

Nanoscale mapping of oceanic crust samples from Rainbow hydrothermal vent field: Apatite characterization as a bioavailable phosphorus source

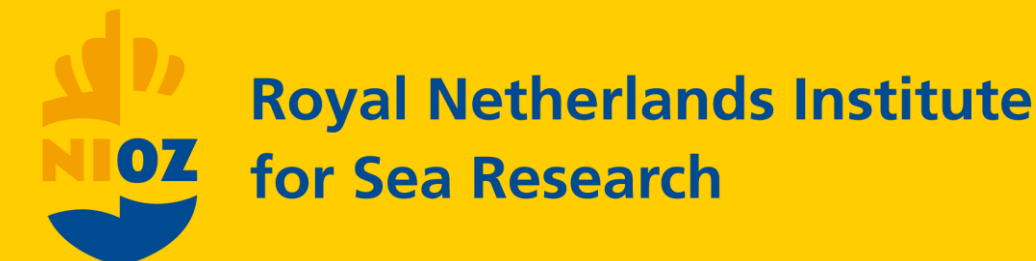
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Background and knowledge gaps:

A cruise (64PE441-NICO leg 12, July 16th – July 25th, 2018) through the Mid-Atlantic ridge transited over the serpentine hosted Rainbow vent field (Figure 1), sampling a chimney slope. Among the rock samples retrieved, one revealed a Calcium and Phosphorus phase with a tabular hexagonal morphology resembling apatite $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$, to our knowledge never recorded in such a mafic environment.

Hydrothermal Vent fields have recently been in the spotlight in origin of life studies. High (~300°C) temperatures and catalytic properties of the vent fluids promote Fischer-Tropsch (FTT) type reactions, leading to abiotic hydrocarbon synthesis (Figure 2). A long-standing question however is the supply of certain minor elements. Although these settings are enriched in relevant transition metals, one element that is not easily accounted for is **Phosphorus**: essential in metabolic processes yet not commonly found in meaningful quantities as a bioavailable (ortho)phosphate compound in aqueous media.

