**Université de Liège**
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Laboratoire de Minéralogie

# Petrogenetic significance of the triphylite + sarcopside intergrowths in granitic pegmatites: an experimental investigation of the $Li(Fe,Mn)(PO_4)$-$(Fe,Mn)_3(PO_4)_2$ system

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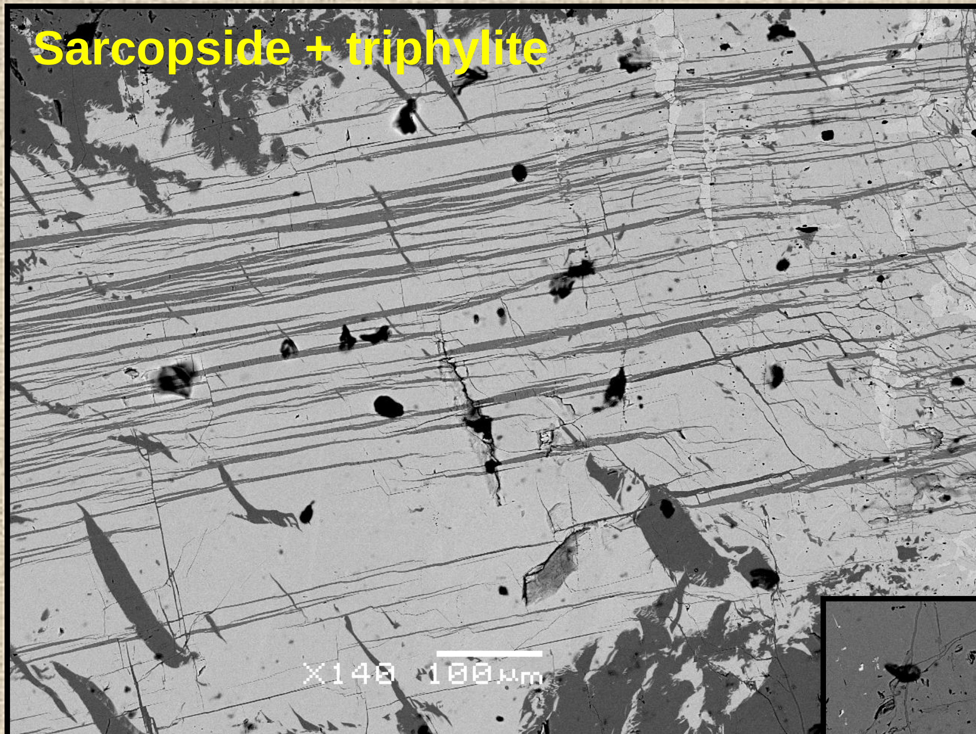
Granitic pegmatites – The State of the Art

Porto, May 7th 2007

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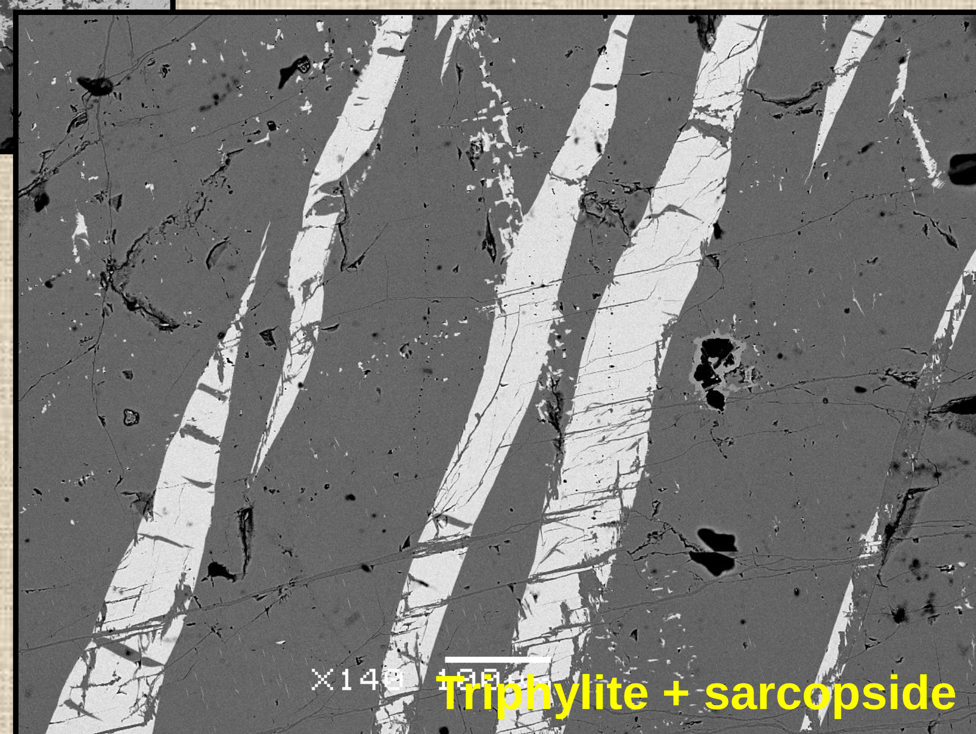
**Cañada pegmatite, Spain**

