



Estonian Journal of
Earth Sciences
2023, 72, 1, 34–37

<https://doi.org/10.3176/earth.2023.12>

www.eap.ee/earthsciences
Estonian Academy Publishers

SHORT COMMUNICATION

Received 27 March 2023
Accepted 31 March 2023
Available online 9 June 2023

Keywords:

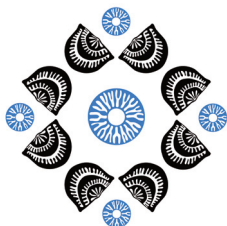
phosphorites, sedimentary apatite,
brachiopods, carbonate fluorapatite,
biomineralisation, early diagenesis

Corresponding author:

Sophie Graul
sophie.graul@taltech.ee

Citation:

Graul, S., Kallaste, T., Moilanen, M.,
Ndiaye, M. and Hints, R. 2023. Early
diagenetic transformation stages
revealed by micro-analytical studies of
shelly phosphorites, Rakvere region.
Estonian Journal of Earth Sciences, 72(1),
34–37. <https://doi.org/10.3176/earth.2023.12>



14TH ISOS
ESTONIA 2023

Early diagenetic transformation stages revealed by micro-analytical studies of shelly phosphorites, Rakvere region

Sophie Graul^a, Toivo Kallaste^a, Marko Moilanen^b,
Mawo Ndiaye^a and Rutt Hints^a

^a Department of Geology, Tallinn University of Technology, Ehitajate 5, 19086 Tallinn, Estonia

^b Oulu Mining School, University of Oulu, P.O. Box 3000, FI-90014 Oulu, Finland

ABSTRACT

Furongian–Tremadocian phosphorites of Estonia are sandstone rich in biogenic apatite, represented by brachiopod detritus. The study focuses on the mineralogical and micro-analytical characterisation of phosphorites from the Aseri, Toolse, and Kabala deposits based on FE-SEM and EPMA analyses. The shell fragments are composed of alternating compact and porous laminae, but with considerably poor preservation of pristine textures, superseded by the formation of authigenic CAF-apatite during the early diagenesis. In all settings, the shells showed preferential uptake of Sr into the porous cryptocrystalline laminae. The altered areas are composed of massive apatite crystallites with Mn-enriched layers. They are frequently covered with pyrite, indicating progressive recrystallisation under the influence of interstitial fluids and fluctuations in redox gradients in coastal environments.

Introduction

In sedimentary phosphorites, P₂O₅ can occur in several forms, such as fossilised bones, nodules, or other biochemogenic phosphates (Godet and Föllmi 2021). The precipitation of biochemogenic phosphates in marine sediments is restricted to the transition zone between oxic and suboxic environments close to the sediment–water interface. The most common phosphate encountered belongs to the apatite mineral group, with cryptocrystalline carbonate fluorapatite (CAF-apatite), also referred to as ‘francolite’, dominating in the occurrence of cryptocrystalline grains (Lécuyer et al. 1998; Ptáček 2016). Francolites are non-stoichiometric minerals with the generalised formula (Ca_{10-a-b}Na_aMg_b(PO₄)_{6-x}(CO₃)_{x-y-z}(CO₃F)_y(SO₄)_zF₂) and numerous structural and chemical variations. Chemical substitutions can occur in all its lattice sites (the two Ca²⁺ sites, PO₄³⁻ and F⁻) (McLennan 2001; Veiderma et al. 2005). Bioapatites, another sedimentary apatite source, originate from phosphate biomineralisation of the hard skeleton of vertebrates and some invertebrates. For the precipitation of vertebrate bones and teeth, the nucleation by proteins and macromolecular matrices provides casts that control crystal growth. Such processes presumably also control the segregation of the skeleton of invertebrates (Trappe 1998). In inarticulate brachiopods, direct biomineralisation occurs as precipitation of phosphate to stabilise the exoskeletons. Their shells are initially composed of hard tissues, amorphous hydrogels, phosphate precipitates, and organic matter (Lowenstam and Weiner 1989). Post-mortem, during the diagenesis, the biogenic phosphatic matter chemically evolves toward CAF-apatite composition through various substitutions, together with an increase in crystallite size and formation of authigenic apatite phases (Trappe 1998). However, such alteration pathways are still only fragmentally understood (Ferretti et al. 2021).

