

Structural Study On The Chemical Environment Surrounding Phosphorus In Ash Fractions Suitable For Nutrient Recovery

Elbashir, S¹.; Ramstedt, M².; Thyrel, M³.; Broström, M¹.; Skoglund, N¹.

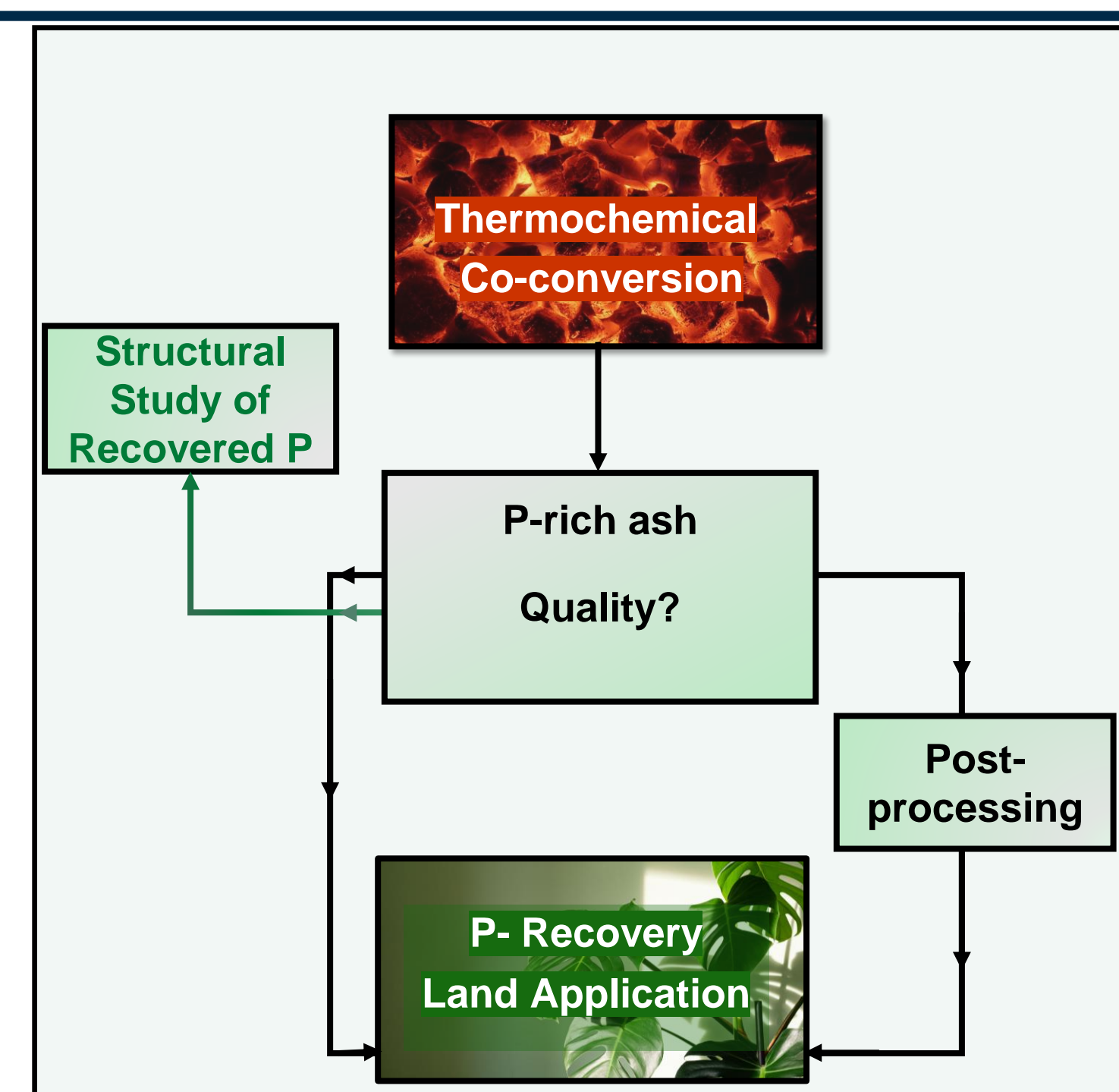
¹Thermochemical Energy Conversion Laboratory (TEC-Lab), Department of Applied Physics and Electronics, Umeå University, Umeå, Sweden.

