The association of natural hydrogen and nitrogen : the ammonium clue ?
-
Insights from geochemical modeling

<u>Nicolas Jacquemet</u>[1] & Alain Prinzhofer[2]

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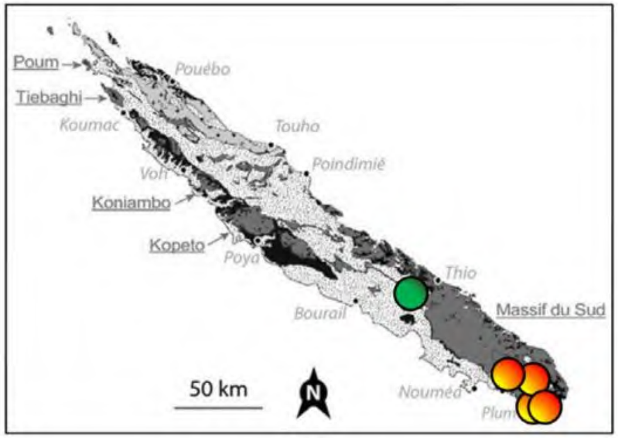
[2] Scientific director of GEO4U

Colloque annuel du GdR HydroGEMM / édition 2024 / IPGP & IFPEN

Motivation of the study

Seepage of H2… and N2



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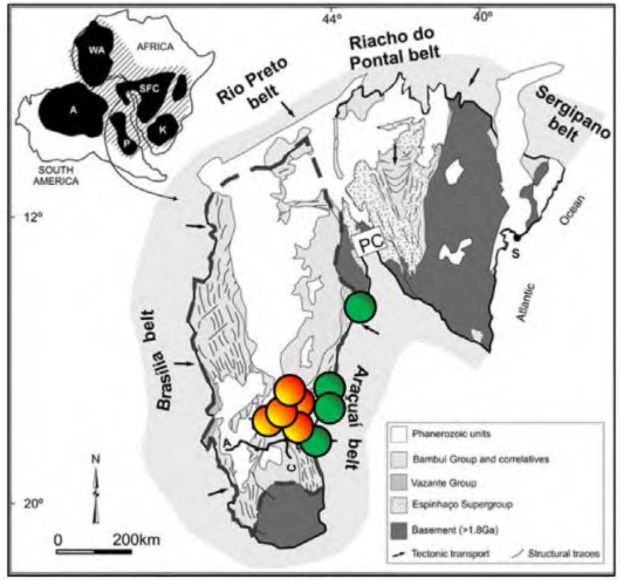

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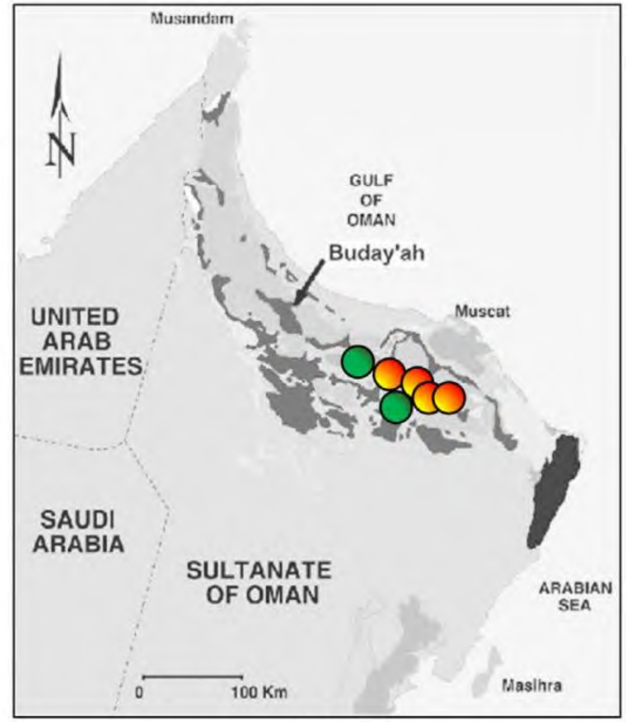


(c)

: H_2 and N_2 seep
: pure N_2 seep

- Hydrogen systems of the Oman and New Caledonian ophiolite and of the Brazil’s Sao Francisco Basin :
  - Seep of H2 associated with N2 at the central part of the hydrogen systems
  - Seep of (almost) pure N2 at the periphery of the hydrogen systems

Ammonium (NH_4^+) as the source of N_2 ?

- NH_4^+ (ammonium)-bearing natural minerals are reported in the literature
- NH_3 (ammonia; the conjugate base of NH_4^+) is known to decompose into N_2 and H_2 with temperature :

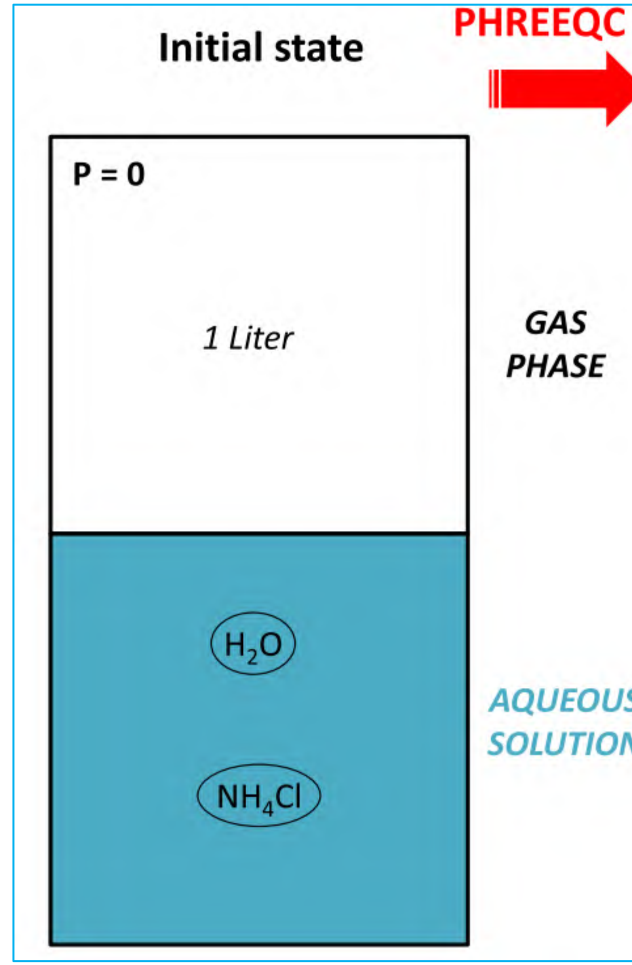
$$2\ NH_3 = N_2 + 3\ H_2$$

- In the lower crust, at temperature around 250 °C, an isotopic study of Bebout et al. (1992) demonstrated that nitrogen generation was linked to ammonium reactivity
- ➔ Does NH_4^+ could be the source/precursor of the emitted N_2 in the hydrogen systems ?

Geochemical models set-up

Initial chemical systems = 'simple' model systems

- **<u>(A) Redox-unbuffered systems</u>**
  - Water + FeCl2 $$Fe^{2+} + H^{+} = Fe^{3+} + 0.5\, H_2$$
  - Water + NH4Cl
  - Water + NH4Cl + FeCl2
- FeCl2 and NH4Cl salts provide ferrous iron & ammonium to the water
- Plus one volume of 1 L possibly hosting a multicomponent gas phase

