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Crystal chemistry of lithium in pegmatite phosphates: a SIMS investigation of natural and synthetic samples

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The role of lithium in pegmatites

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Two petrogenetic families of pegmatites: LCT and NYF

LCT = Lithium-Cesium-Tantalum

Primary lithium-bearing minerals:

- **Spodumene [$LiAlSi_2O_6$]**
- **Petalite [$LiAlSi_4O_{10}$]**
- **Lepidolite [$K(Li,Al)_3(Si,Al)_4O_{10}(F,OH)_2$]**
- **Elbaite [$Na(Al,Li)_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$]**
- **Amblygonite-montebrasite [$LiAlPO_4F$ – $LiAlPO_4(OH)$]**
- **Triphylite-lithiphilite [$LiFePO_4$ – $LiMnPO_4$]**

Experimental: SIMS analyses

- **Instrument**: Cameca IMS 4f ion microprobe
- **Analyst**: Dr. Luisa Ottolini, CNR-IGG Pavia, Italy
- **Primary-ion beam**: 12.5 kV accelerated O^{2-}
- **Current intensity**: 0.8-4 nA
- **Beam diameter**: 3-6 µm
- **Pt-coated sample**: thickness 400 Å
- **Secondary-ion signals from**: $^{6}Li^{+}$, $^{31}P^{+}$, $^{57}Fe^{+}$
- **Acquisition time**: 3 seconds (Li, P) and 6 seconds (Fe)
- **Standard**: triphylite from the Buranga pegmatite (9.96 wt. % Li_2O; wet chemical analysis by Héreng, 1989)

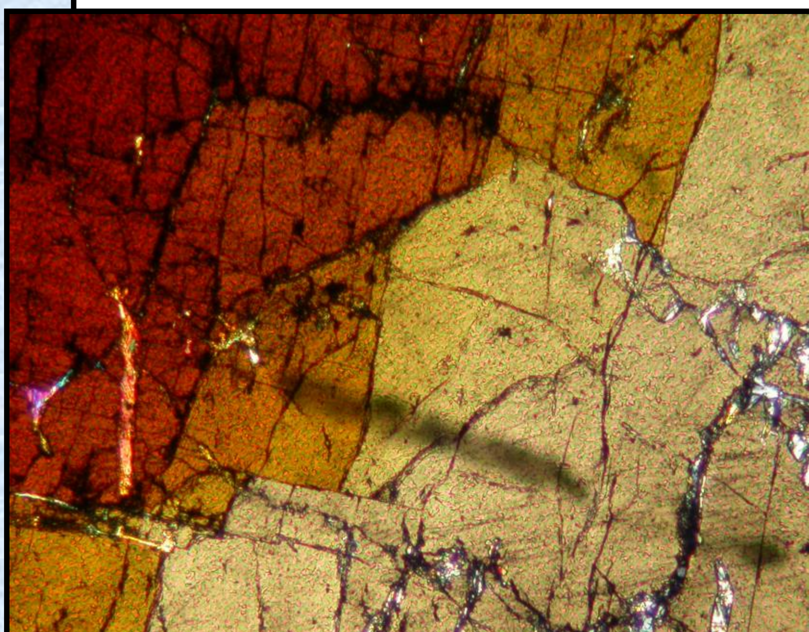
Phosphates with the olivine structure: the « Quensel-Mason » sequence

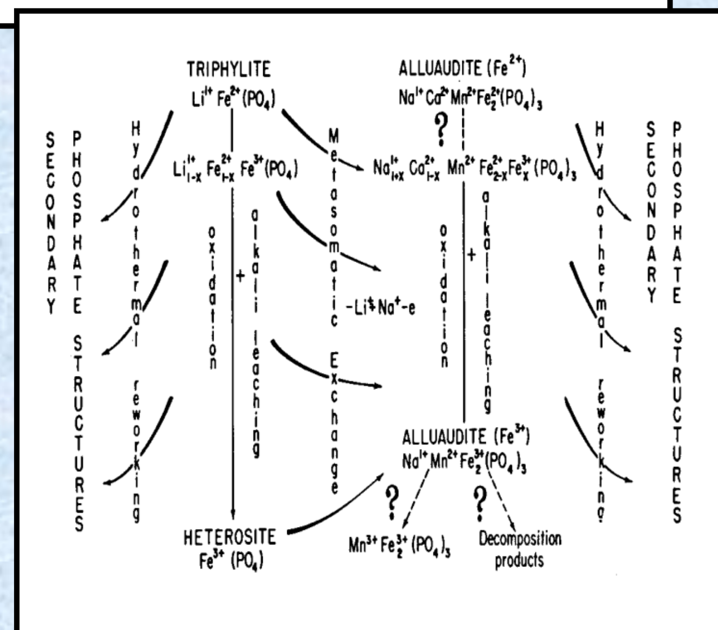
$Li(Mn^{2+},Fe^{2+})PO_4 \Rightarrow \square_x Li_{1-x}(Mn^{2+},Fe^{3+})PO_4 \Rightarrow \square(Mn^{3+},Fe^{3+})PO_4$

(Lithiophilite) (Sicklerite) (Purpurite)