²Department of Chemistry, Umeå University. Umeå, Sweden.

³Department of Forest Biomaterials and Technology, Swedish University of Agricultural Sciences. Umeå, Sweden.

Introduction

Nutrient recovery is an integral part of sustainable clean energy production where one of the most important nutrients is phosphorus (P). Many factors drive the strong interest in recovering P from various biomass and waste ashes. Both the scarcity and the vital importance of P represent the major driving factors for examining a sustainable and environmentally-friendly recovery processes [1]. The thermochemical **co-conversion** of sewage sludge and biomasses is a promising technique to recover P [2]. One of the main challenges related to the P-rich ash fractions is the presence of heavy metals (HM). Therefore, understanding the speciation of phosphates in the ash fractions is crucial for optimizing P recovery from the co-conversion. Nonetheless, the removal of the associated HM is pivotal for the safe application of the P- rich ash fractions in fertilizers industry [3]. Trial and error approaches are applied to reduce the amount of HM through fuel design and/or additives during thermochemical processes. However, the connection between P and HM in these ash fractions is yet to be understood. So, detailed speciation of these elements in the P- rich ash fractions is important to create a natural link for sustainable energy production and nutrient recovery.



Aim and Objectives

Aim

To understand the connection between P and HM in the P-rich ash fractions from co-conversion of sewage sludge and biomasses.

Objectives

- Synthesize reference phosphates that are commonly found in the P- rich ashes.
- Investigate the inclusion of HM such as Zn, Cu and Ni in the phosphate structures.
- Determine the speciation of P and HM in ashes via synchrotron-based analyses.

Methodology

Solid state synthesis

Reference phosphates compounds that are known to be found in ashes are selected based on literature. Table (1) shows the candidate phosphates considered in the study. The synthesis method is based on a high temperature route (solid state reaction) using a muffle furnace. The selected heating protocols are varied depending on the target compound (700°C–1100°C).

Analyses

Various analytical techniques are used to study reference phosphate materials:

- Powder X-rays diffraction (XRD).
- SEM-EDS measurements.
- FTIR and Raman spectroscopy.

These analyses will be complemented with X-ray absorption spectroscopy(XAS) to identify bond distances between P and HM in ash fractions.

Table 1. Reference phosphate compounds.

Whitlockites/ Merrillite	Orthophosphates	Pyrophosphates
$\beta\text{-Ca}_3(\text{PO}_4)_2$	CaKPO_4	$\text{Ca}_2\text{P}_2\text{O}_7$
$\text{Ca}_3\text{KMg}(\text{PO}_4)_7$	KMgPO_4	$\text{CaK}_2\text{P}_2\text{O}_7$
$\text{Ca}_3\text{NaMg}(\text{PO}_4)_7$		$\text{K}_2\text{MgP}_2\text{O}_7$
$\text{Ca}_{10}\text{K}(\text{PO}_4)_7$		



Figure 1. P- rich ash pellets.