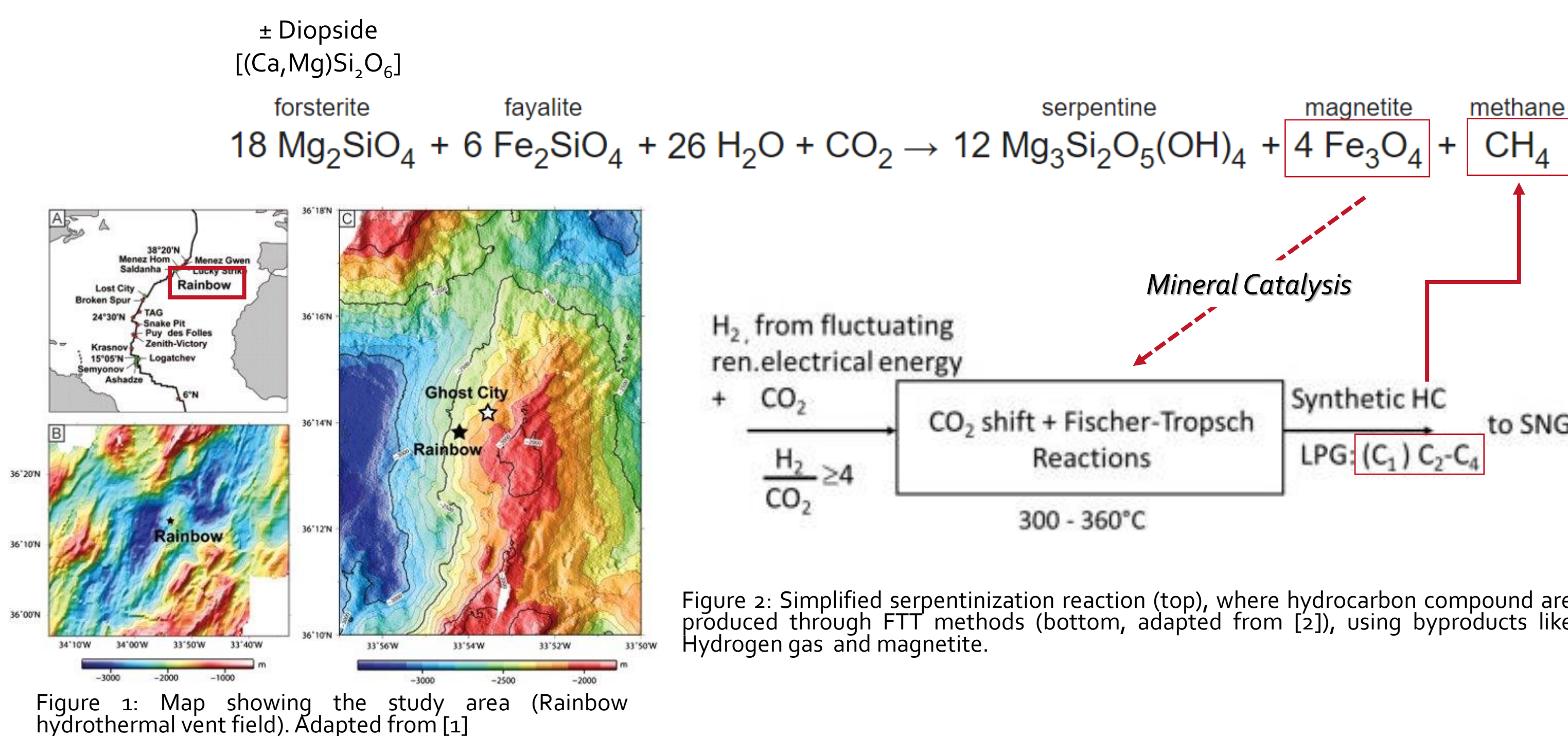


Figure 1: Map showing the study area (Rainbow hydrothermal vent field). Adapted from [1]