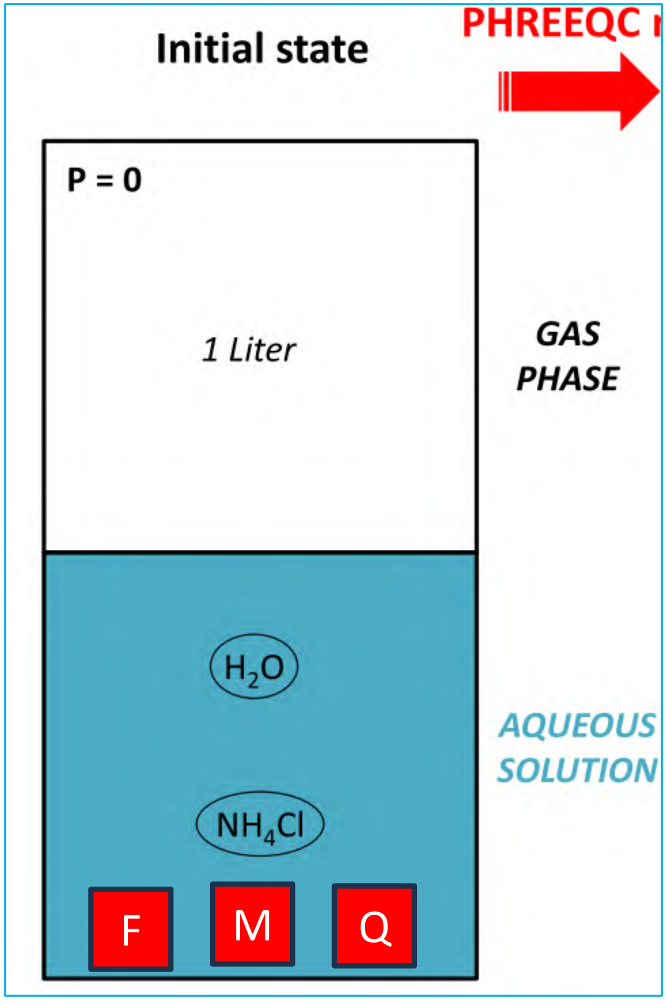


Initial chemical systems = ‘simple’ model systems

- **<u>(B) Redox-buffered systems</u>**
  - Water + Magnetite-Hematite (*‘Control’ system)*
  - *Water + Fayalite-Magnetite-Quartz (‘Control’ system)*
  - Water + Magnetite-Hematite + NH4Cl
  - Water + Fayalite-Magnetite-Quartz + NH4Cl
- The FMQ & MH mineral assemblages set the oxygen fugacity within the systems ; and provide ferrous & ferric iron sources & sinks
- FMQ: highly reducing conditions; MH: lower ;
- Plus one volume of 1 L possibly hosting a multicomponent gas phase

Initial chemical systems = 'simple' model systems

- **(B) Redox-buffered systems (water-mineral systems)**
  - Water + Fayalite-Magnetite-Quartz + NH4Cl



(Thermod.) Equilibrium calculations on initial systems

- Done with the version 3 of the PHREEQC software with the BRGM's Thermoddem database
- Within the 25-300 °C temperature range (Earth surface to ~10 km depth (normal geothermal gradient))
- Considered aqueous, mineral and gaseous species :
  - H2O-Cl-Fe(+II)-Fe(+III)-N(-III)-N(0)-N(+III)-N(+V)-Si
  - Fayalite (Fe_2SiO_4)
  - Magnetite (Fe_3O_4)
  - alpha-Quartz (SiO_2)
  - Hematite (Fe_2O_3)
  - H_2(g), H_2O(g), HCl(g), N_2(g), NH_3(g), O_2(g)

(Thermod.) Equilibrium calculations on initial systems

- Based on Law of Mass Action (LMA) resolution
- The K's of formation-dissolution reactions are calculated as function of temperature

$$log\, K_T = A_1 + A_2 T + \frac{A_3}{T} + A_4 logT + \frac{A_5}{T^2} + A_6 T^2$$

- The pressure conditions of the calculations are (='convention') :
  - 25-100 °C : 1 bar
  - 100-300 °C : Saturation vapor pressure of water : 1 to 86 bar

(Thermod.) Equilibrium calculations on initial systems

- Aqueous solution activity model :
  - B-dot for the charged species (ions)
  - 'Drummond' for dissolved gases (H2(aq), O2(aq), …)
  - Other neutral species : activity of 1
  - H2O(l) (solvent) with a specific equation

$$\log \gamma_i = -\frac{A z_i^2 \sqrt{I}}{1 + a_i^0 B \sqrt{I}} + \dot{B} I$$

$$\log \gamma_{i(aq)} = -\left(C + FT + \frac{G}{T}\right) I + (E + HT)\left(\frac{I}{I+1}\right)$$

- PVTx & gas species activity (fugacity) of the multicomponent gas mixture :

  Peng-Robinson Equation of State (PR EoS)
  - Inputs : critical temperature & pressure & acentric factors (from phreeqc.dat, NIST and Thermosolver database)
  - 'hard-coded' kij's

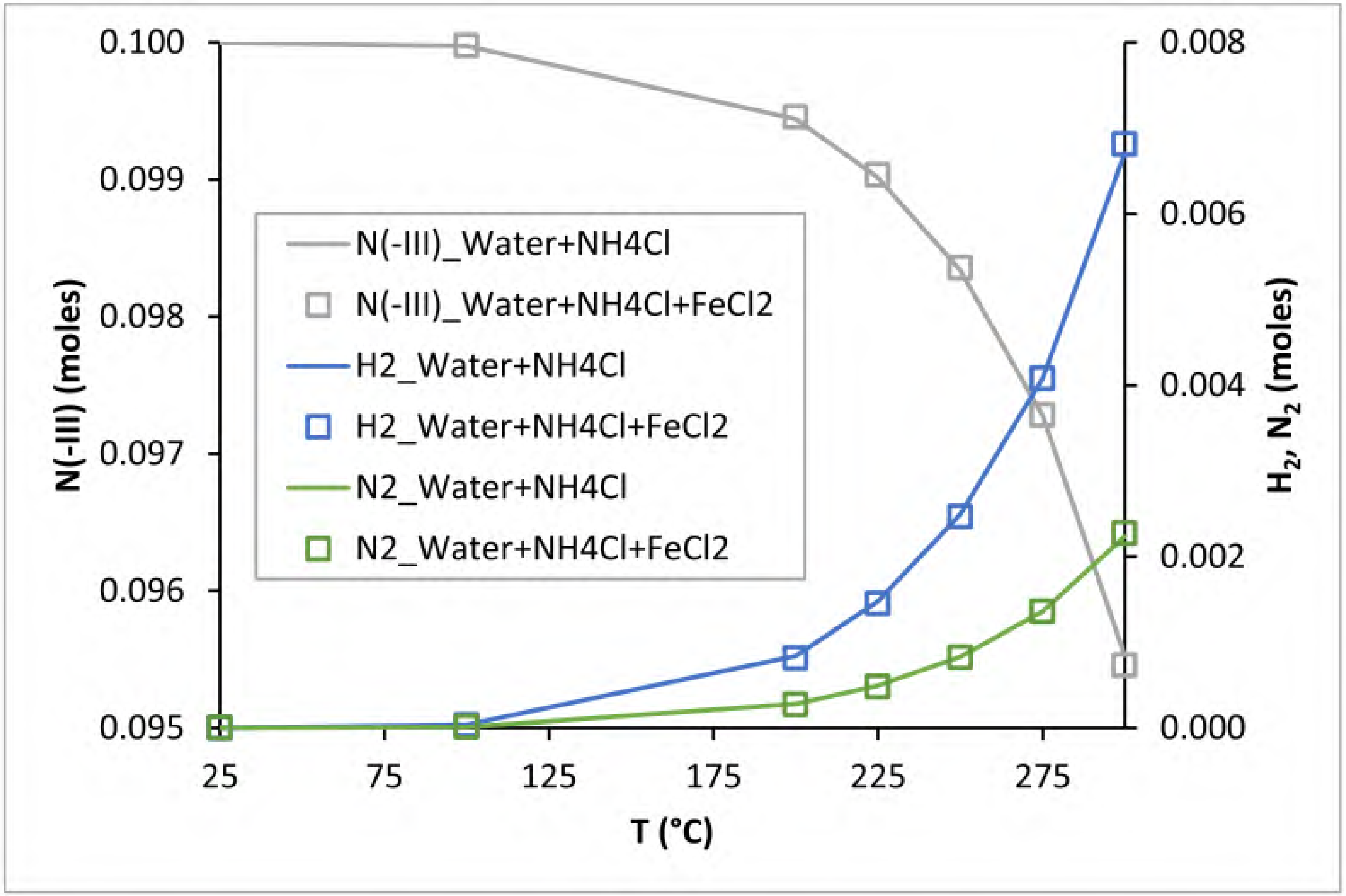
$$a_{H_2O} = 1 - 0.017 \sum_{i}^{N_{aq}} \frac{n_i}{W_{aq}}$$

