Modification of the sewage sludge ash P-mineralogy by thermo-chemical treatment with LF slags

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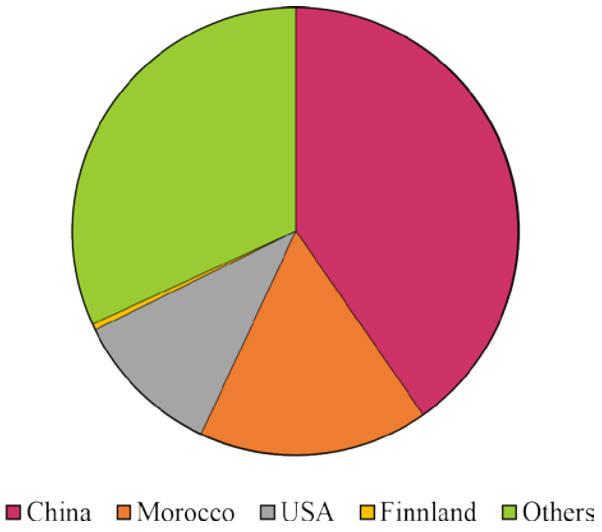
Phosphate use and demand

- P_2O_5 is an essential nutrient for plant growth

→ Widely used as fertilizer

- Production of 223 Mt of phosphate rock:



→ P is CRM on 2020 list

→ High demand and supply risk

- Sewage sludge ash is one major anthropogenic sink for P_2O_5

→ Concentration range: 5-25 wt.%

- P_2O_5 recycling from sewage mandatory in Germany from 2029
- Issue: Major P-Phases show very low plant availability:

Whitlockite (β-TCP) $Ca_9(Mg,Fe)(PO_3(OH)PO_4)_6$

Apatite $Ca_5(PO_4)_3$

Phosphate recycling by thermo-chemical treatment

Sludge2P concept:

- Production of usable gas (H_2,CO, CO_2, CH_4) and sewage sludge ash in integrated system (IPV)

→ Gas delivers (most of) process energy

- Thermo-chemical treatment of SSA with LF-Slag

→ Rich in Ca, fine disintegrated, often landfilled

- Demanded reaction in the melt:

Whitlockite (β-TCP)
Apatite
+ CaO + SiO_2 →

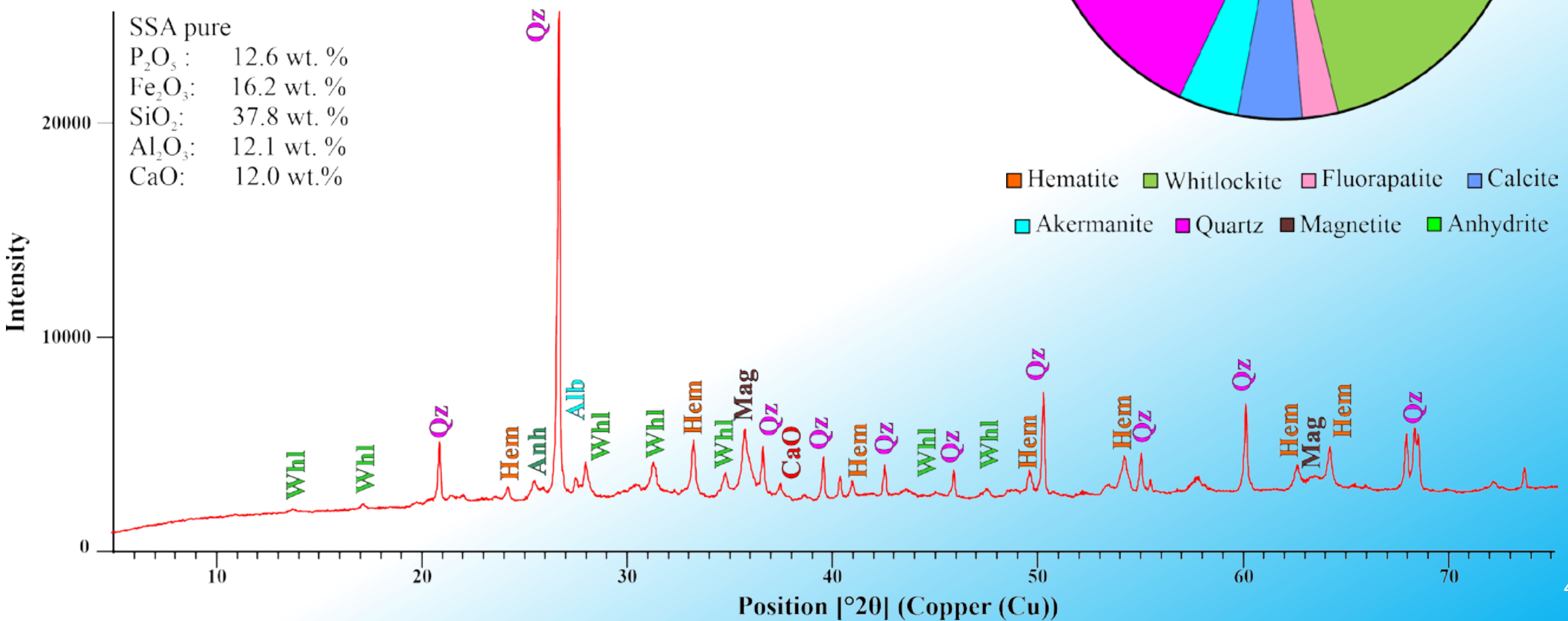
Silicocarnotite
$Ca_5[(PO_4)(SiO_4)](PO_4)$

