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EGU General Assembly 2020

SORBONNE UNIVERSITÉ

ISTeP Institut des Sciences de la Terre de Paris UMR 7193 - SU - CNRS

Partitioning of halogens between hydrated silicates

Analysis and first principles modelling

Sarah Figowy[1*], Benoît Dubacq[1], Philippe D'Arco[1], Yves Noël[1], Benoît Villemant[1], Benoît Caron[1]

Contact: *sarah.figowy@sorbonne-universite.fr

[1]Sorbonne Université, CNRS-INSU, Institut des Sciences de la Terre de Paris, ISTeP UMR 7193, F-75005 Paris, France

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Part I: Main objectives

Studying halogen partitioning by analytics and modelling

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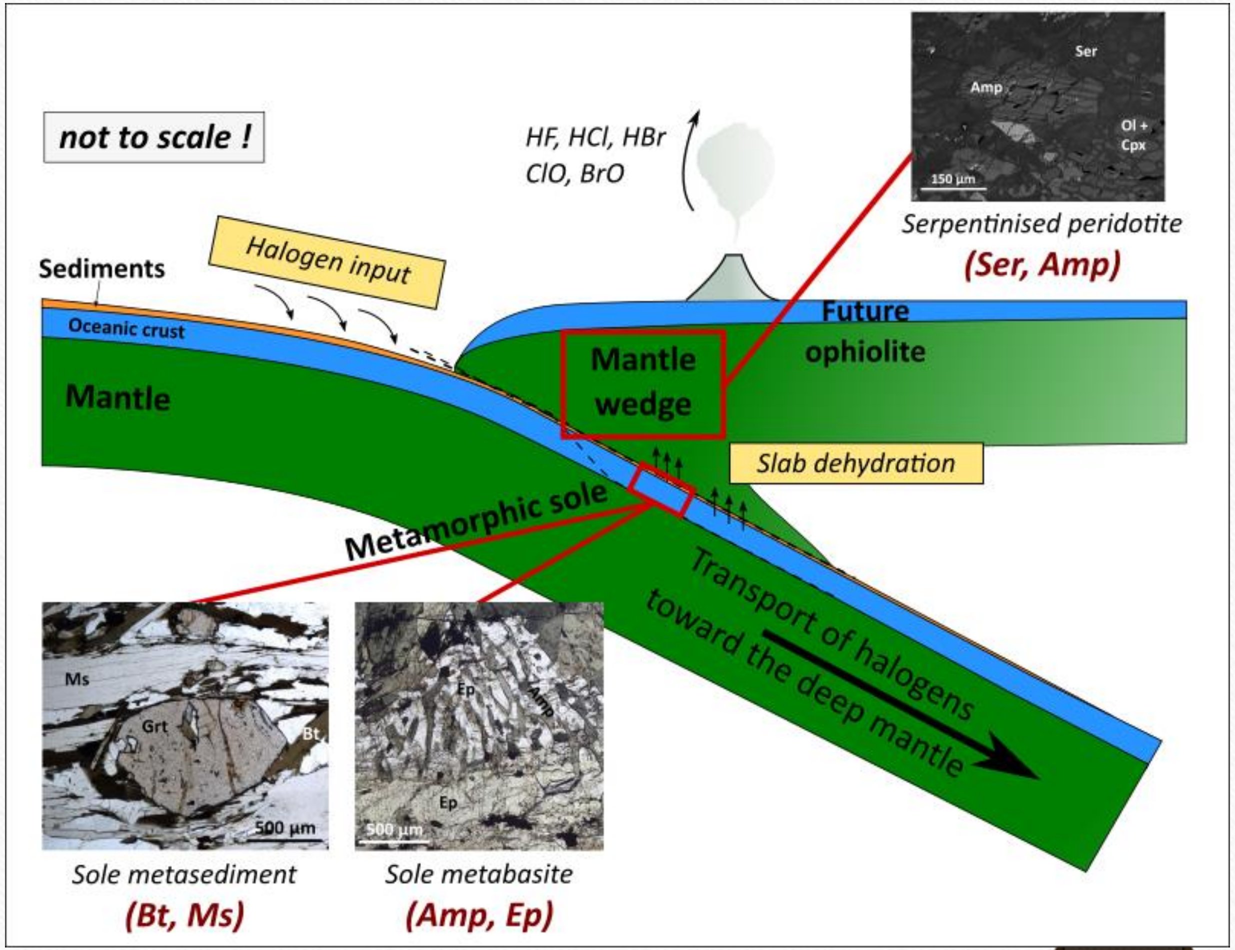
Why studying the partitioning of halogens between minerals in metamorphic and mantle rocks?



Constraints on:

- ✓ Geochemical cycle
- ✓ Metasomatism & fluid/rock interactions

Minerals of interest: hydrated silicates

Biotite (Bt), Muscovite (Ms), Amphibole (Amp), Epidote (Ep), Serpentine (Ser)…

➡ Very abundant ! (main role in deep storage)

➡ But contain very low amount of halogens…

→ Huge analytical & computational challenge !