Results

Chemical reactions

- Redox-unbuffered systems

Water + NH4Cl

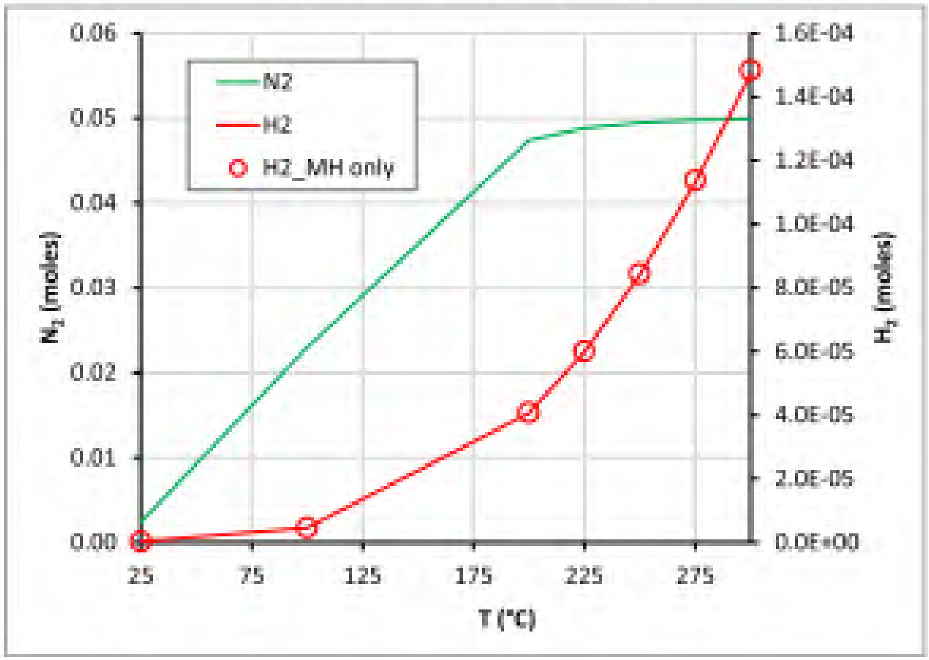


$$NH_4^+ = 1.5\ H_2 + 0.5\ N_2 + H^+$$

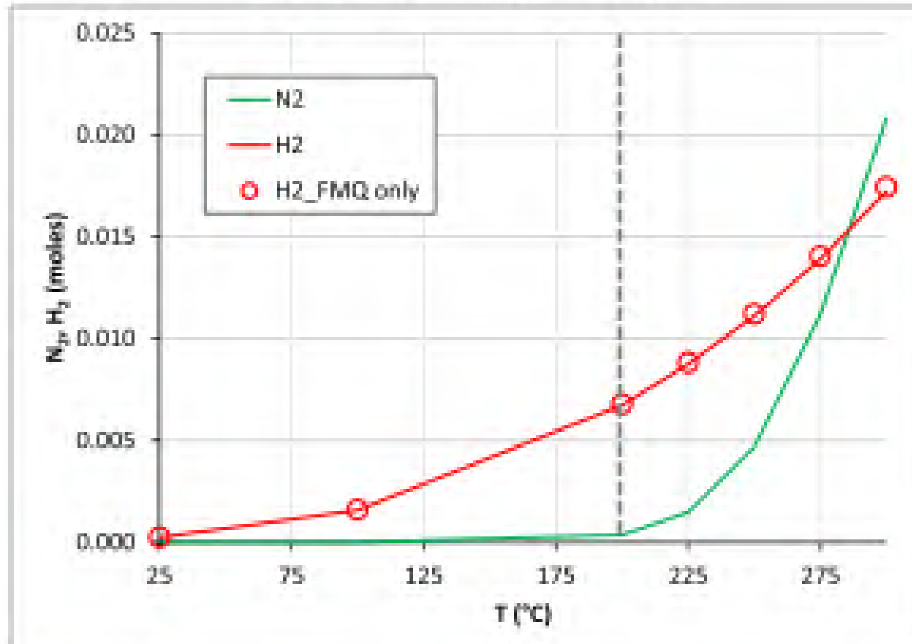
Chemical reactions

- Redox-buffered systems

Water + MH + NH_4Cl



Water + FMQ + NH_4Cl



$H2_{TOT}$ & $N2_{TOT}$
(Gas & Water)

Chemical reactions

- Redox-buffered systems
  - Hydrogen generation
    - Water + Magnetite-Hematite + NH4Cl

$$Fe_3O_4 \text{ (magnetite)} + 0.5\,H_2O = 1.5\,Fe_2O_3 \text{ (hematite)} + 0.5\,H_2$$

- Water + Fayalite-Magnetite-Quartz + NH4Cl

$$1.5\,Fe_2SiO_{4(s)} \text{ (fayalite)} + H_2O_{(l)} = Fe_3O_{4(s)} \text{ (magnetite)} + SiO_{2(s)} \text{ (quartz)} + 0.5\,SiO_{2(aq)} \text{ (aqueous silica)} + H_2$$

$$Fe^{2+} + H^{+} = Fe^{3+} + 0.5\,H_2$$

Chemical reactions

- Redox-buffered systems
- Nitrogen generation
  - Water + Magnetite-Hematite + NH4Cl
    - Nitrogen generation occurs within 25-300°C

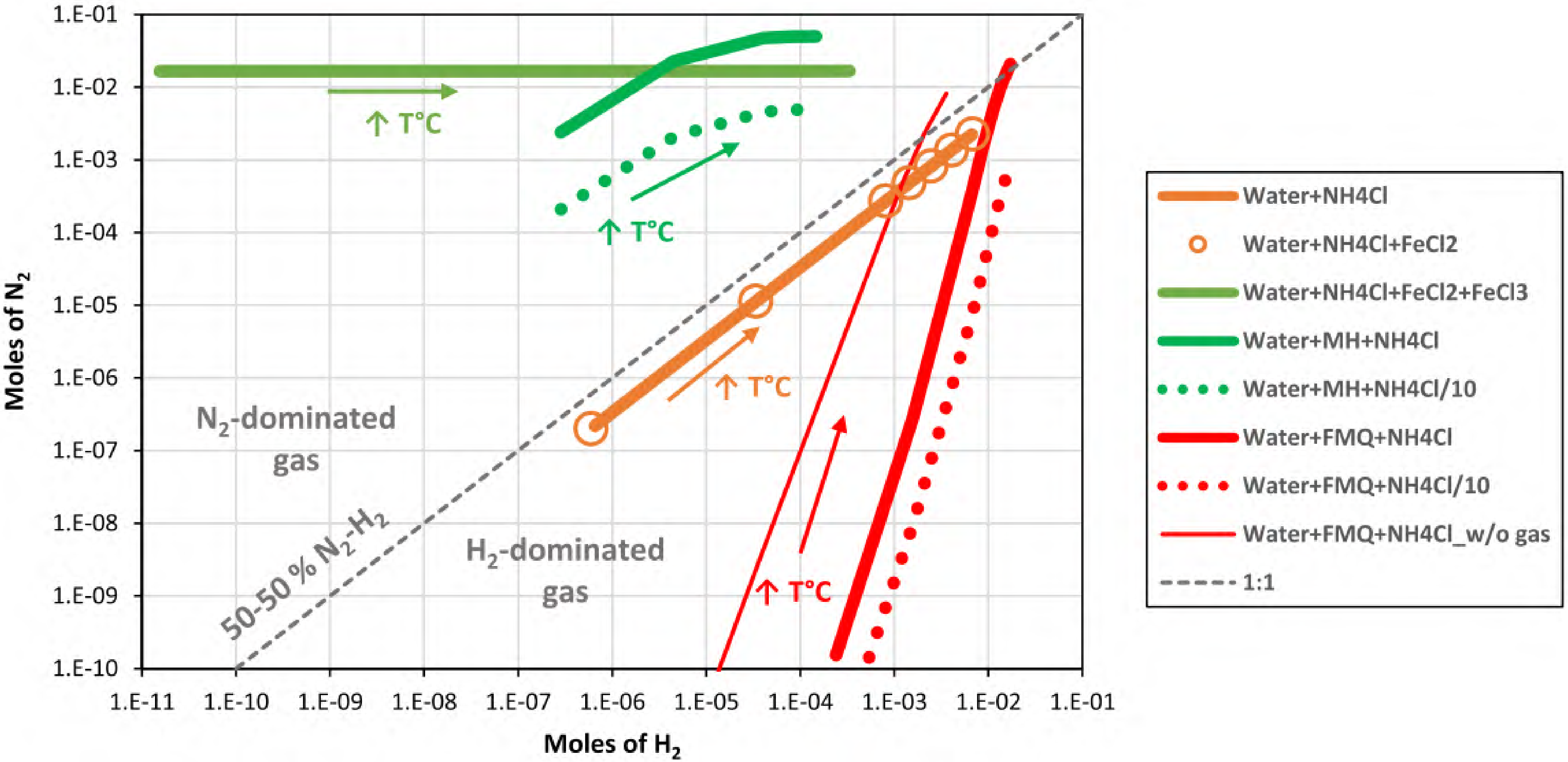
$$4\,Fe_2O_3\text{ (hematite)} + NH_4^+ = 0.5\,N_2 + 2.5\,Fe_3O_4\text{ (magnetite)} + 0.5\,Fe^{2+} + 2\,H_2O$$