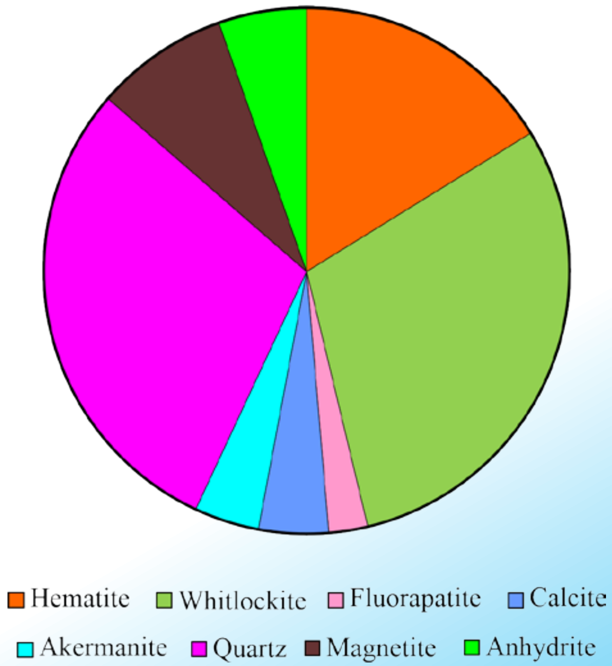
Nagelschmidite
$Ca_3(PO_4)_2 \cdot 2(\alpha\text{-}Ca_2SiO_4)$

Raw materials: SSA

- Ash from „standard“ incineration in fluidized bed furnace → rich in P, Si, Fe
- Major P-Mineral: Whitlockite (TCP) +/- Apatite
- Zn, Pb and Cu → mostly from precipitation (gutter and roofing)
- Ni geogen/mining outcrops → Siegenit $(Ni,Co)_3S_4$

Metal	ppm
As	27
Cd	10
Cr	833
Cu	1,955
Ni	530
Pb	373
Zn	5,530
V	187





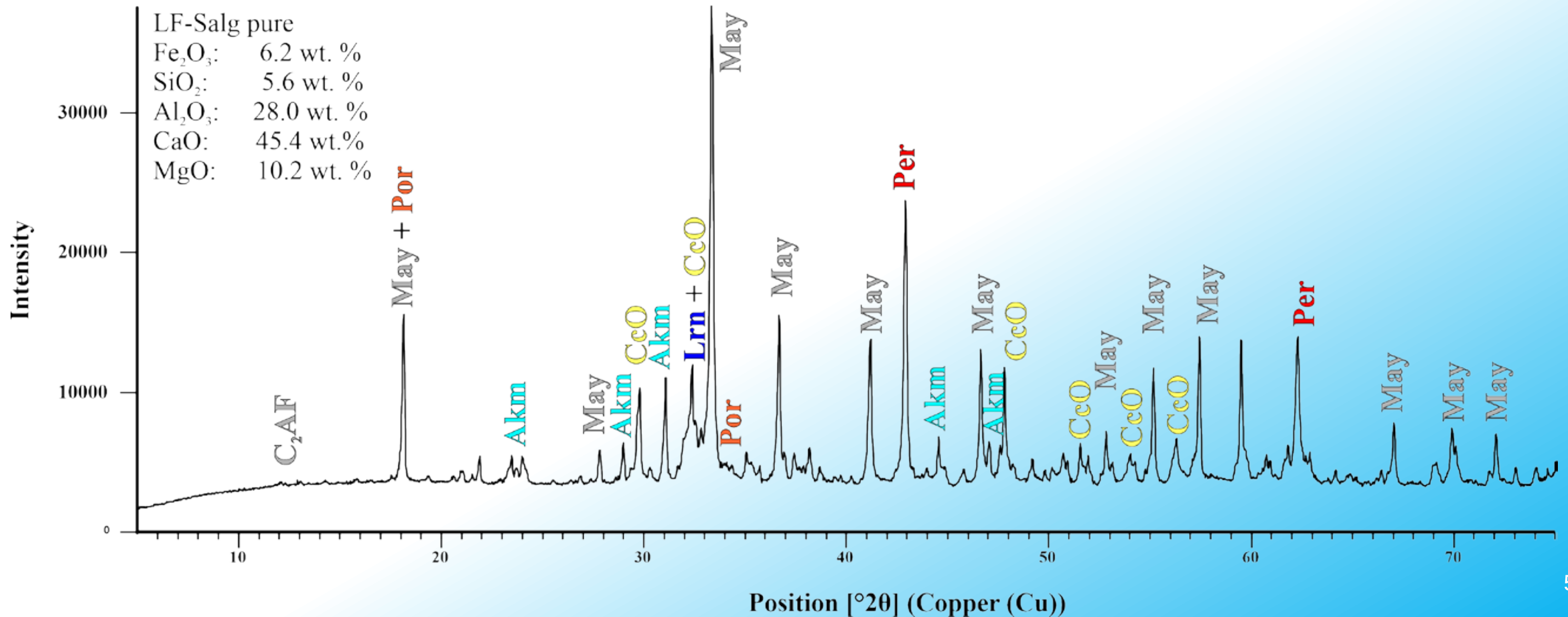
Raw materials: LF-Slag

- Fine disintegrating (γ-C_2S) slag from sec. metallurgy
- Mineralogy: mayenite, calcio-olivine, periclase, melilite

→ rich in Ca + Al and Mg

- Trace metals as Cr, Cu and V from steel refining

Metal	ppm
As	0.6
Cd	0.1
Cr	527
Cu	527
Ni	15.2
Pb	2.5
Zn	28
V	305



Recepies with CaO - Do they melt?

