The missing N conumdrum

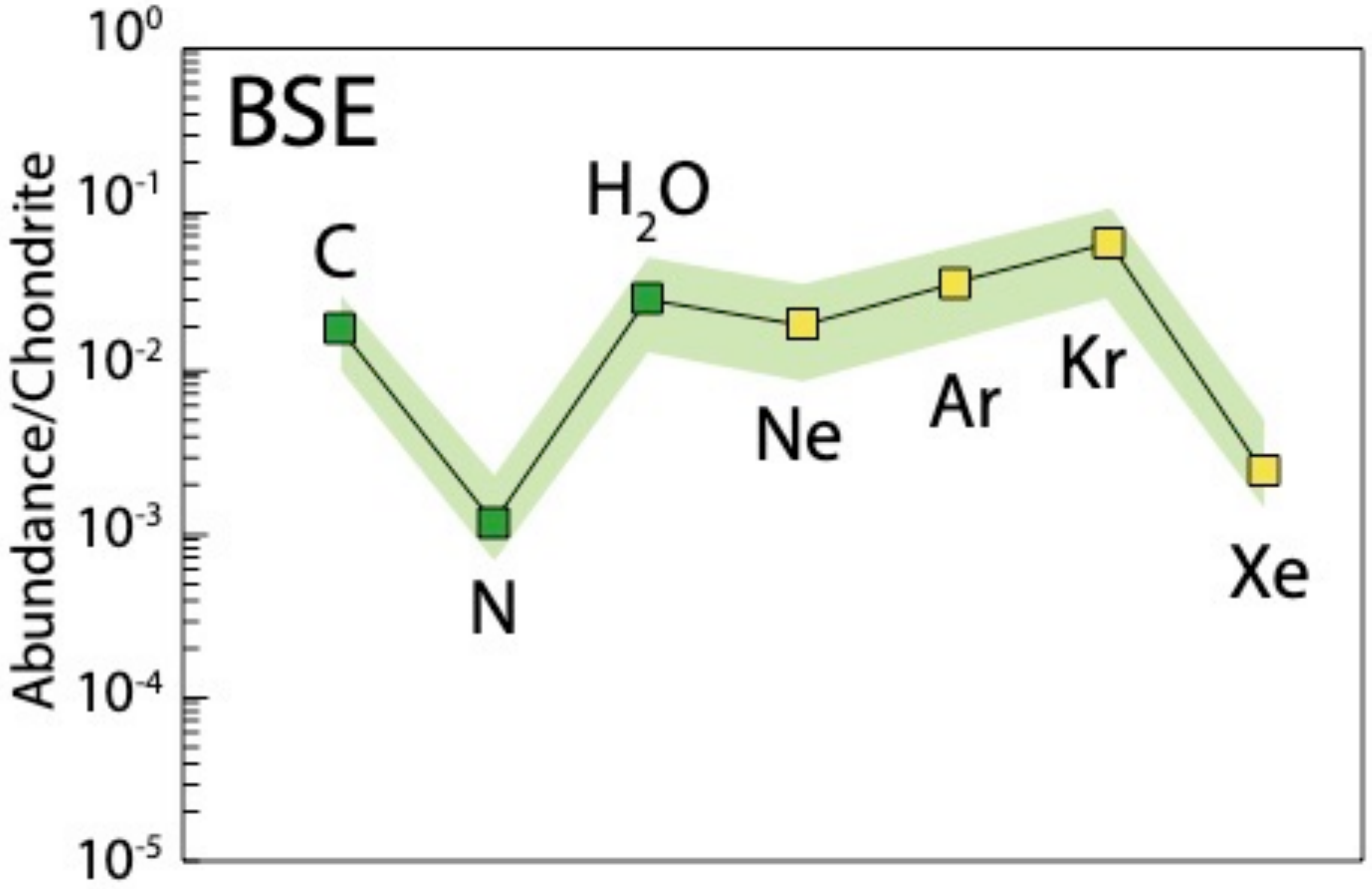
Insights from HP petrology

Celia Dalou

CNRS researcher at the CRPG (Nancy, France)

Why do we study N ?

N depletion of the BSE

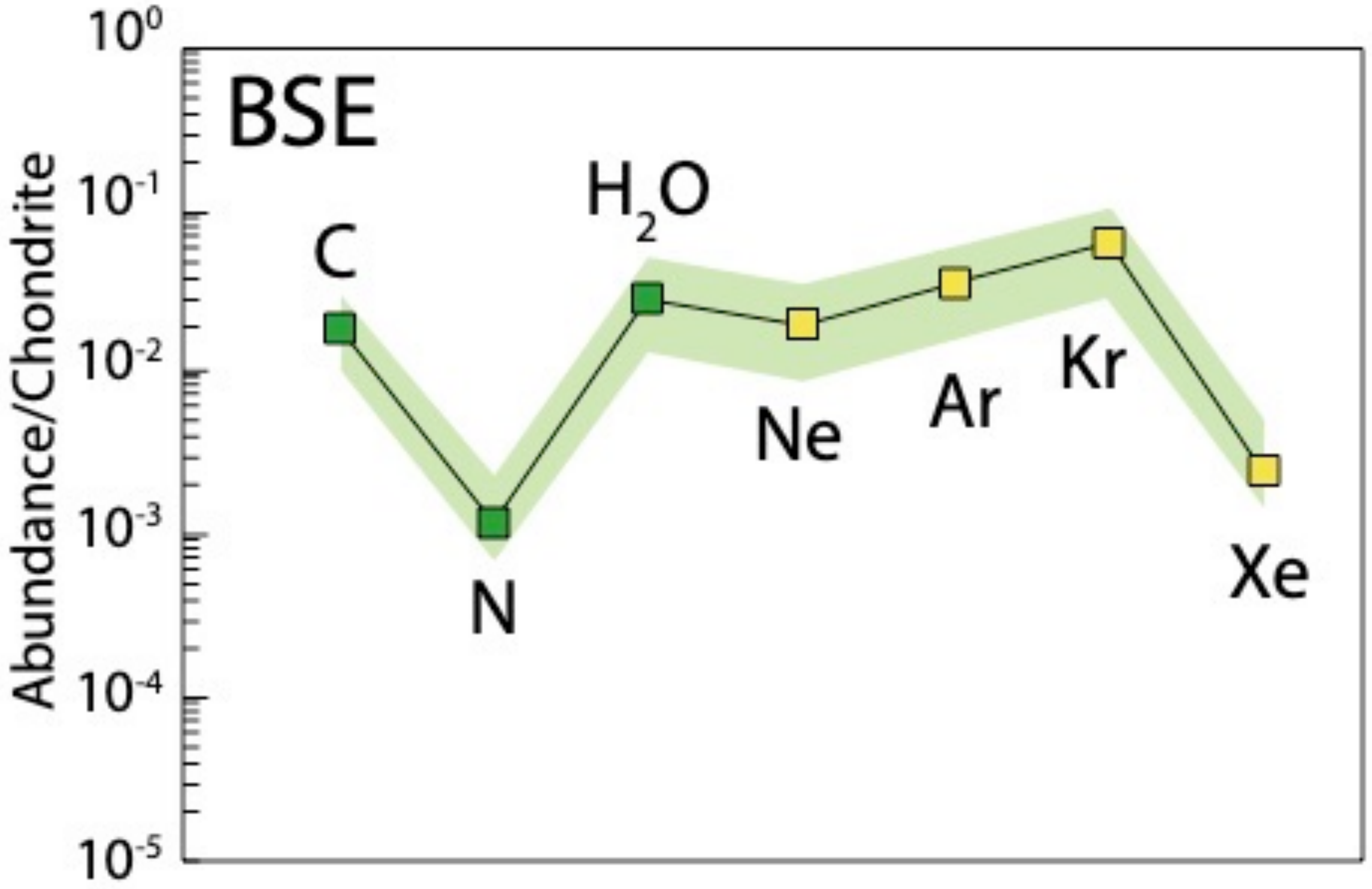


After Marty 2012

Modern Earth mantle = depleted in N compared to other volatiles

N depletion of the BSE

Such as C/N derives from mass balance calculations inventorying the mantle, crust and atmosphere (Marty, 2012; Bergin et al., 2015)



After Marty 2012

Modern Earth mantle = depleted in N compared to other volatiles

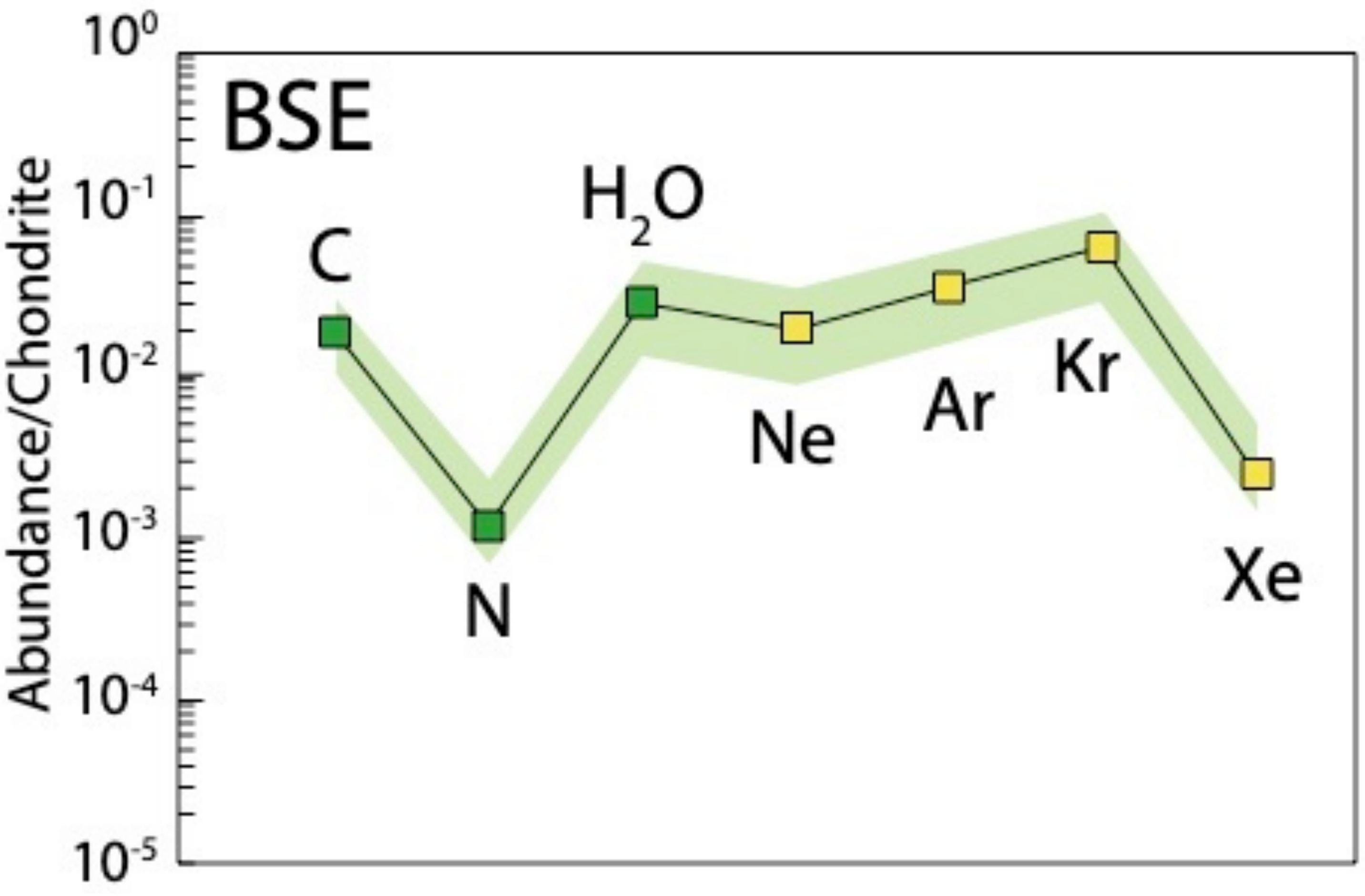
N depletion of the BSE

High C/N ratio

⇩

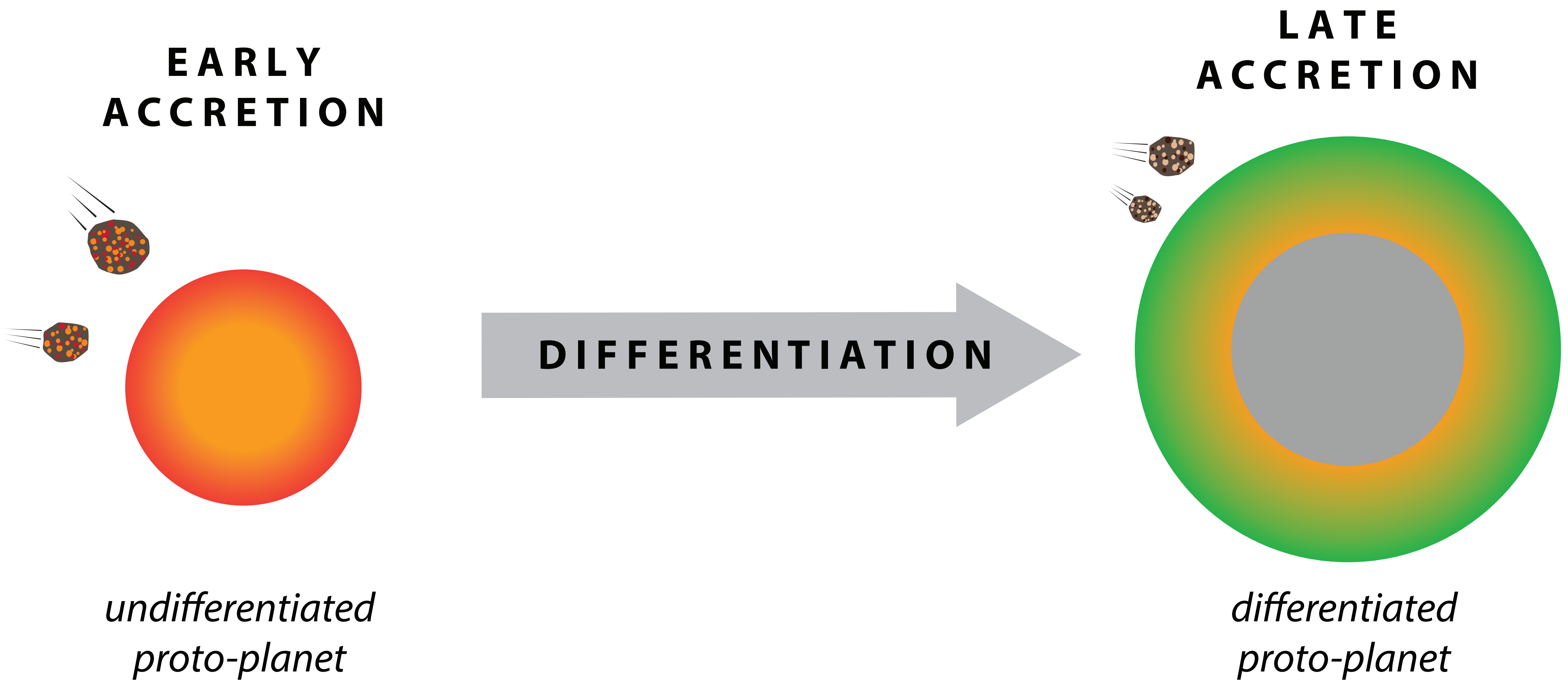
Acquired during planetary differentiation

After Marty 2012



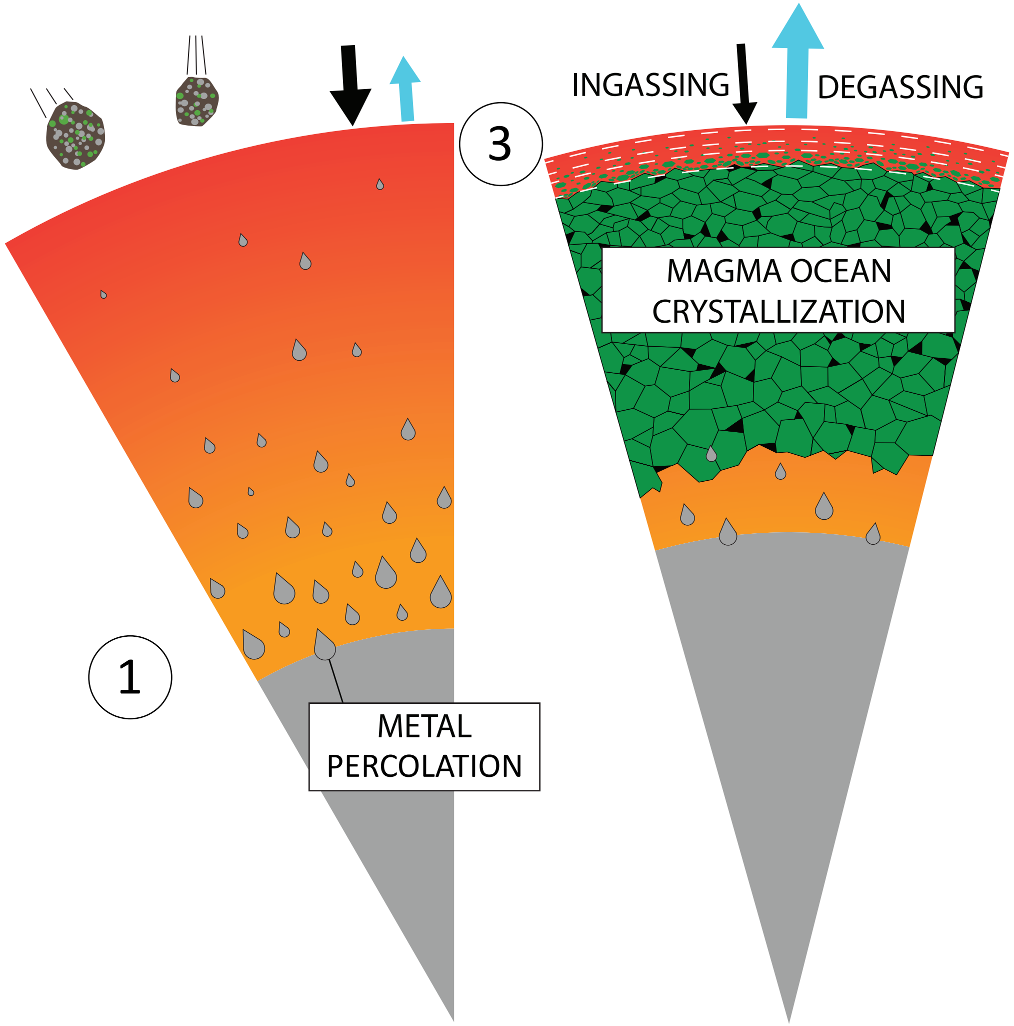
How did the present-day mantle acquired this high C/N ratio ?

How to form a planet?



How to form a planet?

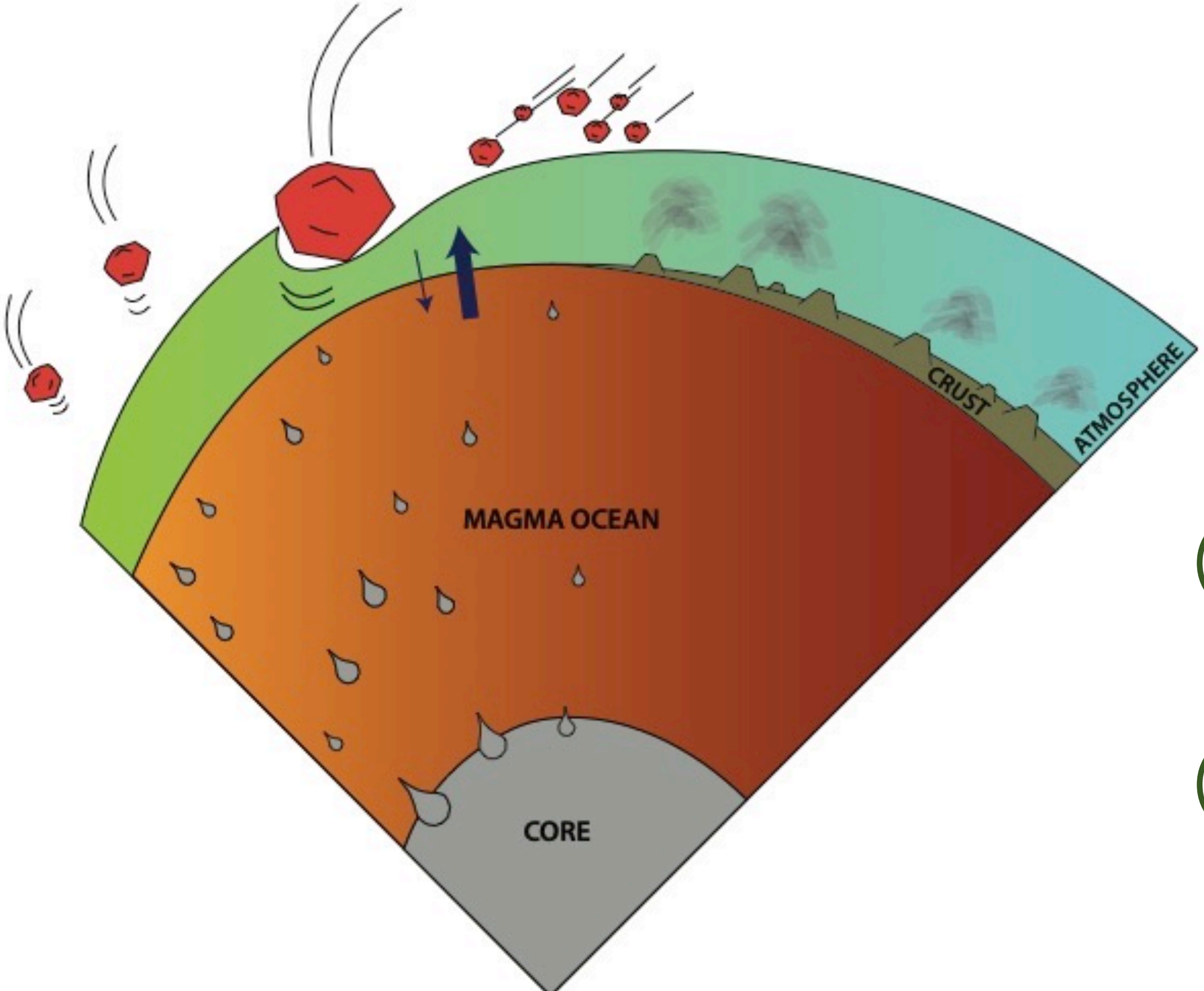
The 3 main processes of rocky planets' differentiation :



1. Core formation
2. Magma ocean's crystallisation
3. Volatile elements' degassing

N depletion of the BSE

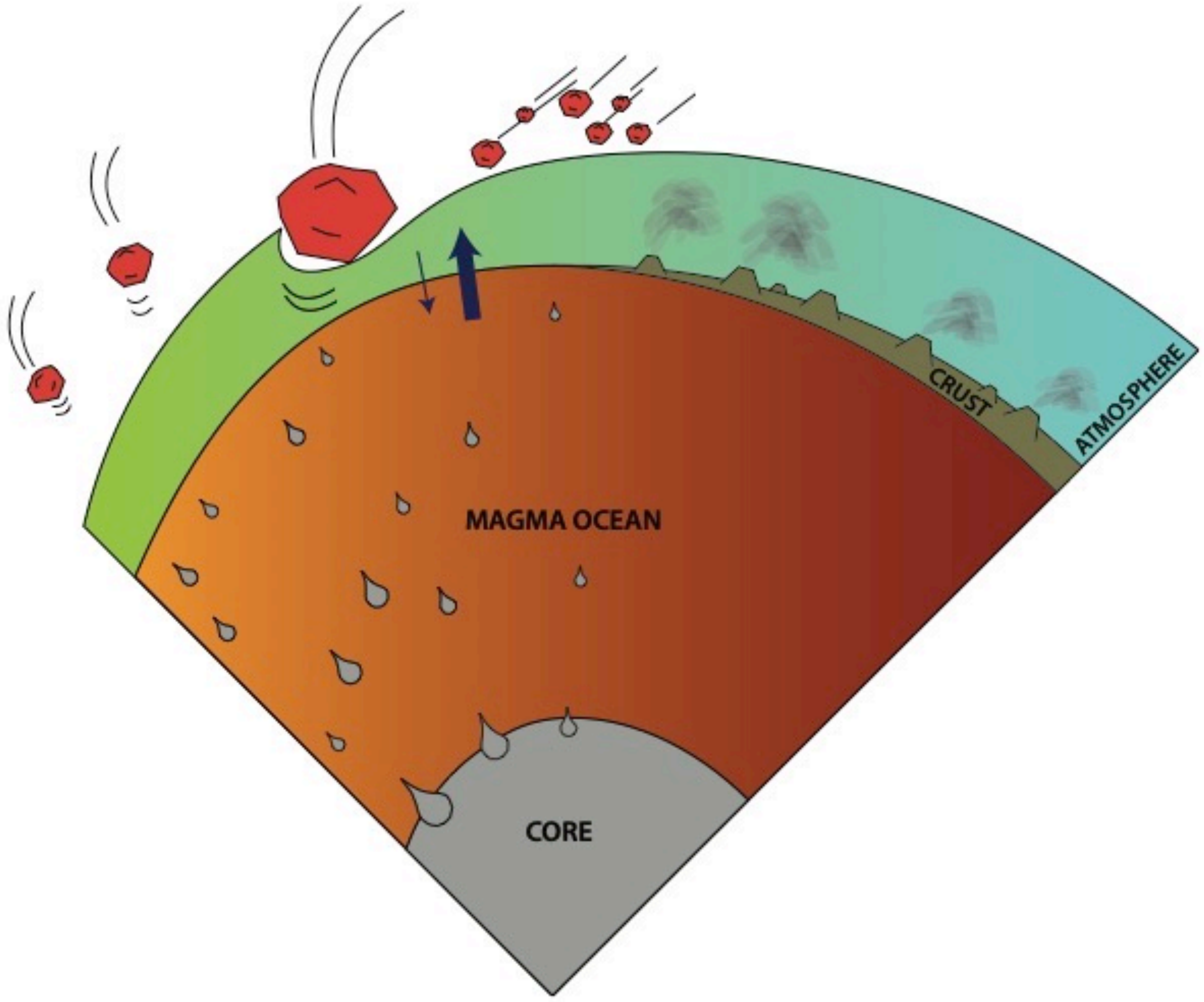
MECHANISMS to explain N depletion of the BSE?

