Doctoral School – Les Houches
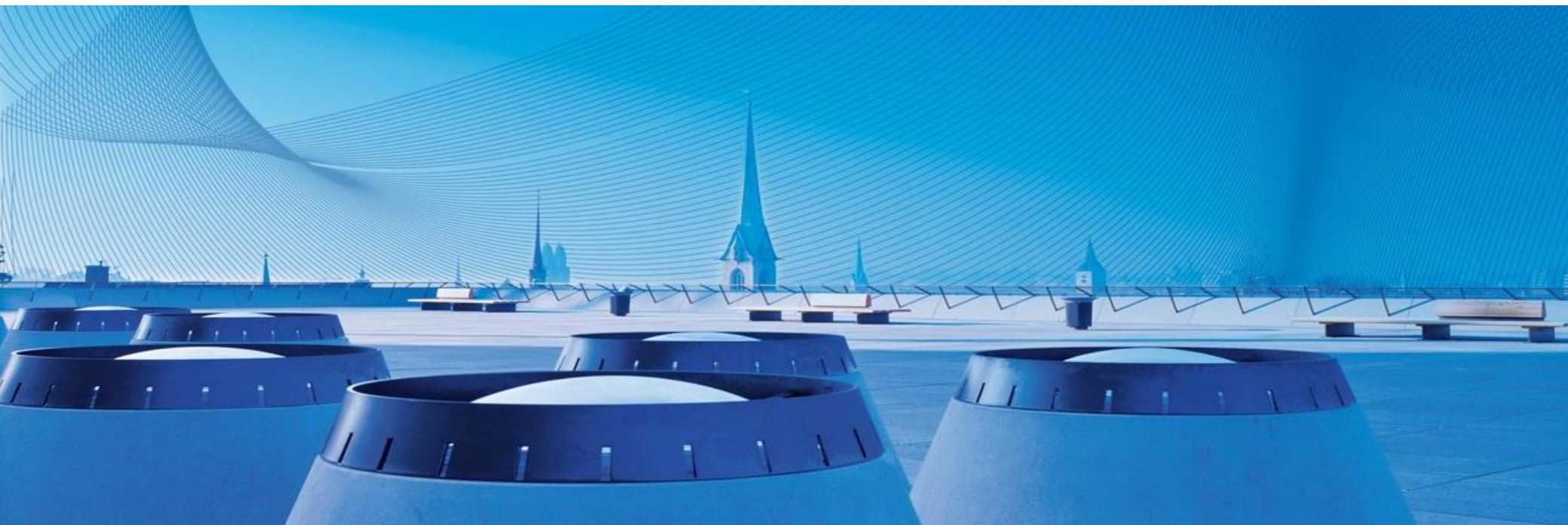## *Geochemistry*

Mechanics of stable isotope fractionation at high temperatures

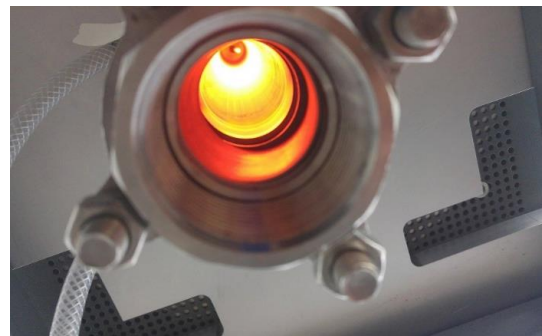*Prof. Paolo Sossi*
ETH Zürich

Course Outline

History and Fundamentals

Experimental Approaches

Applications in Geochemistry

Stable isotope theory

Physical basis for theory of **equilibrium** isotope fractionation developed in the mid 20th century

The Thermodynamic Properties of Isotopic Substances.

LIVERSIDGE LECTURE, DELIVERED BEFORE THE CHEMICAL SOCIETY IN THE ROYAL INSTITUTION ON DECEMBER 18TH, 1946.

By HAROLD C. UREY.
(Institute of Nuclear Studies, University of Chicago.)

THE JOURNAL OF CHEMICAL PHYSICS   VOLUME 15, NUMBER 5   MAY, 1947

Calculation of Equilibrium Constants for Isotopic Exchange Reactions

JACOB BIGELEISEN AND MARIA GOEPPERT MAYER
Argonne National Laboratory, Chicago, Illinois and *Institute for Nuclear Studies, University of Chicago*
(Received February 5, 1947)

Harold Urey
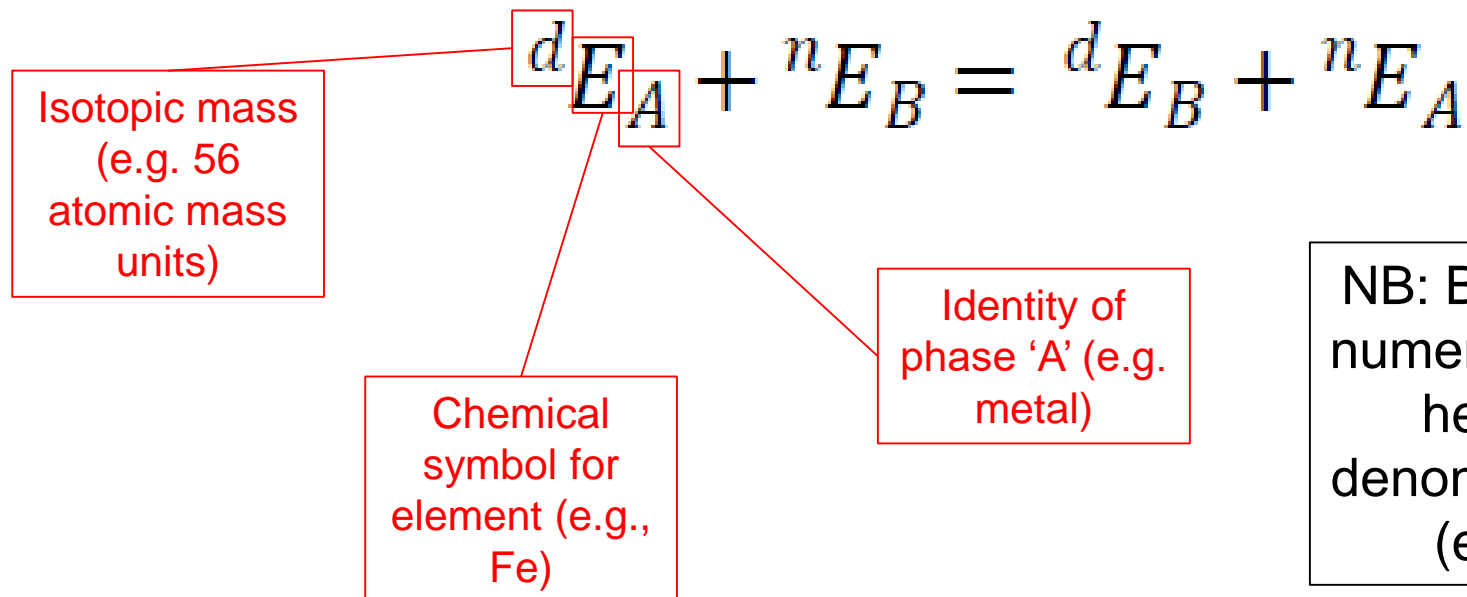(*Nobel Prize 1934*)

Jacob Bigeleisen

Maria Goeppert-Mayer
(*Nobel Prize 1963*)

Work on isotopes → win Nobel prizes

Stable isotope theory – Isotope exchange

Thermodynamic description of how substitution of isotopes affect the free energy of the system

For an element, 'E', the substitution of an isotope 'd' for isotope 'n' between phases A and B is described:

$$^{d}E_{A} + {}^{n}E_{B} = {}^{d}E_{B} + {}^{n}E_{A}$$

Isotopic mass (e.g. 56 atomic mass units)

Chemical symbol for element (e.g., Fe)

Identity of phase 'A' (e.g. metal)

NB: By convention, the numerator isotope 'n', is heavier than the denominator isotope, 'd' (e.g. $^{57}Fe/^{54}Fe$)

Stable isotope theory – The fractionation factor

As per any chemical reaction, an **equilibrium constant** can be written:

The 'fractionation factor'

$$\alpha^{\frac{n}{d}}E_{A-B} = \frac{(^nE/^dE)_A}{(^nE/^dE)_B}$$

NB: When 'B' consists of a monatomic gas of E (e.g., Fe^0 (g)), then $\alpha \rightarrow$ 'β' factor.

This α notation is widely used. If
$\alpha^{n/d}E_{A-B} > 1$, then A is enriched in <u>heavy</u> isotopes
$\alpha^{n/d}E_{A-B} < 1$, then A is enriched in <u>light</u> isotopes

Stable isotope theory – Law of mass action

By law of mass action, fractionation factor, α, is related to the Gibbs free energy change of the reaction:

$$\Delta G = -RT \ln \left(\alpha^{\frac{n}{d}} E_{A-B} \right)$$

Gibbs free energy change of reaction (J/mol)

Gas Constant (8.3145 J/mol.K

Absolute temperature (K)

However, unlike chemical reactions, isotopic substitutions do not involve
i) changes to bond structure
ii) pressure-volume work (PV)
→ ΔG is very **small**

Stable isotope theory – Atomic motion

Instead, isotopic fractionation is governed by *quantum mechanical* effects relating to the **motion** of an atom, which can occur via **three** mechanisms:

Rotation

Translation

Schauble [2004]
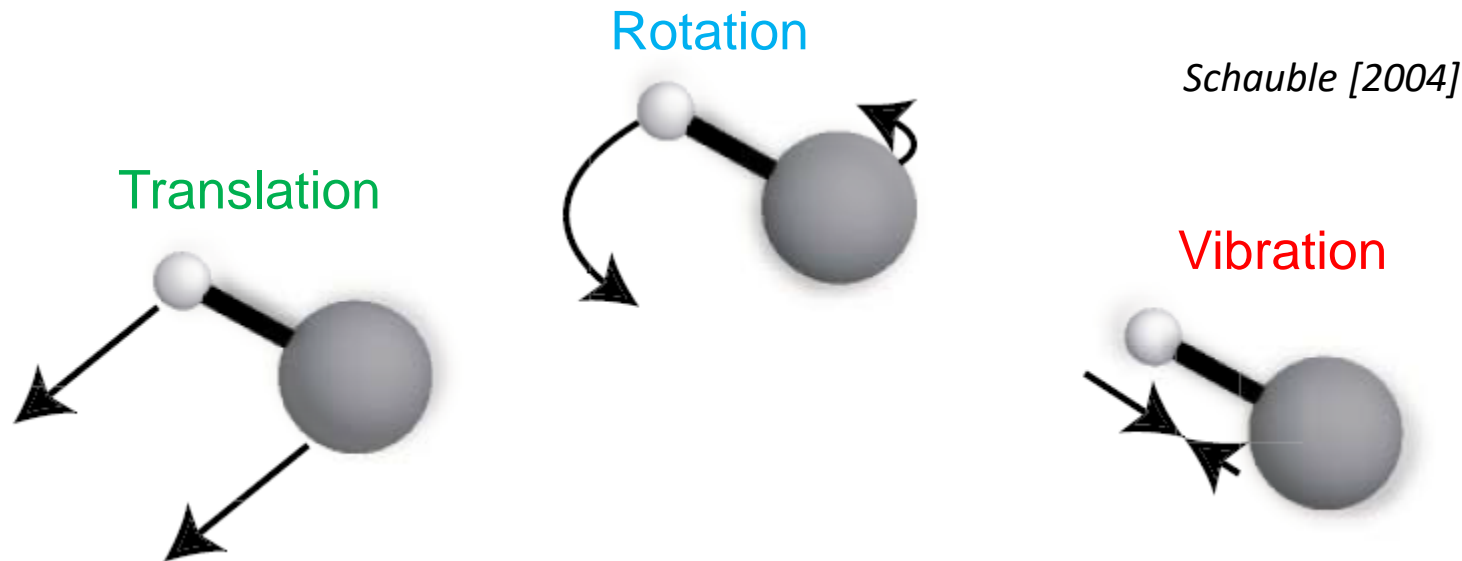
Vibration

The number of degrees of freedom of motion depends on the structure of the molecule