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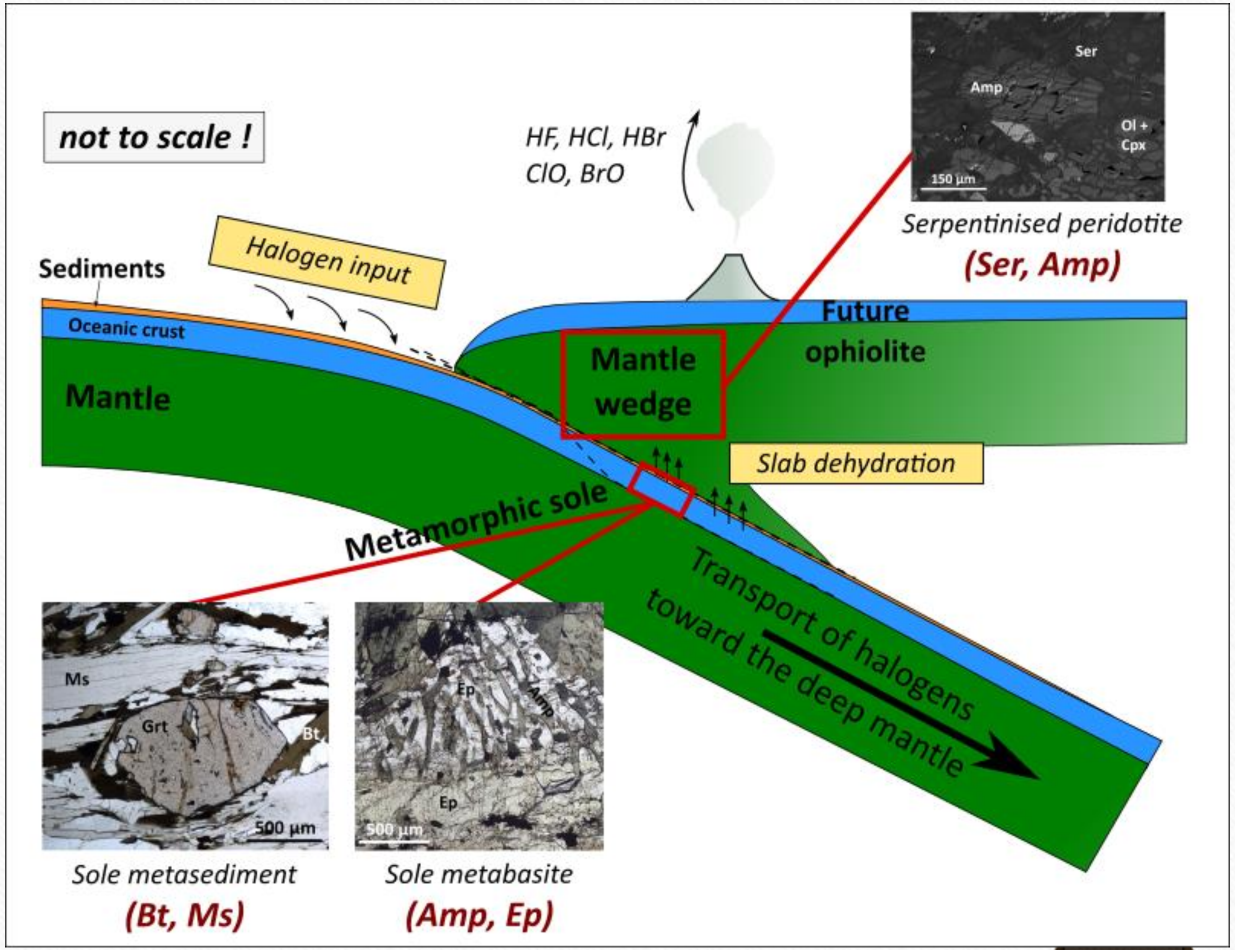

Main objectives:

- Demonstrating the main interest of **LA-ICP-MS/MS** combined to **EPMA** in halogen quantification
- Quantifying the role of **crystal-chemistry and geometry** in halogen uptake by *ab initio* modelling
- Quantifying and comparing **Gibbs free energies of halogen exchange** between modelled minerals

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Part II: Analysis

Quantifying halogens in metamorphic and mantle rocks by EPMA & LA-ICP-MS/MS

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State of the art: analytics

1) *Bulk* measurement ***e.g.: ICP-MS solution***

- ✓ Very low detection limit
- ✓ Pagé et al. (2018): 0.03 ppm Br and I in serpentines

Inadequate for mineral-mineral partitioning

2) Point measurement ***e.g.: SIMS***

- ✓ In glasses, minerals, fluid inclusions
- ✓ Hughes et al. (2018): 350 ppb Br in olivine

Complex sample preparation and signal processing + low availability

Huge need to develop a method:

- ✓ for point analyses
- ✓ « en routine »
- ✓ *in situ*
- ✓ suited for trace to ultra-trace quantification

Candidate: ICP-MS/MS (laser ablation mode)

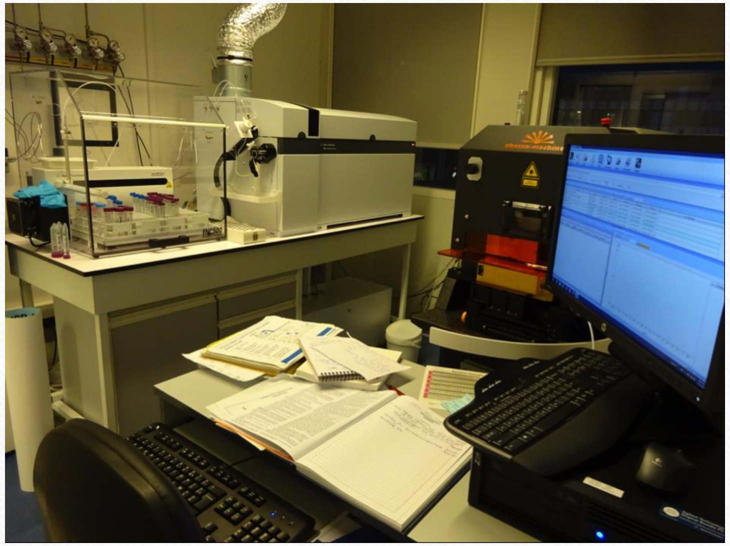

Photo: LA-ICP-MS/MS 8800 Agilent (ALIPP6)

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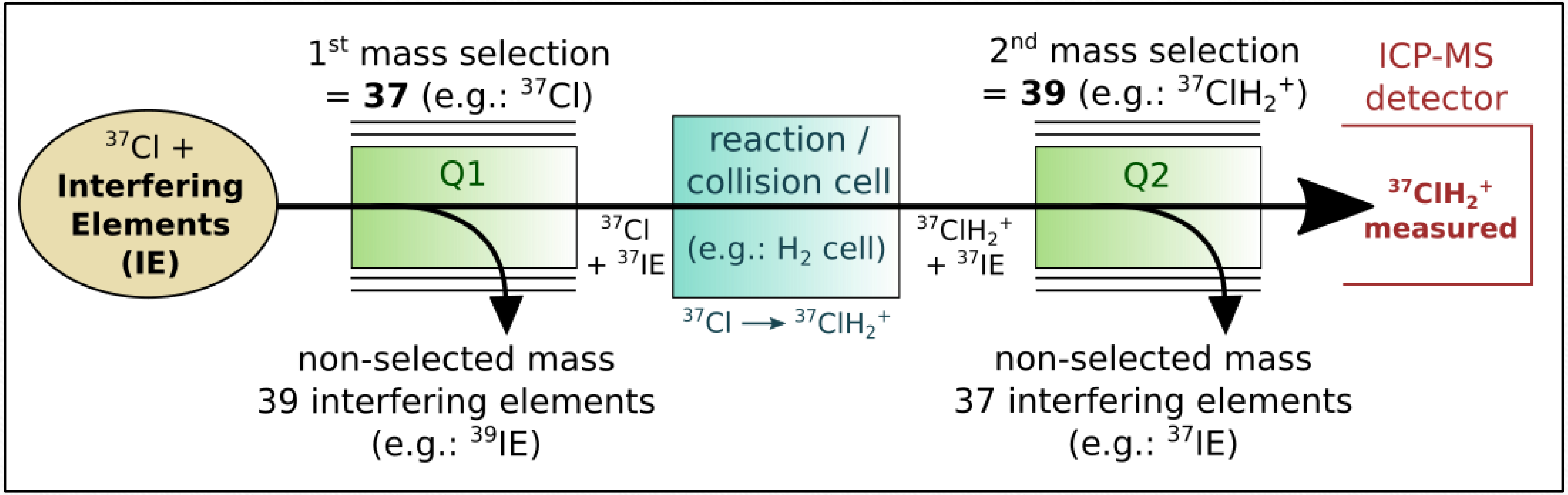
The LA-ICP-MS/MS (triple quad)



two quadrupoles + reaction/collision cell to optimise the mass/charge separation of isotopes

LA-ICP-MS/MS

$\searrow$ Sensibility

$\searrow\searrow$ Mass interferences

$\nearrow$ $\frac{\text{Signal}}{\text{Noise}}$ ratio

F non accessible by ICP-MS !