  - Water + Fayalite-Magnetite-Quartz + NH4Cl
    - Nitrogen generation starts at 200 °C

$$2\,NH_4^+ + 3\,Fe_3O_{4(s)}\text{ (magnetite)} + 4.5\,SiO_{2(s)}\text{ (quartz)} = N_2 + 4\,Fe_2SiO_{4(s)}\text{ (fayalite)} + 0.5\,SiO_{2(aq)}\text{ (aqueous silica)} + Fe^{2+} + 4\,H_2O$$

$$3\,Fe^{3+} + NH_4^+ = 0.5\,N_2 + 3\,Fe^{2+} + 4\,H^+$$

Typology of the produced gases



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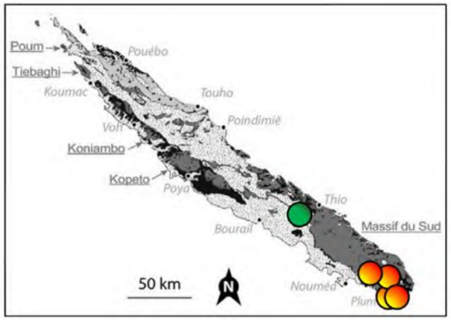
Implications for hydrogen systems comprehension



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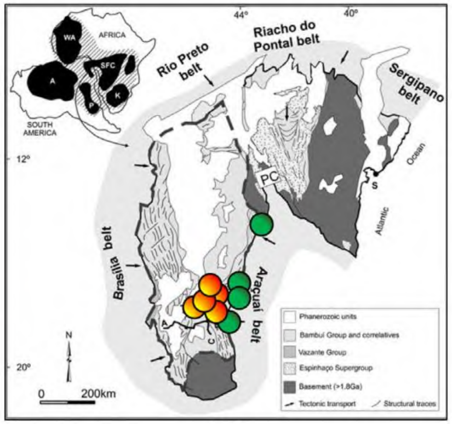

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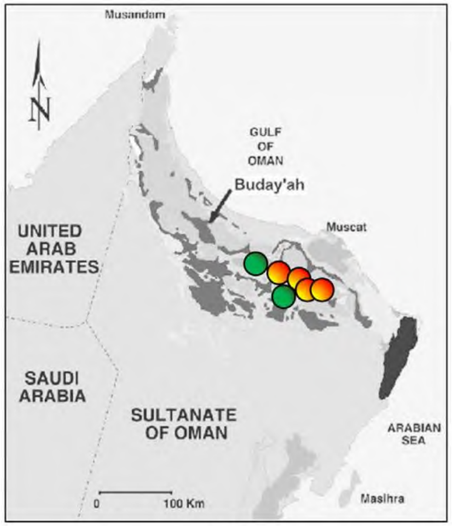

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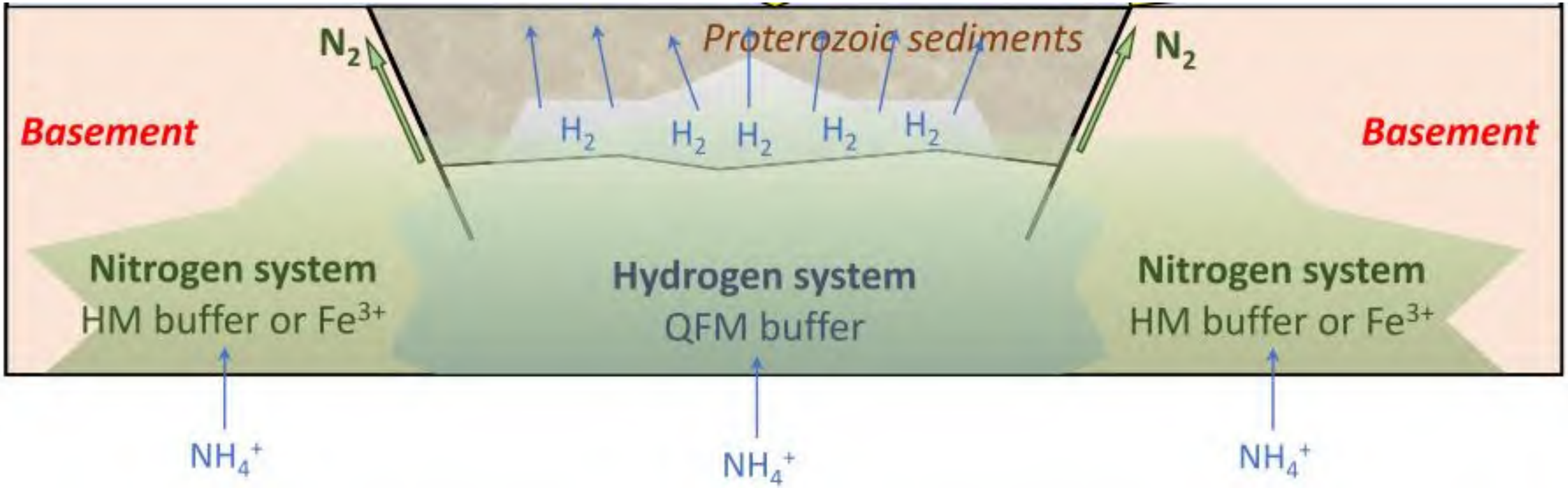

More info

International Journal of Hydrogen Energy
Volume 50, Part B, 2 January 2024, Pages 161-174

The association of natural hydrogen and nitrogen: The ammonium clue?

Nicolas Jacquemet [a], Alain Prinzhofer [b]

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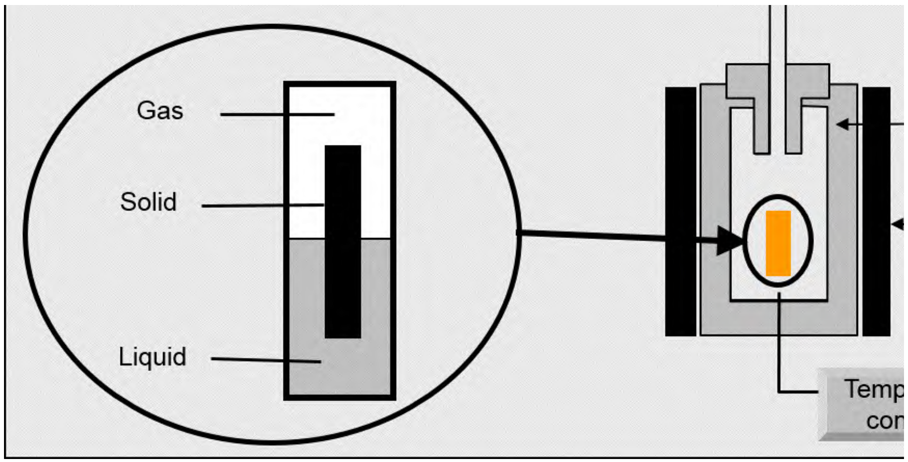
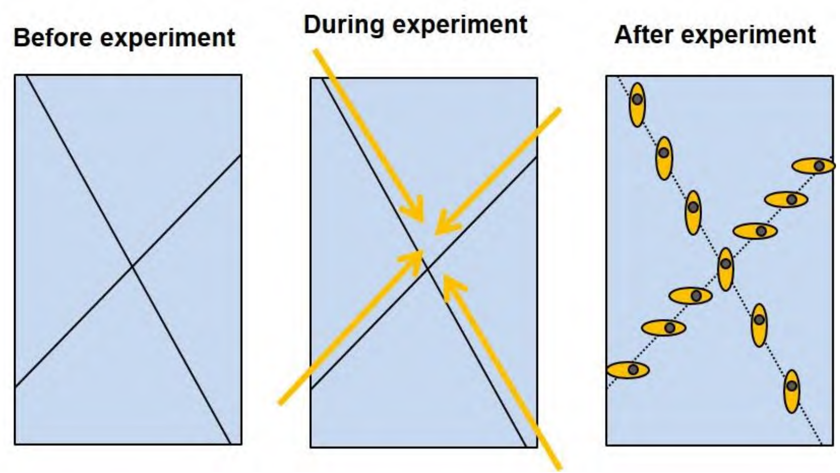
https://doi.org/10.1016/j.ijhydene.2023.07.265

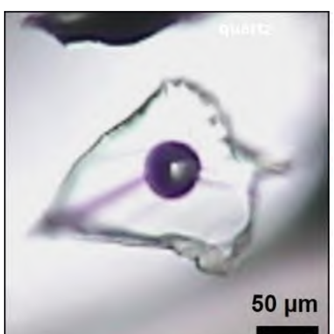
Outlooks / improvements of the study

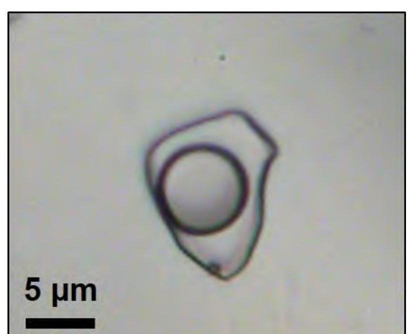
To compare with 'hydrothermal' lab experiments