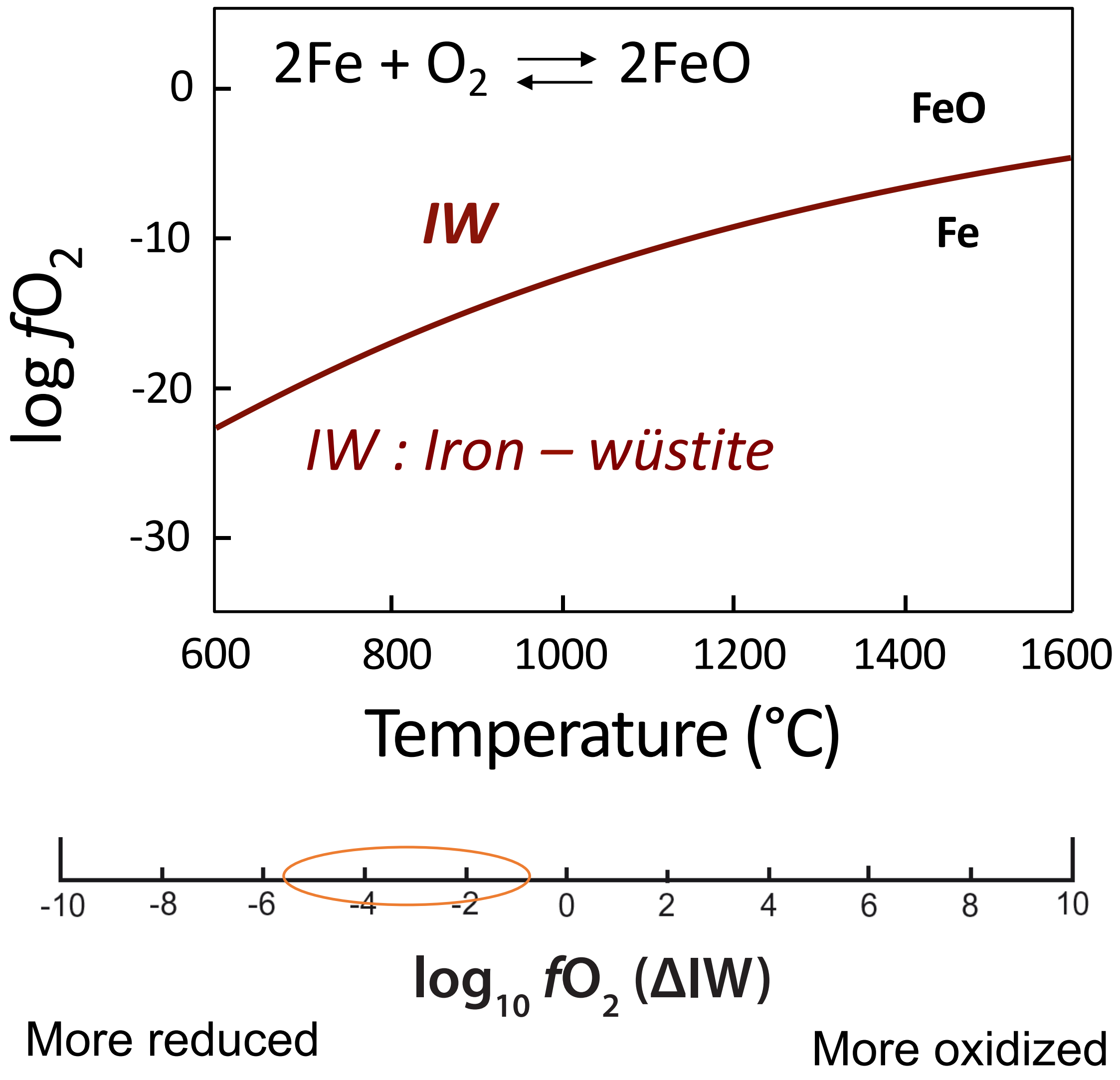


① Core formation

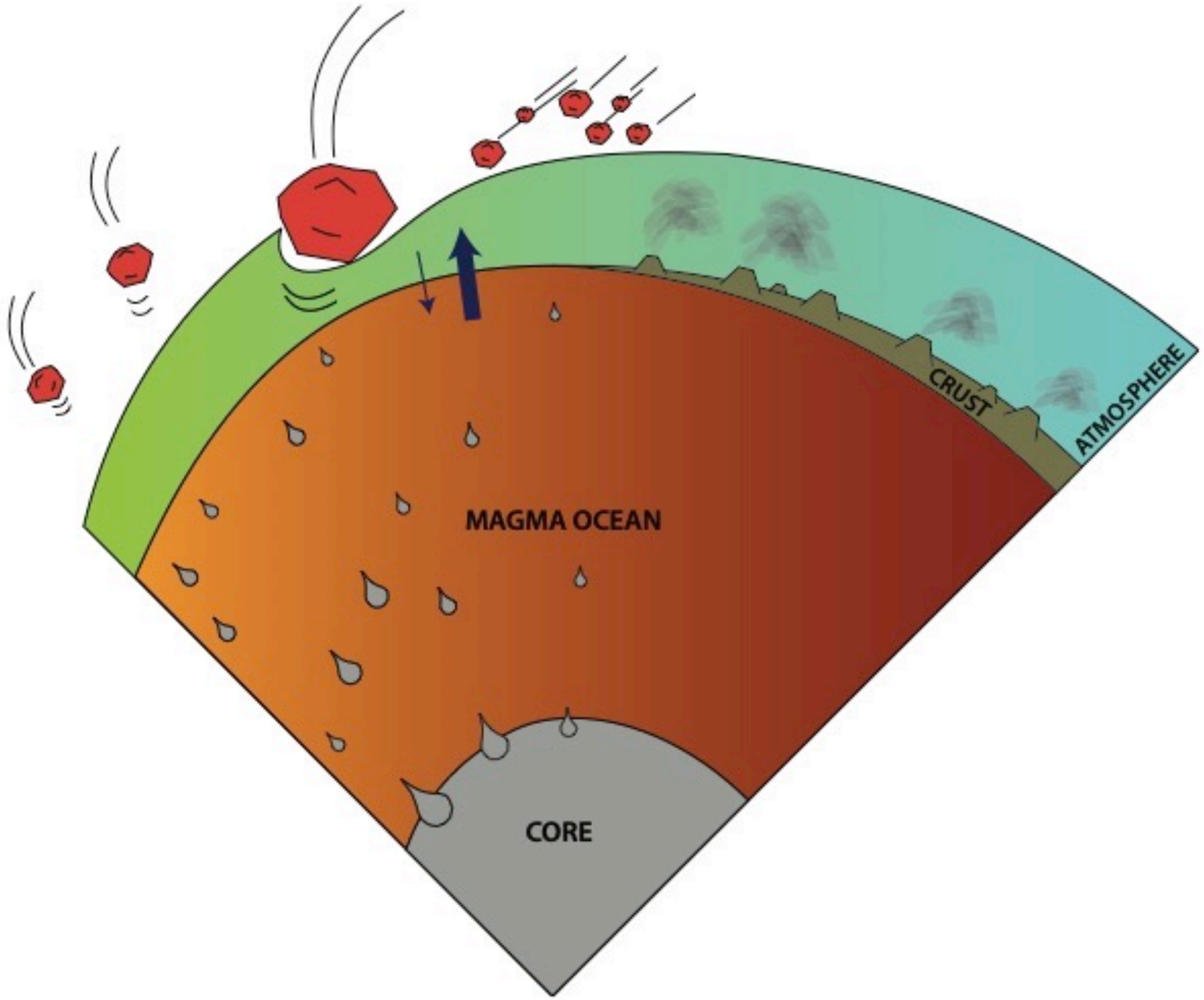
② MO degassing

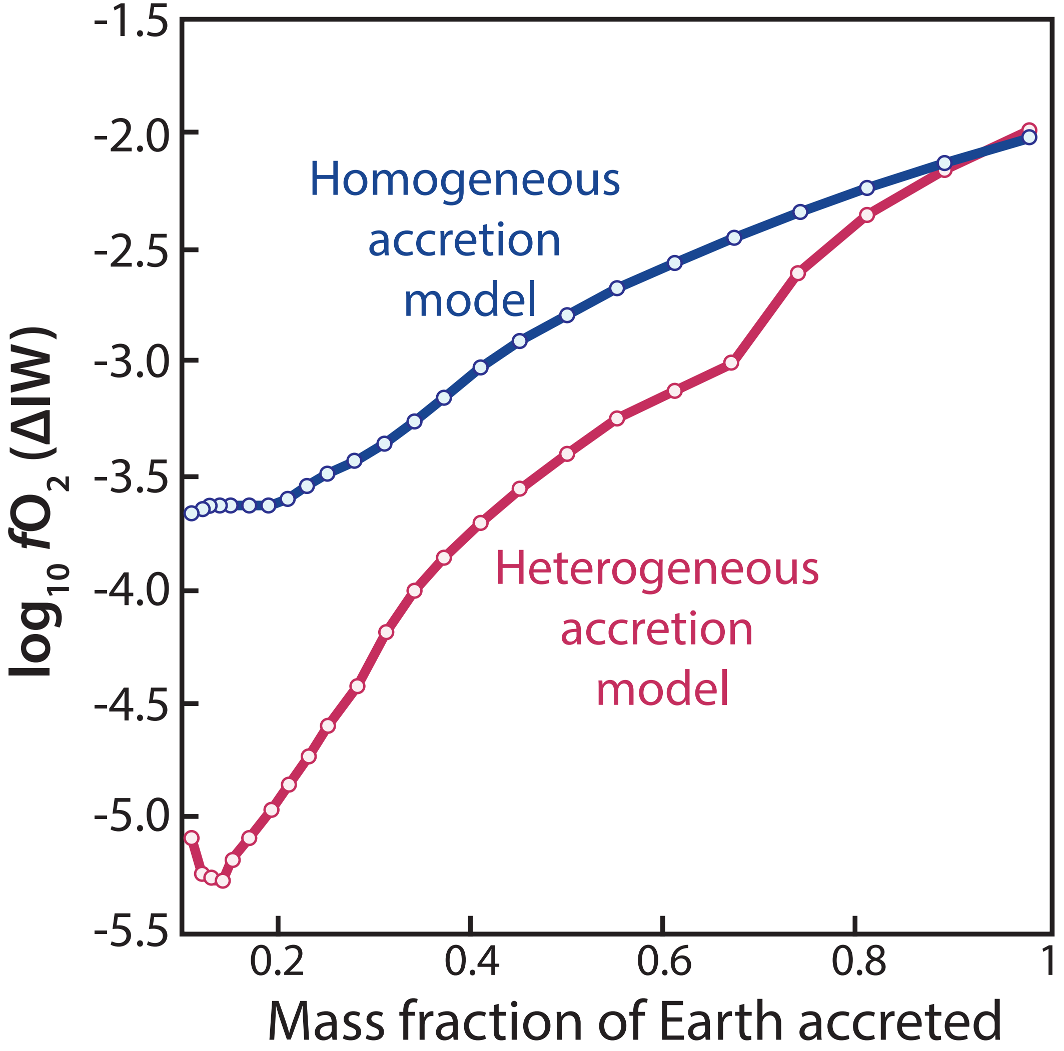
Focus on fO_2 during planetary differentiation





Focus on fO_2 during planetary differentiation

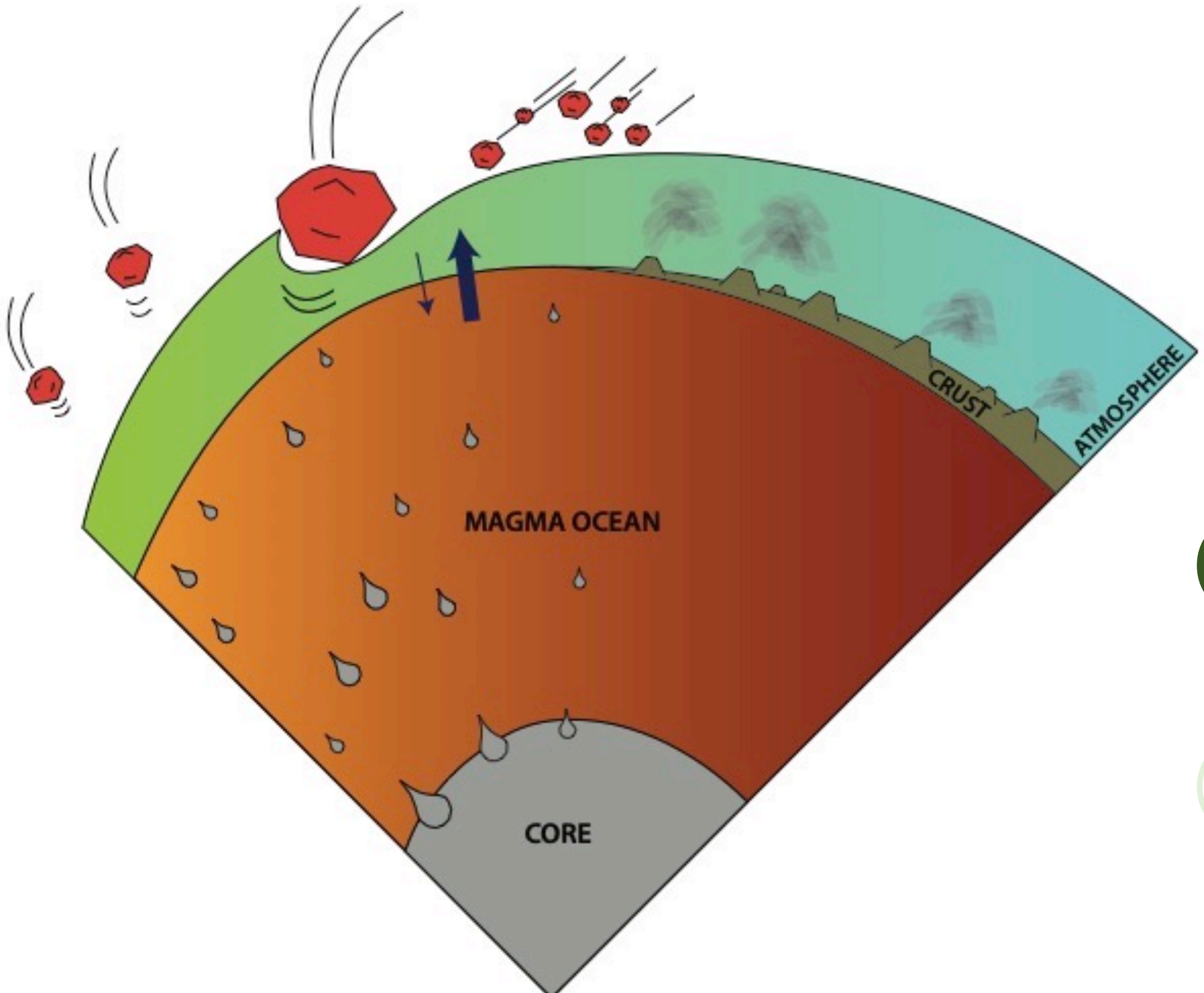




Rubie et al. (2011)

N depletion of the BSE

MECHANISMS to explain N depletion of the BSE?



① **Core formation**

② MO degassing

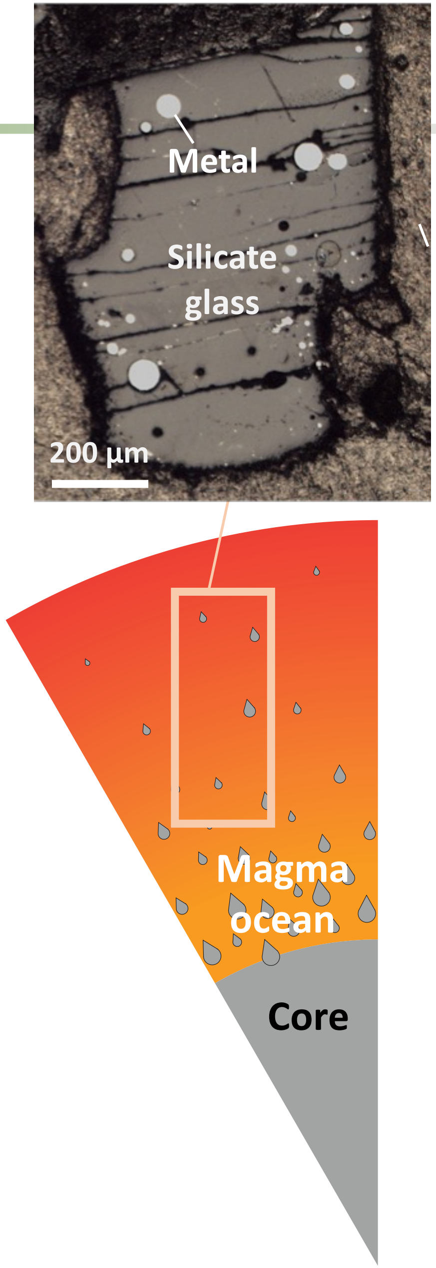
N metal-silicate partitioning

Experiments

From 1 to 25 GPa and up to 2000°C

Graphite capsules – Pure MgO and Fo capsules

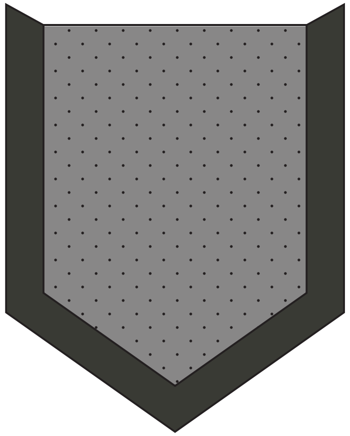
Piston-cylinder + multi-anvil experiments
(two studies in DAC up to 26 GPa)



N metal-silicate partitioning

Experiments

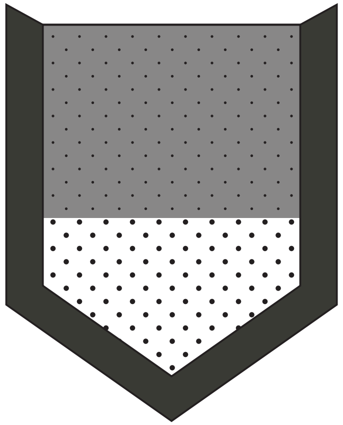
Different protocols used



Basalt (primitive basalt, MORB) or martian basalt
+ Si_3N_4 ± Si

Mixed -> loaded in capsule

$$6\ FeO_{\text{silicate melt}} + Si_3N_{4\ \text{nitride}} = 6\ Fe_{\text{alloy}} + 3\ SiO_{2\ \text{silicate melt}} + 2\ N_{2\ \text{silicate melt or alloy}}$$



Fe-free and N-freeBasalt (primitive basalt, MORB) or martian basalt

Fe ± Fe_7N_3 ± FeS ± Si

Mixed -> loaded in capsule

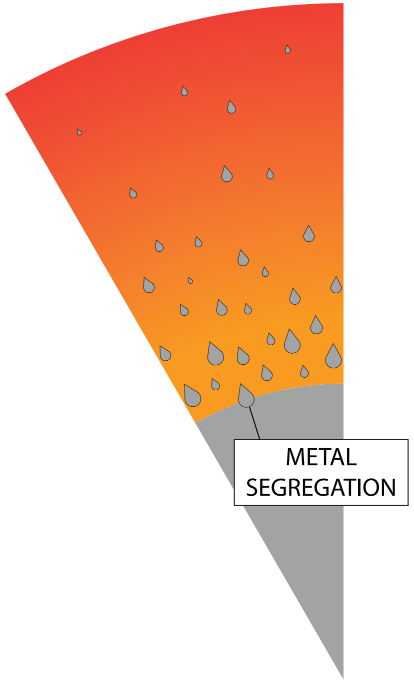
$$Fe_7N_{3\ \text{nitride or alloy?}} = 7\ Fe + 3/2\ N_{2\ \text{silicate melt or alloy}}$$

N metal-silicate partitioning

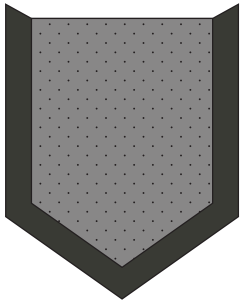
Experiments

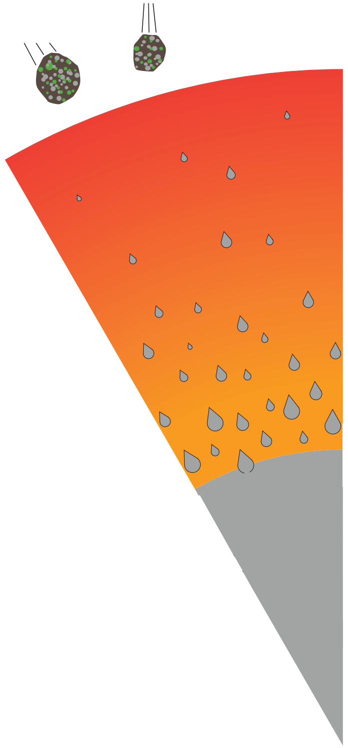
Different protocols used

core formation processes



$$2FeO \longrightarrow 2Fe + O_2$$

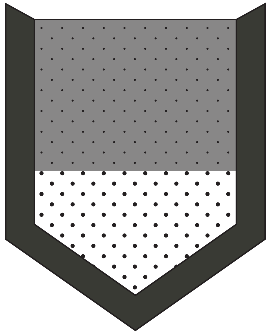




Metal delivered by
Earth building blocks

⬇

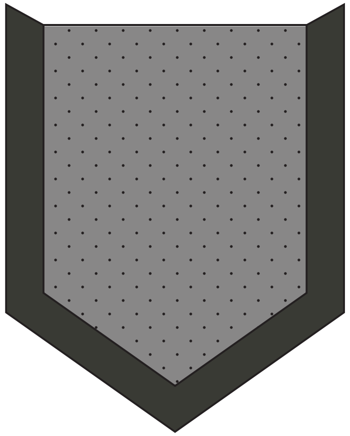
Volatile elements already
in the metallic phase



N metal-silicate partitioning

Experiments

Different protocols used



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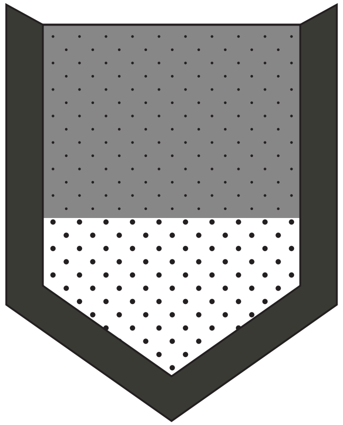

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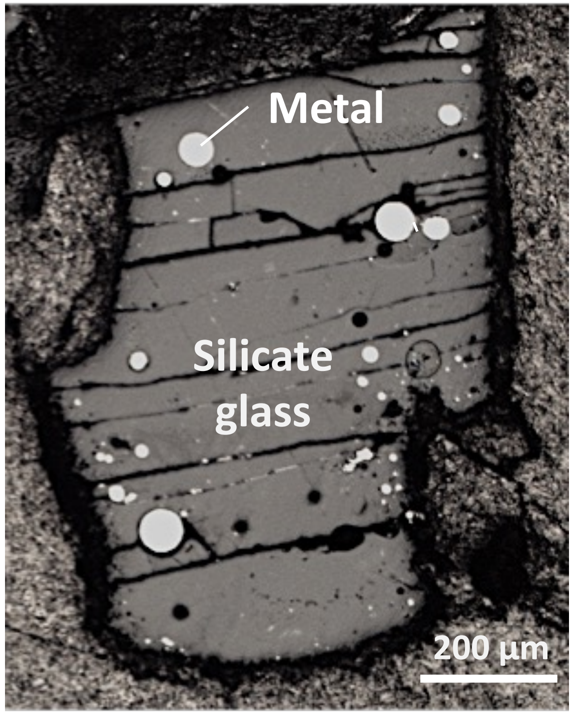

Basalt (primitive basalt, MORB) or martian basalt

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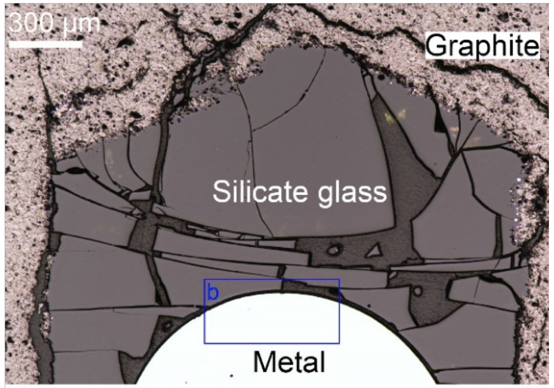
Mixed -> loaded in capsule



Li et al. (2016)

Fe-free and N-freeBasalt (primitive basalt, MORB) or martian basalt

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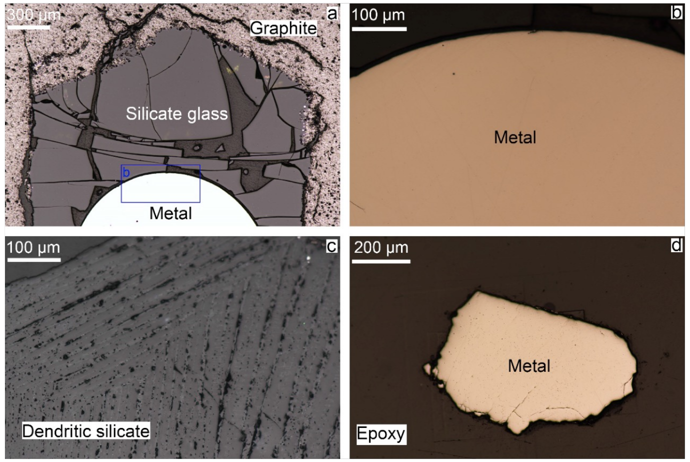
N metal-silicate partitioning

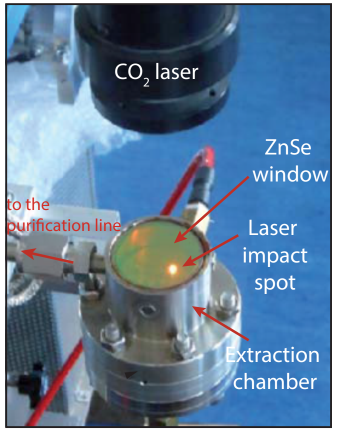
Measurements

Noble gas mass spectrometry

Li et al. (2016)