Stable isotope theory – Energy quanta

Schauble [2004]
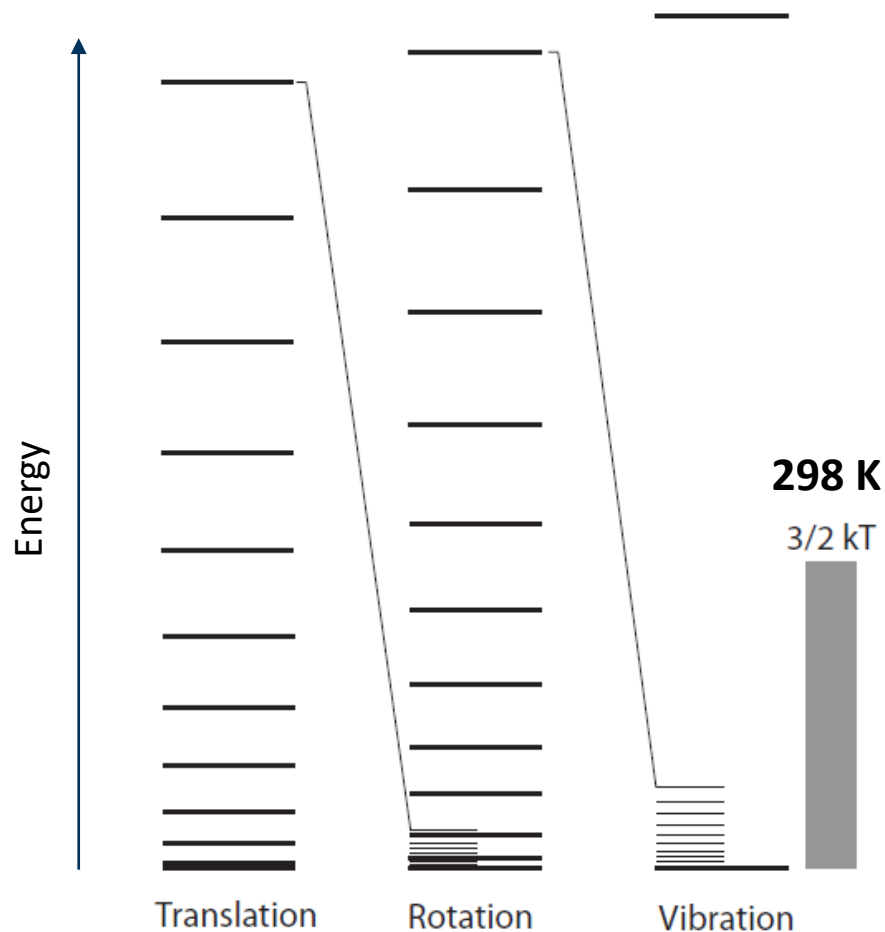
Only **vibrational** motions have energy sufficient relative to thermal (3/2 kT) to drive isotopic fractionation

Energy levels occur in evenly-spaced **quanta**, and are related to the vibration frequency;

$$E_{vib,\,i} = \left(n_i + \frac{1}{2}\right) h \nu_i$$

Energy of the ith vibration

Quantum number (excited states)

Planck's constant (J.s)

Vibrational frequency (s^{-1})

When $n_i = 0$, the system is in its **ground state**

Stable isotope theory – Zero-point energy

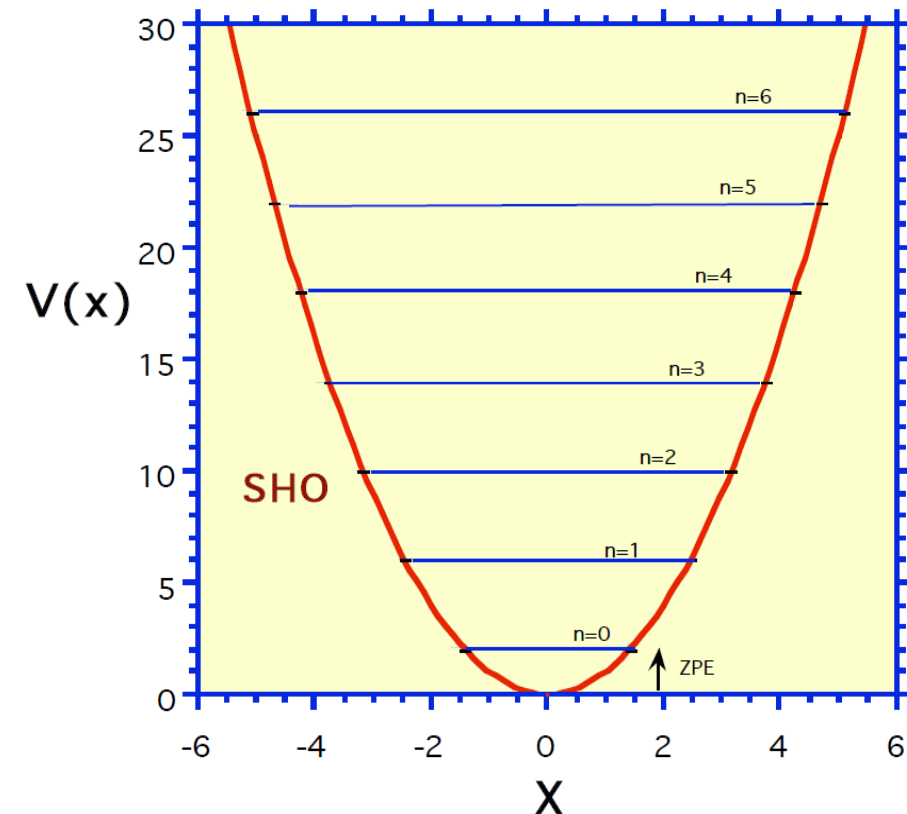Energy state of the system solved by statistical mechanics (Boltzmann equation)

Partition function, Q
is likelihood that a molecule will occupy a given energy level:

$$Q = \sum_n \exp(-E_n / kT)$$

if *T* is high, atoms fall from their high energy states more slowly

Under reasonable *T*, *n* ~ 0 and isotopic fractionation is driven by differences in **zero point energy**
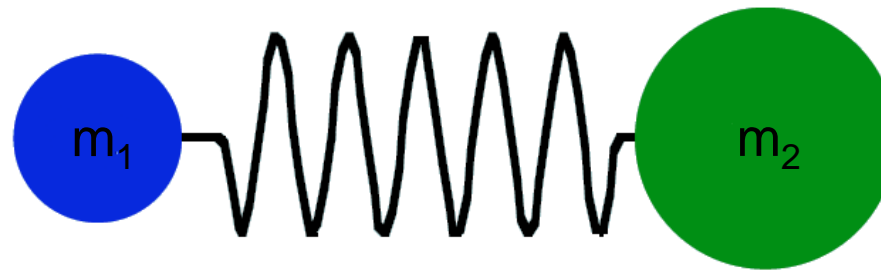

But even at the zero-point, the atom is **not** at rest!

Stable isotope theory – Force constant

For a simple harmonic oscillator, force is proportional to displacement;

$$F = -Kx$$

Hooke's Law shows that the frequency is related to the **force constant** (spring constant) and the **masses, m_1 and m_2**

$$*\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$v = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$$

Force Constant (N/m)

Reduced mass*

Stable isotope theory – Force constant measurement

Frequencies measured spectroscopically (Raman, IR, NRIXS)

Typical wavenumbers between 100 cm^{-1} to 4000 cm^{-1} (K = 50 – 2000 N/m)

Crude estimate of isotopic fractionation obtained by difference of zero point energies:

$$\Delta G = \sum \frac{1}{2} h v_{products} - \sum \frac{1}{2} h v_{reactants}$$

More quantitative → use partition function (Q), related to the Gibbs free energy

$$G = -RT ln(Q)$$

Q may be simplified as

$$Q = \frac{e^{-u/2}}{1 - e^{-u}}, \text{ where } u = h v / kT$$

Frequency (measured!)

Stable isotope theory – Bigeleisen-Mayer approximation

Force constants can be simply related to the fractionation factor (α) if:

$$hv/kT \; < \; 5$$

(i.e., 1000 cm^{-1} at 288 K or higher temperature → condition is widely met)

$$10^3 \ln \alpha^{\frac{n}{d}} E_{A-B} = \Delta^{\frac{n}{d}} E_{A-B} = \frac{10^3 3N}{96} \left(\frac{h}{\pi kT}\right)^2 \left(\frac{1}{m_d} - \frac{1}{m_n}\right)[K_A - K_B]$$

See Bigeleisen and Mayer 1947 for derivation

Stable isotope theory – Qualitative rules

1. Equilibrium isotope fractionations decrease proportional to **$1/T^2$**

2. All else being equal, magnitude of fractionation scales with **$\Delta m_{n\text{-}d}/\overline{m}^2$**

3. Heavy isotopes are concentrated in phases in which the element is more strongly bound. Bond stiffness (short, strong) correlates with:

    a.   High oxidation state

    b.   Low co-ordination number

    c.   Strong-field ligands in the spectrochemical series

    d.   Covalent bonds

    e.   Low spin state (for Fe and other *d*-group metals)

Calculation of force constants

Force constants in crystals (and crystal-like structures) can be estimated by the ionic model based on **Born-Landé** repulsion terms (Born and Mayer, 1932)

Bond valence = Z/C_N

Charge on electron

Born exponent (=12)

$$K_T = -\frac{\frac{1}{4\pi\varepsilon_0}\left(\frac{s_{Fe}s_O e^2(1-B)}{r_{Fe-O}{}^3}\right)}{I}$$

Coulomb's constant

Mean Fe-O bond distance

Ionicity

= 1-exp(-1/4 * (χ_{Fe}- χ_O)^2)

Experimental Approaches
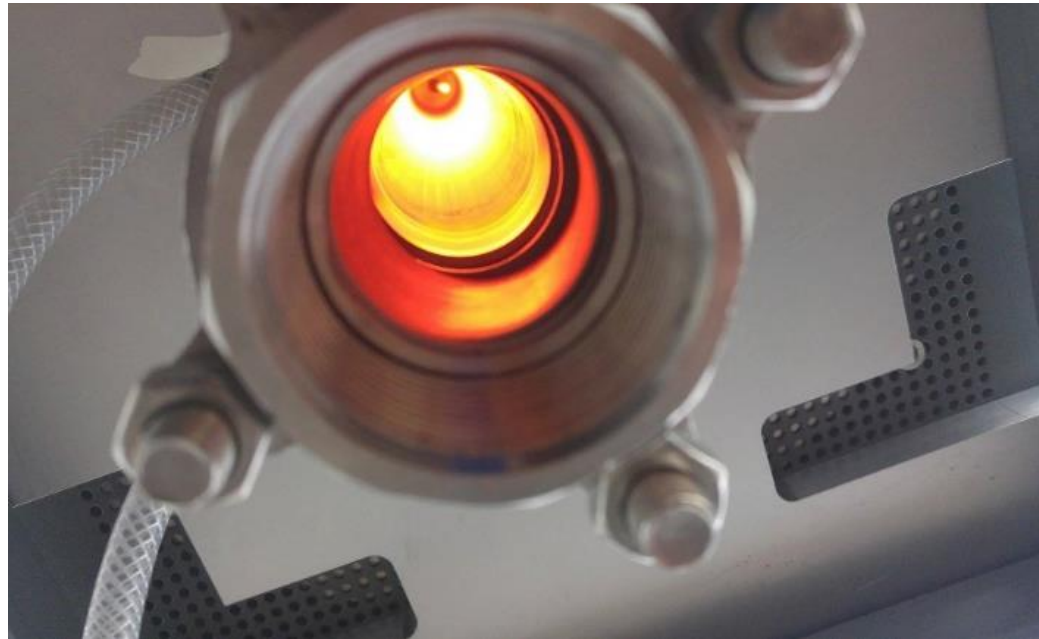
Simulating the Earth: Key parameters