The shelly phosphorites found in northern Estonia were deposited during the Cambrian–Ordovician transition in the coastal zone of a shallow, epicontinental sea (Heinsalu and Viira 1997; Nielsen and Schovsbo 2011). They belong to the Kallavere Formation, which spreads over most of northern Estonia and parts of the Leningrad region in northwestern Russia (Fig. 1; Kaljo et al. 1988). The Kallavere Formation in the study area has low thermal maturity. It exhibits no evidence of hydrothermal influence due to overall tectonic stability and shallow burial of the region (Kirsimäe

et al. 1999). The mineral matter of loosely cemented rock comprises quartz and phosphatic detritus, composed of lingulid remnants, and is enriched in rare earth elements (REE) and Sr. The abundance of phosphatic detritus and the presence of organic-rich mudstones have been interpreted to reflect a nutrient-rich palaeoenvironment with high primary productivity (Artyushkov et al. 2000; Baturin and Ilyin 2013). Previous studies have shown that shelly phosphorite deposits are highly variable in the mineralisation characteristics of phosphates, the type of accessory phases, the state of preservation, and consequently are likely to reflect alteration under somewhat different diagenetic environments (Nemliher and Puura 1996; Lang et al. 2015; Lumiste et al. 2021; Vinn et al. 2021).

This contribution aims to decipher the diagenetic transformation pathways in shelly phosphorites by combining textural analyses and geochemical mapping with a field emission scanning electron microscopy (FE-SEM) and a field emission electron probe micro-analyser (EPMA). We focus on distributions of P, Mn, Fe, and Sr to trace diagenetic variations in brachiopod fragments, along with the microstructures of the shells and associated carbonate cement. All selected minor compounds could fit into Ca^{2+} sites of apatite. Due to the same ionic charge and the close radii of Sr^{2+} to Ca^{2+} , such uptake is expected to take place readily, starting in vivo and continuing during post-deposition together with F^- uptake to bioapatite lattice (Trueman and Tuross 2002; Martin and Scher 2004). Mn and Fe (oxy)hydroxides are known to be major carrier phases transporting P to the sea bottom and releasing bounded P to sediments in the course of reduction and thus supporting diagenetic phosphatisation.

Materials and methods

The 21 studied samples originate from five drill cores within the Toolse, Kabala, and Aseri deposits (Fig. 1). The Kallavere Formation was sampled across its entire section in the new

cores of Toolse and Aseri, in the framework of broader geochemical research on REE resources of phosphorites (Graul et al. in press). Additional spot samples from previous studies were included from the Kabala deposit. The materials were prepared as thick sections for micro-analytical investigations using cold-curing resin. The textural analysis was performed at the Center for Material Analysis, University of Oulu. FE-SEM investigations of selected carbon-coated polished thick sections were conducted on a Zeiss ULTRA plus instrument using a backscattered electron detector (AsB). Quantitative wavelength dispersive spectrometer (WDS) analysis of major and trace elements was performed with a JEOL JXA-8530F Plus (EPMA). The following analytical conditions were used for the WDS point analyses: a beam size of 5–10 μm , an acceleration voltage of 15 kV, and a current of 15 nA. The peak counting time was set at 10 seconds for the element peaks and at 5 seconds for the background measurements. The following elemental lines and standards were analysed: Fe ($\text{K}\alpha$, magnetite), Mn ($\text{K}\alpha$, Mn), P ($\text{K}\alpha$, apatite), Sr ($\text{L}\alpha$, SrF_2). Matrix correction with the ZAF iterative method was applied to all analyses. This correction considers three effects influencing the X-ray characteristics: atomic number (Z), absorption (A), and fluorescence excitation (F). For the analysis of the WDS elemental map, the following elemental lines were used: Mn ($\text{K}\alpha$), P ($\text{K}\alpha$), Fe ($\text{K}\alpha$), and Sr ($\text{L}\alpha$). A focused spot, an accelerating voltage of 20 kV, a current of 20 nA and a dwell time of 50 ms were used for measurements.