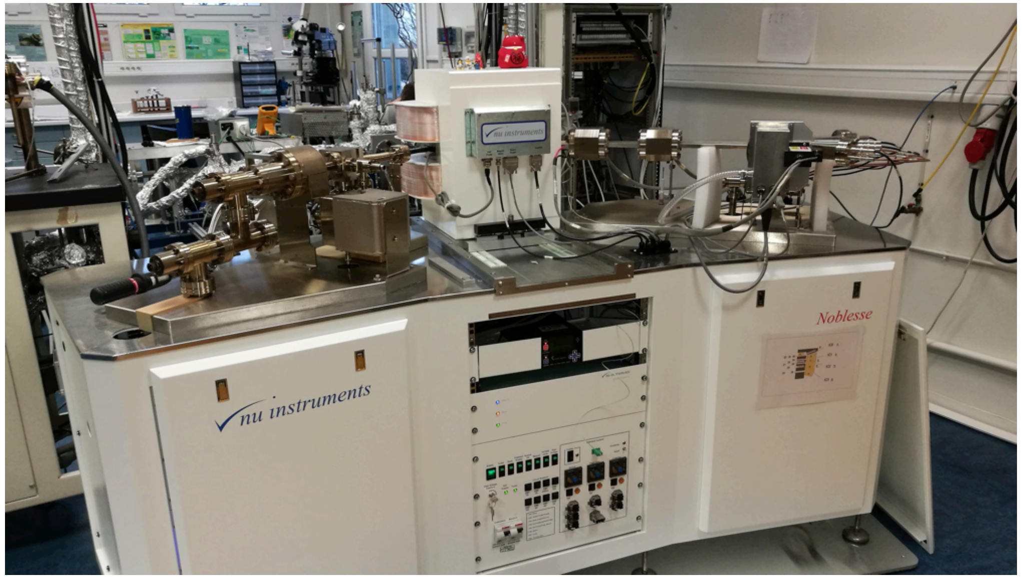


After separation of
metal and silicate phases :



Purification step

Measured by
noble gas static mass spectrometry



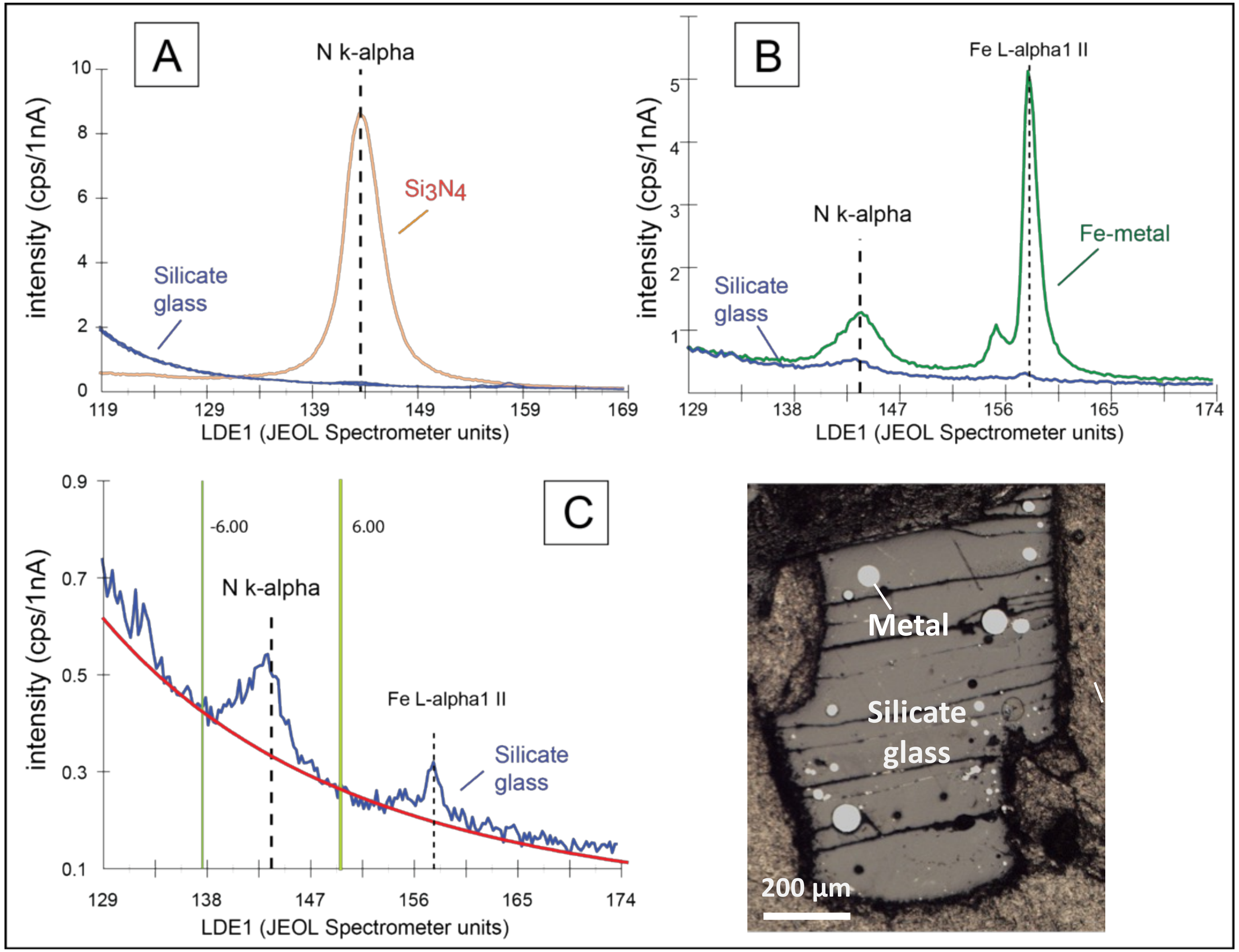
N metal-silicate partitioning

Measurements

EPMA

Von der Handt and Dalou (2016):

- resolves concentrations down to a **detection limit of 0.04 wt% N…**
- With an analytical errors **better than 3% for concentrations > 0.6 wt%.**



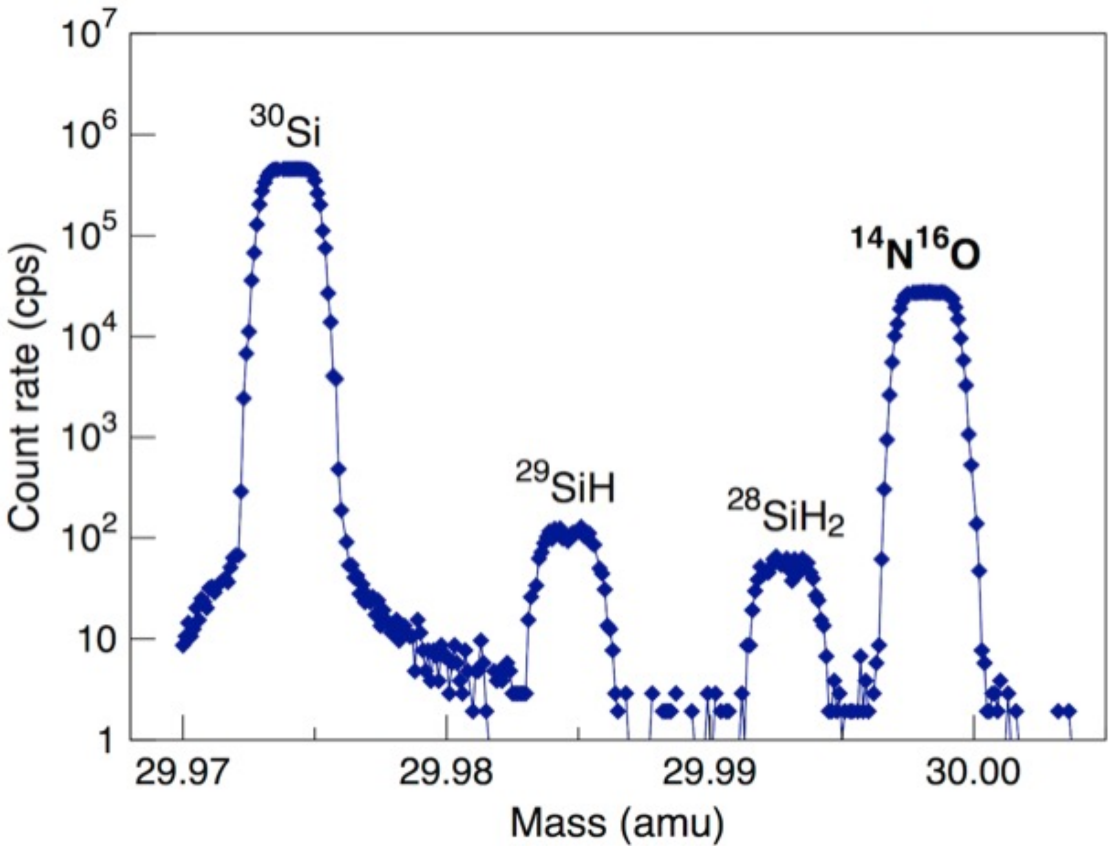
N metal-silicate partitioning

Measurements

SIMS

Silicate glass analysis
following Füri et al. (2018)

$^{14}N^{16}O^{-}$ molecular ions at
a nominal mass resolution m/Δm = 14,000



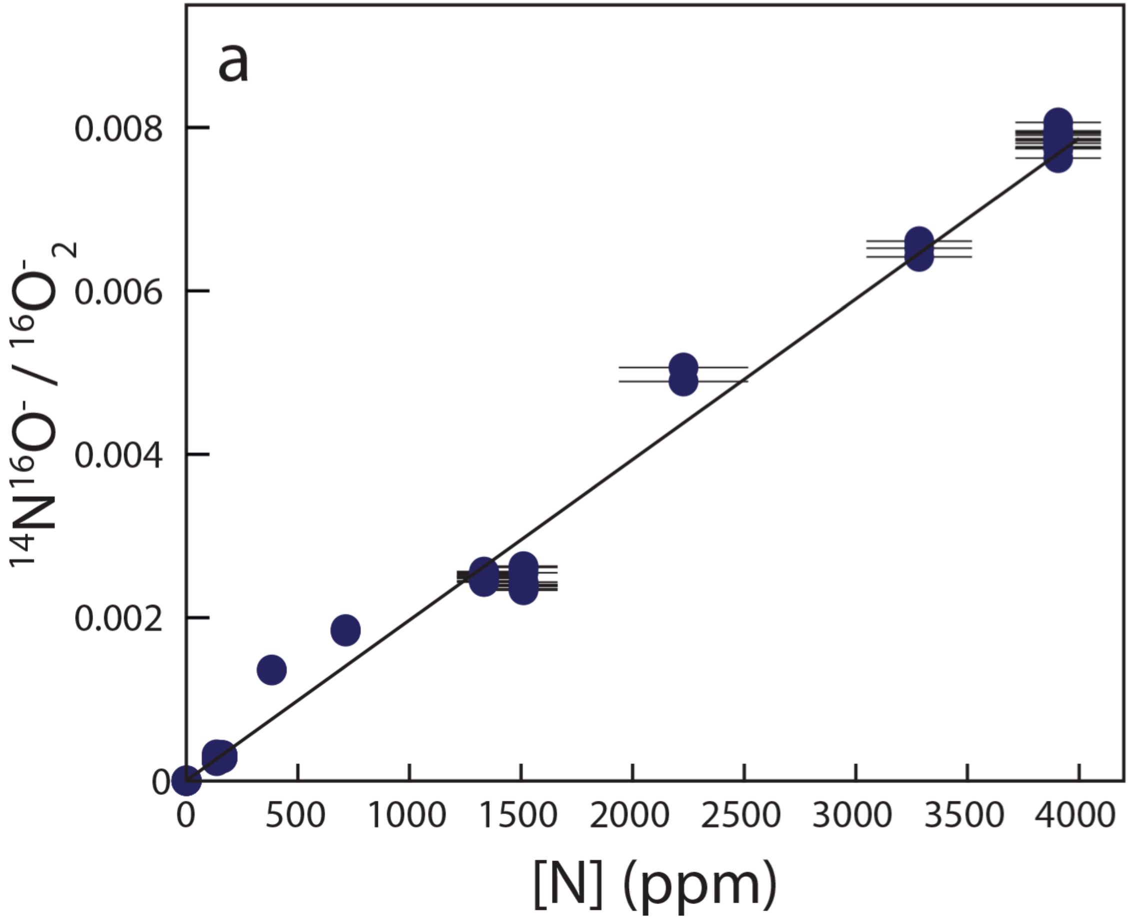
N metal-silicate partitioning

Measurements

SIMS

Silicate glass analysis following Füri et al. (2018)

Silicate glasses used as reference materials

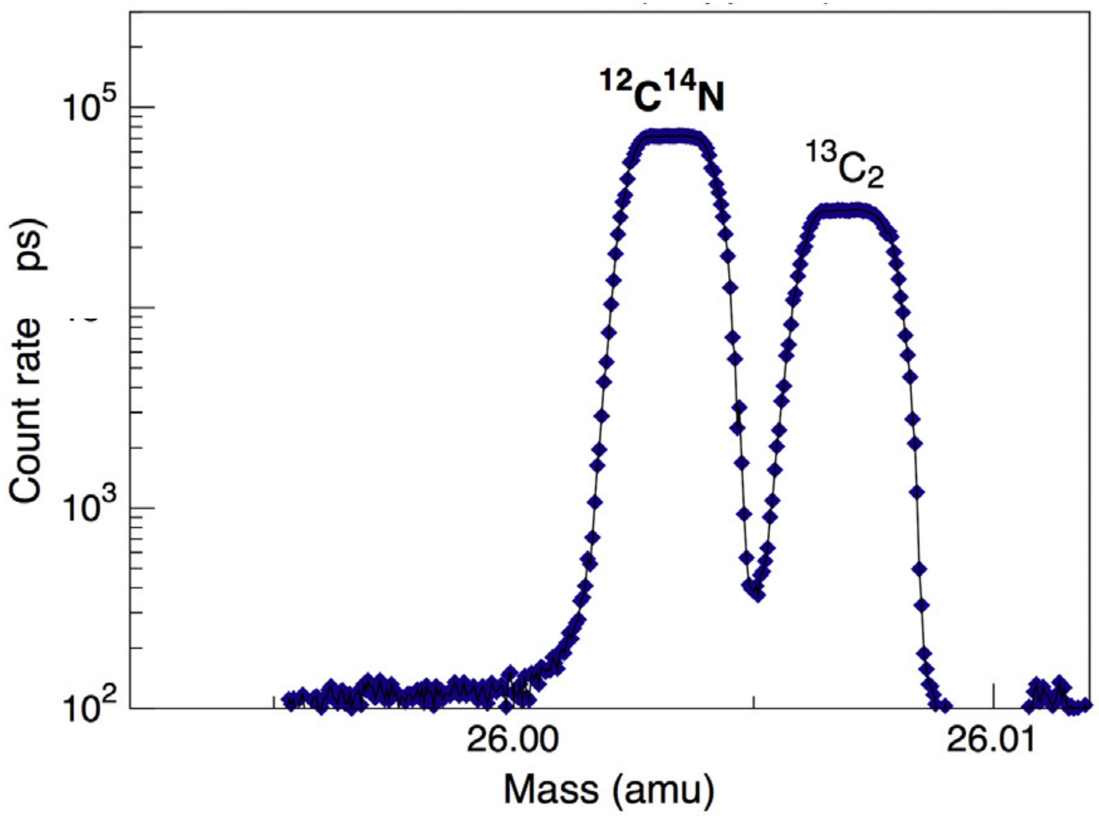


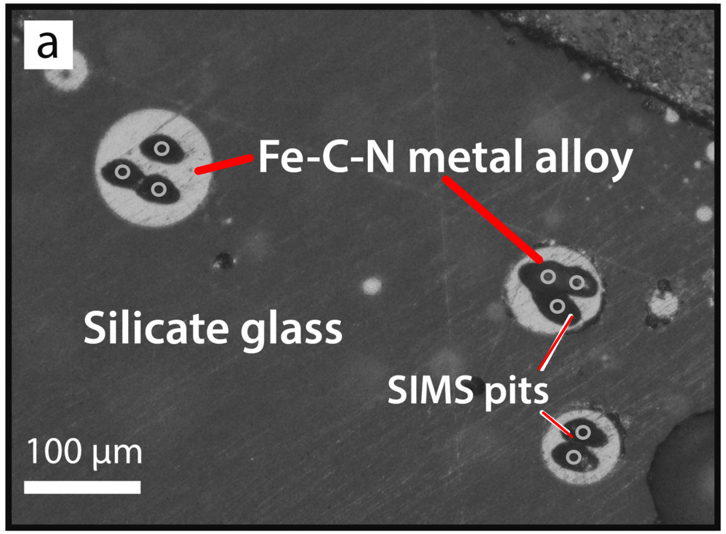
N metal-silicate partitioning

Measurements

SIMS

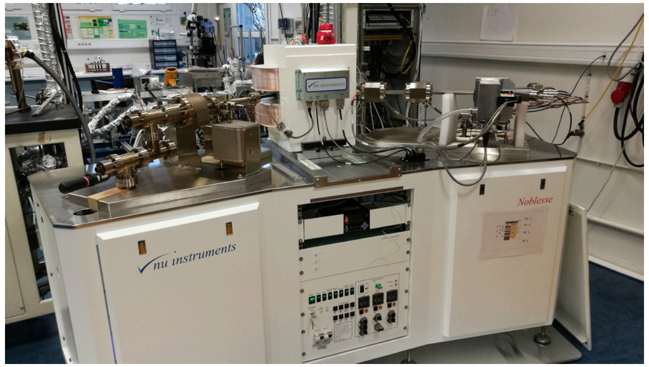
$^{12}C^{14}N^{-}$ molecular ions
at a nominal mass resolution m/Δm = 8,000





Metal standards:

metal beads analyzed by noble gas static mass spectrometry

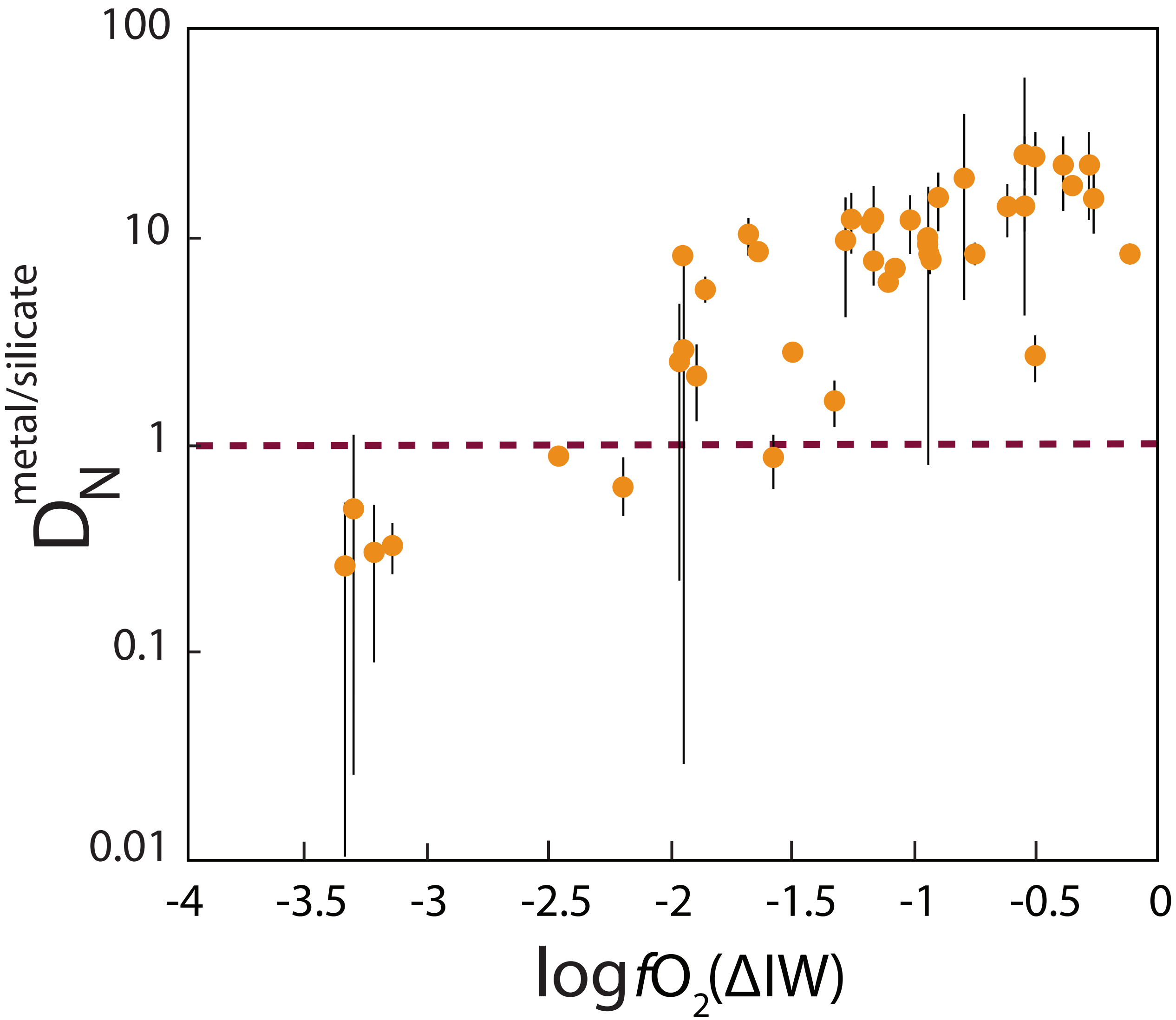


Füri et al. (2018)

N metal-silicate partitioning

Results

EPMA – 2017

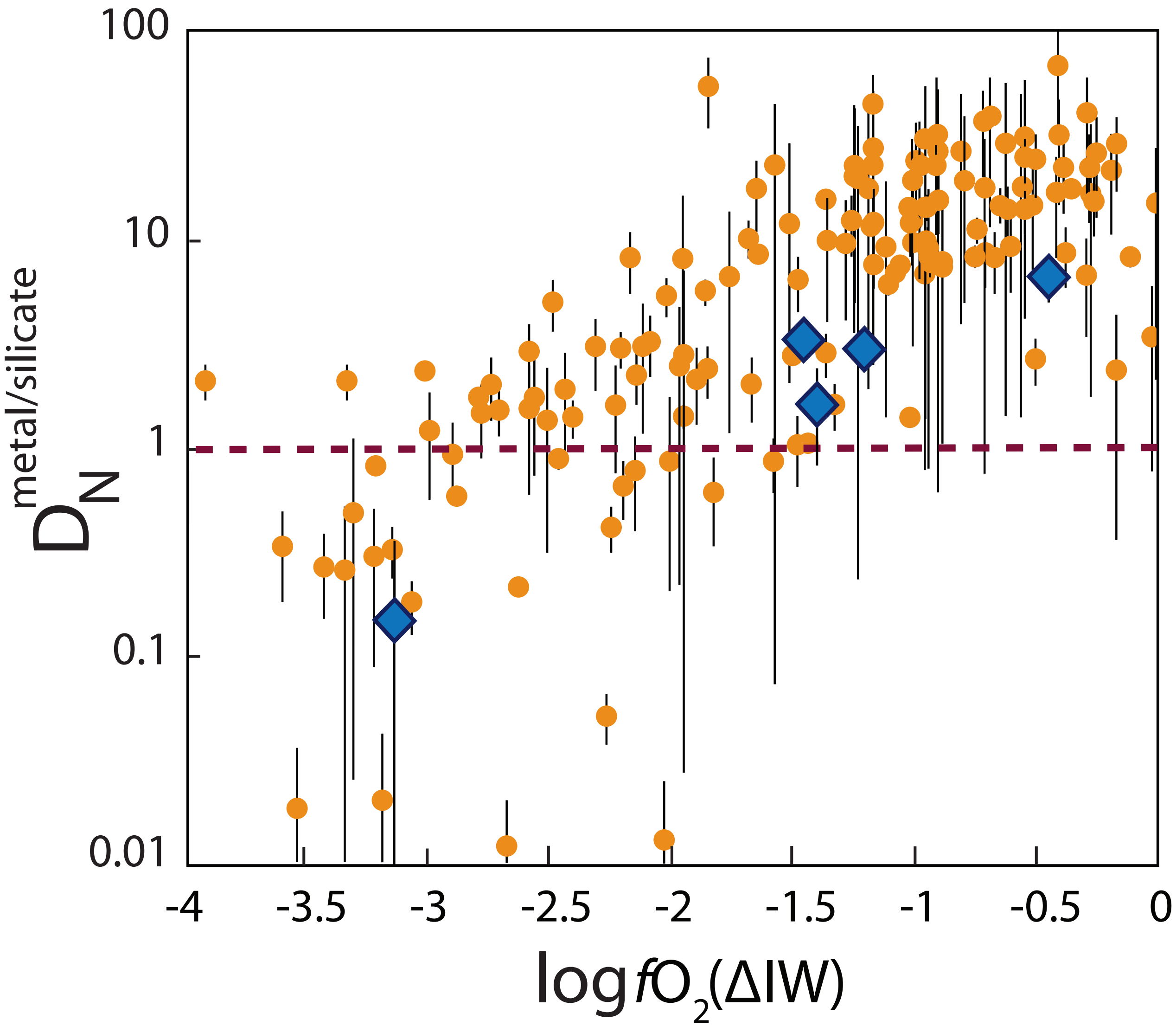


Kadik et al. 2011; 2013; 2015
Roskosz et al. 2013
Li et al. 2016
Dalou et al. 2017

N metal-silicate partitioning

Results (data before 2020):