$Li(Fe^{2+},Mn^{2+})PO_4 \Rightarrow \square_x Li_{1-x}(Fe^{3+},Mn^{2+})PO_4 \Rightarrow \square(Fe^{3+},Mn^{3+})PO_4$

(Triphylite) (Ferrisicklerite) (Heterosite)





Analyses of natural olivine-type phosphates

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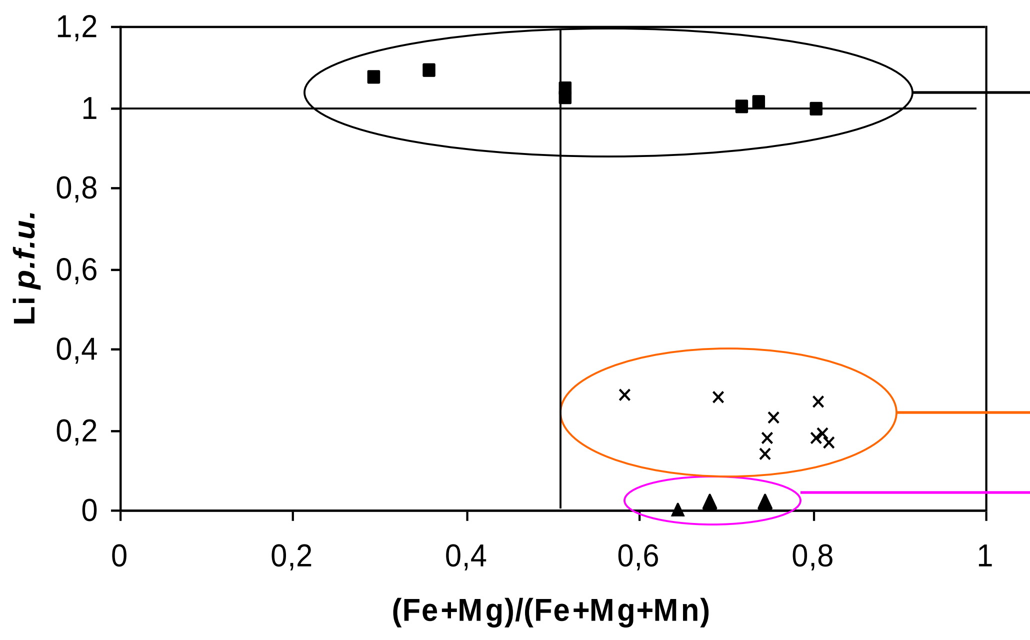
19 samples from several pegmatites in Namibia, Spain, Portugal, Germany



Triphylite-lithiophilite
0.99-1.07 Li *p.f.u.*

Ferrisicklerite
0.14-0.29 Li *p.f.u.*

Heterosite
0.00-0.02 Li *p.f.u.*

Heterosite may contain up to 0.21 wt. % Li_2O, and ferrisicklerite may show a low Li-content of 1.31 wt. % Li_2O

Close Li-contents!

Which difference between heterosite and ferrisicklerite?

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Triphylite-lithiophilite: $M^{2+}/(M^{2+}+M^{3+})$ = 0.93-1.00
Ferrisicklerite: $M^{2+}/(M^{2+}+M^{3+})$ = 0.14-0.38
Heterosite: $M^{2+}/(M^{2+}+M^{3+})$ = 0.02-0.06

→ **Significant amount of divalent cations in ferrisicklerite, and low Mn^{2+}-content in heterosite**

↓

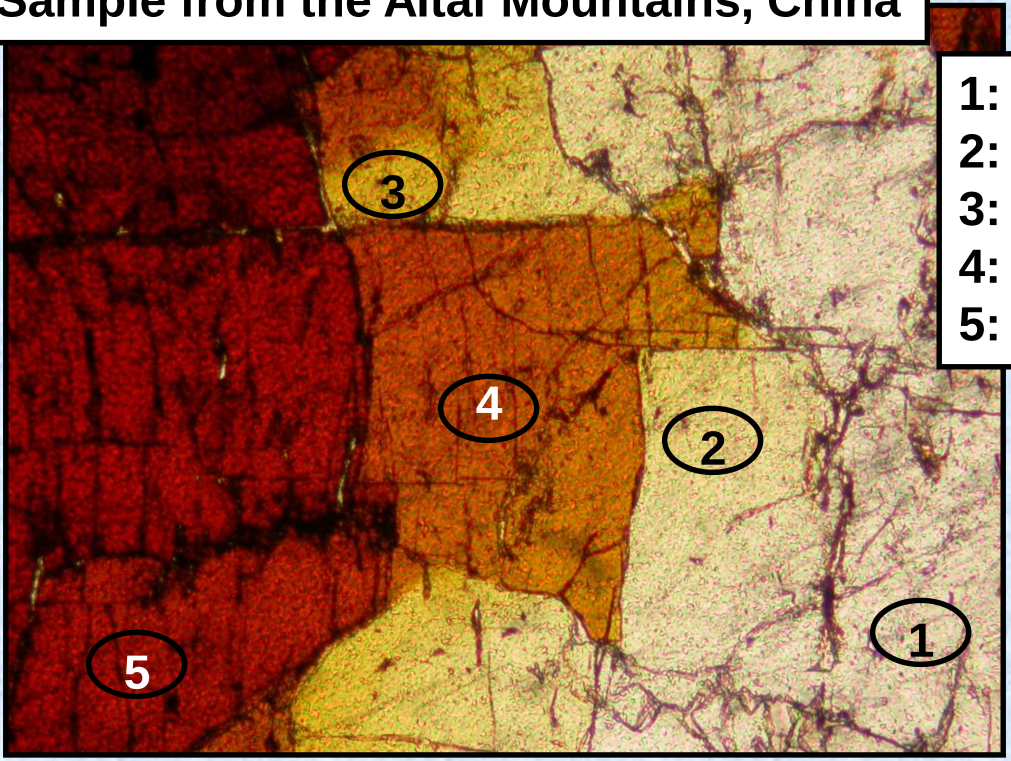
Different optical properties, due to Mn^{3+}???