Results and discussion

The typical original valve structure of these inarticulate brachiopods displays an alternation of thin, compact laminae and thicker, baculate laminae (Fig. 2A; Cusack et al. 1999; Nemliher 2006). Baculate laminae are interpreted as remnants of the organic matrix of brachiopods, while compact laminae are interpreted as densely mineralised apatite structures (Lang

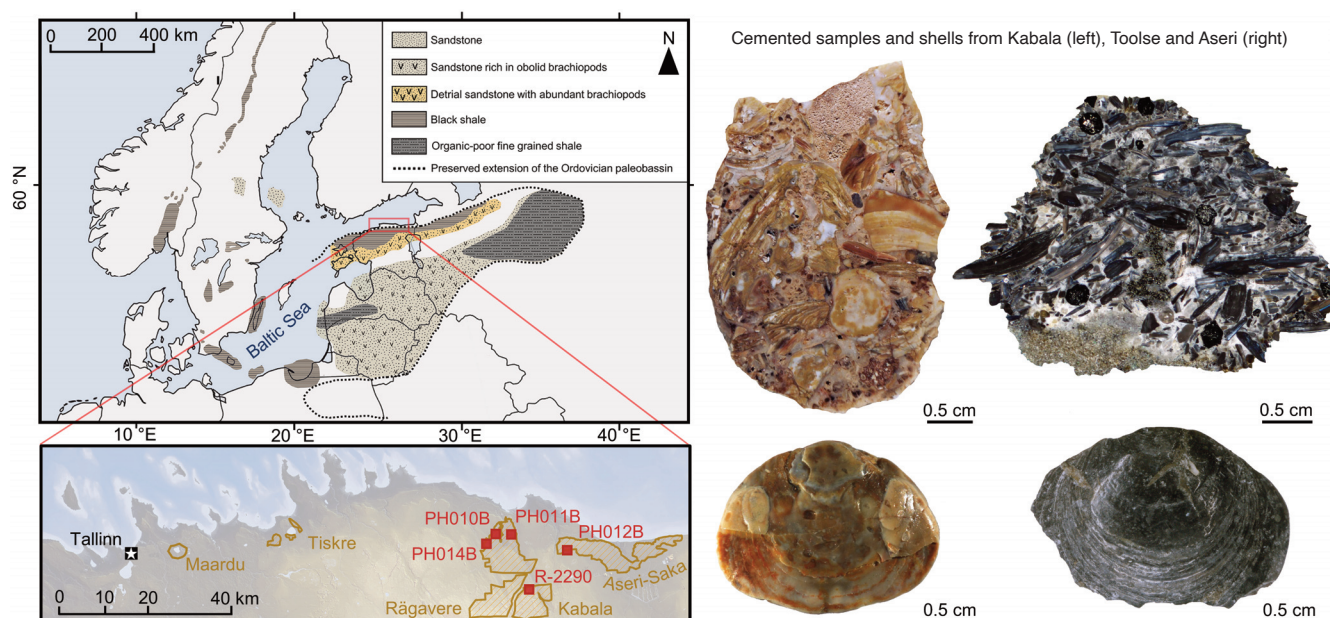


Fig. 1. Preserved extension of the Ordovician Palaeobasin, after Popov et al. (2019). Location of analysed drill cores and phosphorite deposits. Examples of analysed materials from the Kabala, Toolse, and Aseri deposits.

