AMS SFIS “Calcul atomistique du fractionnement isotopique”
Toulouse, 9 juin 2015

# Fractionnement isotopique du fer dans les minéraux et du magnésium entre minéral et solution

Marc Blanchard

# PLAN

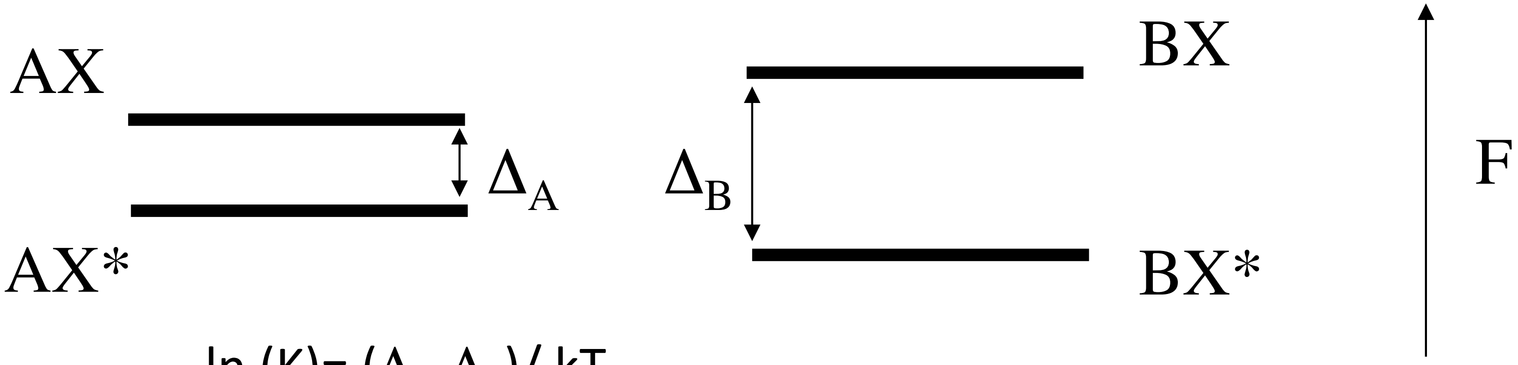
- Theoretical isotopic fractionation
- Fe isotope fractionation in minerals: DFT – Mössbauer – NRIXS
- Mg isotope fractionation between aqueous solution and carbonate minerals
- Isotopic signature of chemical impurities in minerals: Mg and sulfate in calcium carbonates

# THEORETICAL ISOTOPIC FRACTIONATION

An essential basis for interpreting isotopic compositions in natural samples is to know the equilibrium isotopic fractionation factors

X isotope exchange between phase A and phase B:

$$AX + BX^{*} \leftrightarrow AX^{*} + BX$$



$$\ln(K) = (\Delta_A - \Delta_B) / kT$$

$$F = -kT \ln(Q) \Rightarrow K = (Q_{AX^*}/Q_{AX})/(Q_{BX^*}/Q_{BX})$$

Mass-dependent equilibrium isotopic fractionation is controlled by vibrational properties.

# The reduced partition functions ratio or *β*-factor

X isotope exchange between phase A and an ideal gas of element X:

$$AX + X^* \Leftrightarrow AX^* + X \qquad \beta(A,X) = \frac{\left(n_{X*}/n_X\right)_A}{\left(n_{X*}/n_X\right)_{gas}}$$

$$10^3 \ln \alpha\left(A,B,X\right) = 10^3 \ln \beta\left(A,X\right) - 10^3 \ln \beta\left(B,X\right)$$

## From vibrational properties

$$\beta(A,X) = \frac{Q(AX^*)Q(X)}{Q(AX)Q(X^*)} \qquad Q = \left[\prod_{i=1}^{3Nat}\prod_{\{q\}}\frac{e^{-h\nu_{q,i}/(2kT)}}{1-e^{-h\nu_{q,i}/(kT)}}\right]^{1/N_q}$$

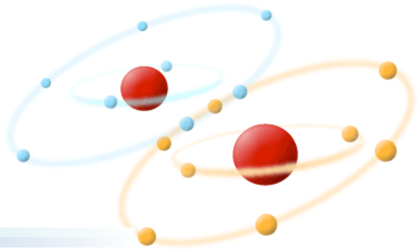
## From the kinetic energy

$$\frac{\partial F}{\partial m} = -\frac{\langle K\rangle}{m}$$

$$\ln\beta(A,X) = -\frac{3}{2}\ln\left(\frac{m^*}{m}\right) + \frac{1}{k_B T}\int_m^{m^*}\frac{\langle K(m')\rangle}{m'}\,dm'$$

- Path Integral Molecular Dynamics
- Mössbauer, Nuclear Resonant Ineastic X-ray Scaterring (NRIXS)

# AB INITIO CALCULATIONS



First-principles calculations determine the electronic structure and the properties of well-defined systems without involving empirical parameters.

- Total energy of the system as a function of the geometry (atomic positions, cell parameters)
- Solution of the Schrödinger equation for a system of nuclei and electrons: density functional theory (DFT)
- The relaxed structure corresponds to the minimum of the total energy (accuracy w.r.t. exp. ≈ few %)
- Derivatives of the total energy w.r.t. the atomic positions and/or the electric field lead to the properties

DFT = Exact theory but its application requires approximations:

- Generalized Gradient Approximation (PBE)
- Plane-waves basis set (periodic system, cutoff)
- Calculation restricted to valence electrons (pseudo-potentials)
- Optionally, addition of a Coulomb repulsion between electrons at the same atomic orbitals = Hubbard U

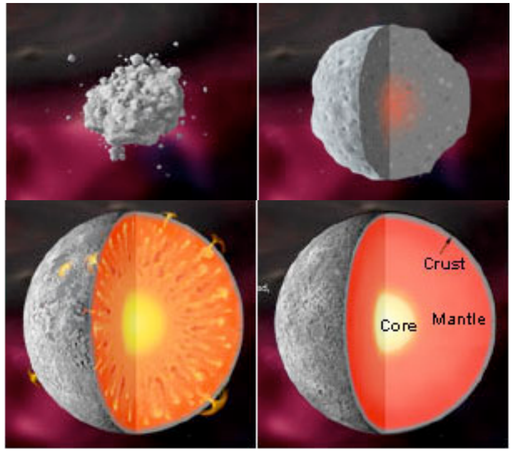
Codes PWscf, CP and PHonon (Quantum-espresso package)

# FE ISOTOPE FRACTIONATION IN MINERALS:
# DFT – MÖSSBAUER - NRIXS

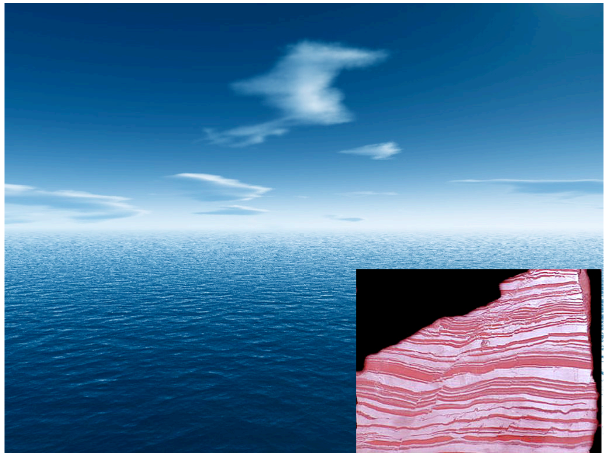
$^{54}$Fe (5.84 %), $^{56}$Fe (91.76 %), $^{57}$Fe (2.12 %), $^{58}$Fe (0.28 %)

⇒ **Proxy complementary to traditional stable isotopes**

The most important Fe isotope fractionations occur in low-T environments and with redox gradients.



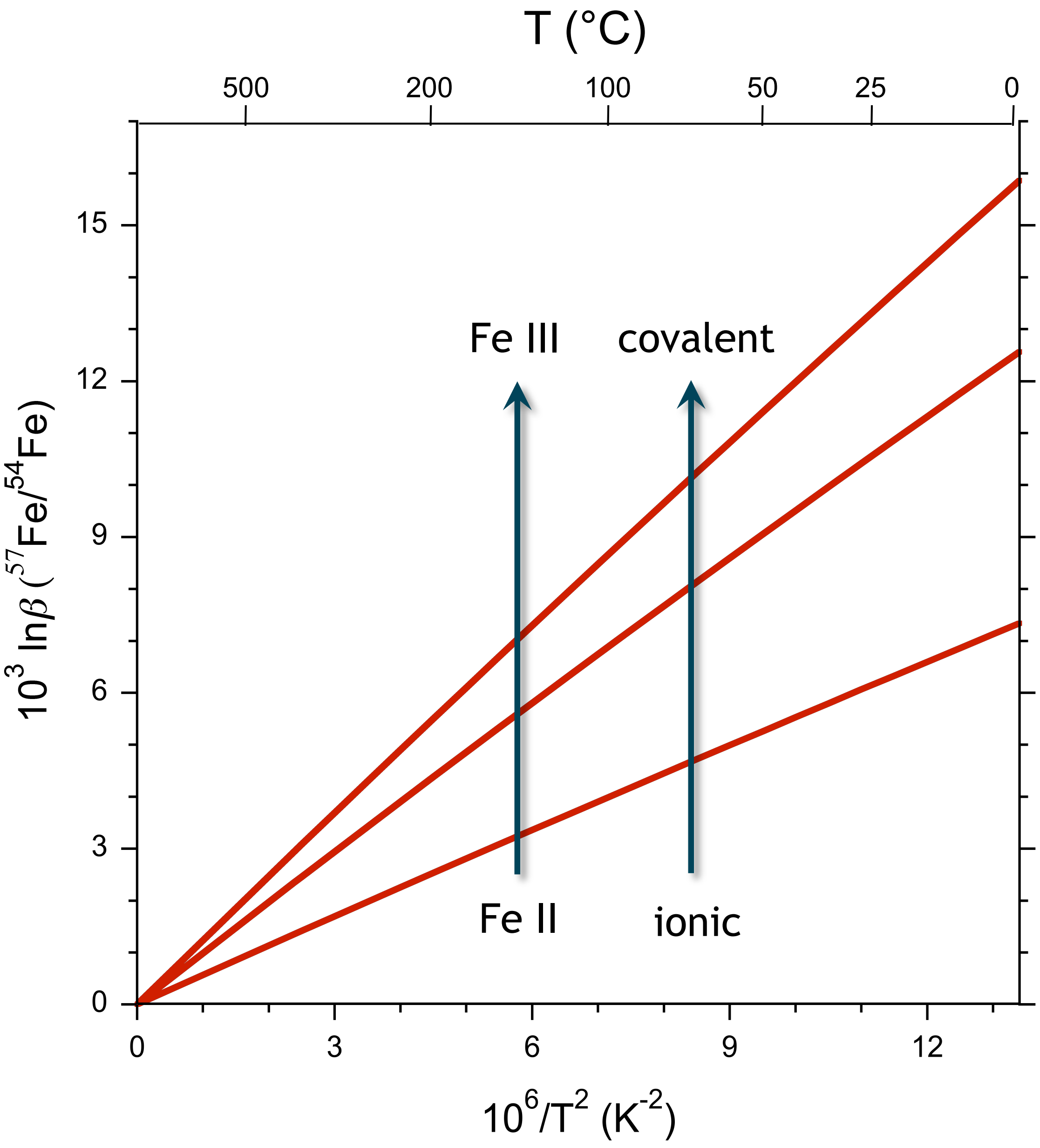
Planetary formation



Redox evolution of the ocean

Laterite, Brazil

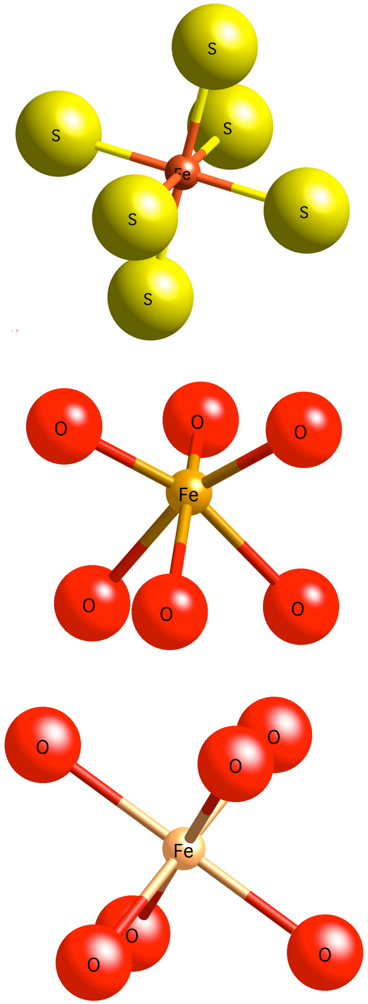
# Parameters controlling the Fe $\beta$-factor in minerals



Pyrite
$FeS_2$

Hematite
$Fe_2O_3$

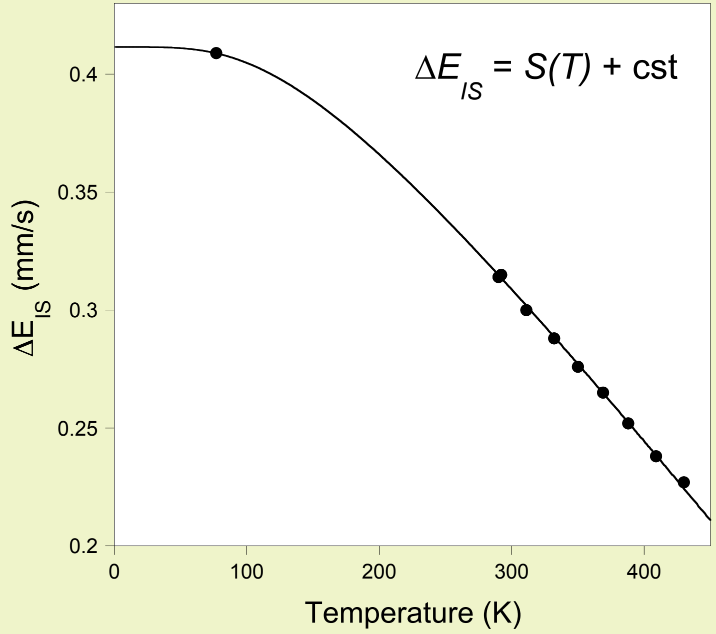
Siderite
$FeCO_3$



Blanchard et al. (2009, GCA)

From 1st order thermodynamic perturbation theory:

$$\ln\beta = \frac{m^* - m}{m}\left(\frac{K}{RT} - \frac{3}{2}\right)$$



In **Mössbauer**, the kinetic energy of the iron sublattice is related to the second-order Doppler shift (*S(T)*)

$$S(T) = -\frac{K(T)_{^{57}Fe}}{m\,c}$$

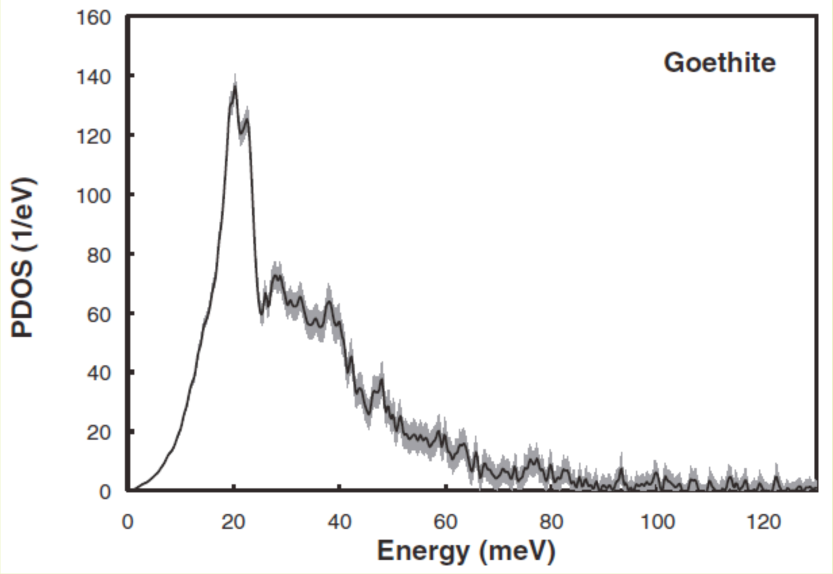
velocity of light

In **Nuclear Resonant Inelastic X-ray Scattering** (NRIXS), the kinetic energy is related to the partial vibrational density of state (PDOS)

