Estonian Paleozoic shelly phosphorites: a continent-scale resource for phosphorus and potential for rare earth elements

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What is Estonian phosphorite?

<table>
<thead>
<tr>
<th>Chem. composition (n=12):</th>
<th>Chem. composition (n=6):</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_2O_5$ – 37.11%</td>
<td>$P_2O_5$ – 35.37%</td>
</tr>
<tr>
<td>MgO – 0.67%</td>
<td>MgO – 0.63%</td>
</tr>
<tr>
<td>$Fe_2O_3$ – 1.17%</td>
<td>$Fe_2O_3$ – 3.15%</td>
</tr>
<tr>
<td>FeS$_2$ – 0.21%</td>
<td>FeS$_2$ – 3.36%</td>
</tr>
<tr>
<td>$P_2O_5$ citric acid – 11.06%</td>
<td>$P_2O_5$ citric acid – 10.39%</td>
</tr>
</tbody>
</table>

Soesoo & Kirmsmae, 2020: Estonian Paleozoic shelly phosphorites...; EGU 2020
Estonian phosphorite is a sedimentary rock, which contains Lingula valves and detritus, rich in phosphorus.
Estonian Deposits (Millions tons of $\text{P}_2\text{O}_5$)

- **Maardu** - ca 3.4 Mt (not in registry)
- **Tsitre** - 4.1 Mt
- **Aseri** - 22.5 Mt
- **Toolse** - 27.4 Mt
- **Rakvere** - ca 735 Mt $\text{P}_2\text{O}_5$

Soesoo & Kirsimäe, 2020: Estonian Paleozoic shelly phosphorites...; EGU 2020
Estonian sedimentary shelly phosphate rock – a multi-resource of P and REE

Soesoo & Kirmsa, 2020: Estonian Paleozoic shelly phosphorites...; EGU 2020
Rare Earth Elements in apatite as an additional value to phosphorite?

\[ Ca_{10}(PO_4)_6(OH)_2 \]

Na, Mg, …REE

F, Cl, CO_3

# ionic radii of Ca and REEs is similar, and as the result REEs are concentrated in apatite

# sedimentary phosphates are considered as REE ores

Photo: Liisa Lang

SOESOO & KIRSIMÄE, 2020: Estonian Paleozoic shelly phosphorites...; EGU 2020
Apatite crystal aggregates in phosphatic brachiopod

Internal structure of shells - inarticulate brachiopods

Soesoo & Kirsimäe, 2020: Estonian Paleozoic shelly phosphorites...; EGU 2020
Element distribution within shells

Soesoo & Kirsimäe, 2020: Estonian Paleozoic shelly phosphorites...; EGU 2020
Distribution of Trace and REE elements?

TOF-SIMS
elemental mapping of shell structures

Soesoo & Kirsimäe, 2020: Estonian Paleozoic shelly phosphorites...; EGU 2020
Ce distribution in shells

REE distributions “copy” an internal structure of the shell

Soesoo & Kirsimäe, 2020: Estonian Paleozoic shelly phosphorites...; EGU 2020
• REE elements in shelly apatite?

REE concentration in single shell

Number of analyses -- 103
Why Estonian phosphorite is in good quality?

Weak cementation

Simple enrichment and processing technology

Low content of heavy metals - Cd <0.5 ppm (in shells)
3-165 ppm in Moroccan phosphate rock (>300 ppm in apatite phase)

Low to moderate content of U <<70 ppm (in shells)
100-300 (600) ppm in Moroccan phosphate deposits

Mar & Okazaki, 2012
The calculation!

- Take annual mining (raw) – 5 Mt
- P @ 12% → 600 000 t P₂O₅
- tot REE – 1200 ppm → 720 t
- tot REE – 1500 ppm → 900 t

- REE recovery – 50% → **360-450 t** total REEs
Conclusions

• Estonian phosphorite reserves – the biggest in EU?
• Open pit and underground mining possible
• REEs – as a co-product of phosphorites; the size is meaningful
• Historical knowledge on technologies, REE plant in Estonia
• Technologically easy & good infrastructure (railway, seaports)
• Willingness to be developed
• Knowledge-based society

Soesoo & Kirsimäe, 2020: Estonian Paleozoic shelly phosphorites...; EGU 2020
THANK YOU FOR YOUR ATTENTION!