## Lamellar textures

↓

## EXSOLUTIONS??



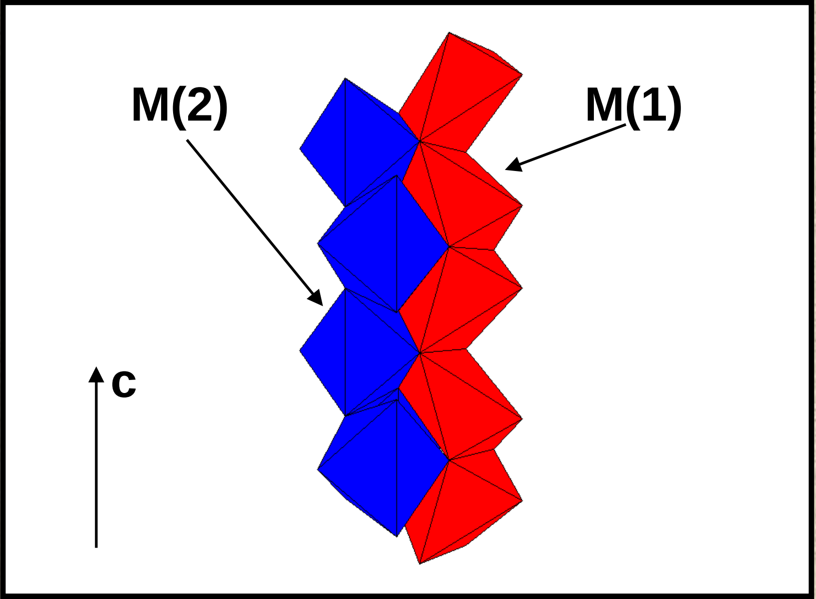
# Crystal structures

## Triphylite

$Li_4\ Fe^{2+}_4\ (PO_4)_4$

***Pnam***

***a* = 10.36, *b* = 4.71, *c* = 6.03 Å**

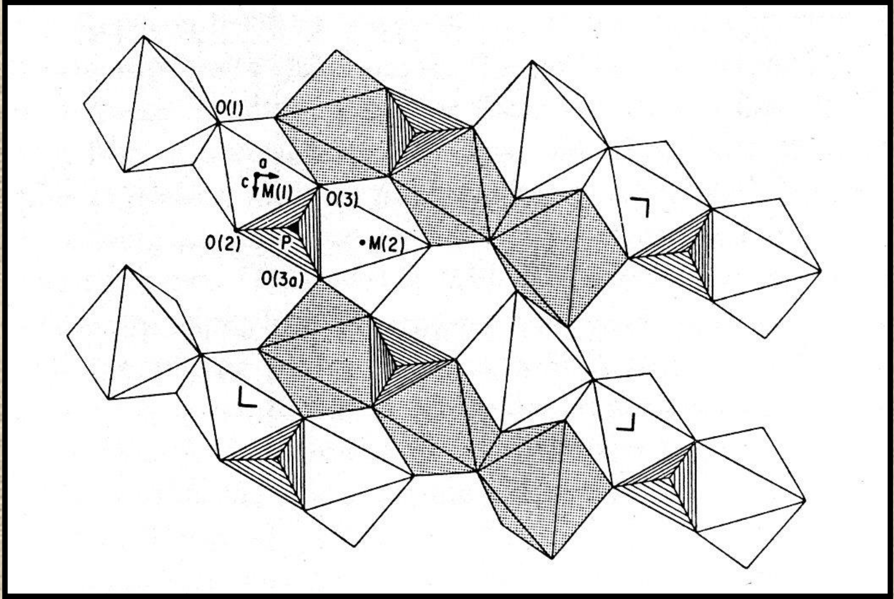



## Sarcopside

$\square_2 Fe^{2+}_2\ Fe^{2+}_4\ (PO_4)_4$

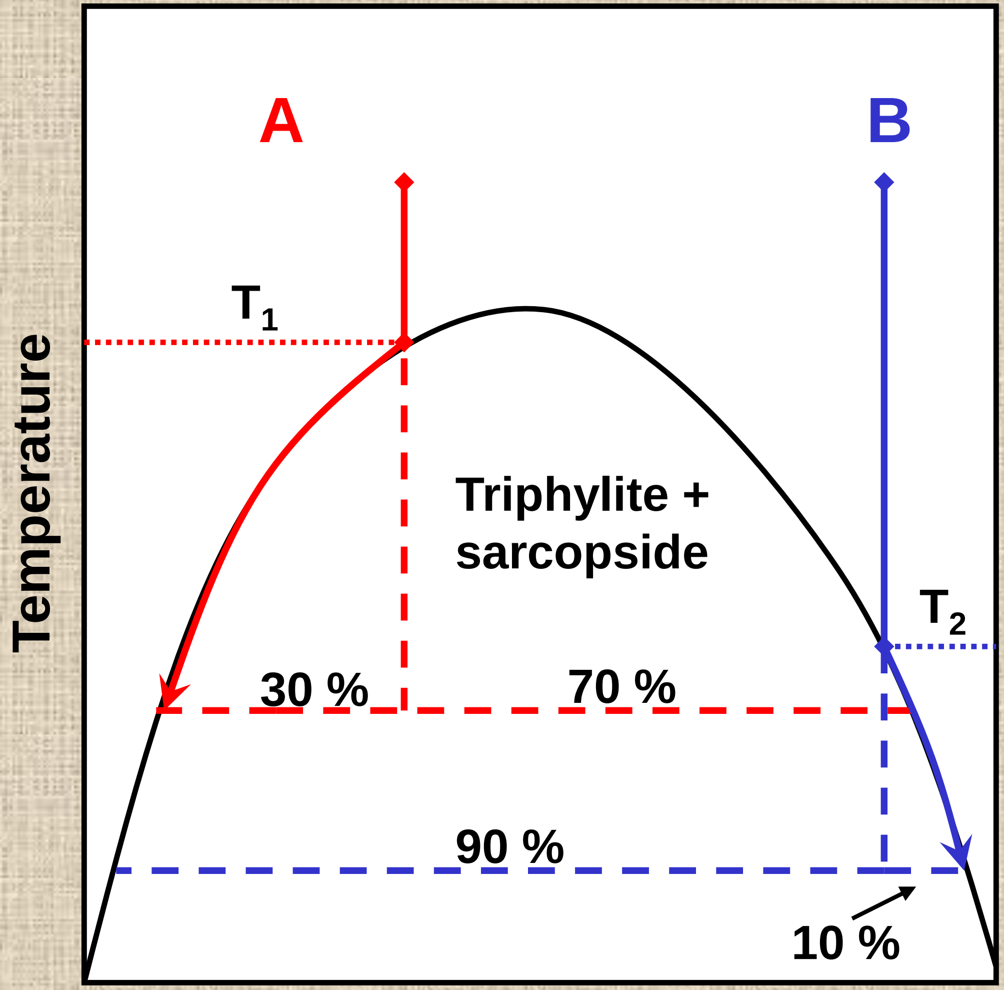
***P2₁/a***

***a* = 10.44, *b* = 4.77, *c* = 6.03 Å, *β* = 90.0 °**




Moore (1972): **«All evidence indicates that sarcopside is an exsolution product… its association with triphylite is particularily interesting since sarcopside is indisputably the exsolved phase, suggesting that triphylites at high temperature are at least partially disordered, extending our interest to the series $Li_2Fe_2(PO_4)_2$-$\square FeFe_2(PO_4)_2$. »**

# The idea…




$LiFe^{2+}(PO_4)$
Triphylite

$Fe^{2+}_3(PO_4)_2$
Sarcopside

**Starting composition A**

**70 % triphylite +**
**30 % sarcopside**
**Min. temperature $T_1$**

**Starting composition B**

**90 % sarcopside +**
**10 % triphylite**
**Min. temperature $T_2$**

# Natural assemblages

| | Cañada, Spain (SS-3) | | Tsaobismund, Namibia (8501-39) | |