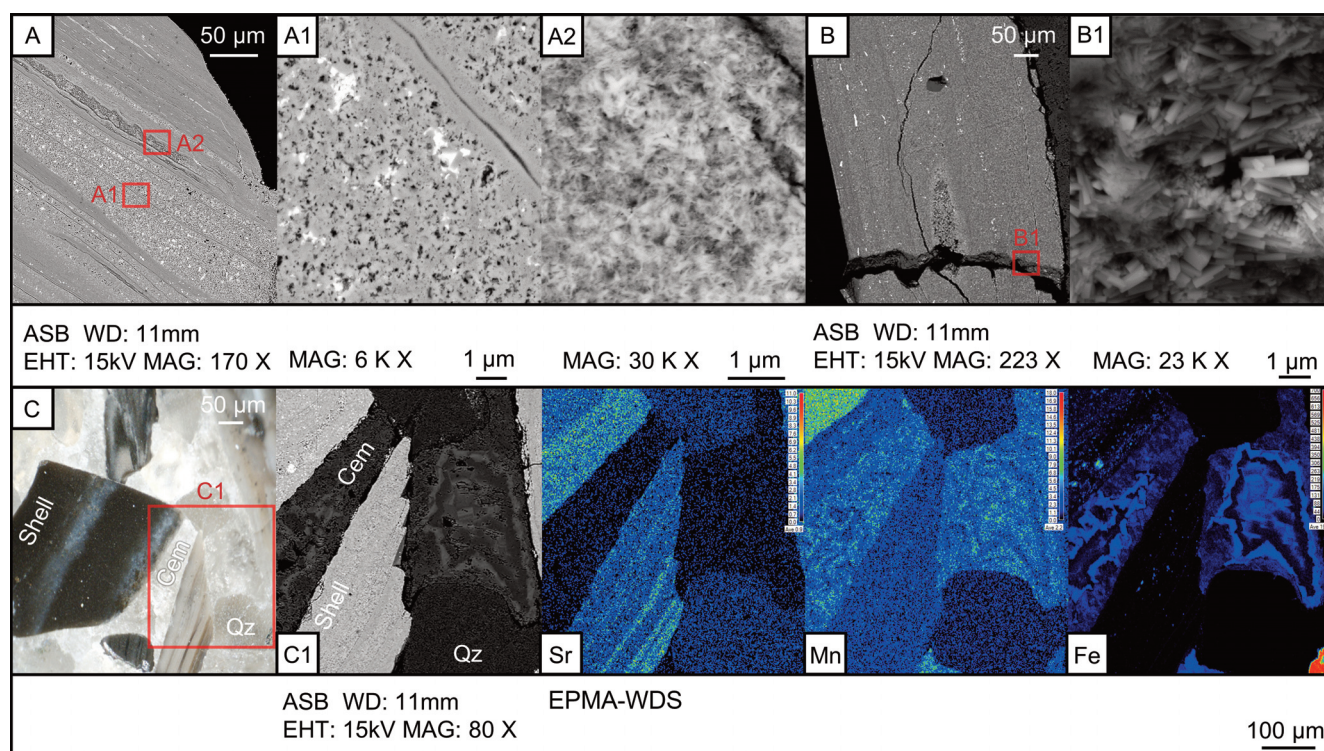


Fig. 2. SEM-AsB texture examples of shelly phosphorites. **A** – brachiopod section from the Kabala deposit. **A1** – crystallised compact laminae by phosphogenisation and diagenetic alteration. **A2** – porous baculate lamina with fibrous aggregates; **B** – fractured brachiopod section from the Toolse deposit. **B1** – tabular crystallites of CAF-apatite in a fresh fracture; **C** – optical microscopy image of an altered coquina section in carbonated cement from the Toolse deposit. Abbreviations: Qz – quartz grain, Cem – carbonated cement, Shell – shell fragments. **C1** – EPMA-WDS quantitative analysis of Sr, Mn, and Fe.

et al. 2015). However, in Toolse and Aseri, massive shell structures are abundant, indicating homogenisation of the laminae due to secondary apatite formation, with little preservation of the original material (Holmer 1989; Nemliher 2006). The presence of hydroxyapatite and authigenic CAF-apatite was reported by Nemliher et al. (2004) in Estonian lingulate shells based on X-ray diffraction analyses. The secondarily formed authigenic CAF-apatite is interpreted as the product of post-mortem phosphatisation of organic matter in the shells, combined with a later diagenetic alteration. The altered structures could be commonly identified via dark laminae with a high pyrite content in shell fragments from the Toolse and Aseri settings. Pyrite is predominantly present as microcrystals aligned along the laminae of the valve, with occasional occurrences of aggregates encasing brachiopod detritus. In some cases, secondary apatite has filled the original porosity to such an extent that it is complex to distinguish crystallites, apart from fresh fracture surfaces (Fig. 2B), indicating significant diagenetic recrystallisation. In contrast, in the Kabala deposit, Fe has been preserved in the form of goethite ($\text{Fe}^{3+}\text{O}(\text{OH})$) and brachiopod laminae tend to be considerably more porous with needle-shaped or fibrous aggregates, or compact laminates exhibiting remaining porosity (Fig. 2A). This suggests various degrees of precipitation and recrystallisation according to different rates and diagenetic conditions.