BUT

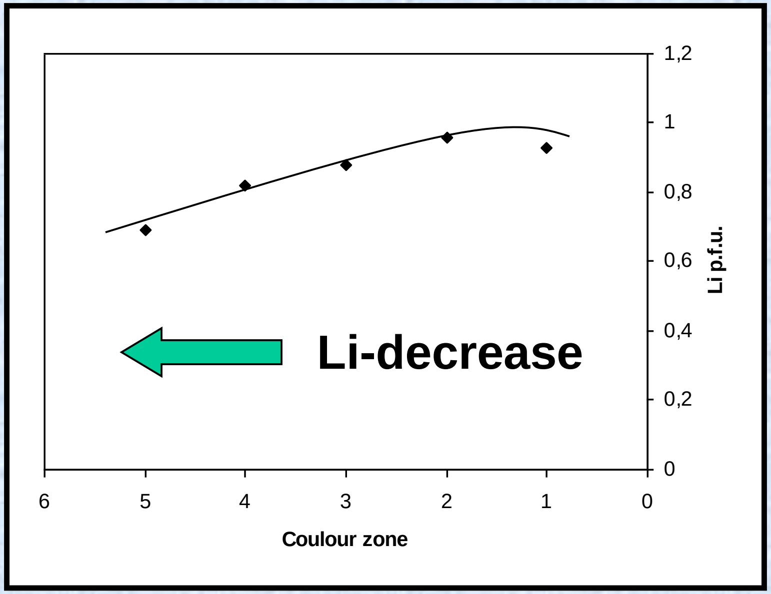
- **Triphylites-lithiophilites generally contain significant amounts of Fe^{3+} (up to 3.52 wt. % Fe_2O_3)**
- **Ferrisicklerites generally contain significant amounts of Mn^{3+} (up to 10.24 wt. % Mn_2O_3)**
- **Heterosite still contain significant amounts of Mn^{2+} (up to 2.12 wt. % MnO)**

