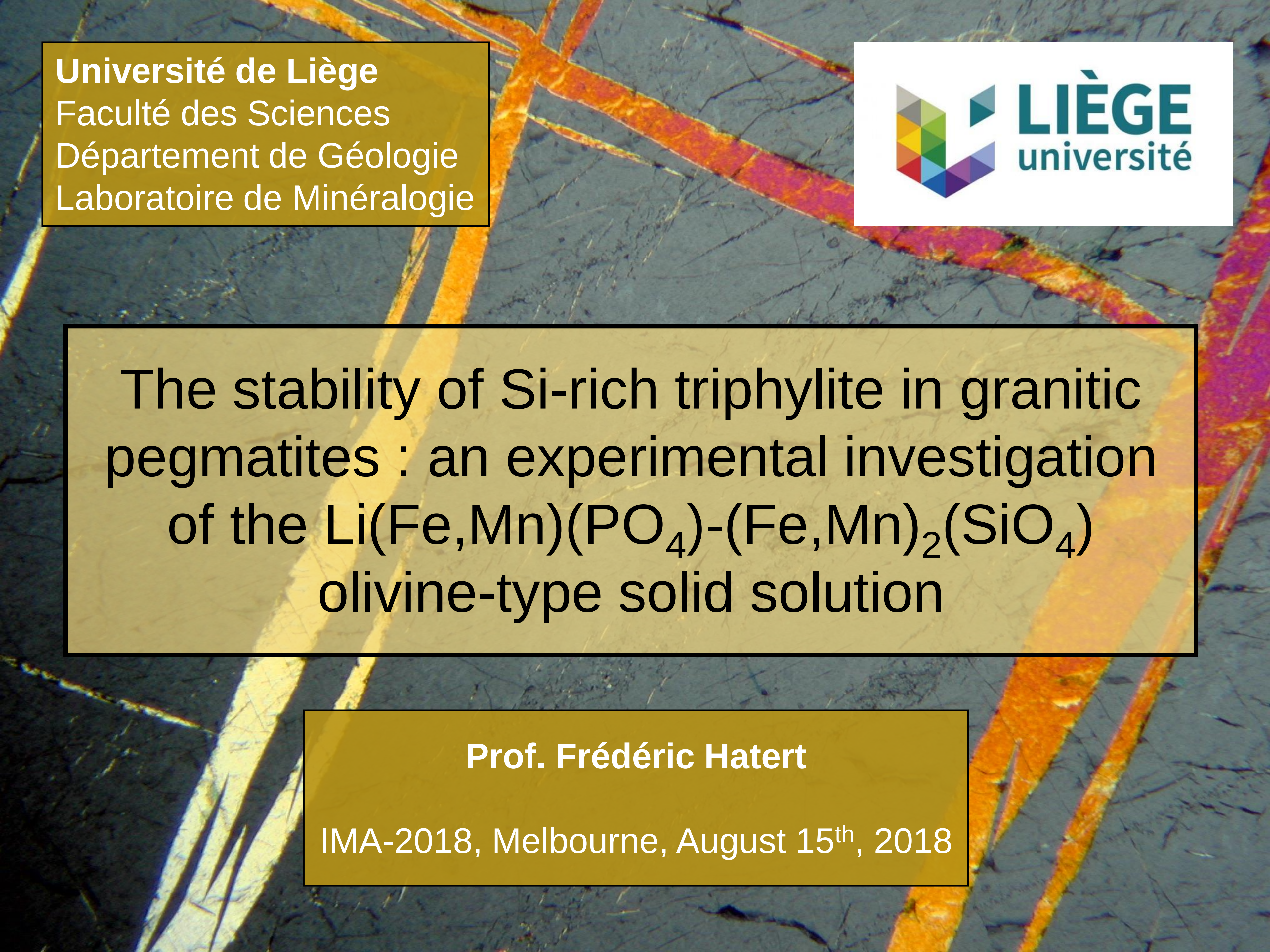
Université de Liège
Faculté des Sciences
Département de Géologie
Laboratoire de Minéralogie

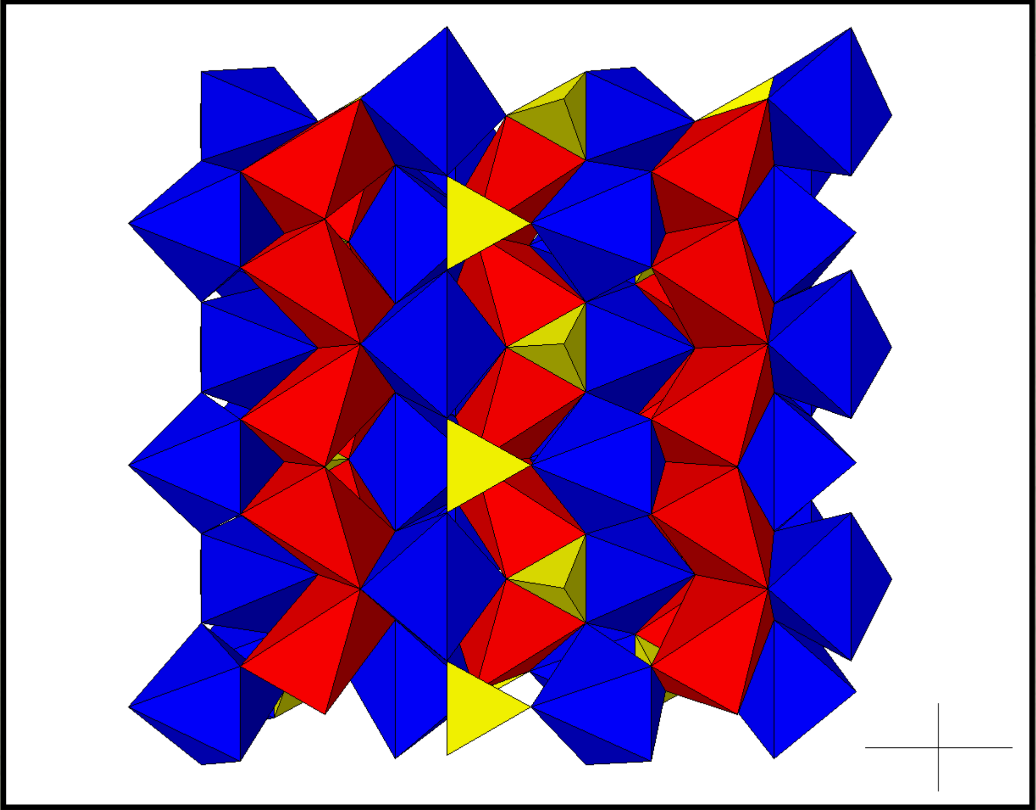


The stability of Si-rich triphylite in granitic pegmatites : an experimental investigation of the Li(Fe,Mn)(PO$_4$)-(Fe,Mn)$_2$(SiO$_4$) olivine-type solid solution