Combined with EPMA for F and Cl

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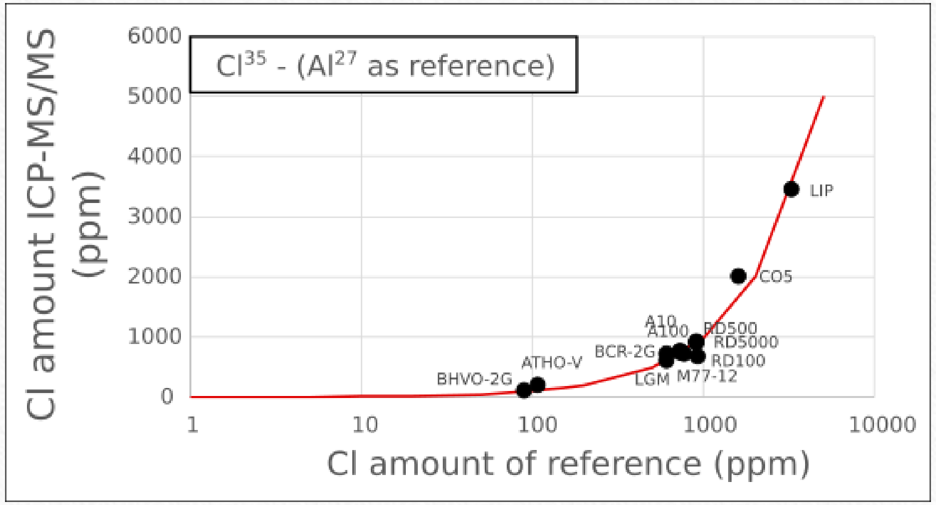
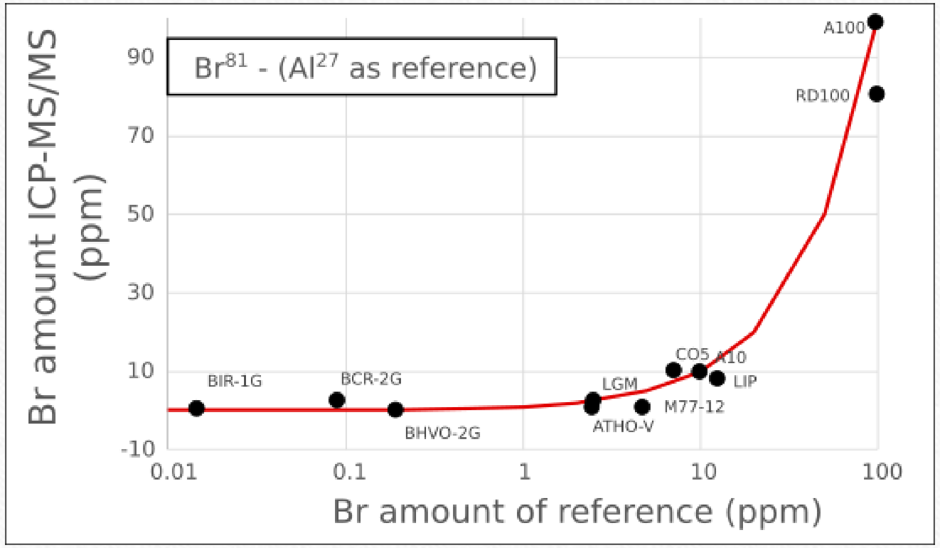
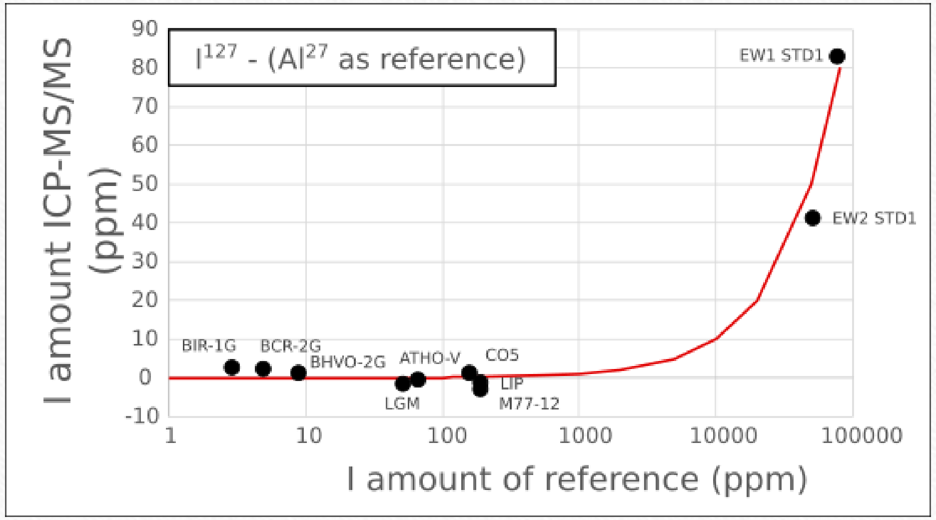
ICP-MS calibrations of Cl, Br and I

With international and in-house glass standards

- ✓ Cl : about 80 ppm
- ✓ Br : about 0.1 ppm
- ✓ I : < 1 ppm (work in progress)