EPMA versus SIMS



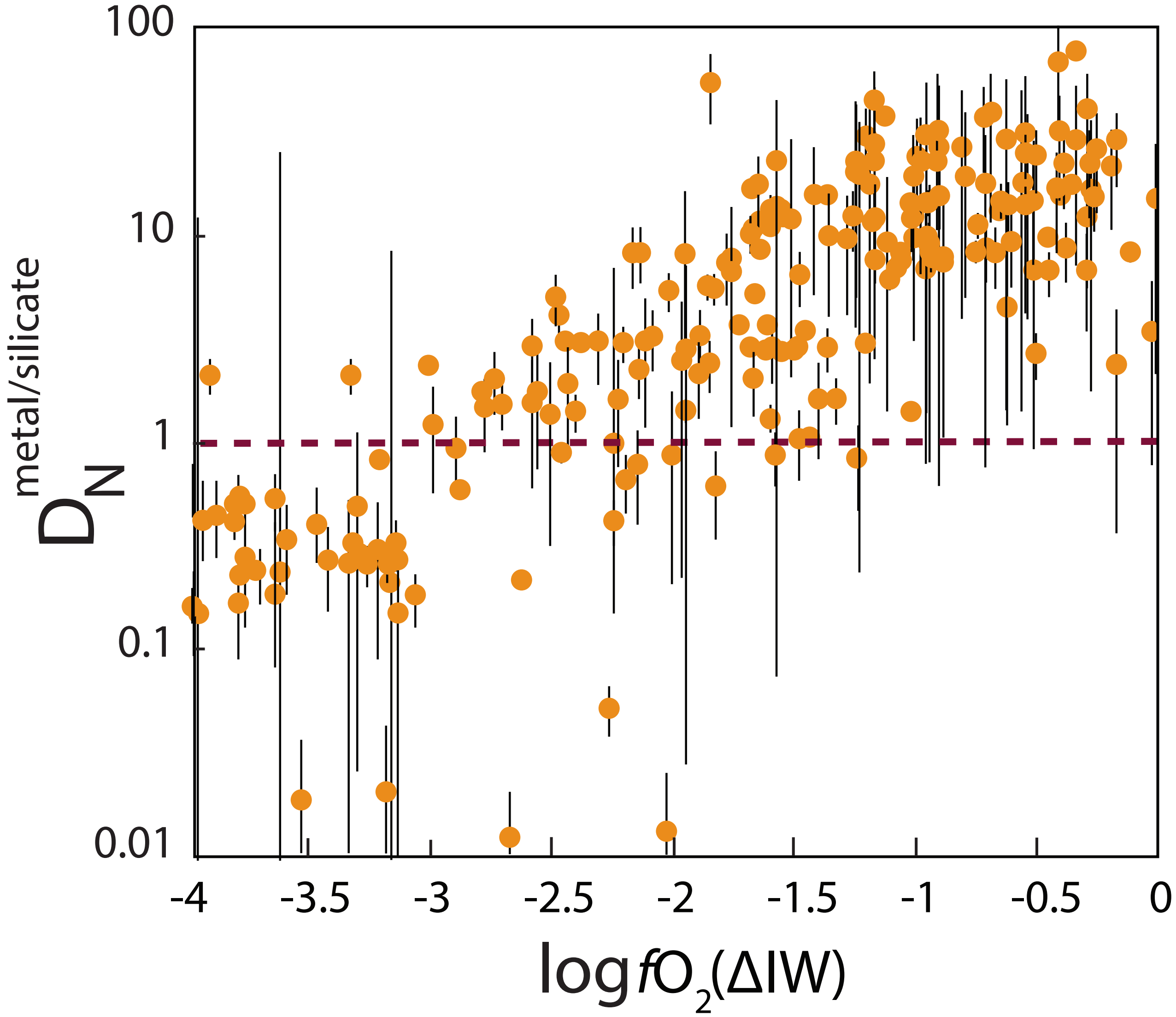
Kadik et al. 2011; 2013; 2015; 2017
Roskosz et al. 2013
Li et al. 2016
Dalou et al. 2017; 2019
Speelmanns et al. 2018; 2019
Grewal et al. 2019a, b, 2021

N metal-silicate partitioning

Results (data in 2022):

Graphite capsules

Kadik et al. 2011; 2013; 2015; 2017
Roskosz et al. 2013
Li et al. 2016
Dalou et al. 2017; 2019
Speelmanns et al. 2018; 2019
Grewal et al. 2019a, b
Jackson et al. 2021
Shi et al. 2022
Dasgupta et al. 2022

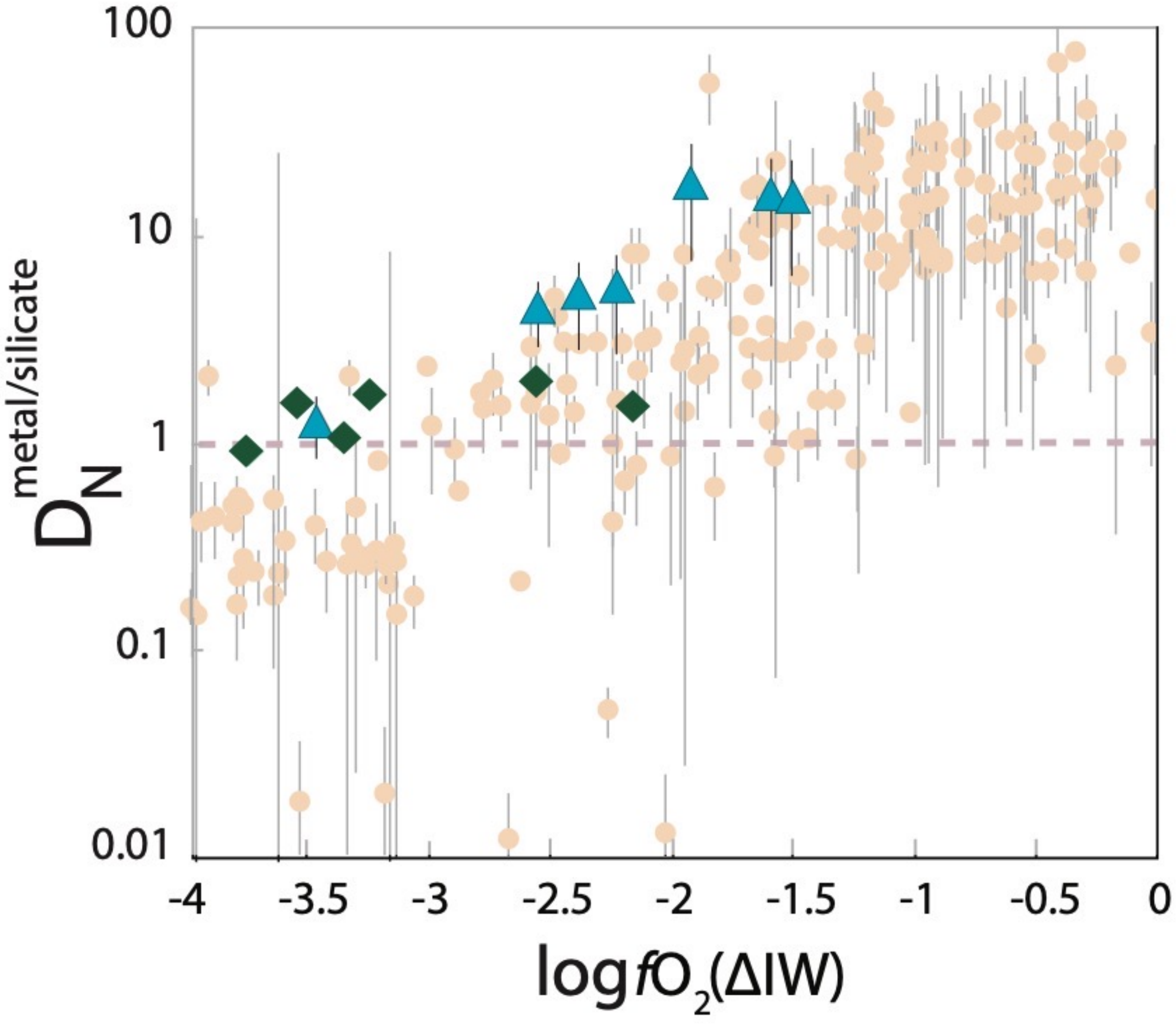


N metal-silicate partitioning

Results (data in 2022):

Graphite ● versus
MgO ▲ and Fo ◆ capsules

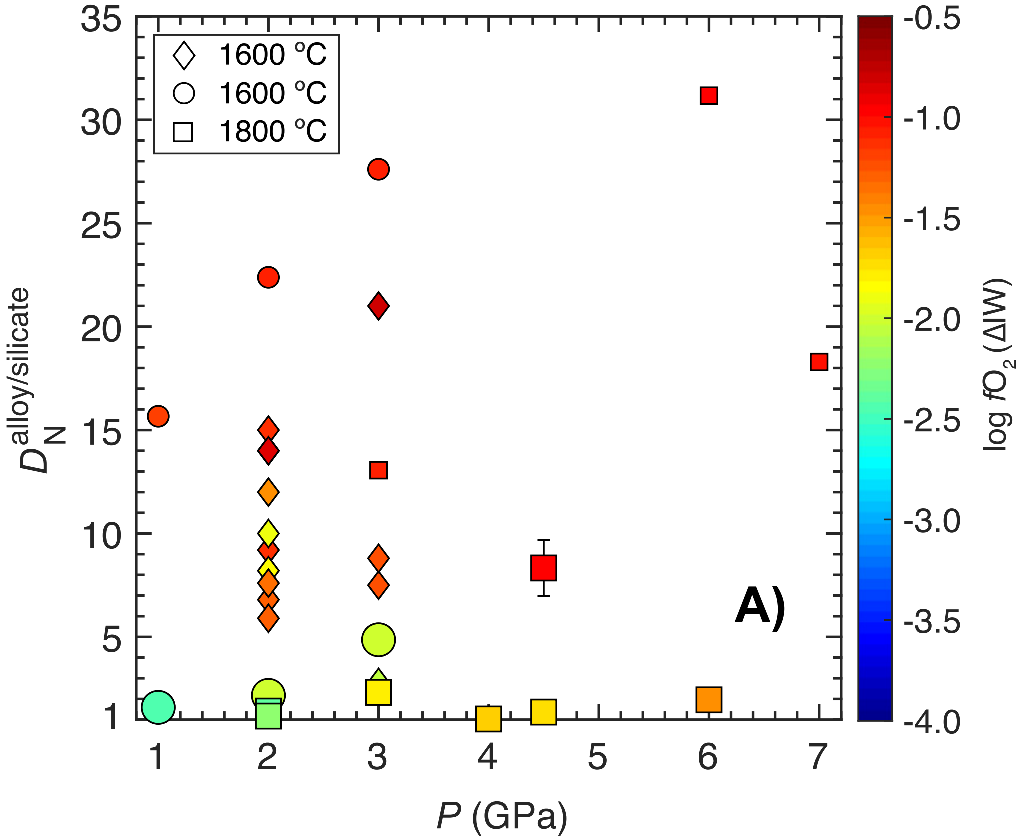
Grewal et al. 2021 Dalou et al. *In prep*

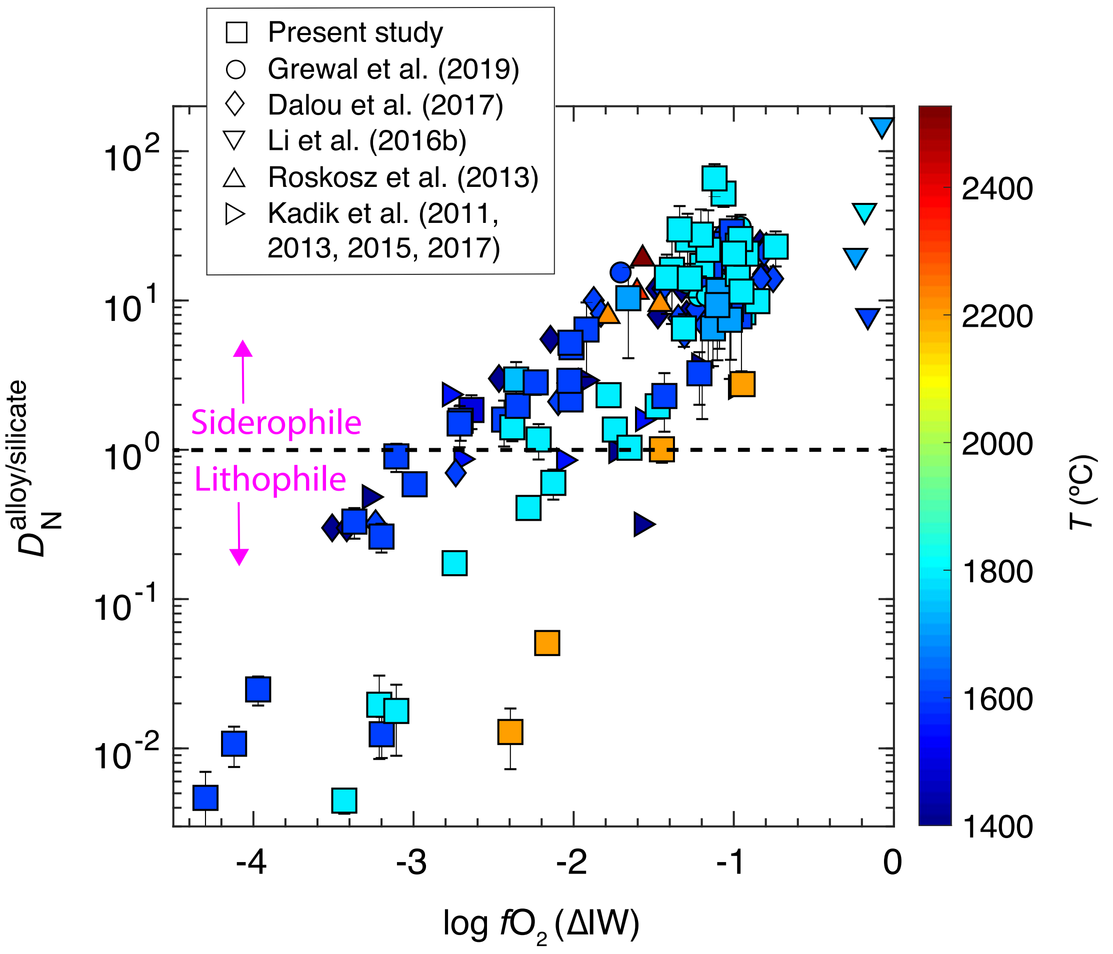


N metal-silicate partitioning

Results

Scatter in the data ? ➡ *P-T conditions :*





From Grewal et al. 2020

N metal-silicate partitioning

Results

Why fO_2 controls on N metal-silicate partitioning ?

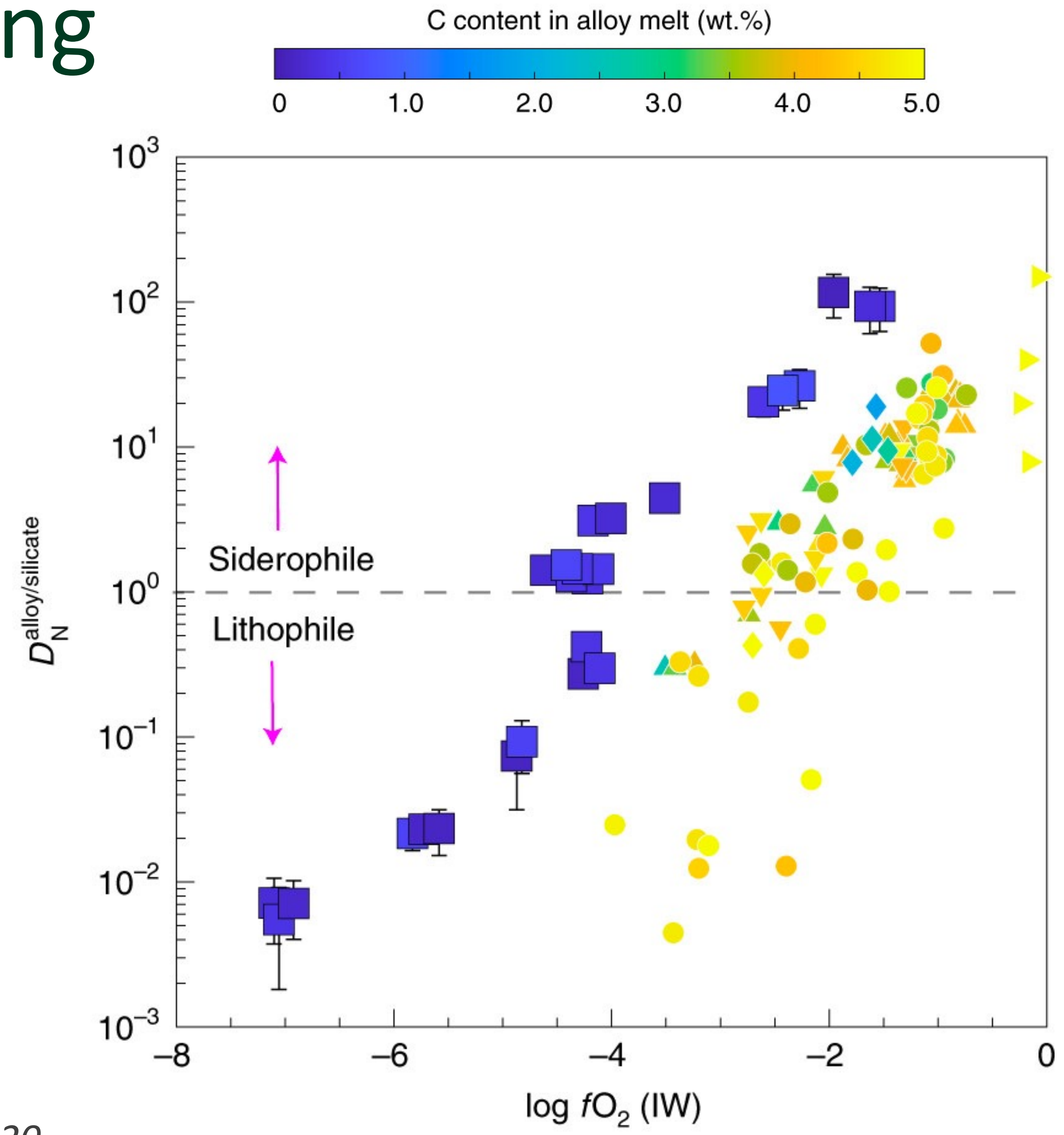
N metal-silicate partitioning

Results

Why fO_2 controls on N metal-silicate partitioning ?

1. Metal composition ?

- fO_2 drives the solubility of C and Si, and indirectly that of N in core-forming metals.



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N metal-silicate partitioning

Results

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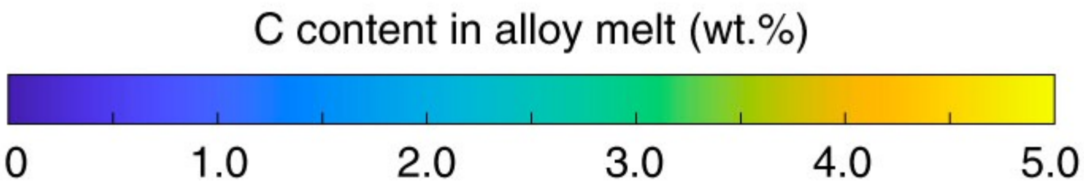

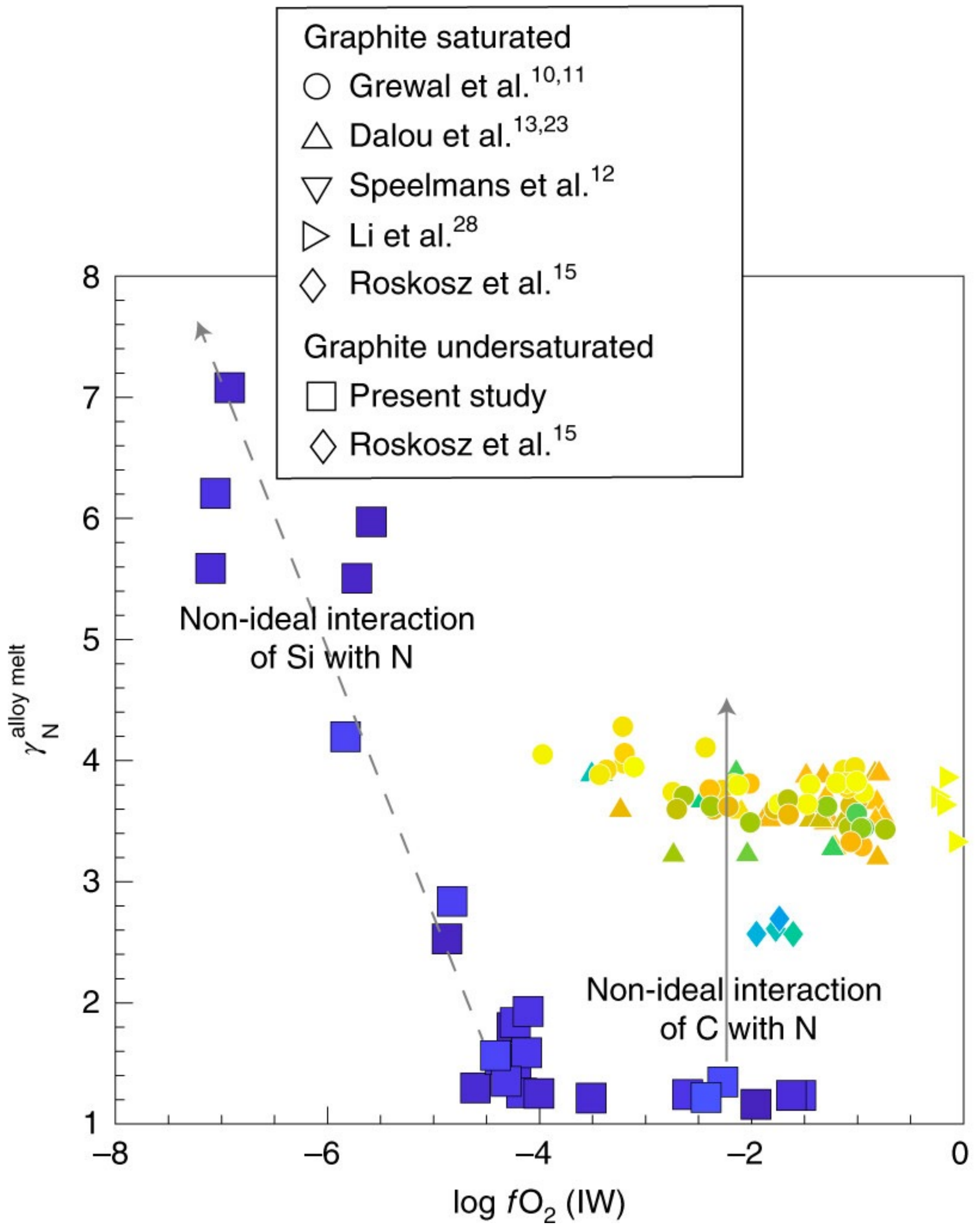

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N metal-silicate partitioning

Results

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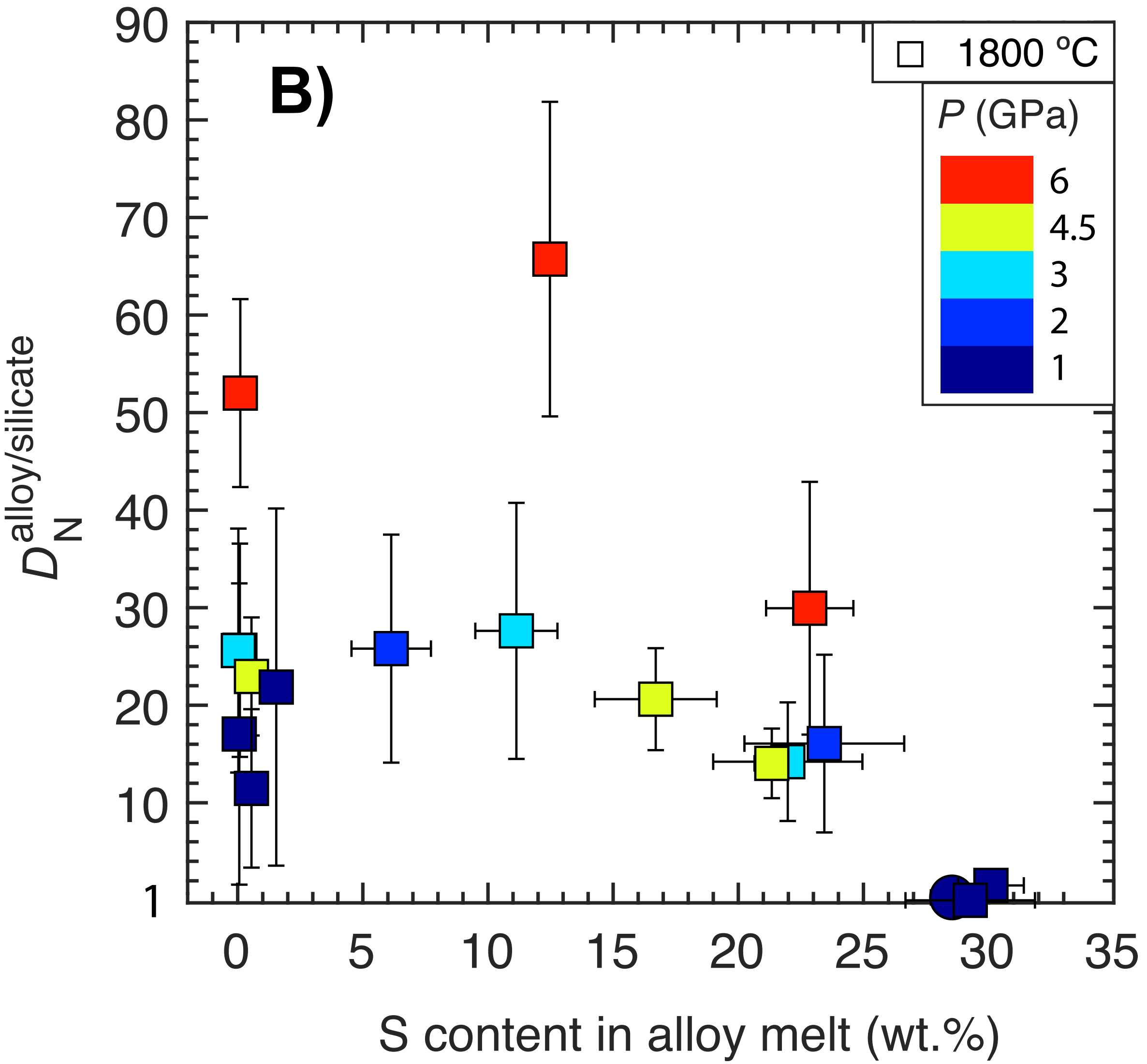


From Grewal et al. 2020

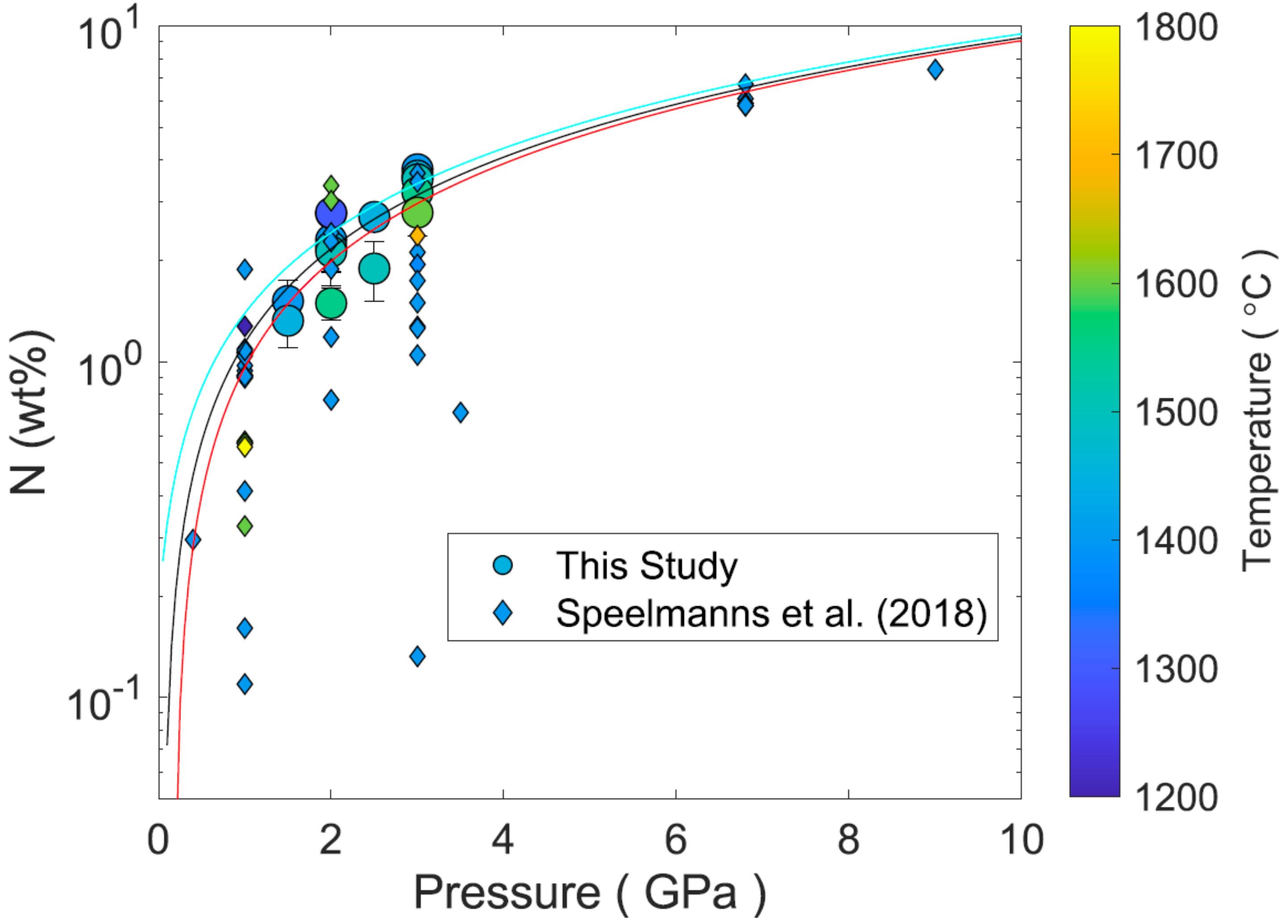
N metal-silicate partitioning

Results

Why fO_2 controls on N metal-silicate partitioning ?