Prof. Frédéric Hatert

IMA-2018, Melbourne, August 15th, 2018

The olivine structure



Phosphates

- Triphylite, $LiFe^{2+}(PO_4)$
- Lithiophilite, $LiMn(PO_4)$
- Natrophilite, $NaMn(PO_4)$
- Karenwebberite, $NaFe^{2+}(PO_4)$

Silicates

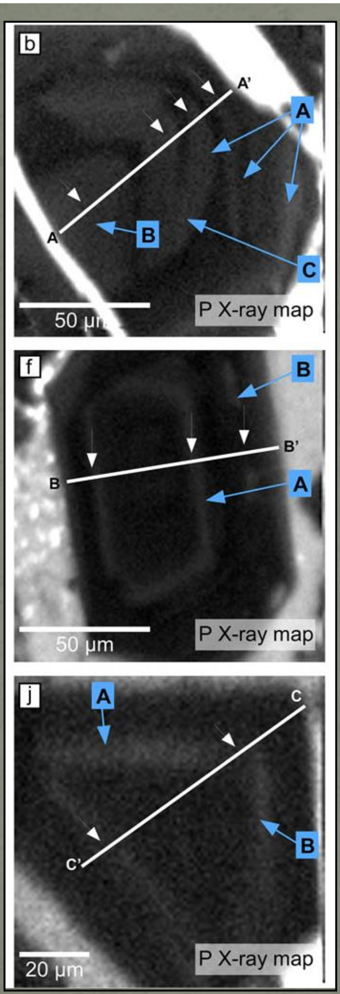
- Fayalite, $Fe^{2+}_2(SiO_4)$
- Forsterite, $Mg_2(SiO_4)$
- Tephroite, $Mn^{2+}_2(SiO_4)$

Red octahedra: M1 (Li, Na, Fe, Mn, Mg)
Blue octahedra: M2 (Fe, Mn, Mg)
Yellow tetrahedra: (Si, P)

S.G. *Pmnb*
a = 6.092 Å
b = 10.429 Å
c = 4.738 Å

Phosphorous in olivine-type silicates

Semarkona LL chondrite

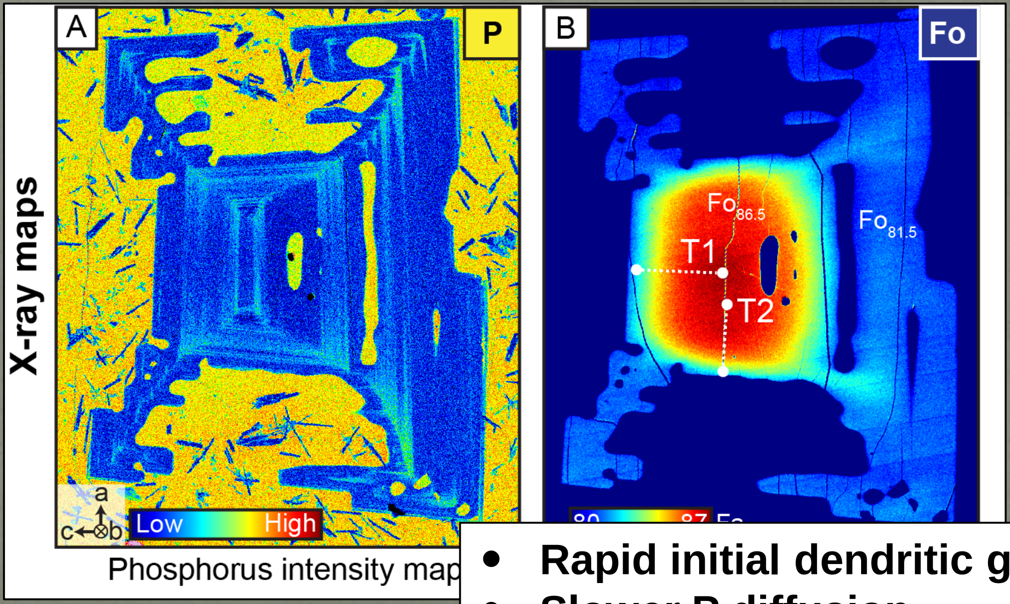


McCanta *et al*. (2016)

P_2O_5 in olivines

- Generally below 1 wt. %
- In meteorites: up to 5 wt. %

Kilauea volcano, Hawaii



- **Rapid initial dendritic growth**
- **Slower P diffusion**

Shea *et al*. (2015)

