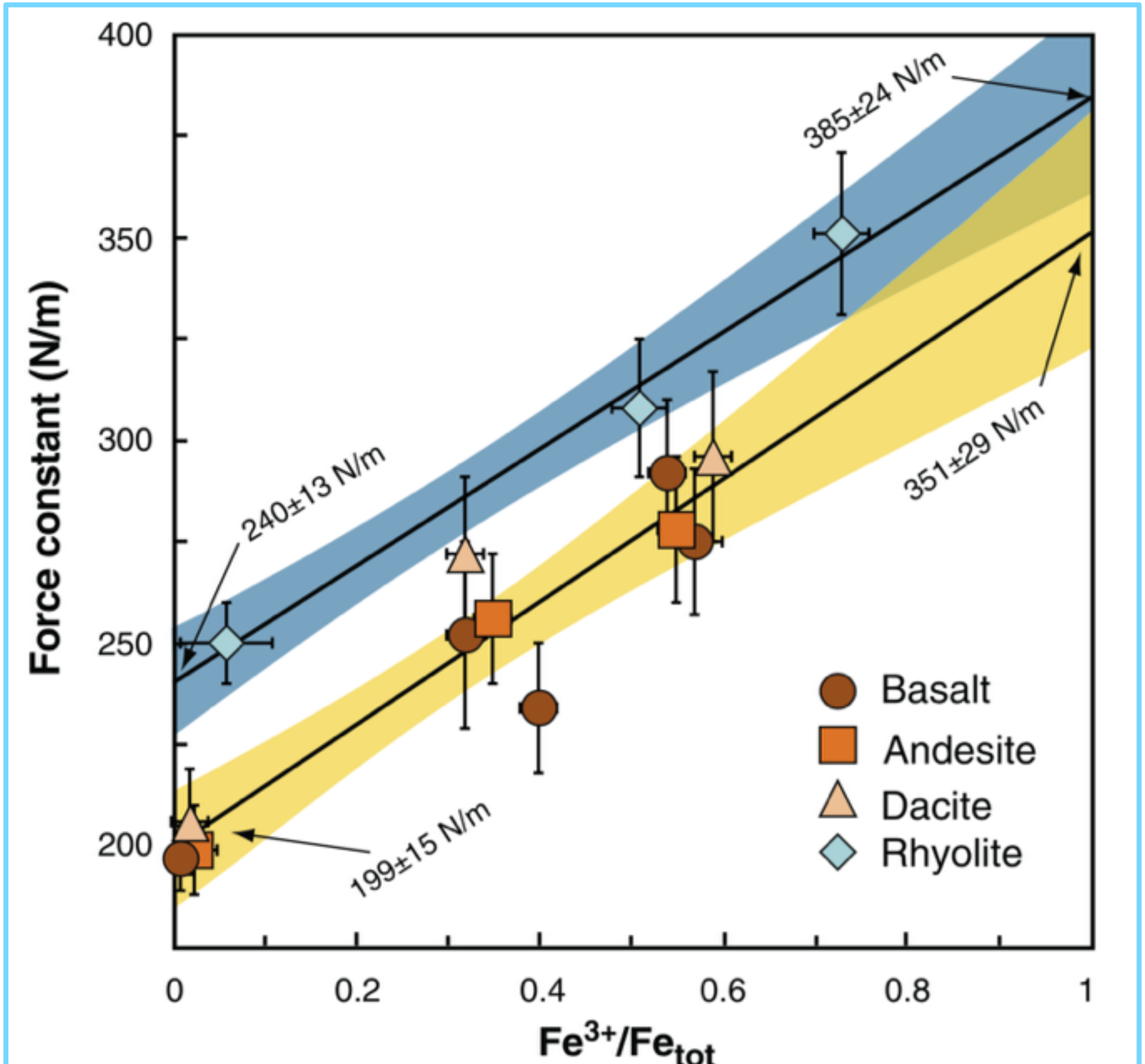
$$\ln \boxed{\alpha_{A-B}} = \ln\ \beta_A - \ln\ \beta_B$$