The progressive transition from lithiophilite to sicklerite

Sample from the Altaï Mountains, China

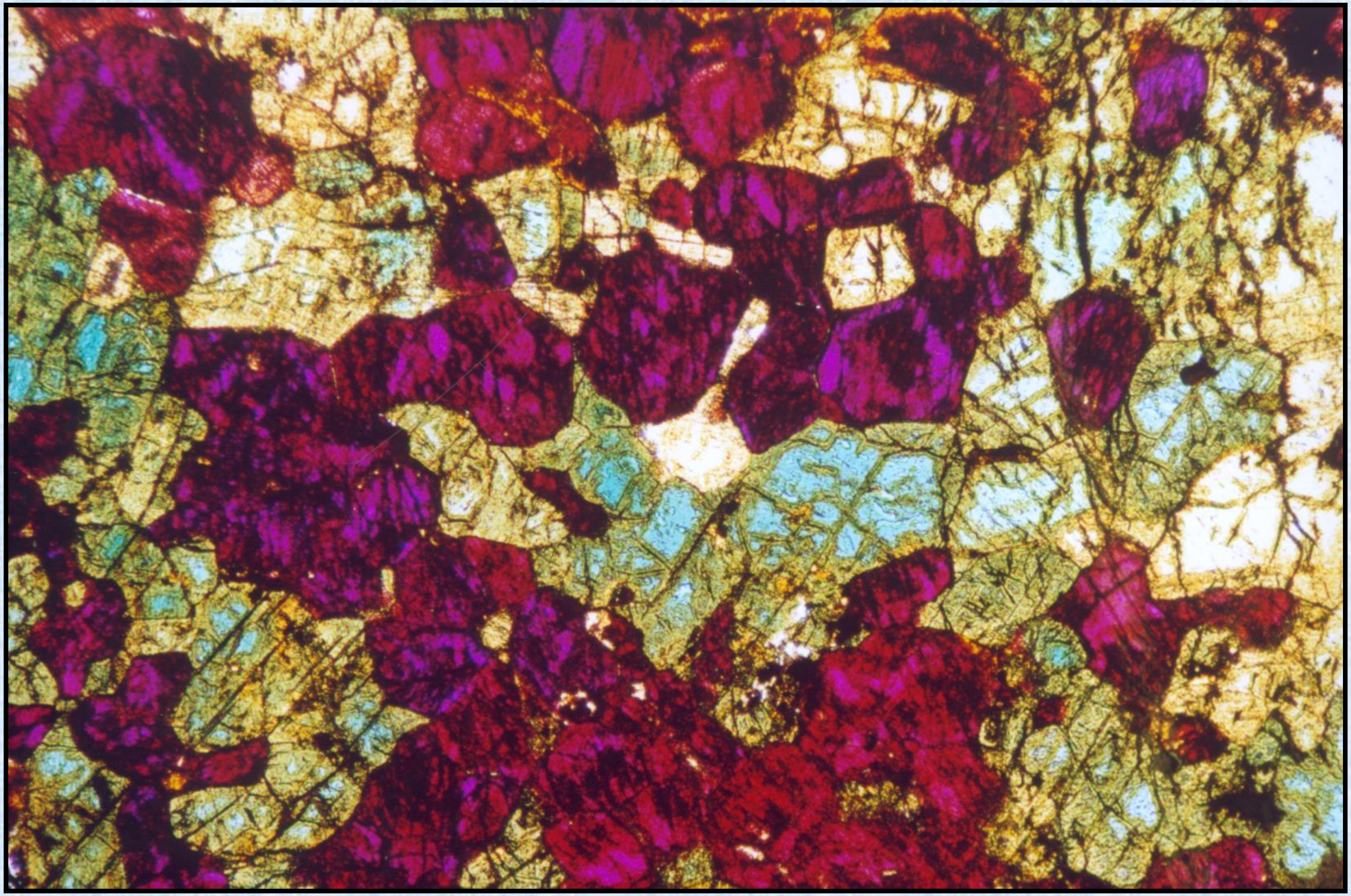


1: $Li_{0.93}(Fe^{2+}_{0.03}Fe^{3+}_{0.13}Mn^{2+}_{0.80})(PO_4)$
2: $Li_{0.96}(Fe^{2+}_{0.08}Fe^{3+}_{0.08}Mn^{2+}_{0.81})(PO_4)$
3: $Li_{0.88}(Fe^{3+}_{0.16}Mn^{2+}_{0.80}Mn^{3+}_{0.01})(PO_4)$
4: $Li_{0.82}(Fe^{3+}_{0.16}Mn^{2+}_{0.75}Mn^{3+}_{0.06})(PO_4)$
5: $Li_{0.69}(Fe^{3+}_{0.16}Mn^{2+}_{0.62}Mn^{3+}_{0.19})(PO_4)$



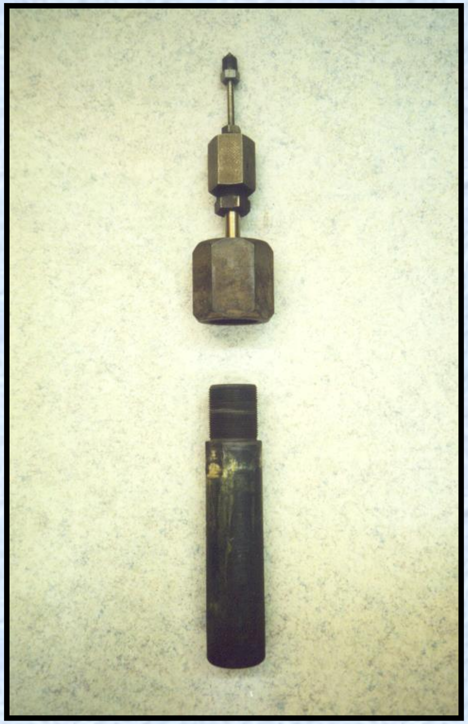
- The transition from lithiophilite to sicklerite is progressive
- The change in colour is due to the presence of Mn^{3+}