Temperature, T

Pressure, P

Chemical composition, x

Oxygen fugacity, fO_2

| Fe^0 | Fe^{2+} | Fe^{2+}/Fe^{3+} | Fe^{3+} |

Fe - metal   Olivine (Fayalite)   Magnetite   Hematite
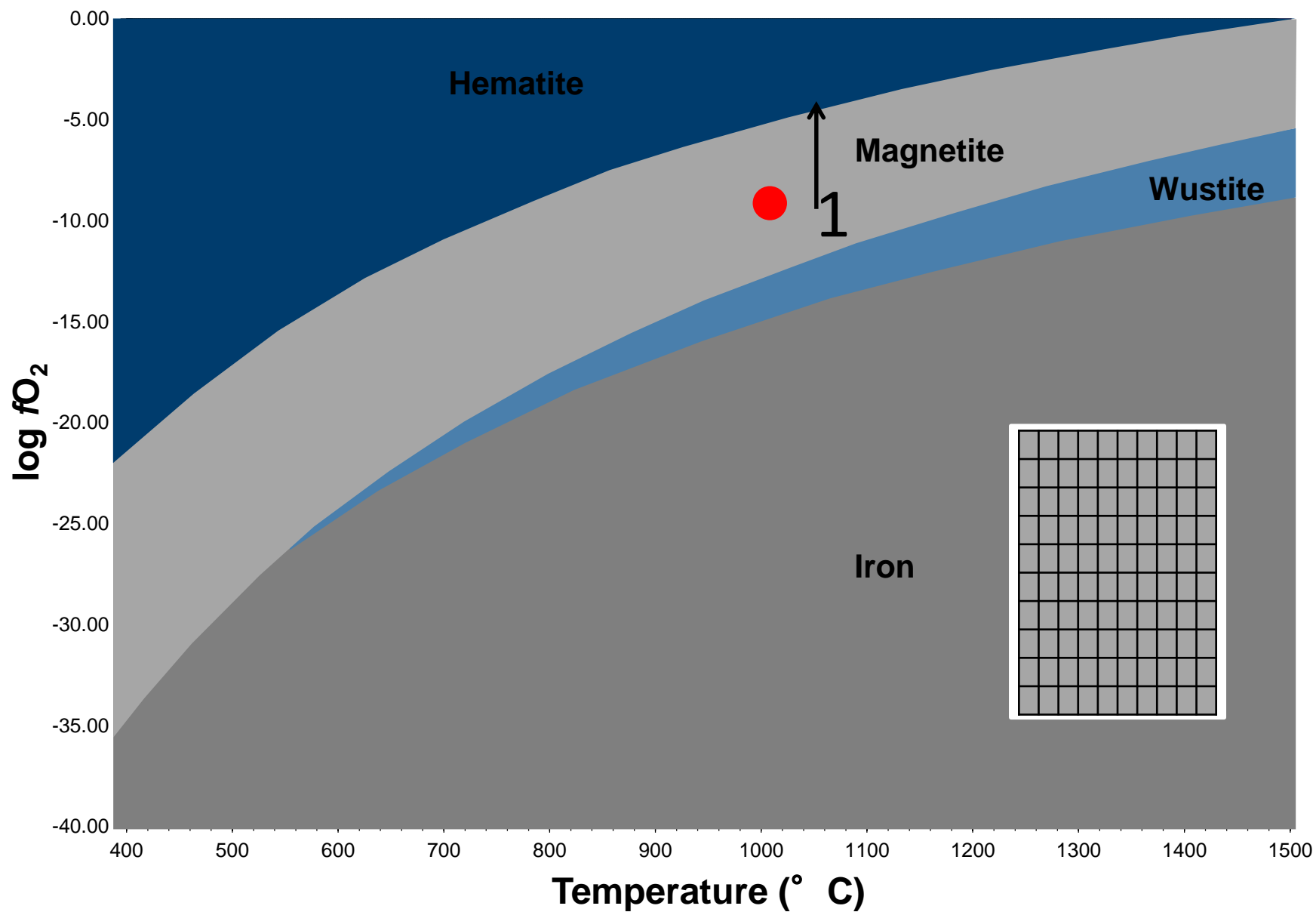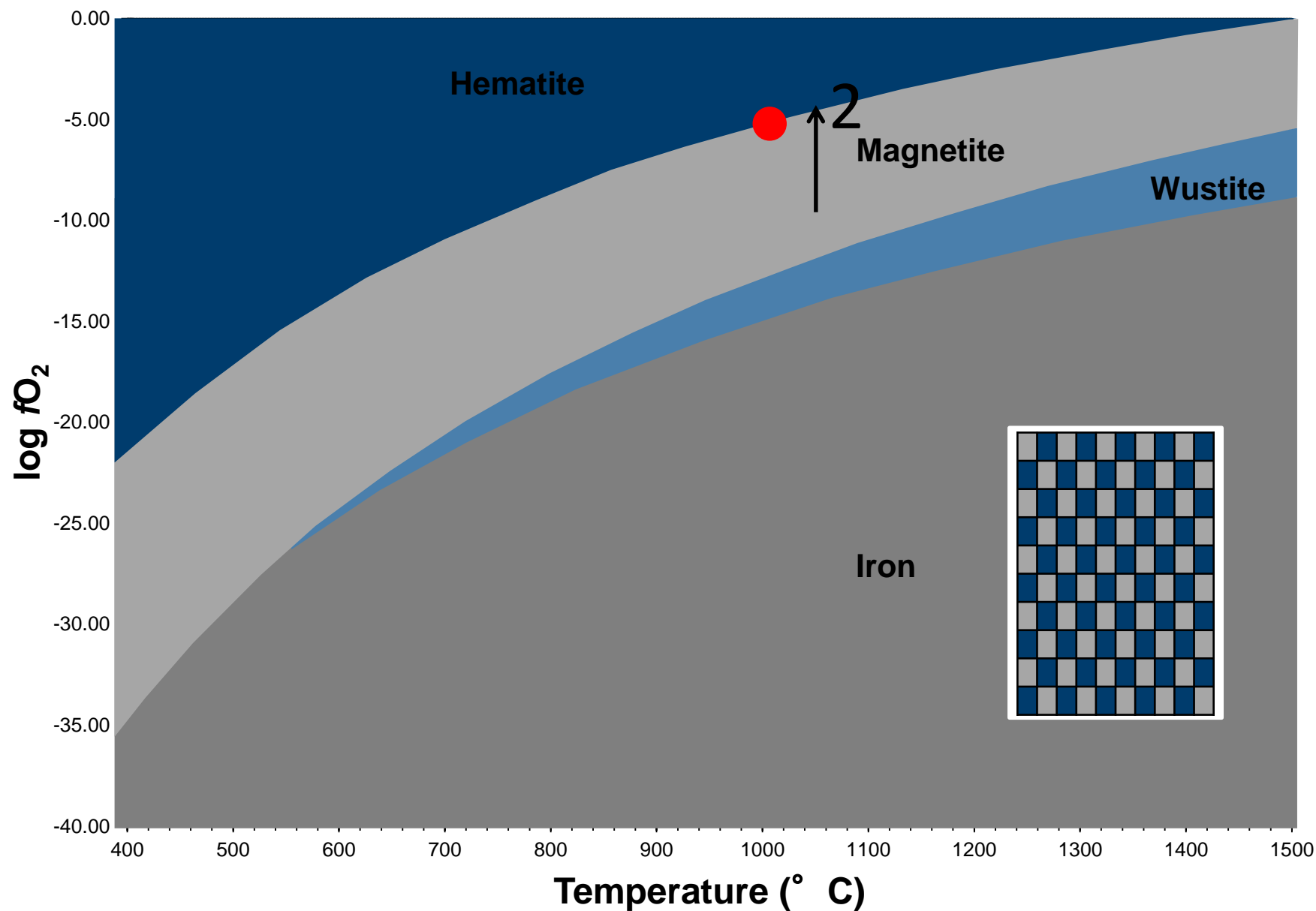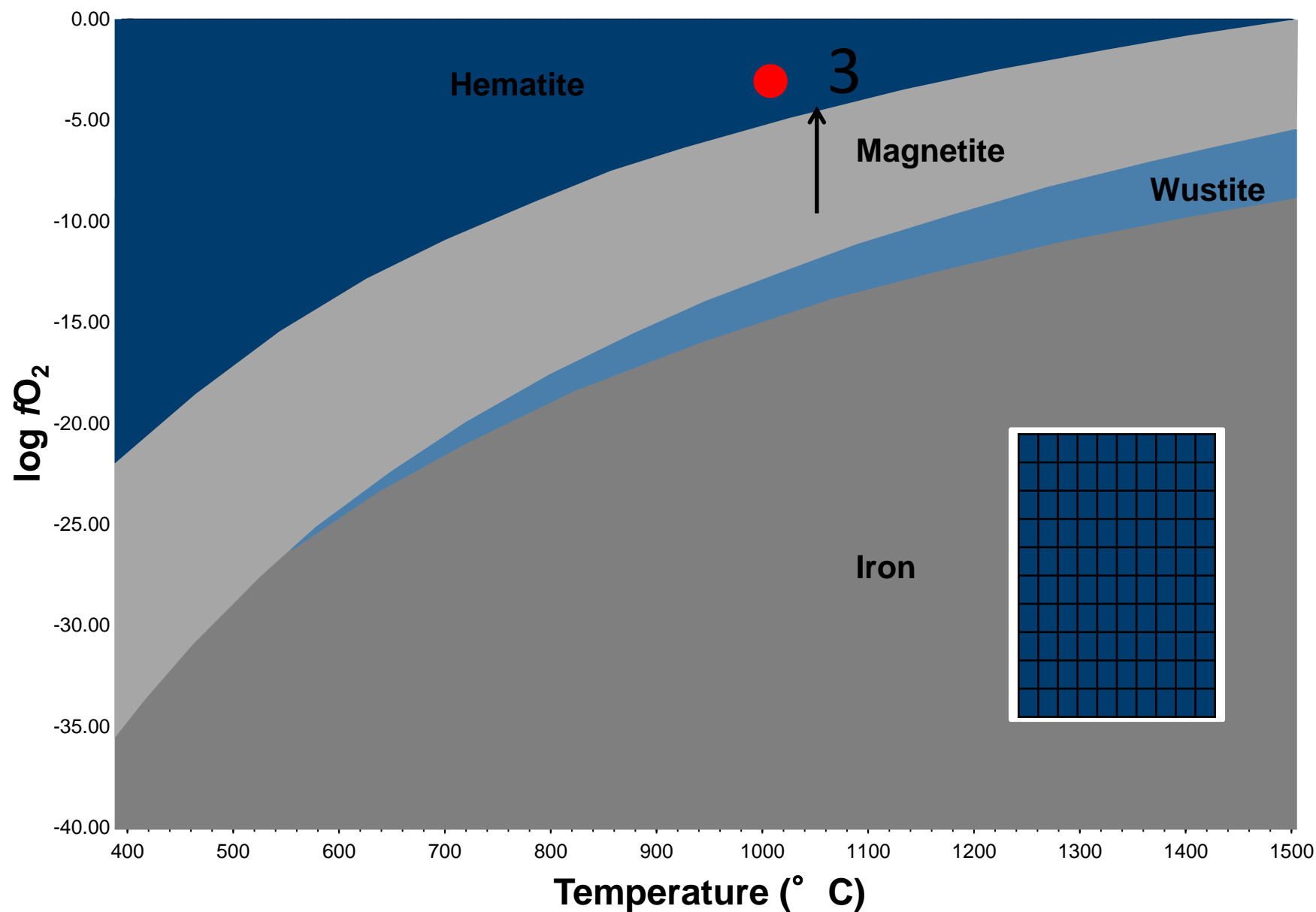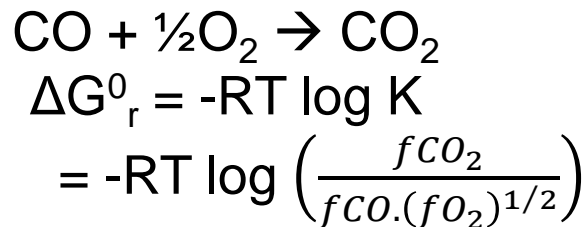
Experimental approaches – 1 atm furnace

