

X-ray absorption spectroscopy of condensed sugar-phosphates

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1 Introduction

One of the most important acids in biological systems is phosphoric acid (H_3PO_4) that is usually present in its ionized form, phosphate (PO_4^{3-}). Phosphate is a key element in building blocks of life; forming the nucleic acids DNA and RNA, as phosphodiester backbone [1]. ATP (adenosine triphosphate), an anhydride of phosphoric acid acts as energy storage and transfer within the cell. Phospholipids consisting of two fatty acid tails and a phosphate group head are the structural basis of all cell membranes. Despite importance of phosphate compounds in biological systems, their electronic structures are less understood than those of inorganic phosphates. In order to understand electronic structures of condensed sugar-phosphates, X-ray absorption spectroscopy (XAS) spectra were measured near the P *K*-edge.

2 Experiment

Experiments were performed at beamline BL-27A with an InSb(111) double-crystal monochromator with an energy resolution of ca. 0.8 eV around P *K*-edge. The XAS spectra of polycrystalline thymidine 5'-monophosphate calcium salt (TMPCa), thymidine 5'-monophosphate disodium salt (TMPNa₂), and α -tricalcium phosphate (α -Ca₃(PO₄)₂: α -TCP) were measured using monitoring sample drain current near the P *K*-edge (2145–2185 eV) and normalized to the incident flux with a thin aluminum film detector downstream of the sample chamber. Such energies were chosen to excite the P 1*s* core electron to 3*p* and 4*p* unoccupied orbitals. The X-ray energy was calibrated by reference to the lowest sharp peak of tetraphenylphosphonium bromide (PPh₄Br) as 2147.8 eV.

3 Results and Discussion

Fig. 1 shows P *K*-edge XAS spectra of polycrystalline TMPCa, TMPNa₂, and α -TCP. TMPNa₂ has deliquescence property and absorbed moisture from the atmosphere during mounting, transforming into gel phase before entering vacuum chamber. Based on previous study [2], peak A is assigned to P 1*s* \rightarrow 3*p* transition. Peak B and C are assigned to P 1*s* \rightarrow P-O-P chains in condensed phosphates corresponds to a chemical variation in the 2nd coordination sphere of P. Features of peak A in TMPCa and TMPNa₂ are resemble in each other but the peak position of TMPNa₂ is slightly shifted to higher energy (\sim 0.2 eV) than that of α -TCP. This shift would be caused by difference in P oxidation states, which depends on the charge density of counterions and crystalline structures.

The shoulder peak B is slightly observed in both TMPCa and TMPNa₂, as broad features. The intensity of peak B in TMPCa is larger than that in TMPNa₂. The result is in agreement with the case of inorganic phosphates, where Na salt shows only small amount of peak B. In general, peak B and C are characteristic signatures of Ca-P and extensively used as distinct fingerprints for Ca-phosphates in minerals [3]. The peak C was not observed in TMPNa₂ but very slightly in TMPCa. This suggests that structural configurations are more effect to produce the peak C. The mechanisms of interaction between metal cations and sugar-phosphates will be investigated further.

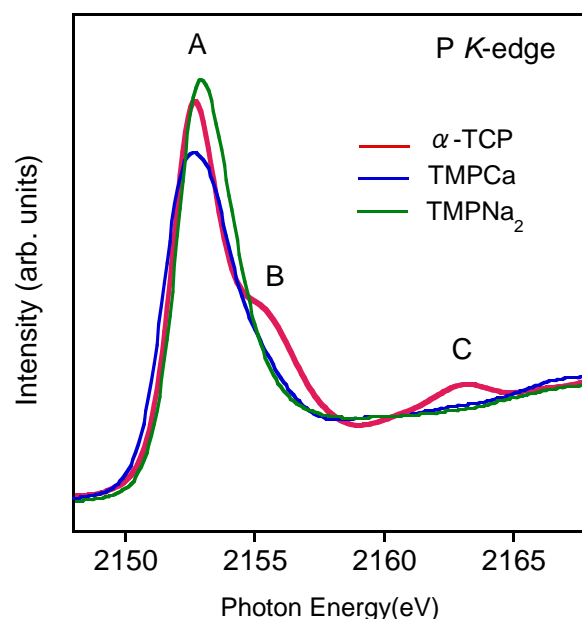


Fig. 1: P *K*-edge XAS of polycrystalline TMPCa (blue spectrum), TMPNa₂ (green spectrum), and α -TCP (red spectrum).

References

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