The triphylite + alluaudite assemblage



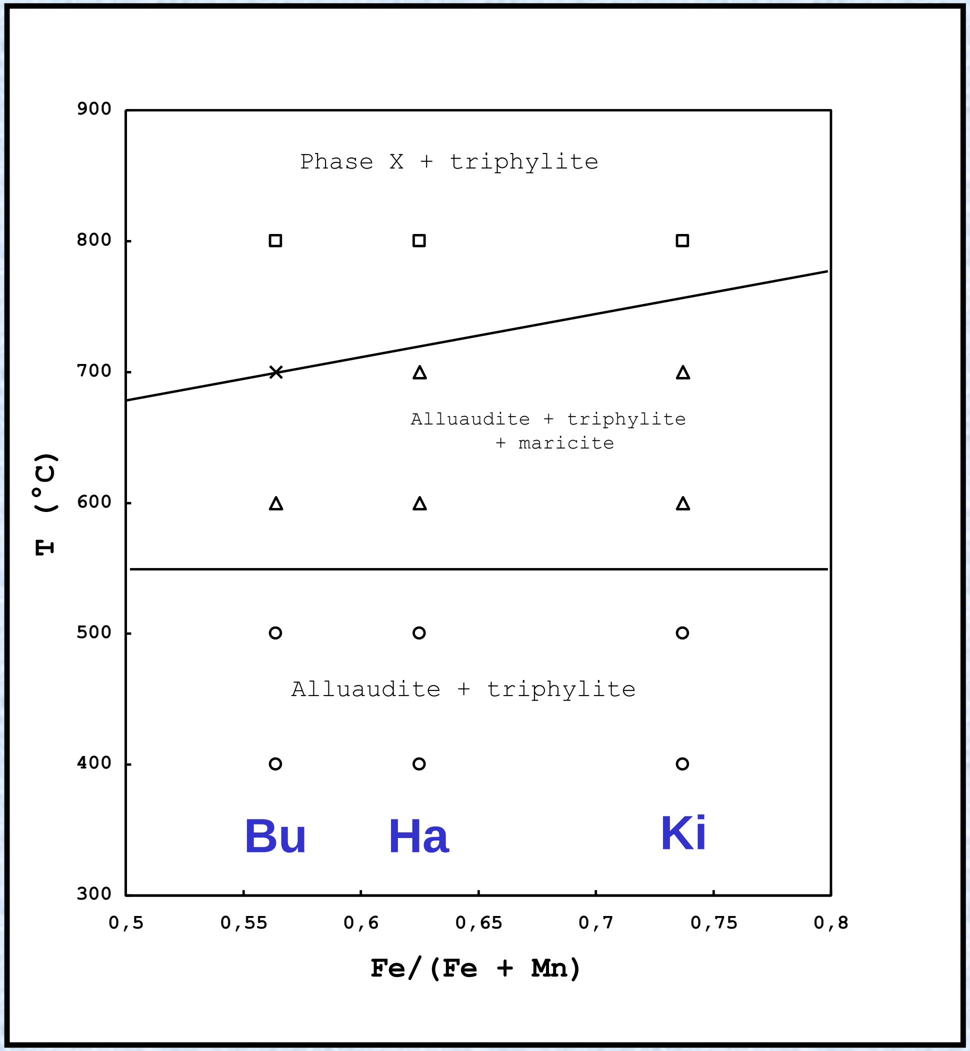
Hagendorfite, alluaudite, and heterosite, Kibingo pegmatite, Rwanda

Experimental: Hydrothermal synthesis



- Hydrothermal synthesis
- Tuttle-type cold-seal bombs
- T = 400-800 °C
- P = 1 kbar
- Double capsule method (Au 4 mm, $Ag_{70}Pd_{30}$ 2 mm)
- Oxygen fugacity: Ni/NiO (NNO) buffer

Stability of the triphylite + alluaudite asemblage



No maricite in pegmatites

Alluaudite + triphylite assemblage stable up to 500-600°C

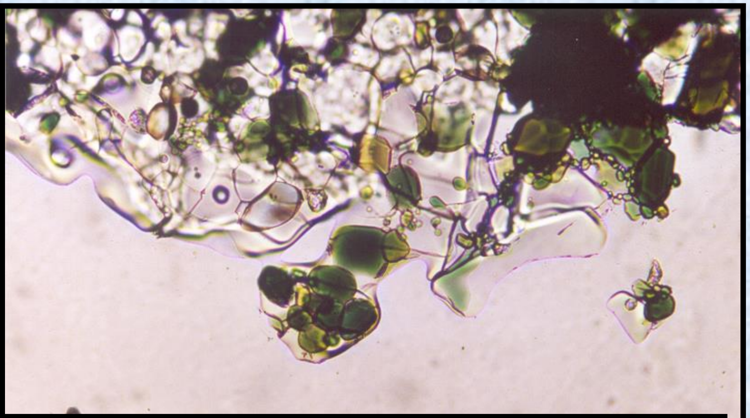
Bu = Buranga, Rwanda
Ha = Hagendorf-Süd, Germany
Ki = Kibingo, Rwanda

Li-content of synthetic phosphates

- **Triphylite-type phosphates**: **6.14-10.65 wt. % Li_2O (0.64-1.11 *a.p.f.u*.)**
- **Maricite-type phosphates**: **0.22-0.93 wt. % Li_2O (0.03-0.11 *a.p.f.u*.)**
- **Alluaudite-type phosphates**: **0.06-0.22 wt. % Li_2O (0.02-0.07 *a.p.f.u*.)**
- **X-phase**: **0.66-1.17 wt. % Li_2O (0.30-0.54 *a.p.f.u*.)**