Silicon in olivine-type phosphates

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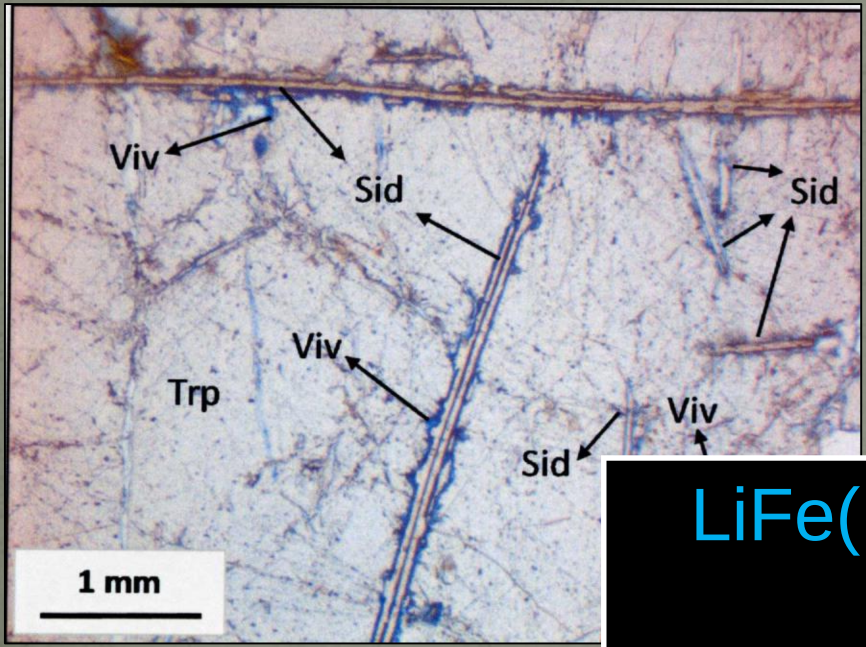
SiO_2 in triphylite

- Generally below 1 wt. %
- Pøibyslavice granite: 1 to 17 wt. % (Škoda *et al*., 2013)



Baijot (2015)

$$LiFe(PO_4) \longrightarrow Fe_2(SiO_4)$$

$$Li^+ + P^{5+} \longrightarrow Fe^{2+} + Si^{4+}$$

Previous experiments

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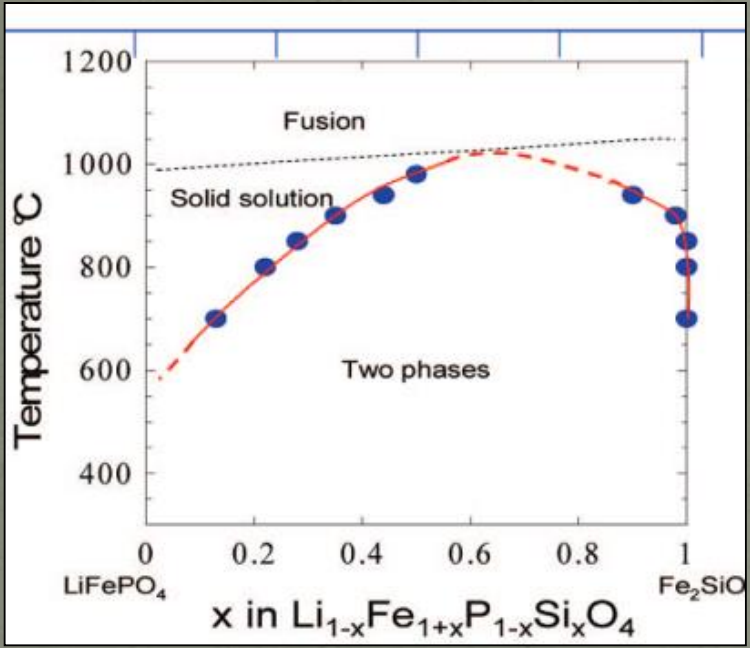
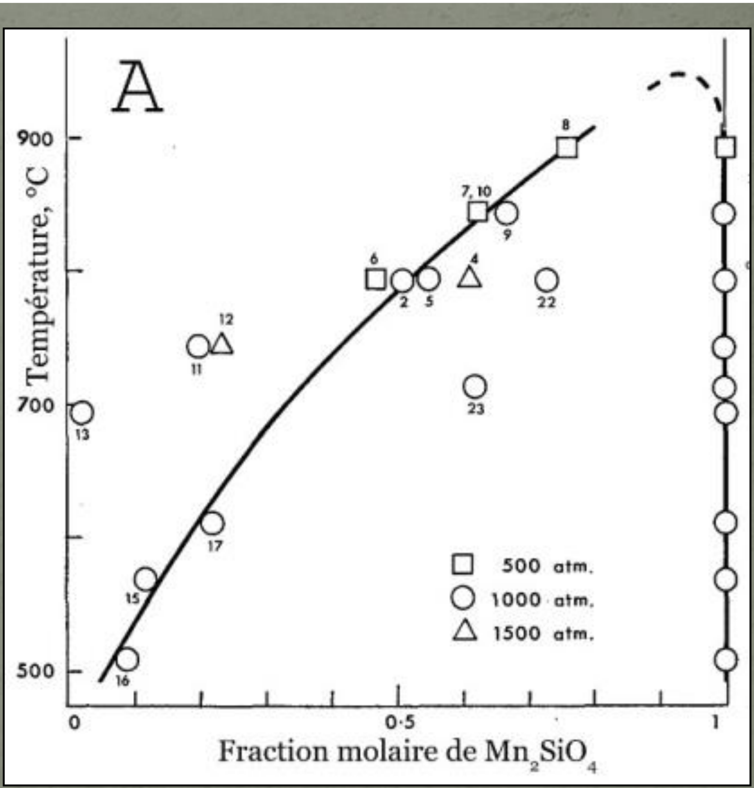
$LiFe(PO_4)$ – $Fe_2(SiO_4)$ system



Recham *et al*. (2008)

