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

Zavalíaite, $(Mn^{2+},Fe^{2+},Mg)_3(PO_4)_2$, a new primary phosphate from the La Empleada pegmatite, San Luis province, Argentina

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1st European Mineralogical Conference

Frankfurt, Germany, September 6th, 2012

Field-trip in Argentina

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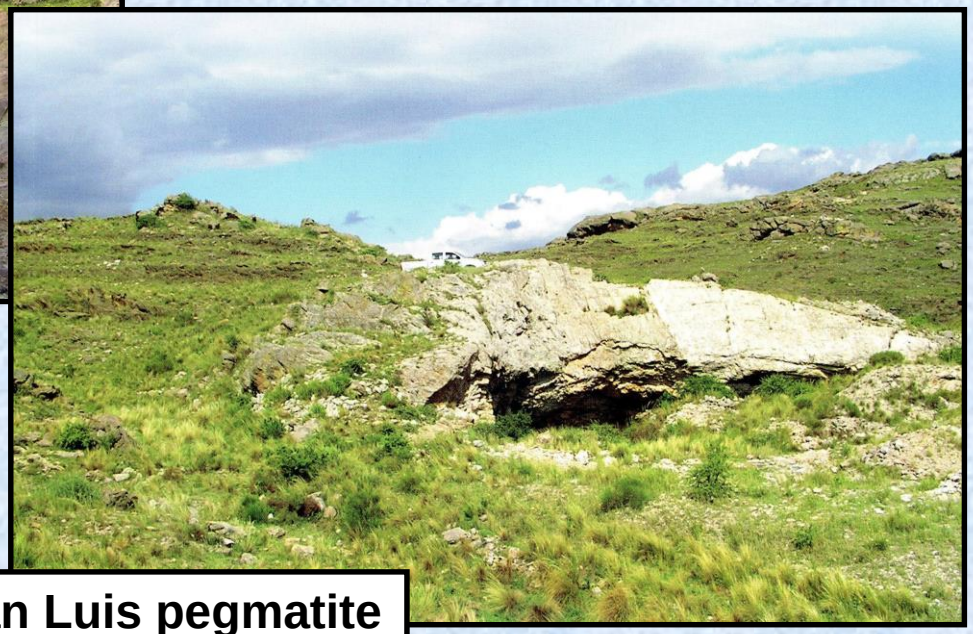
Paso del Rey granite

February 2008

- **Field-trip organized by M. Galliski**
- **San Luis Province (Argentina)**
- **Rare element pegmatites**