|---|---|---|---|---|
| | Sarc. | Tri. | Sarc. | Tri. |
| $P_2O_5$ | 39.71 | 45.19 | 38.69 | 43.65 |
| MgO | 0.77 | 1.10 | 1.42 | 1.03 |
| MnO | 12.11 | 8.86 | 11.48 | 16.01 |
| FeO | 45.47 | 35.15 | 46.67 | 28.69 |
| $Li_2O^*$ | 0.00 | 9.51 | 0.00 | 9.19 |
| TOTAL | 98.06 | 99.81 | 98.26 | 98.57 |
| Cation numbers | | | | |
| P | 2.000 | 1.000 | 2.000 | 1.000 |
| Mg | 0.068 | 0.043 | 0.127 | 0.041 |
| Mn | 0.611 | 0.196 | 0.595 | 0.367 |
| $Fe^{2+}$ | 2.262 | 0.768 | 2.386 | 0.649 |
| Li | 0.000 | 1.000 | 0.000 | 1.000 |
| % | 35.3 | 64.7 | 15.2 | 84.8 |

* : Calculated values.

$Fe^{2+}$-dominant compositions

- **5 samples from the Cañada pegmatite (Spain)**
- **2 samples from the Tsaobismund pegmatite (Namibia)**

- **Electron microprobe analyses (Toulouse, France)**
- **Measurement of the proportions of triphylite and sarcopside**

# Hydrothermal experiments

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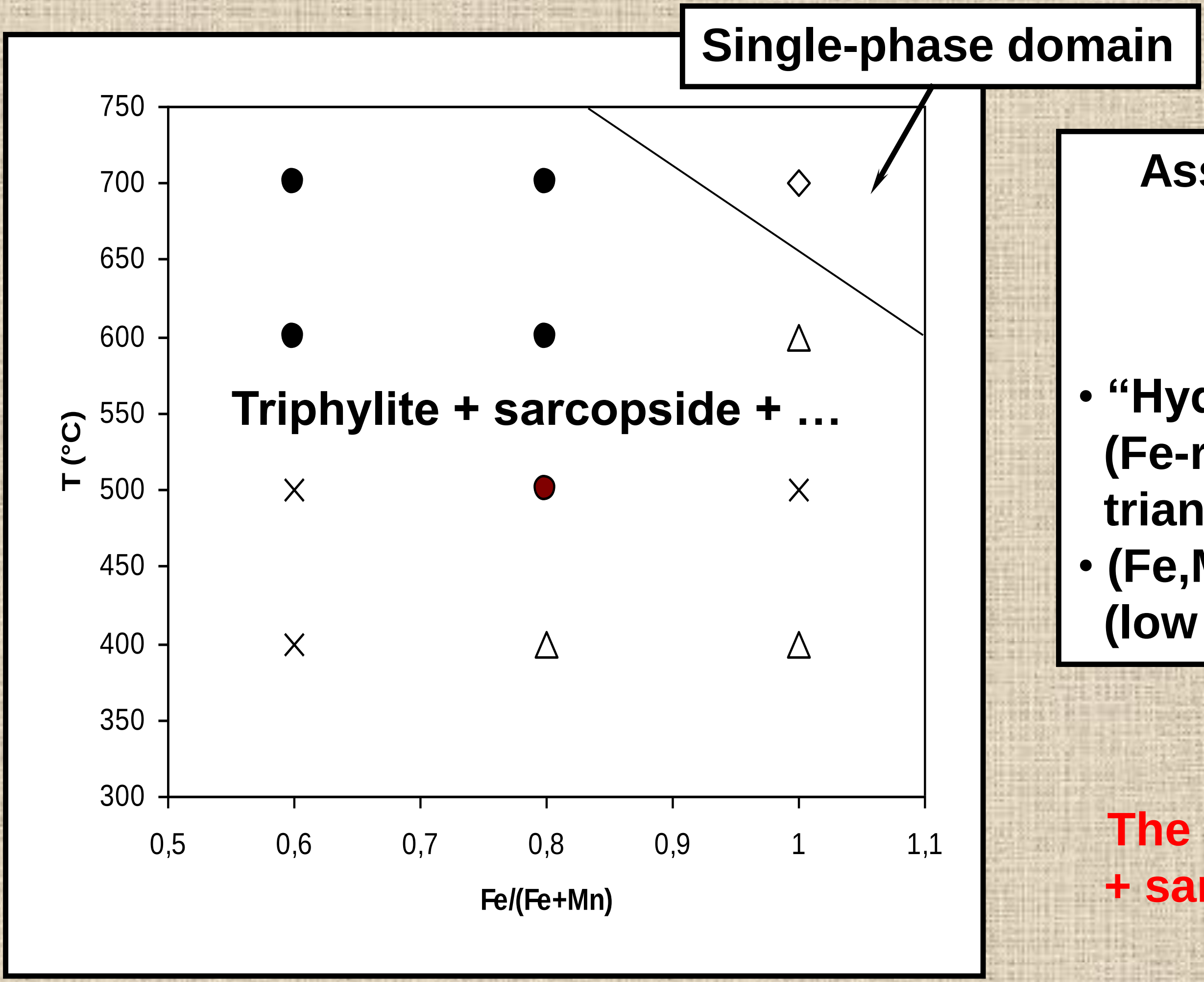
$LiFe^{2+}_{2.5}(PO_4)_2$
$LiMn_{0.50}Fe^{2+}_{2}(PO_4)_2$
$LiMnFe^{2+}_{1.5}(PO_4)_2$