1. Metal composition ?

- N solubility in metal alloys



From Dasgupta et al. 2022

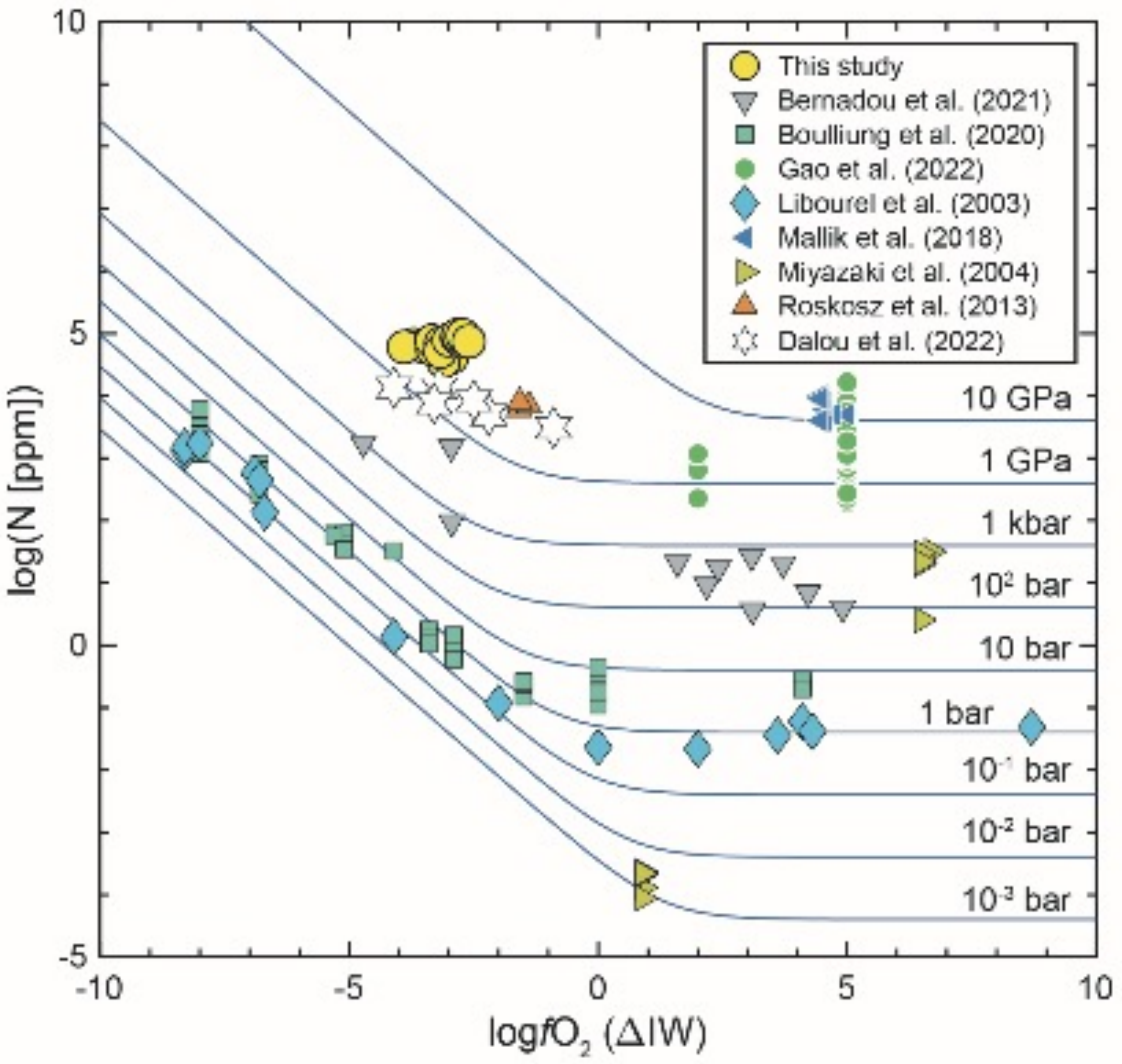
N metal-silicate partitioning

Results

Why fO_2 controls on N metal-silicate partitioning ?

2. Silicate melt composition ?

- fO_2 drives N solubility in silicate melts



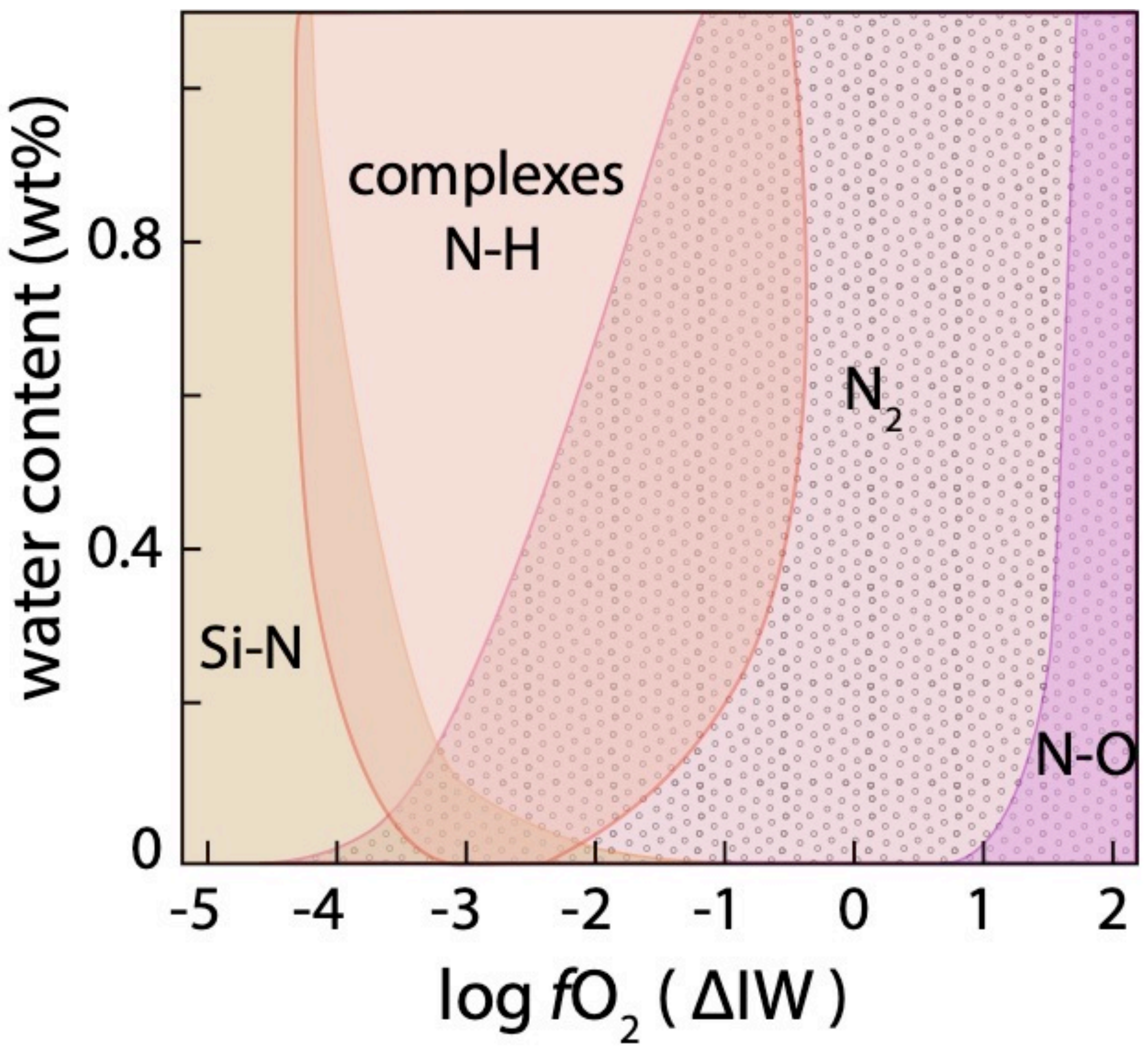
From Dasgupta et al. 2022

N metal-silicate partitioning

Results

Why fO_2 controls on N metal-silicate partitioning ?

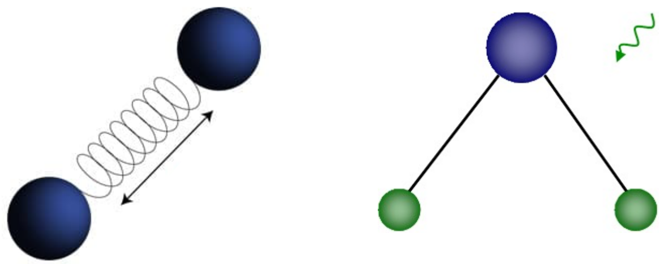
- fO_2 drives N solubility in silicate melts by changing N speciation



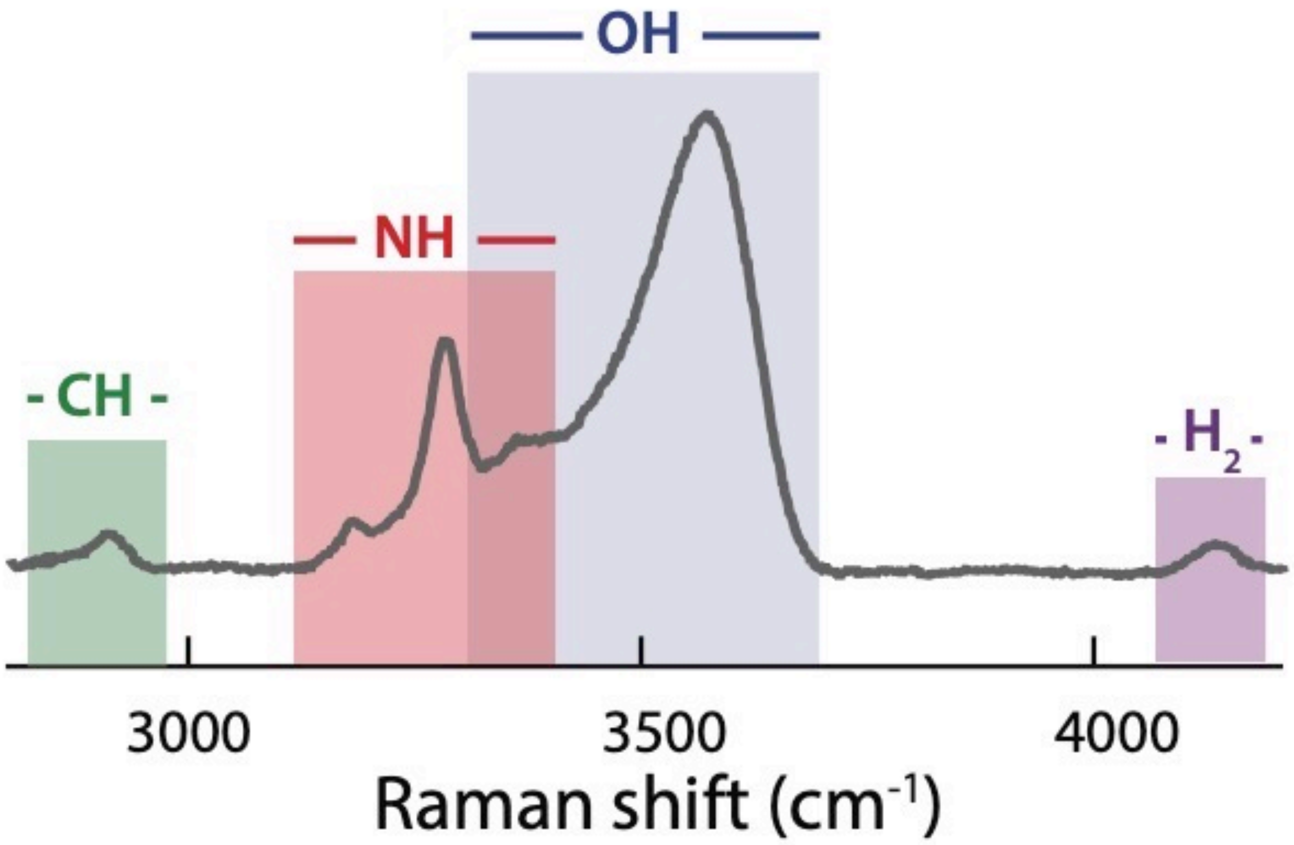
From Dalou et al. (2019b); Grewal et al. (2020)

How to measure N speciation in melts ?

N speciation can be observed by Raman spectrocopy :



Vibrational frequency



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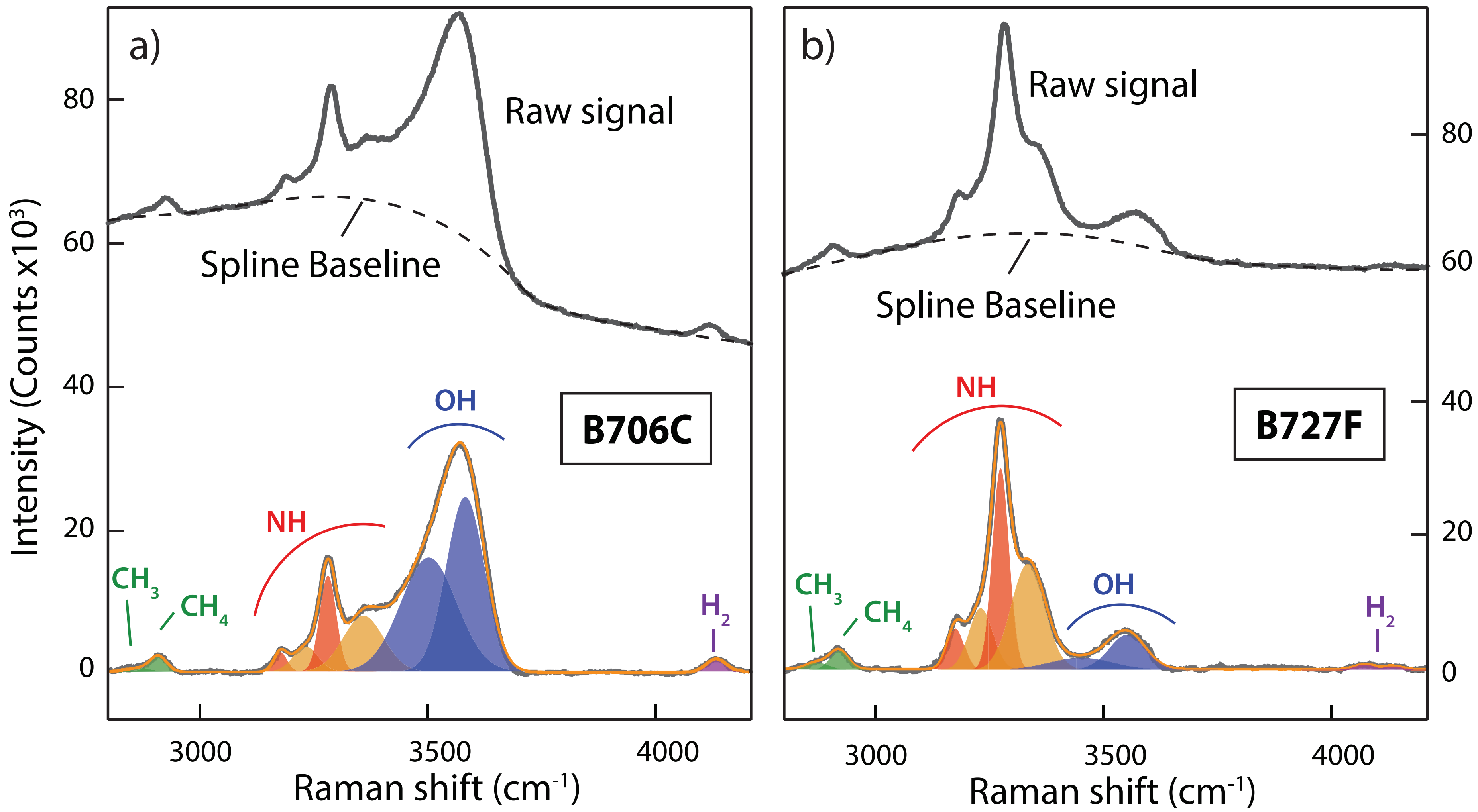
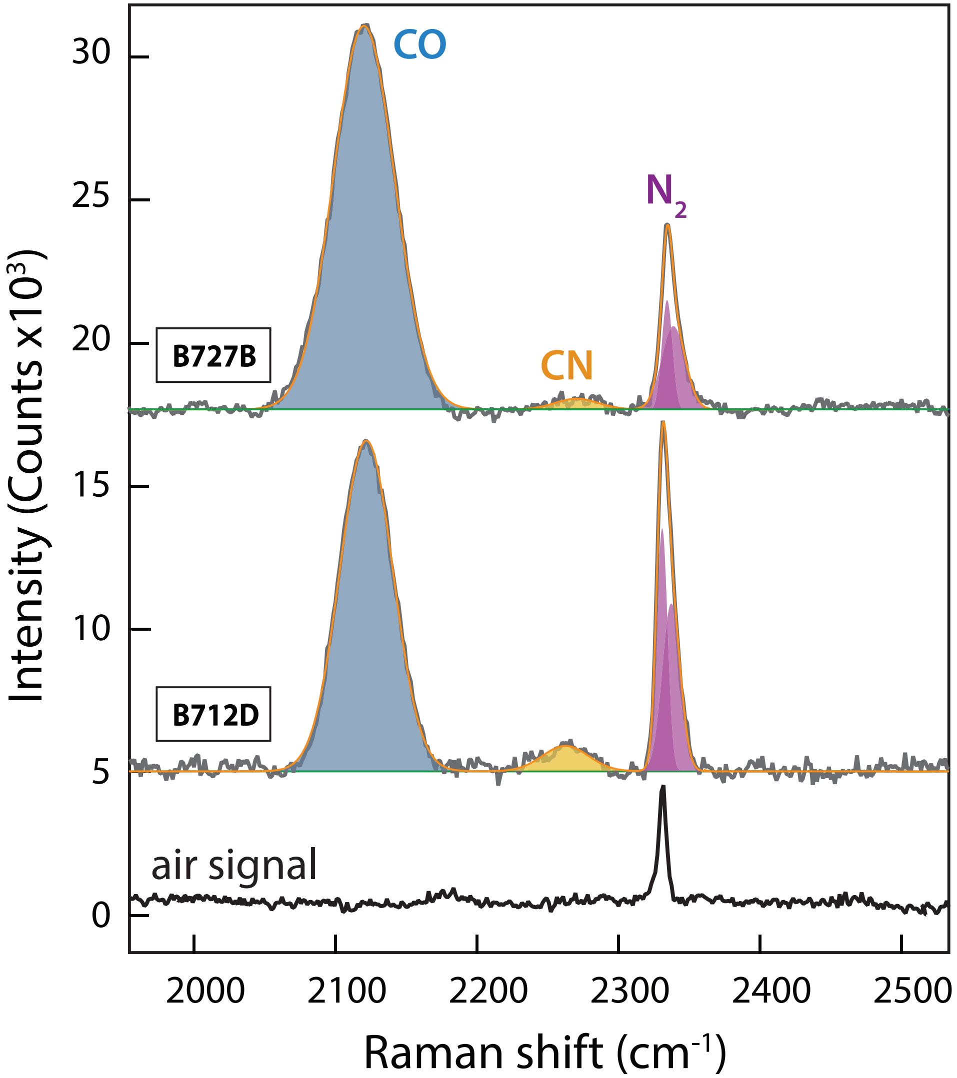


From Dalou et al. 2019

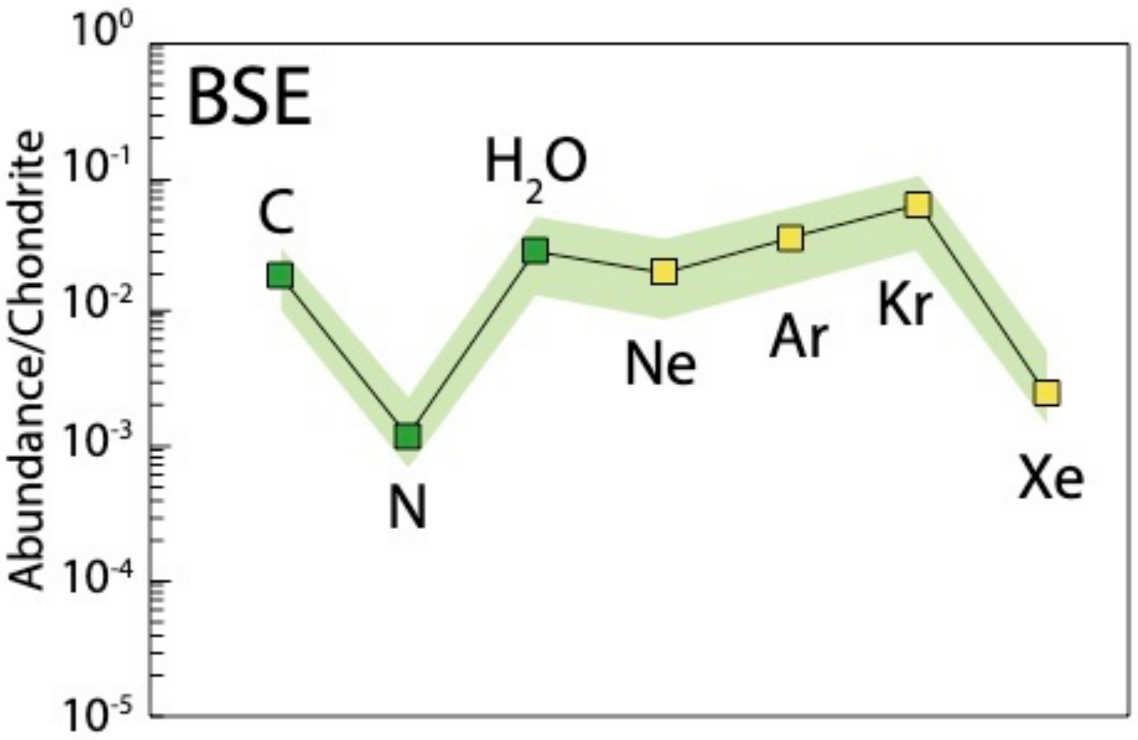
How to measure N speciation in melts ?