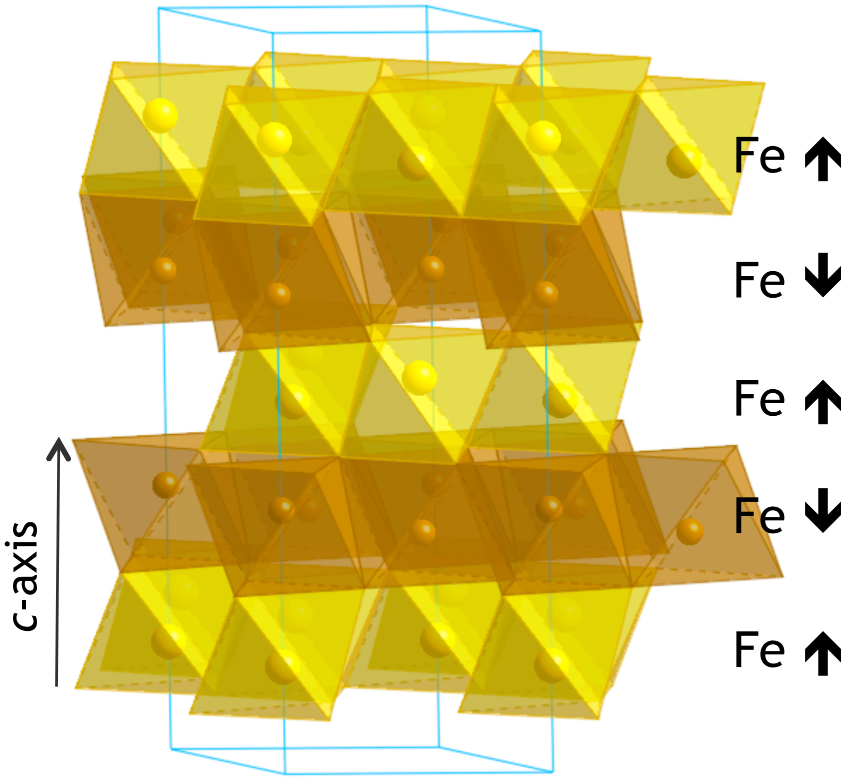
$$K_{^{57}Fe} = \frac{3}{2}\int_0^{e_{\max}} E(e,T)\,g(e)\,de$$

Einstein function

PDOS norm. to 1



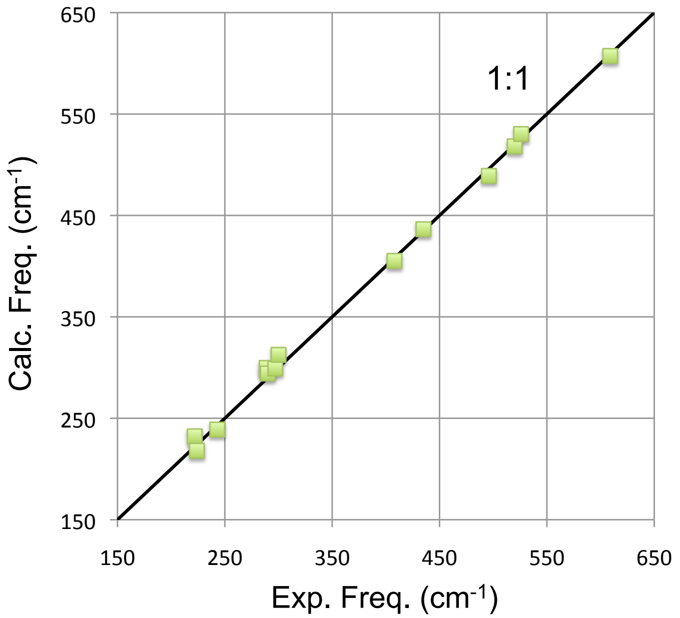
**Hematite** ($\alpha$-$Fe_2O_3$), rhombohedral sym., antiferromagnetic

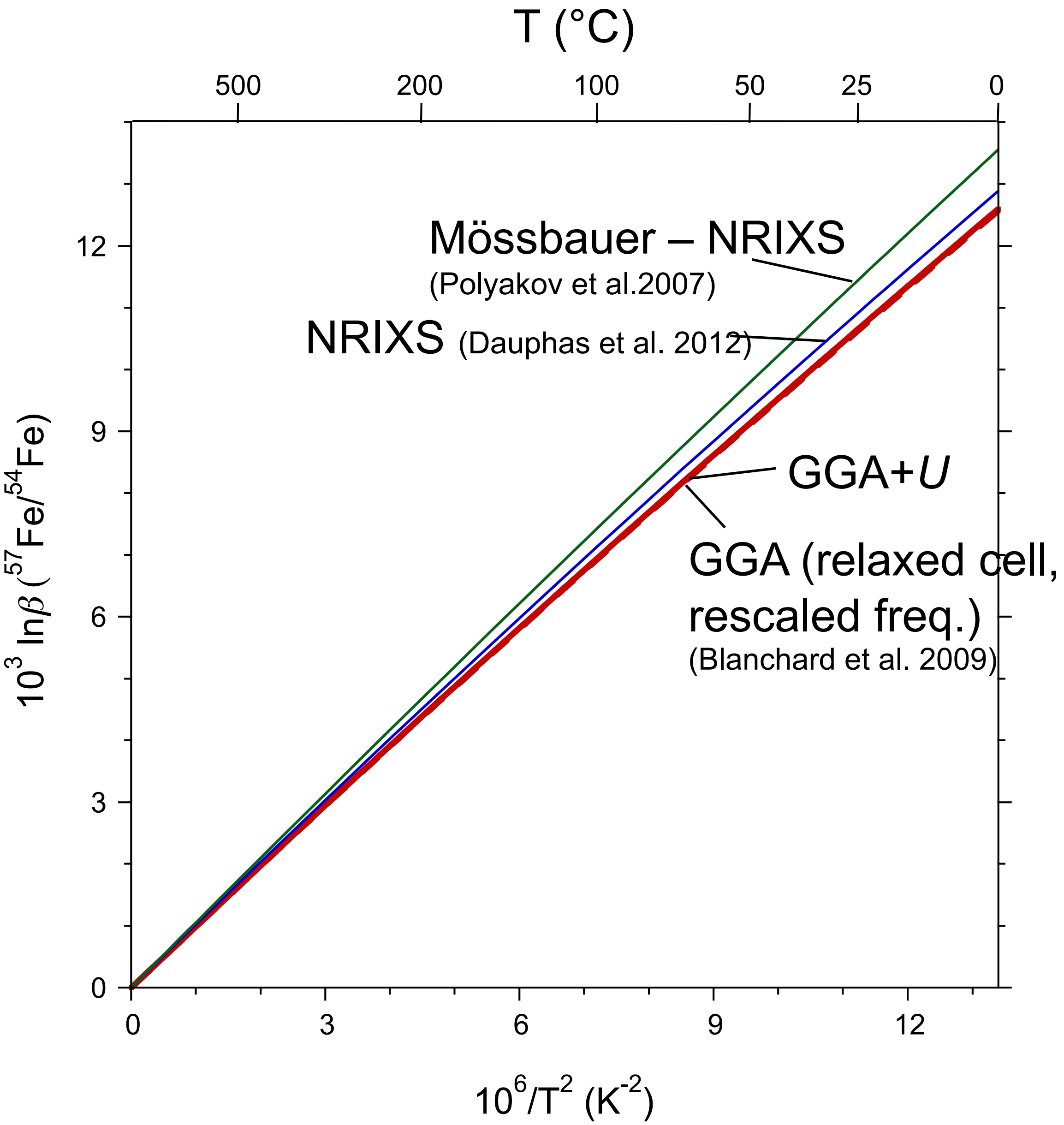


Atomic positions

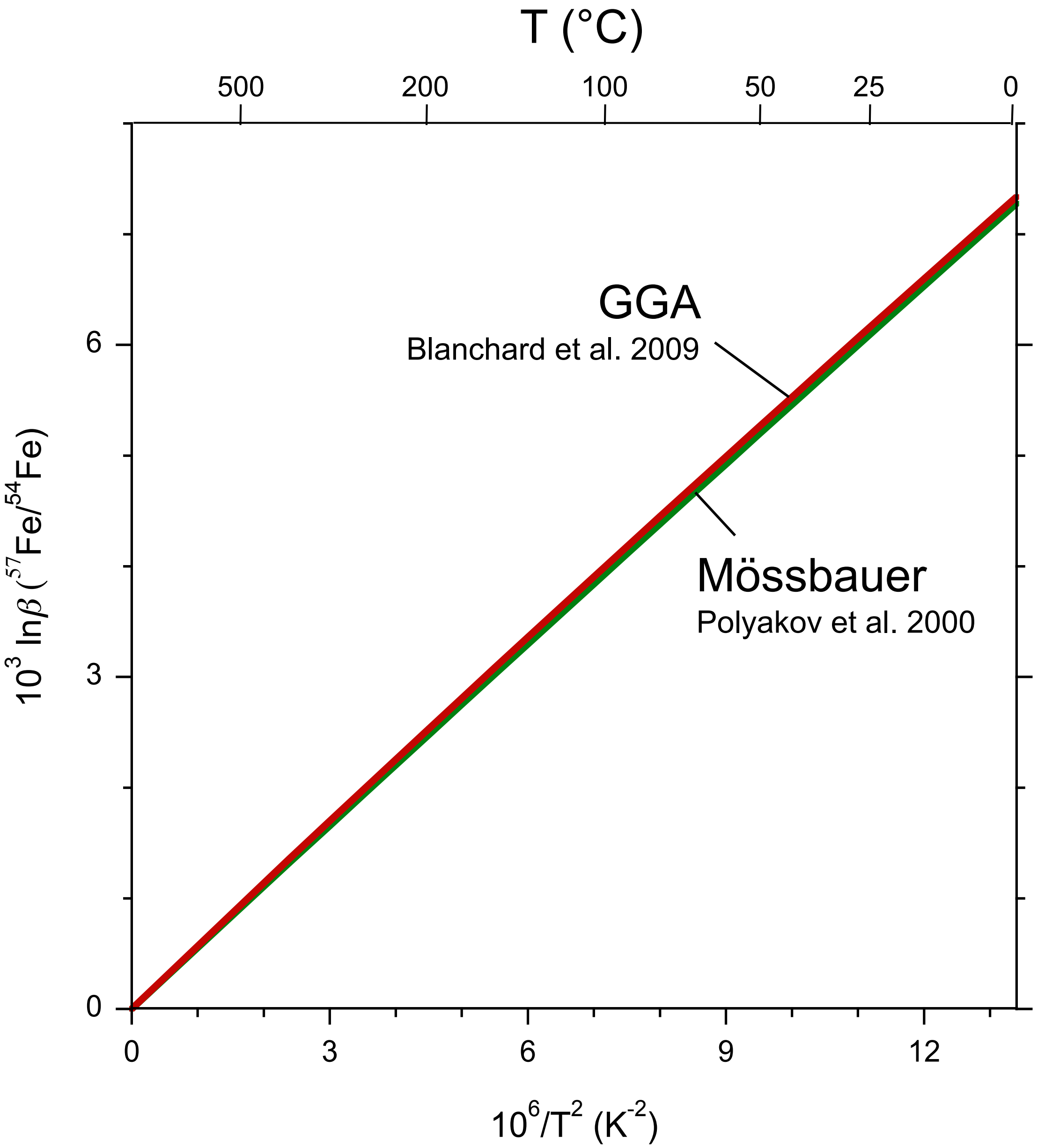
| | $x_{Fe}$ | $x_O$ |
|---|---|---|
| Calc. | 0.1449 | -0.0558 |
| Exp. | 0.1447 | -0.0556 |

Raman and IR frequencies

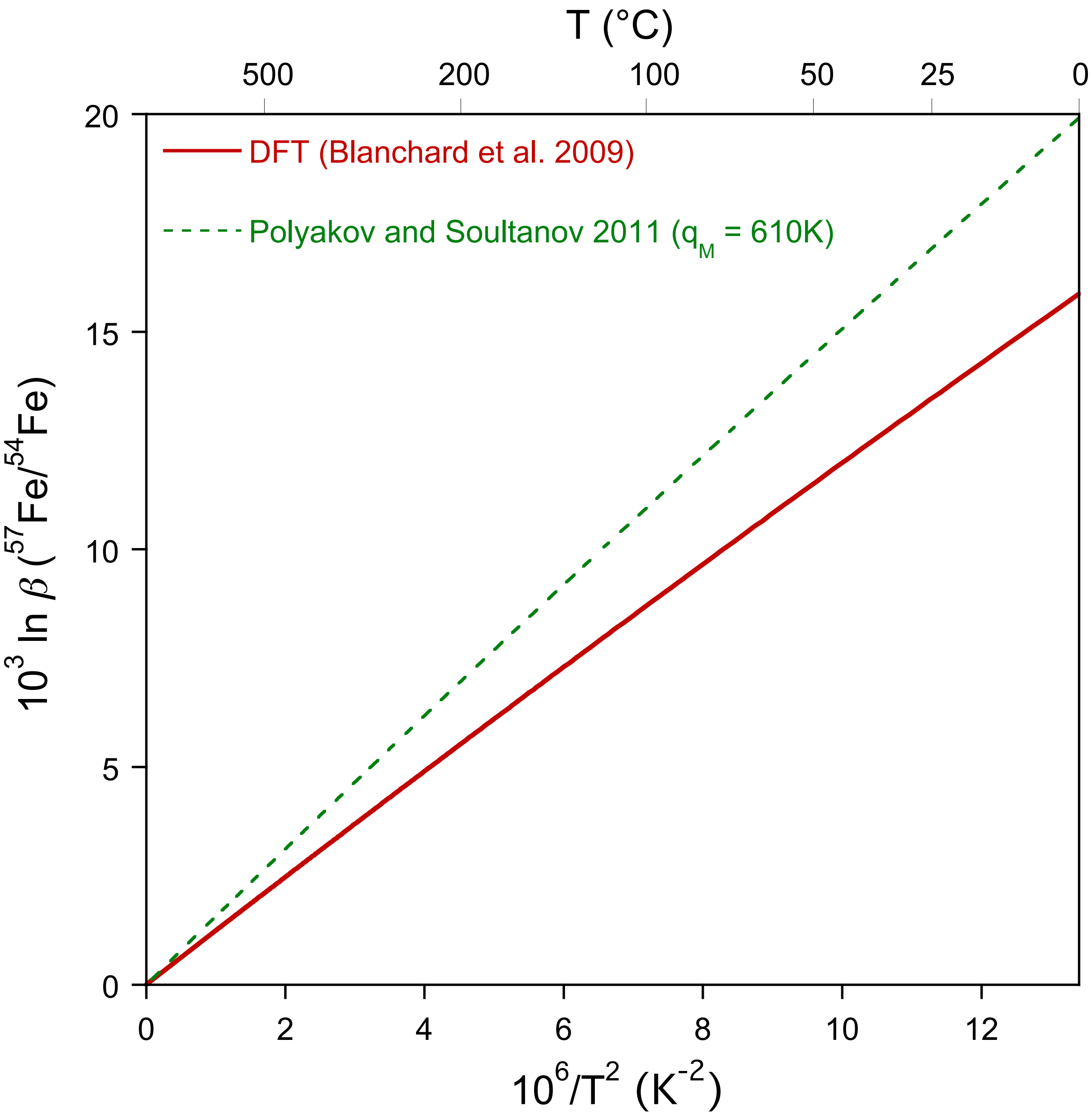



T (°C)
500
200
100
50
25
0
Mössbauer – NRIXS
(Polyakov et al.2007)
NRIXS (Dauphas et al. 2012)
GGA+U
GGA (relaxed cell, rescaled freq.)
(Blanchard et al. 2009)
$10^3 \ln\beta\,(^{57}Fe/^{54}Fe)$
0
3
6
9
12
$10^6/T^2\ (K^{-2})$