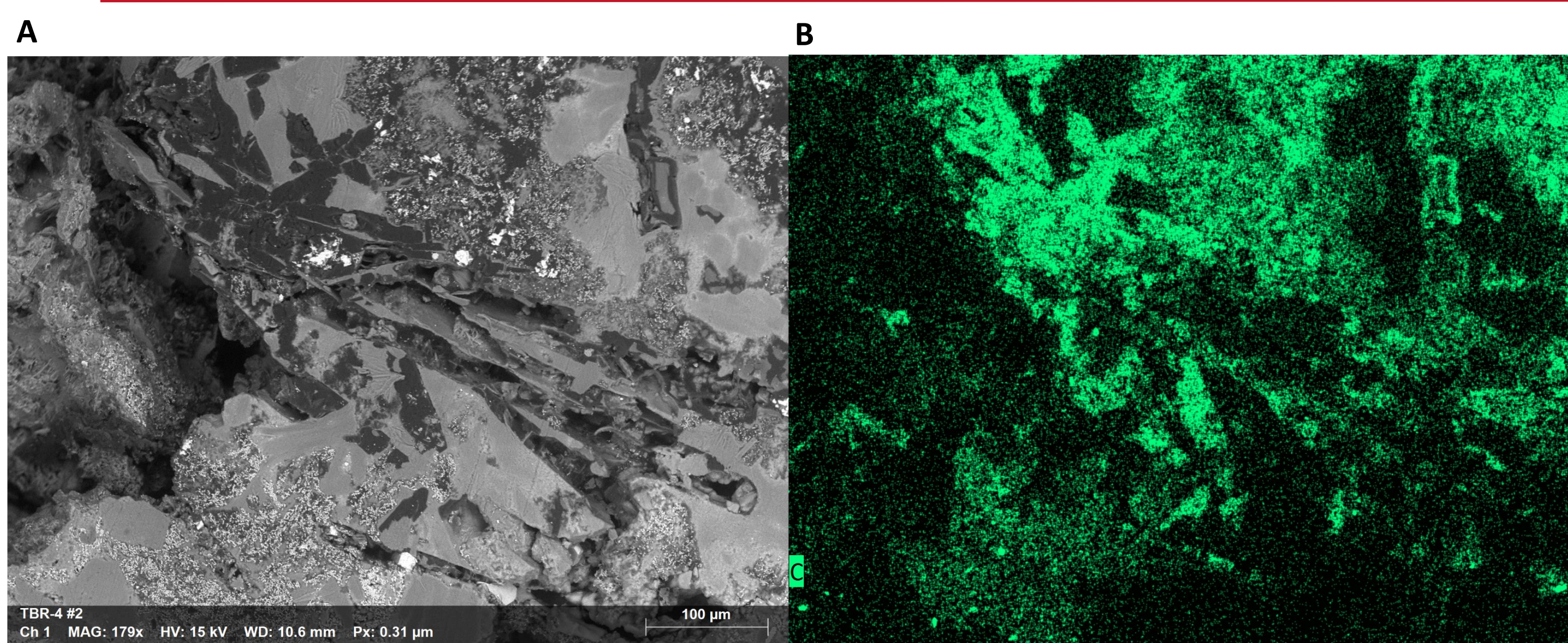


Figure 4: SEM image (A) of a Condensed Carbonaceous Mass found, and its respective elemental map (B). The absence of O in multiple analysis cements that this is not likely abiogenic phase.

Conclusions:

EDX and Raman data substantiates the classification of apatite, likely formed through hydrothermal precipitation, in support:

- Small, equigranular and present always inside porosity support fluid intrusion, not a part of the original paragenesis.
- Stronger similarities to Hydroxyapatite (Figure 6), suggesting stronger similarities to seawater composition. Moreover, the “drip experiment” demonstrates this phase would’ve been in equilibria with Rainbow plume pH, and thus may have precipitated from it.
- The internal “spongy” texture suggests non-equilibria precipitation. Considering it is a single phase (Ap in Fig.5.D), these are likely remnants from nucleation clusters aggregated with oriented attachment.

The influence of iron in the system is beyond expected. Apatite grains appear often associated with Iron oxy-hydroxides (Figure 3.B and 3.D), and may even predate it, as Figure 5.E suggests. Moreover, abundant Condensed Carbon masses were found, a signal that these FTT reactions may not only be taking place in the plume [3] but also on the seafloor.

The presence of a crystalline phosphate phase appeals to the theory of heterogeneous uptake, and the mineral surface catalysis the removal from its own structure. Nevertheless, uptake from solution may be possible when sufficiently close to the vent opening, as solubility of orthophosphate compounds greatly increases with decreasing pH (Figure 8). This discovery could divert attention to acidic hydrothermal vent systems, as serpentinizing systems may provide not only the necessary short-chain hydrocarbons, but also a phosphorus source in two forms.