San Luis pegmatite

Geological context

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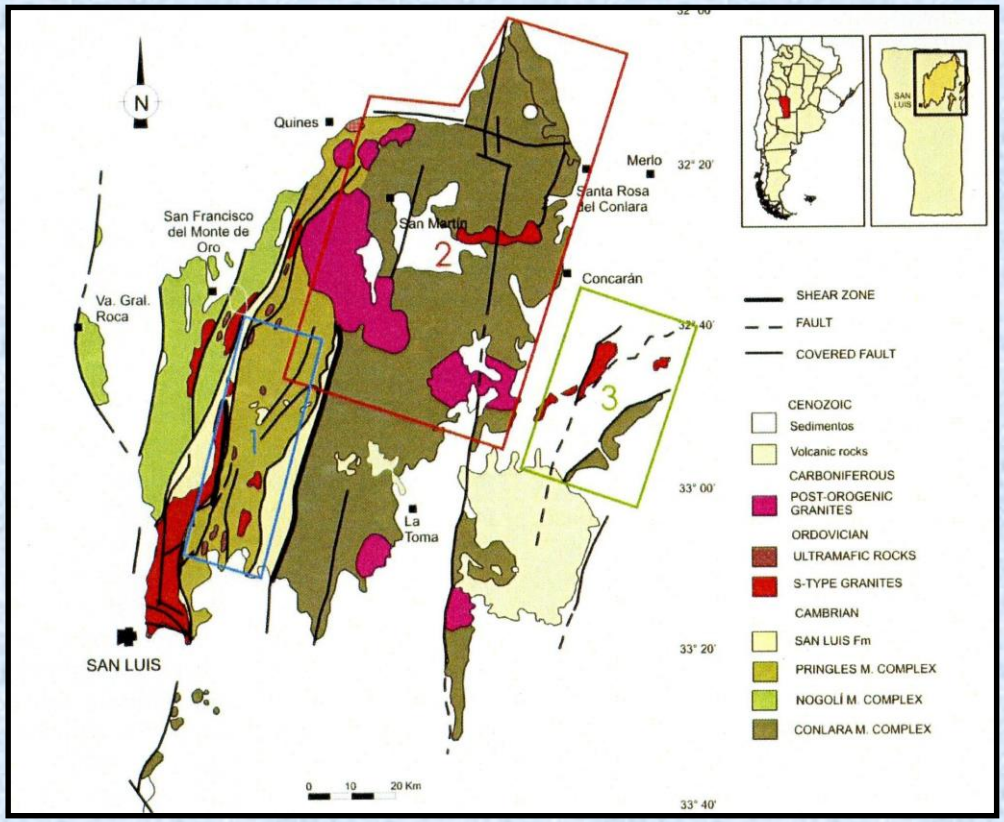
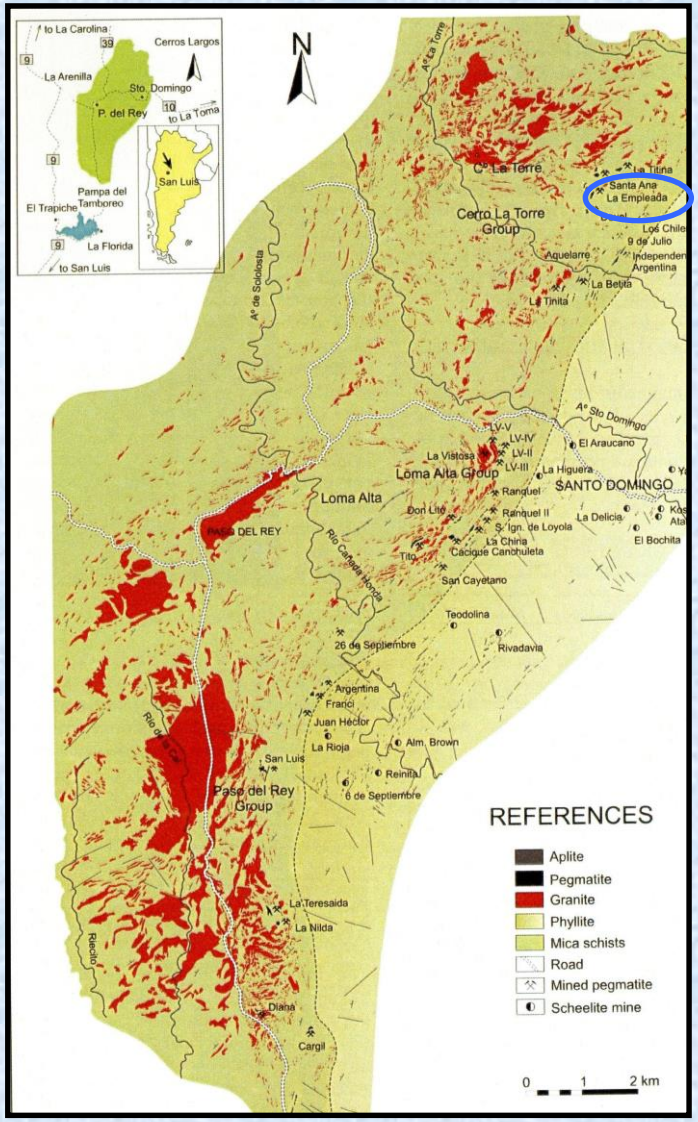
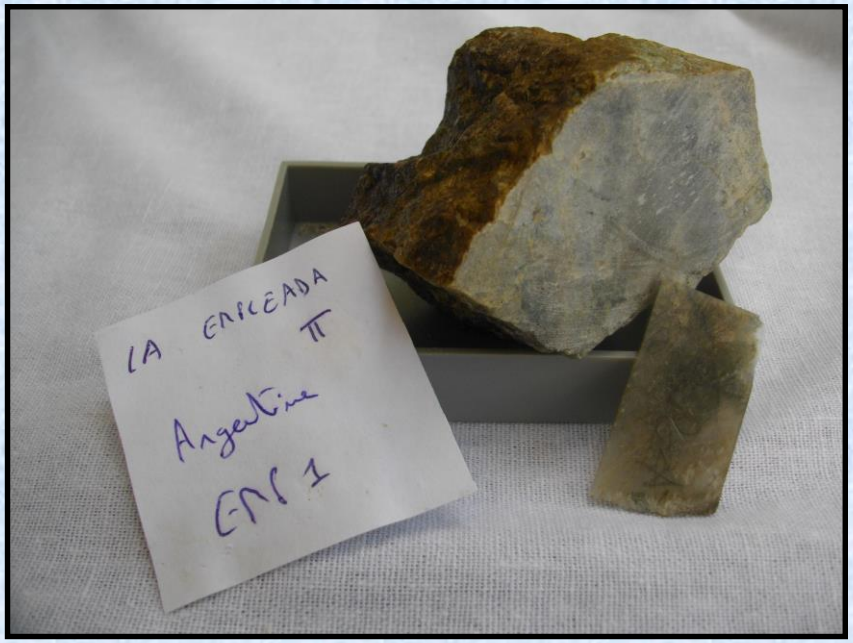