## **Siderite** ($FeCO_3$), rhombohedral sym., antiferromagnetic

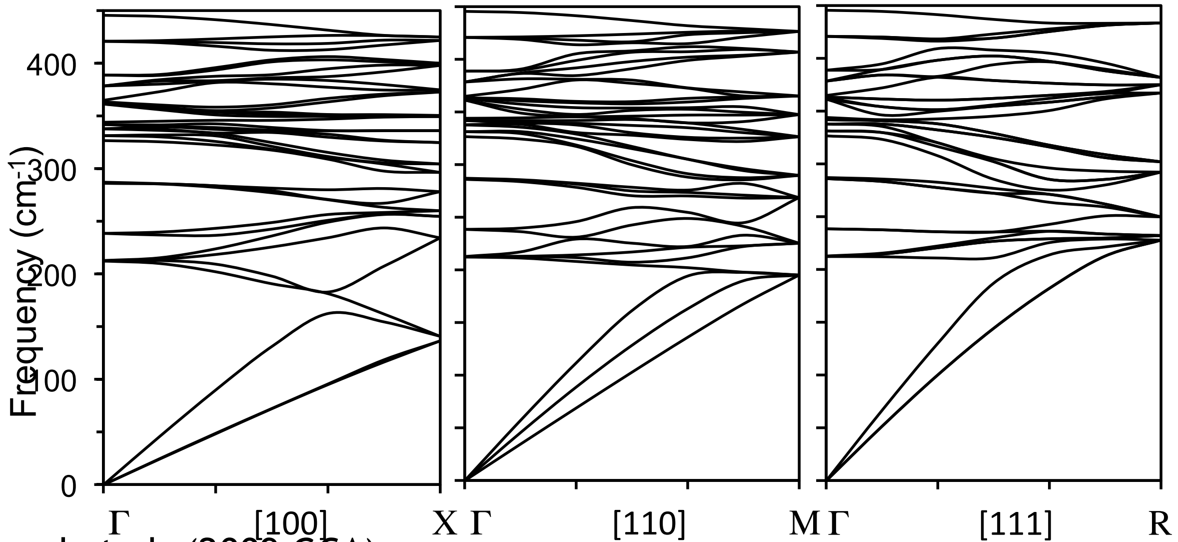


## **Pyrite** ($FeS_2$), cubic sym., diamagnetic



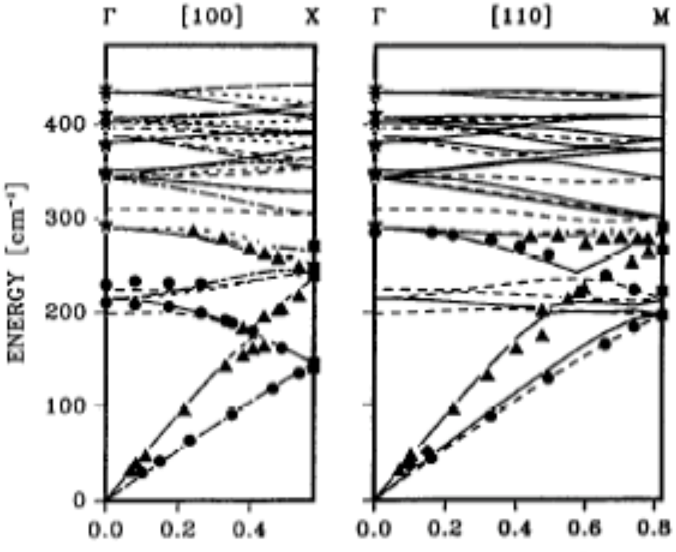
# Vibrational properties: theory vs. experiment

## Phonon dispersion curves

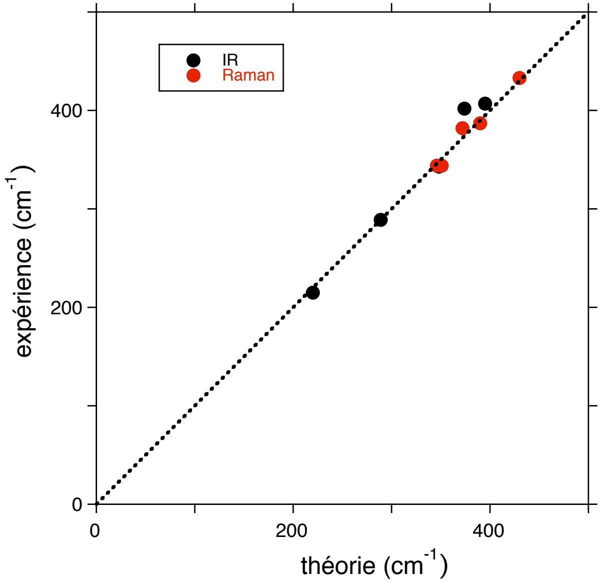


Blanchard et al. (2009 GCA)

IR and Raman frequencies

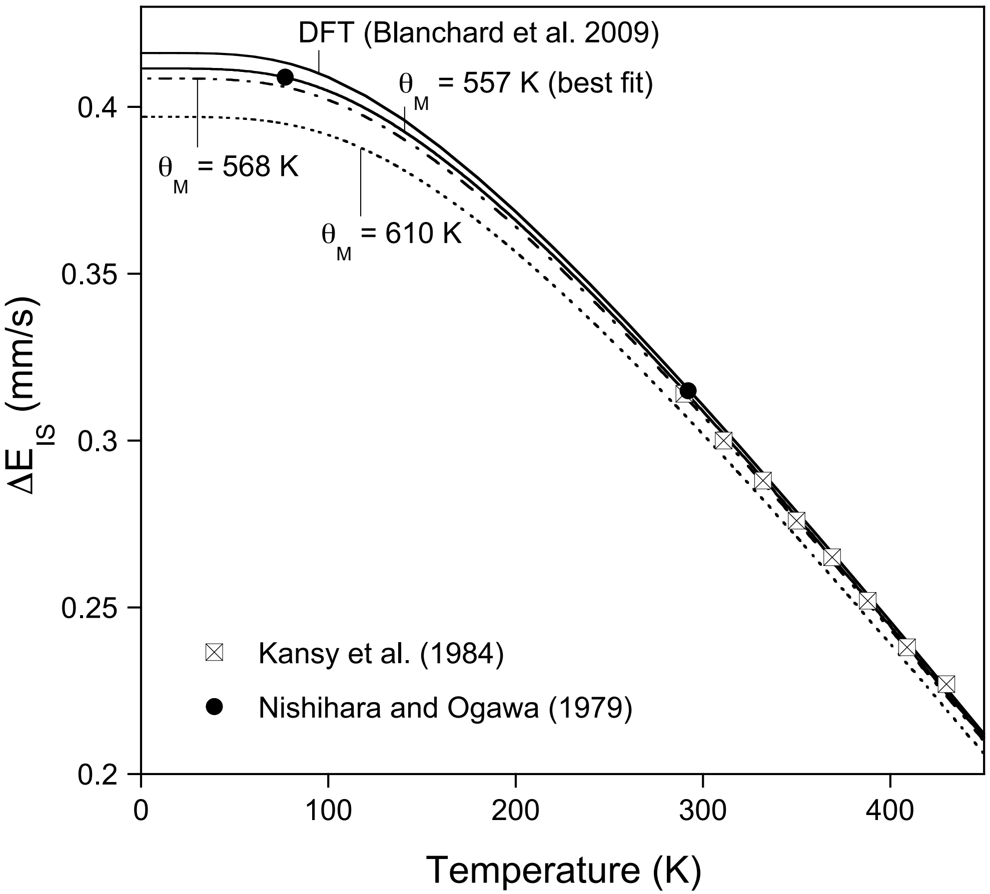


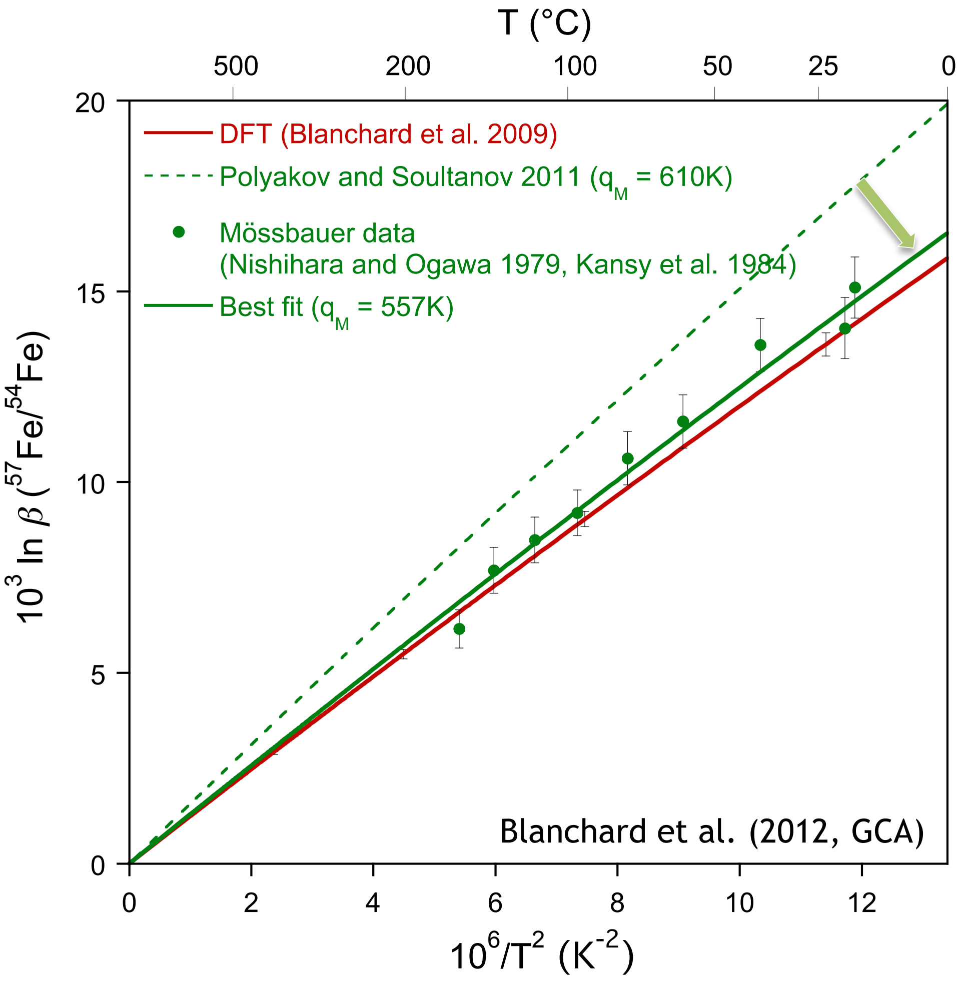
Bührer et al. 1993



# Revision of Mössbauer-derived $\beta$-factor

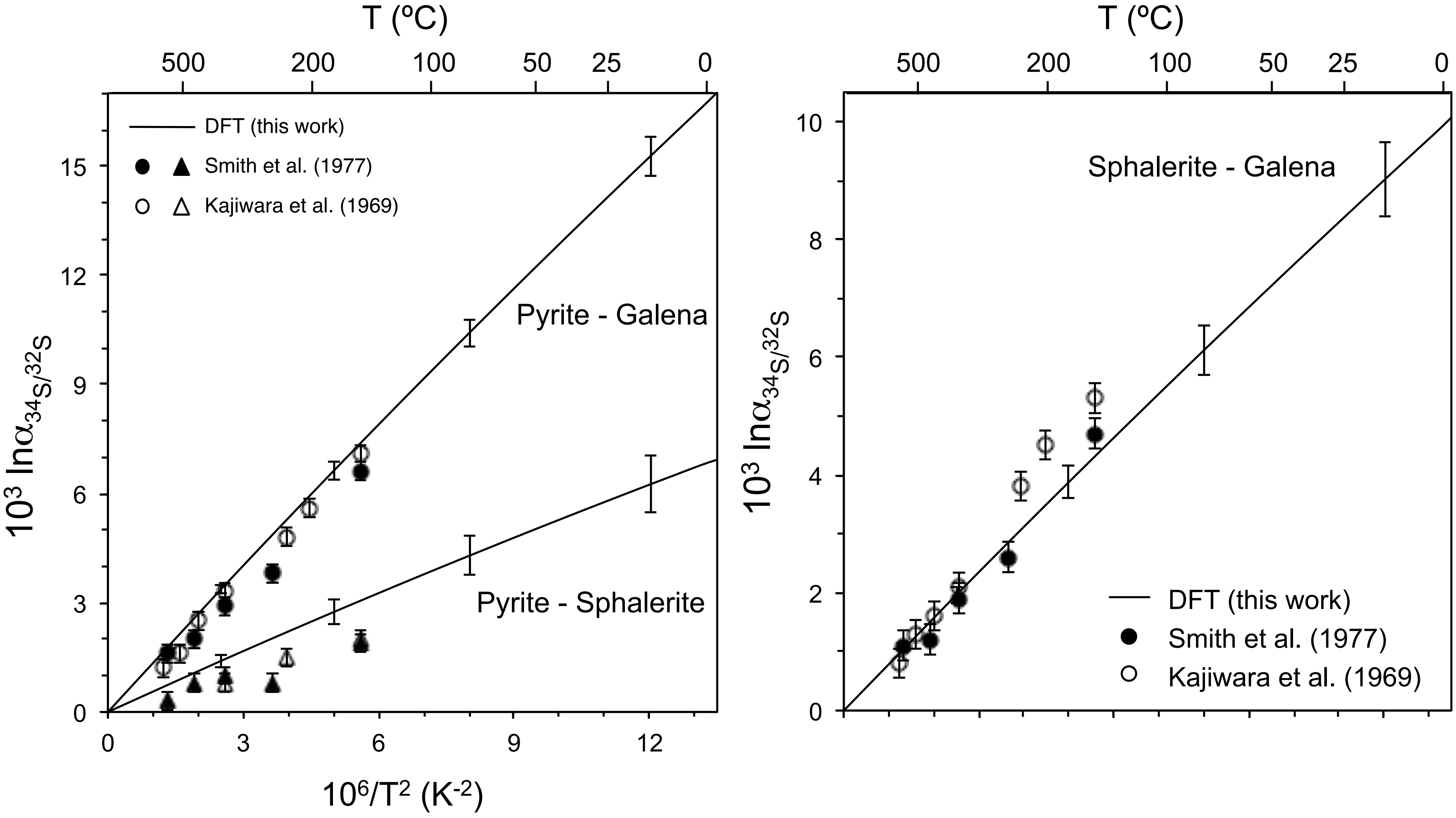
## T dependence of the Mössbauer isomer shift