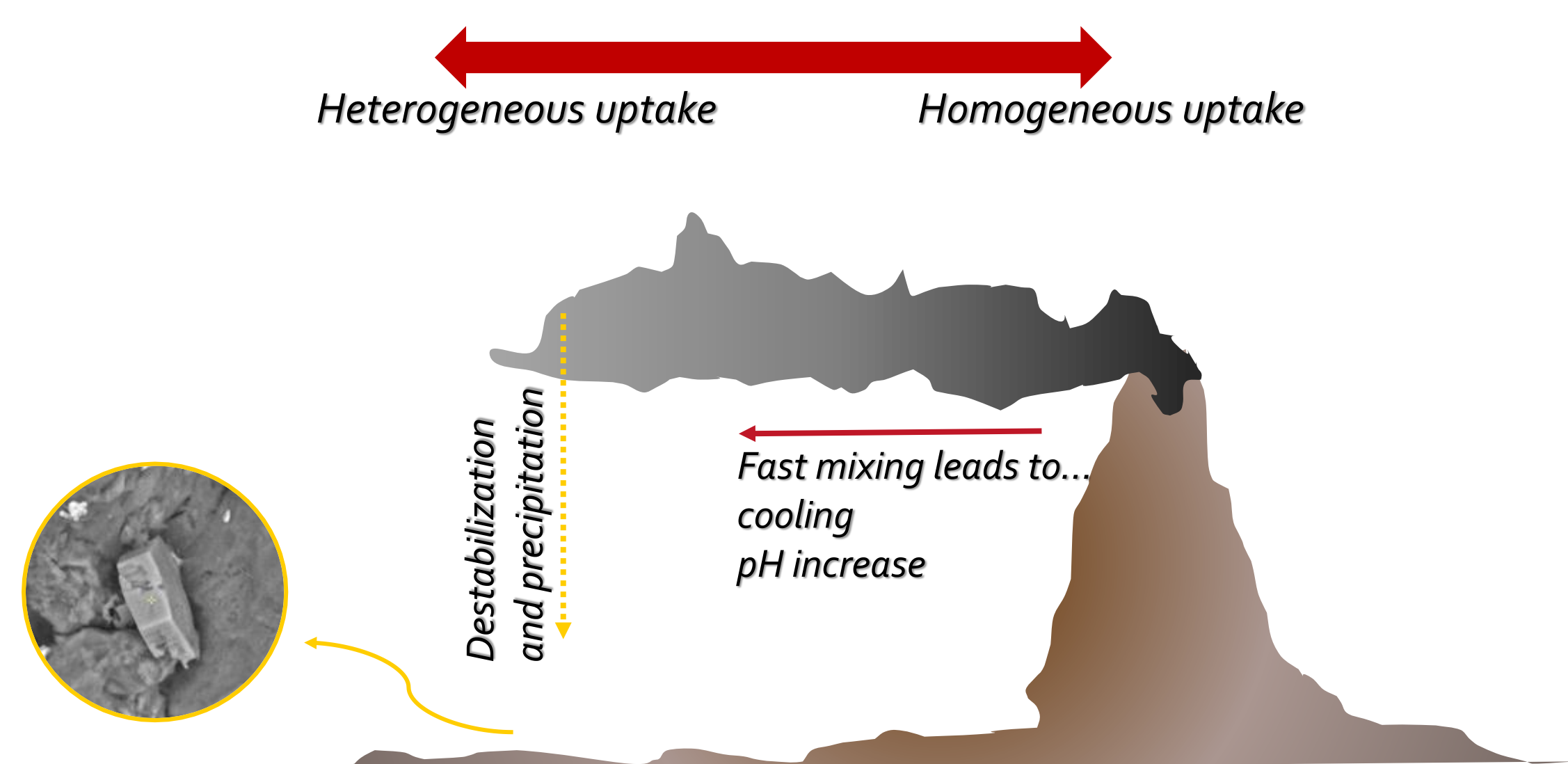


Figure 8: Schematic illustrating the distal effect discussed above.

The source of this Phosphorus is unknown. Authors^[3] sustain the existence of a brine at depth in Rainbow that could, through phase separation, retain mobile elements such as Cl, F, P and REE. In the future, more detailed plume water analysis should be conducted, and more chimney samples analysed, to constrain the origin and extent of this mineralization.

Objectives:

Full characterisation of the Phosphorous phase present was the priority, motivated by its novelty in a serpentinising environment. For this, chemical composition, mineral structure and relation to its surroundings were studied to justify its origin and possibility of biological uptake.

Moreover, the catalytic potential of Rainbow vent plumes is of interest. Is there was a catalytic mineral present capable of promoting FTT reactions?

Methods and Results:

➡ Morphological and chemical characterisation: Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray spectroscopy (EDX);