- Tuttle-type cold-seal bombs
- T = 400-700 °C
- P = 1 kbar
- Gold capsules, 2 mm diameter

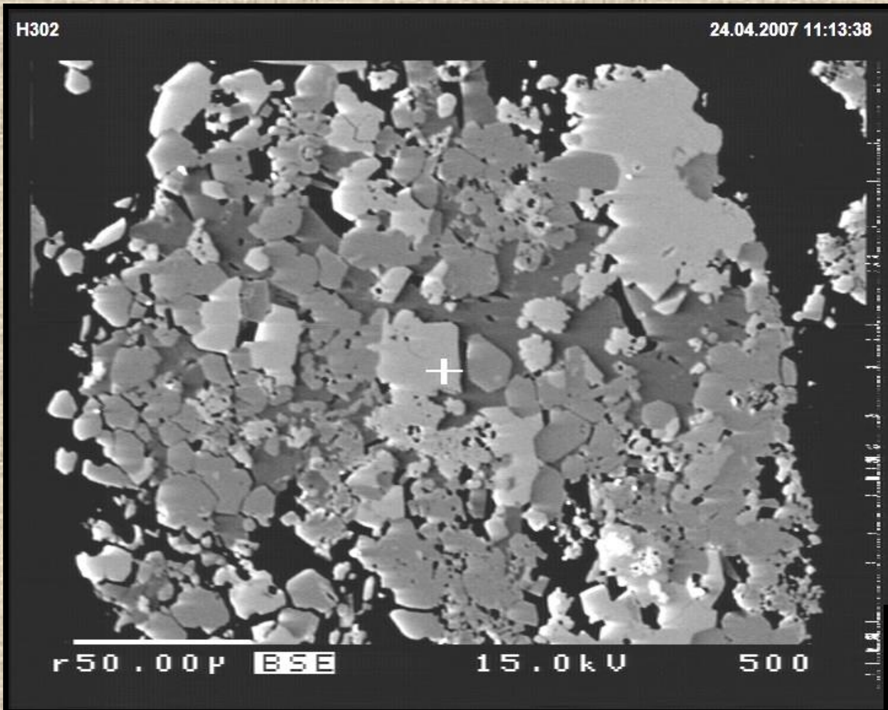
# Stability of the triphylite + sarcopside assemblage




**Associated phosphates**

- **“Hydrated sarcopside” (Fe-rich compositions, triangles)**
- **$(Fe,Mn)_2P_2O_7$ (low temperature, crosses)**