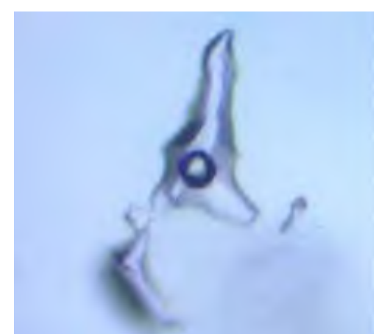
- Ideally on the same 'simple' systems
- <u>Synthetic fluid inclusions in flexible gold cells experiments</u>





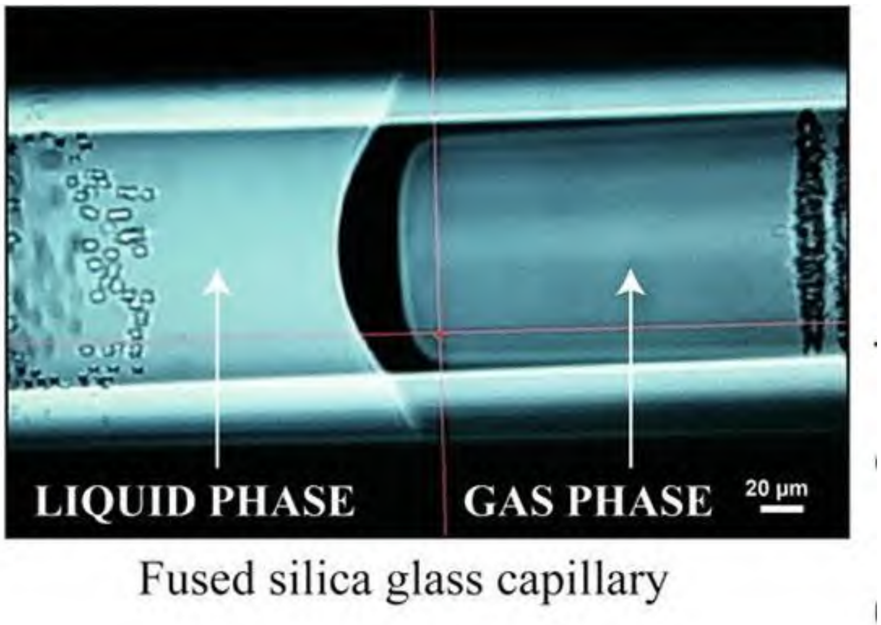




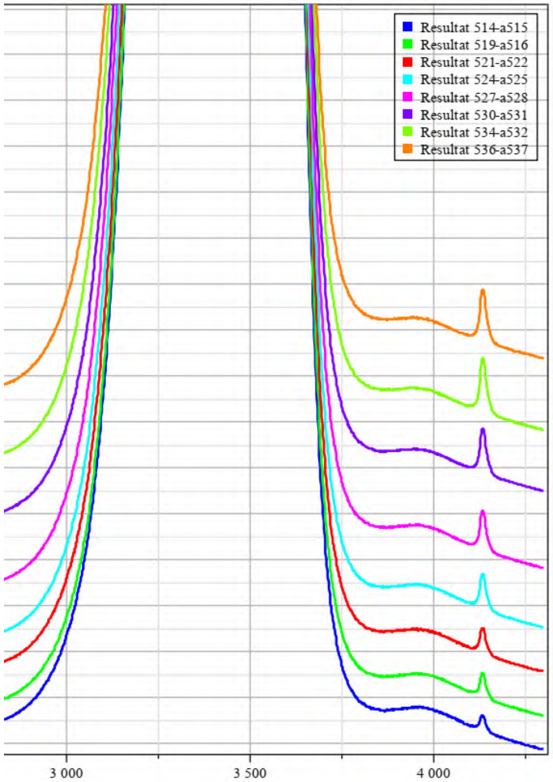


To compare with ‘hydrothermal’ lab experiments

- Coupled Fused Silica Capillary Capsules (FSCCs) and Raman micro-spectroscopy experiments
- …



Carocci et al. (2022)



Jacquemet et al. (2016)

To explore more realistic sources of NH4+ than NH4Cl

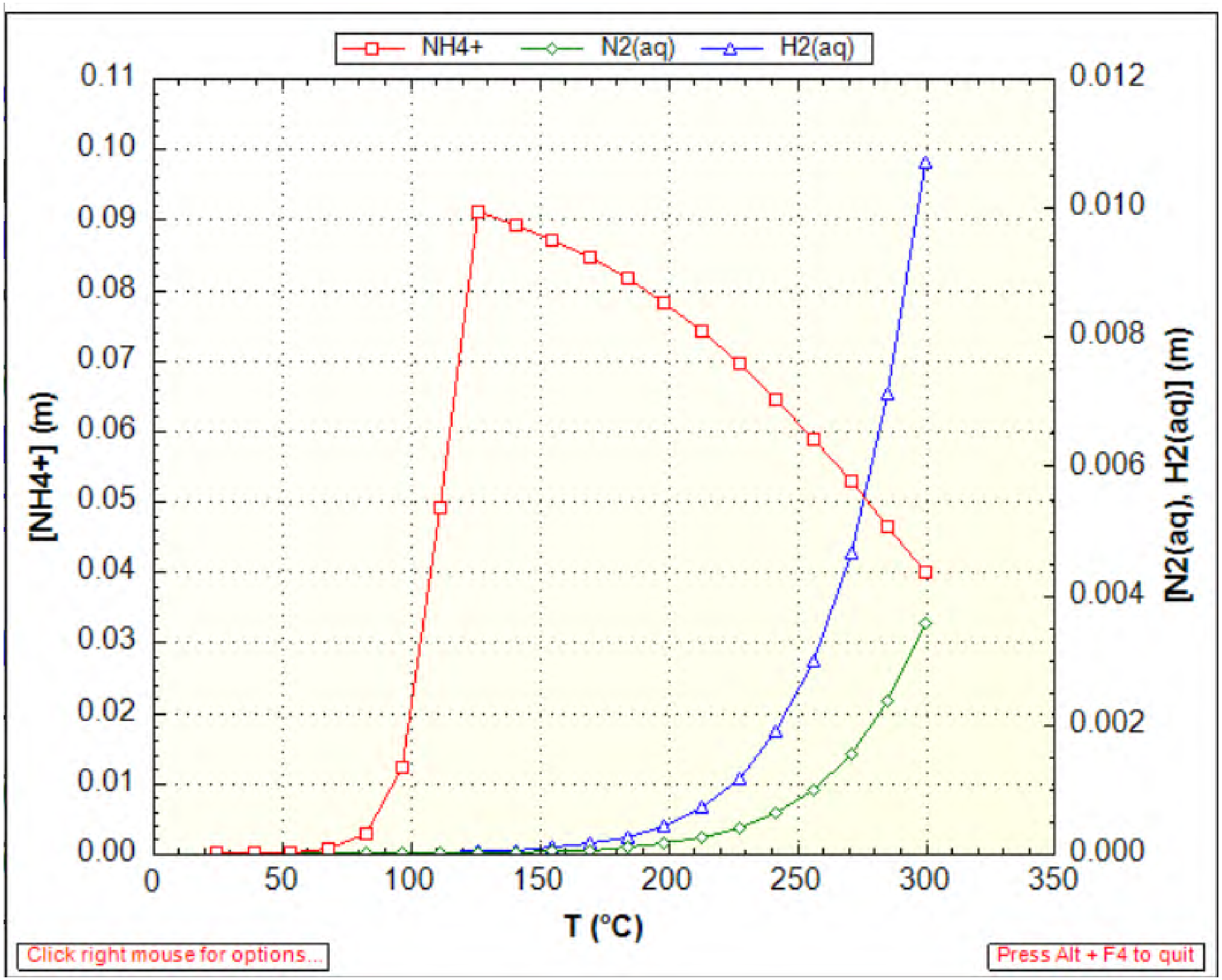
- NH4-bearing minerals dissolution

Holloway and Dahlgren (2002)