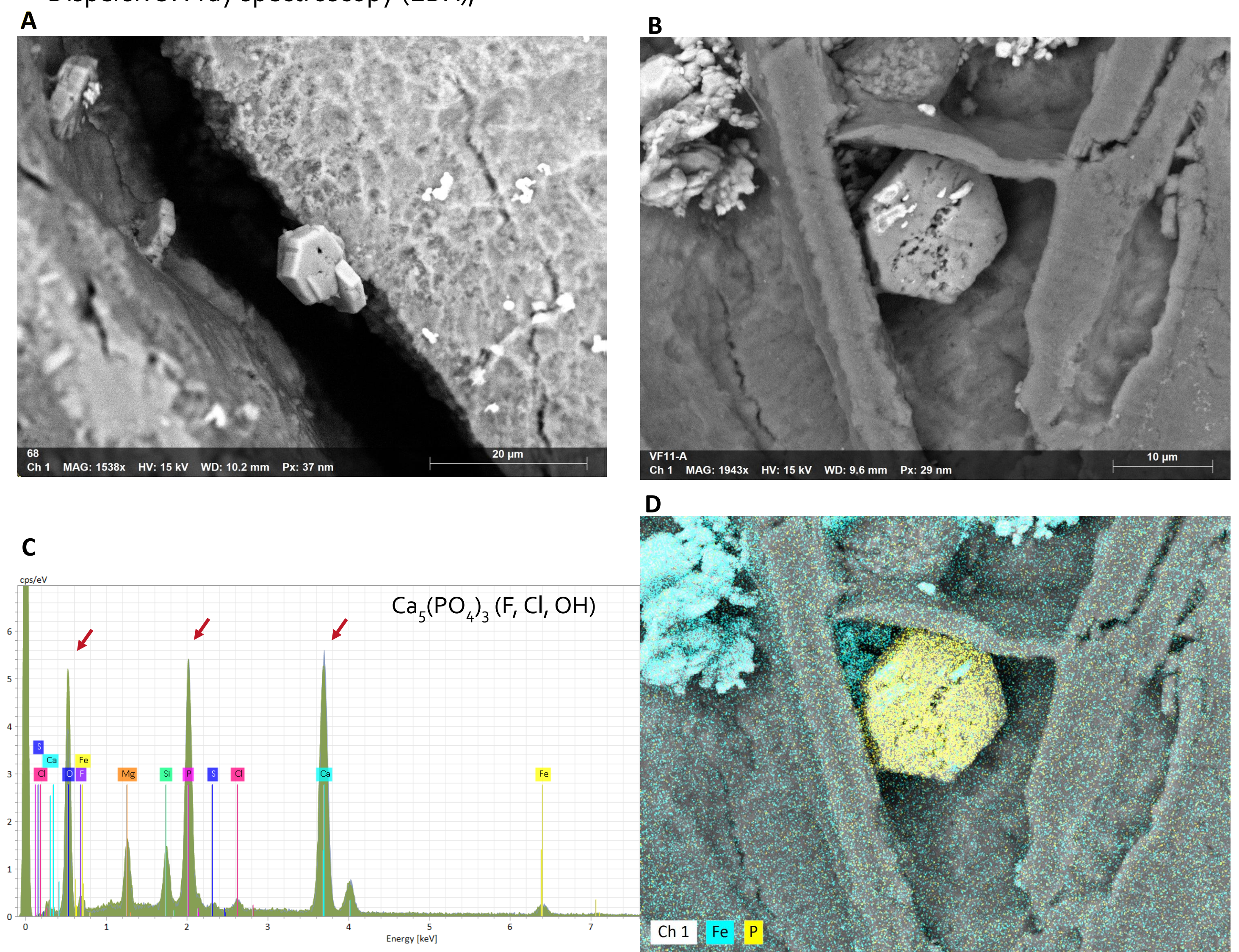


Figure 3: Data compilation from SEM sessions. C shows an EDX spectra of an average grain, such as those represented in A, B and D. The chemistry aligns well with the proposed apatite.

➡ Detailed chemistry and morphology: Transmission Electron Microscopy (TEM) on an extracted representative grain.