1 atm gas-mixing furnace

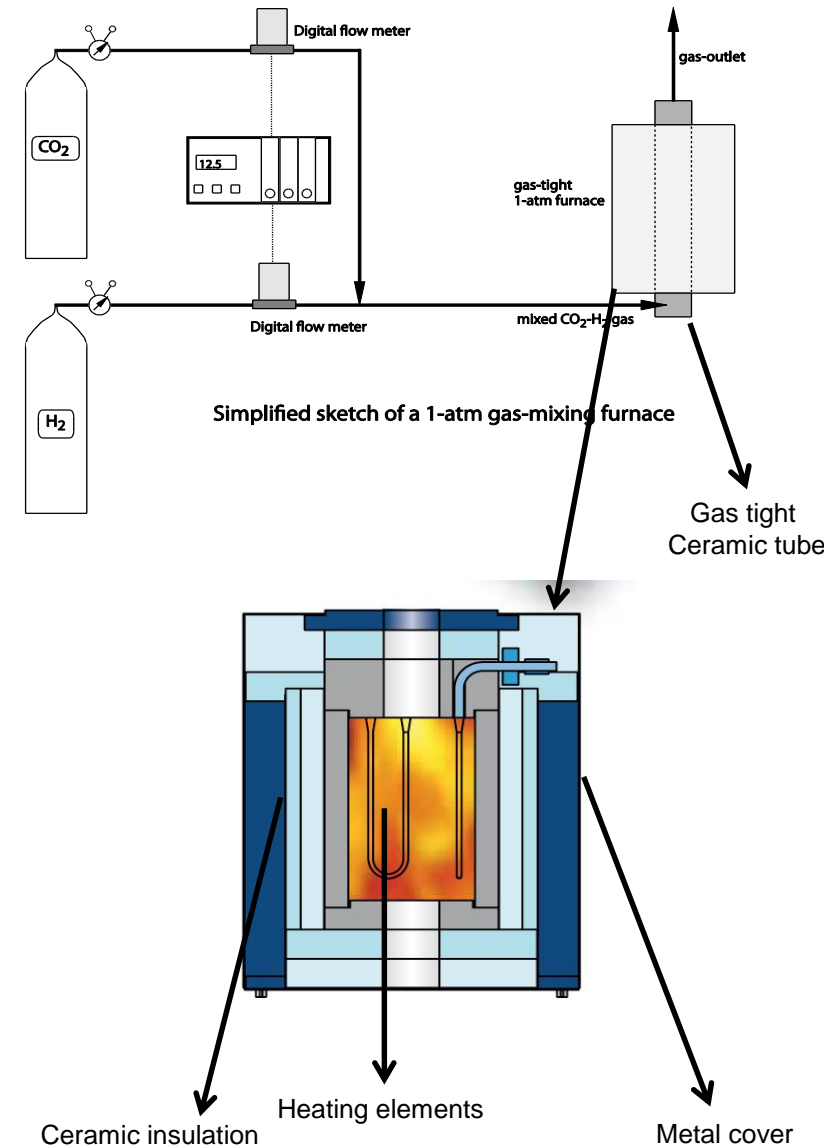**Temperature:** up to ~1650 °C
Pressure: 1 bar (total)
Composition: Nominally volatile-free
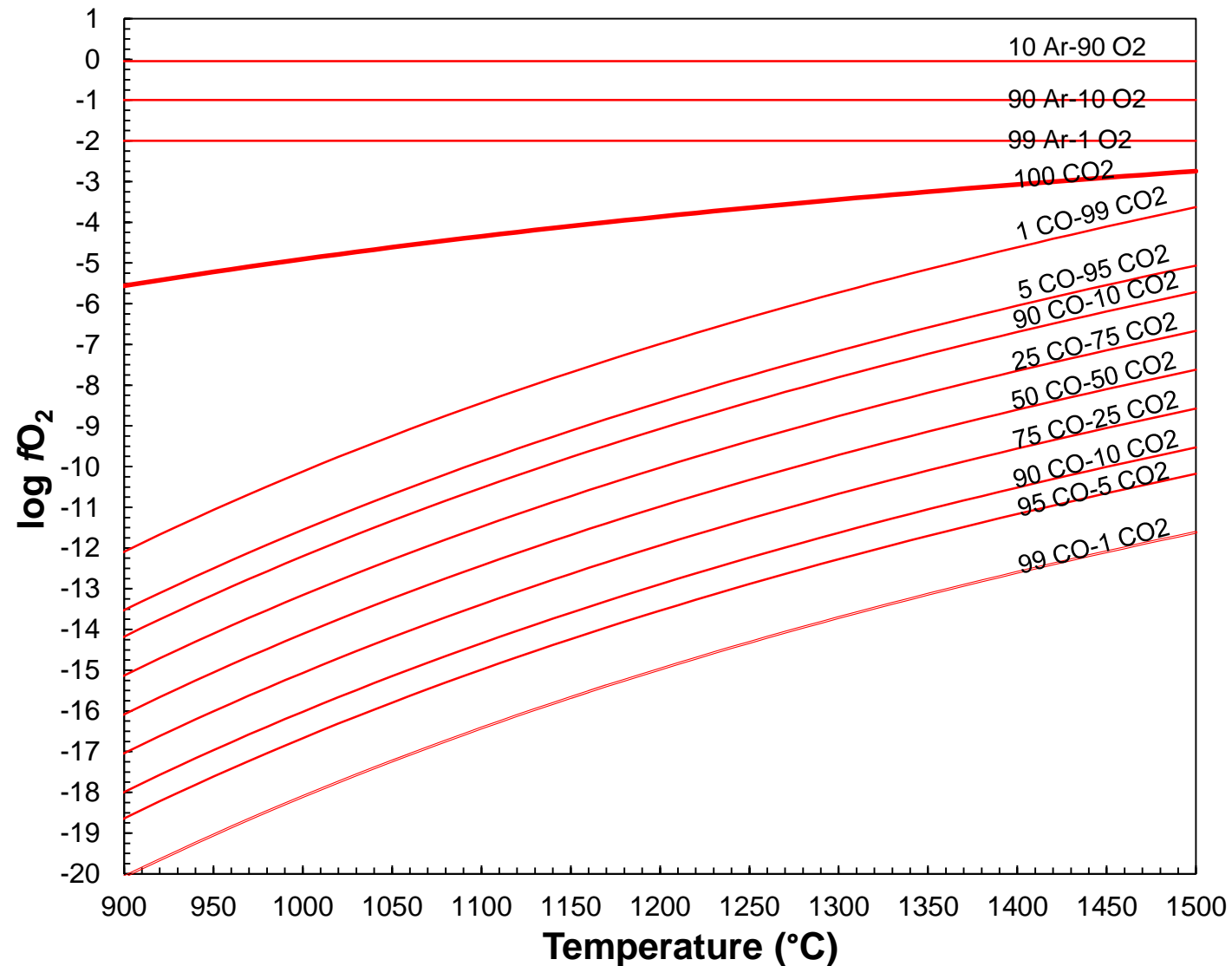fO_2: Controlled by CO-CO$_2$ (or CO$_2$-H$_2$)
gas mixing

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2$$

$$\Delta G^0_r = -RT \log K$$

$$= -RT \log \left(\frac{fCO_2}{fCO.(fO_2)^{1/2}} \right)$$

$$\left(\frac{\Delta G^0}{-RT} \right) = \log fCO_2 - \log fCO - 0.5 \log fO_2$$

$$\log fO_2 = 2\left[\log pCO_2 - \log pCO - \left(\frac{\Delta G_r}{-RT} \right) \right]$$

CO$_2$

Digital flow meter

12.5

gas-tight
1-atm furnace

gas-outlet

mixed CO$_2$-H$_2$ gas

Digital flow meter

H$_2$

Simplified sketch of a 1-atm gas-mixing furnace

Gas tight
Ceramic tube
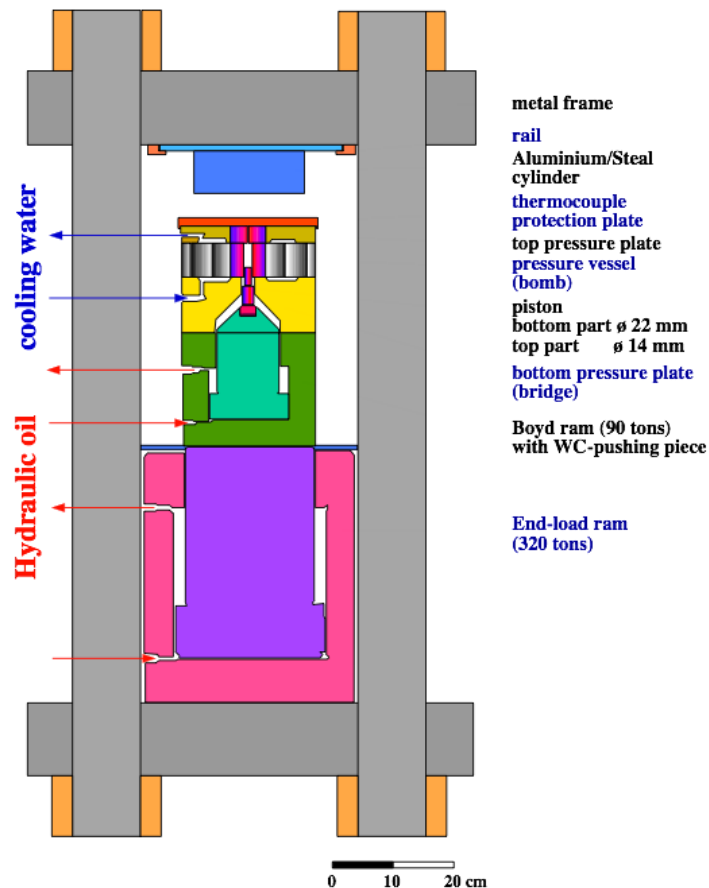
Ceramic insulation   Heating elements   Metal cover

Experimental approaches – 1 atm furnace

Experimental approaches – The Piston Cylinder

Boyd & England Type Piston Cylinder

metal frame

rail
Aluminium/Steal
cylinder

thermocouple
protection plate

top pressure plate

pressure vessel
(bomb)

piston
bottom part ø 22 mm
top part   ø 14 mm

bottom pressure plate
(bridge)

Boyd ram (90 tons)
with WC-pushing piece

End-load ram
(320 tons)

cooling water

Hydraulic oil

0   10   20 cm

End-loaded piston cylinder

Temperature: up to ~2000 °C
Pressure: 5 kbar – 40 kbar (crust +
upper mantle)
Composition: Any
fO_2: Generally imposed by capsule set-
up and/or starting materials

Use in isotope geochemistry

- Simulation of core formation (metal-
silicate partitioning)
- Fluid-mineral / Fluid-melt exchange
- Partial melting (mantle/crust)

Experimental approaches - Aim

Objective: Quantify the value of the fractionation factor (α) between two phases at given temperature and pressure