- **San Luis Province**
- **NE of San Luis city**
- **El Totoral pegmatitic fiels (1)**
- **Cerro La Torre Group**

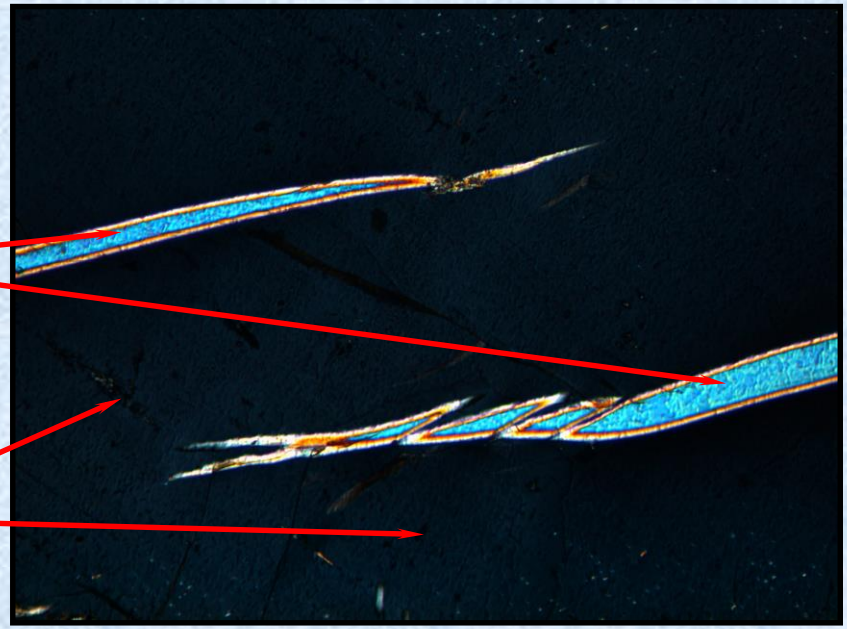
Appearance & chemical composition



- **Phosphates nodules**
- **Lithiophilite, $Li(Mn,Fe)PO_4$**
- **Lamellar mineral in thin sections?**

$(Mn^{2+}_{1.31}Fe^{2+}_{1.19}Mg_{0.52})_{\Sigma 3.02}(PO_4)_2$

$Li(Mn^{2+}_{0.39}Fe^{2+}_{0.29}Mg_{0.32})_{\Sigma 1.00}(PO_4)$



New mineral species!