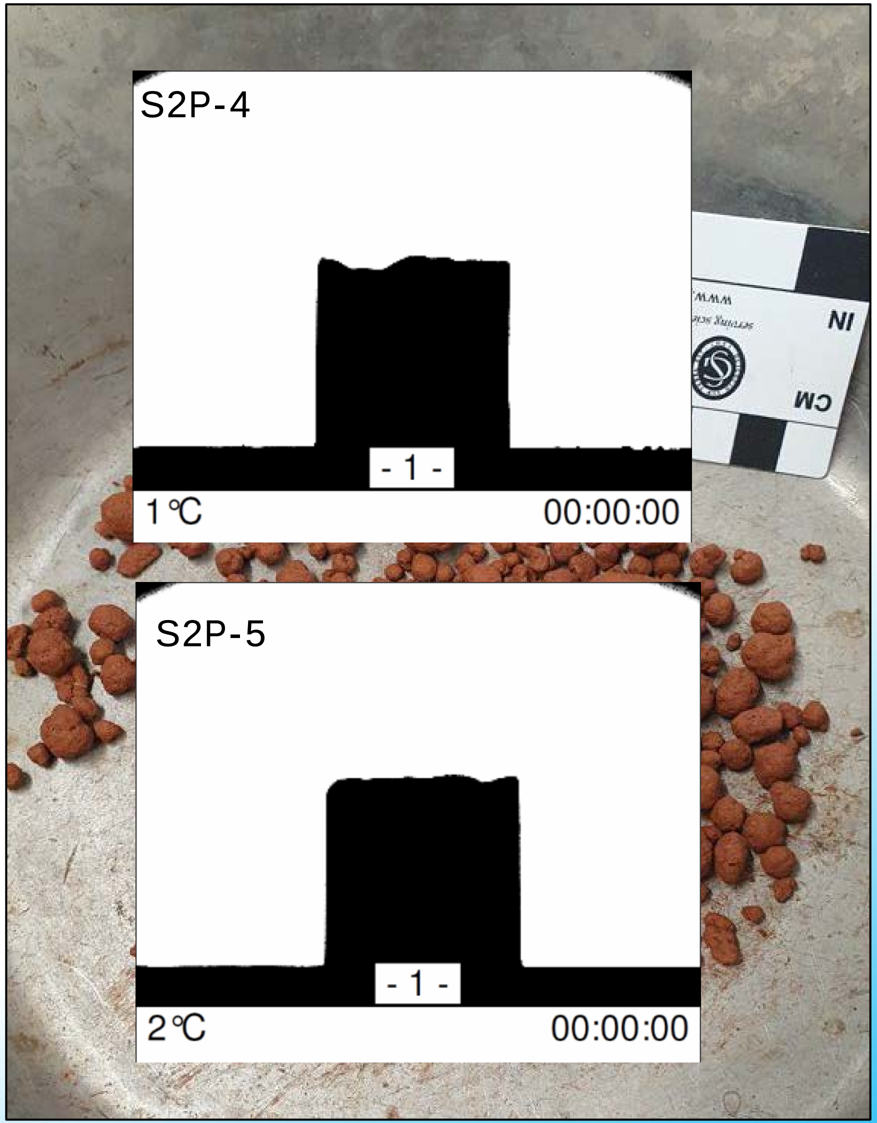
- 3 Mixtures of SSA + LF-Slag + Lime

S2P-1: 70 % SSA + 30 % Lime
→ Adding CaO exceeding Ca-Si-P stabilization
→ Melting: 1232 °C

S2P-4: 40 % SSA + 60 % LF-Slag
→ Adding CaO only by LF-Slag
→ Melting: 1298 °C

S2P-5: 50 % SSA + 40 % LF-Slag + 10 % Lime
→ Total CaO content equivalent to S2P-1
→ Melting: 1288 °C