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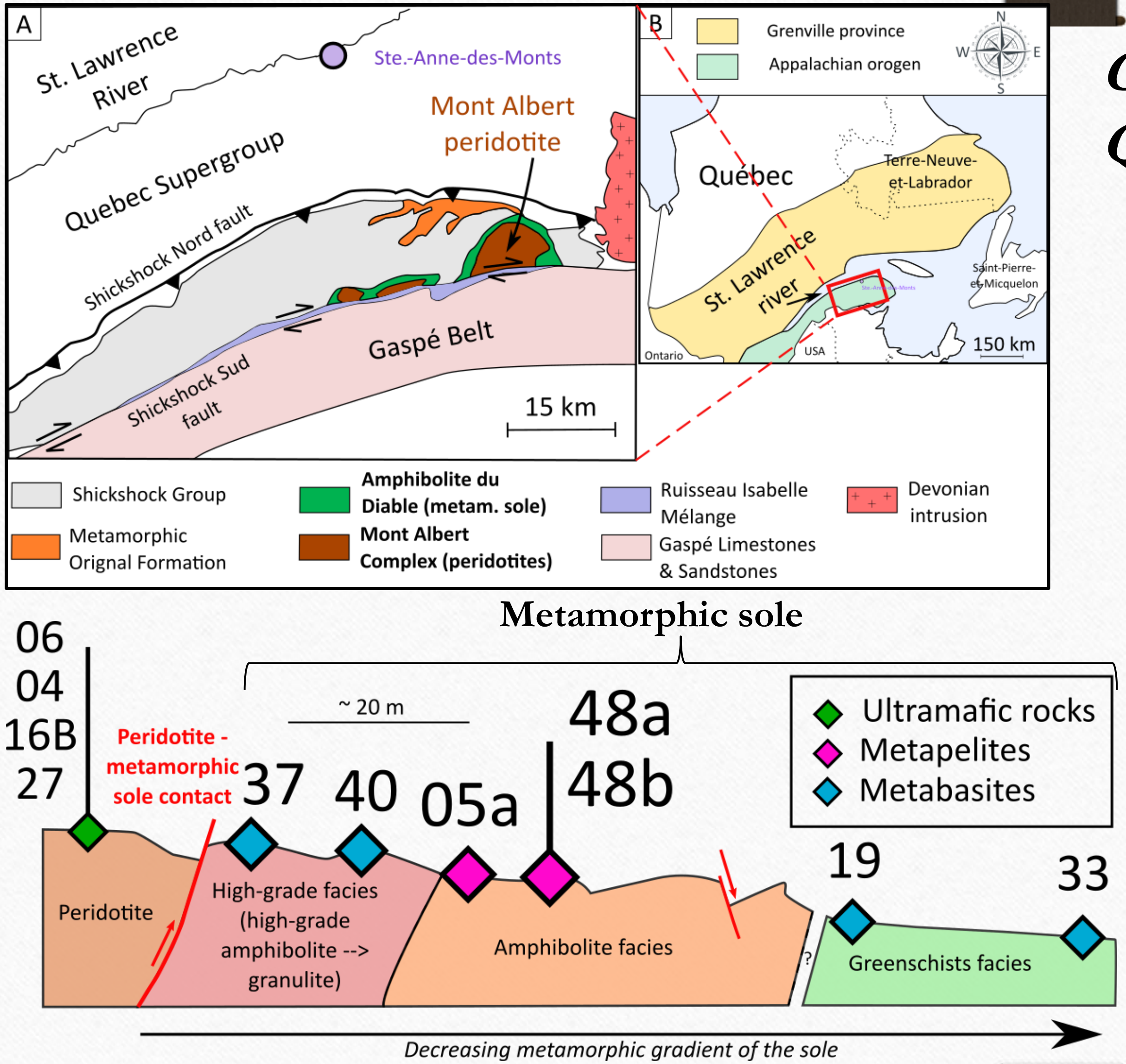

After Dubacq et al., 2019

Case study: Mont Albert (Gaspésie, Québec, Canada)

Metamorphic sole (metasediments + metabasites) at the base of the **peridotite body**

Metamorphic sole (**hydrated**)

Fluid exchanges ??

Mantle wedge (**should be anhydrous!**)

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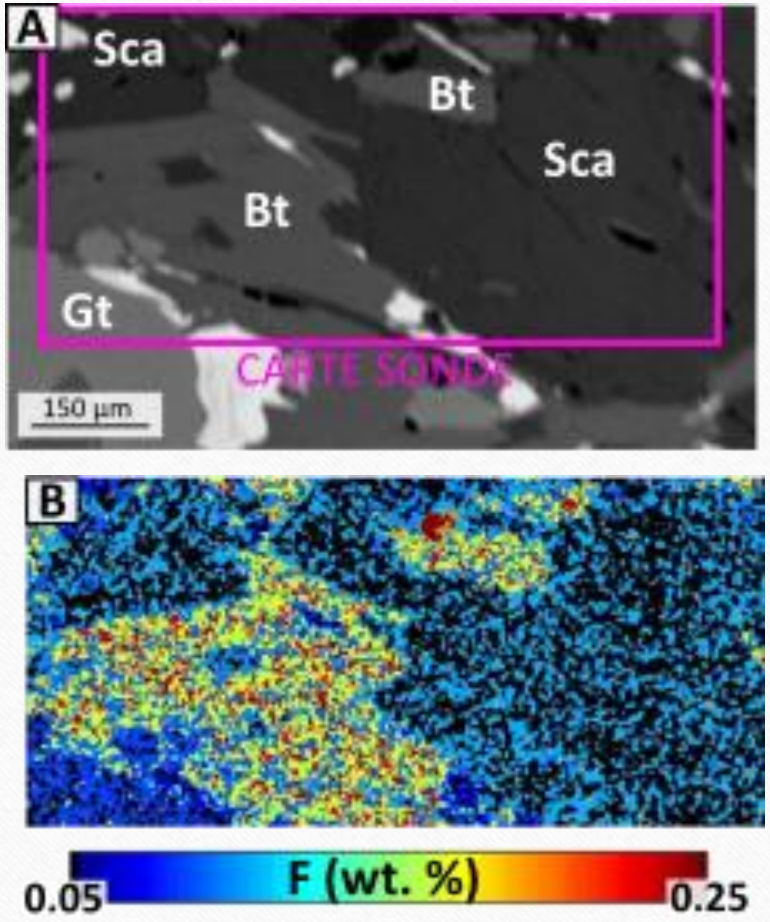
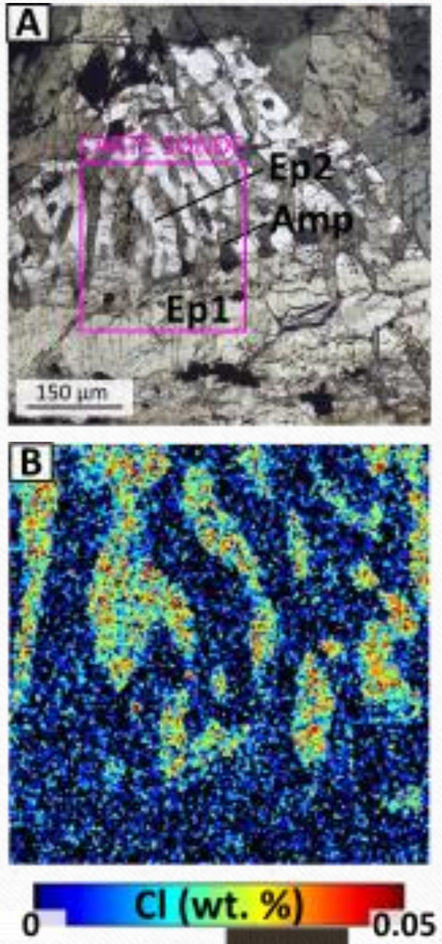
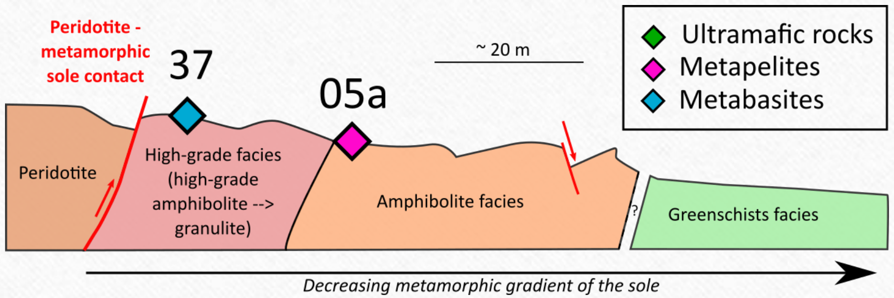
EPMA: F and Cl amount in the metamorphic sole