Equilibrium must be achieved or established.
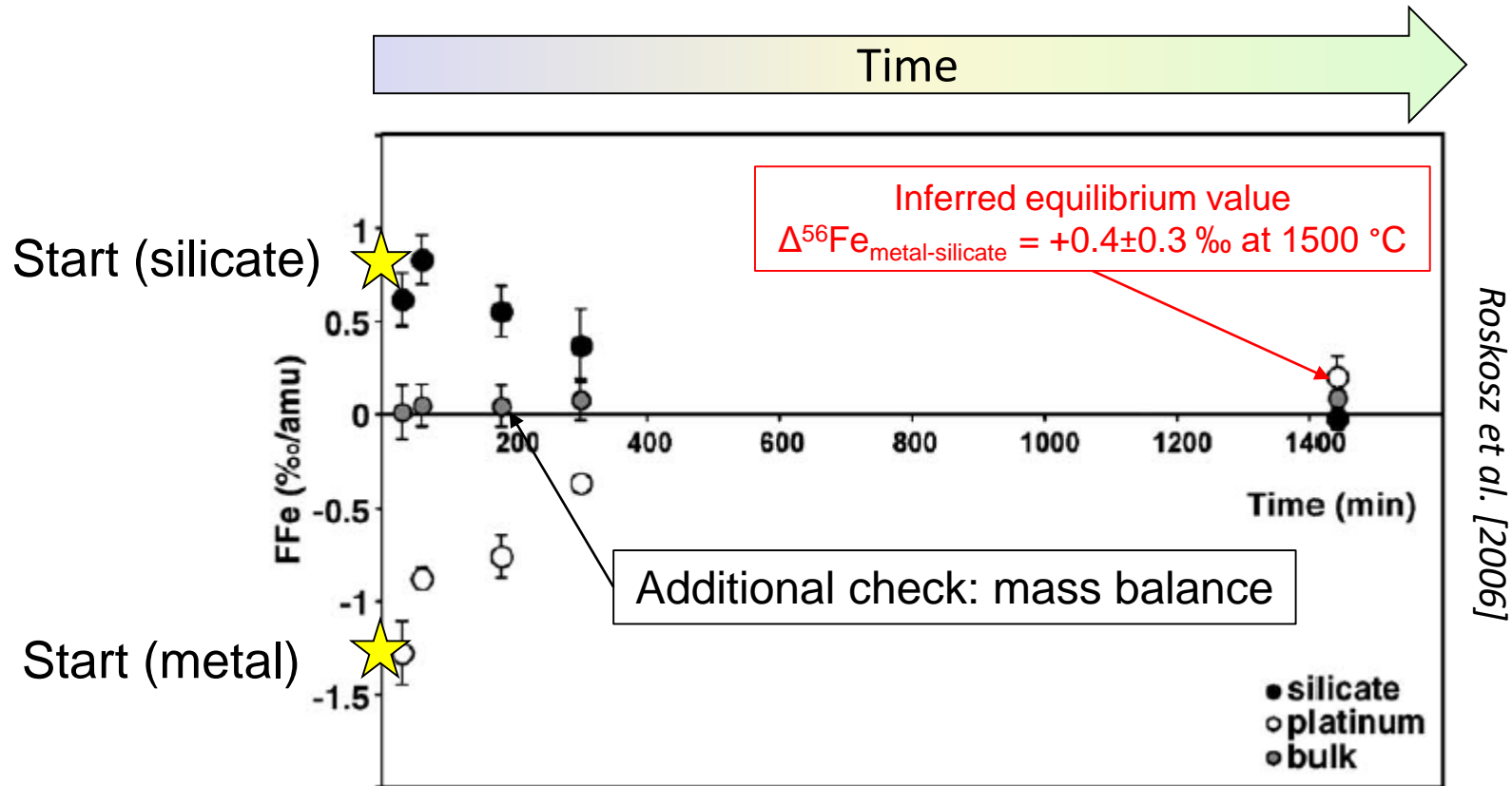This can be demonstrated by three approaches:

1. Time series

2. Reversal

3. Three-isotope method

Experimental approaches – Time series

The same experiment performed for different durations

Direct, empirical assessment of equilibrium

Experimental approaches – Mass balance

Mass balance equation

$$\delta^{n/d}E_{bulk} = \delta^{n/d}E_A f_A^E + \delta^{n/d}E_B f_B^E$$

For a two-phase system;

$$\delta^{n/d}E_{bulk} = \delta^{n/d}E_A f_A^E + \delta^{n/d}E_B (1 - f_A^E)$$
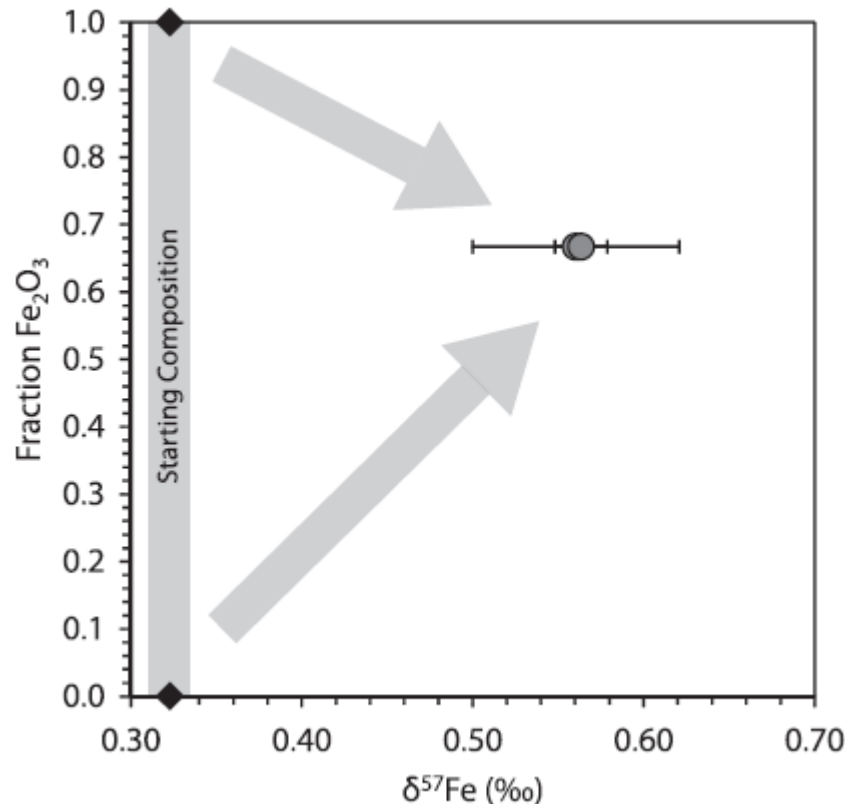
Need to know at least 3 of 4 unknowns
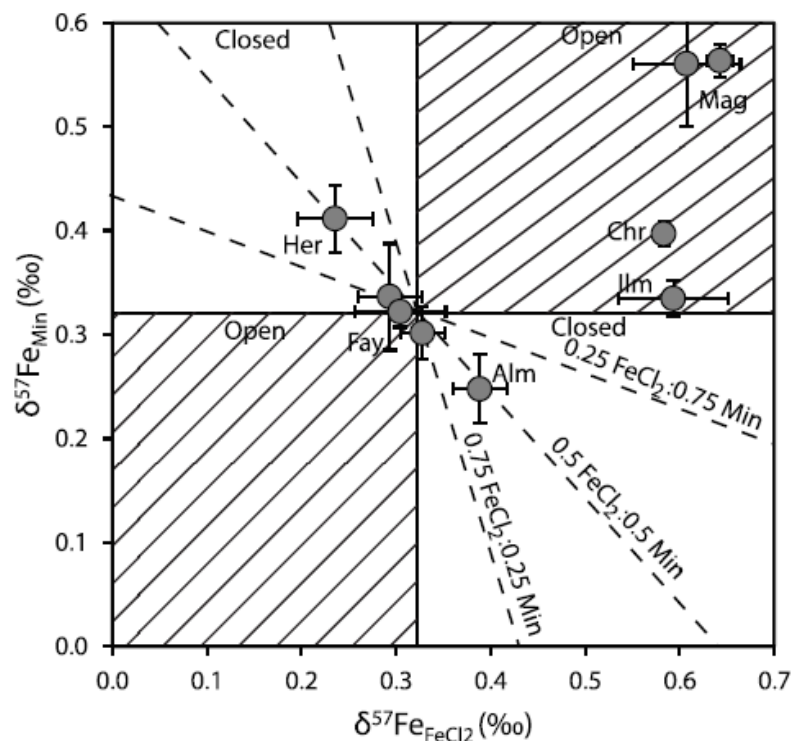
Check for open-system behaviour

Sossi and O'Neill [2017]

Experimental approaches – Reversal

A **reversal** is the repetition of an experiment using different **initial conditions**
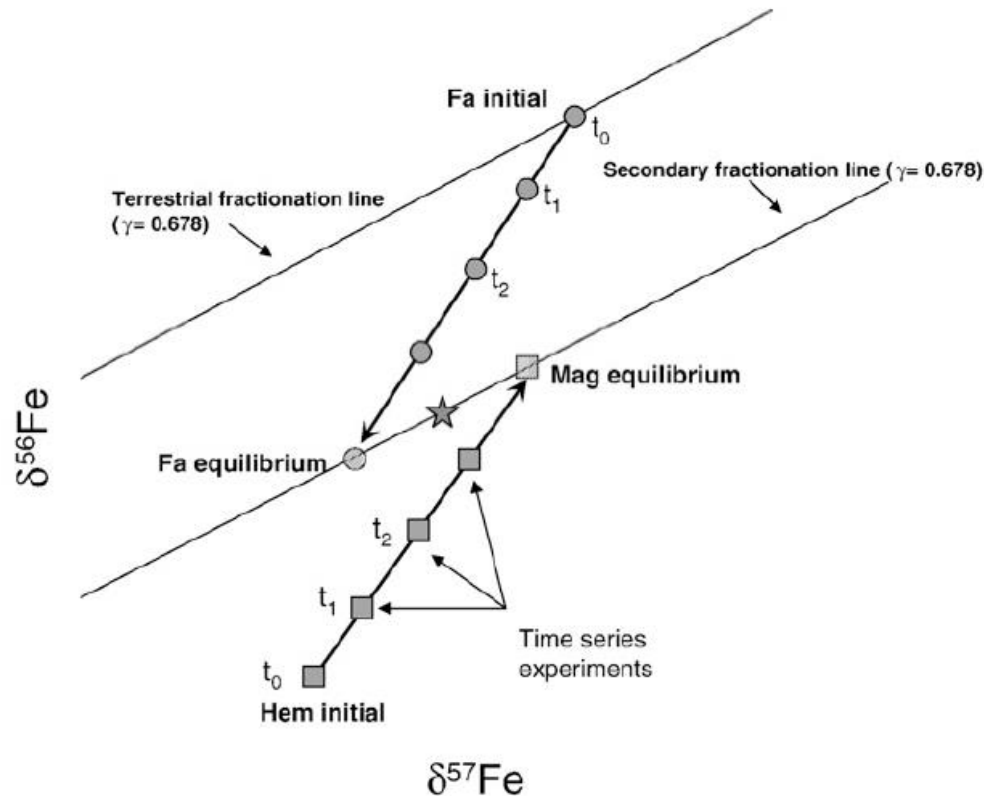
If successful, the end result is the same (equilibrium is **independent** of the path taken)

Example:
Experiment 1 – FeO + $FeCl_2$(ex) = Fe_3O_4 ($\delta^{57}Fe = 0.56\pm0.01$ ‰)
Experiment 2 – Fe_2O_3 + $FeCl_2$(ex) = Fe_3O_4 ($\delta^{57}Fe = 0.56\pm0.01$ ‰)

Sossi and O'Neill [2017]

Experimental approaches – Three Isotope Method

Shahar et al. [2008]

First developed by Matsuhisa et al. (1978) for O isotopes (mineral – fluid reaction)

Principles
- Two phases (A, B)
- A spike with an **unnatural** isotope composition is added to one phase
- Reaction between A and B defines a **new** bulk composition
- Intersection of time series arrays with SFL gives the equilibrium value

Rate of reaction is proportion to degree of disequilibrium

$$\frac{dR_A}{dt} = \alpha_{Eq} k R_B - k R_A$$

Change in isotope ratio

Change in time

Reaction constant

Experimental approaches – Three Isotope Method

Ideal for **solids** at **low temperatures** because

i)   Full equilibration is difficult

Rate constant $\quad\longrightarrow\quad$ $k = Ae^{-\frac{\Delta G}{RT}}$

ii)   Satisfies the condition of a closed system

Fraction (f) of element E in phase A $\quad\longrightarrow\quad$ $f_A^E \dfrac{dR_A}{dt} + f_B^E \dfrac{dR_B}{dt} = 0$

iii) Composition of phases does not change appreciably

- Mass balance equations (see earlier slide) are valid
    - Linear trajectories results