Mineral	Formula	Occurrences
Ammoniojarosite	$(NH_4)Fe^{3+}(SO_4)_2(OH)_6$	ore deposits: WY & UT, USA; hydrothermal: The Geysers, CA
Boussingaultite	$(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$	hydrothermal: The Geysers, CA
Lecontite	$(NH_4,K)Na(SO_4) \cdot 2H_2O$	evaporite, Pakistan
Letovicite	$(NH_4)_3H(SO_4)_2$	hydrothermal: The Geysers, CA, USA; Campi Flegrei, Italy
Mascagnite	$(NH_4)_2SO_4$	hydrothermal: The Geysers, CA, USA
Sal-ammoniac	$(NH_4)Cl$	hydrothermal: Etna and Vesuvius, Italy
Tschermigite	$(NH_4)Al(SO_4)_2 \cdot 12H_2O$	hydrothermal: The Geysers, CA. USA; Campi Flegrei, Italy; Taupo, New Zealand
Mundrabillaite	$(NH_4)_2Ca(HPO_4)_2 \cdot H_2O$	cave deposit: Australia
Ammonian fluorapophyllite	$(NH_4,K)Ca_4Si_8O_{20}(F,OH) \cdot 8H_2O$	hydrothermal: Calvinia, South Africa and Guanajuato, Mexico
Ammonioleucite	$(NH_4)AlSi_2O_6$	metamorphosed volcanic rock: Japan; hydrothermal: The Geysers, CA
Buddingtonite	$NH_4AlSi_3O_8$	hydrothermal: Sulphur Bank Mine, CA; Cedar Mt, NV, USA; Japan; Phosphoria Fm.: ID, USA; oil shale: Australia
Tobelite	$(NH_4,K)Al_2(Si_3Al)O_{10}(OH)_2$	hydrothermally altered clay: Japan; UT, USA; oil shale: North Sea

To explore more realistic sources of NH4+ than NH4Cl

Buddingtonite	$NH_4AlSi_3O_8$



To explore more realistic sources of NH4+ than NH4Cl

- K+/NH4+ exchange on clay minerals' surface → cation exchange

Appelo and Postma

To investigate T and P conditions beyond 300 °C and 86 bar

- <u>Pressure</u> :

PHREEQC is ‘designed’ to explore ‘high’ pressures

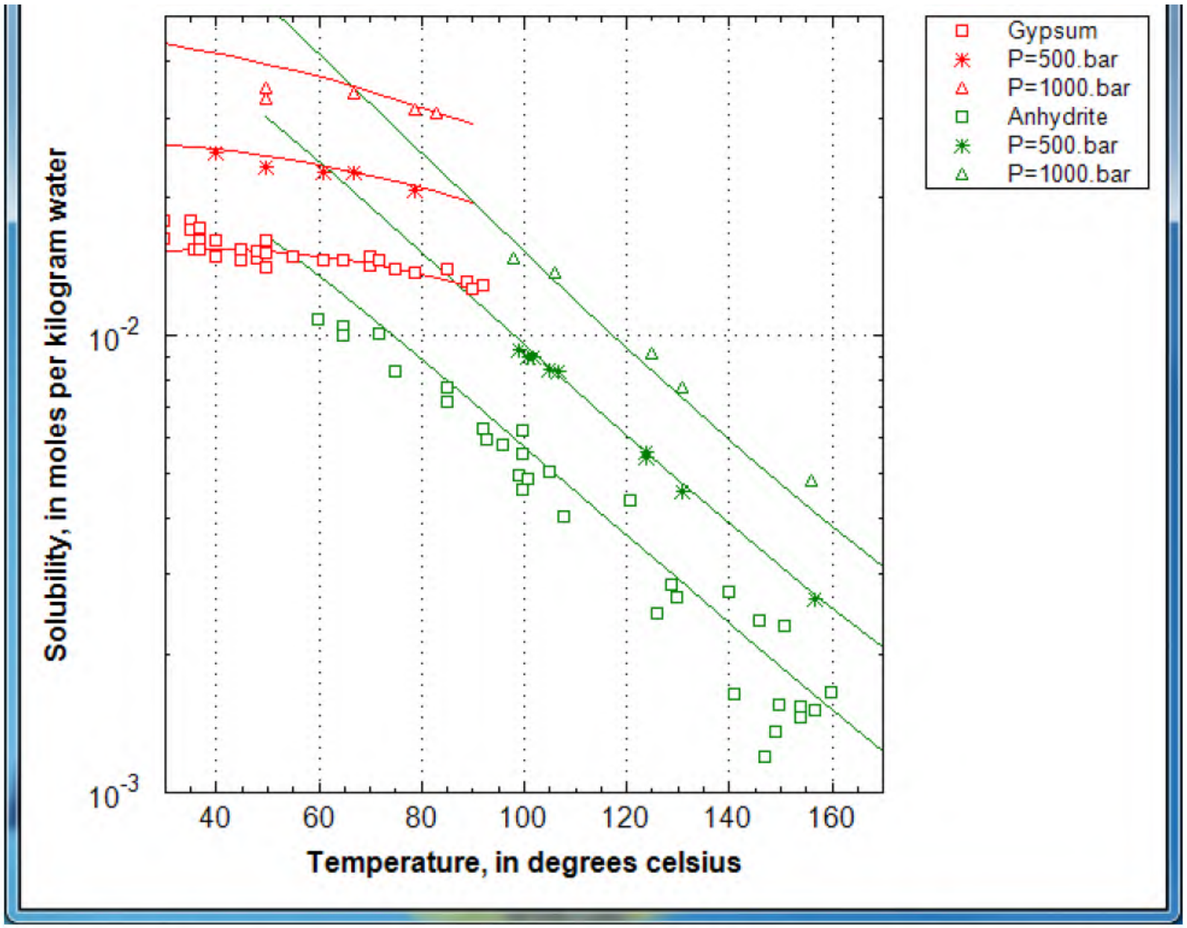


Figure 5. The solubility of gypsum and anhydrite as a function of temperature at 1, 500, and 1,000 bars. Data points from Blount and Dickson (1973); lines calculated by PHREEQC.

PHREEQC user’s guide

To investigate T and P conditions beyond 300 °C and 86 bar

- Temperature :
  - PHREEQC calculations above 300 °C
    - B-dot model : extrapolation of the A(T), B(T) and Bdot(T) parameters to T > 300 °C BUT below the critical T of water (374 °C) ?

$$\log \gamma_i = -\frac{A\, z_i^2 \sqrt{I}}{1 + a_i^0 B \sqrt{I}} + \dot{B} I$$

  - Use of other softwares :
    - SupPHREEQC
    - HCh (Shvarov, 2008) (Gibbs Energy Minimization, not Law of Mass Action)
    - …

ELSEVIER
Computers & Geosciences
Volume 143, October 2020, 104560

SupPhreeqc: A program for generating customized Phreeqc thermodynamic datasets from Supcrtbl and extending calculations to elevated pressures and temperatures

Guanru Zhang [a, b], Peng Lu [c], Yilun Zhang [b], Kevin Tu [d], Chen Zhu [b]

- *geothermal.dat* with T-P grid of 0–300°C at Psat and *bl.dat* up to 1000°C and 5000bars.

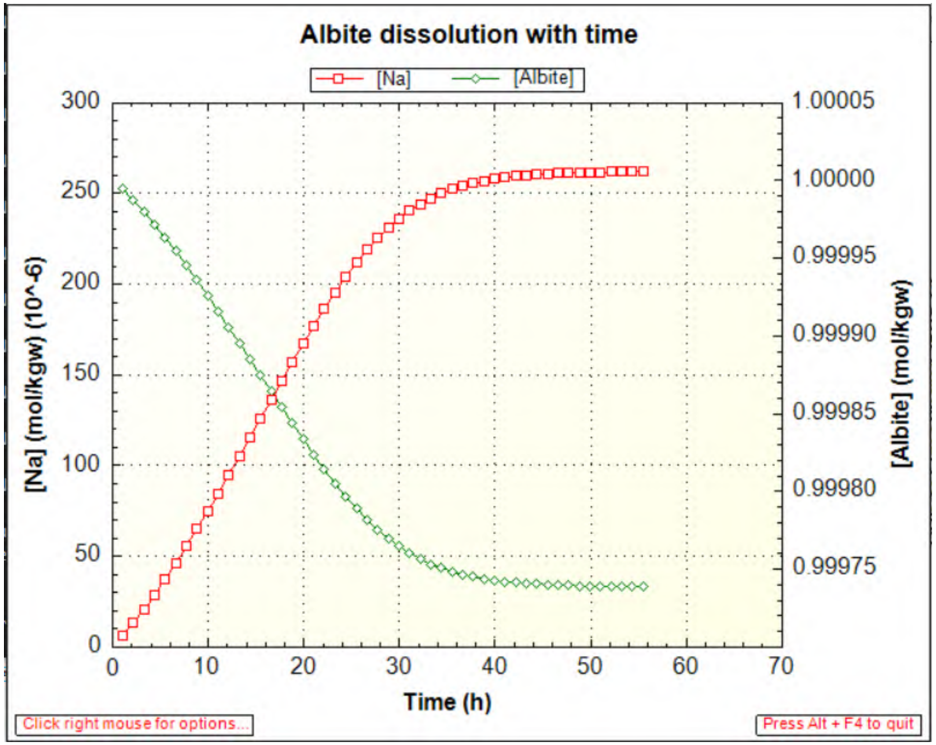
HCh: New Potentialities for the Thermodynamic Simulation of Geochemical Systems Offered by Windows