→ Low melting temp. decreases energy demand



Method: Furnace Experiments

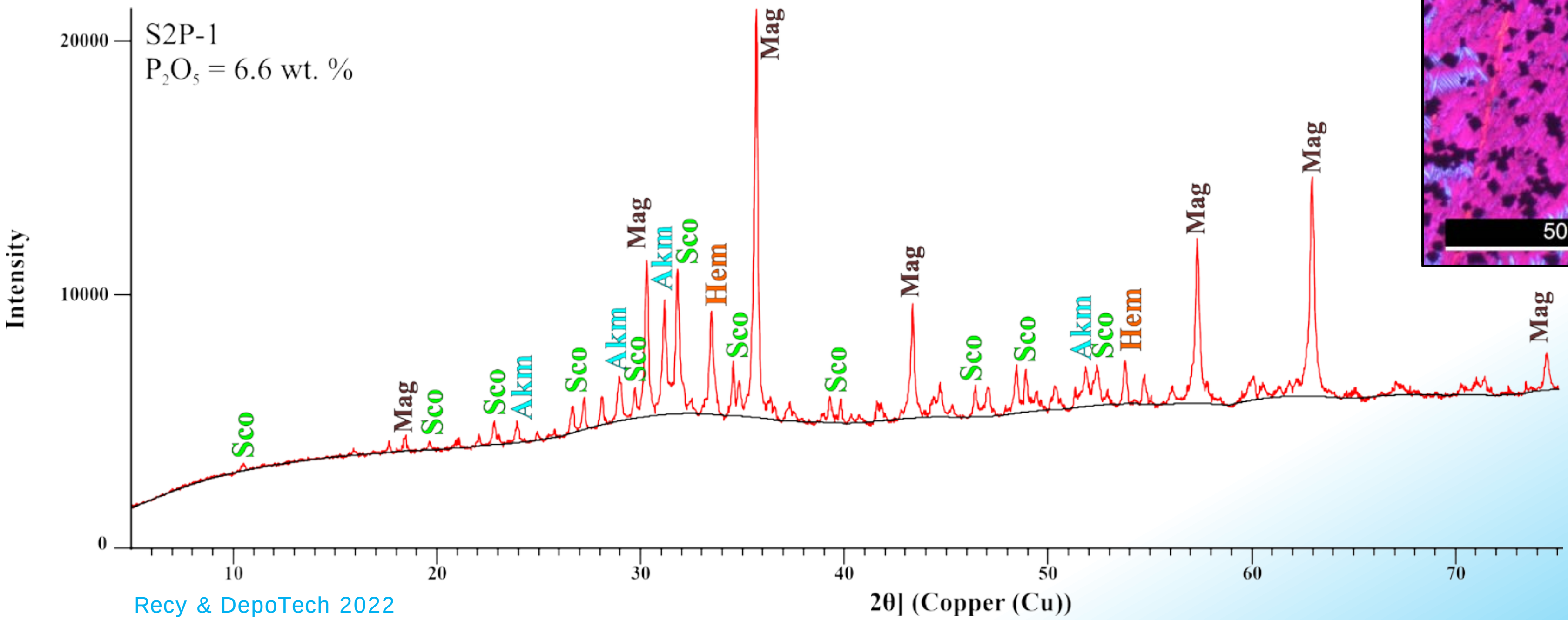
- TBRC 40 L at MU Leoben
- MgO refractory, CH_4-O_2 burner at λ=0.8 – 1.0
- Charing: 2x30 kg pellets at 1450 °C
- Tapping after reaching 1450 °C into ZrO_2 lined pots

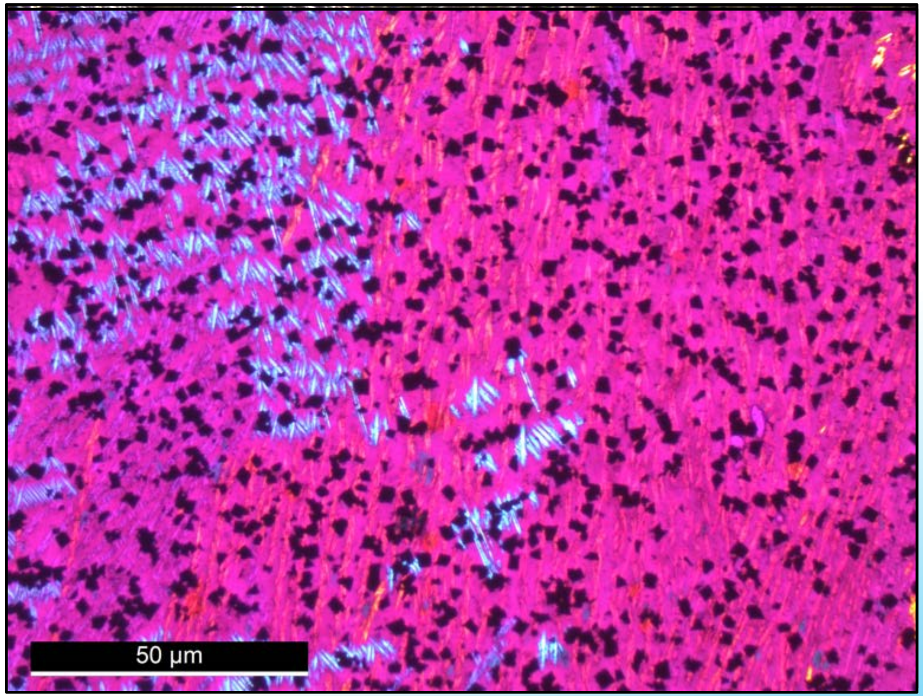
Results: P-Mineralogy S2P-1

- Silicocarnotite can be identified as P-carrier

→ Vitreous matrix within very fine skeletal grains (trachitic)

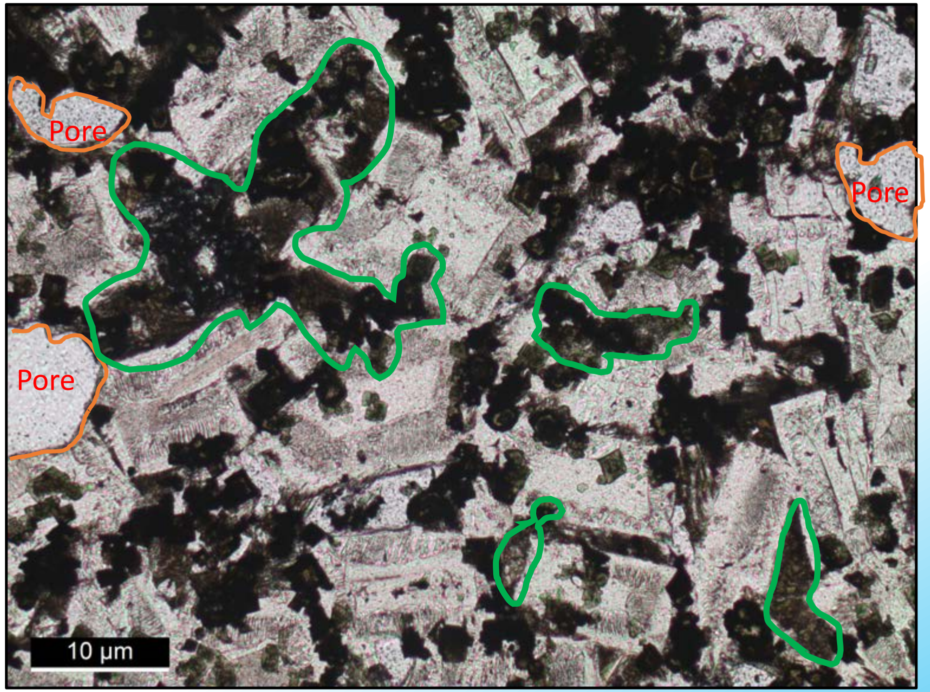
- Idiomorphic and disseminated magnetite
- Low amounts of melilite can be found