Preliminary Results

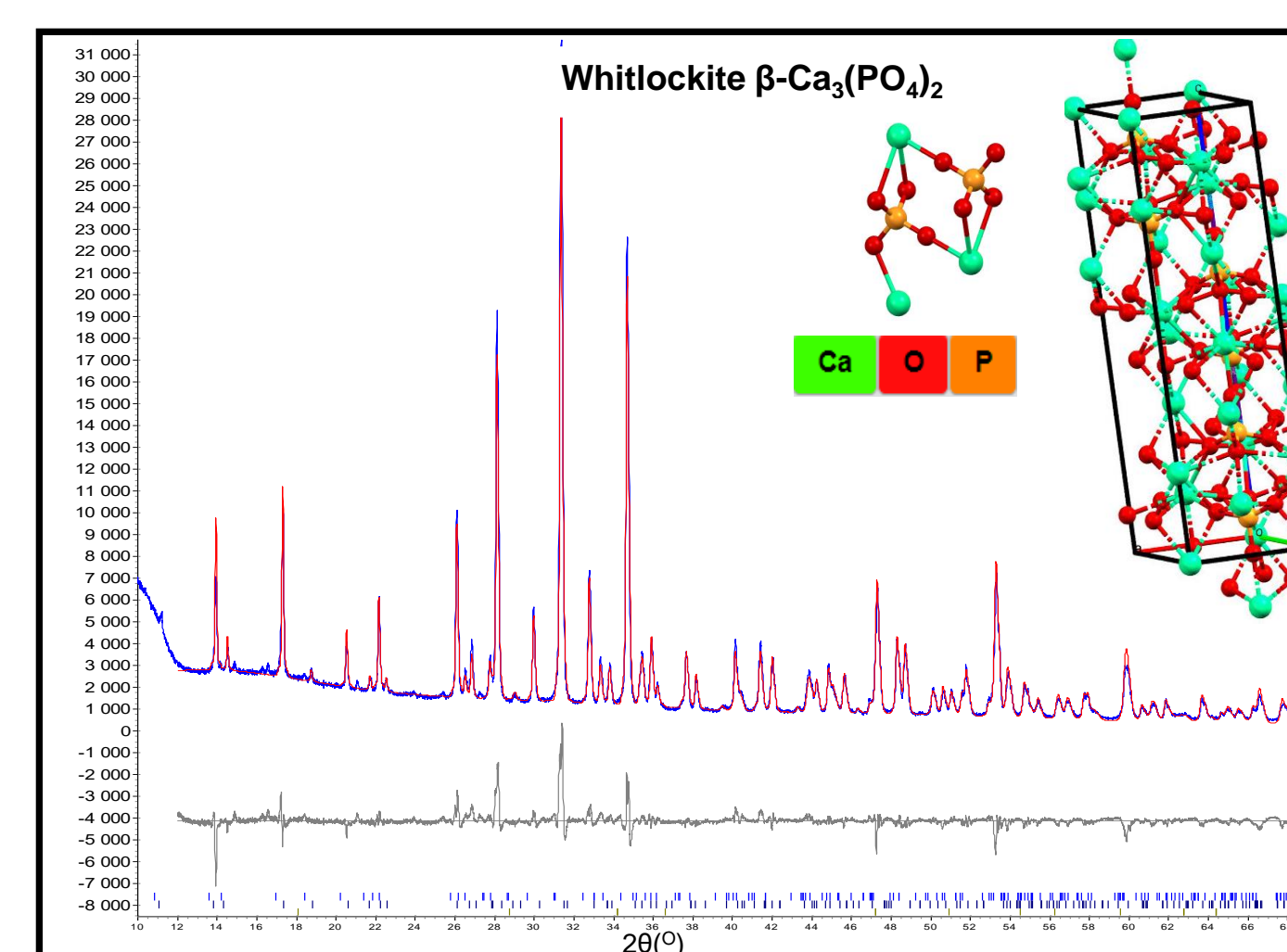


Figure 2. XRD pattern of pure whitlockite $\beta\text{-Ca}_3(\text{PO}_4)_2$.