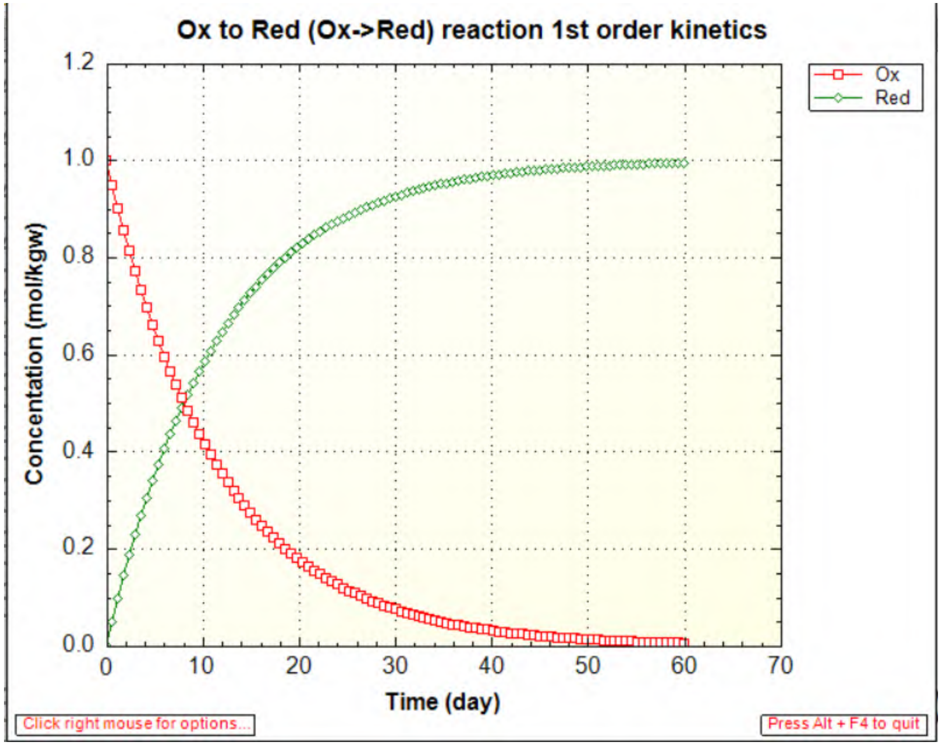
Yu. V. Shvarov
Geological Faculty, Moscow State University, Vorob'evy gory, Moscow, 119992 Russia

Received April 22, 2007

To consider the kinetics of redox and mineral reactions

- Mineral reactions = mineral dissolution-precipitation reactions
- Redox reactions kinetics : catalysts, … ?





A page of advertising

My offer

n.jacquemet@geochemical-consulting.com

- Collaboration with labs (master and PhD students supervision, …)
- Execution of R&D modeling studies (mainly) with PHREEQC
  - 0D geochemical models
  - Reactive Transport (RT) models
- PHREEQC training courses :

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---------------------------------------
!!! Next PHREEQC course training !!!
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11, 12 and 13 February 2025

In-person ; in (the beautiful town of) Paris

https://geochemical-consulting.com/phreeqc-training-courses
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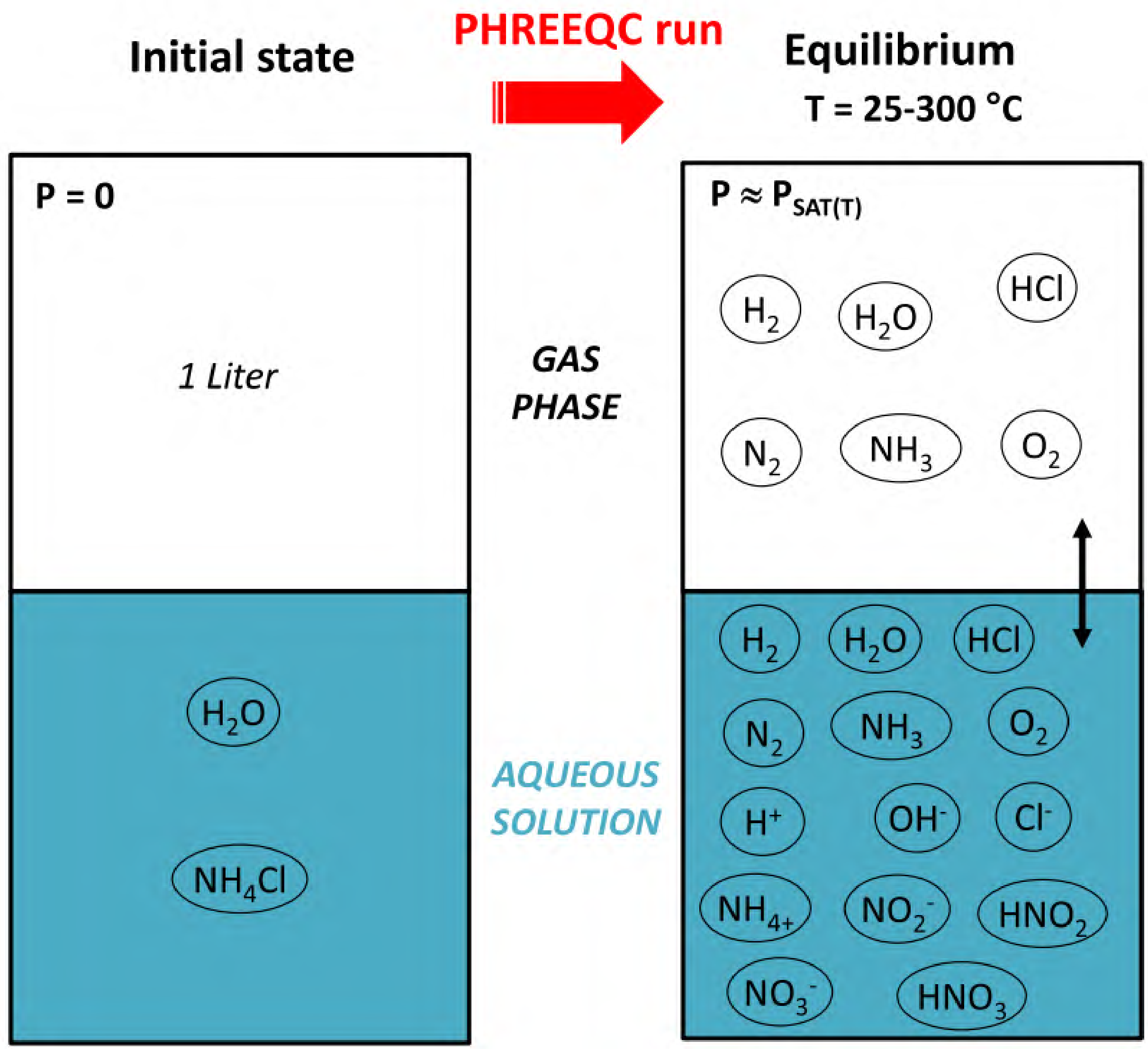
Thanks for your attention !