**The assemblage triphylite + sarcopside is of primary origin**

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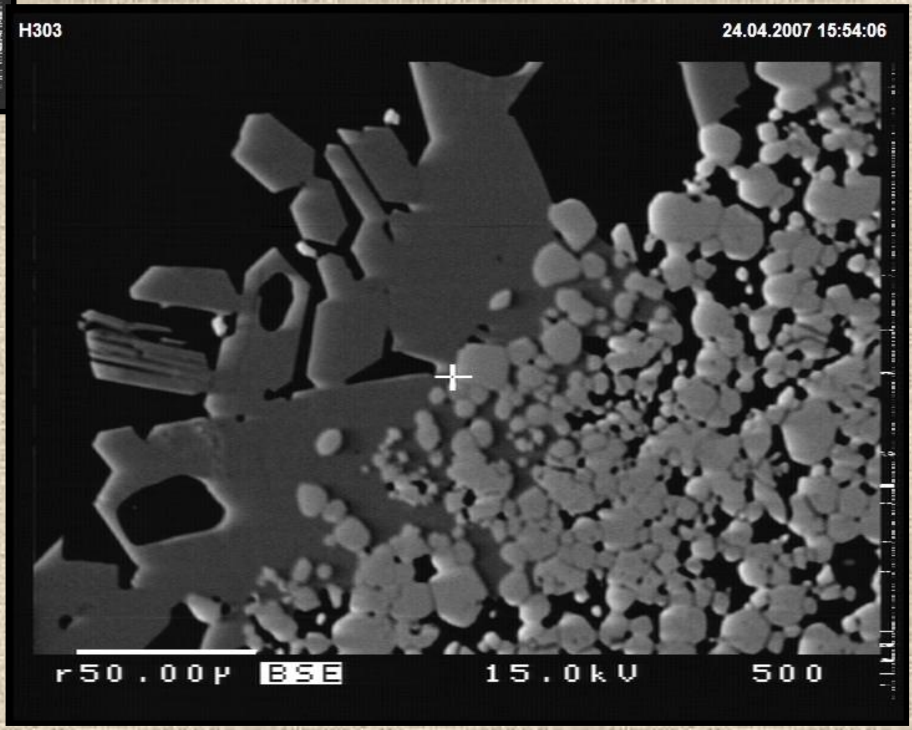
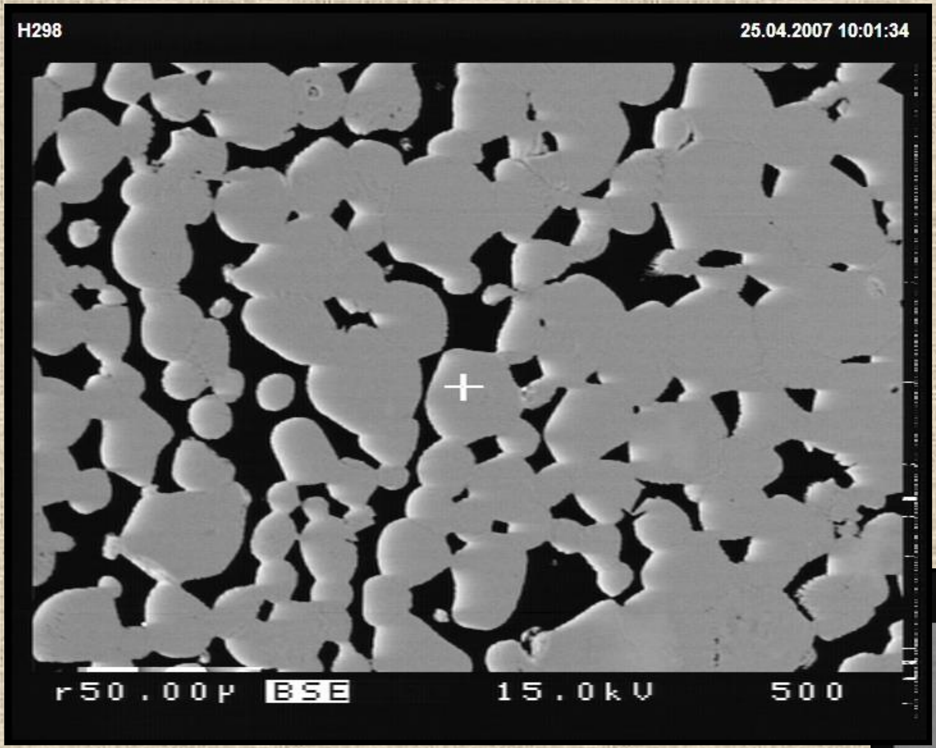
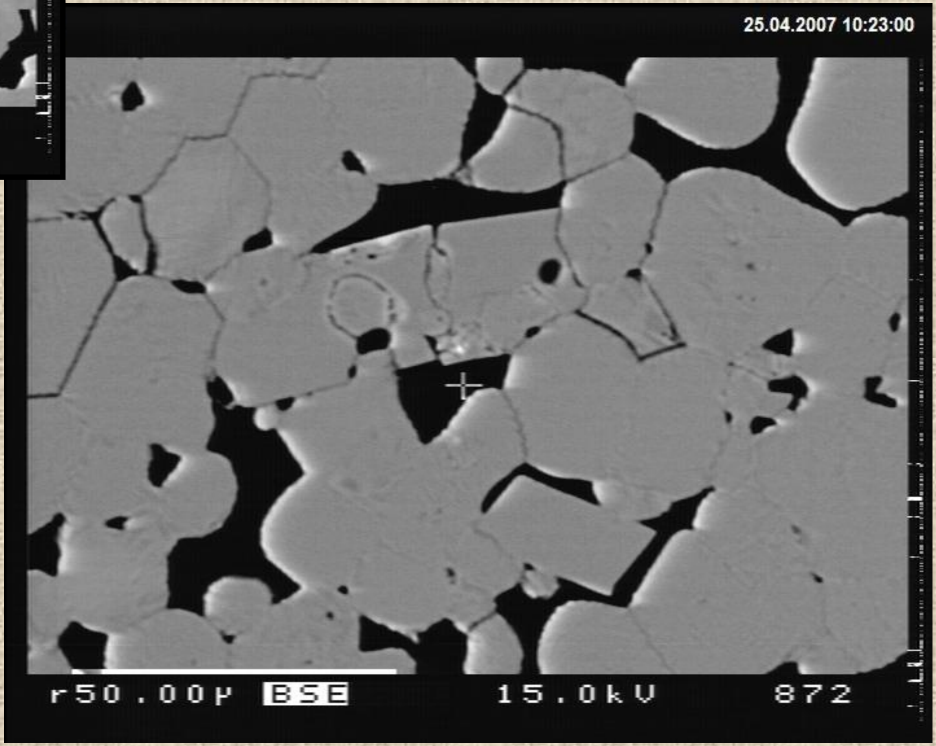
400°C

Triphylite + sarcopside + « hydrated sarcopside »