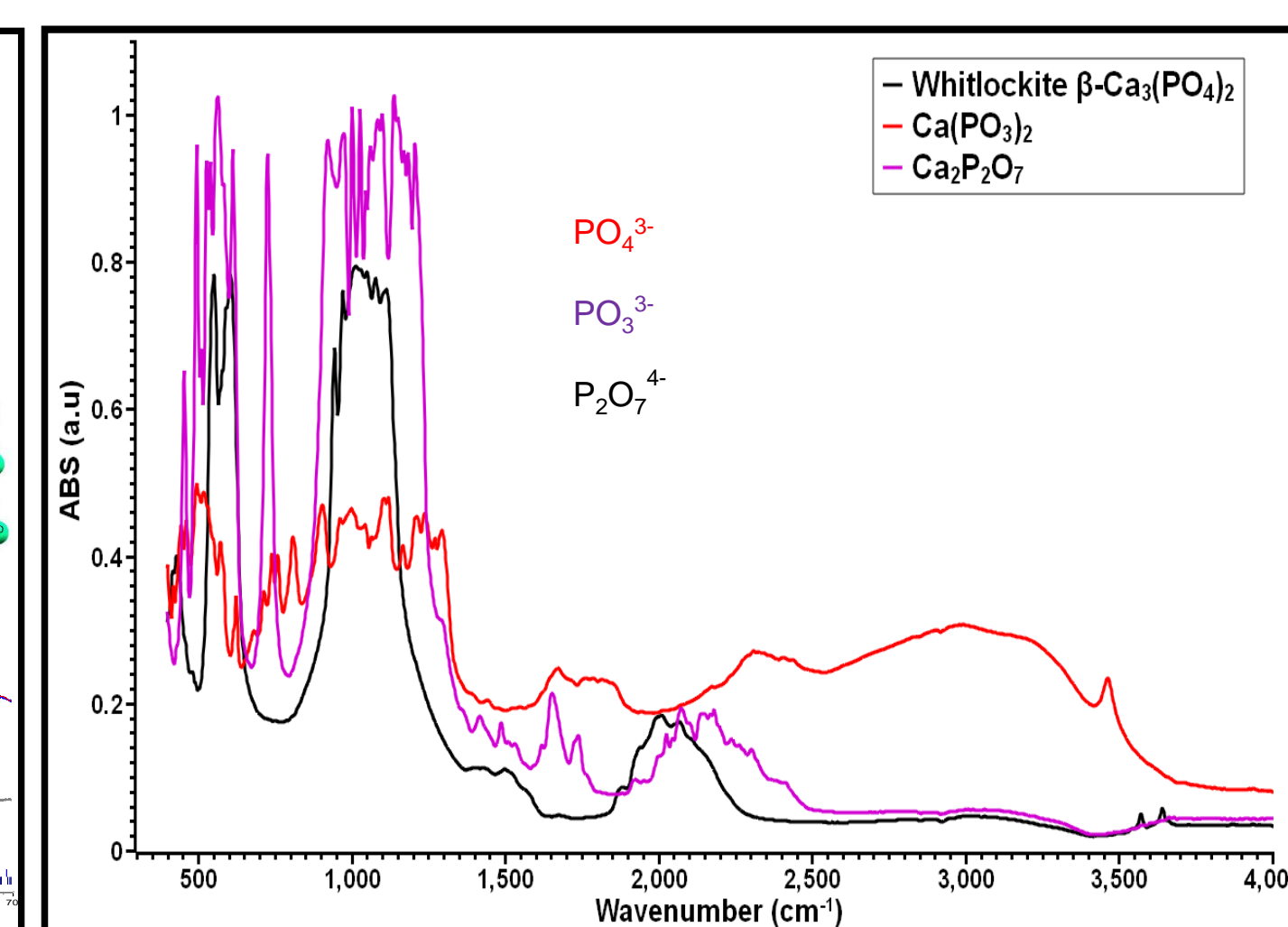


Figure 3. FTIR spectra of different phosphates.