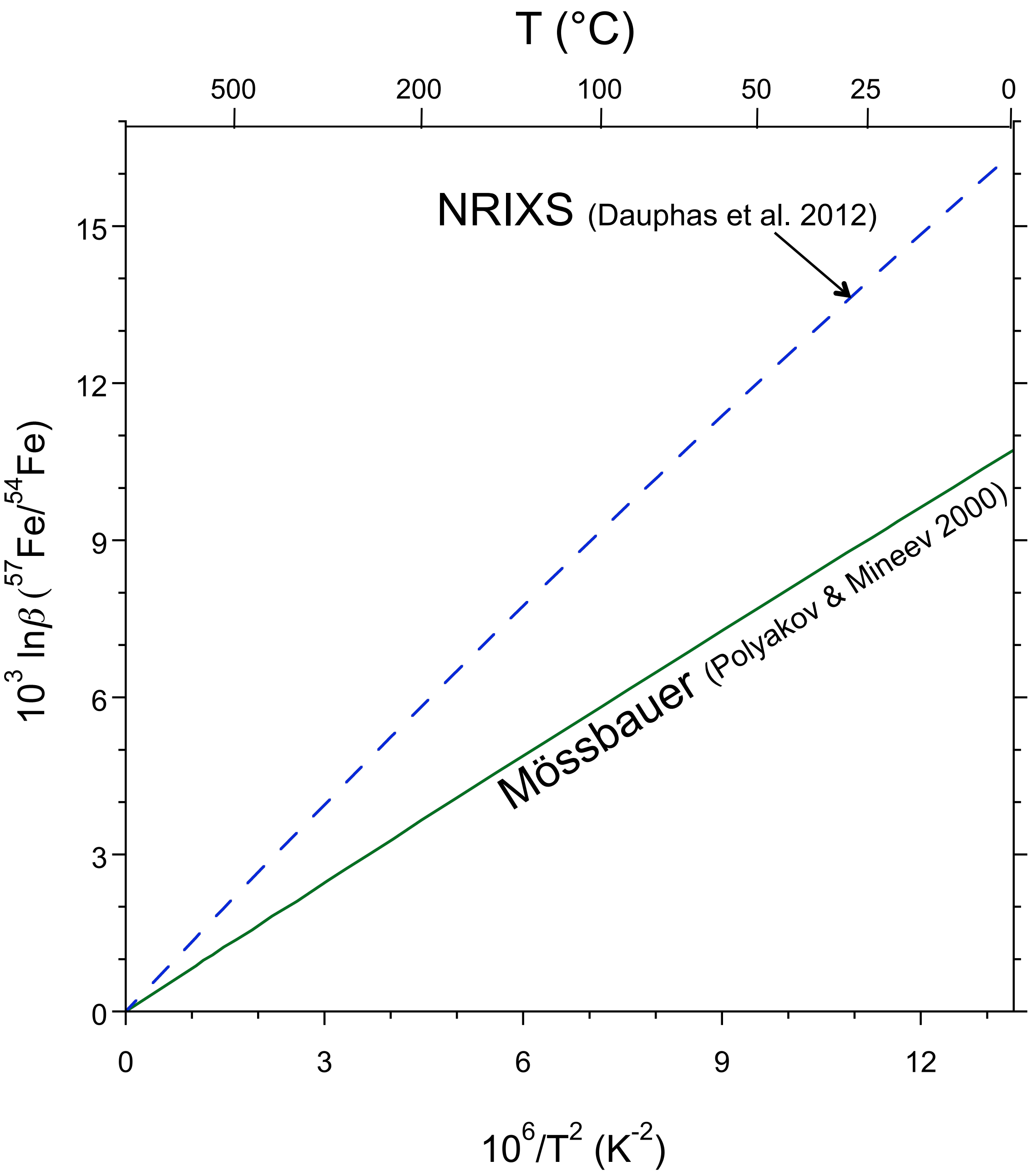


Fe $\beta$-factor of pyrite confirmed by recent NRIXS measurements (Polyakov et al. 2013 Goldschmidt abstract) and experiments (Syverson et al. 2013 GCA)

# Implications for sulfur isotope fractionation

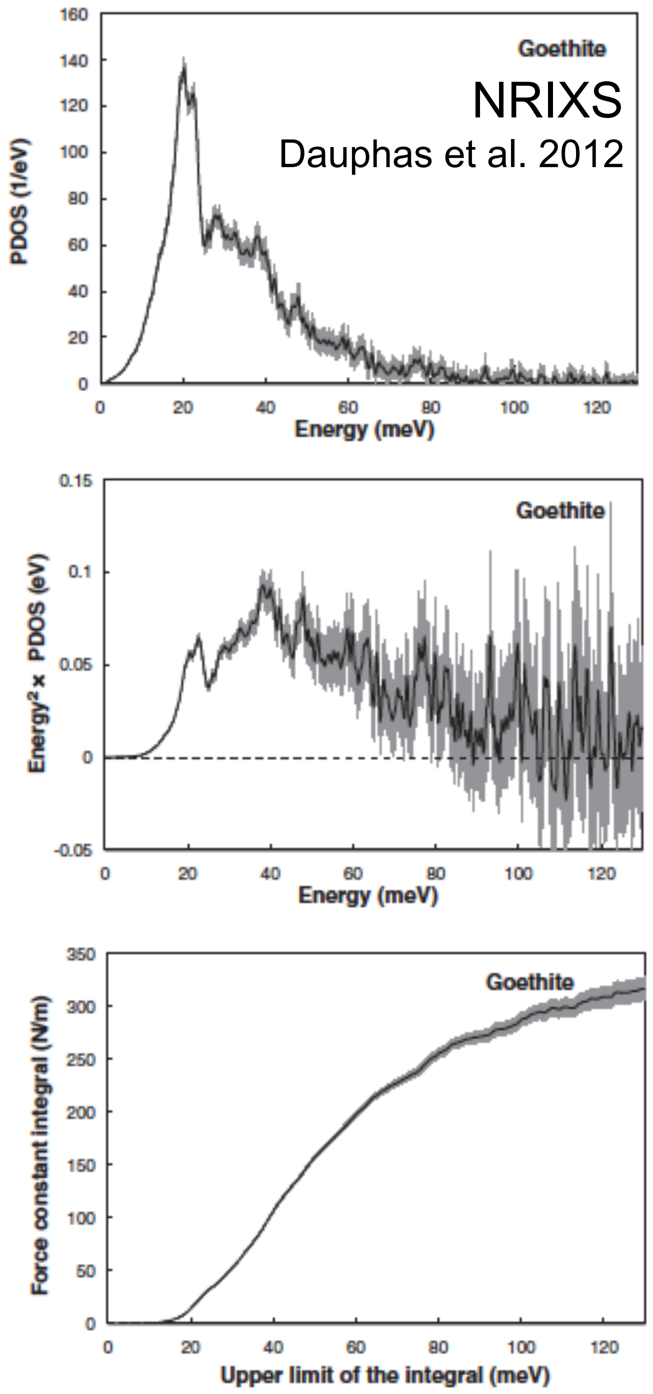


# **Goethite** (α-FeOOH), orthorhombic sym., antiferromagnetic



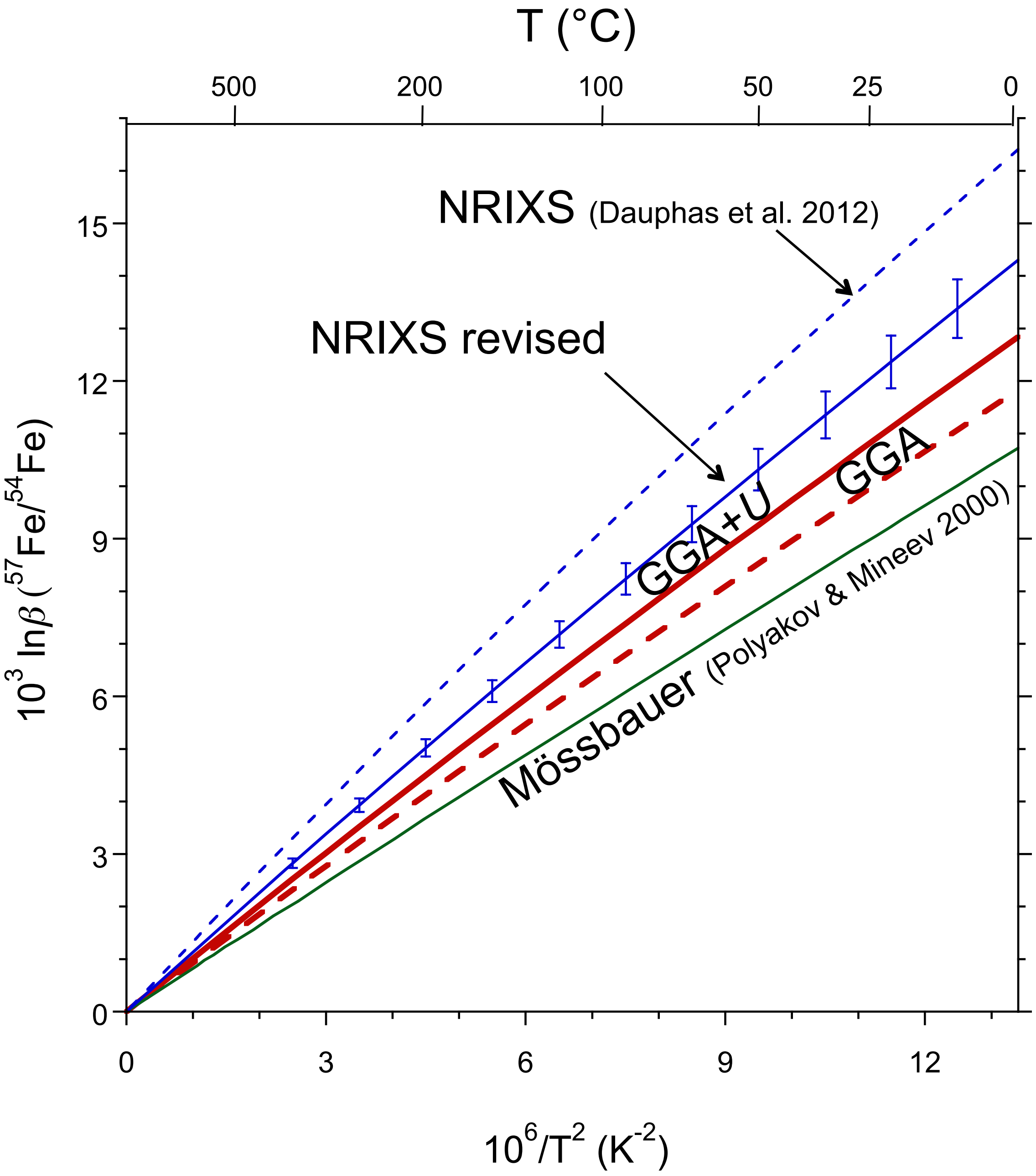
NRIXS (Dauphas et al. 2012)

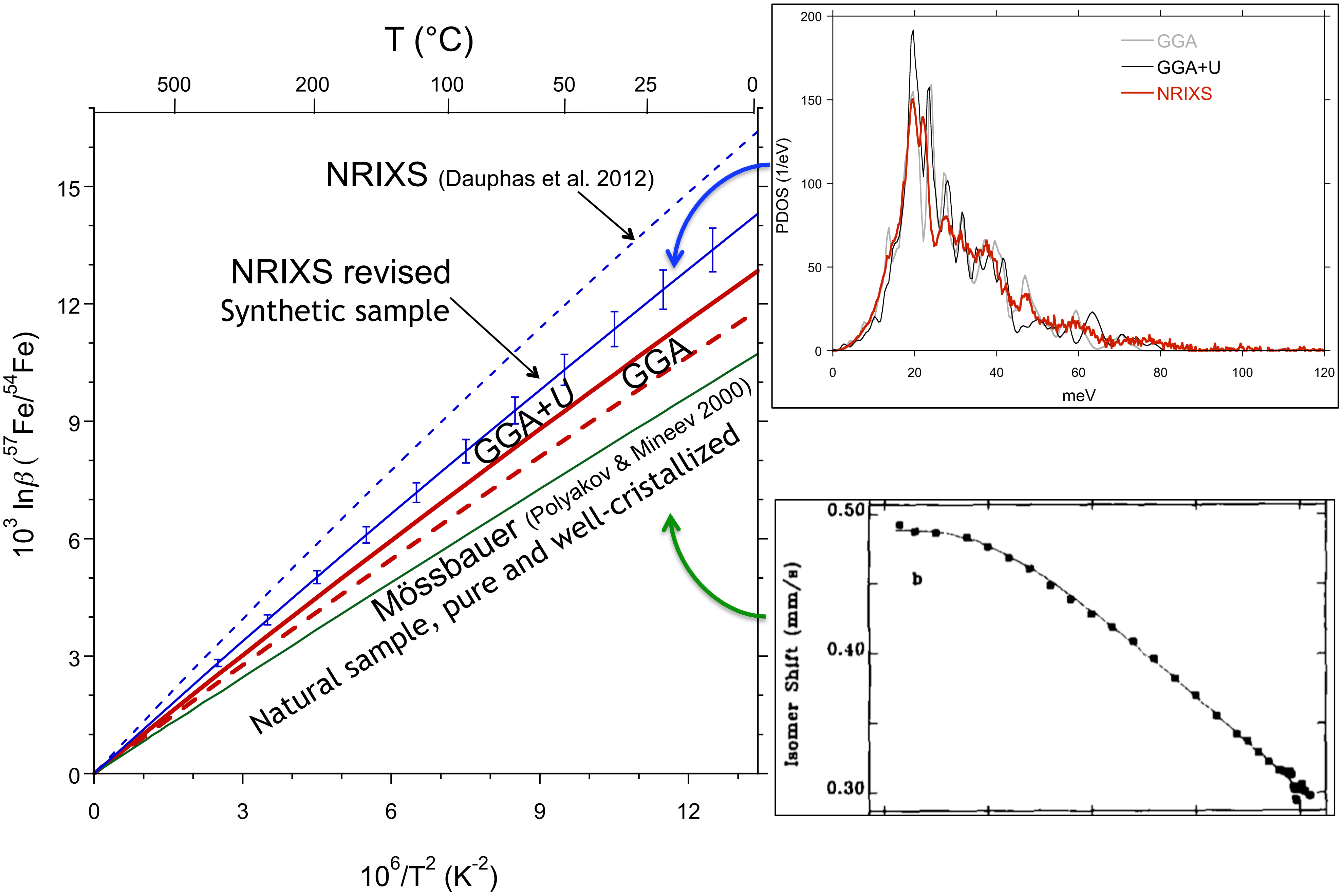
Mössbauer (Polyakov & Mineev 2000)



NRIXS

Dauphas et al. 2012


T (°C)
500
200
100
50
25
0
NRIXS (Dauphas et al. 2012)
NRIXS revised
GGA+U
GGA
Mössbauer (Polyakov & Mineev 2000)
$10^3 \ln\beta\,(^{57}Fe/^{54}Fe)$
0
3
6
9
12
15
0
3
6
9
12
$10^6/T^2$ ($K^{-2}$)


T (°C)
500
200
100
50
25
0
NRIXS (Dauphas et al. 2012)
NRIXS revised
Synthetic sample
GGA+U
GGA
Mössbauer (Polyakov & Mineev 2000)
Natural sample, pure and well-cristallized
15
12
9
6
3
0
$10^3 \ln\beta$ ($^{57}$Fe/$^{54}$Fe)
0
3
6
9
12
$10^6/T^2$ (K$^{-2}$)
200
150
100
50
0
PDOS (1/eV)
GGA
GGA+U
NRIXS
0
20
40
60
80
100
120
meV
0.50
0.40
0.30
b
Isomer Shift (mm/s)