Equilibrium Fractionation Factor

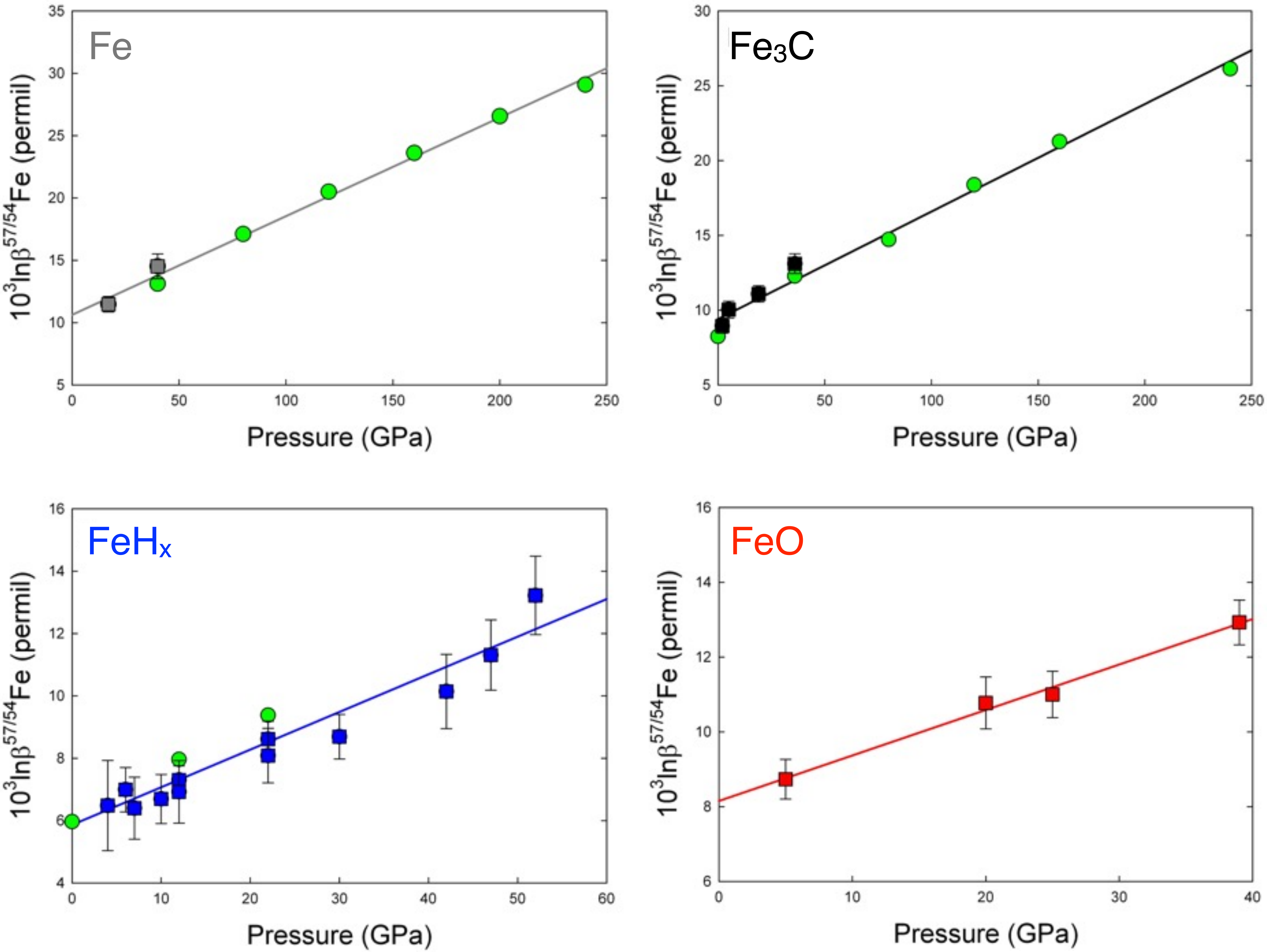
$$10^3 \ln \alpha_{A\text{-}B} \cong \delta^i E_A - \delta^i E_B = \Delta_{A\text{-}B}$$