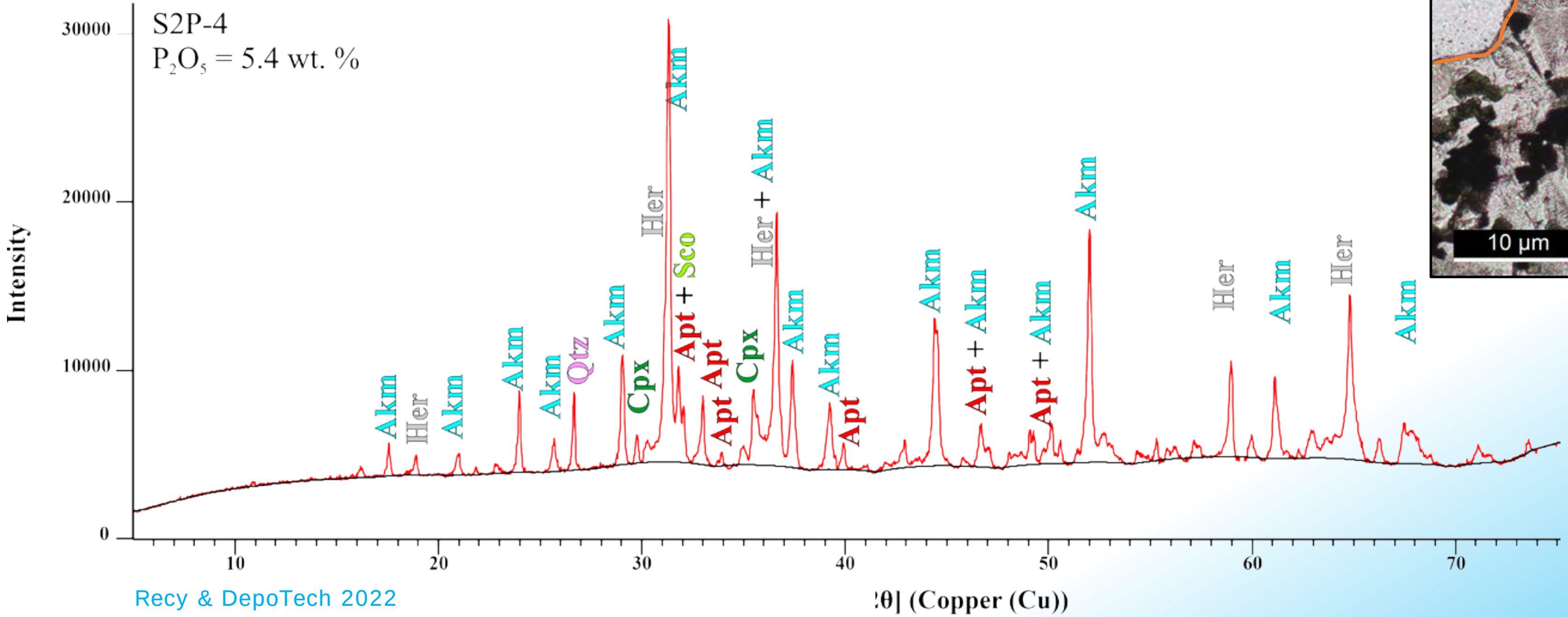




Results: P-Mineralogy S2P-4

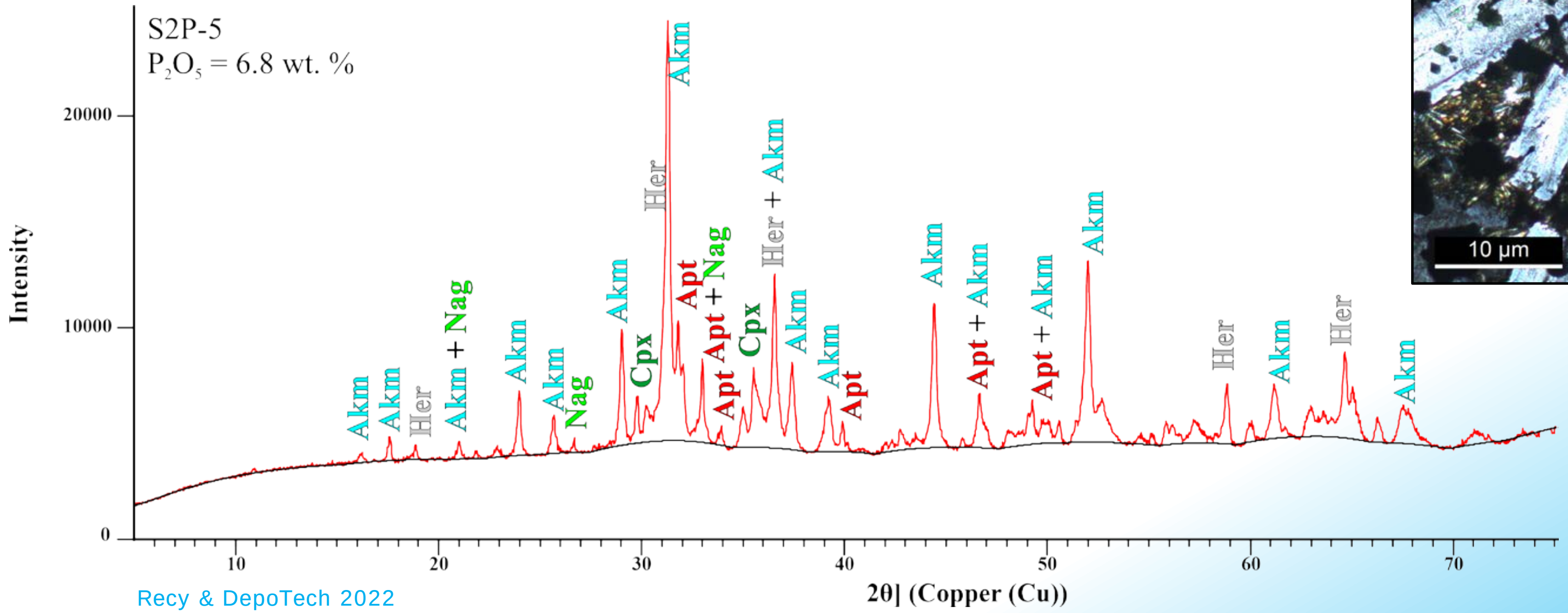
- As major P-carrier apatite and minor Sco were observed
- Melilite idiomorphic, interstitial voids filled with fine Cpx+Sco
- Porosity can be observed microscopically (10 µm)