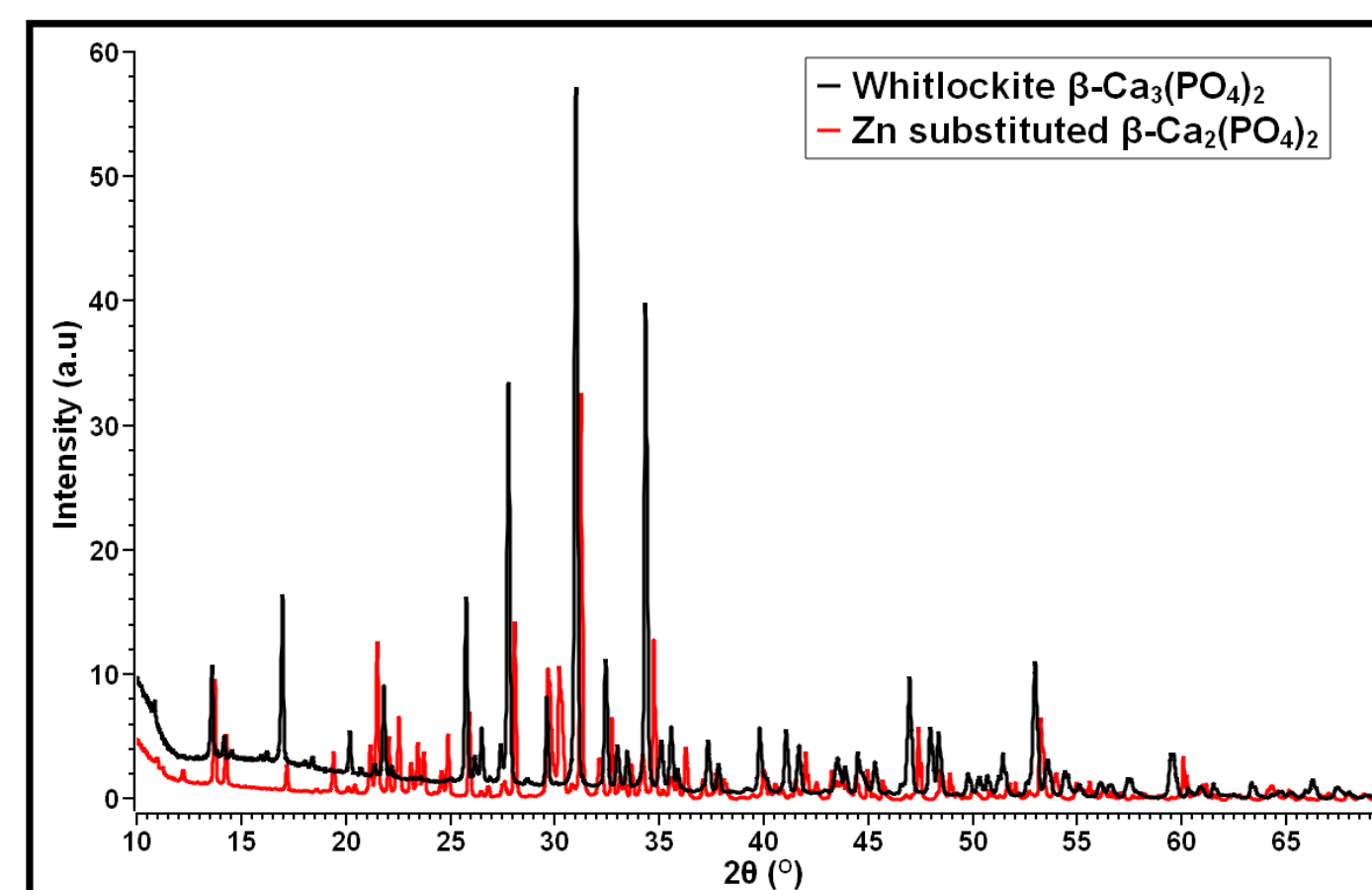


Figure 4. XRD patterns of whitlockite $\beta\text{-Ca}_3(\text{PO}_4)_2$ and Zn-substituted $\beta\text{-Ca}_3(\text{PO}_4)_2$ (solid solution of $\text{CaZn}_2(\text{PO}_4)_2$ and $\text{Ca}_{19}\text{Zn}_2(\text{PO}_4)_{14}$).