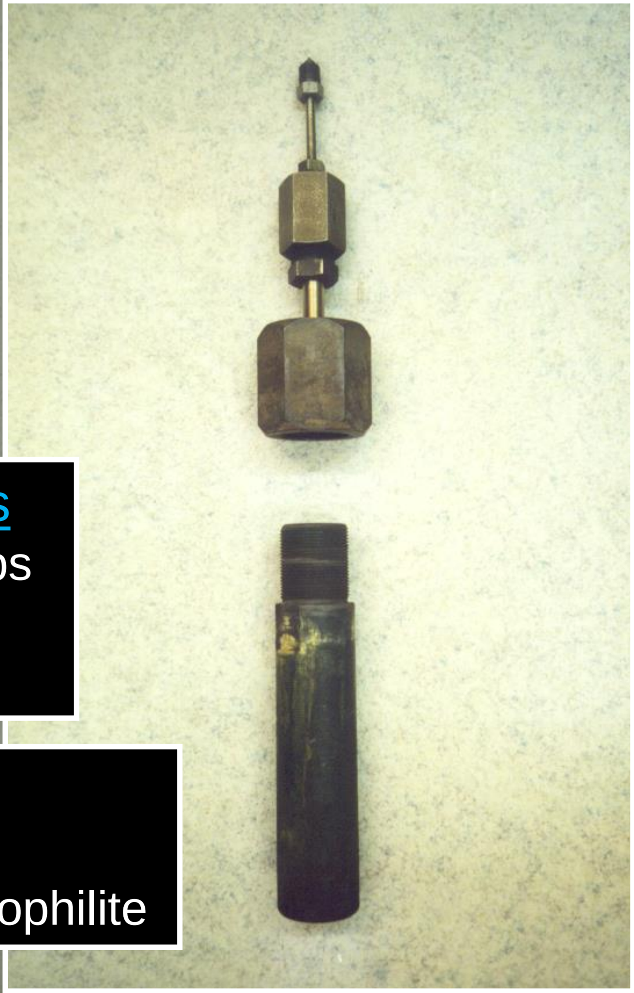
- **Solid-state experiments**
- **Asymmetric miscibility gap**
- **No P in olivine below 900°C**
- **No Si in triphylite below 500°C**

$LiMn(PO_4)$ – $Mn_2(SiO_4)$ system



Bradley *et al*. (1966)

New hydrothermal experiments



Hydrothermal experiments

- Tuttle-type cold-seal bombs
- T = 400-700°C
- P = 1 kbar

Starting material

- Mixture of chemicals
- 50 % fayalite/tephroite and 50 % triphylite/lithiophilite

Synthesized compounds

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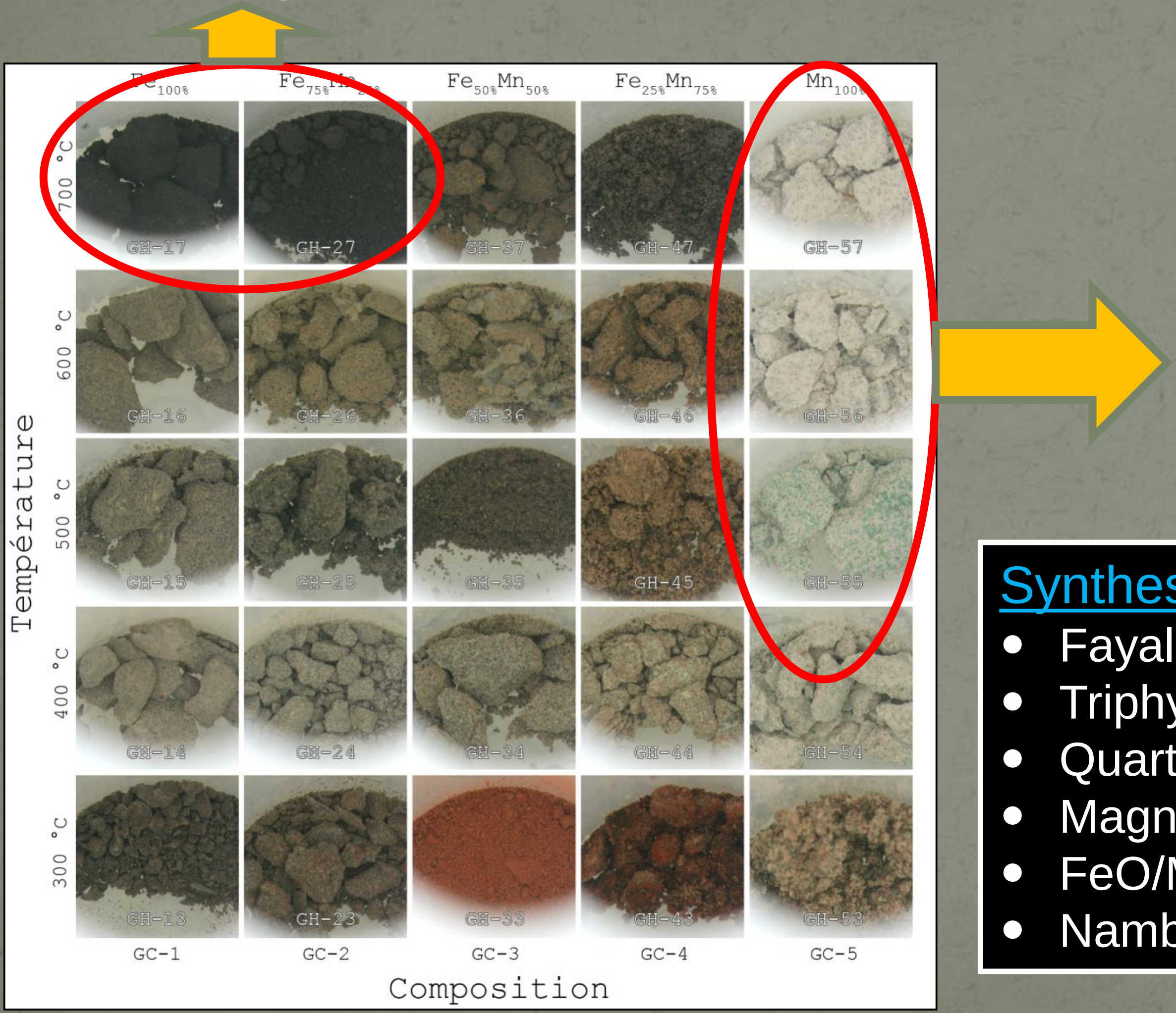
Rich in magnetite/jacobsite