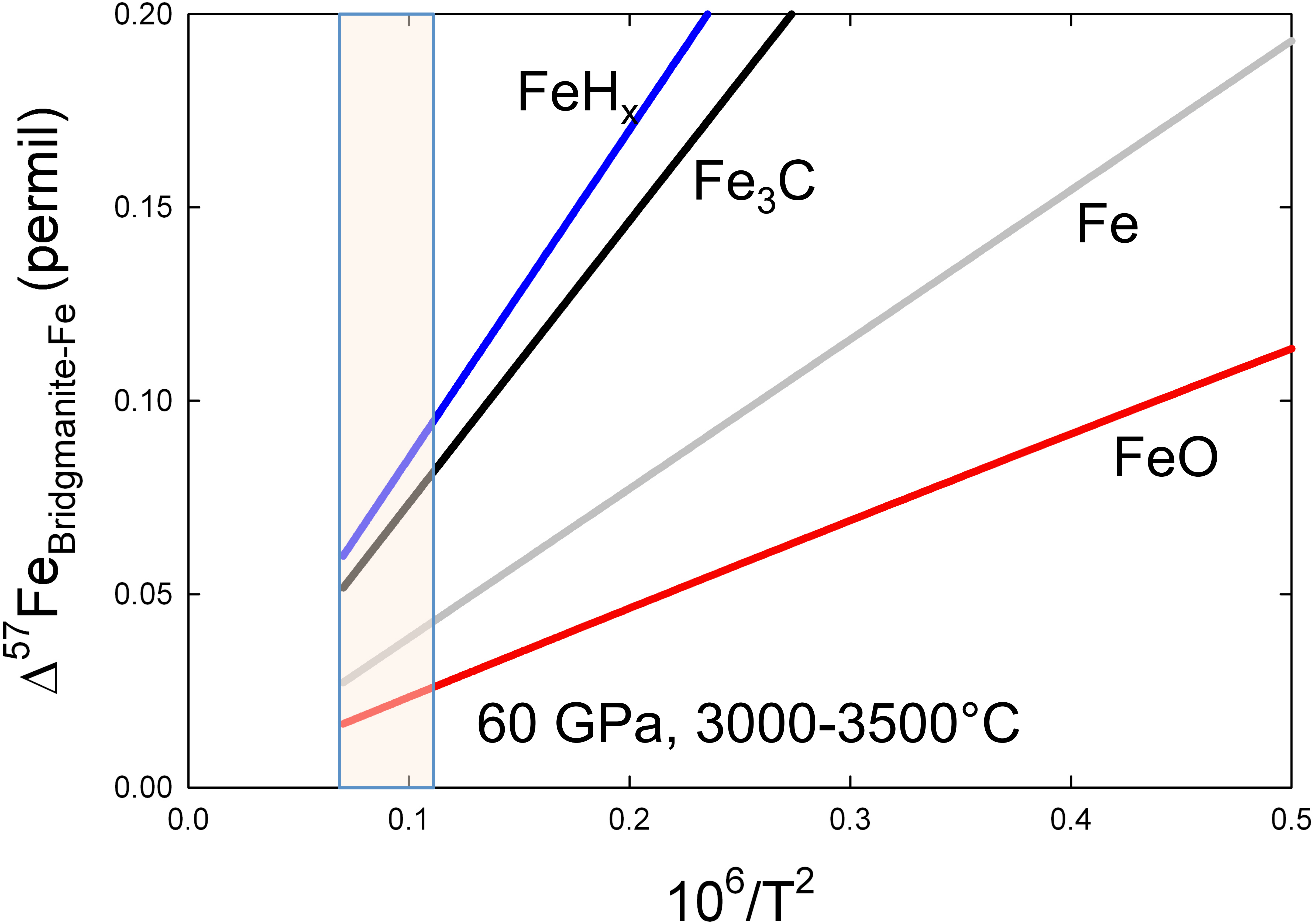


Dauphas et al., 2014

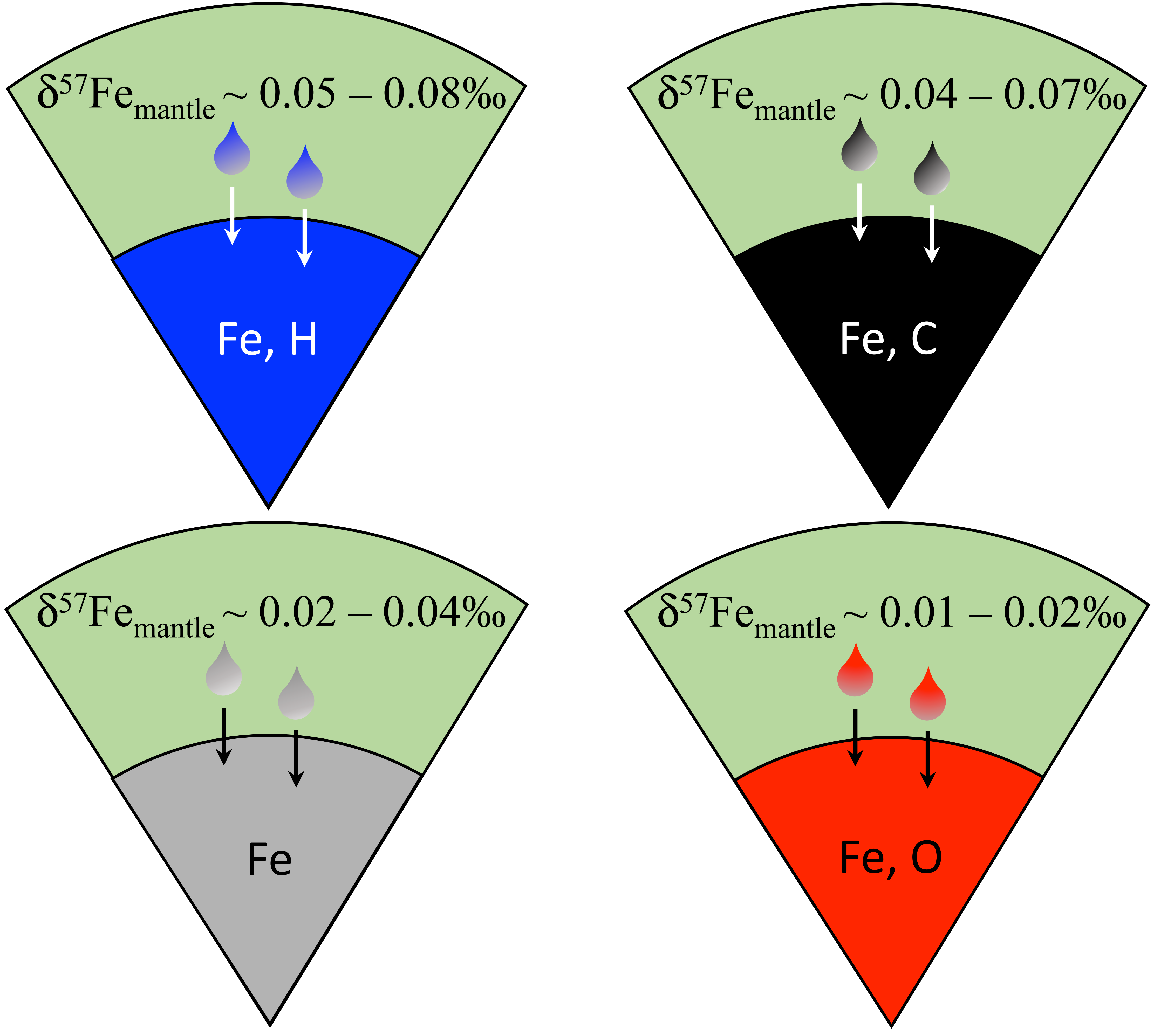


Dauphas et al., 2014


Fe
Fe3C
FeHx
FeO
10^3lnβ^57/54Fe (permil)
Pressure (GPa)



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



$\delta^{57}Fe_{mantle} \sim 0.05 - 0.08‰$
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

Geochemistry 2: Experimental and Stable Isotope Perspectives on the Deep Earth

While significant work has already been done in this field, there remains tremendous opportunities to discover new and exciting ways to use stable isotopes in order to understand more about the deep Earth!