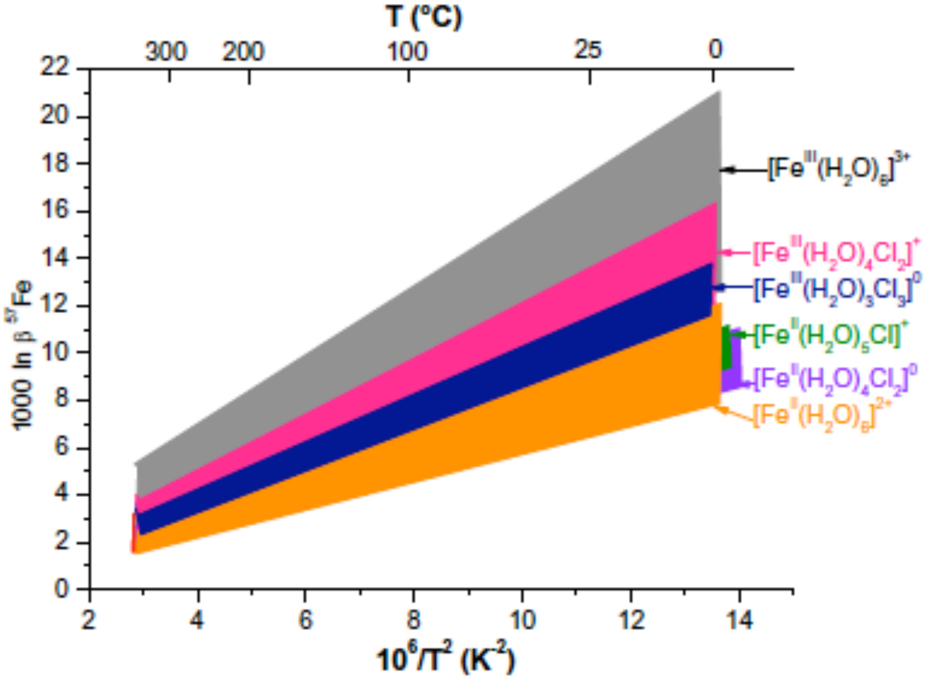
# MG ISOTOPE FRACTIONATION BETWEEN AQUEOUS SOLUTION AND CARBONATE MINERALS

# Solid-liquid reactions are ubiquitous and control many natural processes (like for instance isotopic fractionations)

Theoretical $\beta$-factors of $^{57}$Fe

of iron aqueous complexes

(Saunier et al. 2011)



Challenge:

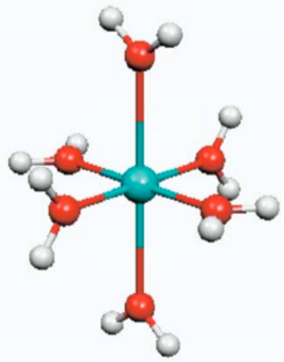
Accurate calculation of isotopic properties of a solvated ion

&

Modeling of both the solid and liquid phase at the same level of theory

# Various theoretical approaches in litterature

- *From a static molecular cluster*



Relaxation of atomic positions

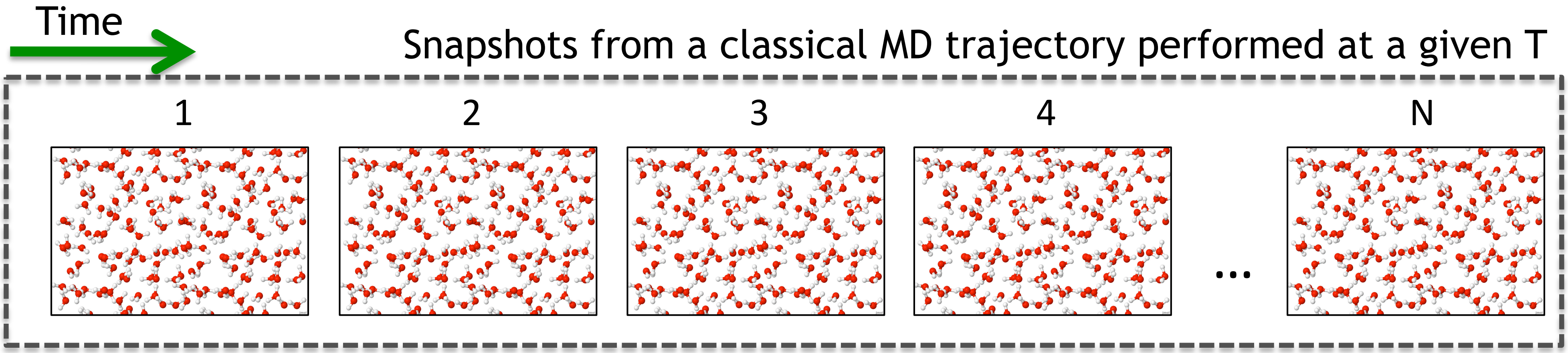
↓

Vibrational properties

↓

$$\beta(A,X)=\frac{Q(AX^{*})Q(X)}{Q(AX)Q(X^{*})} \qquad Q=\left[\prod_{i=1}^{3Nat}\prod_{\{q\}}\frac{e^{-h\nu_{q,i}/(2kT)}}{1-e^{-h\nu_{q,i}/(kT)}}\right]^{1/N_q}$$

- *From a molecular dynamics (MD) simulation*



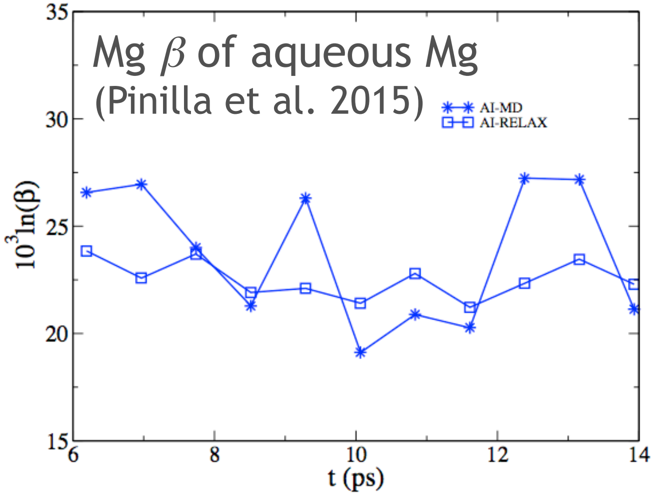
Time

Snapshots from a classical MD trajectory performed at a given T

w/ or w/o relaxation of atomic positions

Vibrational properties

$$\ln(\beta) = \frac{1}{N}\sum_{i=1}^{N}\ln(\beta_i)$$

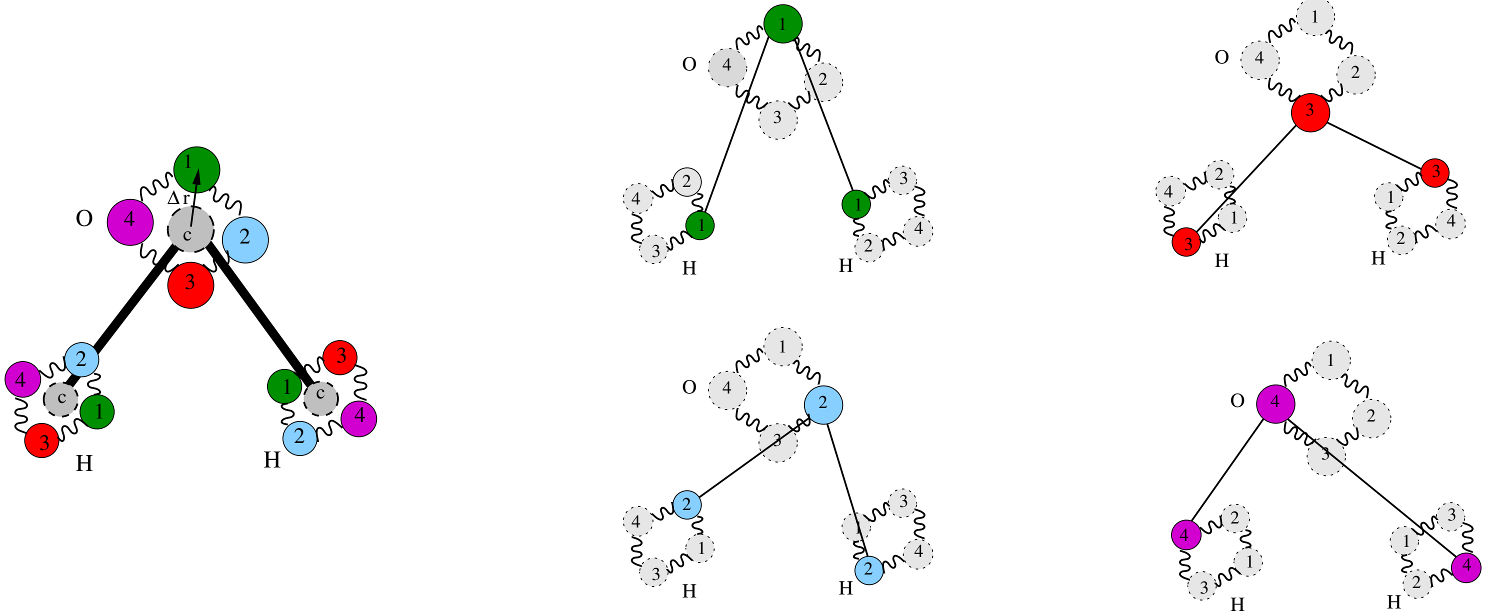


Mg $\beta$ of aqueous Mg
(Pinilla et al. 2015)

- *From a path integral molecular dynamics (PIMD) simulation*

**From the kinetic energy**

$$\ln \beta(A,X) = -\frac{3}{2}\ln\left(\frac{m^*}{m}\right) + \frac{1}{k_B T}\int_{m}^{m^*} \frac{\langle K(m')\rangle}{m'}\, dm'$$

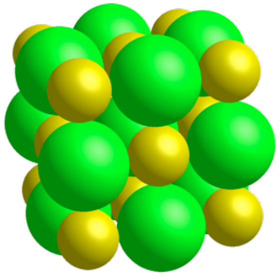


- Ideally P -> 1 gives classical mechanics and P -> ∞ quantum mechanic

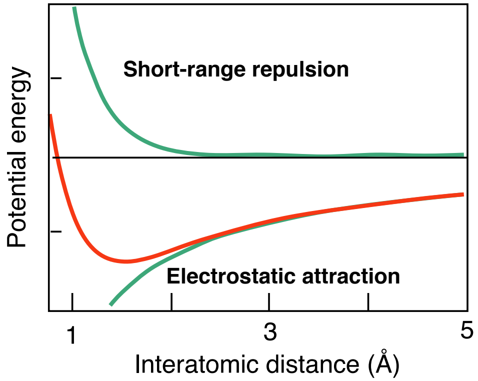
= exact result for a given force field
(includes quantum and anharmonic effects)

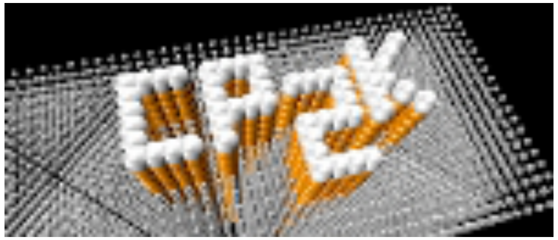
➔ Systematic study of equilibrium fractionation factors in pure water and aqueous Mg, using several levels of theory within the simulations

# Computational details

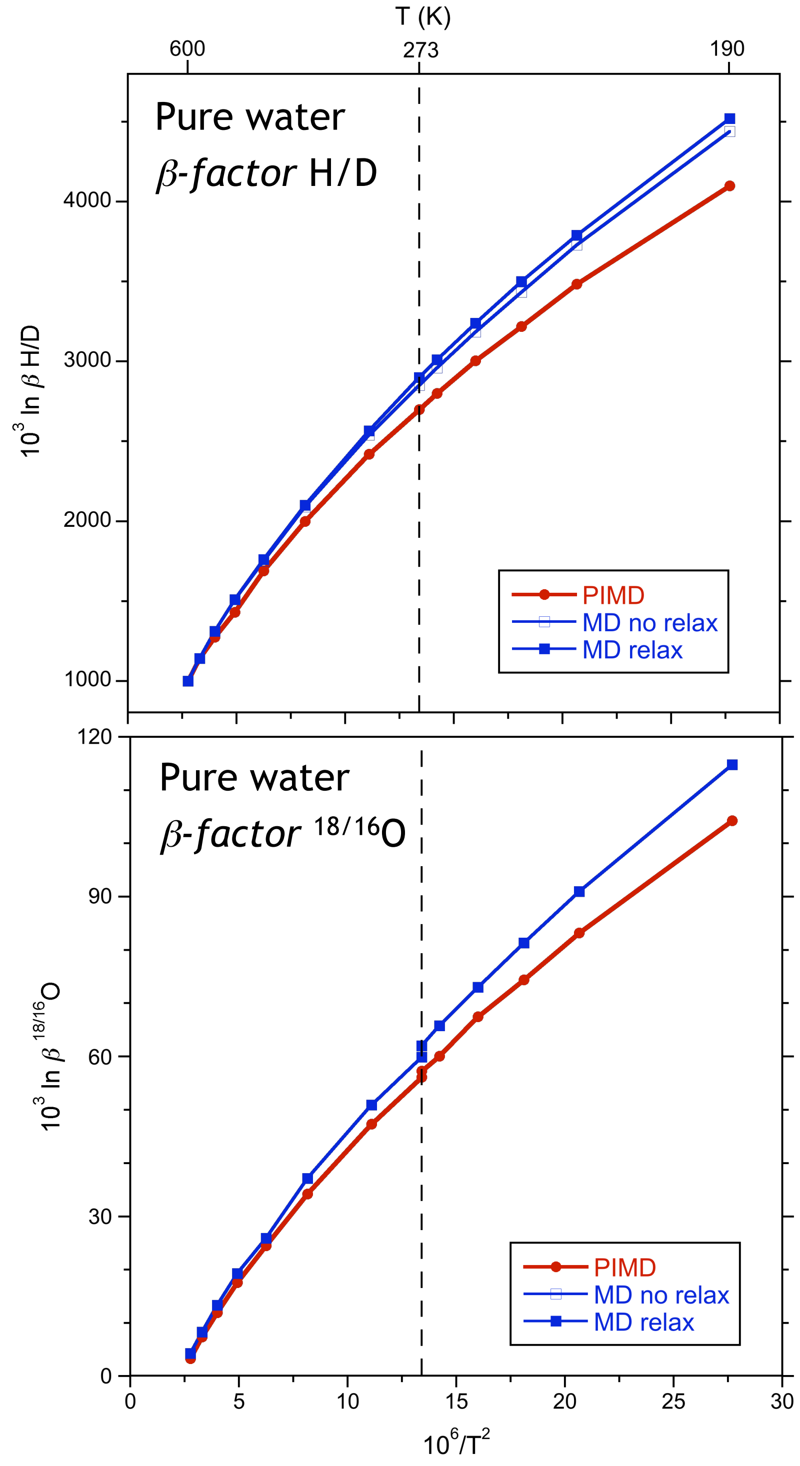


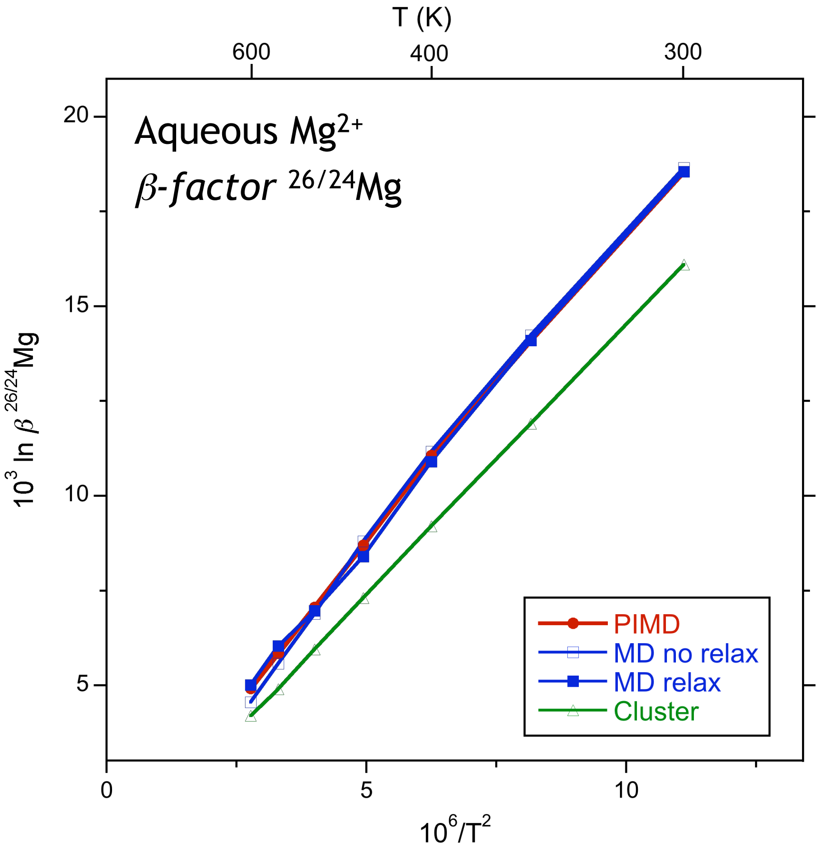
- PINT module of the CP2K suite of codes (open source molecular dynamics)
- The potential is approximated by an empirical function that is fitted to approximately reproduce known interactions.
- Up to 256 water molecules
- NVT ensemble / several T
- P = 32 beads
- At least 3 x $10^5$ MD steps (time step = 0.5 fs)
- Up to 3000 snapshots