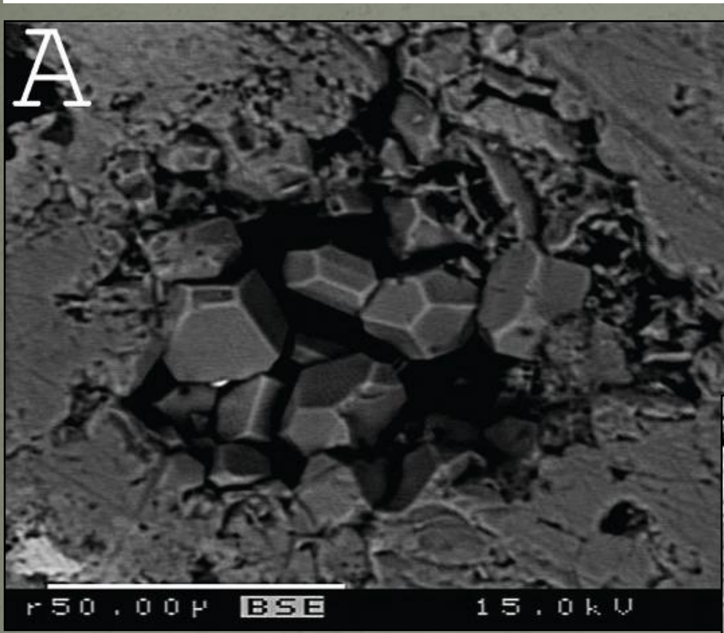
Rich in olivine-type compounds

Synthesized compounds

- Fayalite/tephroite (1-71 %)
- Triphylite/lithiophilite (17-55 %)
- Quartz (< 16 %)
- Magnetite/jacobsite (< 36 %)
- FeO/MnO (< 17 %)
- Nambulite (< 22 %)