From Dalou et al. 2019

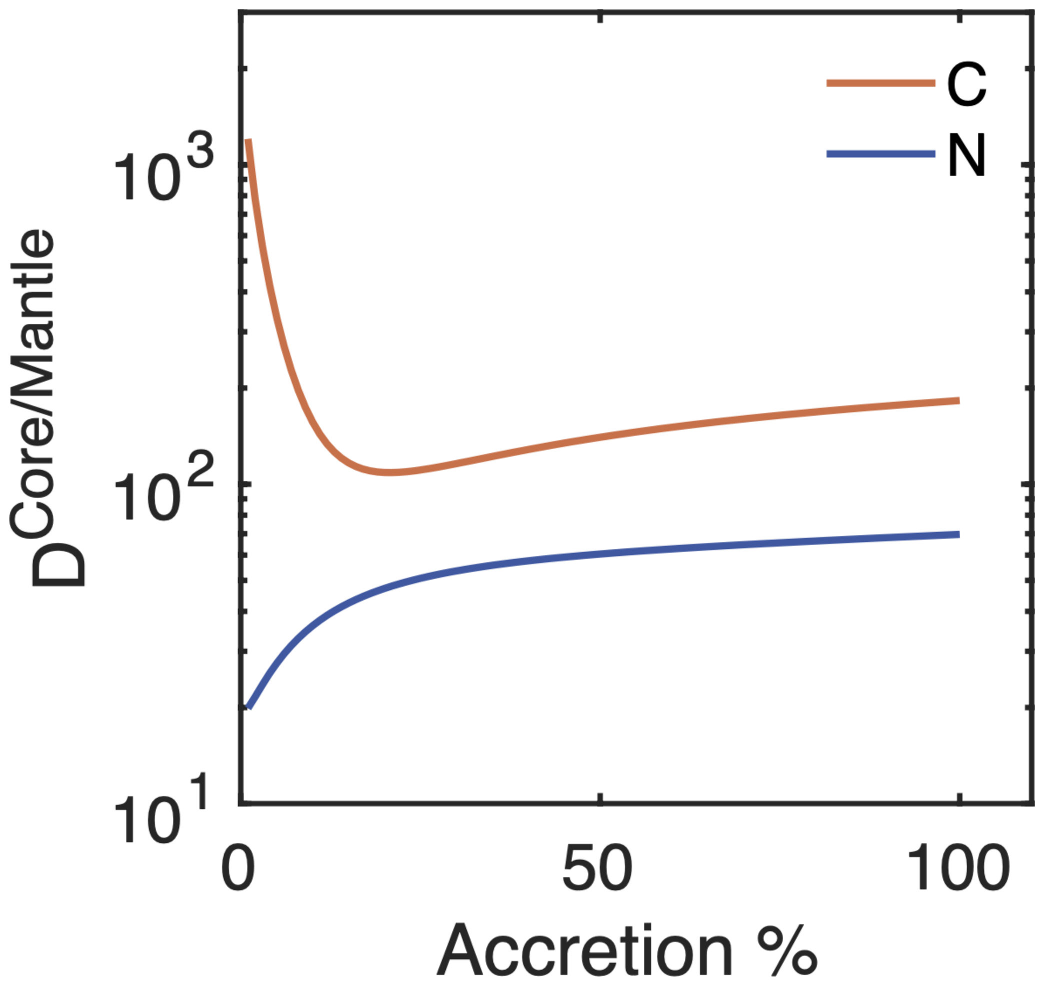
N metal-silicate partitioning

Can N metal – silicate partitioning explain ? :



After Marty 2012

C/N during core formation

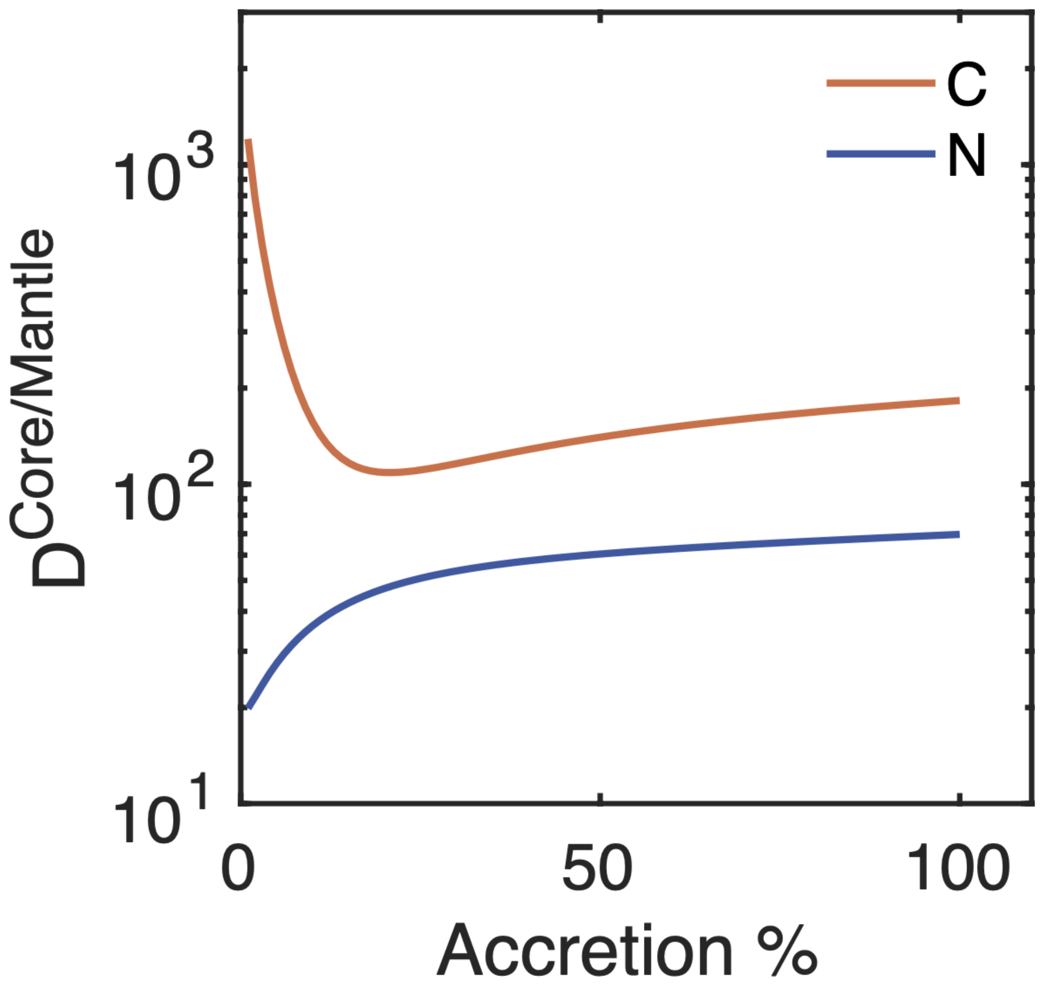


Huang et al. in prep :

Over a large range of *P-T-f*O_2 conditions :

N remains less siderophile than C (data from Fisher et al. 2020)

C/N during core formation

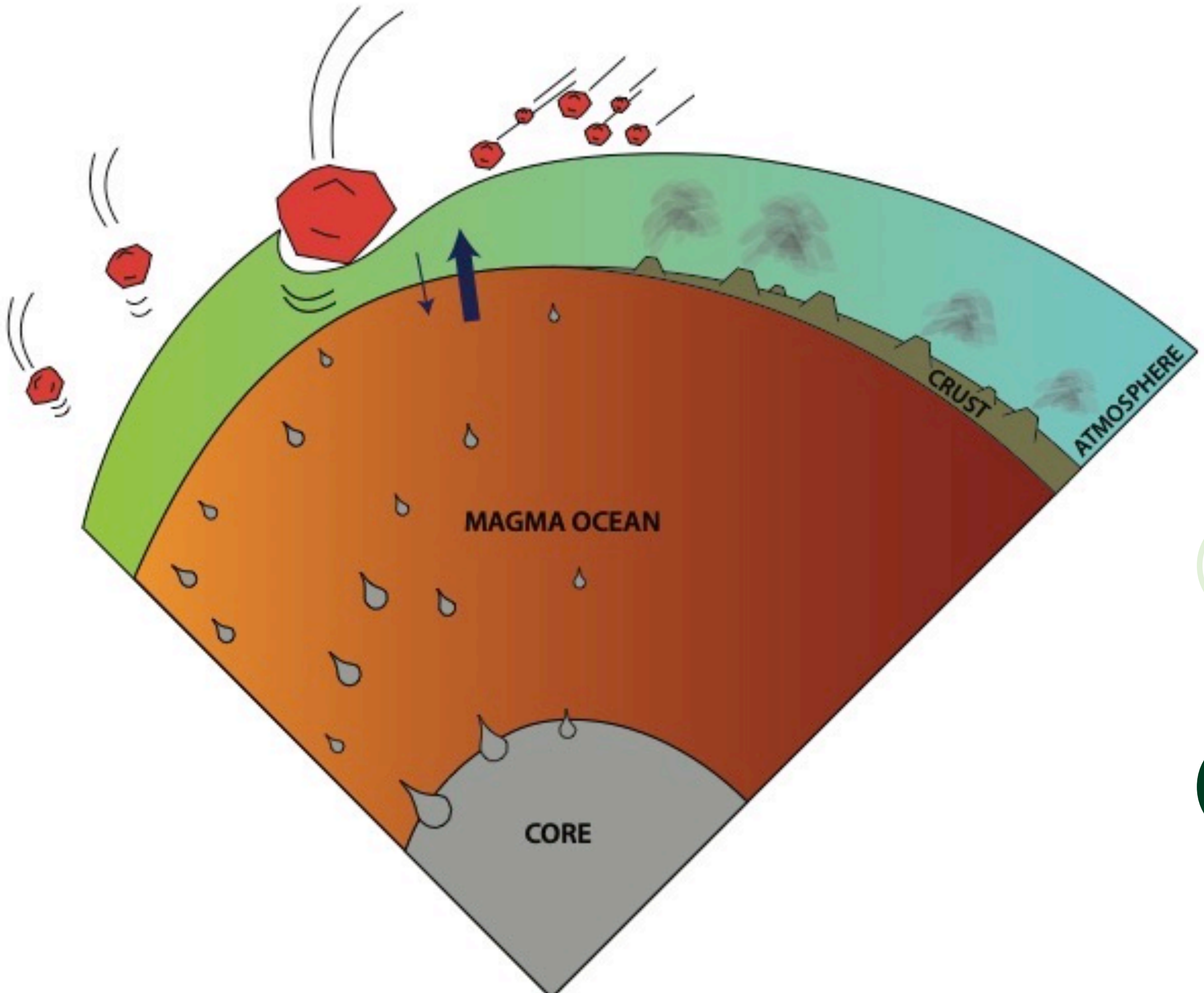


N remains less siderophile than C

Core formation alone decreased the C/N of the BSE

N depletion of the BSE

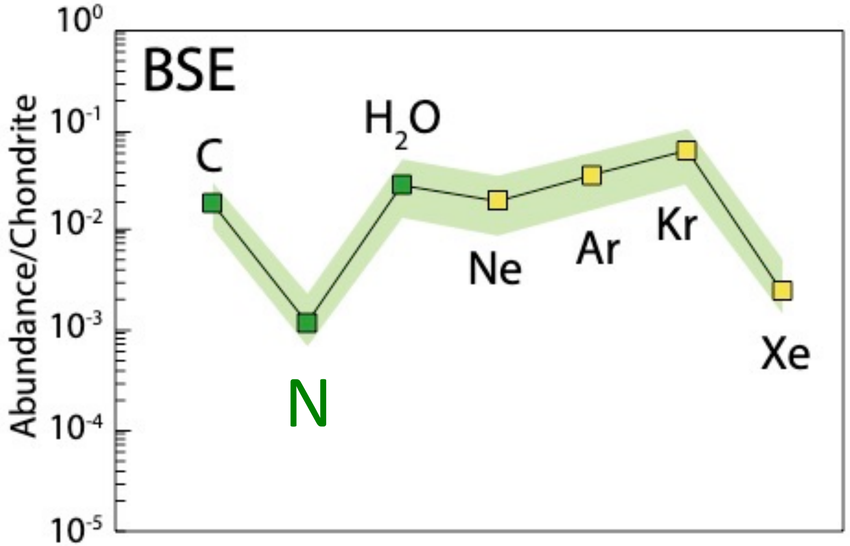
MECHANISMS to explain N depletion of the BSE?



① Core formation

② MO degassing

N depletion of the BSE



After Marty 2012

N should have been significantly more degassed or evaporated than C and H ???

N solubility in the magma ocean

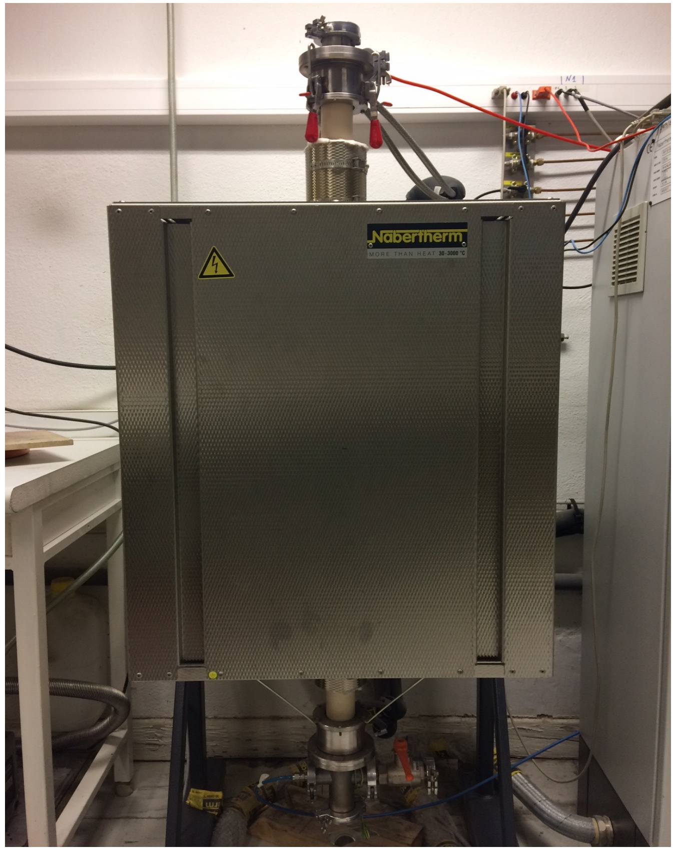
Experiments

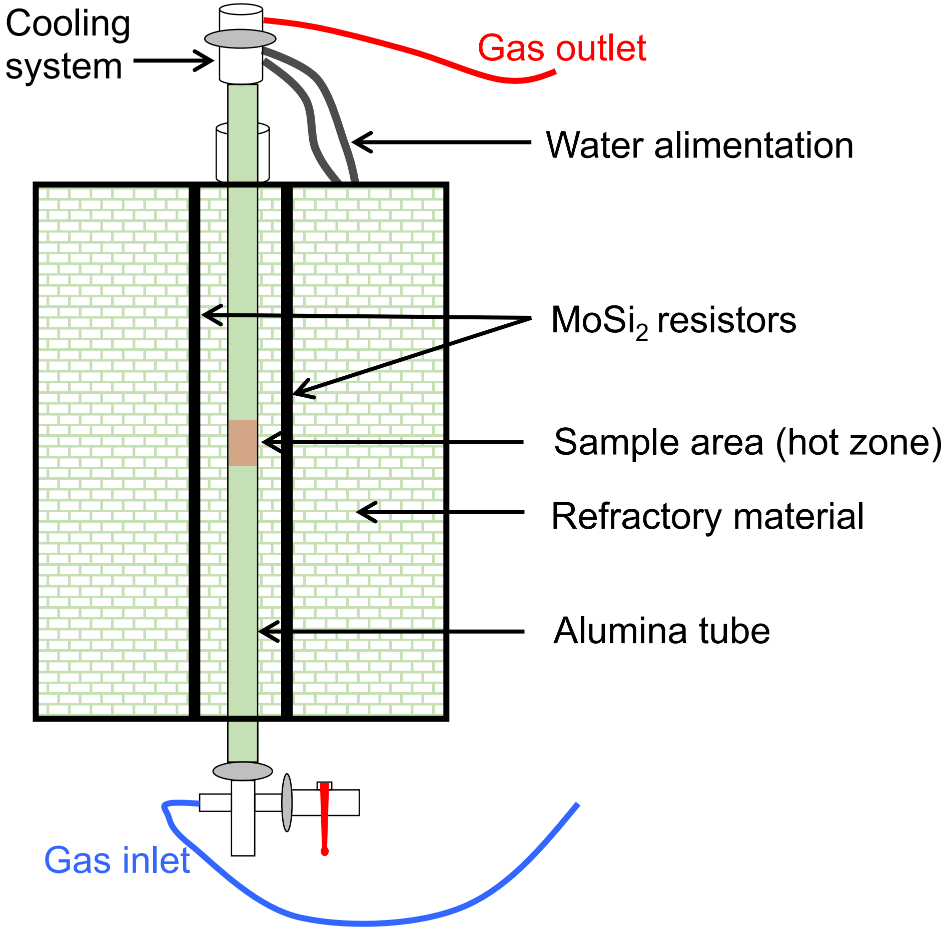
IW -8 to IW +4.1

Different methods :

- 1 atm

Courtesy of Julien Boulliung





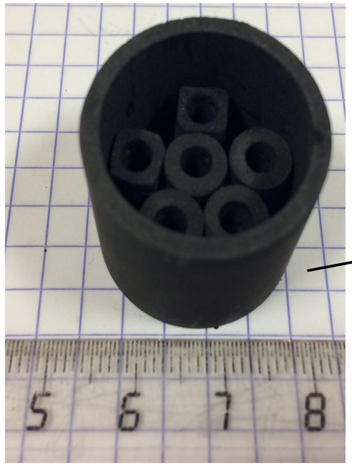
Atmosphere-controlled furnace (1 bar)
Controlled gas flow (300 cc/min)

N solubility in the magma ocean

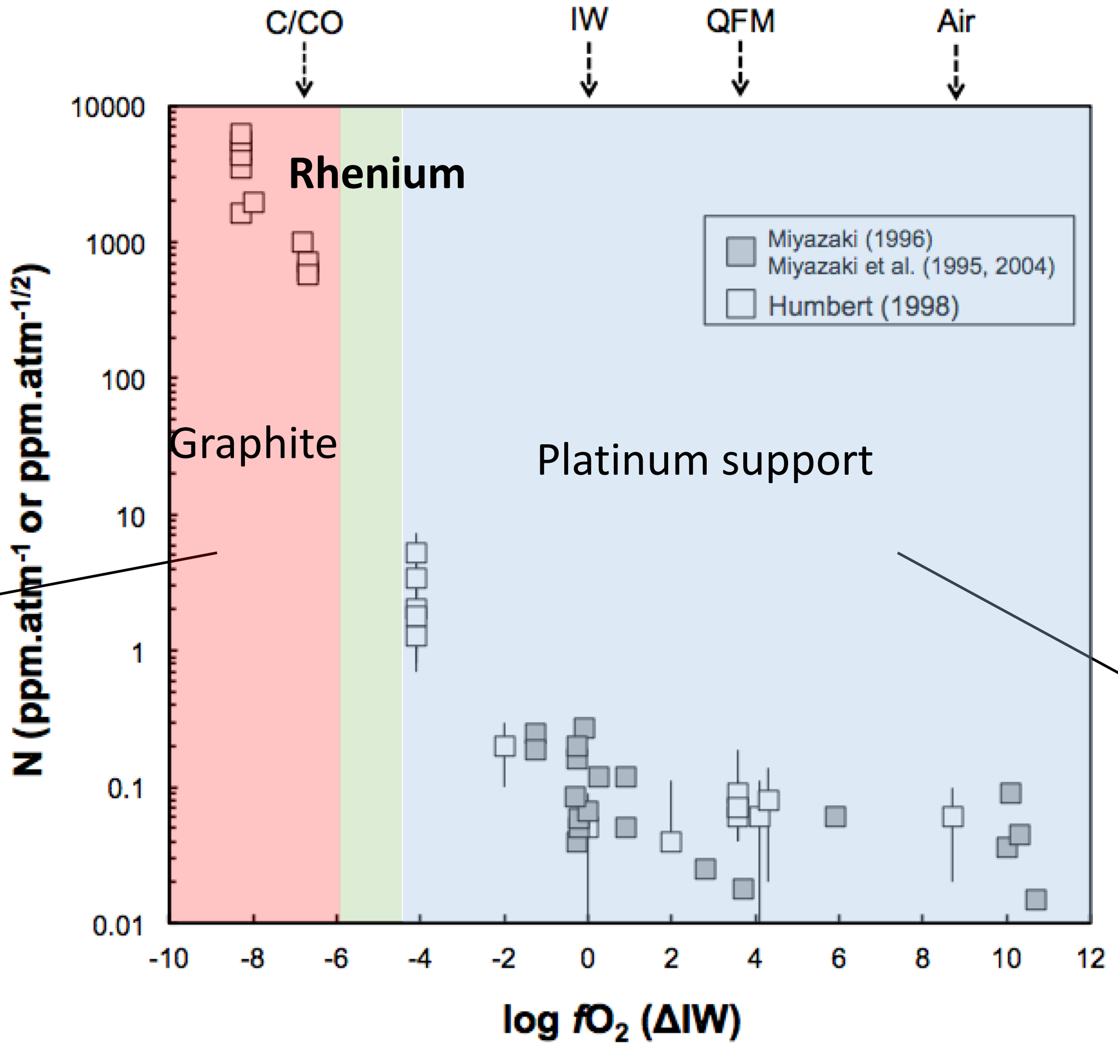
Experiments

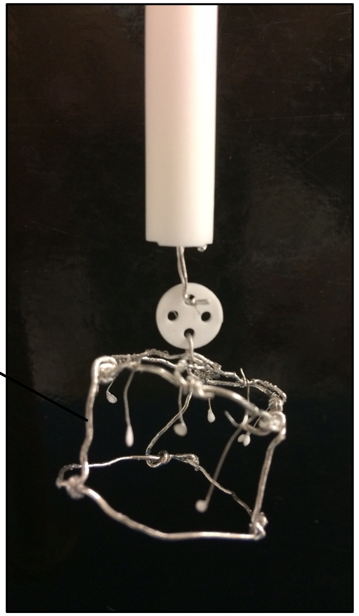
Different methods :

- 1 atm



Graphite crucible





Platinum support

Courtesy of Julien Boulliung

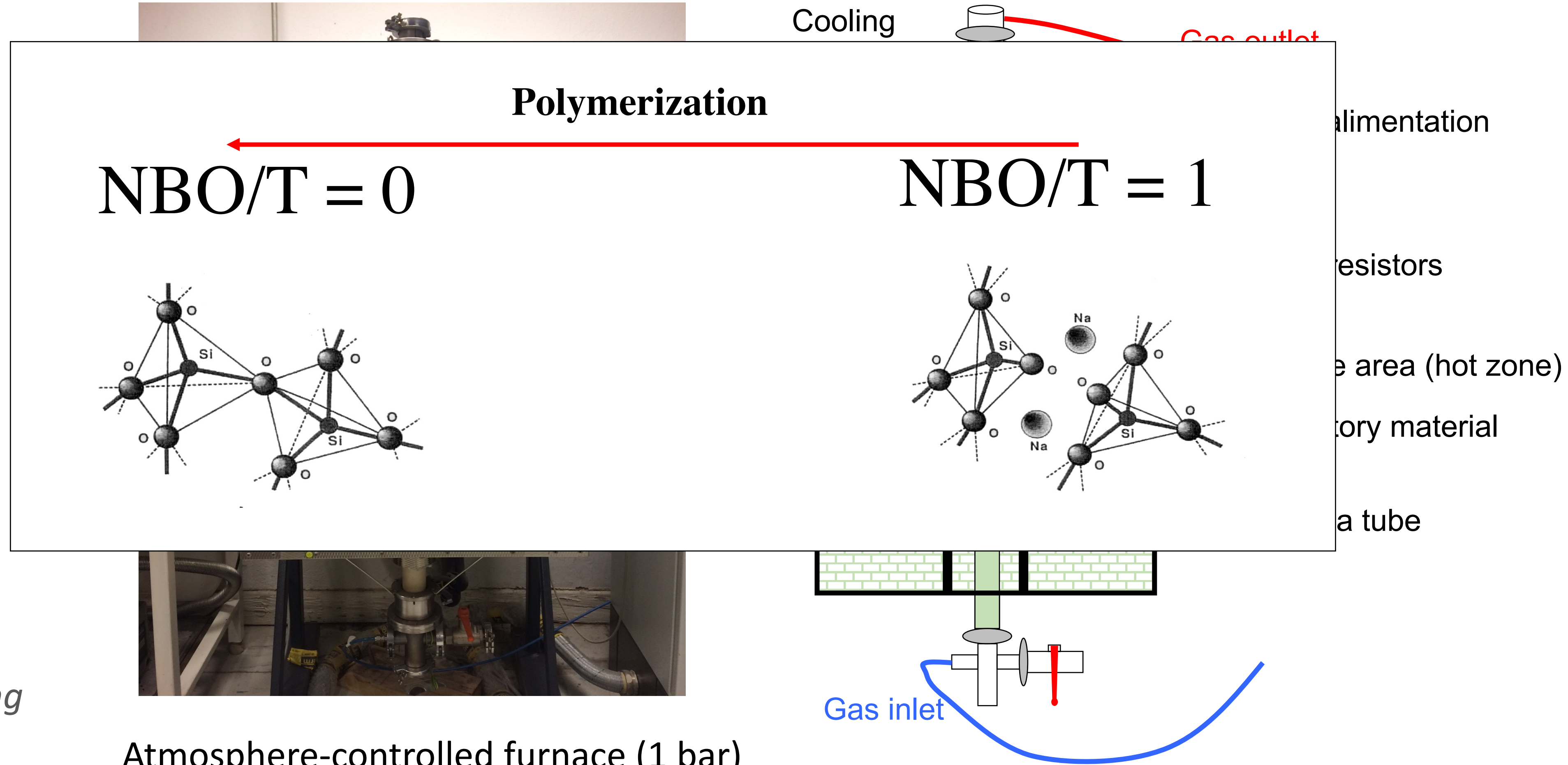
N solubility in the magma ocean

Experiments

$0 < NBO/T < 2.1$

Different methods :

- 1 atm



Courtesy of Julien Boulliung

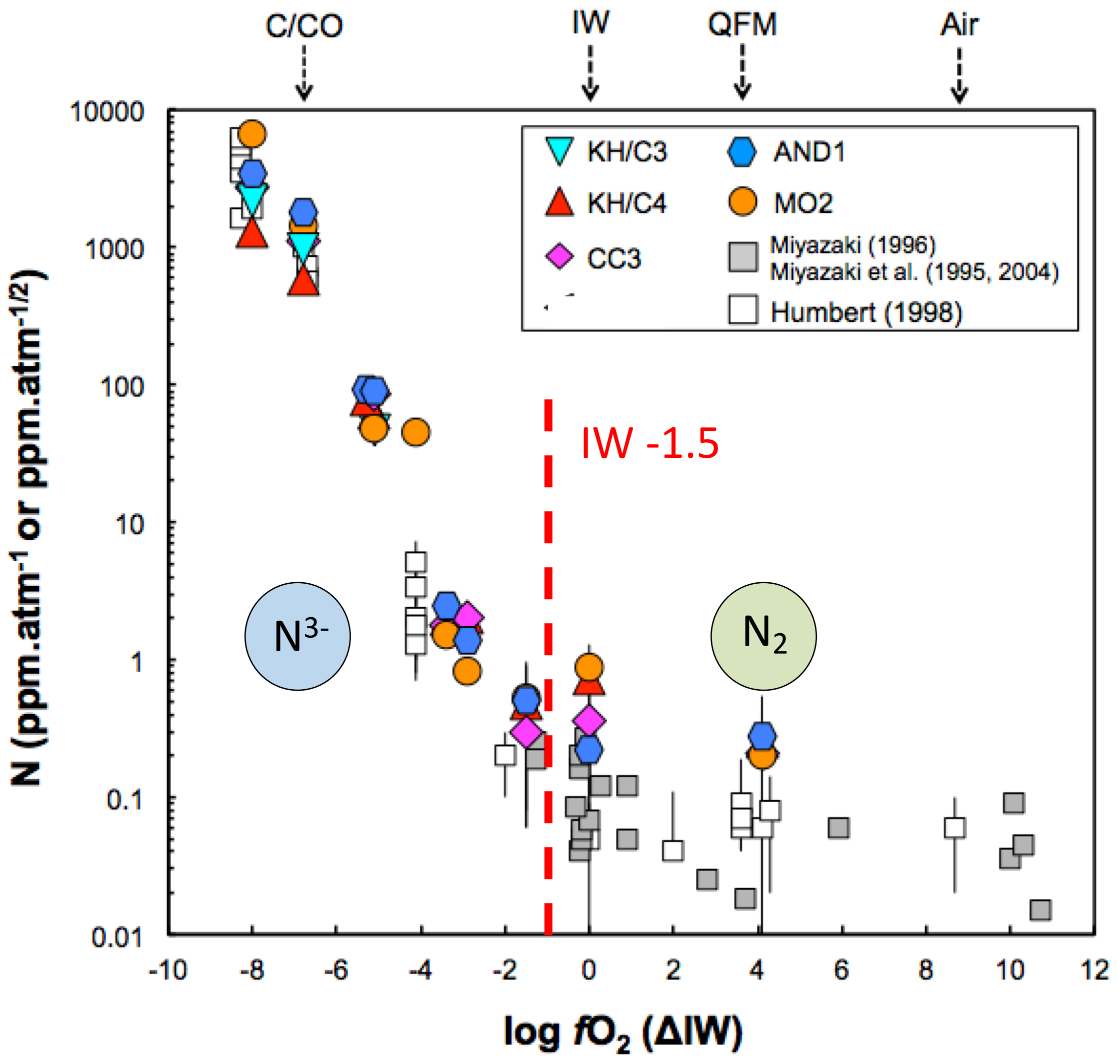
Atmosphere-controlled furnace (1 bar)
Controlled gas flow (300 cc/min)