EPMA-WDS analyses demonstrate variations in the abundances of Fe, Mn, and Sr. In the Aseri and Toolse deposits, Fe is found either as microcrystalline pyrite along the shell

laminae or in concentric rims in secondary apatites formed along the edges of the quartz grains, and in carbonate cements that occur in the basal part of the Kallavere Formation (Fig. 2C). In the latter, iron presents zonal distribution. Compared to Fe, the Mn distribution appears to be more complex. Mn is also contained in zonal distribution in the phosphatic rims and the carbonate cement, but Mn also appears in significant concentrations in the dark, more altered areas of the valves. These discrepancies could indicate local variations in the degree of sulphidic conditions and the composition of the interstitial, early diagenetic pore water.

Regardless of locality, Sr is highly concentrated in the porous laminae of the brachiopod detritus and minimally distributed in other parts of shells or carbonate cement. This most likely suggests a major early uptake by poorly crystalline bioapatite with a high surface area controlled by Sr:Ca ratio of the seawater and adsorption onto crystallite surfaces (Trueman et al. 2002). As Sr uptake has shown to considerably strengthen hydroxyapatite-type phases, this process might have been significant for the preservation of originally organic-rich laminae in brachiopod valves.

Conclusions

The brachiopod fragments of Estonian phosphorites from the Rakvere phosphorite region are dominated by packed structures, with little preservation of original laminae textures overprinted by the formation of secondary CAF-apatite. The degree of diagenetic alteration varies between localities, as

well as the distribution patterns of Sr, Fe, and Mn, which are subject to local redox conditions. The high primary productivity and steep redox gradient close to the sediment-water interface allowed extensive authigenic apatite growth and extensive recrystallisation upon deposition and early diagenesis.

Acknowledgements

This study was supported by the ERDF and the Estonian Research Council via project RESTA23. The publication costs of this article were partially covered by the Estonian Academy of Sciences.