Significance and Future

Iron isotopes - Minerals

Sossi and O'Neill, 2017
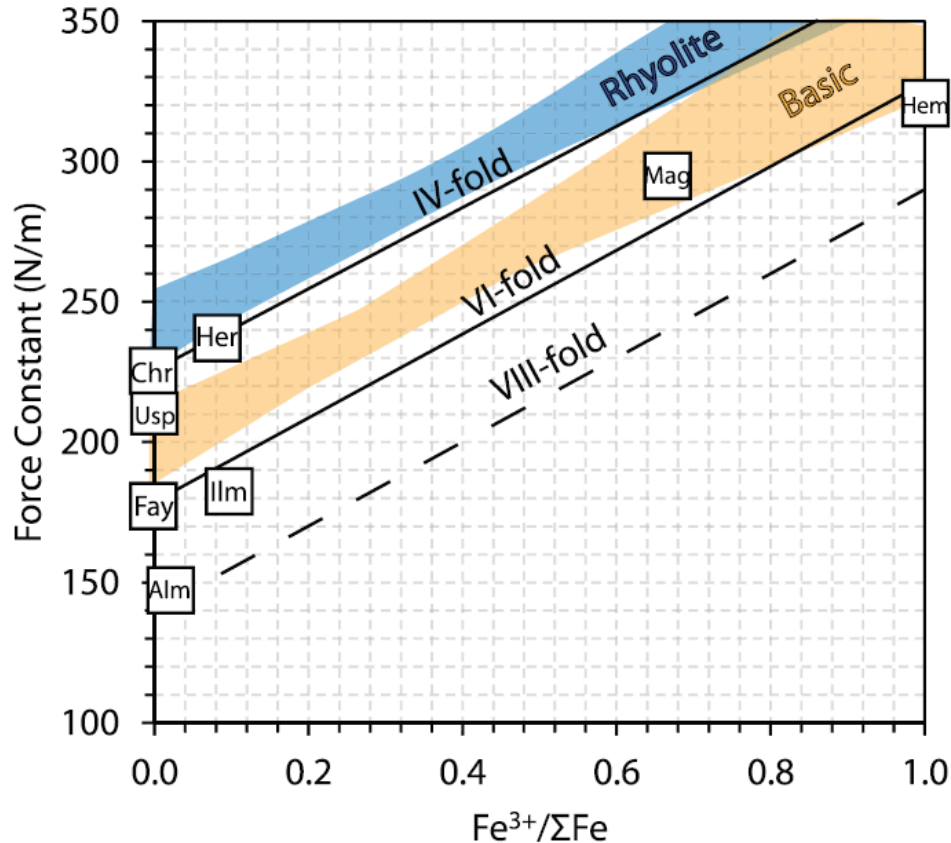
Predict K_T as function of
- Oxidation state, Z
- Co-ordination Number C_N

Slope | Intercept

$$K_{Fe-O} = a \times \frac{Fe^{3+}}{\Sigma Fe} + b$$

a ≈ 140 (Nm^{-1}/Fe^{3+}ΣFe^{-1})

b_{VIII} = 145 Nm^{-1}
b_{VI} = 185 Nm^{-1}
b_{IV} = 225 Nm^{-1}

(IV-fold − VIII-fold) ~ 2/3 × (Fe^{3+} - Fe^{2+})

Iron isotopes - Glasses

Silicate glasses synthesised under controlled fO_2

Force constant derived from NRIXS measurements

a ~ 150 N/m/(Fe^{3+}/Fe^T)

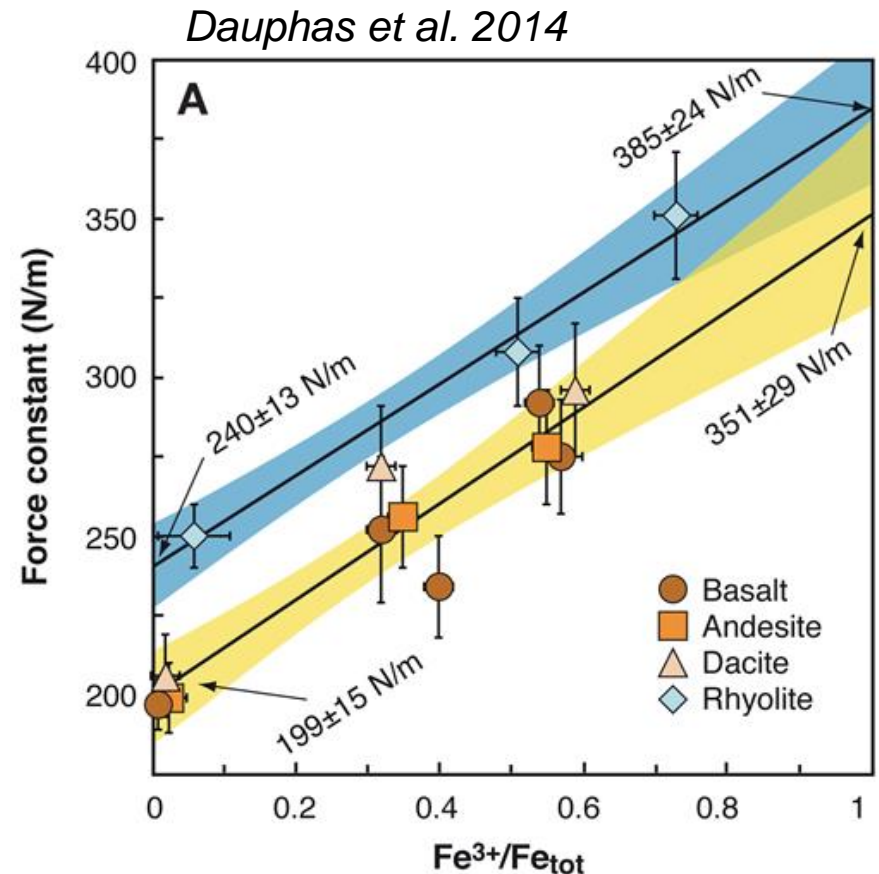Basalt/Andesite/Dacite
b ~ 200 N/m

Rhyolite
b ~ 240 N/m

Likely related to change in structural environment of Fe^{2+} (addition of Na, K…)

Dauphas et al. 2014

Stable isotope fractionation not controlled only by redox state!

Partial Melting Model

Can compute fractionation factor between
mineral and **melt**
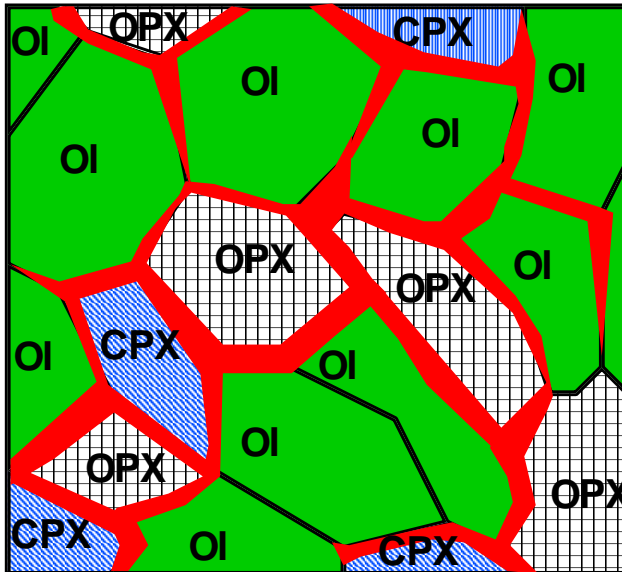
$$10^3 \ln \alpha^{\frac{n}{d}} E_{A-B} = \Delta^{\frac{n}{d}} E_{A-B} = \frac{10^3 3N}{96} \left(\frac{h}{\pi kT}\right)^2 \left(\frac{1}{m_d} - \frac{1}{m_n}\right) [K_A - K_B]$$

Reduces to a constant × $[K_A - K_B]$

For $^{56}Fe/^{54}Fe$,

$$10^3 \ln \alpha \,^{56/54} Fe_{A-B} = 2804 \times \frac{[K_A - K_B]}{T^2}$$

Letting A = basalt with 15 % Fe^{3+} and B = olivine;

K_{basalt} = 220 N/m
$K_{olivine}$ = 190 N/m

$$10^3 \ln \alpha \,^{56/54} Fe_{basalt-olivine} = 0.084 \times \frac{10^6}{T^2}$$

Partial Melting Model

Can compute fractionation factor between
mineral and **melt**

Isotope fractionation is the *ratio* of partition coefficients of isotope *i* and *j*

$$\frac{(^iC_E)_1/(^iC_E)_2}{(^jC_E)_1/(^jC_E)_2} = \frac{D^i_{1-2}}{D^j_{1-2}} = \alpha E^{i/j}_{1-2},$$

Recast Shaw (1970) equations for abundance of isotope, *i*, by multiplying D^i_{1-2} by the fractionation factor, $\alpha E^{i/j}_{1-2}$ (batch melting):
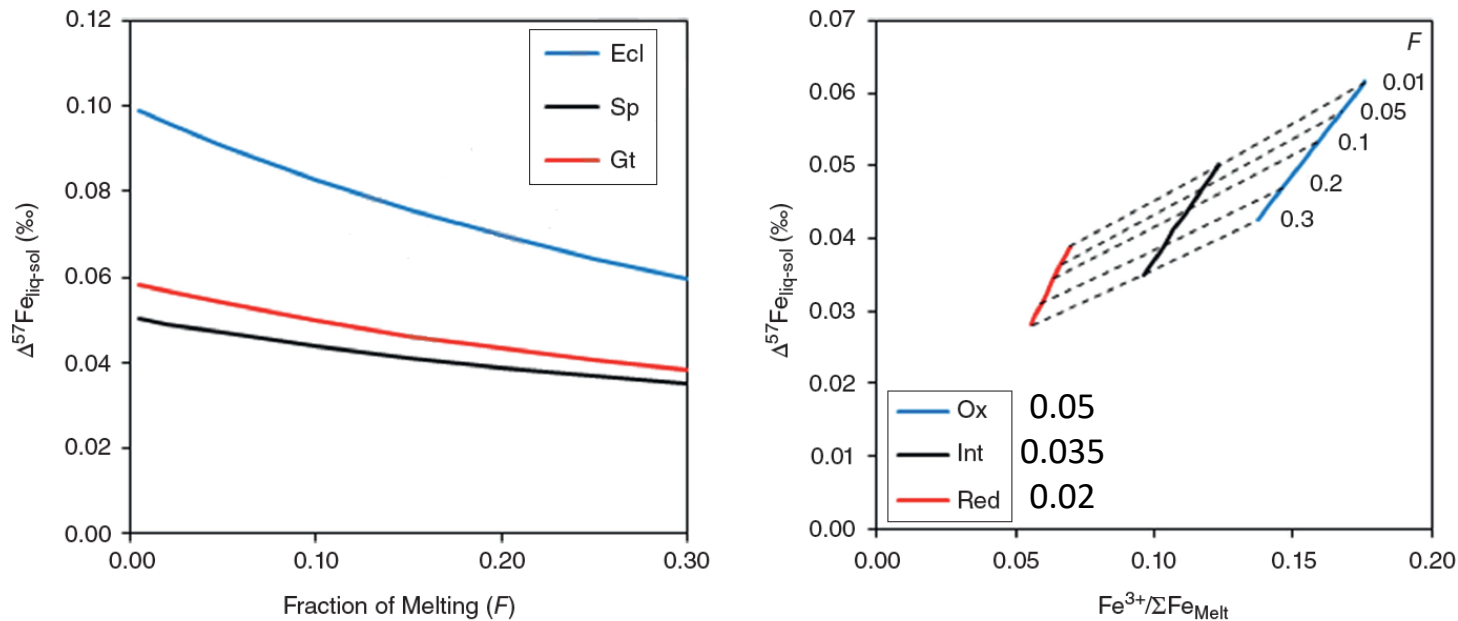
$$\frac{C^i_l}{C^i_o} = \frac{1}{\left(\left(D^i_{1-2}\alpha^{i}_{j}E_{1-2}\right) + F\left(1 - P^i_{1-2}\alpha^{i}_{j}E_{1-2}\right)\right)},$$

Isotope composition (delta notation) is given by

$$10^3 \ln\left(\frac{C^i_l}{C^j_l}\right) = \delta^i E$$

Partial Melting Model

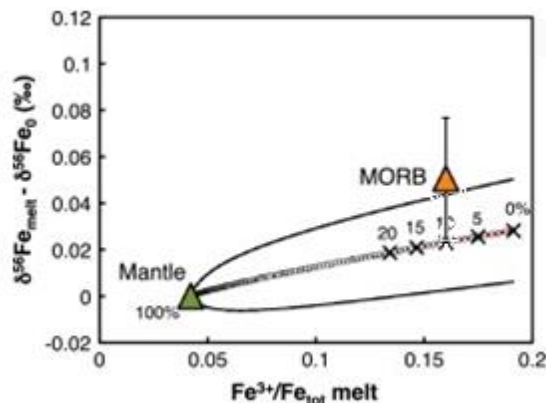Can compute fractionation factor between
mineral and **melt**

1473 K

$\Delta^{57}Fe_{liq\text{-}sol} \sim 0.05 \text{ to } 0.10 \text{ ‰}$
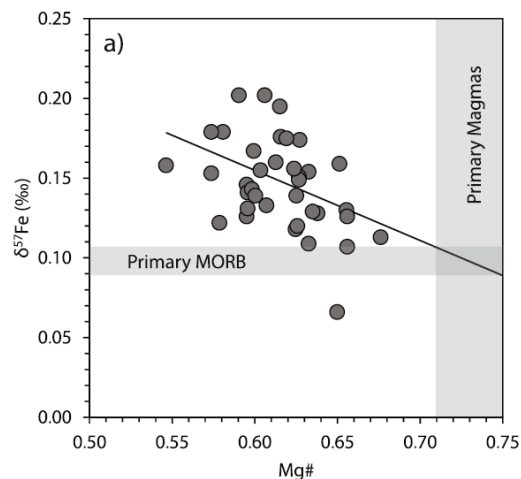
$\delta^{57}Fe = 1.5 \times \delta^{56}Fe$

Composition of MORB

Does partial melting explain the iron isotope composition of MORB?