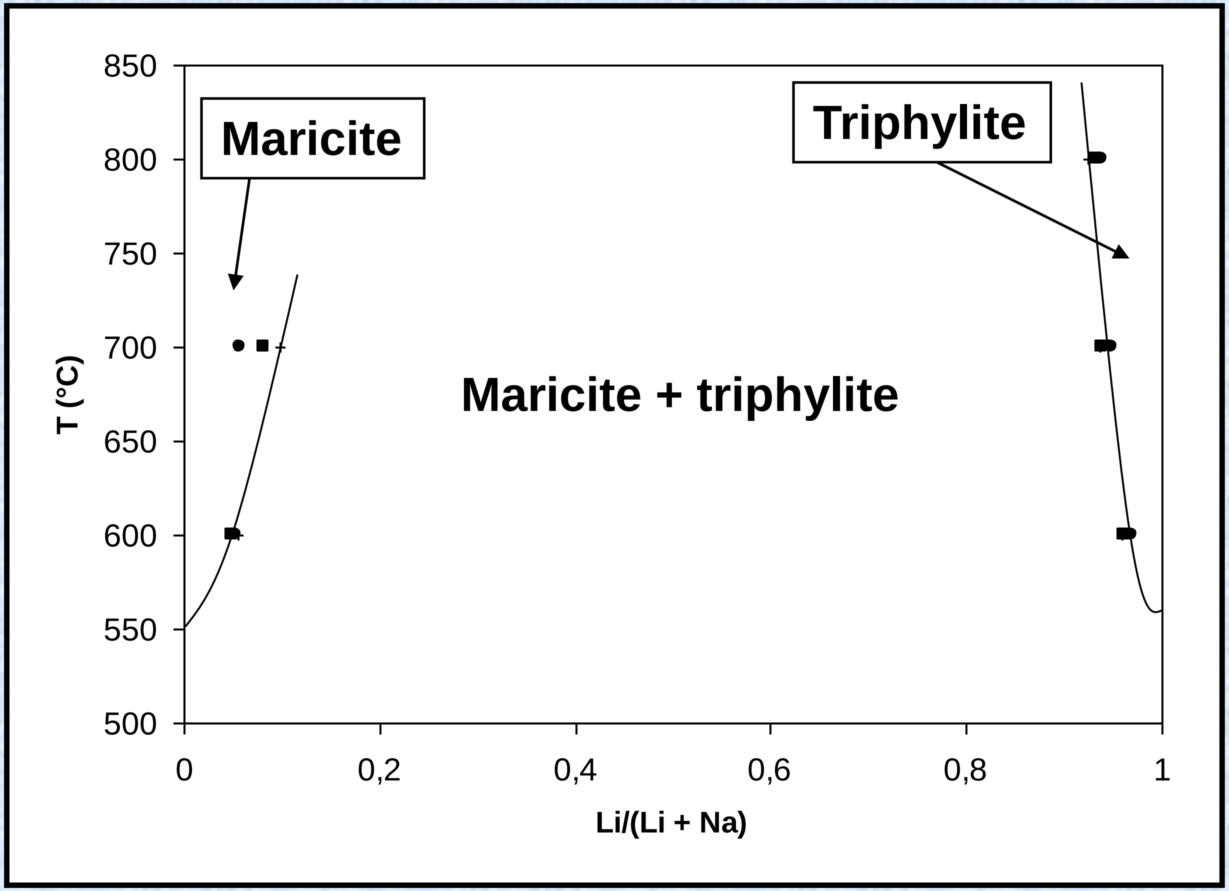
Natural alluaudites
0.004 to 0.010 wt. % Li_2O

First occurrence of Li in natural alluaudites!



700°C
Alluaudite + triphylite + maricite

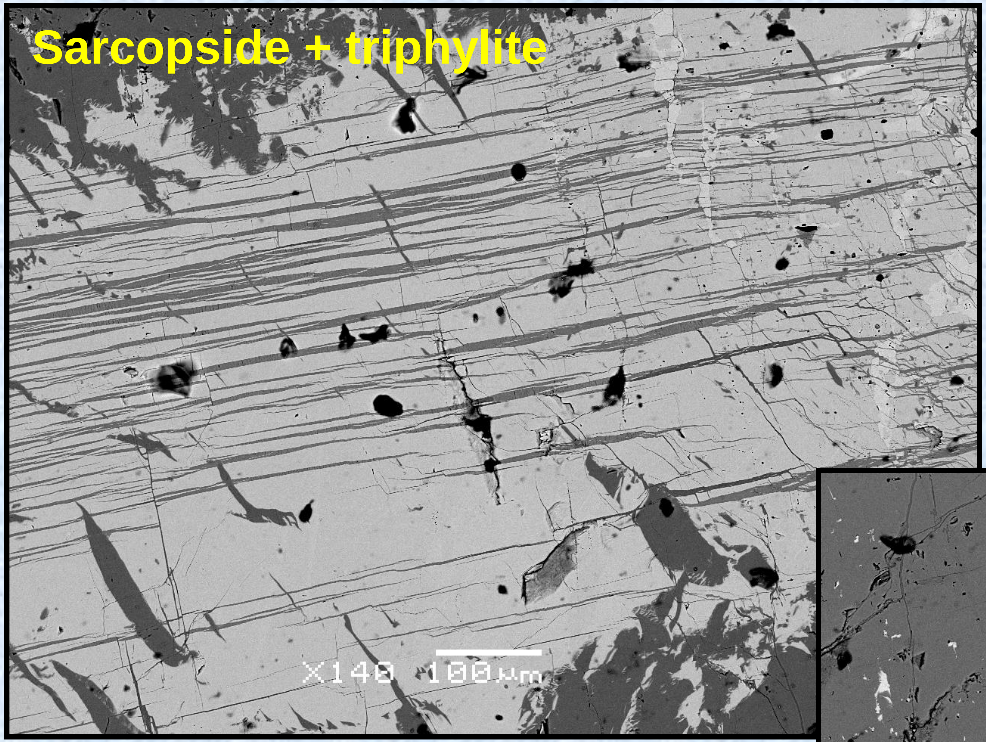
Triphylite-maricite phase diagram



- In triphylite, Na can reach 0.08 *a.p.u.f.* at 800°C
- In maricite, Li can reach 0.10 *a.p.u.f.* at 700°C
- No partitioning below ca. 550°C

Geothermometer!