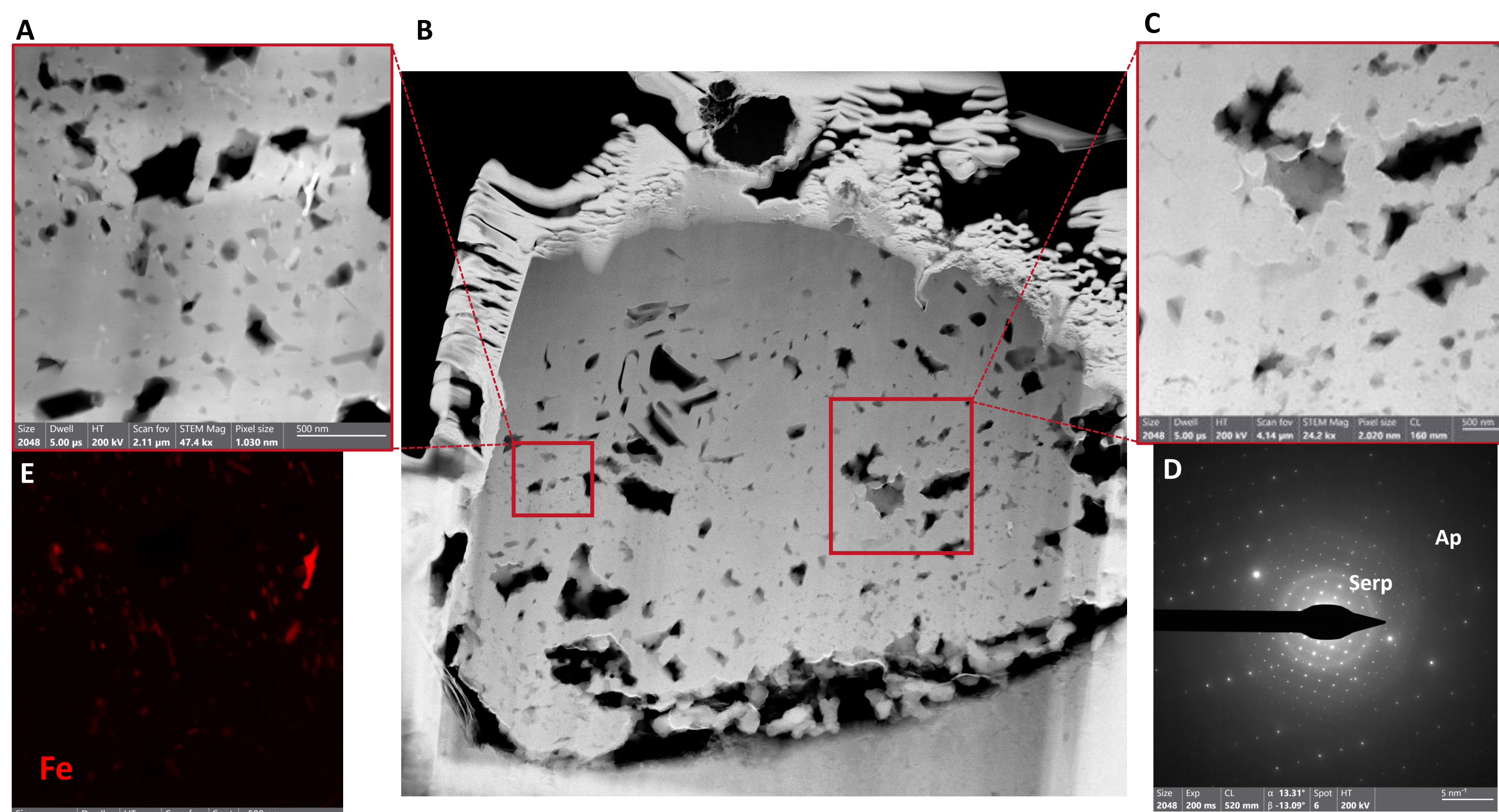


Figure 5: Data compilation from the TEM session. In the center (B), the rain overview. The imperfect, botryoidal structure can be seen in detail in C. D shows a representative diffraction pattern of the bulk grain, with a serpentine signal in the center and phosphate phase at the periphery. Finally, A and E show in detail the relationship between Iron clusters and the phosphate phase, the latter being a Fe channel elemental map.