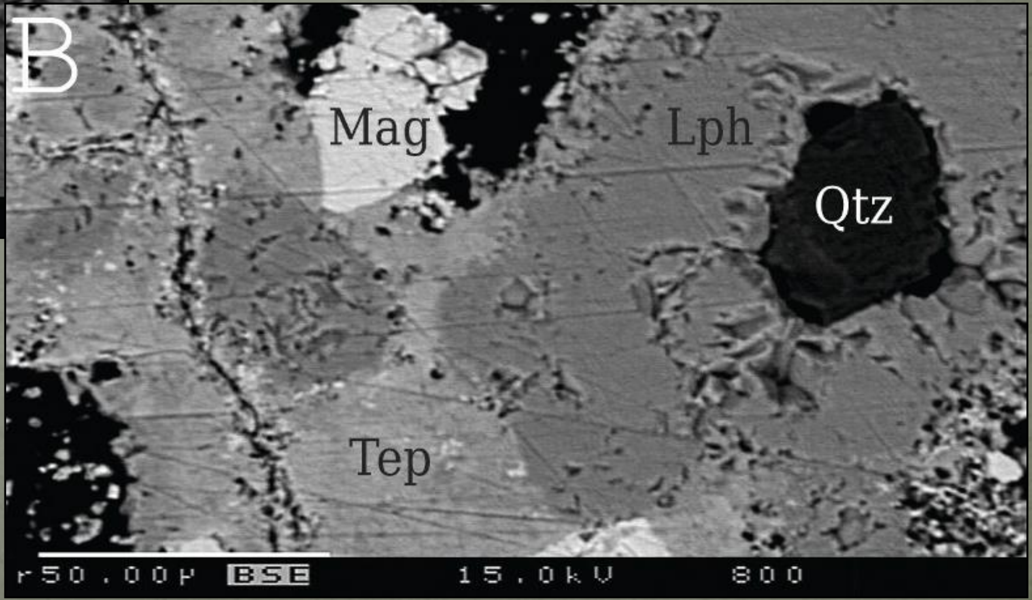
Synthesized phases

Idiomorphic lithiophilite crytals



Sample GH-37

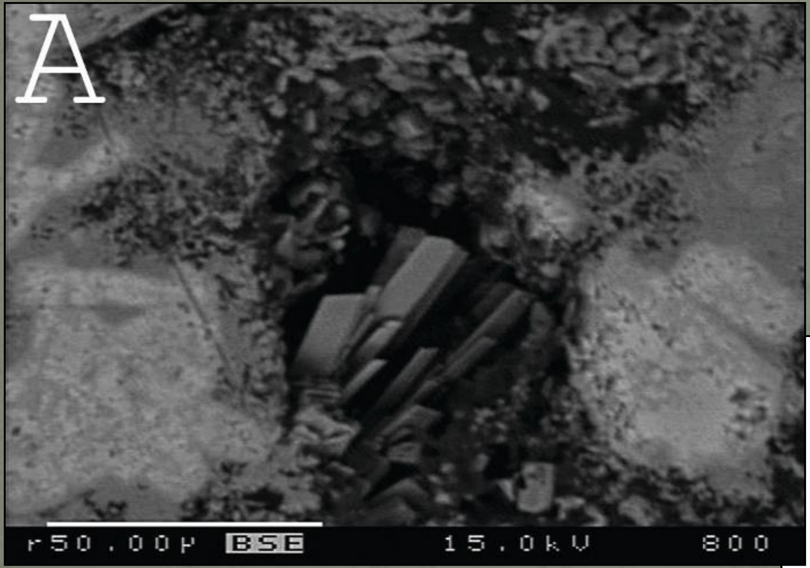
Lithiophilite + tephroite assemblage



Sample GH-37

Nambulite, $LiMn_4Si_5O_{14}(OH)$

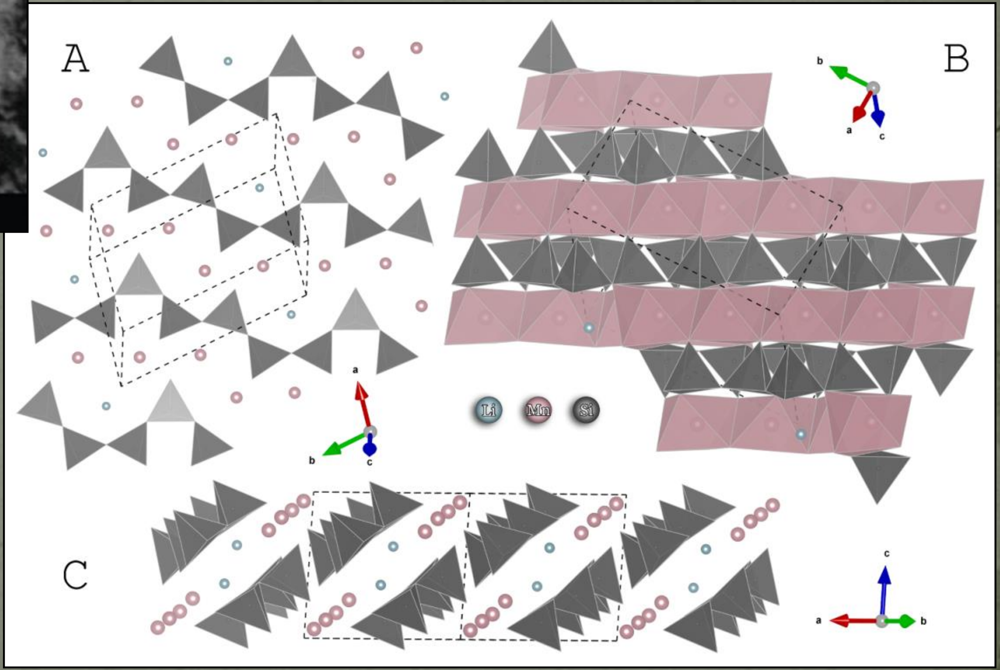
Nambulite crystals



Sample GH-54

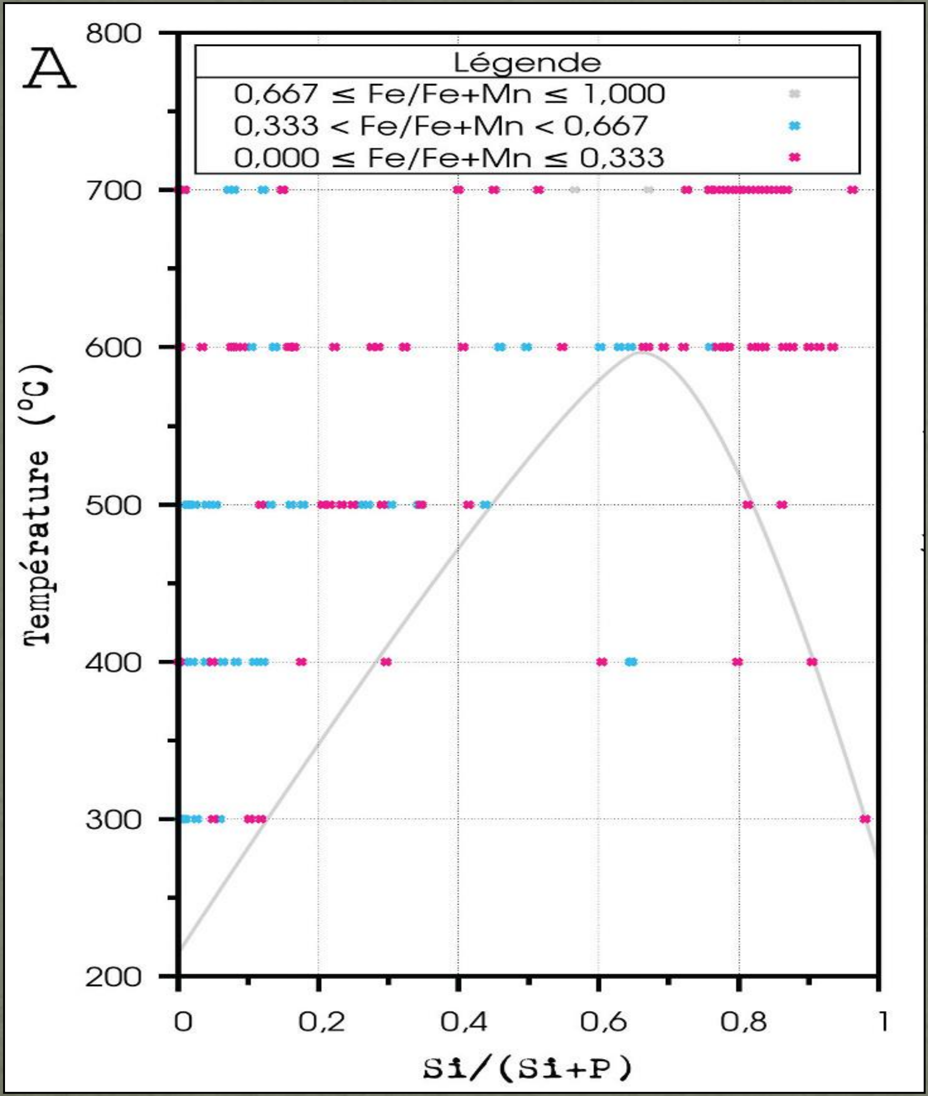
- **Alteration of rhodonite**
- **Pyroxenoid structure**
- **MnO_6 layers and SiO_4 layers**

Nambulite structure



Narita *et al*. (1975)