References

- Artyushkov, E. V., Lindström, M. and Popov, L. E. 2000. Relative sea-level changes in Baltoscandia in the Cambrian and early Ordovician: the predominance of tectonic factors and the absence of large scale eustatic fluctuations. *Tectonophysics*, **320**(3–4), 375–407.
- Baturin, G. N. and Ilyin, A. V. 2013. Comparative geochemistry of shell phosphorites and dictyonema shales of the Baltic. *Geochemistry International*, **51**(1), 23–32.
- Cusack, M., Williams, A. and Buckman, J. 1999. Chemico-structural evolution of linguloid brachiopod shells. *Palaeontology*, **42**(5), 799–940.
- Ferretti, A., Medici, L., Savioli, M., Mascia, M. T. and Malferrari, D. 2021. Dead, fossil or alive: Bioapatite diagenesis and fossilization. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **579**, 110608.
- Godet, A. and Föllmi, K. B. 2021. Sedimentary phosphate deposits. In *Encyclopedia of Geology*. Elsevier, 922–930.
- Graul, S., Kallaste, T., Pajusaar, S., Urston, K., Gregor, A., Moilanen, M. et al. 2023 (in press). REE+Y distribution in Tremadocian shelly phosphorites (Toolse, Estonia): multi-stages enrichment in shallow marine sediments during early diagenesis. SSRN. <https://doi.org/10.2139/ssrn.4382862>
- Heinsalu, H. and Viira, V. 1997. Pakerort Stage. In *Geology and Mineral Resources of Estonia* (Raukas, A. and Teedumäe, A., eds). Estonian Academy Publishers, Tallinn, 52–58.
- Holmer, L. E. 1989. Middle Ordovician phosphatic inarticulate brachiopods from Västergötland and Dalarna, Sweden. *Fossils and Strata*, **26**.
- Kaljo, D., Heinsalu, H., Mens, K., Puura, I. and Viira, V. 1988. Cambrian–Ordovician Boundary beds at Tõnismägi, Tallinn, North Estonia. *Geological Magazine*, **125**(4), 457–463.
- Kirsimäe, K., Jørgensen, P. and Kalm, V. 1999. Low-temperature diagenetic illite-smectite in Lower Cambrian clays in North Estonia. *Clay Minerals*, **34**(1), 151–163.
- Lang, L., Kirsimäe, K. and Vahur, S. 2015. Diagenetic fate of bioapatite in linguliform brachiopods: multiple apatite phases in shells of Cambrian lingulate brachiopod *Ungula ingraca* (Eichwald). *Lethaia*, **49**(1), 13–27.
- Lécuyer, C., Grandjean, P., Barrat, J.-A., Nolvak, J., Emig, C., Paris, F. et al. 1998. $\delta^{18}\text{O}$ and REE contents of phosphatic brachiopods: a comparison between modern and lower Paleozoic populations. *Geochimica et Cosmochimica Acta*, **62**(14), 2429–2436.
- Lowenstam, H. and Weiner, S. 1989. *On Biomineralization*. Oxford University Press, New York, London.
- Lumiste, K., Lang, L., Paiste, P., Lepland, A. and Kirsimäe, K. 2021. Heterogeneous REE+Y distribution in Early Paleozoic shelly phosphorites: Implications for enrichment mechanisms. *Chemical Geology*, **586**, 120590.
- Martin, E. E. and Scher, H. D. 2004. Preservation of seawater Sr and Nd isotopes in fossil fish teeth: bad news and good news. *Earth and Planetary Science Letters*, **220**(1–2), 25–39.
- McLennan, S. M. 2001. Relationships between the trace element composition of sedimentary rocks and upper continental crust. *Geochemistry, Geophysics, Geosystems*, **2**(4).
- Nemliher, J. 2006. A new type of shell structure in a phosphatic brachiopod from the Cambrian of Estonia. *Proceedings of the Estonian Academy of Sciences. Geology*, **55**(4), 259–268.
- Nemliher, J. and Puura, I. 1996. Upper Cambrian basal conglomerate of the Kallavere Formation on the Pakri peninsula, NW Estonia. *Proceedings of the Estonian Academy of Sciences*, **45**(1), 1–8.
- Nemliher, J., Kurvits, T., Kallaste, T. and Puura, I. 2004. Apatite varieties in the shell of the Cambrian lingulate brachiopod *Obolus apollinis* Eichwald. *Proceedings of the Estonian Academy of Sciences*, **53**(4), 246–256.
- Nielsen, A. T. and Schovsbo, N. H. 2011. The Lower Cambrian of Scandinavia: Depositional environment, sequence stratigraphy and palaeogeography. *Earth-Science Reviews*, **107**(3–4), 207–310.
- Popov, L. E., Alvaro, J.-J., Holmer, L. E., Bauert, H., Pour, M. G., Dronov, A. V. et al. 2019. Glendonite occurrences in the Tremadocian of Baltica: first Early Palaeozoic evidence of massive ikaite precipitation at temperate latitudes. *Scientific Reports*, **9**, 7205.
- Ptáček, P. 2016. *Apatites and their Synthetic Analogues: Synthesis, Structure, Properties and Applications*. IntechOpen.
- Trappe, J. 1998. *Phanerozoic Phosphorite Depositional Systems: A Dynamic Model for a Sedimentary Resource System*. Springer, Berlin, Heidelberg.
- Trueman, C. N. and Tuross, N. 2002. Trace element in recent and fossil bone apatite. *Reviews in Mineralogy and Geochemistry*, **48**(1), 489–521.
- Veiderma, M., Tõnsuaadu, K., Knubovets, R. and Peld, M. 2005. Impact of anionic substitutions on apatite structure and properties. *Journal of Organometallic Chemistry*, **690**(10), 2638–2643.
- Vinn, O., Holmer, L. E., Wilson, M., Isakar, M. and Toom, U. 2021. Possible drill holes and pseudoborings in obolid shells from the Cambrian/Ordovician boundary beds of Estonia and the uppermost Cambrian of NW Russia. *Historical Biology*, **33**(12), 3579–3584.