Dauphas et al. 2014

Sossi et al. 2016

Iron isotope composition of MORB apparently **too heavy** relative to partial melting

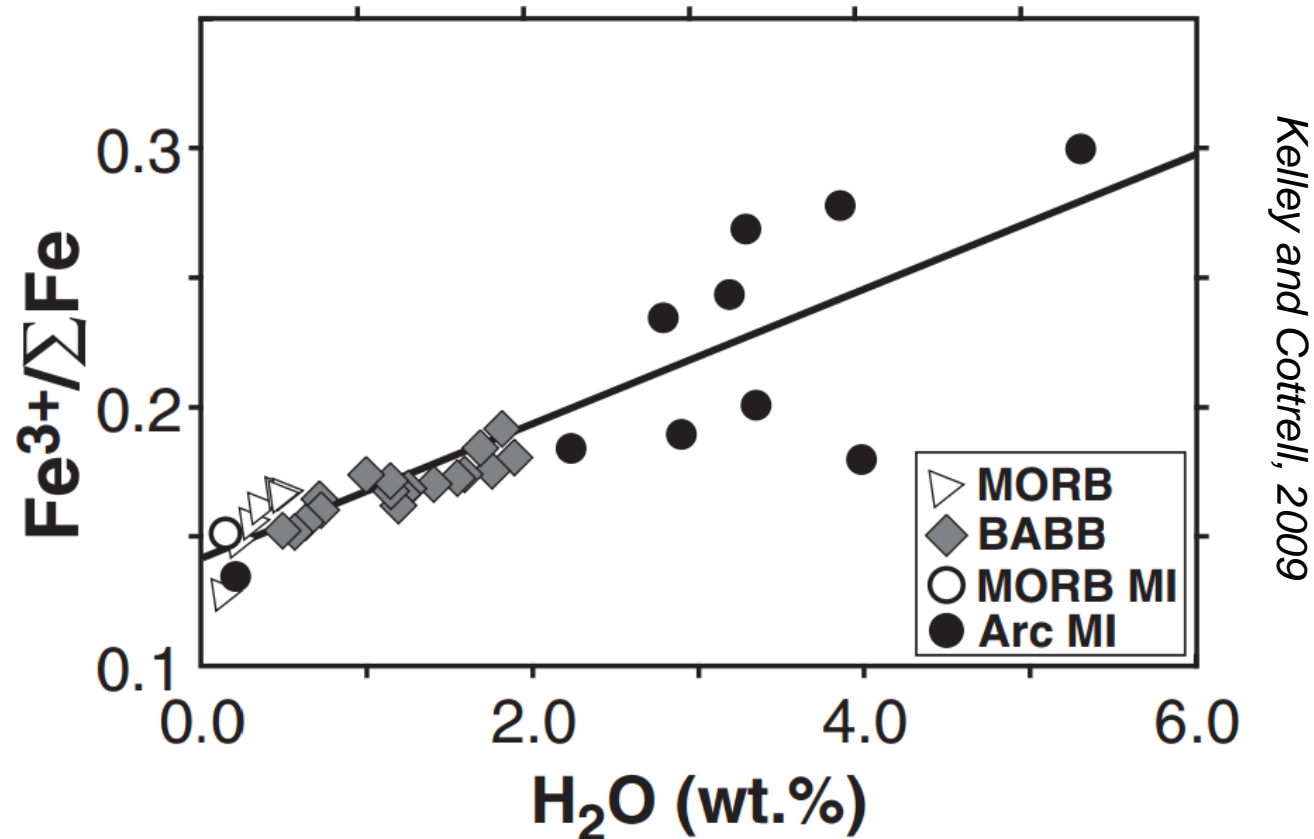**BUT** MORBs are **not** in equilibrium with their mantle sources…

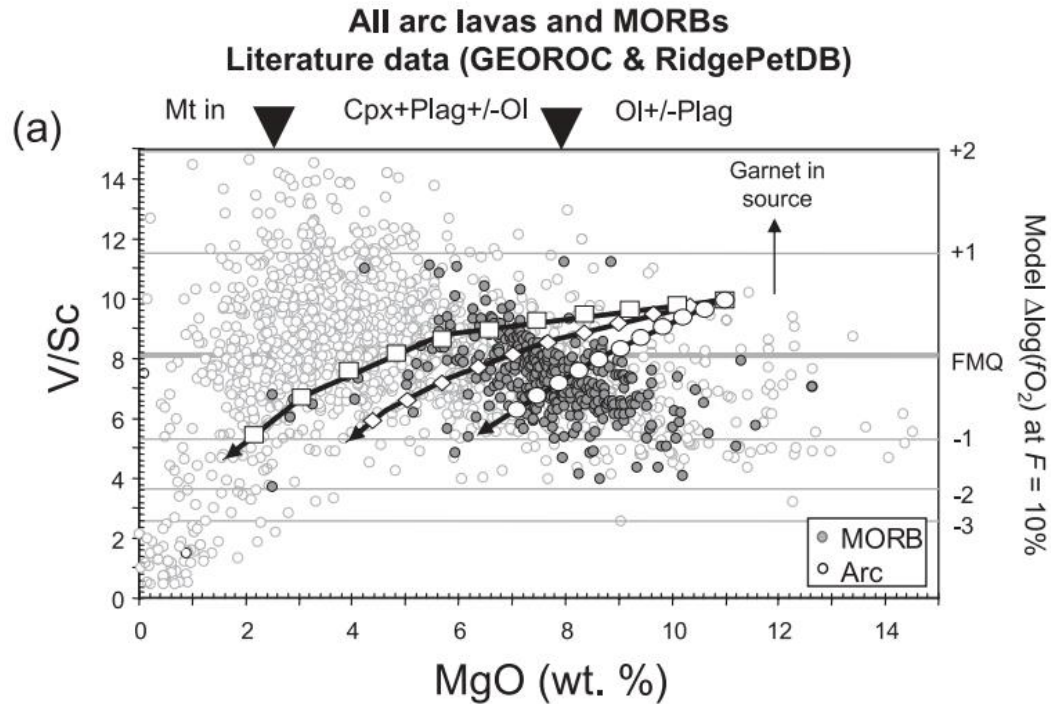Correcting for olivine fractionation, iron isotope composition of MORB ~ 40 % lower

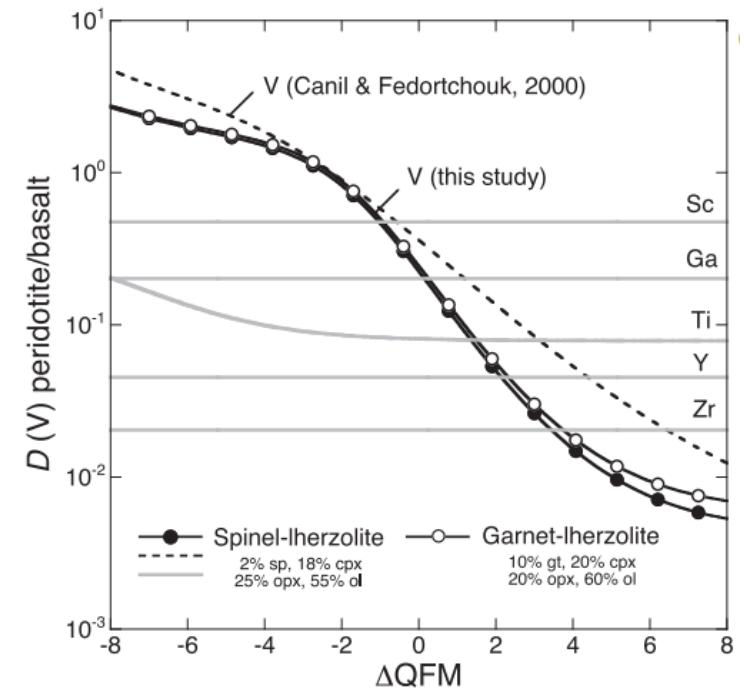# Iron isotopes in magmas – Arcs vs. MORBs

Kelley and Cottrell, 2009

Arcs magmas are more oxidised than MORBs

How do they acquire this?

V/Sc – Arcs vs. MORBs
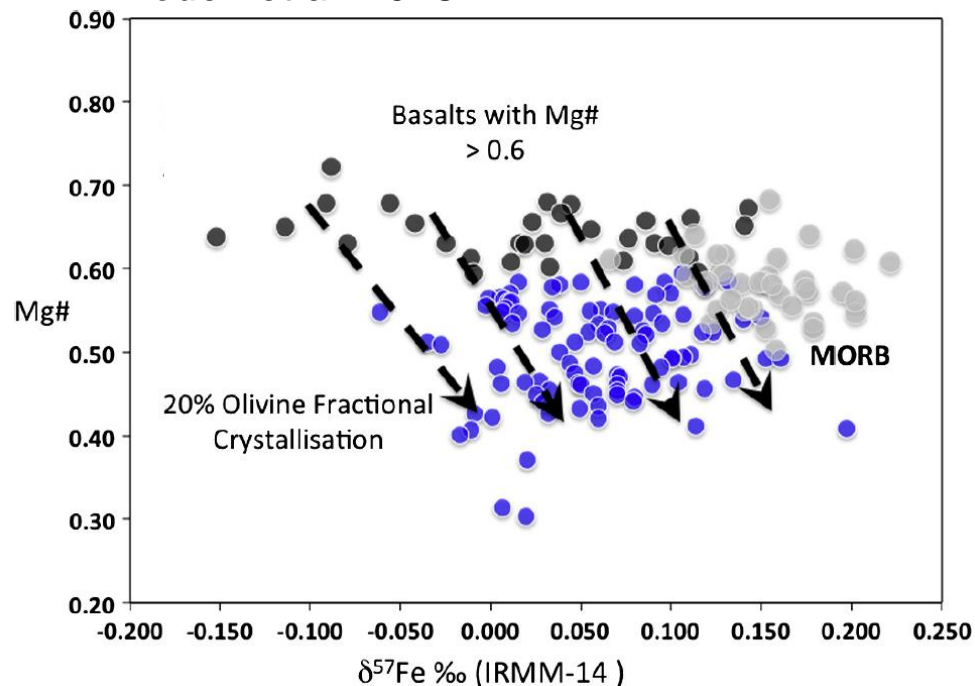

Lee et al. (2005)