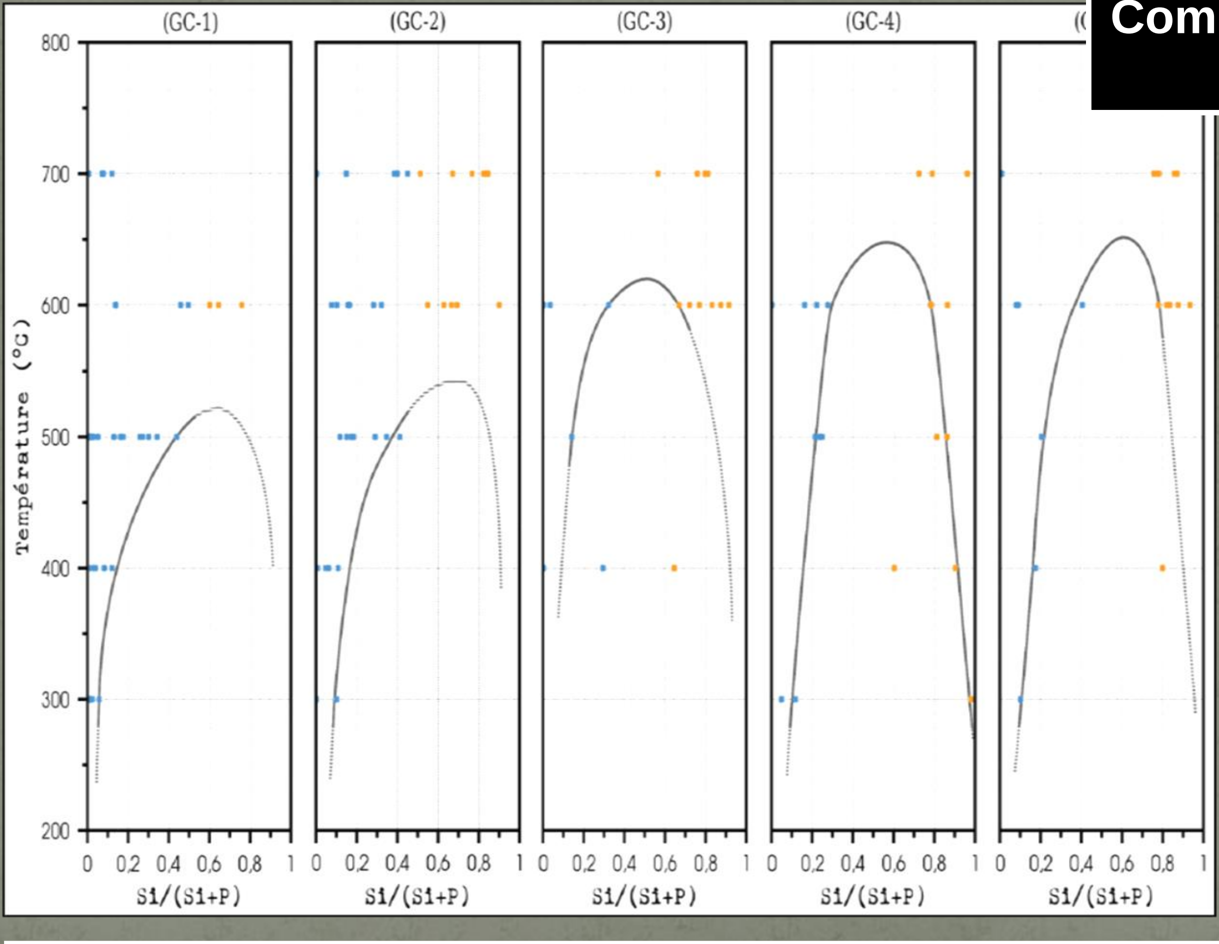
Phase diagrams



- Asymmetric miscibility gap
- No P in olivine below 300°C
- No Si in triphylite below 200°C
- Si-in-triphylite geothermometer