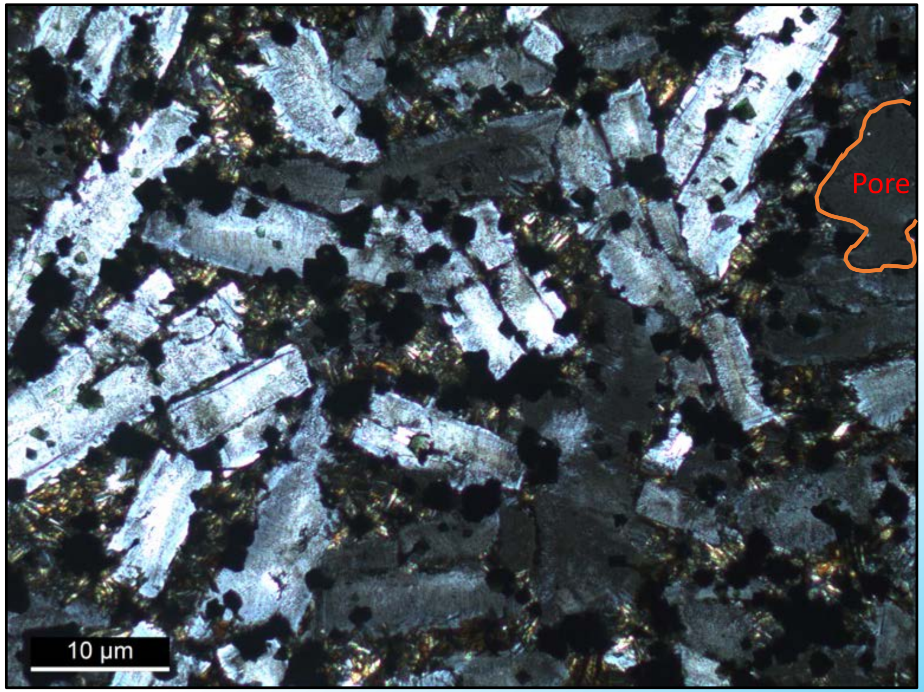




Results: P-Mineralogy S2P-5

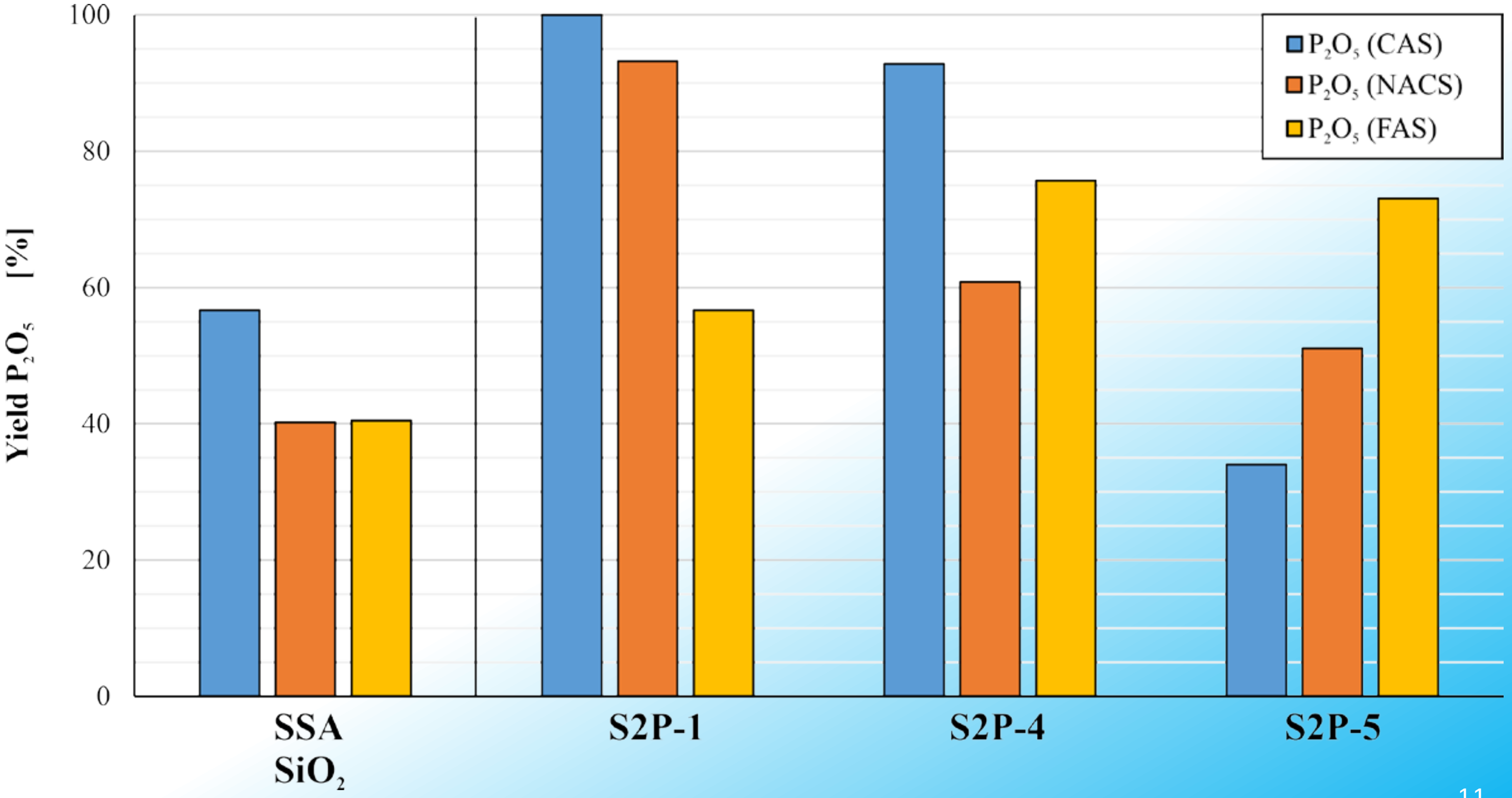
- Idiomorphic melilite is major mineral phase
- Fine pyroxene filling interstitial volume
- Idiomorphic spinel's, disseminated and fine < 5 µm
- As P-carrier nagelschmidtite and apatite were identified





Results: Wet chemistry – P_2O_5 extraction methods

- P_2O_5 extraction was tested with 4 common extractants: Citric acid, neutral ammonium acetate, formic acid and deionized Water
- S2P-1 shows highest yield for CA and NAC
- S2P-5 CA below pure SSA
- Residual P_2O_5 yields >> SSA
- No water soluble P_2O_5



Results: Plant trials

- Pot trials conducted with Maize and Canola (oil seed rape)
- Both species show different sensitivity on P supply
- 3 products, pure SSA, TSP in 2 stages each plus control (no P_2O_5)