N solubility in the magma ocean

Results at 1 atm

- N solubility in silicate melts strongly depends on fO_2

- N chemically incorporated as:
  - N^{3-} at fO_2 < IW -1.5
  - Molecular N_2 at fO_2 ≥ IW -1.5



From Boulliung et al. (2020)

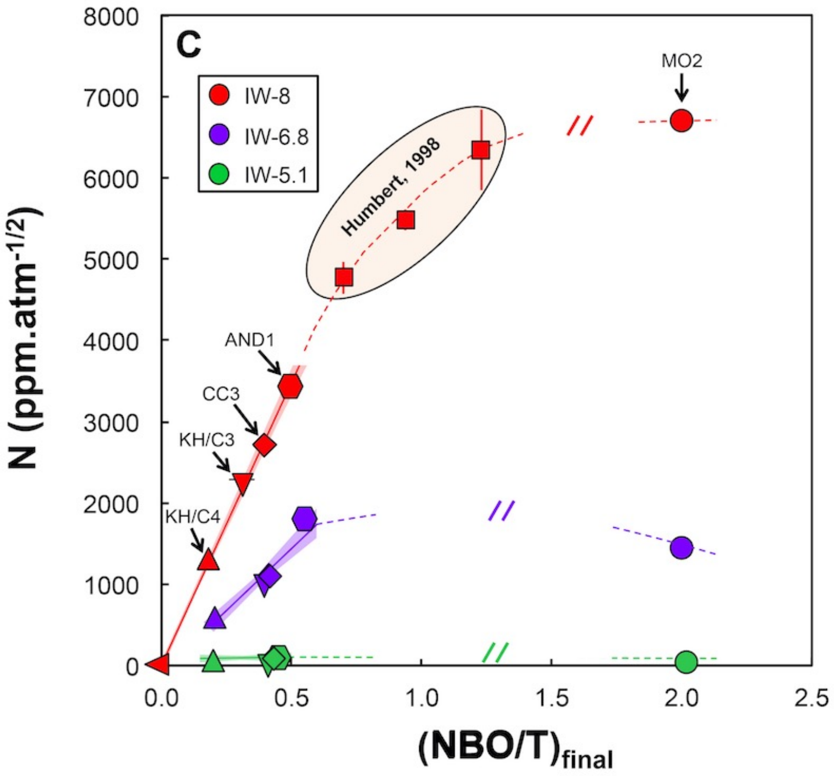
N solubility in the magma ocean

Results at 1 atm

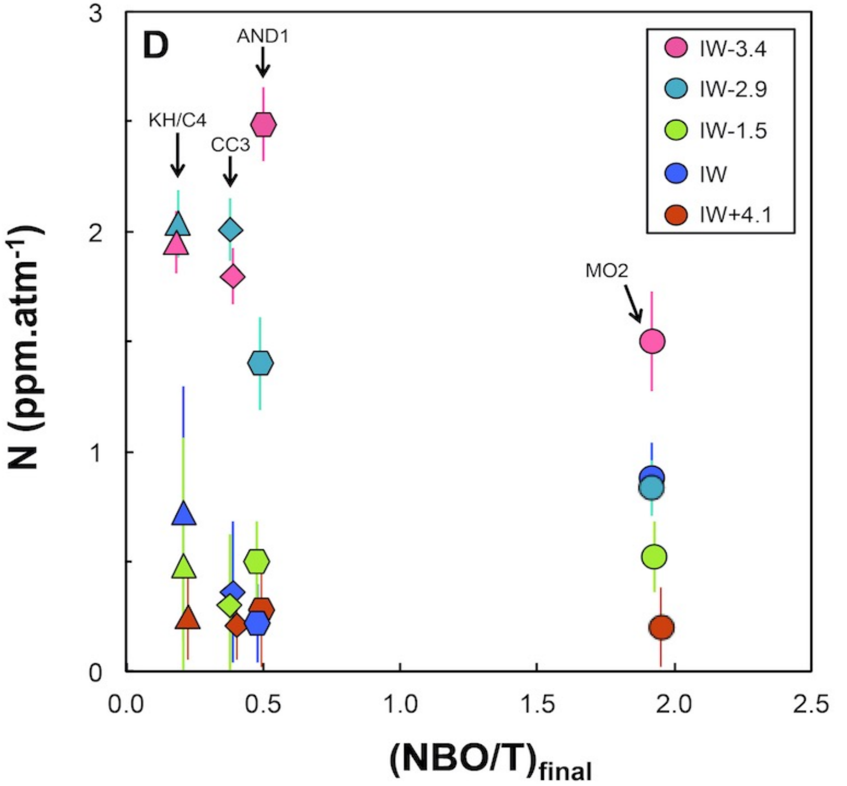
Combined effect of fO_2 and melt composition on N solubility

Courtesy of Julien Boulliung

- Under highly reducing conditions, N solubility increases with increasing NBO/T



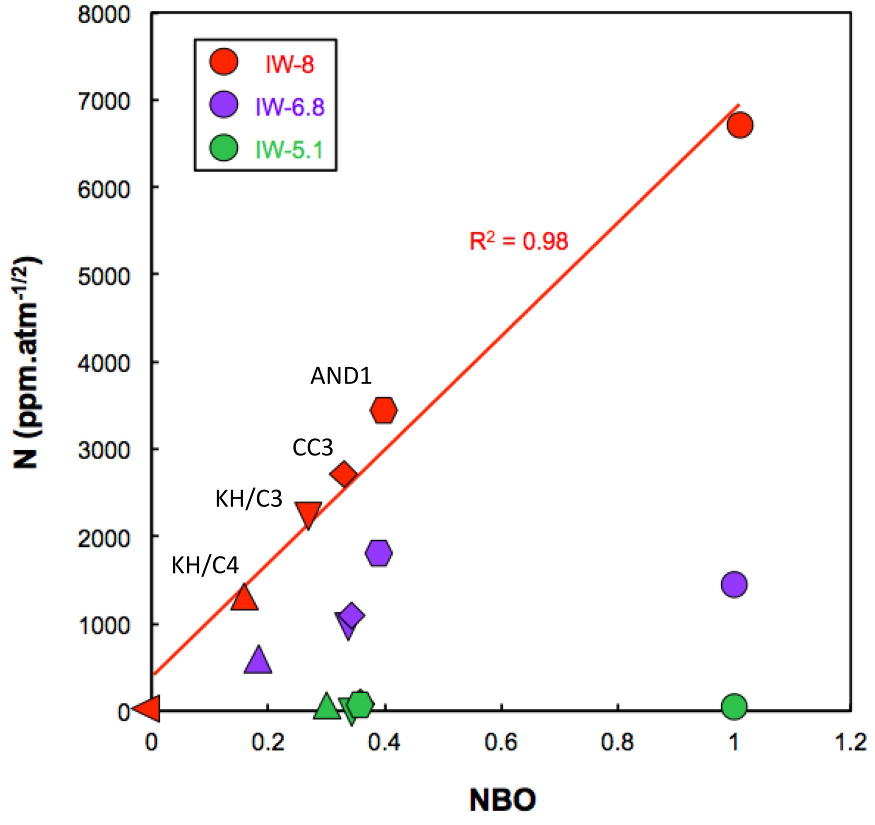
- Under more oxidizing conditions, N solubility is low, irrespective of NBO/T



Boulliung et al., 2020 (GCA)

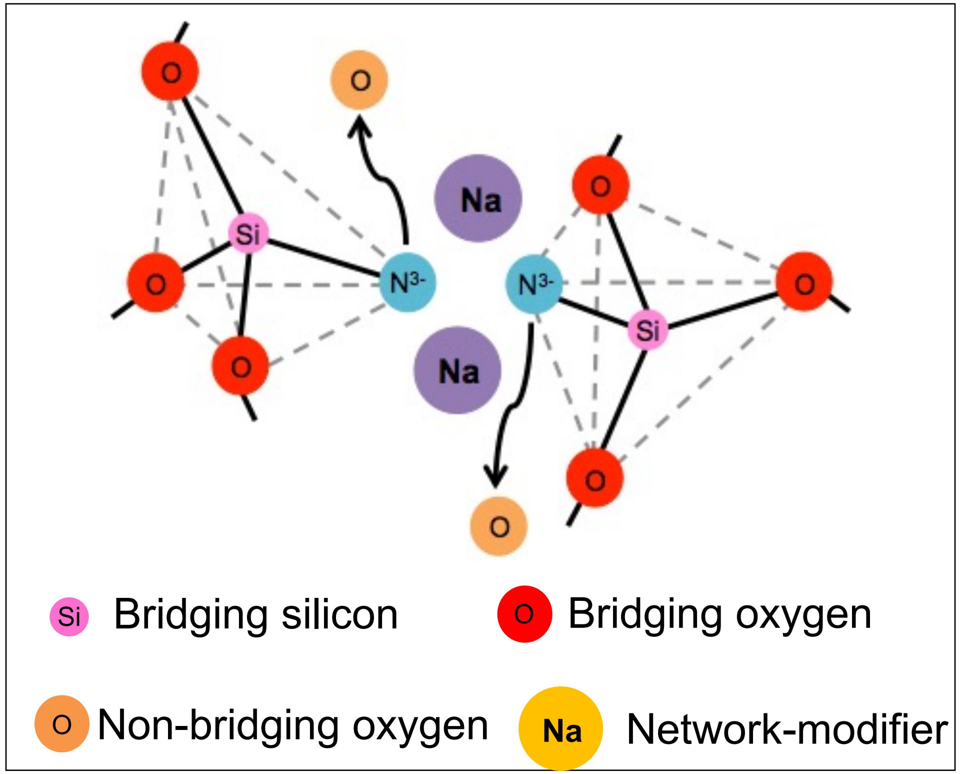
N solubility in the magma ocean

Results at 1 atm



Boulliung et al., 2020 (GCA)

- **Structural sites favorable to the substitution of N^{3-} for O^{2-} are NBOs**

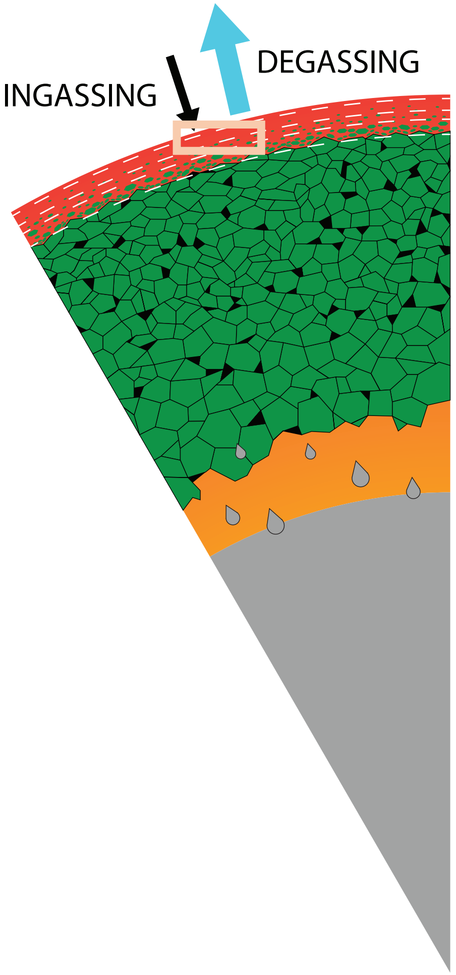


N solubility in the magma ocean

Experiments

Different methods :

- 1 atm
- Under pressure :



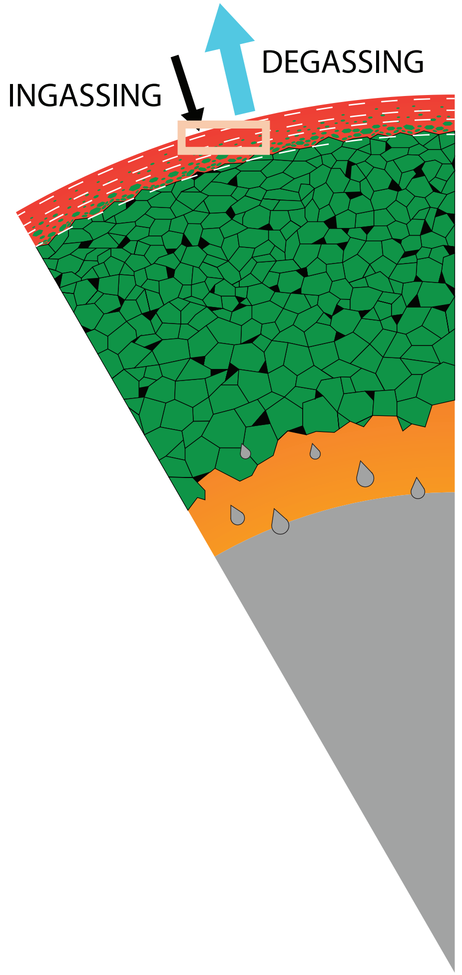
N solubility in the magma ocean

Experiments

- Fe-free primitive basalts (Fichtner et al. 2021)
- 0.5 to 8 wt% N as Si_3N_4

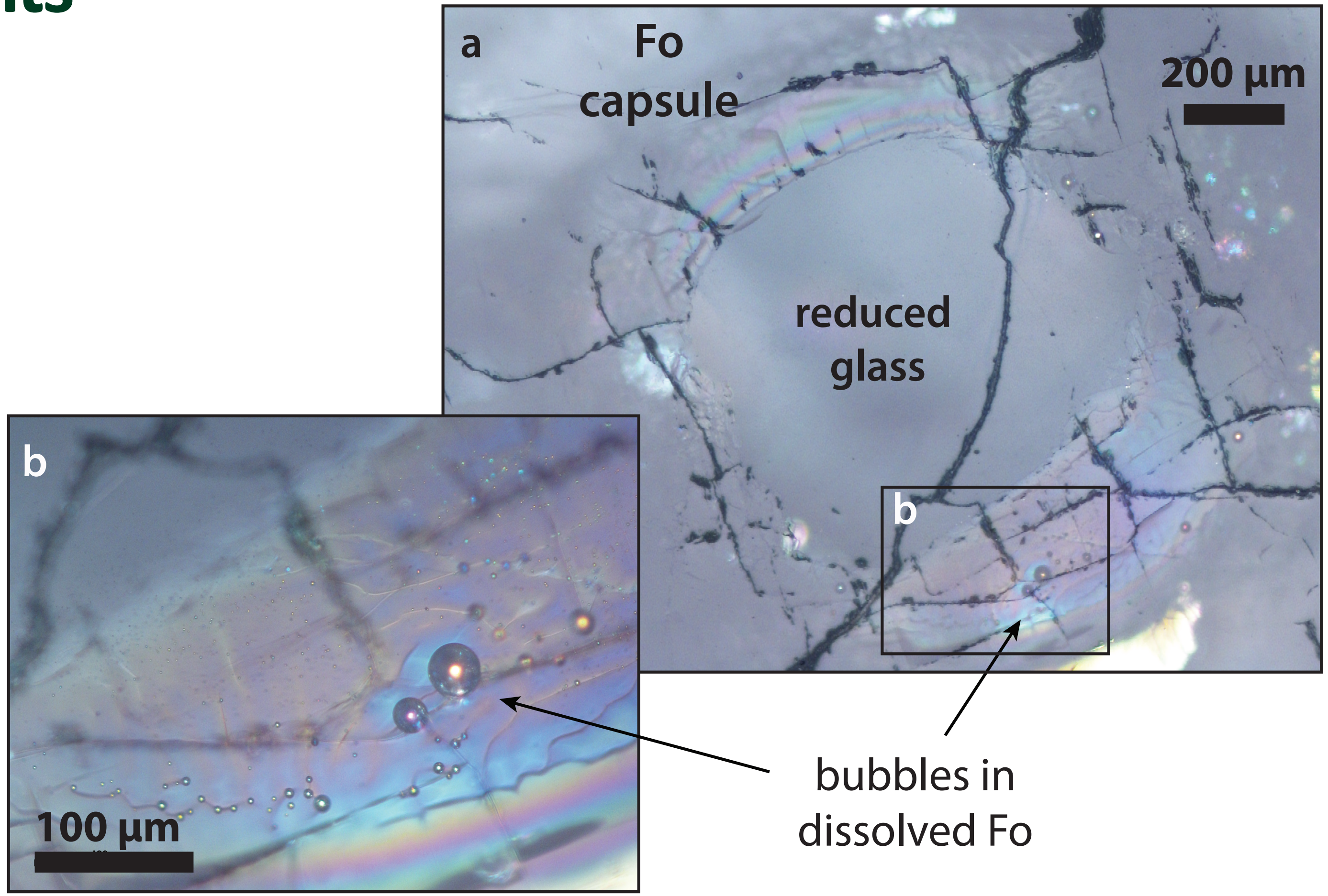
  ➡ Capsules of pure Fo

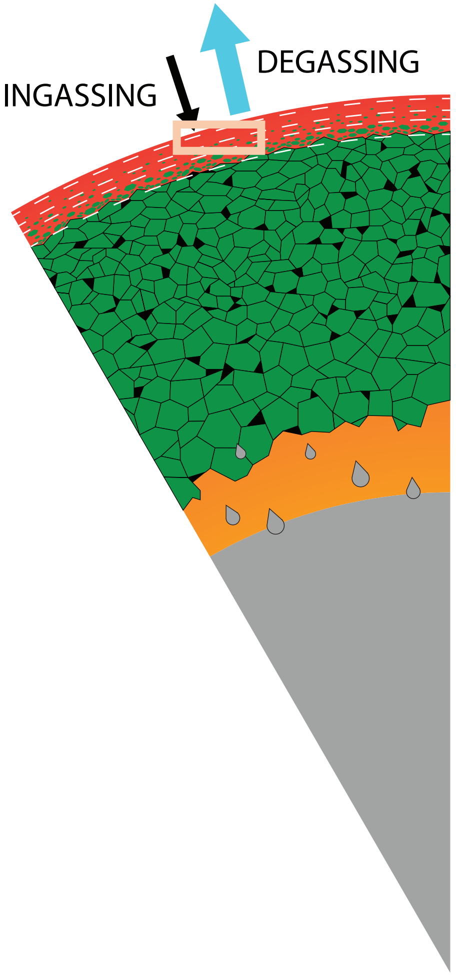
- Piston cylinder experiments at 1.5 GPa, and 1550 °C
- **IW -4.3 < fO_2 < IW**



N solubility in the magma ocean

Experiments



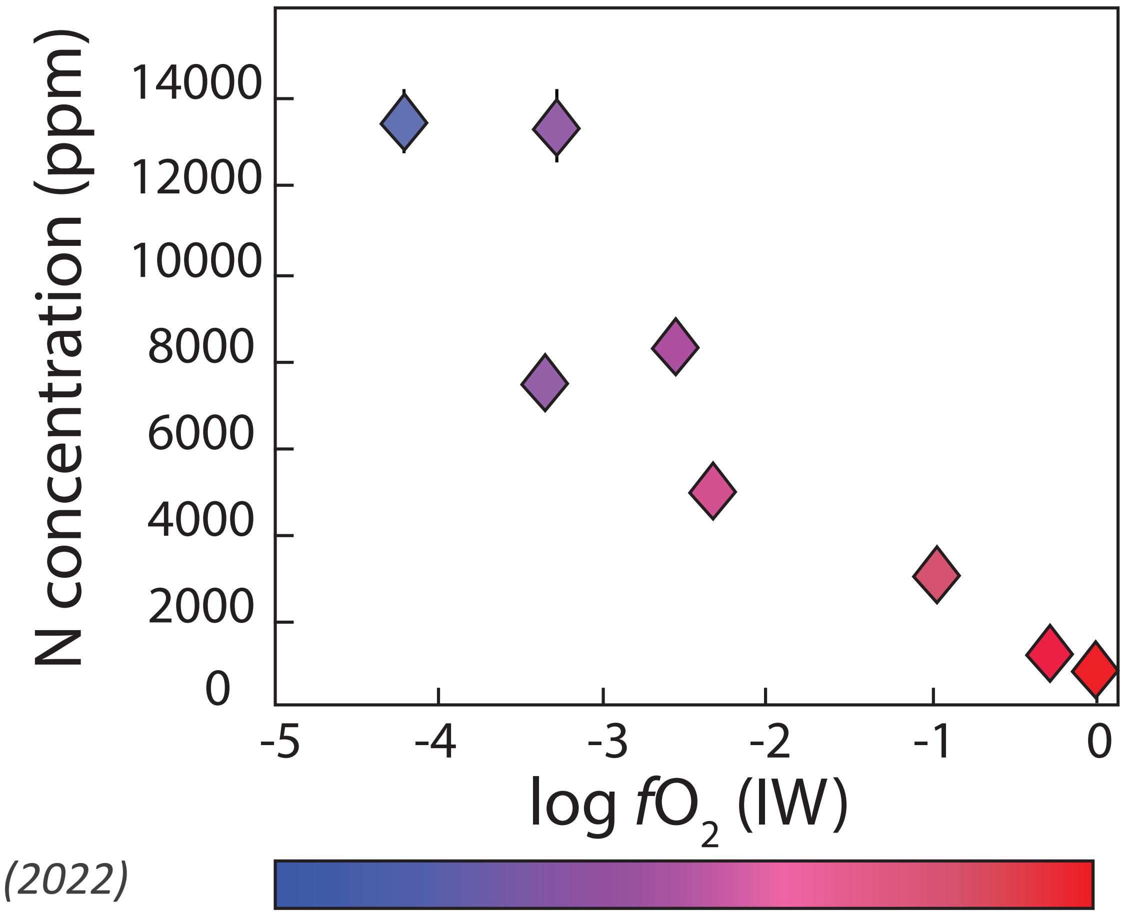


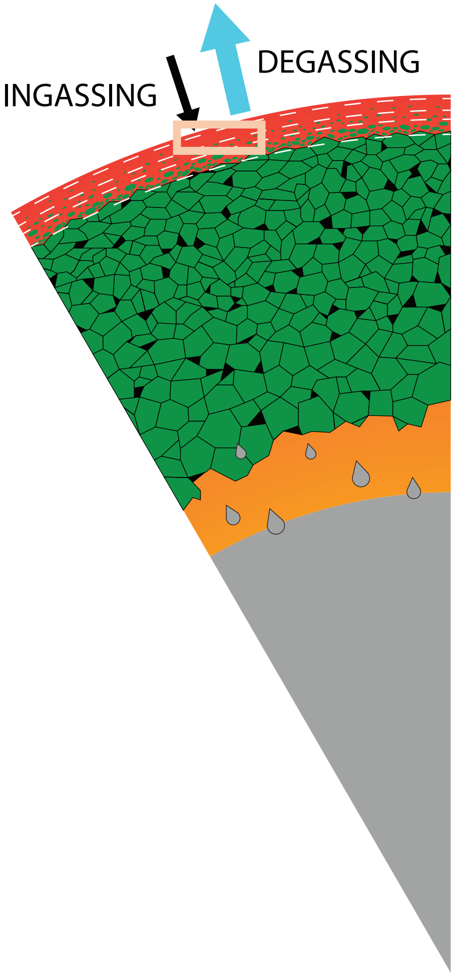
Dalou et al. (2022)

N solubility in the magma ocean

Results

a)

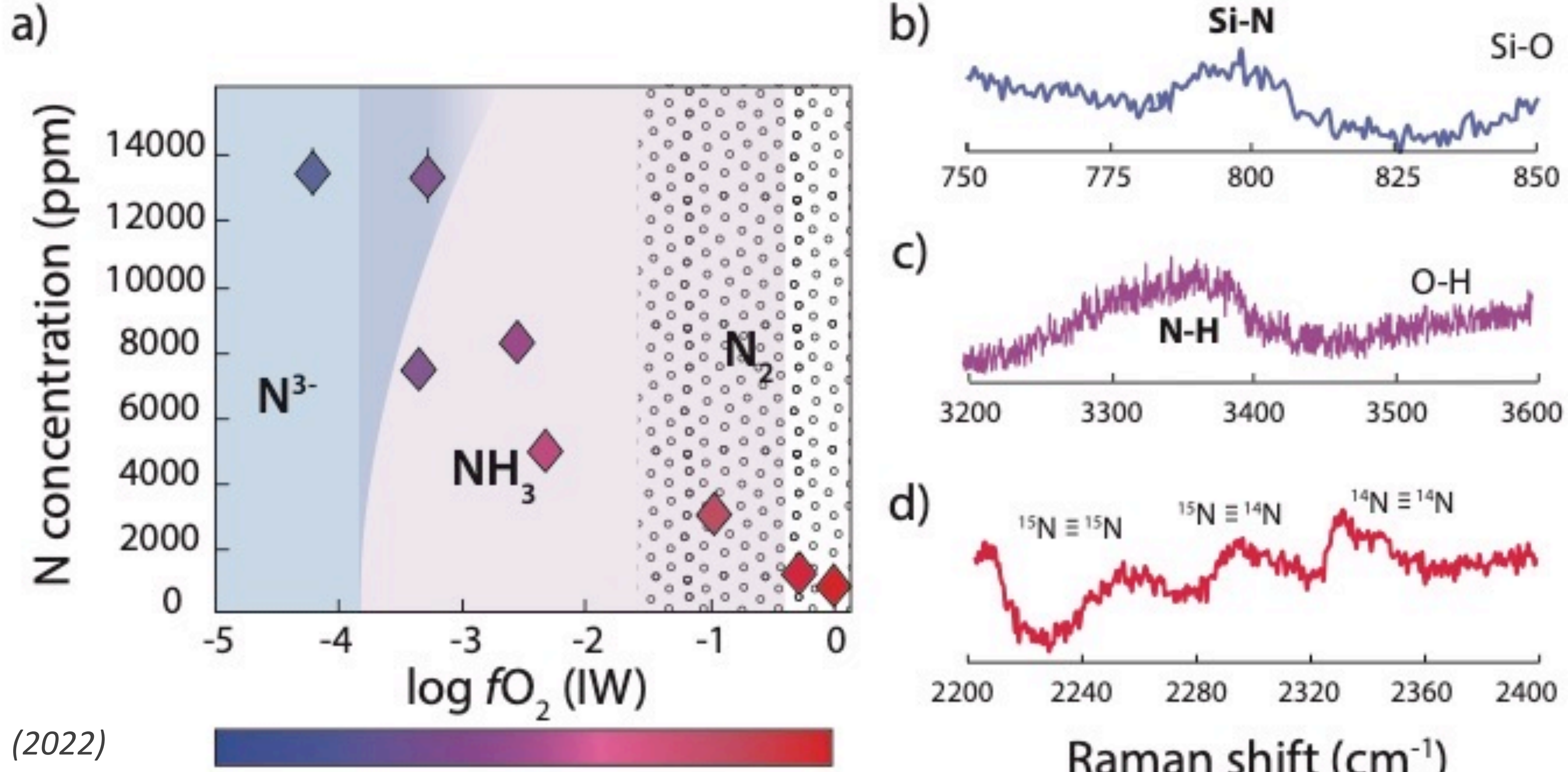




Dalou et al. (2022)