One homogeneous phase with the starting composition




Rare crystals of $Fe_2P_2O_7$

700°C

$LiFe^{2+}_{2.5}(PO_4)_2$

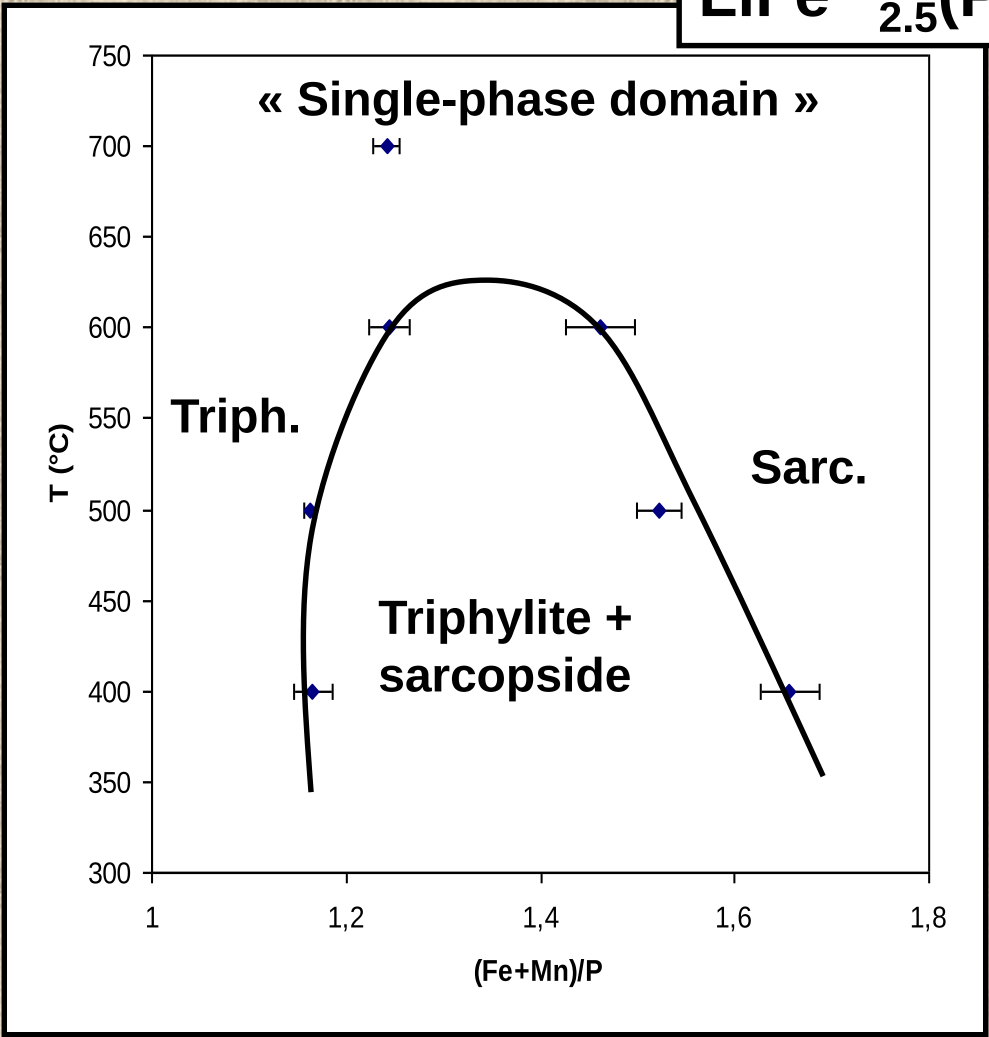
# Microprobe analyses of synthetic phosphates

| | 400°C | | 500°C | | 600°C | | 700°C | |
|---|---|---|---|---|---|---|---|---|
| | Tri. | Sarc. | Tri. | Sarc. | Tri. | Sarc. | Tri. | Sarc. |
| | (Fe+Mn)/P | (Fe+Mn)/P | (Fe+Mn)/P | (Fe+Mn)/P | (Fe+Mn)/P | (Fe+Mn)/P | (Fe+Mn)/P | (Fe+Mn)/P |
| $LiFe^{2+}_{2.5}(PO_4)_2$ | 1.17 | 1.66 | 1.16 | 1.52 | 1.24 | 1.46 | 1.24 | |
| $LiMn_{0.5}Fe^{2+}_2(PO_4)_2$ | 1.01 | 1.46 | 1.18 | 1.60 | 1.19 | 1.43 | 1.33 | 1.60 |
| $LiMnFe^{2+}_{1.5}(PO_4)_2$ | 1.01 | 1.49 | 1.07 | 1.48 | 1.14 | 1.49 | 1.27 | 1.64 |