Metasediment (spl 05a)



Metabasite (spl 37)





Metamorphic sole = enriched in F and Cl

EPMA detection limits :

- ✓ **F : 200 ppm** ✓ **Cl : 25 ppm**

Main hosts in metasediments

- ✓ Biotite : 1500 ppm F, 130 ppm Cl
- ✓ Muscovite : 330 ppm F, < 30 ppm Cl
- ✓ Scapolite : < 200 ppm F, 200 ppm Cl

Main host in metabasites

- ✓ Amphibole : 250 ppm F, 100 ppm Cl

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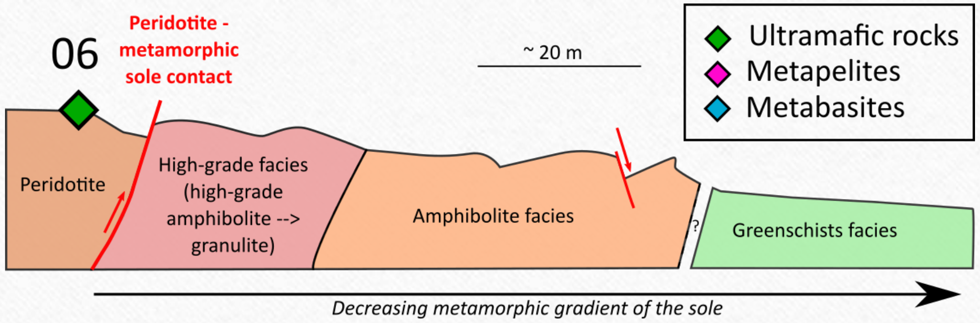
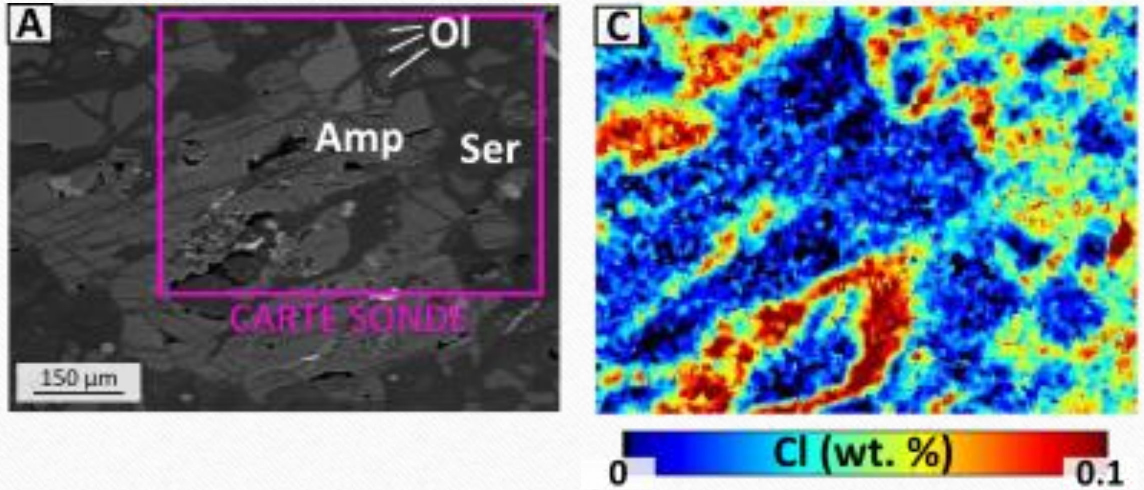
EPMA: F and Cl amount in the mantle wedge



Harzburgite (spl 06)



Main hosts in mantle rocks

- ✓ Serpentine: 500 ppm F, 600-700 ppm Cl
- ✓ Amphibole: <200 ppm F, **40-100s ppm Cl**

- ✓ Serpentine are more enriched in Cl than F
- ✓ **Amphiboles : enriched in Cl in serpentinised harzburgites.**