# Reduced partition functions ratio ($\beta$-factors)

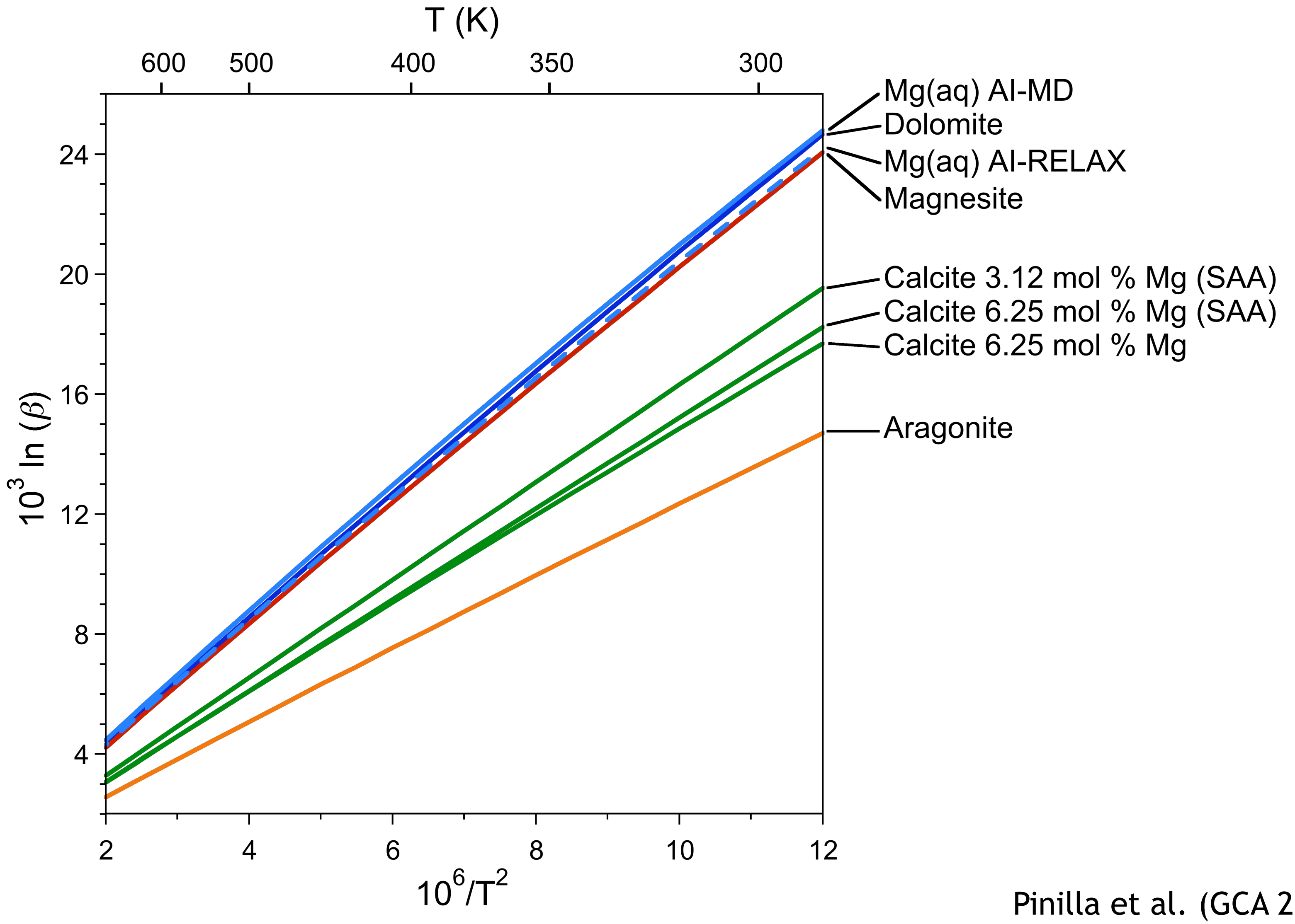




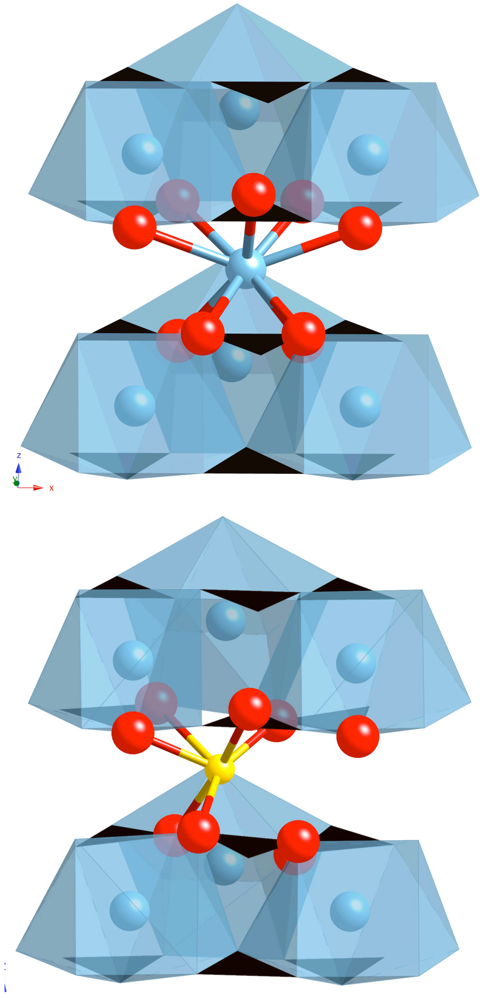
Pinilla et al. (GCA 2014, 2015)

# Mg isotopes in marine carbonates = potential paleoenvironnemental proxies.

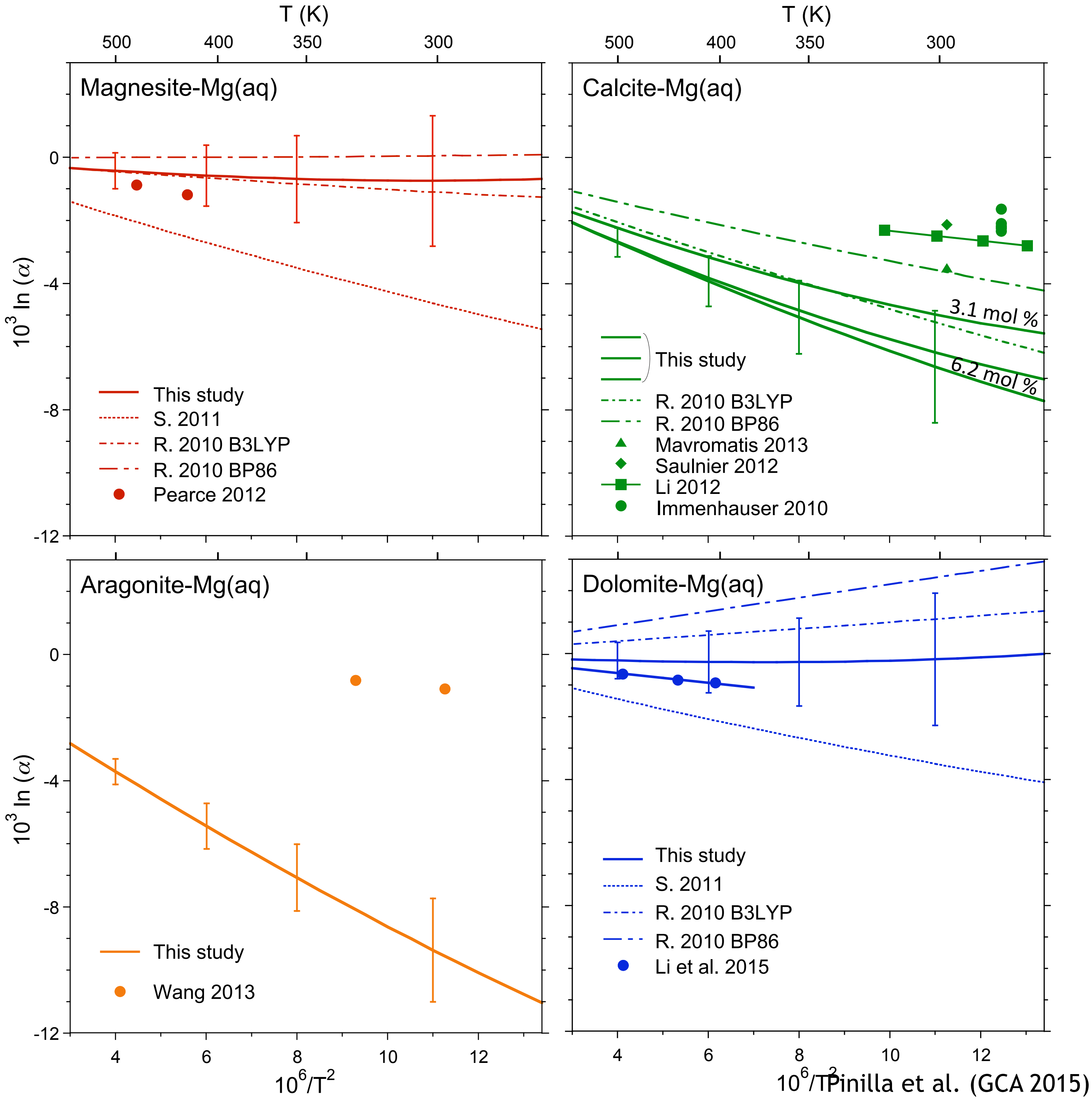
Isotopic variability affected by: mineralogy, T, precipitation rate, Mg concentration, pH (for a review, see Saenger & Wang 2014)



Pinilla et al. (GCA 2015)



Mg-aragonite



Pinilla et al. (GCA 2015)

# ISOTOPIC SIGNATURE OF CHEMICAL IMPURITIES IN MINERALS

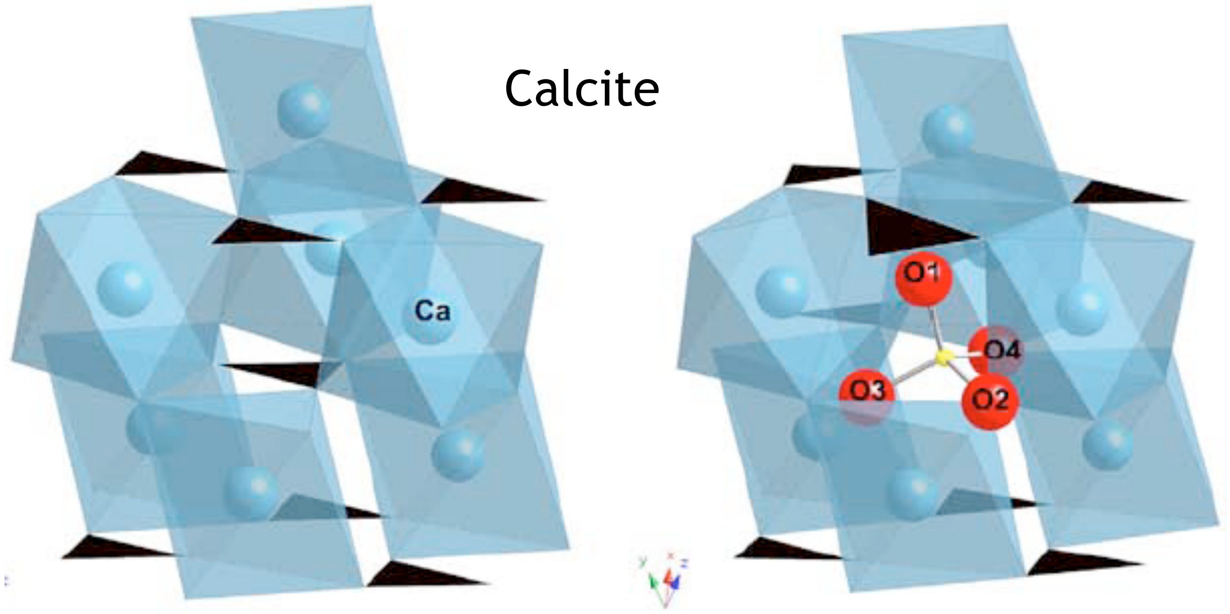
# Sulfate incorporation and $^{34}$S/$^{32}$S isotopic fractionation in different calcium carbonates

The carbonate-associated sulfate is considered as an efficient proxy of the sulfur isotope composition of ancient oceans (Burdett et al. 1989, Kampschulte & Strauss 2004).

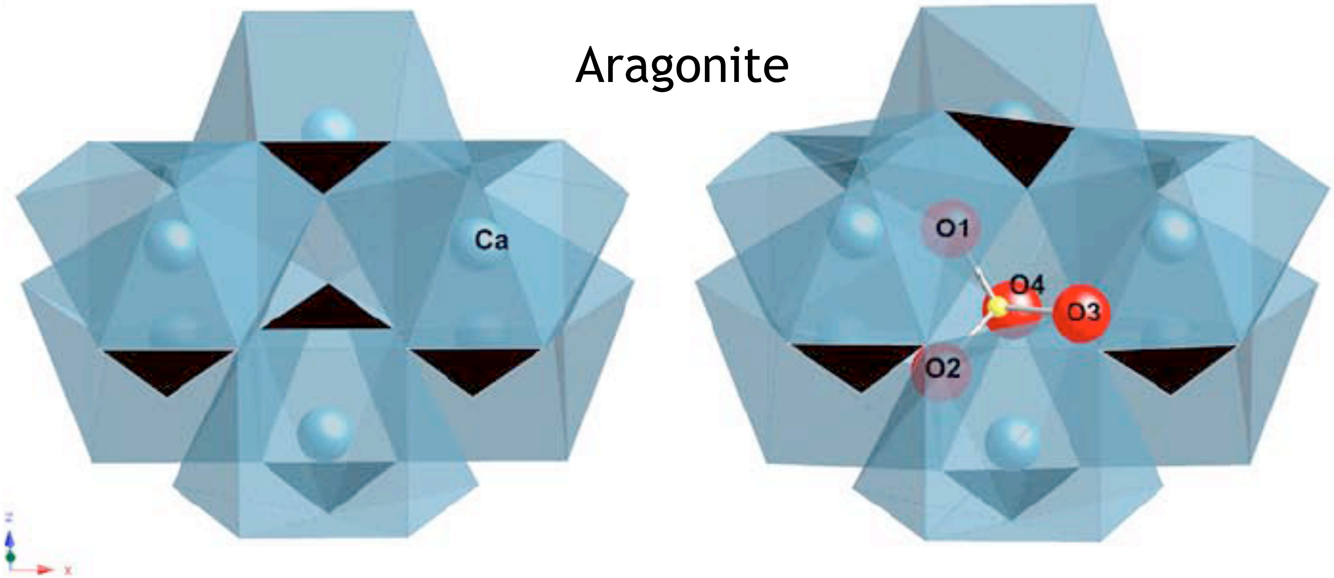
Experimental observations suggest that S is present as sulfate group in the carbonate structure.