The (Fe+Mn)/P ratio of triphylite increases with temperature

# Triphylite-sarcopside phase diagrams

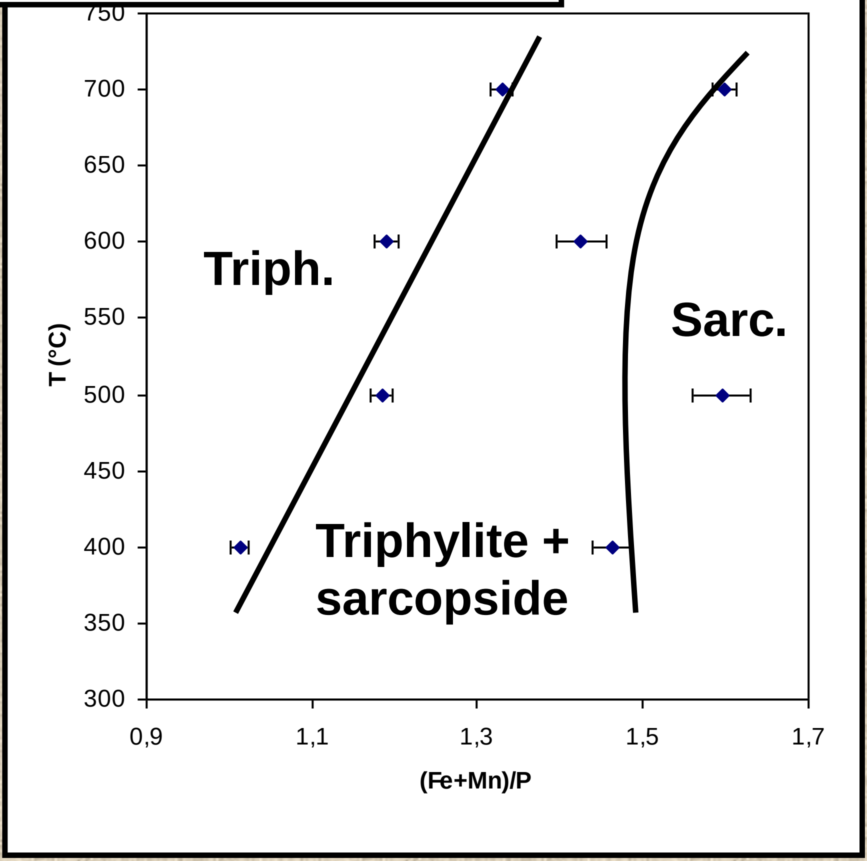
$LiFe^{2+}_{2.5}(PO_4)_2$



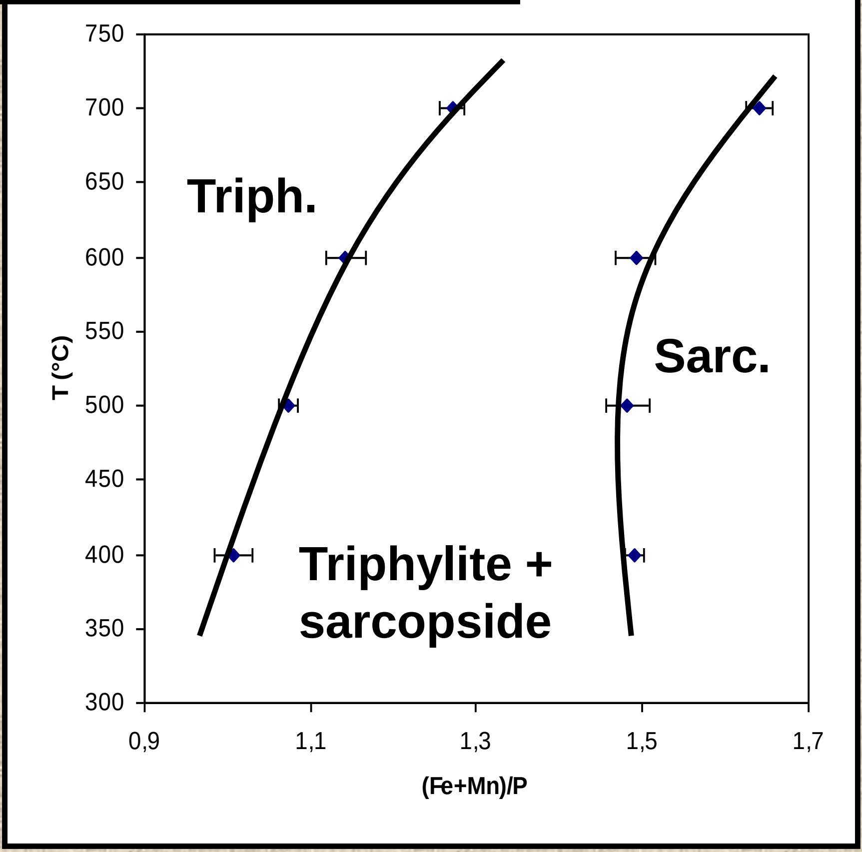

- **When the temperature increases, the Fe-content of triphylite and the Li-content of sarcopside increase.**
- **Above ca. 650°C exists a "single-phase domain"**

# Triphylite-sarcopside phase diagrams

**$LiMn_{0.5}Fe^{2+}_{2}(PO_4)_2$**




**$LiMnFe^{2+}_{1.5}(PO_4)_2$**




**The (Fe,Mn)-content of triphylite increases with temperature, but the (Fe,Mn)-content of sarcopside too → solid solution with wolfeite, $Fe^{2+}_{2}(PO_4)(OH)$??**