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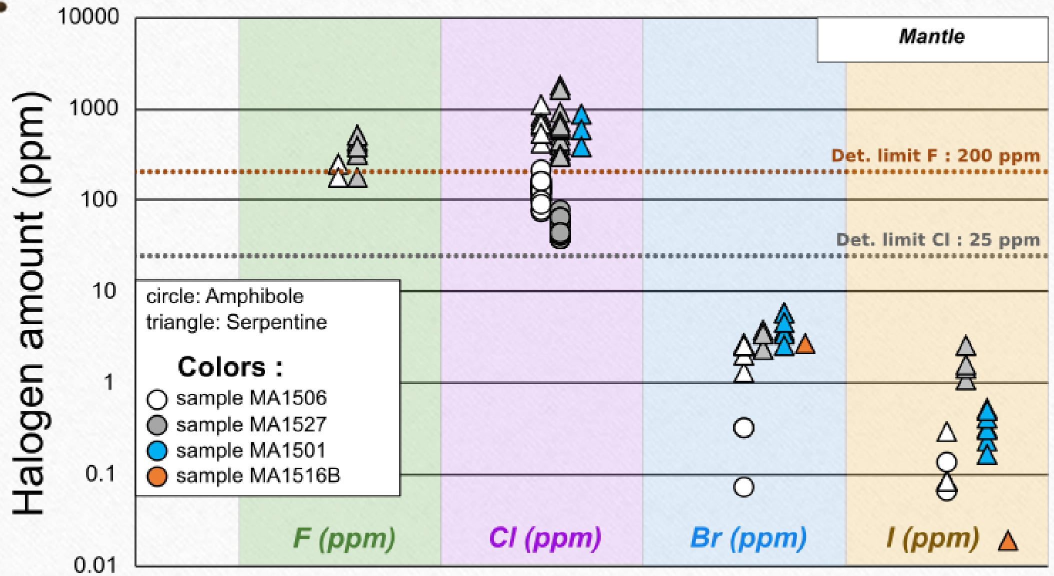
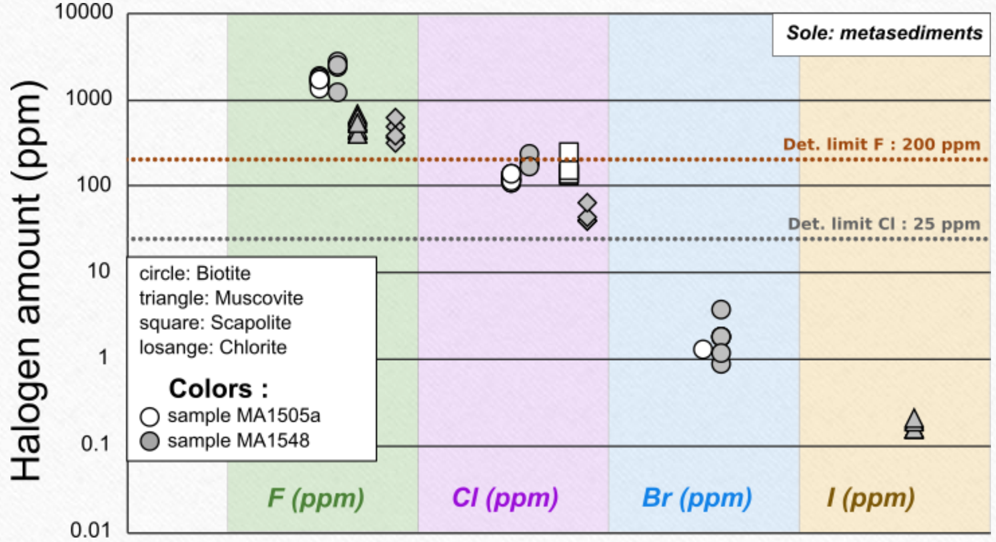
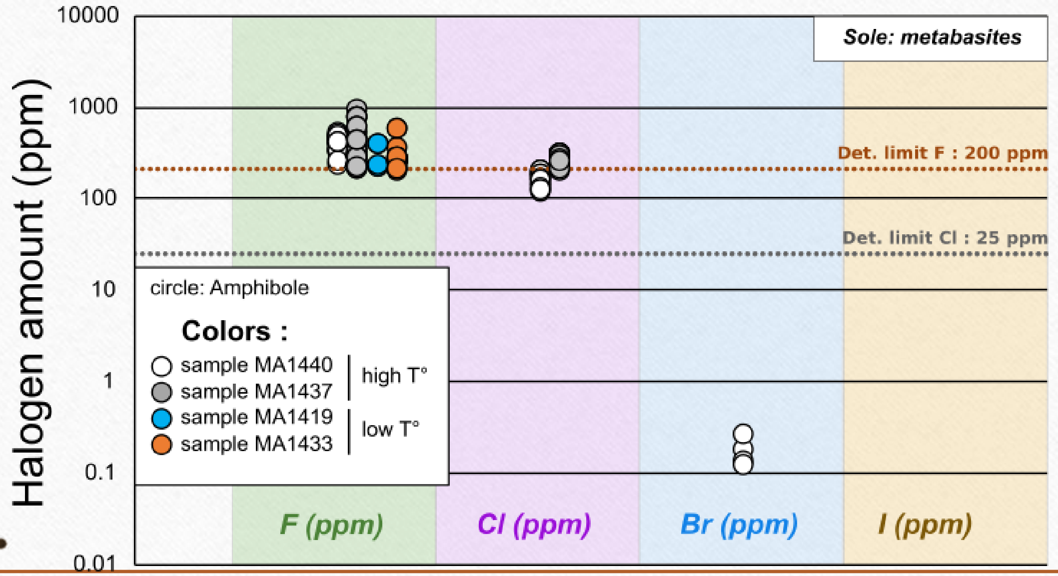
EPMA and ICP-MS/MS results

- ✓ **Metasediment**: biotite is the main host (about 10^3 ppm of F, 10^2 ppm of Cl, 1 ppm of Br)
- ✓ **Mantle**: amphibole are enriched in Cl, Br and I (up to 200 ppm of Cl)

➡ **Dehydration of the metamorphic sole**
➡ **Fluid-rock interaction (from sole to mantle)**
➡ **Halogens incorporated in the mantle wedge**







Detection limits indicated for EPMA (F and Cl)