N solubility in the magma ocean

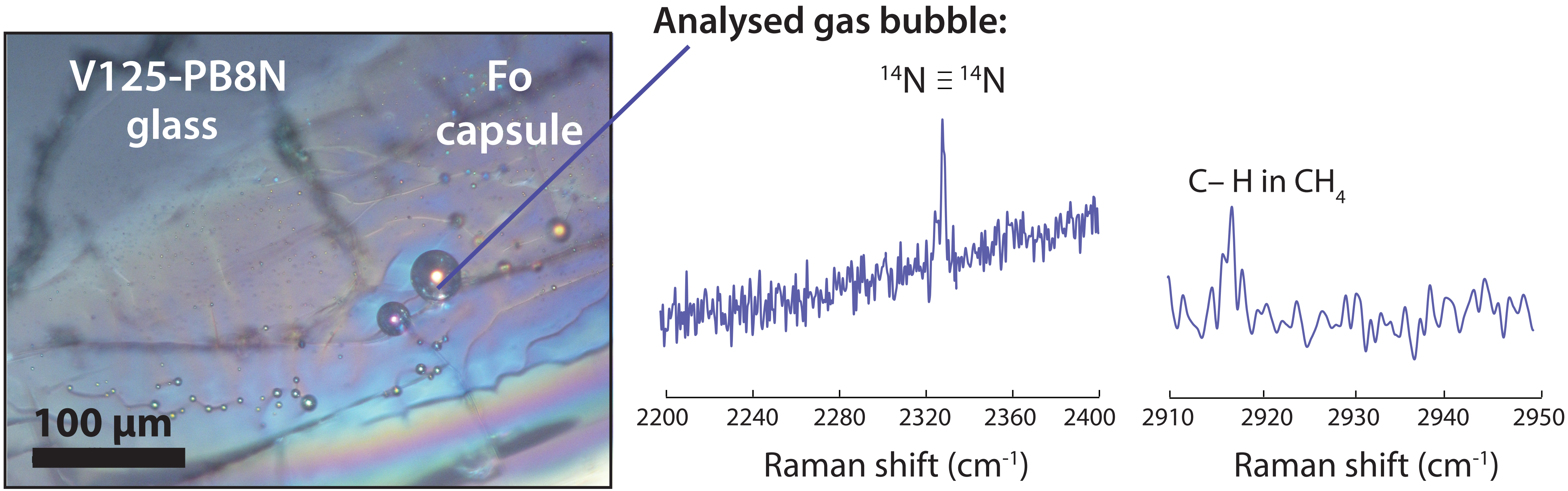
Results



Dalou et al. (2022)

N solubility in the magma ocean

Results



Dalou et al. (2022)

N solubility in the magma ocean

Degassing reactions:

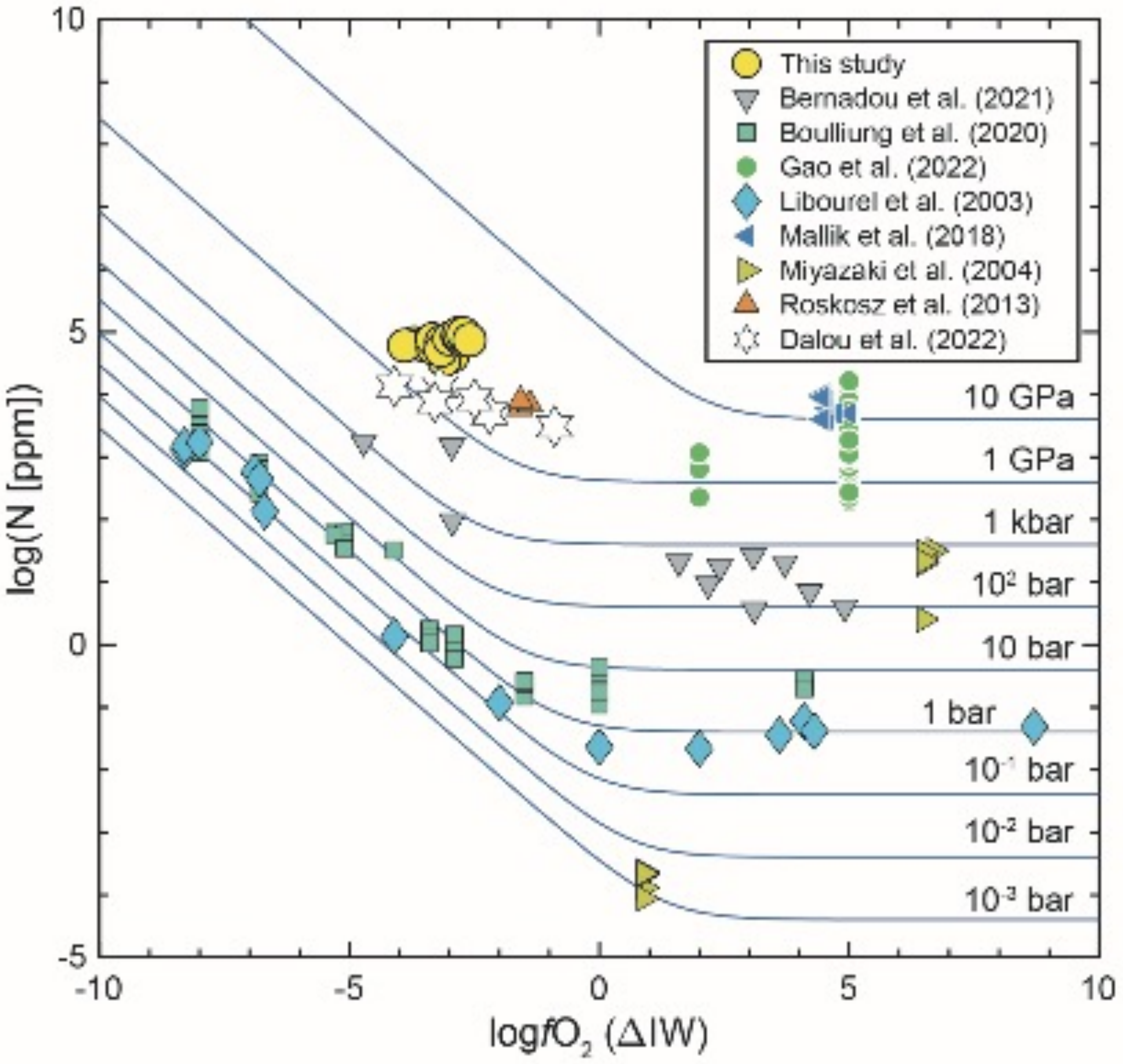
$$N_{2\ (magma)} \Leftrightarrow N_{2\ (gas)}$$

$$2NH_{3\ (magma)} \Leftrightarrow N_{2\ (gas)} + 3H_{2\ (gas)}$$

$$2SiN_{(magma)} + 4OH^{-}_{(magma)} \Leftrightarrow 2SiO_{2(magma)} + N_{2\ (gas)} + 2H_{2\ (gas)}$$

N solubility in the magma ocean

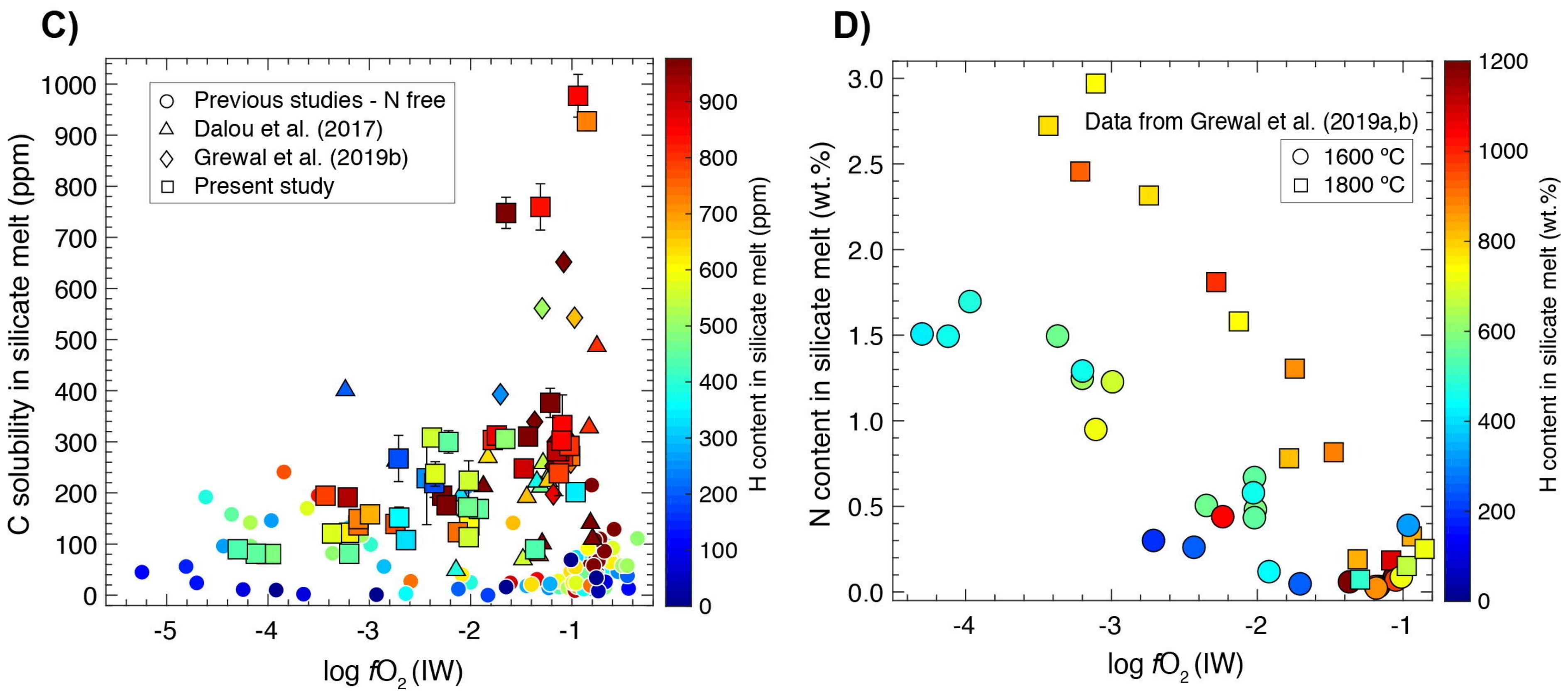
Pressure versus fO_2 effects:



Dasgupta et al. (2022)

C versus N solubility in the magma ocean

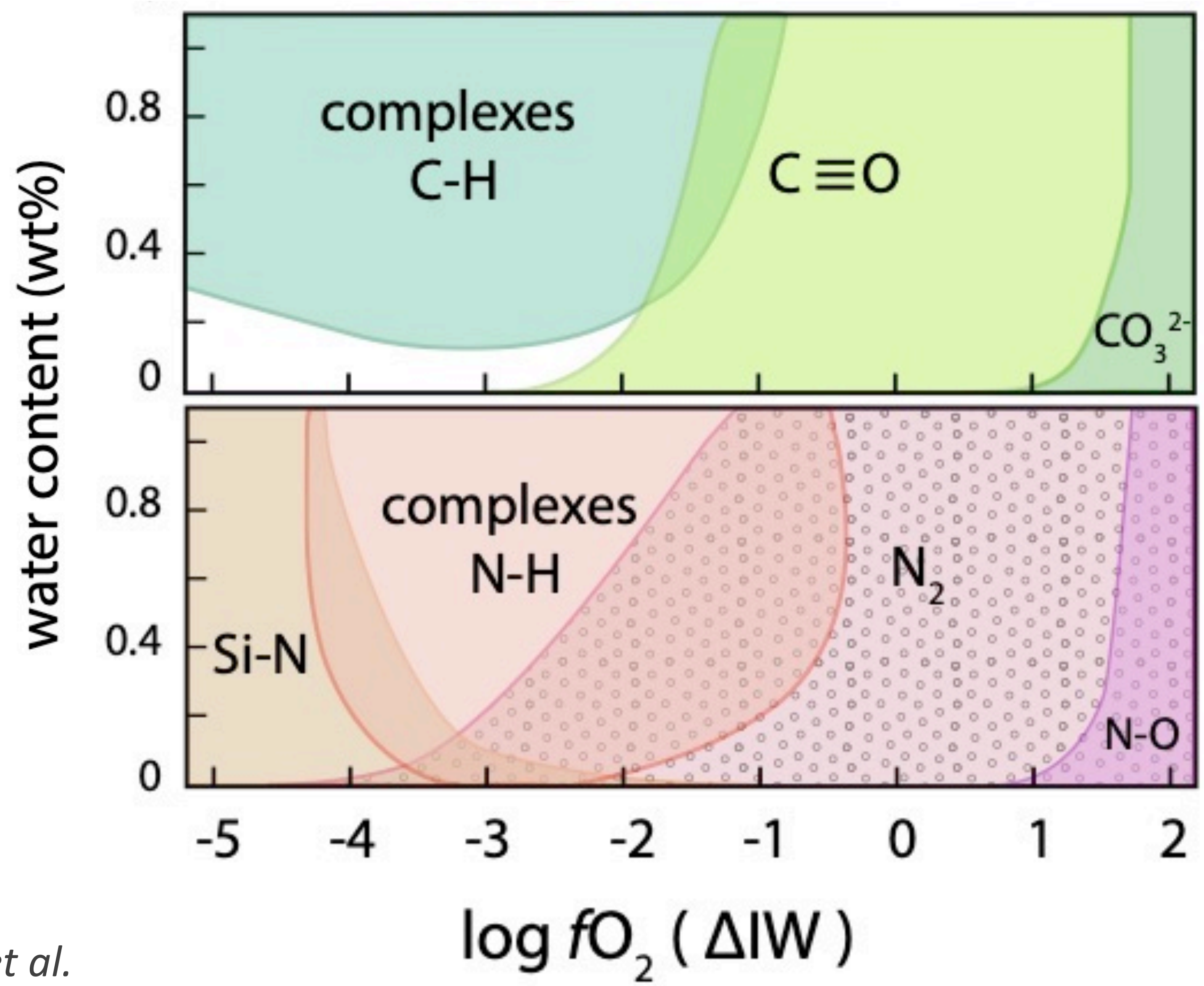
C and N have distinct solubility with increasing fO_2



Grewal et al. (2020)

C versus N solubility in the magma ocean

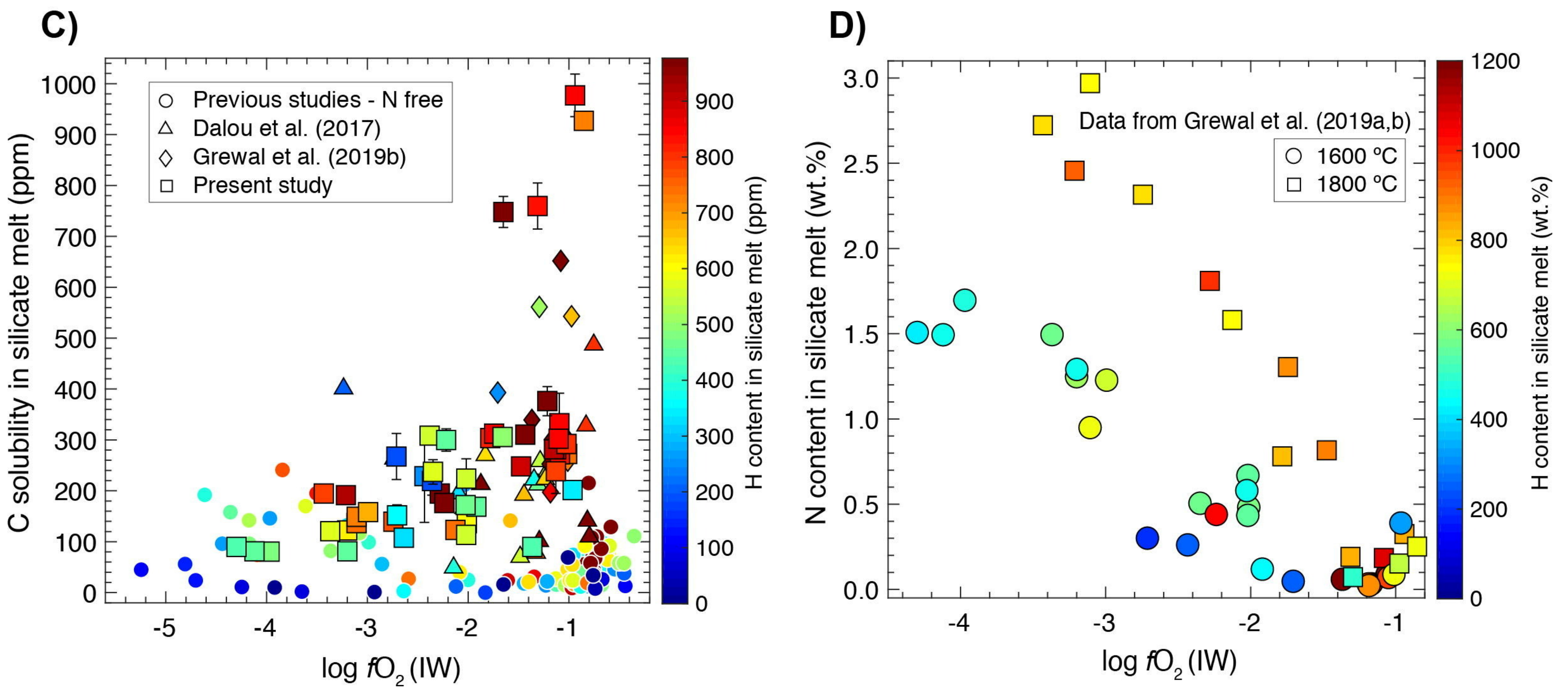
C and N have distinct speciation with increasing fO_2



From Armstrong et al. (2015); Dalou et al. (2019b); Grewal et al. (2020)

C versus N solubility in the magma ocean

C and N have distinct solubility with increasing fO_2



Grewal et al. (2020)

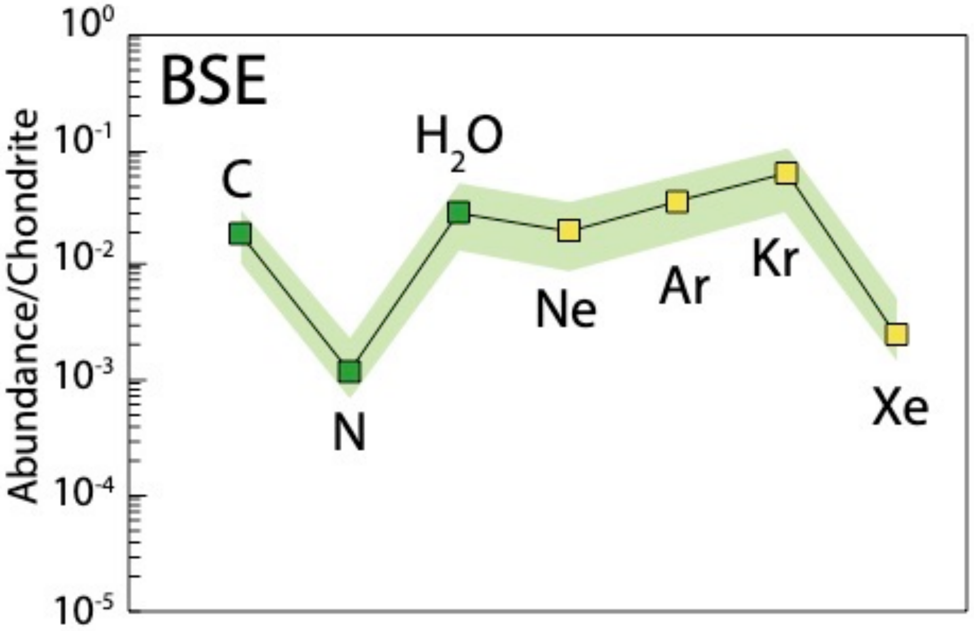
C versus N solubility in the magma ocean

With the increasing fO_2 of the magma ocean:

➡ N degassing increases as C degassing decreases

↳ the C/N of the magma ocean decreases

Magma ocean degassing cannot explain the difference between the C/N ratio of the BSE and the chondrites…



Marty (2012)

Other possibilities…

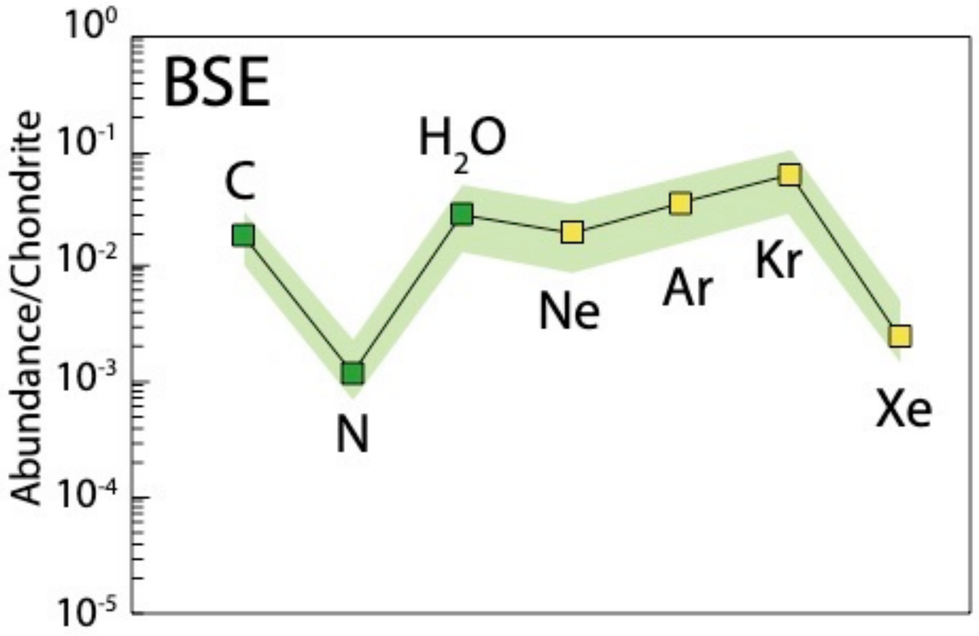
- Misestimation of C/N ratio of the BSE ← hidden N reservoir in the mantle

- The observed C/N ratio is inherited from building blocks, other than CI…

(Alexander 2022)

Other possibilities…

- Misestimation of C/N ratio of the BSE ← hidden N reservoir in the mantle



Marty (2012)

… derives from mass balance calculations inventorying the mantle, crust and atmosphere (Marty, 2012; Bergin et al., 2015).

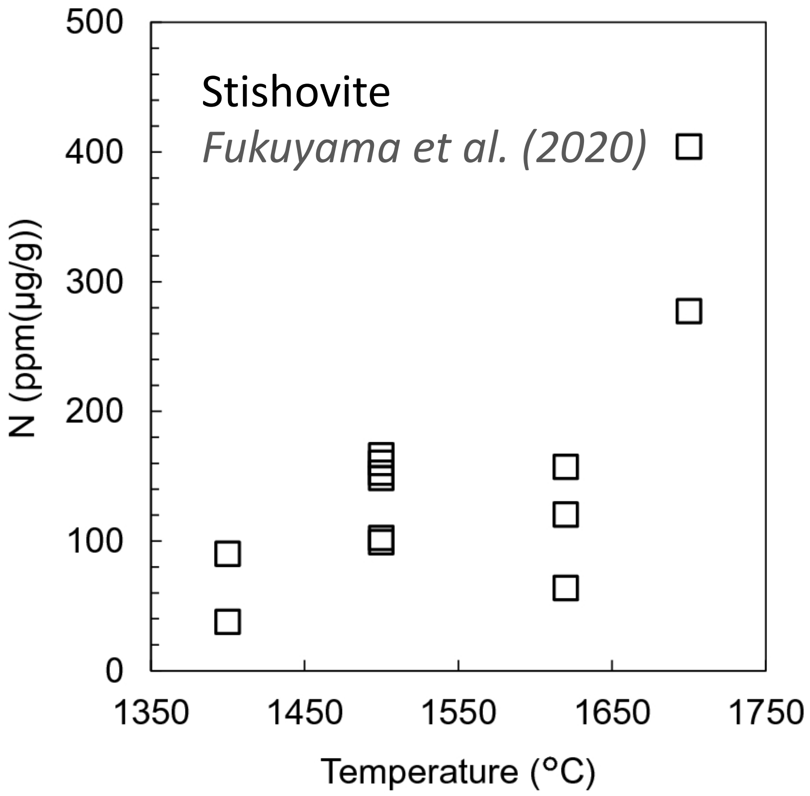
Other possibilities…

- Misestimation of C/N ratio of the BSE ← hidden N reservoir in the mantle

- N highly soluble in transition zone minerals – *Yoshioka et al. (2018)* and lower mantle minerals – *Fukuyama et al. (2020)*

- TiN stable up to 60 GPa – *Daviau et al. (2021)*

- Nitride minerals: Fe_3N, Fe_2N and carbonitrides minerals in inclusions in lower-mantle diamonds: $Fe_9(N_{0.8}C_{0.2})_4$ formed by the infiltration of N-bearing liquid metal → N close to the core ?
– *Kaminsky and Wirth (2017), Huang et al. (2021)*



Other possibilities…

- The observed C/N ratio is inherited from building blocks, other than CI…
  – *Alexander (2022),*

… or from an large differentiated body which impacted the proto-Earth
– *Dasgupta and Grewal (2019)*