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IMA 2011-012: accepted by CNMNC

Mn-dominant analogue of sarcopside!
Ideal formula $(Mn^{2+},Fe^{2+},Mg)_3(PO_4)_2$

Sarcopside	Chopinite	Zavalíaite
$(Fe^{2+},Mn,Mg)_3(PO_4)_2$	$(Mg,Fe)_3(PO_4)_2$	$(Mn,Fe^{2+},Mg)_3(PO_4)_2$
$P2_1/a$	$P2_1/c$	$P2_1/c$
10.44(2)	5.9305(7)	6.088 (1)
4.768(9)	4.7583(6)	4.814(1)
6.026(8)	10.257(1)	10.484(2)
90.0(2)	90.663(9)	89.42(3)

Sarcopside-ferrisicklerite, Cañada, Spain

Name dedicated to María Florencia Márquez-Zavalía (1955-)

- CONICET, Mendoza, Argentina
- Has contributed to improve the knowledge of Argentinean mineralogy
- Pegmatitic to hydrothermal ore minerals
- Participated to the study of new species ferrotitanowodginite, bismutotantalite, and numerous pegmatite phosphate minerals.

Crystal structure (I)

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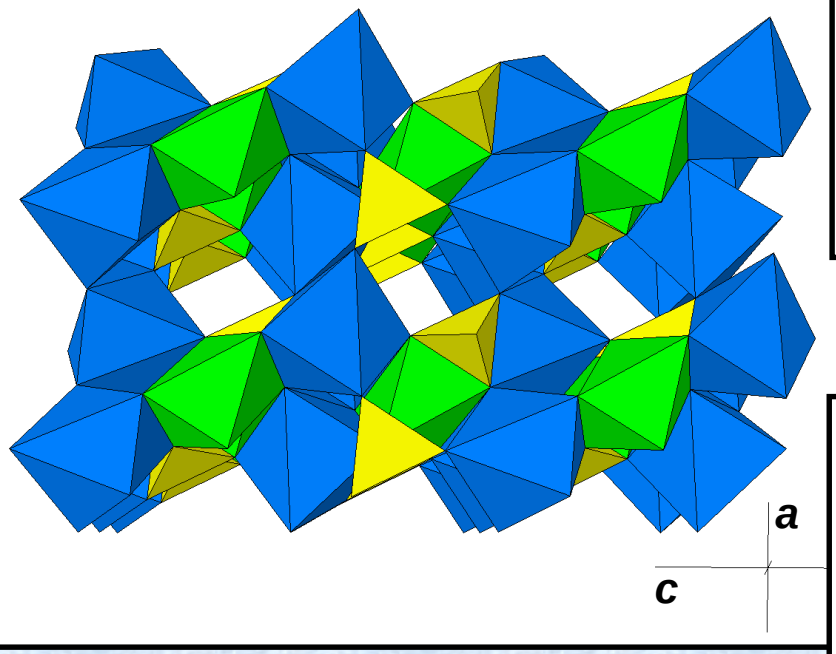
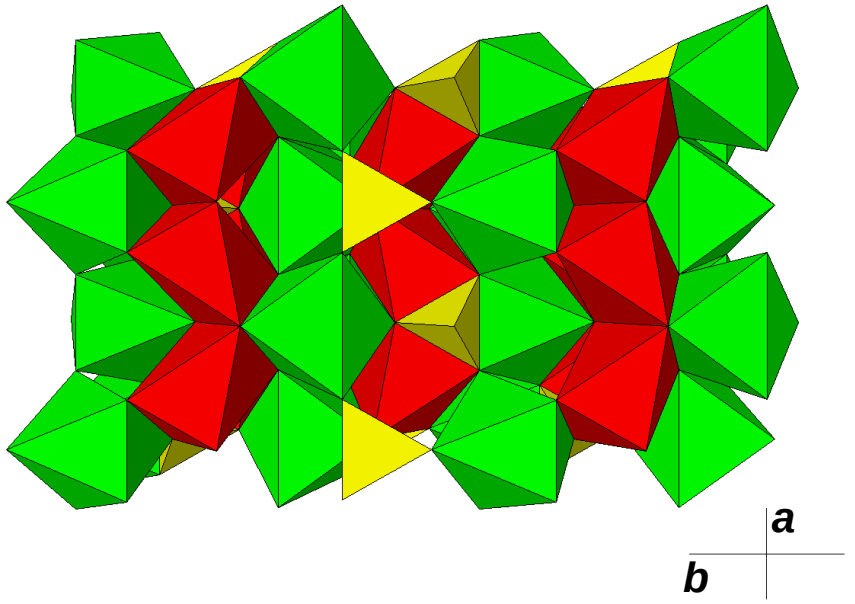
Zavalíaite, $Mn_3(PO_4)_2$