What is the atomic-scale model for the replacement of the triangular molecule by a tetrahedral one? The isotopic fractionations associated?

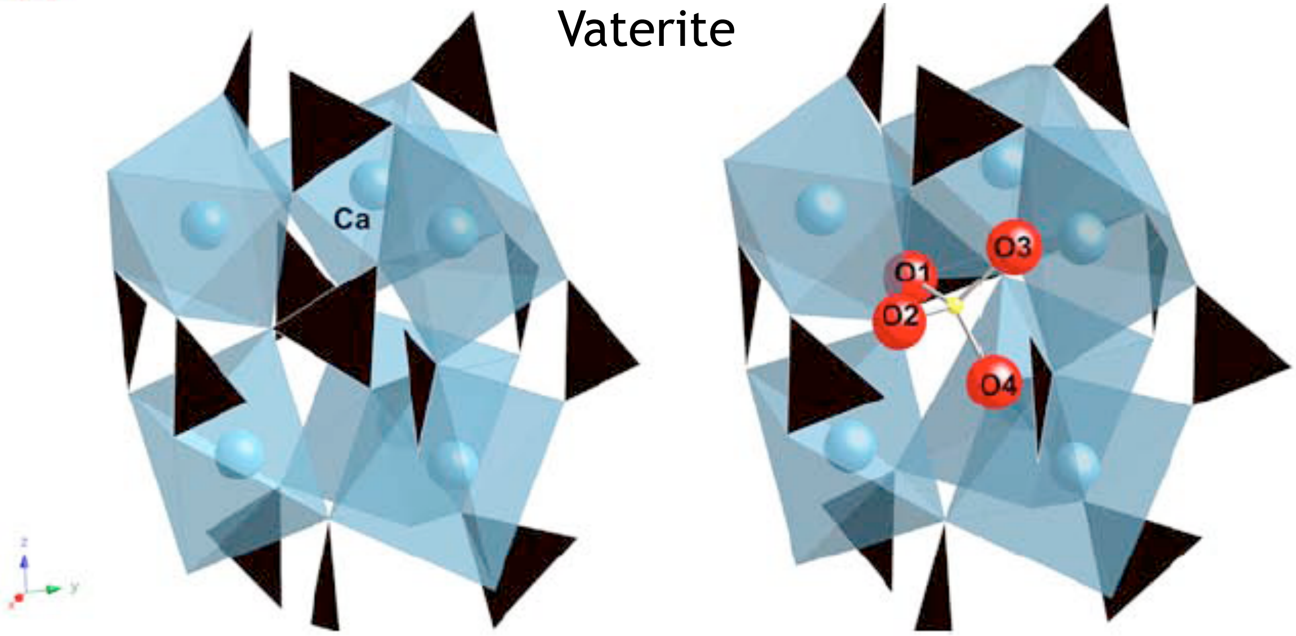
➔ First-principles investigation of S-calcite, S-aragonite, S-vaterite


Calcite

Aragonite



Vaterite

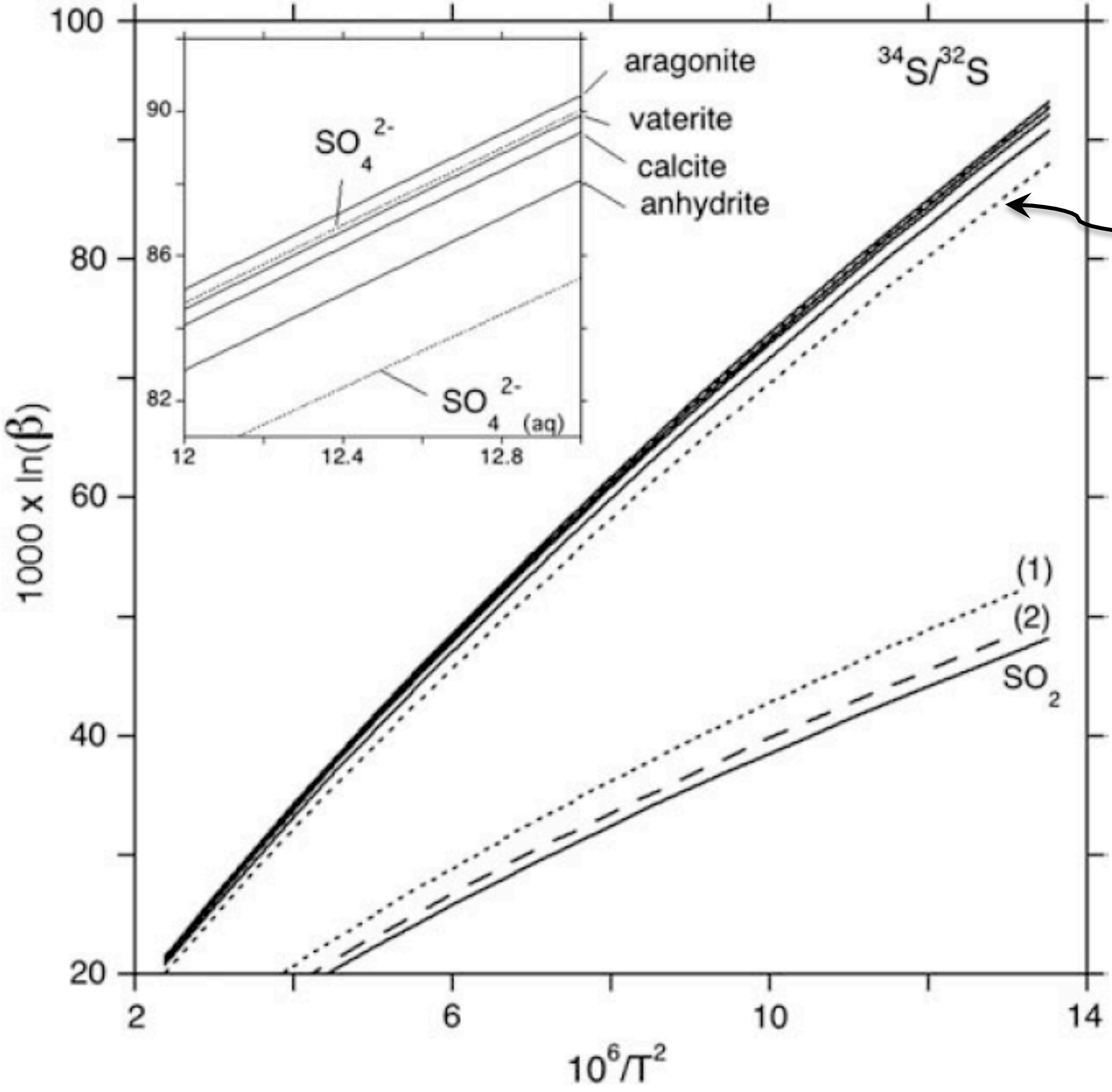


Energetic of sulfate incorporation in carbonate minerals:
Vaterite > calcite >> aragonite

# Theoretical $^{34}S/^{32}S$ $\beta$-factors

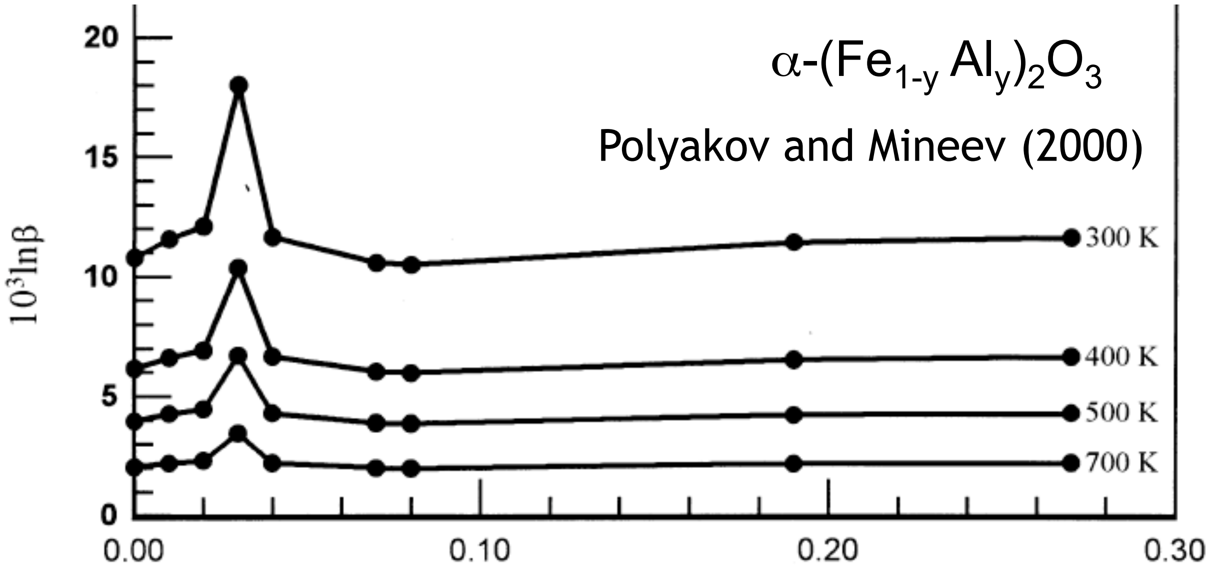
Equilibrium S isotopic fractionation factors between the 3 carbonates are small (< 3‰ at 0 °C).

*“The isotopic fractionation between calcite and aqueous sulfate is smaller than 4‰”*



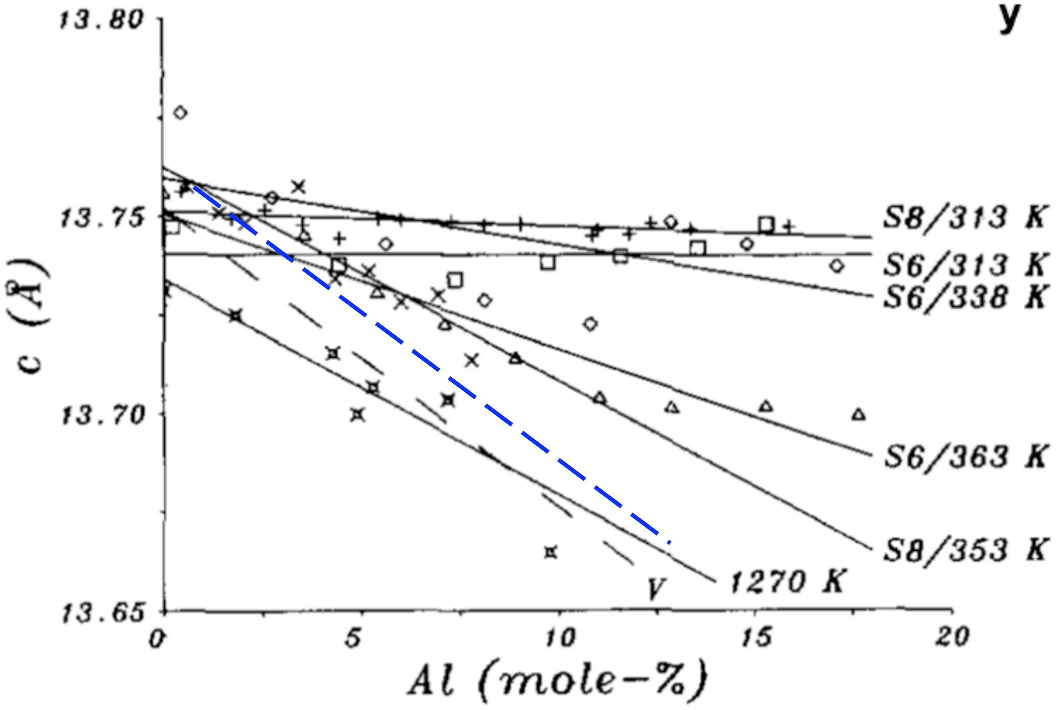
Aqueous sulfate from Otake et al. (2008)

# Effect of Al-substitution on the Fe β–factor of hematite



$\alpha$-$(Fe_{1-y}Al_y)_2O_3$

Polyakov and Mineev (2000)

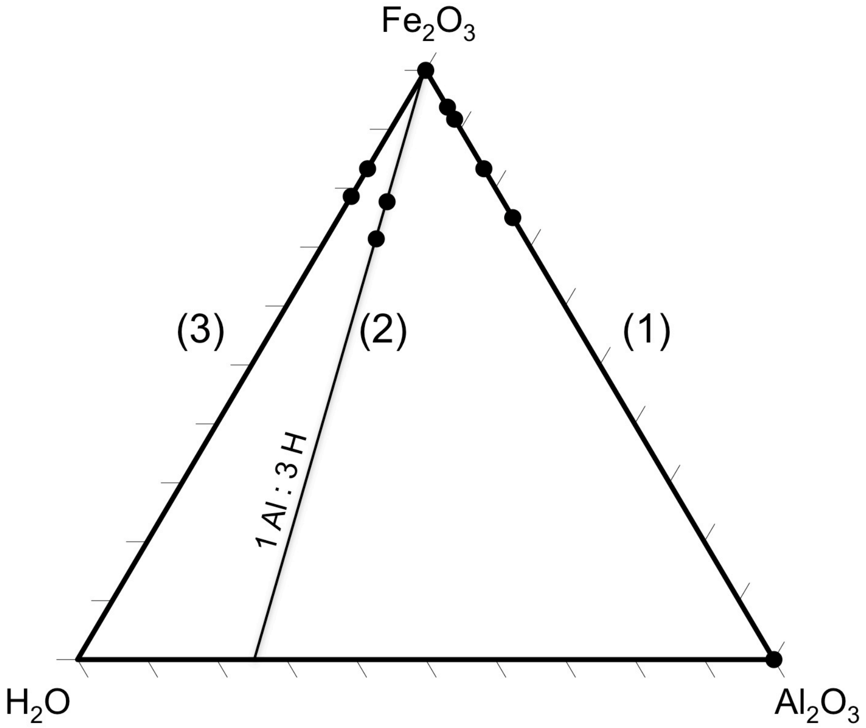


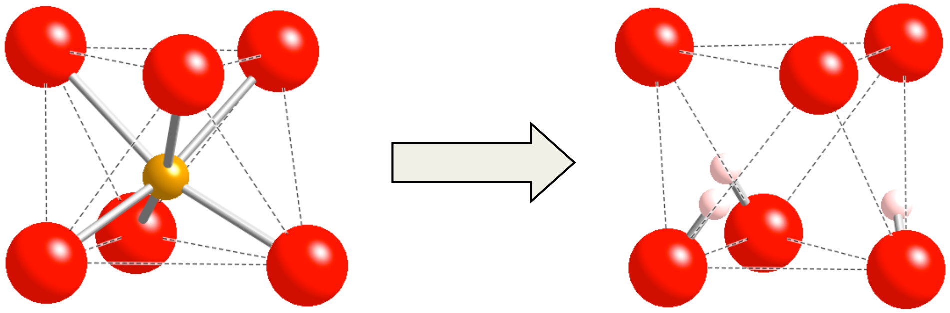
Evolution of lattice parameter (Stanjek & Schwertmann, 1992):

- Deviations from Vegard's rule
- Deviations correlated to synthesis temperatures and to the water content