➡ Chemical bonding: Raman spectroscopy

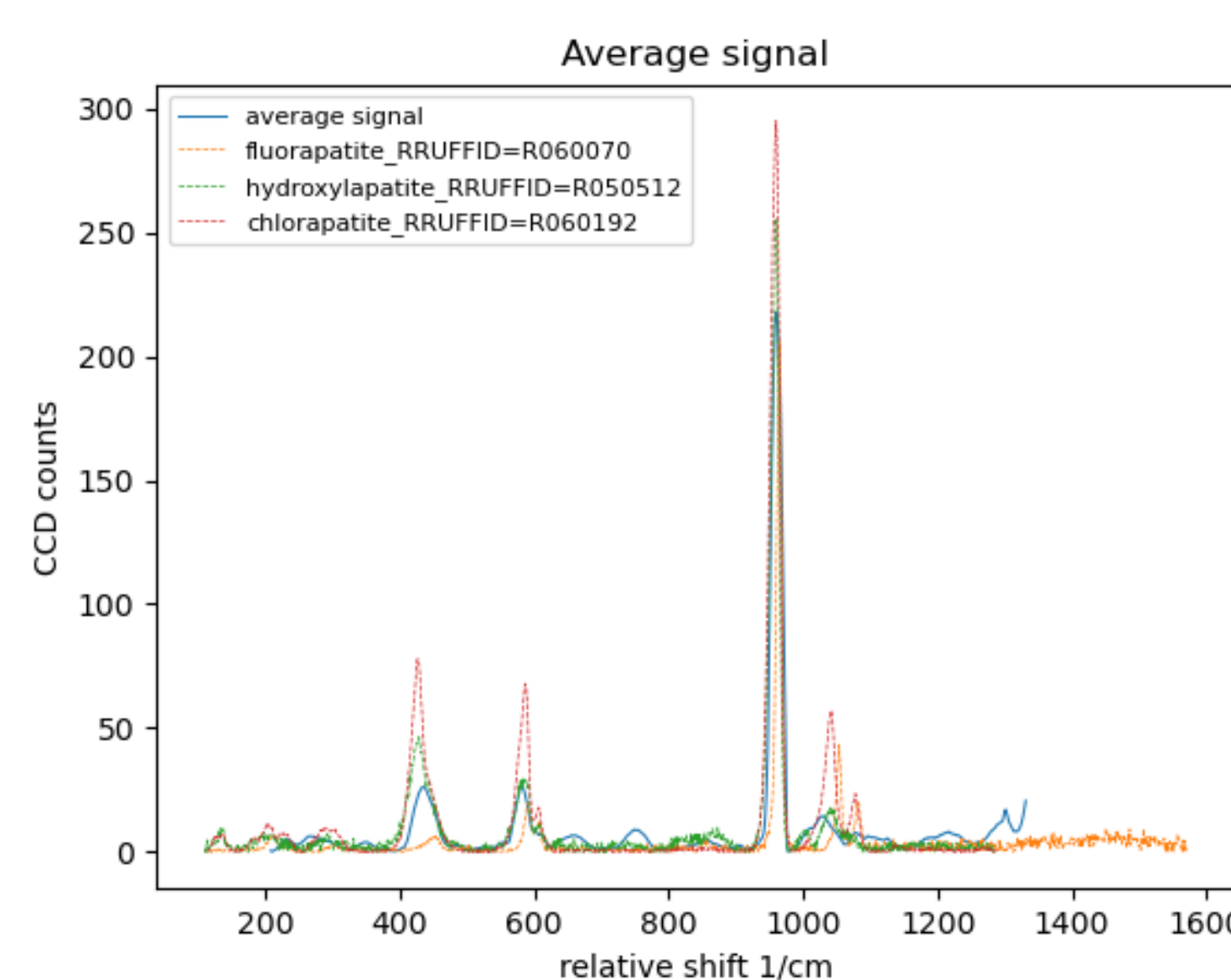


Figure 6: Raman spectra plotting an averaged signal obtained from measurements against known apatite group signals found in databases.