a = 6.088(1) Å
b = 4.814(1) Å
c = 10.484(2) Å
β = 89.42(3)°
S.G. $P2_1/c$
R_1 = 0.0483

Red = Li
Green = Fe
Blue = Mn

Triphylite, $LiFePO_4 = Li_2Fe_2(PO_4)_2$



- Topologically identical crystal structures
- 50 % of M(1) positions are vacant is zavalíaite

a = 5.987 Å
b = 10.286 Å
c = 4.690 Å
S.G. *Pmnb*

Crystal structure (II)

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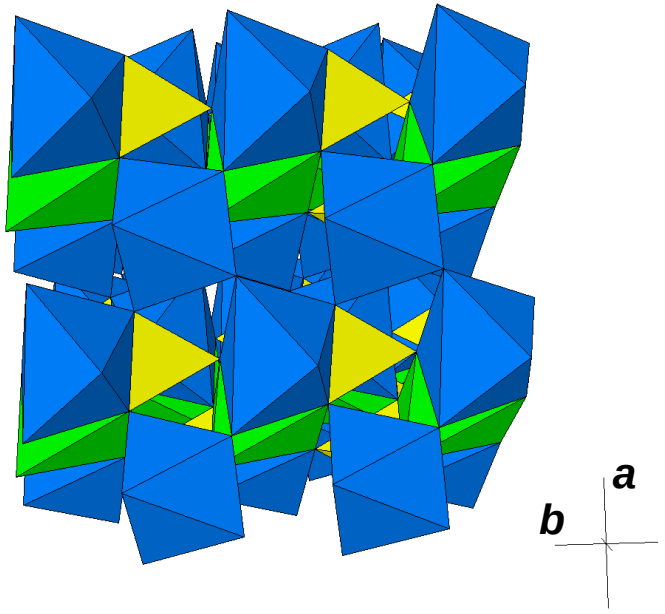
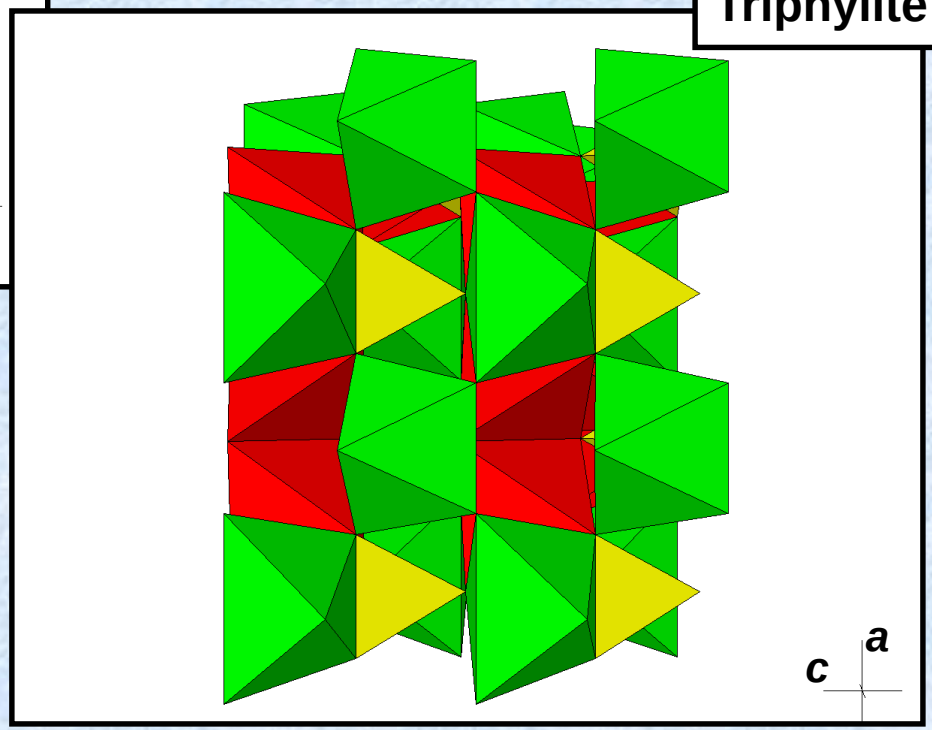
Zavalíaite