The triphylite + sarcopside assemblage



Cañada pegmatite, Spain

Lamellar textures

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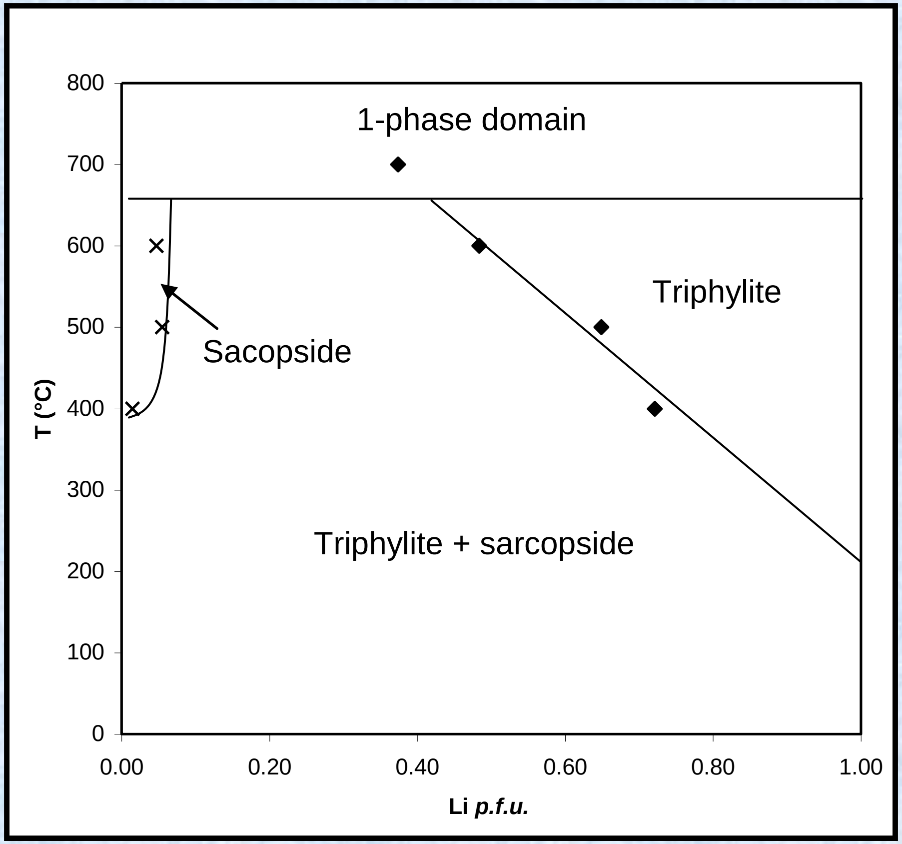
EXSOLUTIONS??