➡ Equilibria (“drip”) experiment

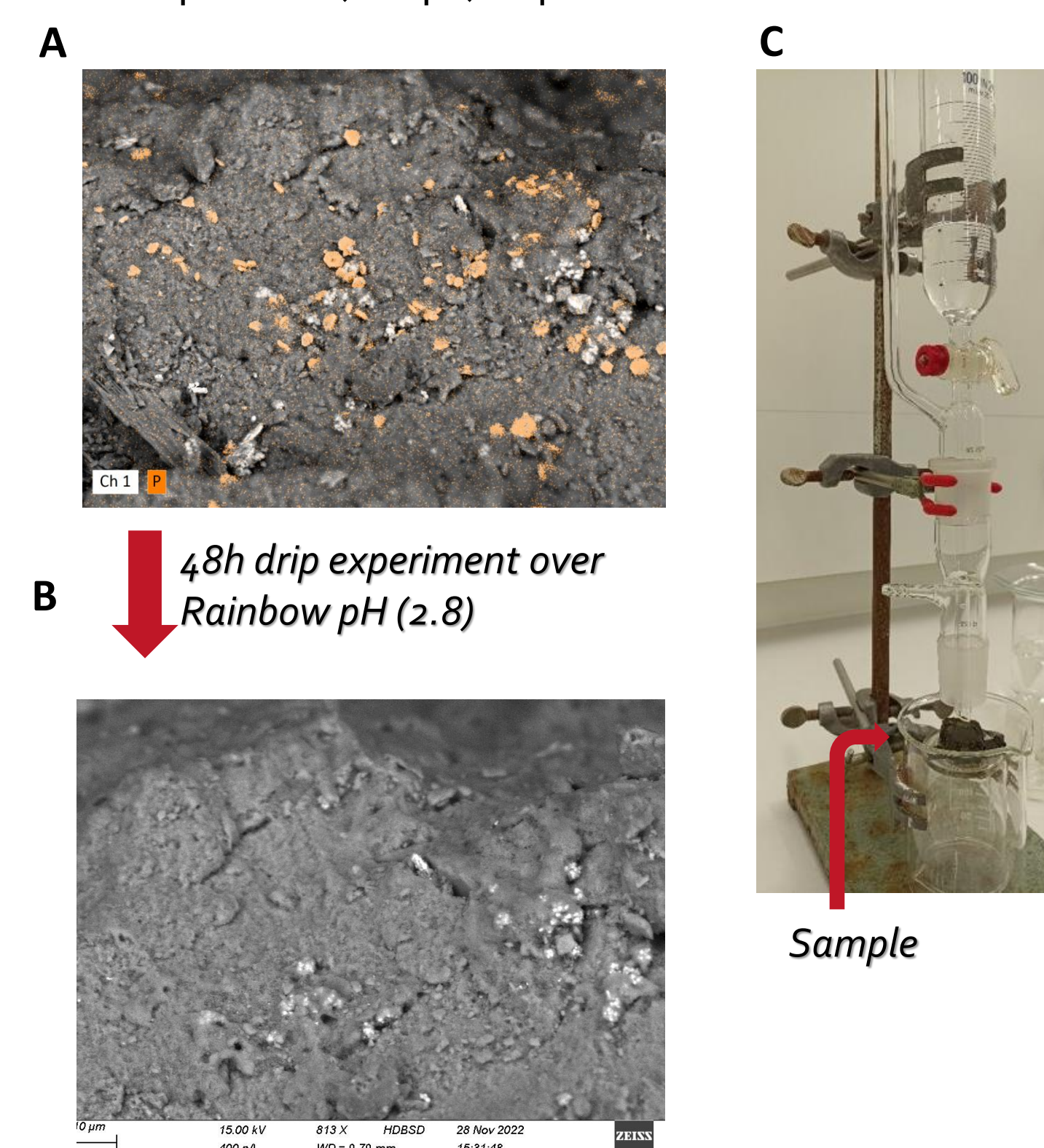


Figure 7: Acid drip experiment results (A-B) and setup (C). It can be seen from image 7.B that hexagonal grains are absent after the acid exposure.