Triphylite



- **Planes constituted by corner-sharing M(2) octahedra**
- **Chains of edge-sharing M(1) octahedra**

Comparison with sarcopside- and olivine-type structures

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Site occupancy factors

	M(1)	M(2)
Sarcopside:	0.78 Fe + 0.22 Mn	0.78 Fe + 0.22 Mn
Chopinite:	0.52 Fe + 0.48 Mg	0.89 Mg + 0.11 Fe
Zavalíaite:	0.85 Fe + 0.15 Mg	0.83 Mn + 0.17 Mg

Bond distances

	M(1)-O	M(2)-O
Sarcopside:	2.18 Å	2.16 Å
Chopinite:	2.13 Å	2.12 Å
Zavalíaite:	2.15 Å	2.18 Å
Triphylite:	2.15 Å	2.16 Å
Fayalite:	2.16 Å	2.18 Å

- M(2) larger than M(1), except for chopinite and sarcopside
- Similar bond distances: difficult to determine site populations!

I.R. Mn^{2+} = 0.830 Å
I.R. Fe^{2+} = 0.780 Å
I.R. Mg^{2+} = 0.720 Å

Nomenclature?

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	M(1)	M(2)	M(1) + 2 M(2)
Sarcopside:	0.78 Fe + 0.22 Mn	0.78 Fe + 0.22 Mn	2.34 Fe + 0.66 Mn
Chopinite:	0.52 Fe + 0.48 Mg	0.89 Mg + 0.11 Fe	2.26 Mg + 0.74 Fe
Zavalíaite:	0.85 Fe + 0.15 Mg	0.83 Mn + 0.17 Mg	1.66 Mn + 0.85 Fe + 0.49 Mg

M(1) contains Fe as dominant cation!

9 possible new species!

FeFe – FeMn – MnFe – MnMn – FeMg – MgFe – MgMg – MgMn – MnMg

Heterosite and sarcopside, Morocco

The Canadian Mineralogist
Vol. 46, pp. 717-728 (2008)
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THE IMA–CNMNC DOMINANT-CONSTITUENT RULE REVISITED AND EXTENDED

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The two sites are considered as a whole for nomenclature purposes

Genesis of zavalíaite

Exsolutions!