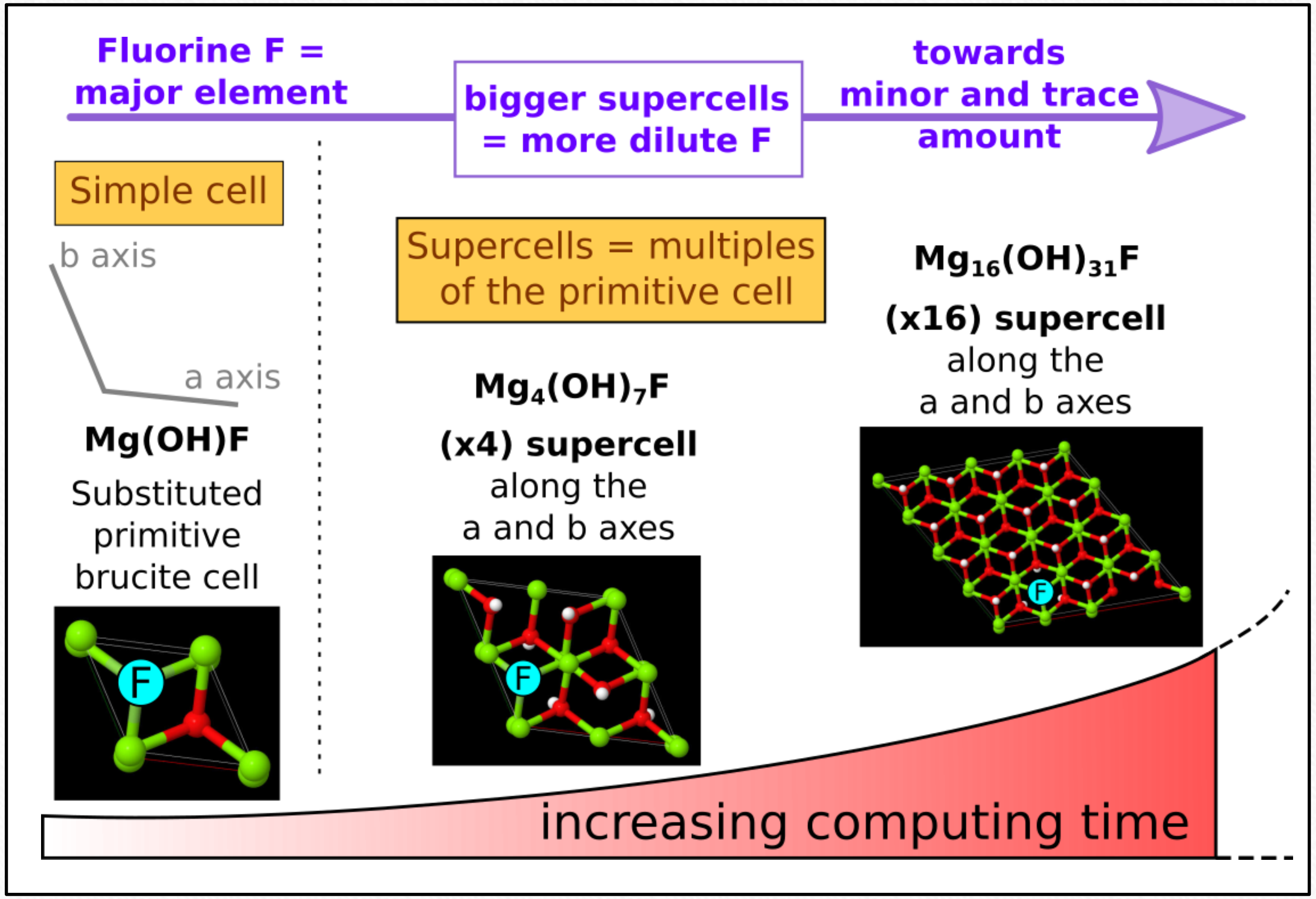
Part III: Modelling

Ab initio modelling of F = OH and Cl = OH exchanges in phyllosilicates

See also the poster presented by Dubacq et al. :

https://doi.org/10.5194/egusphere-egu2020-6962

The *ab* initio modelling of the OH^- = X^- exchange (X⁻ = F⁻, Cl⁻, Br⁻, I⁻)



CRYSTAL17 *ab initio* program (see Dovesi et al., 2004)

- ✓ Reaching lower concentrations: **supercells**
- ✓ Need to work on simplified systems: **end-members**

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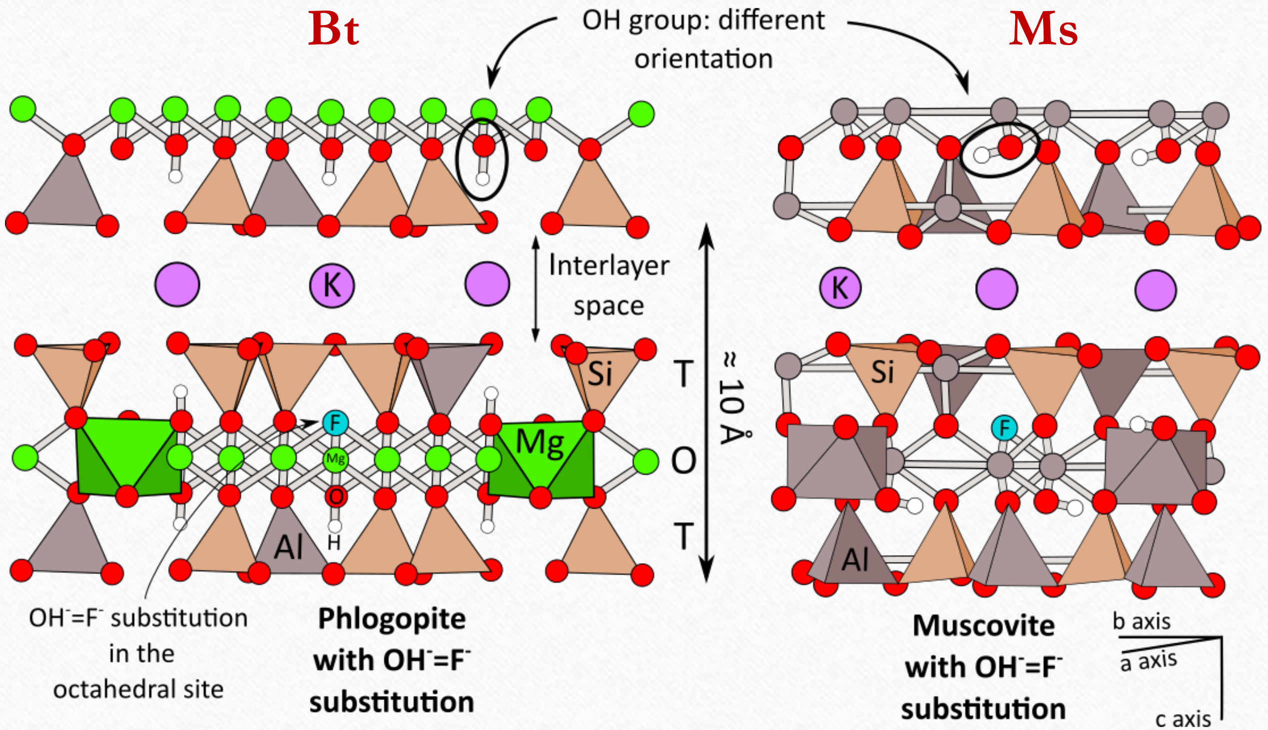
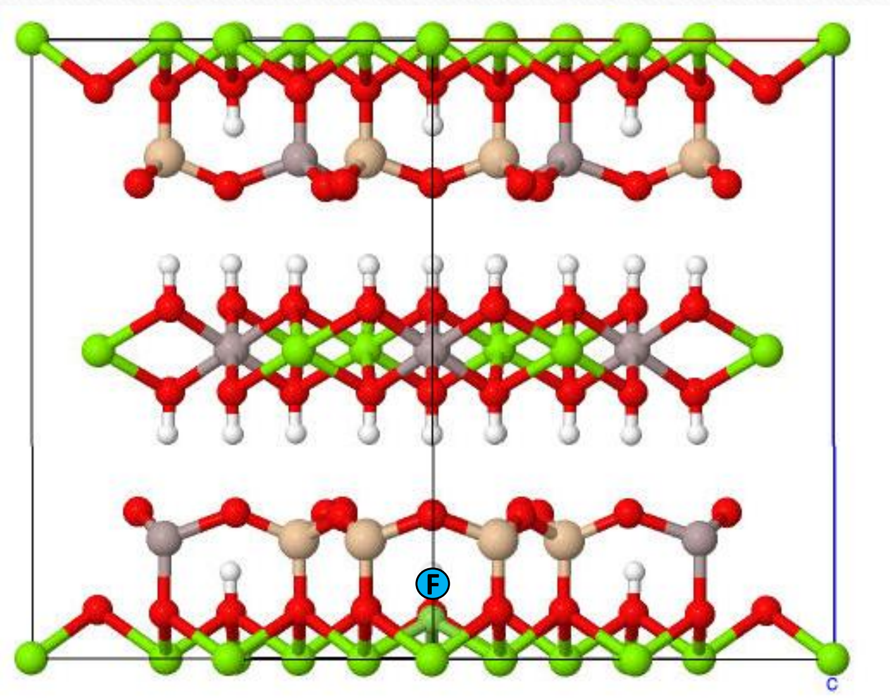
Simulation of F = OH and Cl = OH substitution in three magnesian end-members: phlogopite, muscovite and clinochlore (space group : C2/m)