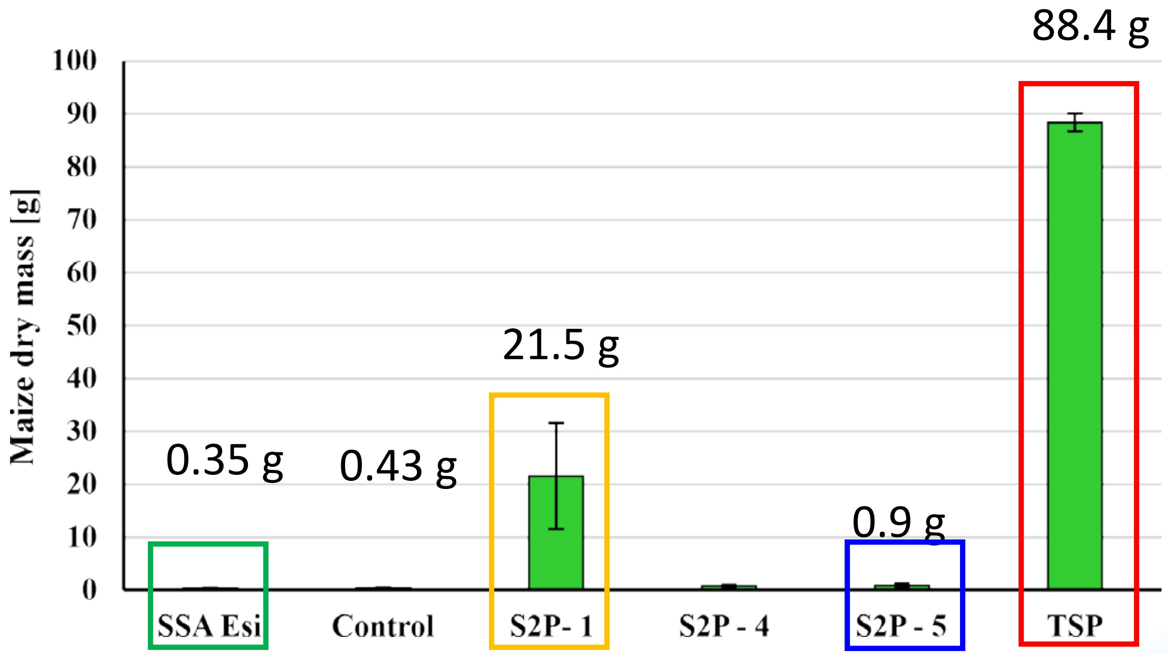
→ Stage 1: suboptimal supply of P

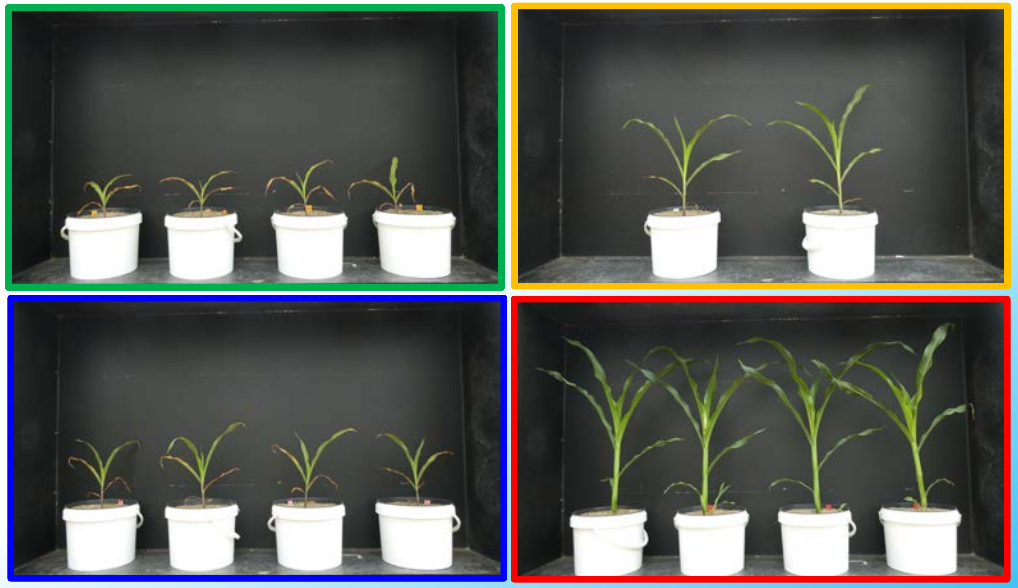
→ **Stage 2: optimal supply of P**

- Bio mass harvested after 3 month growth period
- Sampling of substrate and bio mass for chemical investigation

Results: Plant trials - Maize

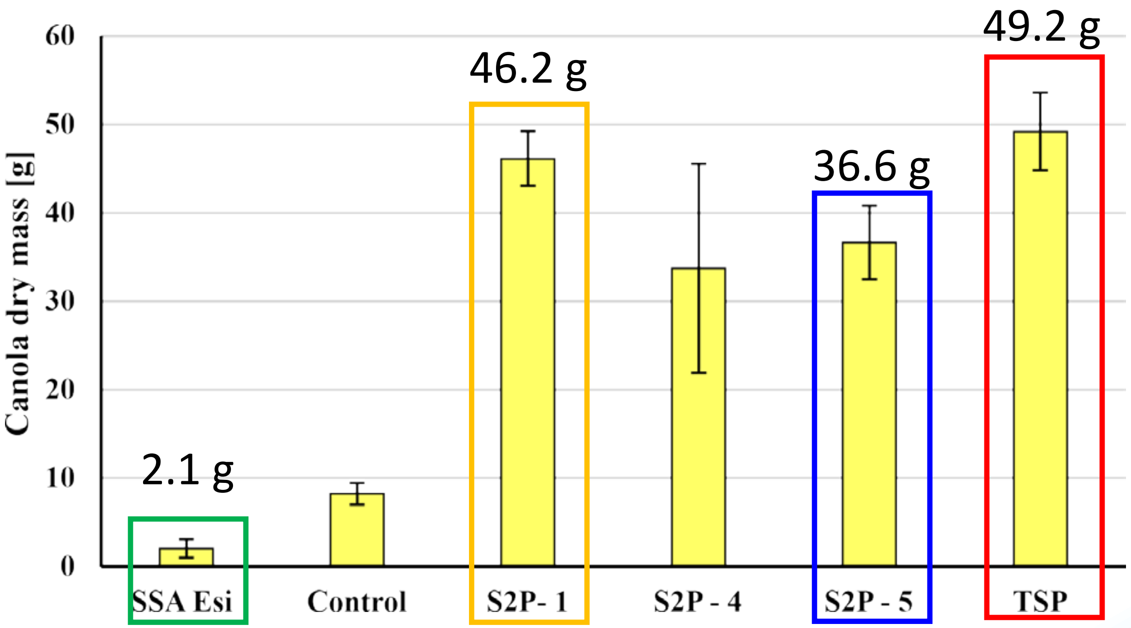
- Maize show very poor plant growth due to selectivity of P_2O_5 uptake
- Application of pure SSA tend to imped growth in comparison to untreated control





Results: Plant trials - Canola

- Canola harvest quite better
- Pure SSA below control (again) → malus elements ???
- S2P-1 within error interval of TSP



Conclusion

- **Mixtures show sufficient melting at desired temperatures**

→ Input data for energy balancing

- **SSA + LF-Slag mixtures produce melilites during cool down**

→ Depletion of Ca + Si from the melt inhibits the formation of Ca-Si-P

→ Lowering the P_2O_5 extraction efficiency

- **Mixtures of SSA, LF-Slag and Lime feature increased P_2O_5 availability**

→ LF-Slag is suitable as Ca-source for thermo-chemical treatment but limited by Mg and Al input

- **Trace elements not critical and mostly inherited from the SSA**

→ Analysis of substrate and bio mass not ready

→ Something in the pure SSA hampers plant growth

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