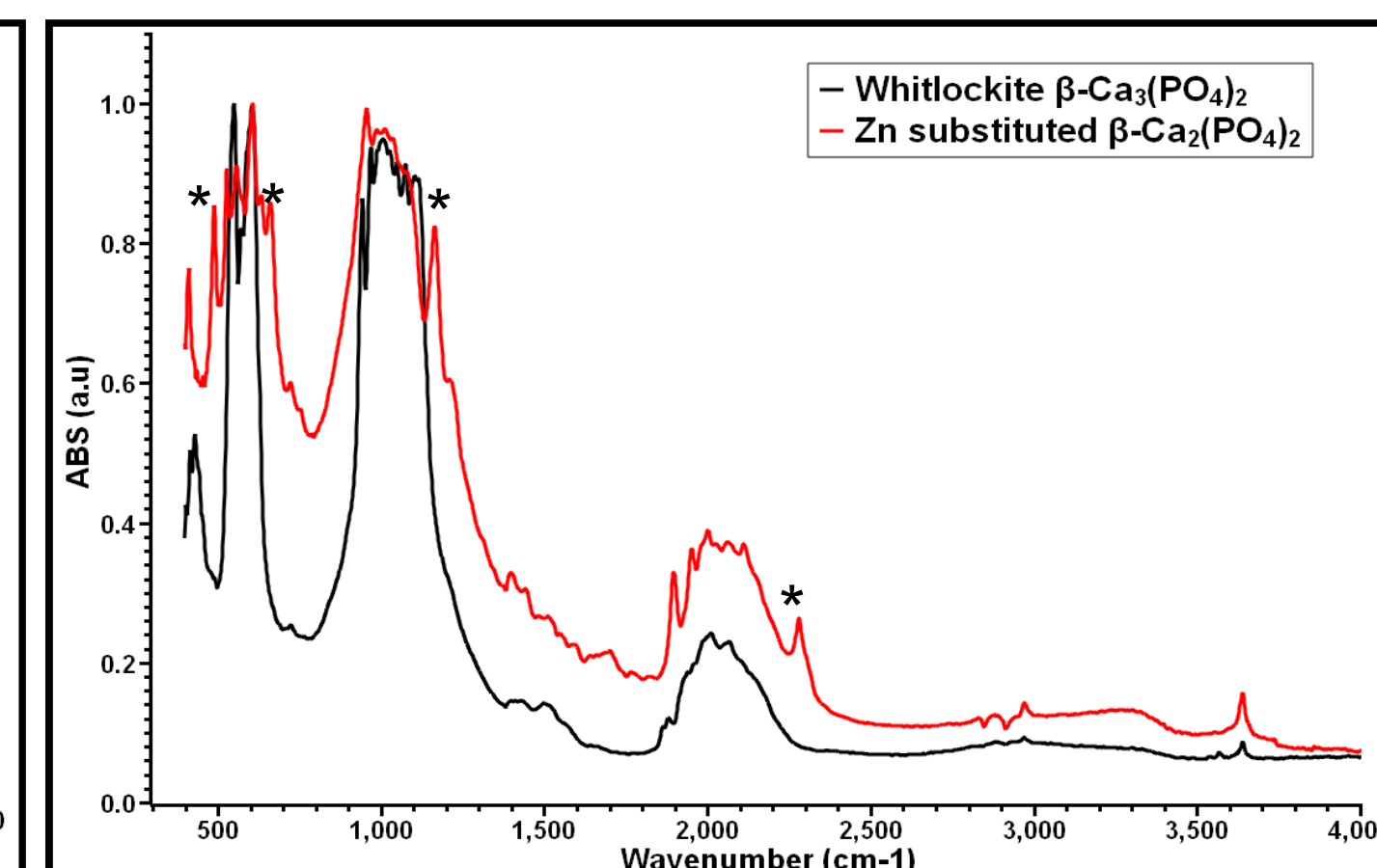


Figure 5. FTIR spectra of whitlockite $\beta\text{-Ca}_3(\text{PO}_4)_2$ and Zn-substituted $\beta\text{-Ca}_3(\text{PO}_4)_2$.