F-Phlogopite
$KMg_3(AlSi_3)O_{10}(OH,F)$
O-H **follows** the c-axis

F-Muscovite
$KAl_2(AlSi_3)O_{10}(OH,F)$
O-H: almost **perpendicular** to c

Cln-1



F-Clinochlore
$Mg_5Al(AlSi_3)O_{10}(OH)_7F$

- ✓ **Cln-1**: F in the TOT sheet
- ✓ **Cln-2**: F in the brucite sheet

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Reaction for this example: *

Exchange from Muscovite to F-Biotite:

$$KMg_3(AlSi_3)O_{10}(OH)_2 + KAl_2(AlSi_3)O_{10}(OH,F) = KMg_3(AlSi_3)O_{10}(OH,F) + KAl_2(AlSi_3)O_{10}(OH)_2$$

Biotite **F-Muscovite** **F-Biotite** **Muscovite**

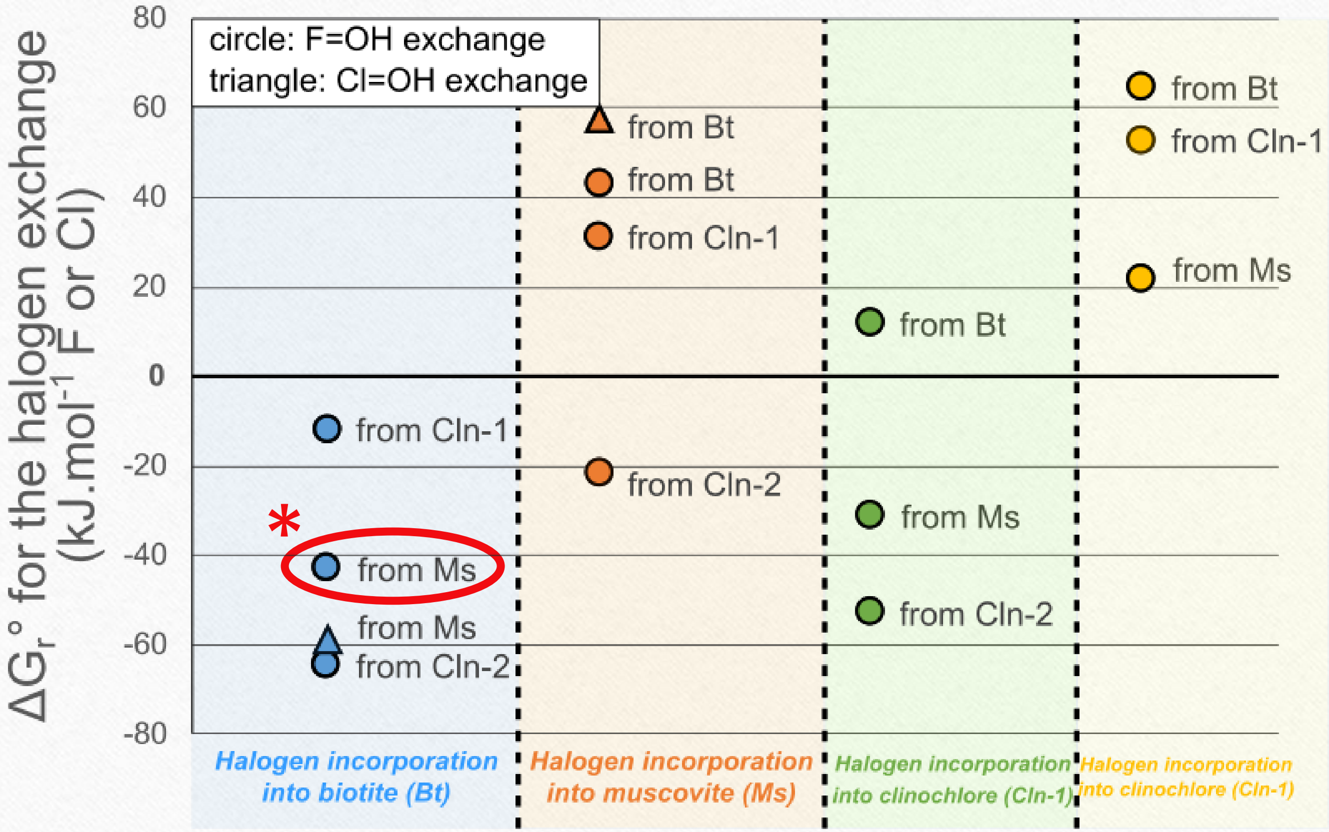
$\Delta G_r° = -11\ kJ.mol^{-1}$ **p.s.f.**

Energy stabilization: phlogopite > clinochlore 1 > muscovite > clinochlore 2

Mg-biotite is systematically favoured

Hypothesis (see also Munoz, 1984):

- ✓ O-H **follows c-axis** in biotite
- ✓ Repulsive effect between H^+ and K^+…
- ✓ …substituted by an attraction between F^- and K^+ !



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To summarize…

- **EPMA and LA-ICP-MS/MS** allow easy ***in situ* measurement** of **F, Cl and Br** in most hydrated silicate phases (Villemant et al., submitted to American Mineralogist). Detection limits are **very satisfying**. Calibration of I may be improved with more reference standards.

- ***Ab initio* modelling** clearly shows that **Mg-biotite is a favoured F- and Cl-host** compared with muscovite and Mg-chlorite, in agreement with natural analyses.

- ***In progress***: halogen incorporation differences between dioctahedral and trioctahedral micas may be linked to electrostatic effects between interfoliar cation, hydrogen and halogen atoms: **but what about vacancy-rich chlorite…? and amphibole…?**

Many thanks for your attention !