# Variations of Li-content and (Fe+Mn)/P ratio in synthetic triphylites

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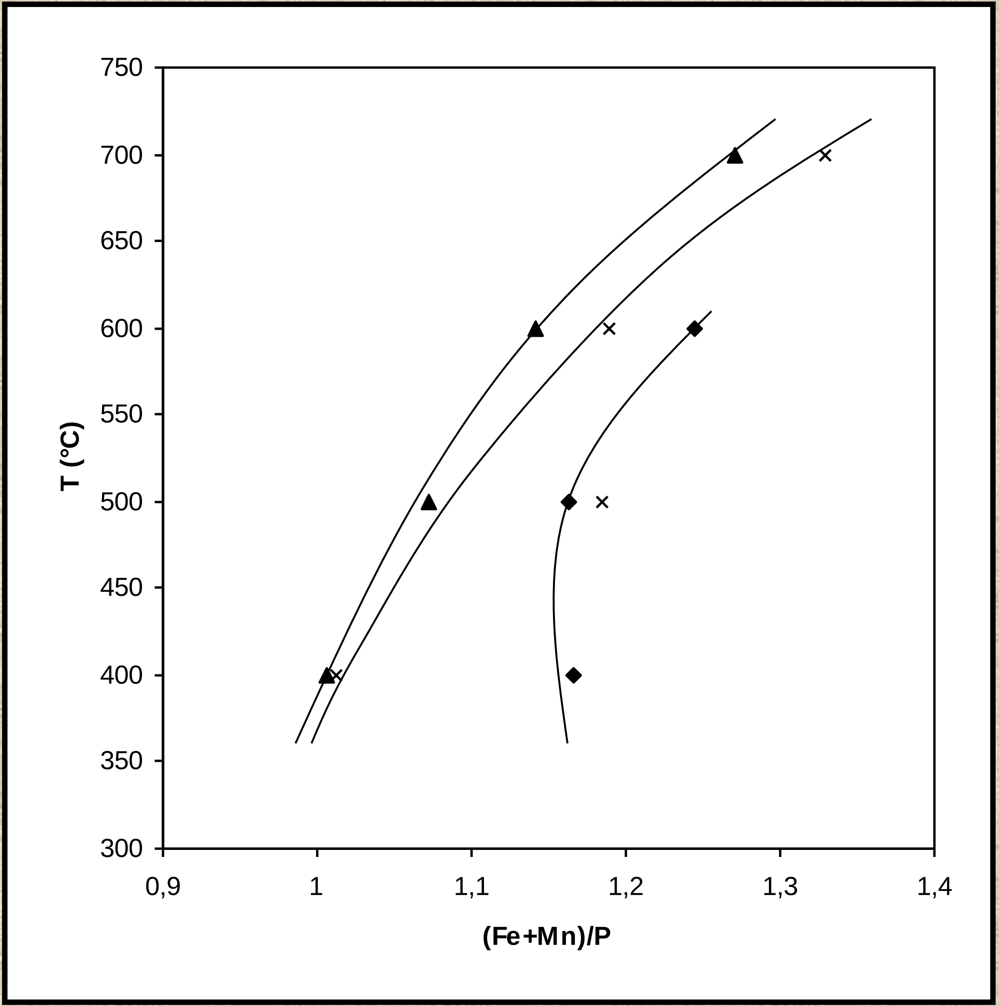
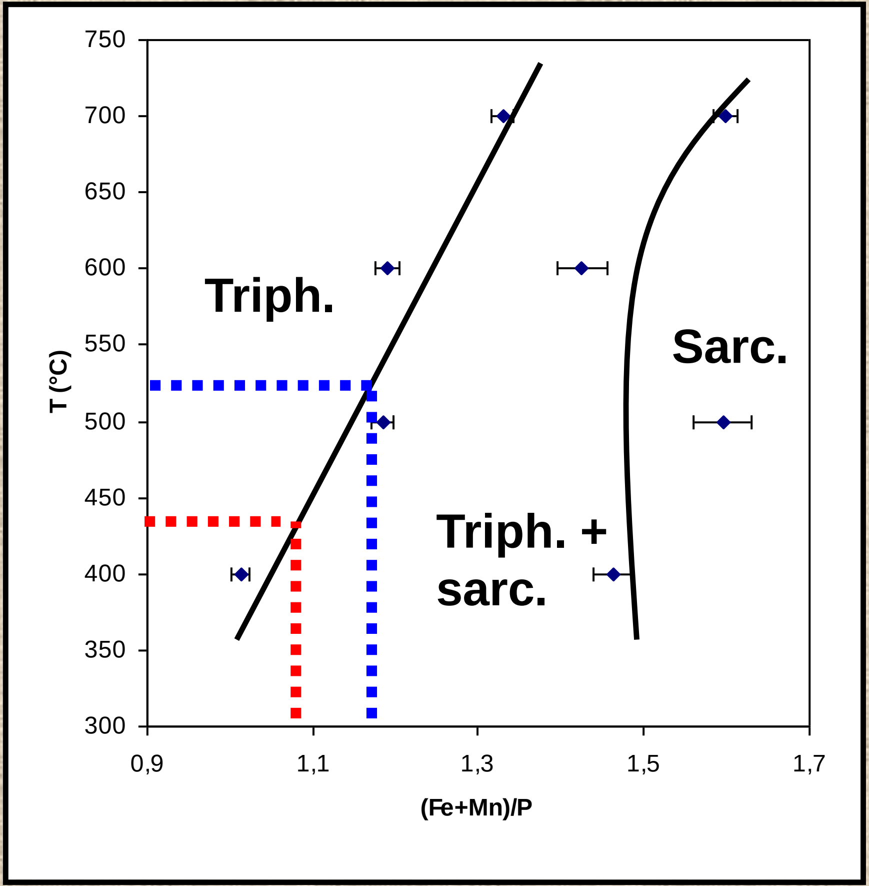



- (Fe,Mn)-content increases with temperature, and Li-content decreases

- When T is constant, (Fe,Mn)/P is higher for the Fe-rich compositions

# Calculation of temperatures for natural assemblages




**Fe/(Fe+Mn) ratios of natural triphylites and sarcopsides close to 0.800 (electron microprobe)**

**Phase diagram for $LiMn_{0.5}Fe^{2+}_2(PO_4)_3$**

**Cañada**

**35 % sarcopside → (Fe+Mn)/P = 1.18**

**T = 500-550°C**

**Tsoabismund**

**15 % sarcopside → (Fe+Mn)/P = 1.08**

**T = 400-450°C**

# Conclusions

- The triphylite+ sarcopside primary assemblage has been reproduced experimentally between 400 and 700°C, and is sometimes associated with minor « hydrated sarcopside » or $(Fe,Mn)_2P_2O_7$.
- For the Mn-free system, a « single-phase domain » has been observed above ca. 650°C. The behavior of the sarcopside field in the Mn-bearing systems is significantly different, with an increase of the (Fe+Mn)/P ratio.
- The experimental phase diagrams can be used to obtain accurate temperature data, starting from the proportions of triphylite and sarcopside in the natural assemblages.