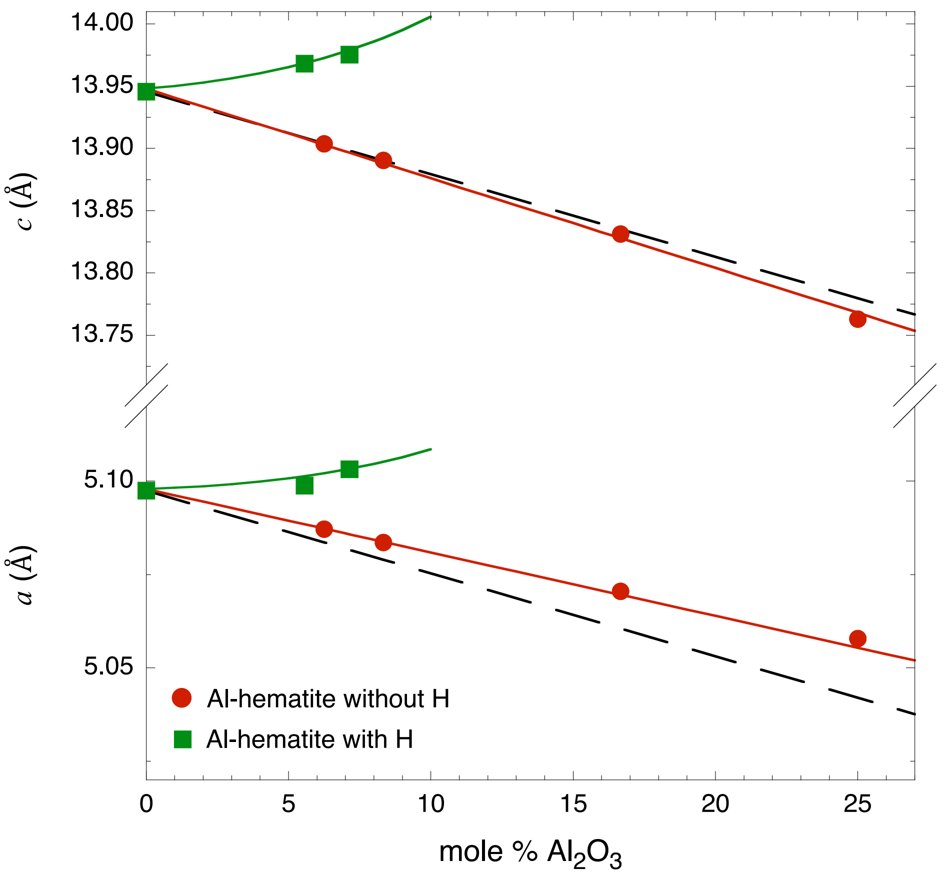
=> Protons associated to Fe vacancies ?

## Ternary diagram showing the compositions investigated:
## Construction of supercells with Al in Fe site and/or 3H in Fe site

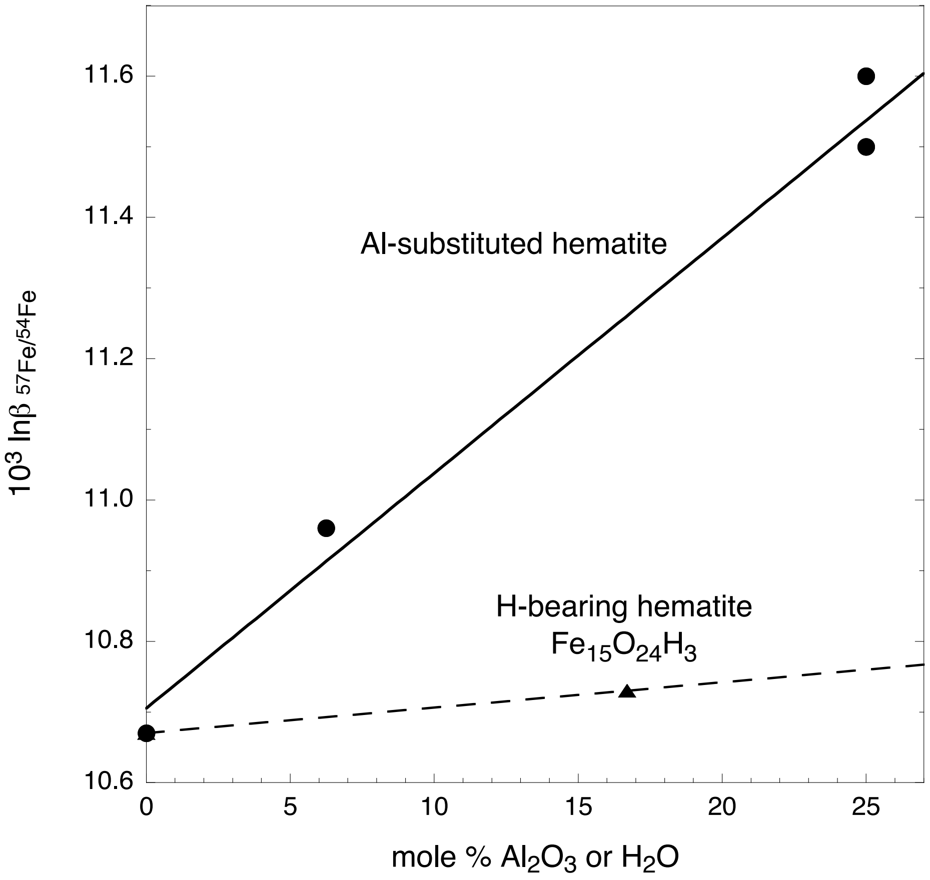


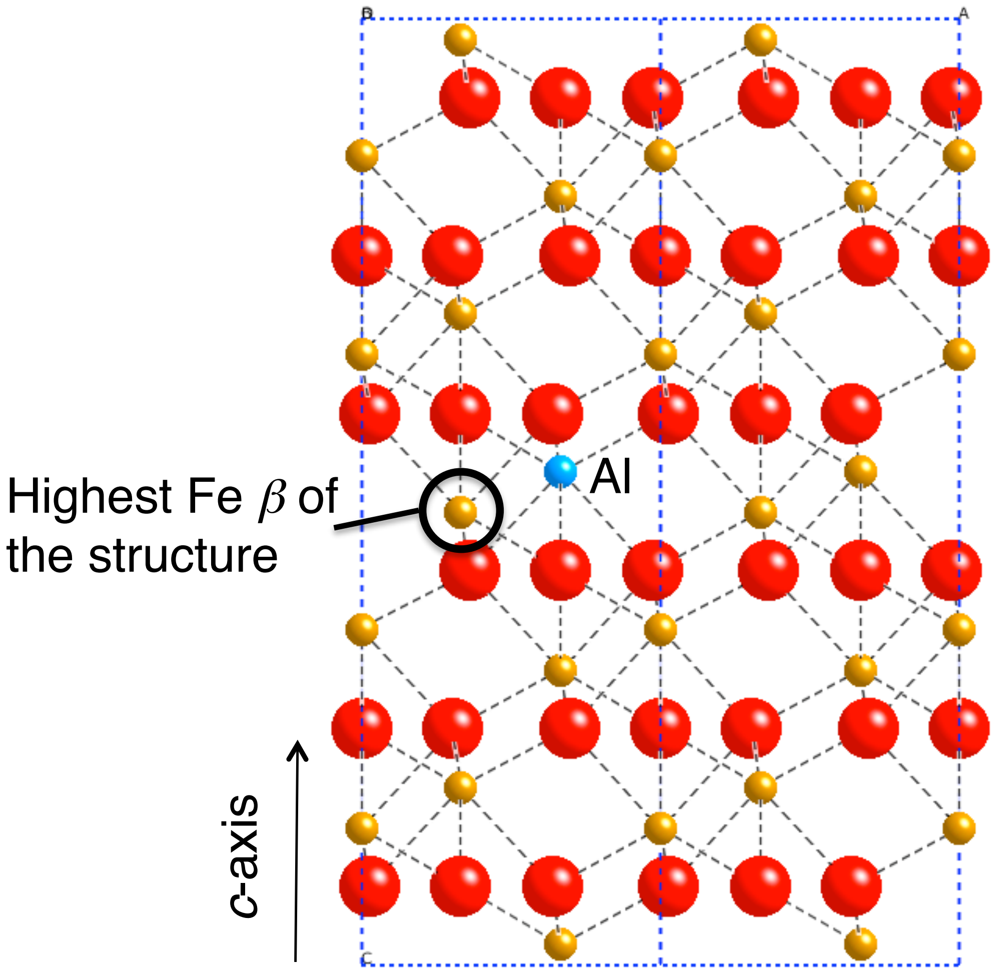


## *Calculated (GGA + U) lattice parameters of hematite versus Al and water contents*



Blanchard et al. (2010, *GCA*)





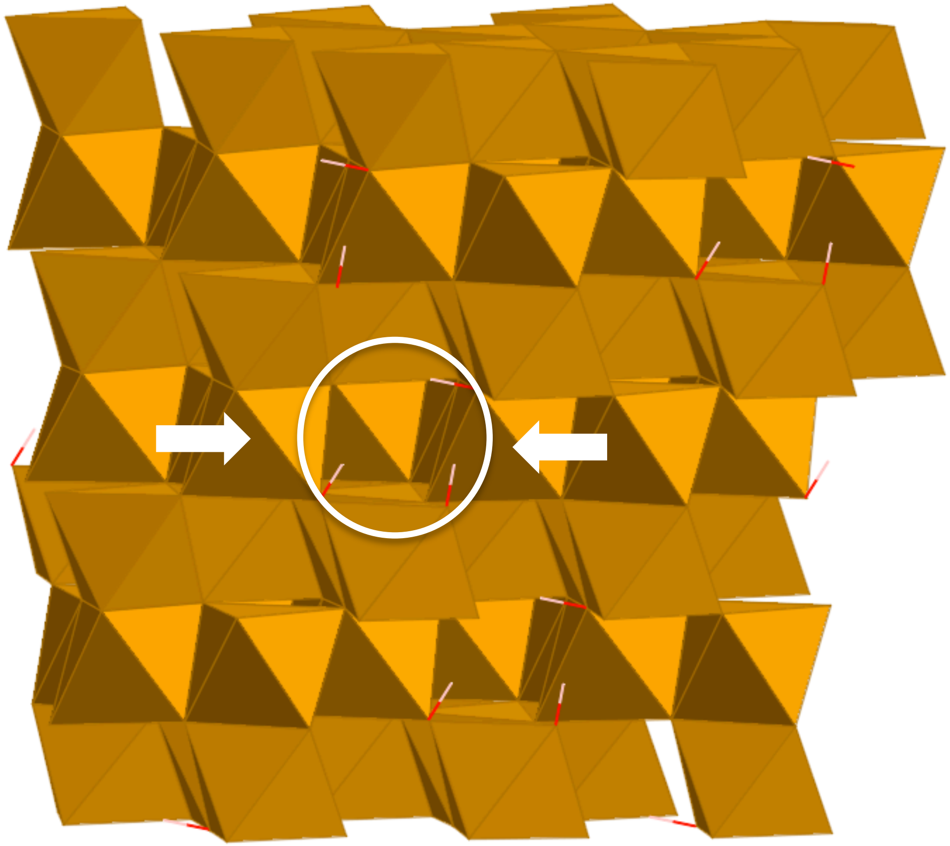
The iron $\beta$ is higher for Fe atoms located next to the Al impurity.
The effect is larger when Al is in the edge-sharing octahedron rather than in the corner-sharing or face-sharing octahedron.

Blanchard et al. (2010, *GCA*)

# β-factors of each Fe site in H-bearing hematite at 0°C (in ‰)

The amplitude of the local iron $\beta$-factors spans over 1.12 ‰ at 0°C, i.e. similar amplitude as in Al-substituted hematite, but compensation of the values due to complex structural relaxation.

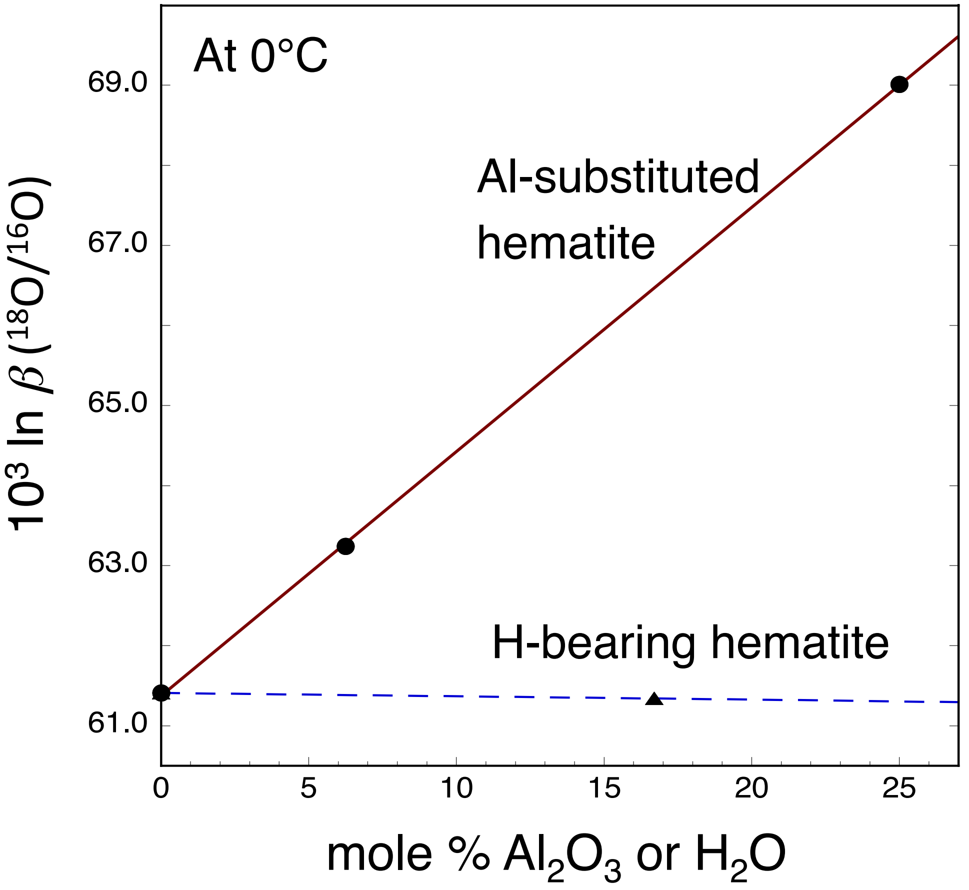
Unlike Al, the protonation has no effect on the average iron $\beta$-factor.



Extreme values for Fe octahedra sharing an edge with the protonated vacancy.

Blanchard et al. (2010, *GCA*)

# *Oxygen $\beta$-factor of hematite vs Al or H content*



- An incorporation of 18 mole % $Al_2O_3$ in hematite would increase the oxygen $\beta$ of ~5.5‰ at 0°C. This effect is sufficiently large to be measurable and to affect the interpretation of natural isotopic compositions.

- The effect of H incorporation is found to be negligible. This is explained by a complex local relaxation of the defective structure leading to a compensation of local $\beta$ values.

Blanchard et al. (2010, *GCA*)

# CONCLUSIONS

- Molecular modeling can contribute significantly to isotopic geochemistry. It is crucial to consider consistent theoretical $\beta$-factors in order to obtain reliable $\alpha$-factors.

- Fe isotopes: DFT $\beta$-factors compares well with Mössbauer- or NRIXS-derived $\beta$-factors. Comparing the data obtained from the different techniques (DFT, Mössbauer, NRIXS) enables to obtain reliable equilibrium isotopic fractionation factors.

- Isotope fractionation is a local property that depends only on the environment surrounding the fractionated isotope.

- Solvation and dynamic effects are important in estimating $\alpha$-factors of liquids

- Ab initio modeling allows to investigate the mechanisms involved at the molecular scale (crystallographic sites, surface effect, adsorption processes …)

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