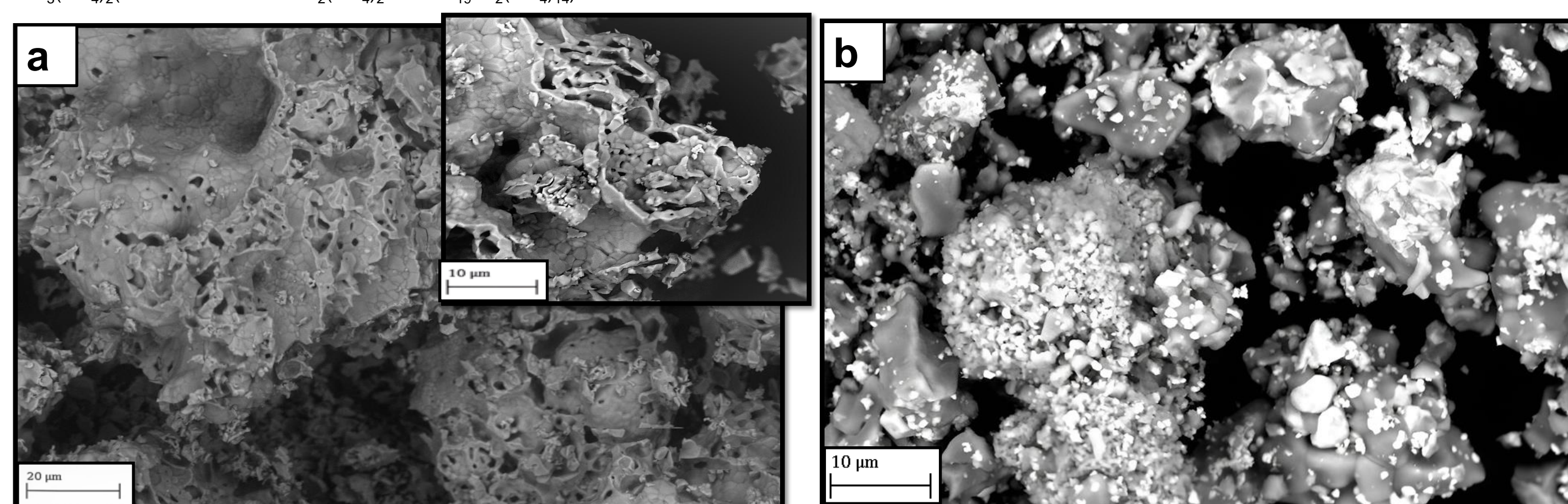


Figure 6. SEM images (BSD) of (a) whitlockite $\beta\text{-Ca}_3(\text{PO}_4)_2$, (b) Zn-substituted $\beta\text{-Ca}_3(\text{PO}_4)_2$.

Discussion

From the preliminary results, the incorporation of Zn into the whitlockite $\beta\text{-Ca}_3(\text{PO}_4)_2$ structure led to the formation of a solid solution consists of two phases ($\text{CaZn}_2(\text{PO}_4)_2$ and $\text{Ca}_{19}\text{Zn}_2(\text{PO}_4)_{14}$) which agrees with the phase diagram of ref [4]. This is evident in the XRD pattern of fig.4; the changes in the peaks position and the present of new peaks suggests the presence of the mixed solid solution mentioned above. Moreover, the FTIR spectrum (fig.5) of the Zn substituted phosphate shows additional peaks assigned as (*) in the region (400-2400 cm^{-1}) and at 2400 cm^{-1} . These new peaks as well as the broadening of the peaks in that region indicate the change in the chemical composition of the whitlockite $\beta\text{-Ca}_3(\text{PO}_4)_2$ induced due to Zn inclusion. In the SEM images of Fig.6, the chalky morphology of the pure whitlockite $\beta\text{-Ca}_3(\text{PO}_4)_2$ is evident. Moreover, from fig. 6b it can be noticed that there are two different phases in the Zn substituted phosphate. This confirms the results obtained by XRD analysis. The elemental distribution mapping (not shown here) of this compound confirmed the presence of Zn in composition. These results are preliminary and yet to be scrutinized, validated and discussed elsewhere. In addition, further work will be devoted to understand the speciation of P and whether the HM are associated in phosphates in ash fractions.

References

1. Jupp, A. R., Beijer, S., Narain, G. C., Schipper, W., & Slootweg, J. C. (2020). Phosphorus recovery and recycling – closing the loop. *Chemical Society Reviews*, 49, 87-101. <https://doi.org/10.1039/D0CS01150A>
2. Garske, B., Stubenrauch, J., Ekardt, F. Sustainable phosphorus management in European agricultural and environmental law. *RECIEL*. 2020; 29: 107– 117. <https://doi.org/10.1111/reel.12318>
3. European Commission. Critical Raw Materials Resilience: Charting a Path towards Greater Security and Sustainability. COM/2020/474 final 2020
4. Kreidler, E. R., & Hummel, F. A. (1967). Phase equilibria in the system calcium phosphate-zinc phosphate. *Inorganic Chemistry*, 6(3), 524-528

Swedish Research Council Grant No. 2017-05331 is acknowledged for supporting this work.