Appendices

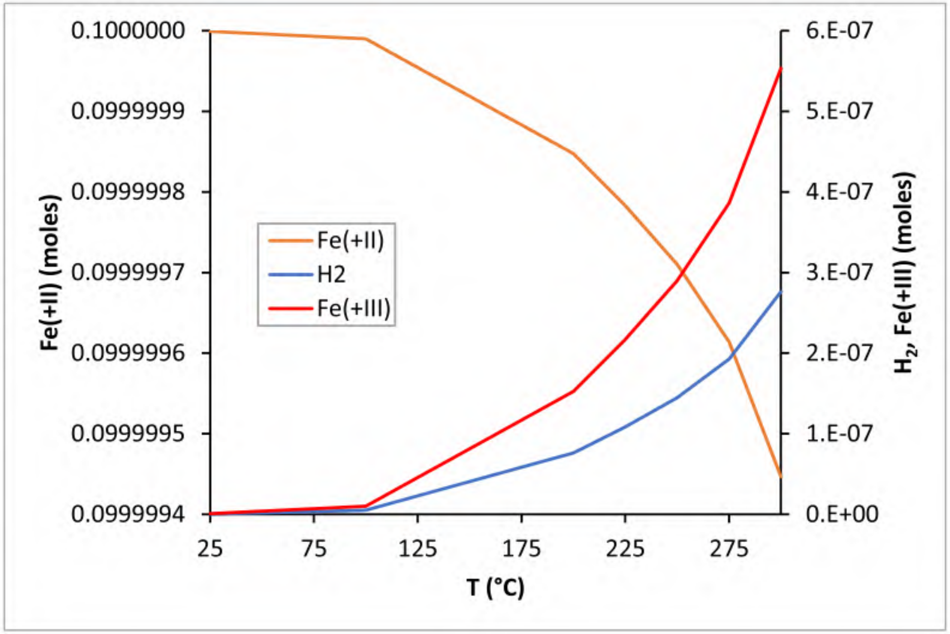
(Thermod.) Equilibrium calculations on initial systems



Chemical reactions

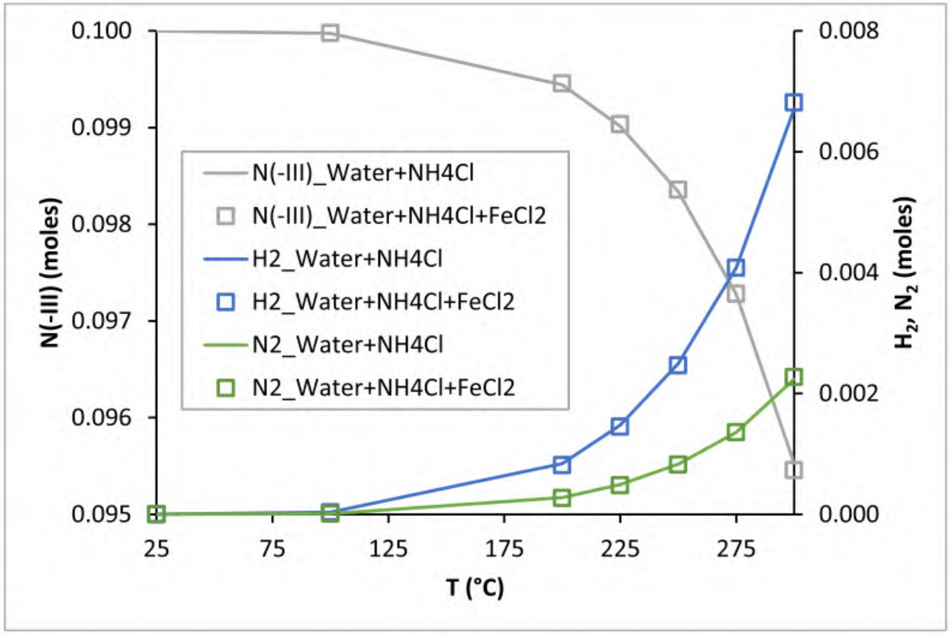
- **Redox-unbuffered systems**

Water + FeCl2



$$Fe^{2+} + H^{+} = Fe^{3+} + 0.5\ H_2$$

Water + NH4Cl +/- FeCl2



$$NH_4^{+} = 1.5\ H_2 + 0.5\ N_2 + H^{+}$$

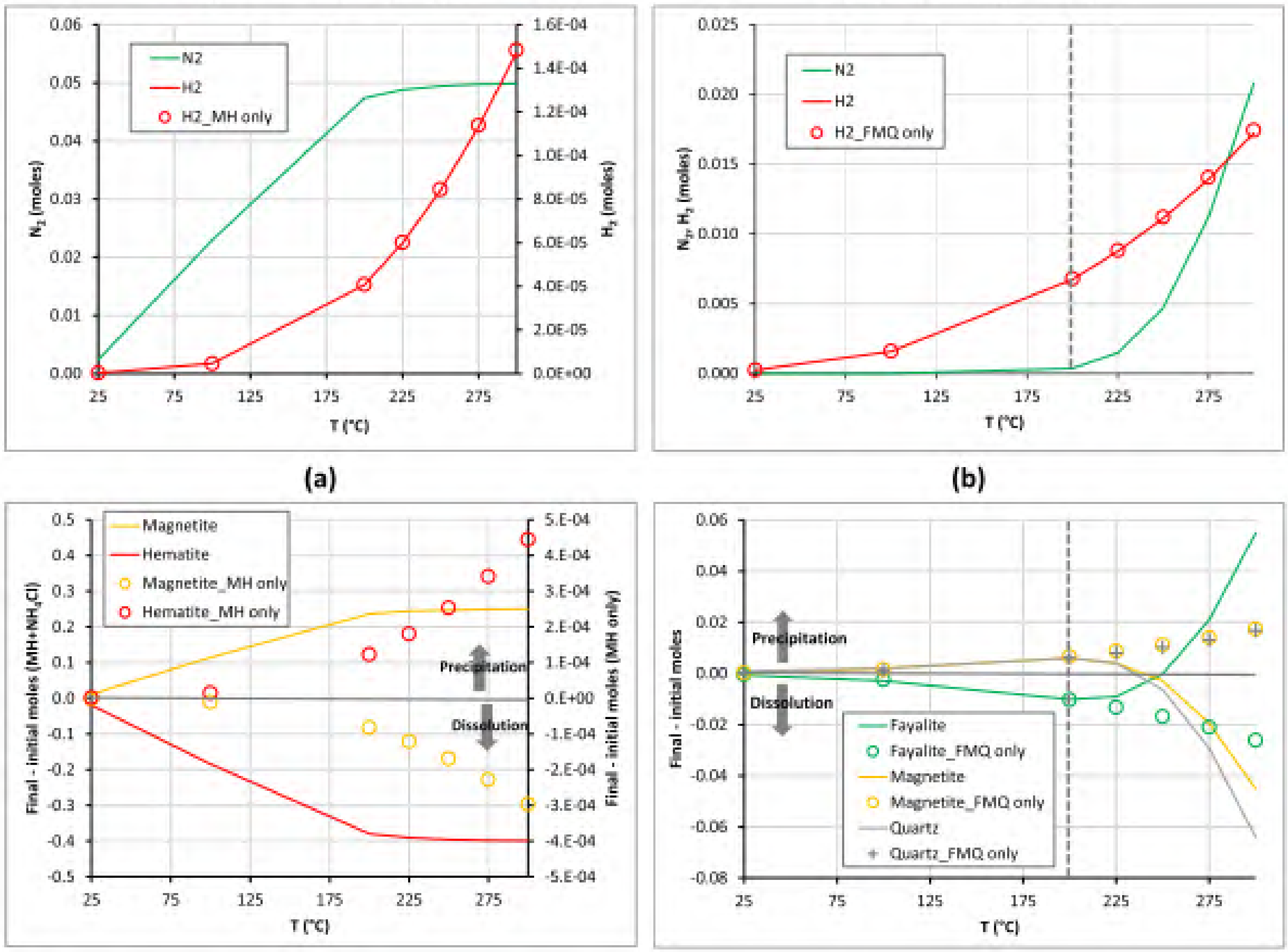
Chemical reactions

- **Redox-buffered systems**

H2$_{TOT}$ & N2$_{TOT}$ (Gas & Water)

Minerals

Water + MH + NH_4Cl | **Water + FMQ + NH_4Cl**



+ Aqueous solution

Conclusion

- Gas-water-mineral equilibrium calculations up to 300°C were executed with PHREEQC on initial model systems including ammonium (NH4+)
- → To see if this ion could be a 'precursor' in the generation of hydrogen and/or nitrogen seeping out of hydrogen systems
- The below reactions involving NH4+ were evidenced
- Under highly reduced redox conditions (FMQ fO2 buffering) the produced gas is mainly hydrogen ; while under lower reduced redox conditions (MH fO2 buffering), the produced gas is mainly nitrogen
- Implications for hydrogen systems comprehension are addressed

$$NH_4^+ = 1.5\ H_2 + 0.5\ N_2 + H^+$$

$$3\ Fe^{3+} + NH_4^+ = 0.5\ N_2 + 3\ Fe^{2+} + 4\ H^+$$

To explore more realistic sources of NH4+ than NH4Cl

```
NH4-feldspar # Buddingtonite
        NH4AlSi3O8 + 4H+ = NH4+ + Al+3 + 3 SiO2 + 2 H2O
        log_k              -2.7243
        -analytic          -7.434e1 3.080e-1 0 0 0 -2.270e-4

NH4-muscovite # Tobelite
        NH4Al3Si3O10(OH)2 + 10 H+ = NH4+ + 3 Al+3 + 3 SiO2 + 6 H2O
        log_k              6.8109
        -analytic          -6.638e1 3.170e-1 0 0 0 -2.386e-4
```