Stability of the triphylite + sarcopside assemblage

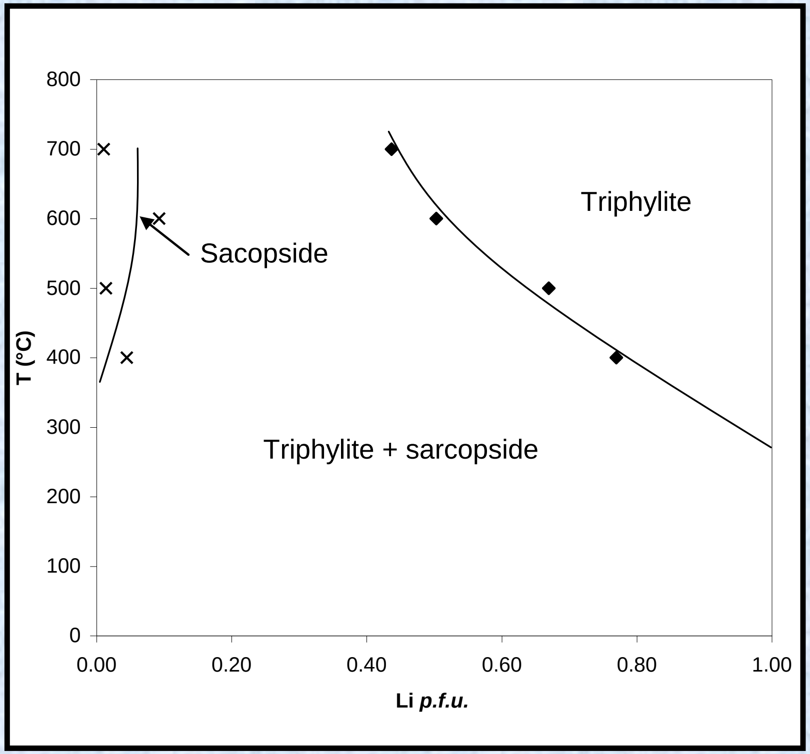


$LiFe^{2+}_{2.5}(PO_4)_2$

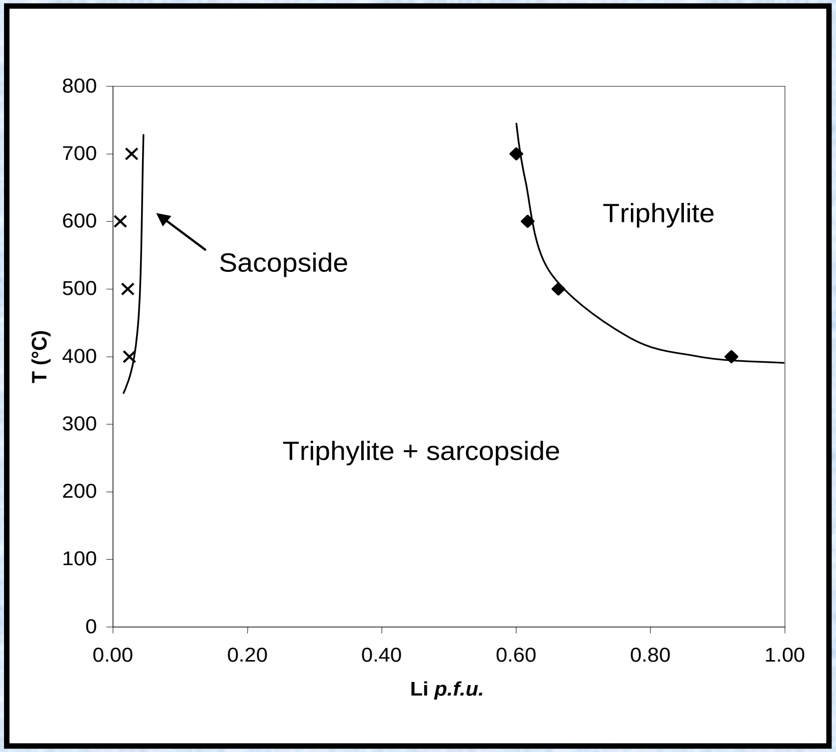
- **Decrease of the Li-content of triphylite, from 0.72 *a.p.f.u.* at 400°C, to 0.48 *a.p.f.u.* at 600°C**
- **Increase of the Li-content of sarcopside, from 0.01 *a.p.f.u.* at 400°C, to 0.05 *a.p.f.u.* at 600°C**
- **1-phase domain above 650°C**

Triphylite-sarcopside phase diagrams

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



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



The Li-content of triphylite decreases with temperature

→ **Geothermometer!**

Calculation of crystallisation temperatures for natural assemblages

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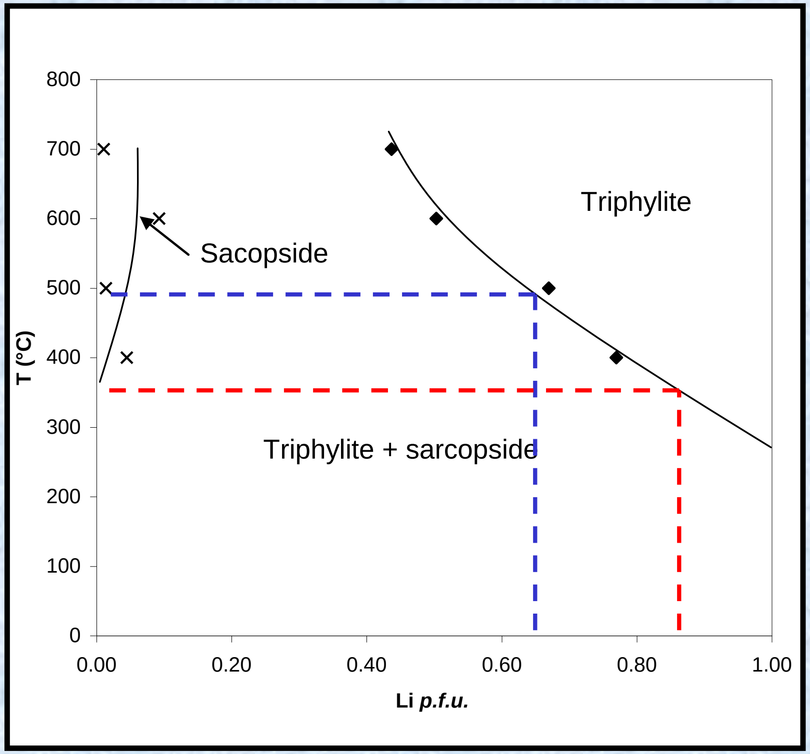

Fe/(Fe+Mn) ratio of natural triphylites and sarcopsides close to 0.800

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

Cañada

35 % sarcopside and 65 % triphylite

T ~ 500°C

Tsoabismund

15 % sarcopside and 85 % triphylite

T ~ 350°C

Conclusions

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- A method was developed to analyse the Li-content of phosphates by SIMS
- The results obtained on natural phosphates with the olivine structure show that the boundary between ferricicklerite and heterosite is not clear
- The transition from lithiophilite to sicklerite is progressive
- As a consequence, the validity of mineral species sicklerite and ferrisicklerite is questionable
- First confirmed occurrence of lithium in natural alluaudite-type phosphates
- Experimental investigations on the alluaudite + triphylite and triphylite + sarcopside assemblages give us results that can be used for geothermometric applications