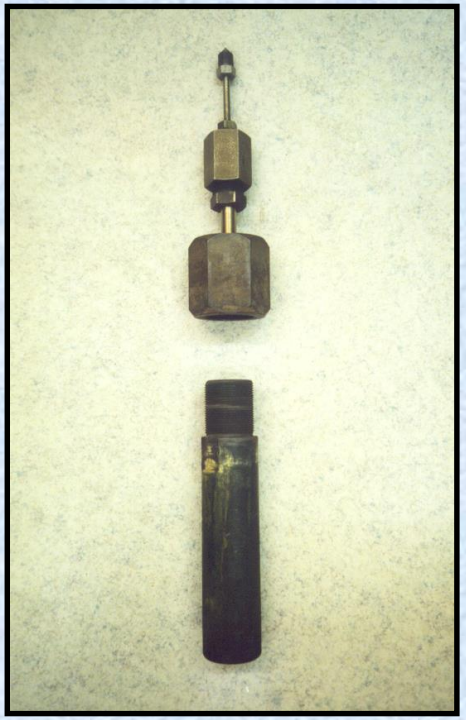
One unique HT phase!

- Generally, no Fe-Mn partitioning
- Mn-rich system in La Empleada
- Fe partitioned preferentially into zavalíaite

Partitioning coefficients

	La Empleada	Cañada	Tsaobismund	Boa Vista
Fe/(Fe+Mn)	0.25	0.83	0.64	0.79
$KD_{Fe\ srcp/trph}$	1.43	1.01	1.04	1.04
$KD_{Mn\ srcp/trph}$	0.91	1.11	0.98	1.08
$KD_{Mg\ srcp/trph}$	0.49	0.61	0.54	0.53

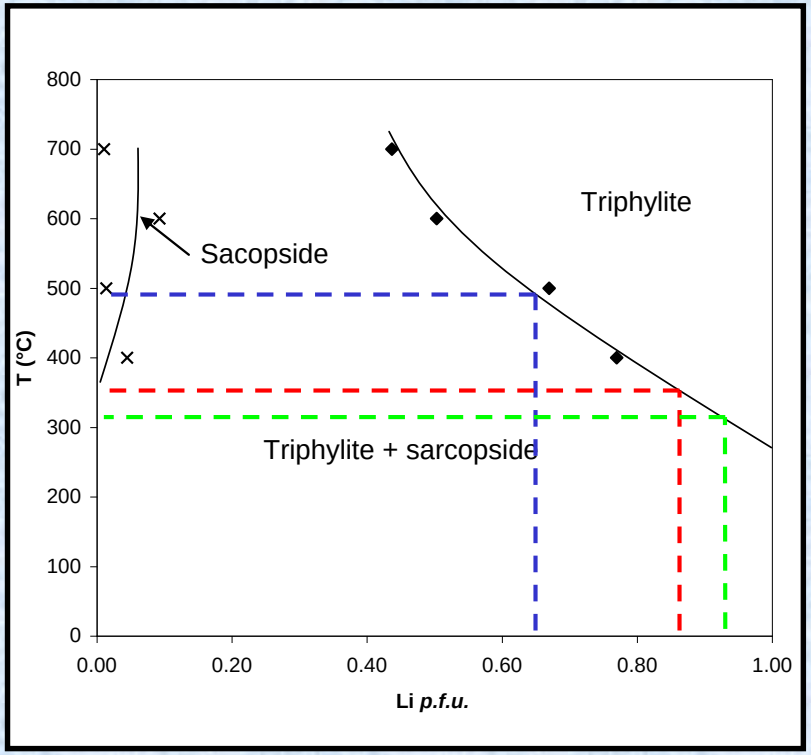
Experimental investigation (I)



- Tuttle-type cold-seal bombs
- T = 400-700 °C
- P = 1 kbar
- Oxygen fugacity: Ni/NiO (NNO) buffer
- Starting compositions close to those of natural triphylite + sarcopside assemblages

Experimental investigation (II)

< 10 % exsolved zavalíaite



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

La Empleada

<10 % zavalíaite and >90 % lithiophilite

T ~ 300°C

Mn-rich phosphates crystallize at low temperatures!

Conclusions

- Zavalíaite has been described in the La Empleada pegmatite, Argentina
- Exsolution lamellae within lithiophilite
- Mn-equivalent of sarcopside, $(Mn,Fe^{2+},Mg)_3(PO_4)_2$
- Crystal structure similar to those of sarcopside and chopinite
- Crystallization temperature of ca. 300°C