Mallmann and O'Neill 2009

Suggests the redox state of arc magmas and MORBs is identical

Iron Isotopes in Arc Magmas

Foden et al. 2018

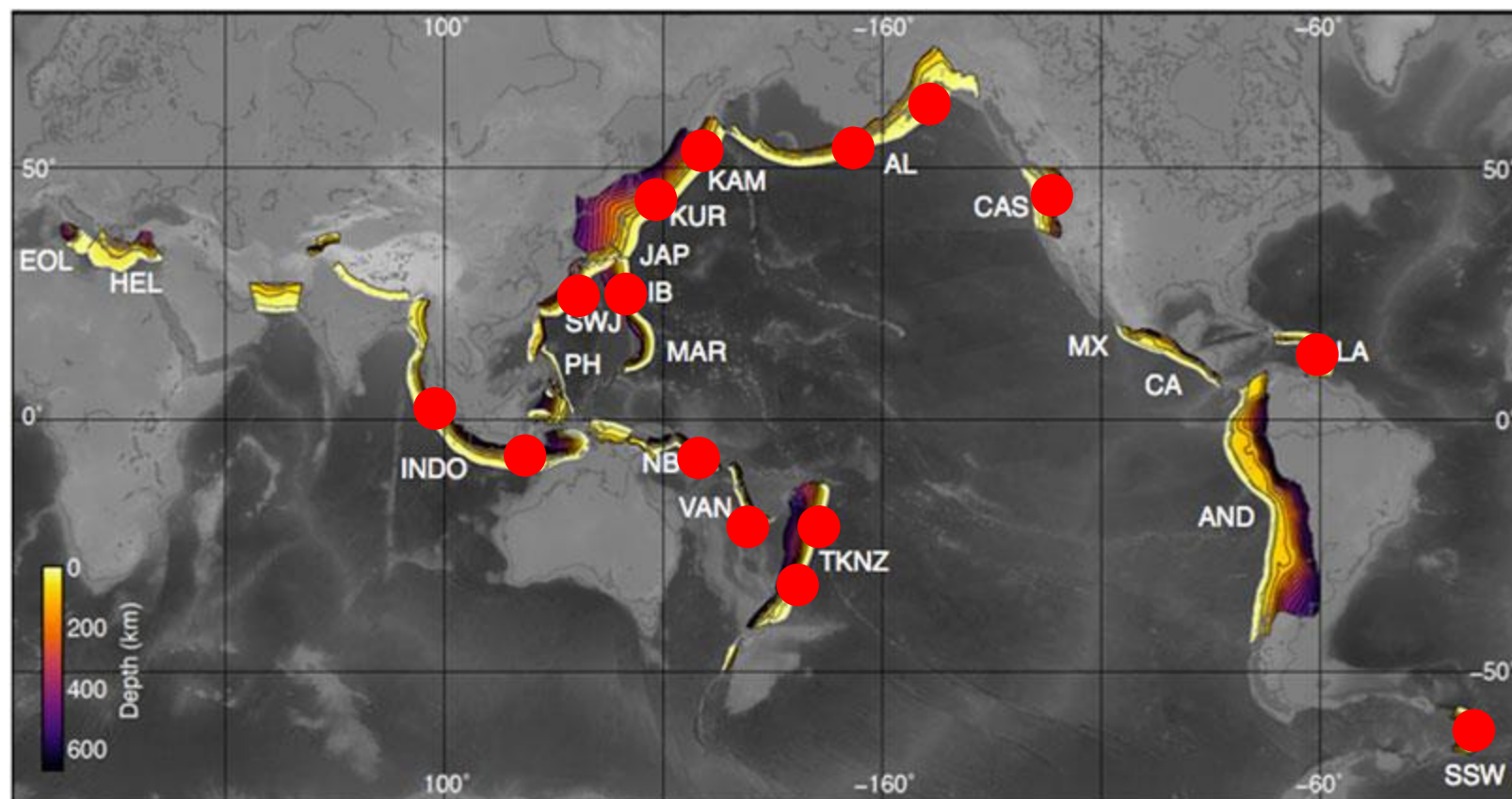For a more oxidised source, arc magmas should be **heavier** than MORB

Opposite is observed

Fractionation (down to -0.05) is **larger** than produced by partial melting alone

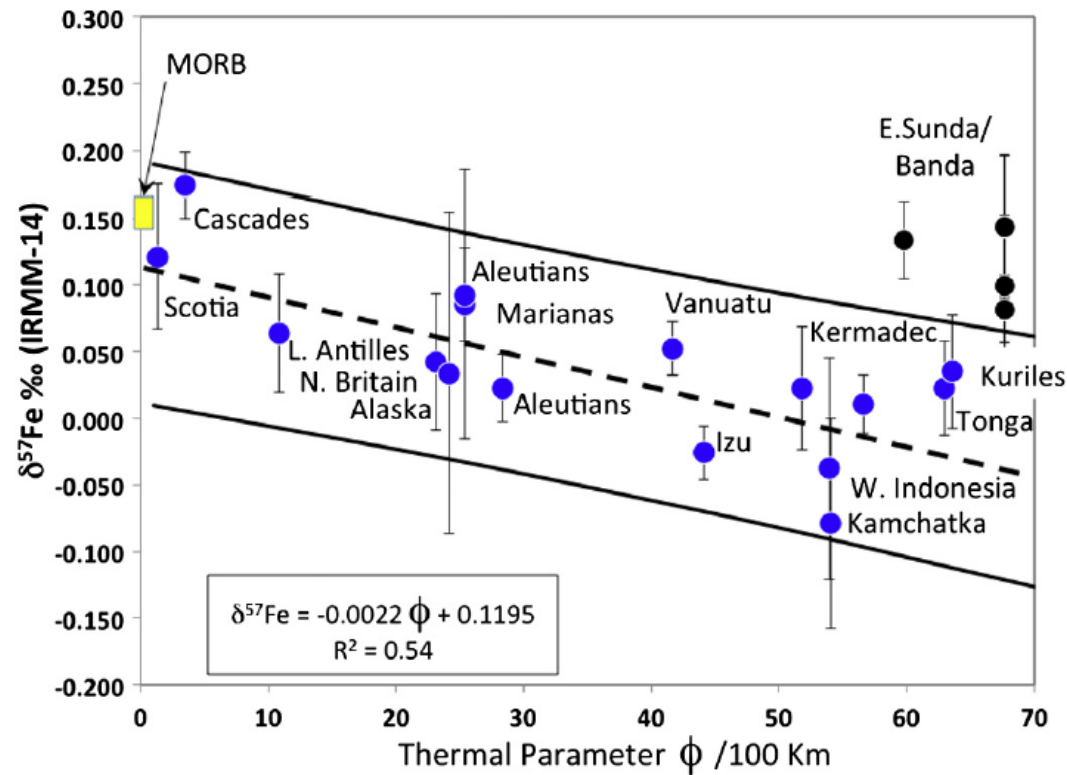*If* arc magma sources were oxidised then Fe is **not** the source of such oxidation → S

Variation with tectonic setting?

Leeman 2020

Arc Magmas

Foden et al. 2018

Φ = slab age (yr) × vertical descent velocity (km/yr)

Cold, old arcs = light
Young, hot arcs = MORB

Conclusions

- **Equilibrium** stable isotope fractionation is caused by differences in **vibrational** frequencies

- Frequency depends on 'force' constant of elements in the bond –**oxidation** state, **co-ordination**, **covalence**, **spin**

- Experiments can provide information on fractionation factors provided at equilibrium (**reversal**, **time series**, **3-isotope**)

- Iron isotope composition of **MORB** explained by **partial melting**

- If **arc magmas** were derived from more **oxidised** mantle than MORB, this oxidation was **not** caused by **Fe**

Iron isotopes – Glasses II
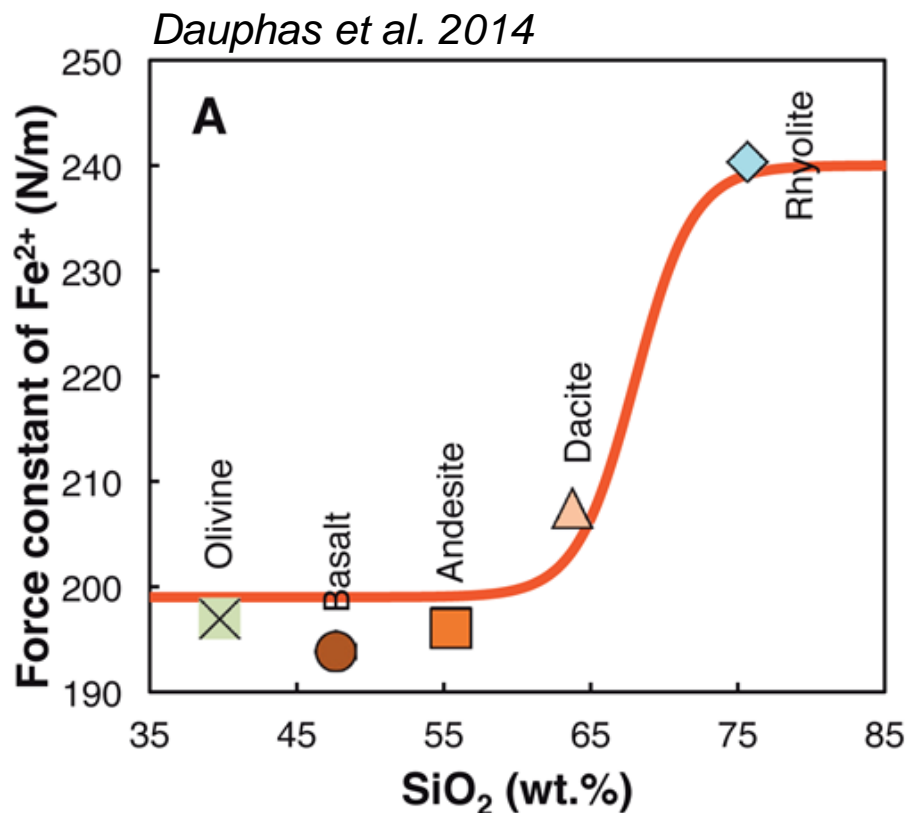
Increasing SiO_2 correlates with increase in K_T at **constant** Fe^{2+}

Likely related to change in structural environment of Fe^{2+}

Addition of Na and K decreases mean co-ordination # of Fe (Jackson et al. 2005; Knipping et al. 2015)

Determination of Force Constants

Estimation of Force Constant (K_T)
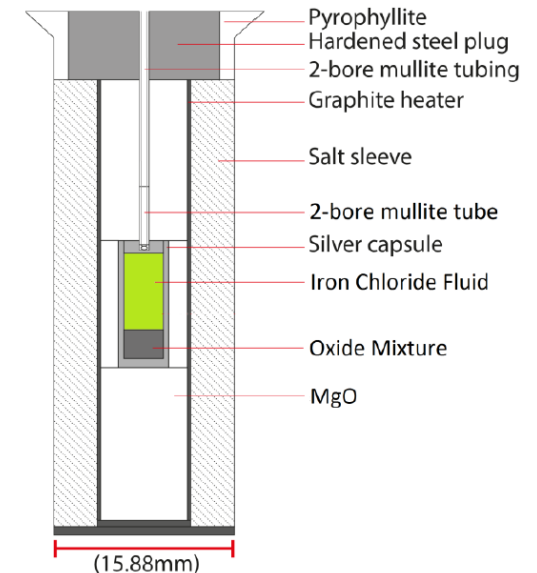- Experimentally
- Spectroscopically
- Ab-initio calculations

Approach of Sossi & O'Neill, 2017

$$\delta^{57}Fe_{min1} - \delta^{57}Fe_{fluid} = \Delta^{57}Fe_{min1-fluid}$$

$$\delta^{57}Fe_{min2} - \delta^{57}Fe_{fluid} = \Delta^{57}Fe_{min2-fluid}$$

For [Fe_{fluid}] >> [Fe_{min}] then

$$\Delta^{57}Fe_{min1-min2} = \delta^{57}Fe_{min1} - \delta^{57}Fe_{fluid} - \delta^{57}Fe_{min2} + \delta^{57}Fe_{fluid}$$

Pyrophyllite
Hardened steel plug
2-bore mullite tubing
Graphite heater

Salt sleeve

2-bore mullite tube
Silver capsule
Iron Chloride Fluid

Oxide Mixture

MgO

(15.88mm)

Experimental approaches – Oxygen fugacity

fO_2 = fugacity of oxygen (=partial pressure for ideal gas)

6 $Fe^{3+}_2O_3$ → **4** $Fe^{2+}Fe^{3+}_2O_4 + O_2^0$

hematite   →   magnetite + oxygen gas

$\Delta G°_{hem-mag(T,P)}$ = - RT ln $K_{hem-mag}$

$\Delta G°_{hem-mag(T,P)}$ = -RT ln $\left(\frac{[aFe_3O_4]^4 \cdot [fO_2]}{[aFe_2O_3]^6}\right)$

$-\Delta G°_{hem-mag(T,P)}/RT$ = **4** ln aFe_3O_4 + ln fO_2 − **6** ln aFe_2O_3

$-\Delta G°_{hem-mag(T,P)}/RT$ = **4** ln 1 + ln fO_2 + **6** ln 1

$-\Delta G°_{hem-mag(T,P)}/RT$ = ln fO_2

Controls phase stability in a chemical system