Phase diagrams

Complete miscibility at 550°C

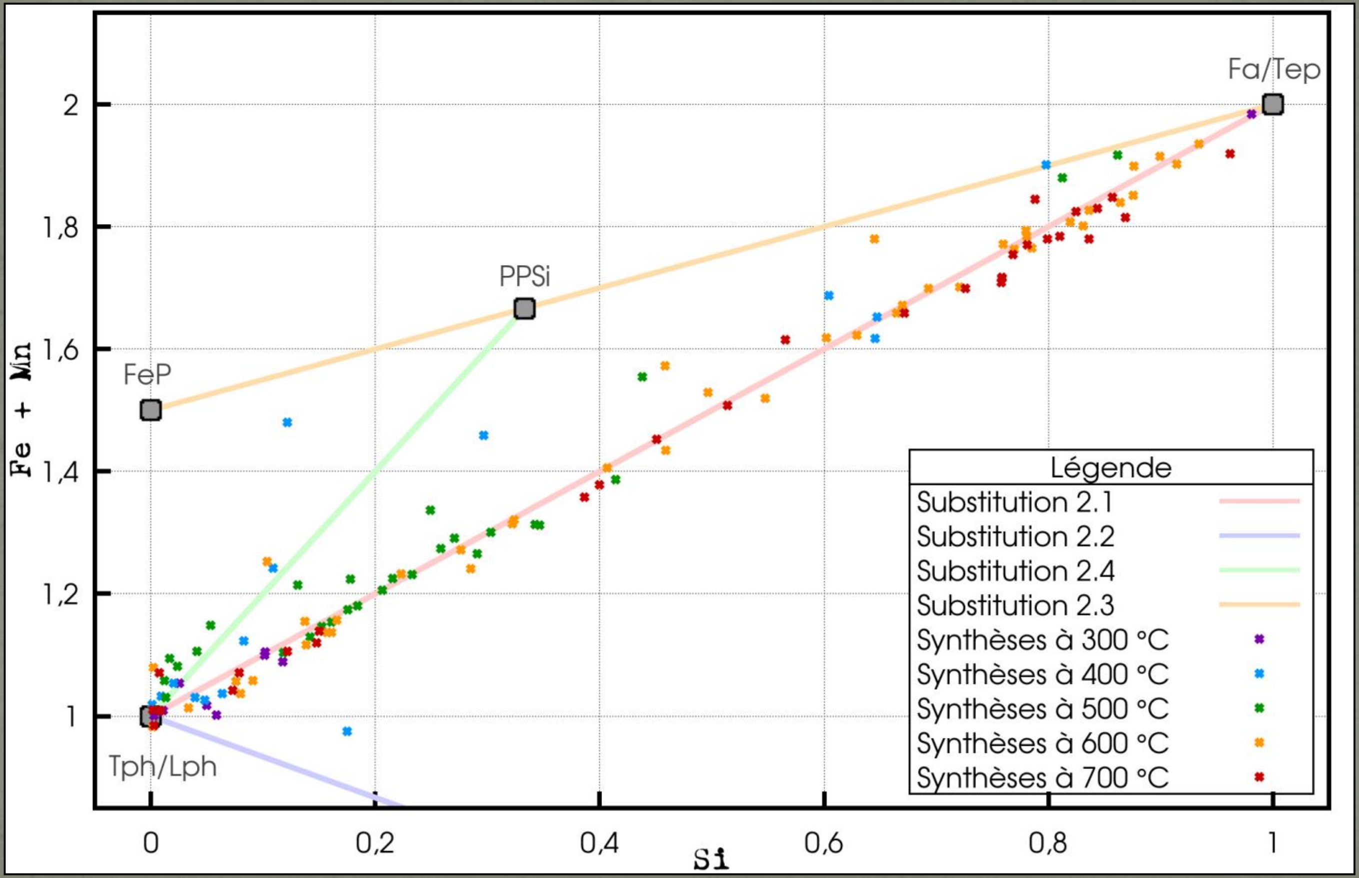


Complete miscibility at 650°C

Mn-rich → **Fe-rich**

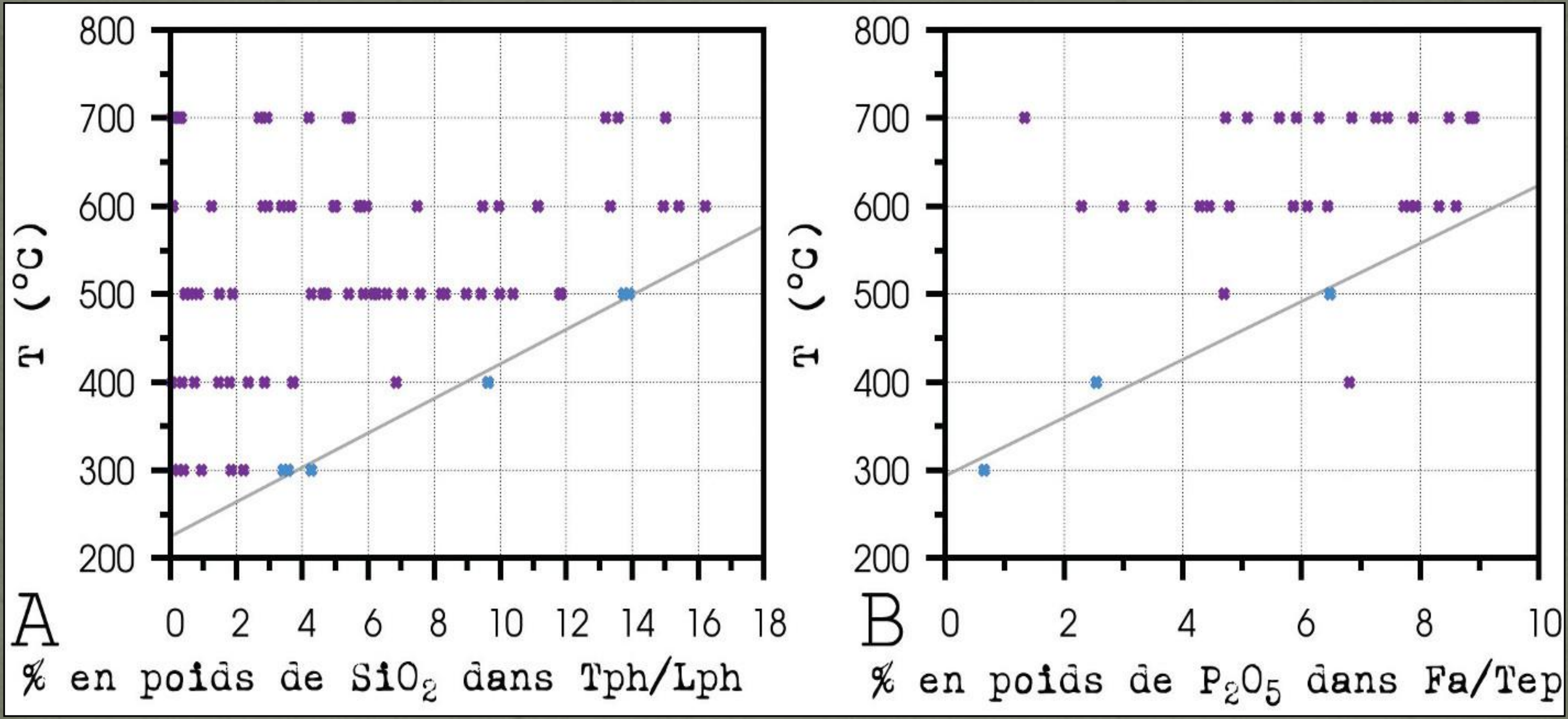
Substitution mechanism

$${}^{M1}\mathrm{Li}^{+} + {}^{T}\mathrm{P}^{5+} \Rightarrow {}^{M1}(\mathrm{Fe}^{2+},\mathrm{Mn}^{2+}) + {}^{T}\mathrm{Si}^{4+}$$



Maximal solubilities

- $T_{phosphate} = 19.6 \cdot [\text{wt. \% } SiO_2] + 224.8$
- $T_{silicate} = 33.0 \cdot [\text{wt. \% } P_2O_5] + 293.7$



Geothermometric applications

Si-bearing pegmatitic triphylites

• Brissago pegmatite, Switzerland:	0.05 to 0.13 wt. % SiO_2	218 – 236 °C
• Newport pegmatite, NH, USA:	0.33 wt. % SiO_2	223 - 240 °C
• Sapucaia pegmatite, Brazil:	0.02 to 0.77 wt. % SiO_2	217 – 249 °C
• Los Aleros pegmatite, Argentina:	0.78 wt. % SiO_2	231 – 249 °C
• Kolmozero pegmatite, Kola, Russia:	0.90 wt. % SiO_2	233 – 251 °C
• Tsaobismund pegmatite, Namibia:	0.12 to 1.0 wt. % SiO_2	219 – 254 °C

Si-bearing granitic triphylite

• Pøibyslavice, Czech Republic:	1.1 to 17 wt. % SiO_2	237 – 582 °C

Very low temperatures → Maximal solubilities are not reached

Phosphates = « closed system », not in equilibrium with silicates

⇓

Immiscibility phosphates/silicates?

Conclusions

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- The triphylite + fayalite assemblage has been obtained experimentally
- Miscibility gap below 550 (Mn-rich compositions) or 650 °C (Fe-rich compositions)
- Si-in-triphylite geothermometer gives too low temperatures, since equilibrium is not reached with enclosing silicates.

Thank you for your attention!