Microanalytical Characterization of REE Phases in a Glauconitic Sandstone

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Abstract

The rare earth elements (REEs) are critical components to numerous modern technologies and identifying alternative sources is essential to stabilizing supply. The glauconitic sandstones of the Bobs Ridge Formation in West Virginia is one possible source, having been identified from previous work as containing ~**700 ppm REEs (LREE [La-Gd] = 770 ppm), HREE [Dy-Lu] = 30 ppm)**. Here we employ multiple microanalytical techniques including XRD, SEM-EDS, FIB-SEM, and EPMA to identify and characterize the REE phases in the Bob's Ridge sandstone.

Pocahontas County, West Virginia

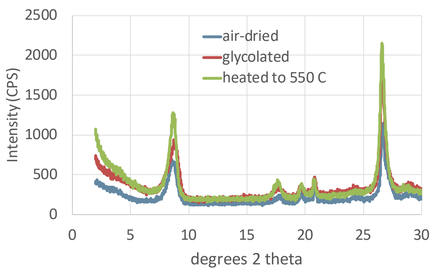
Methods

- FEI Inspect F : 20 kV, beam aperture 3, spot size 5, WD ~10 mm
  - REE phosphate standards (REEP25-15+FC, Astimex Standards Ltd.)
  - REE oxide standards (Standard block #489, Geller Microanalytical Lab.)
- FEI Helios 600i dual beam FIB-SEM
  - 20 µm x 20 µm area, slice thickness ~15 nm (pixel: 9.97 nm, voxel: 1.49 µm³)
- Rigaku III Ultima x-ray diffractometer with Cu anode
  - 40 kV, 44 mA, 4 to 70 degrees two theta, step size 0.02, scan time 2.4 s
- EPMA JEOL 8530F Plus Hyper Probe
  - 15 kV, 95 nA, 25 ms dwell time

XRD results

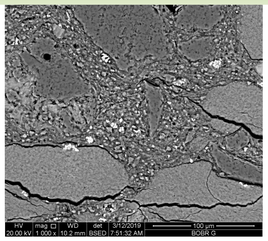
XRD scans on bulk non-oriented powders identify quartz, feldspar, and glauconite as the main minerals present. Glauconite shown to be the dominant clay mineral.

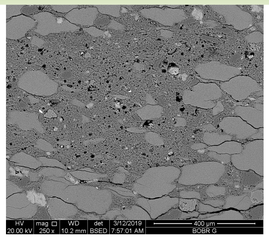
	Weight %
NON-CLAYS	
Quartz	33.8
Kspar (ordered Microcline)	9.7
Total non-clays	43.4
CLAYS	
Glauconite	56.6
Total clays	56.6
TOTAL	100.0



BSE SEM glauconite/quartz/clay matrix

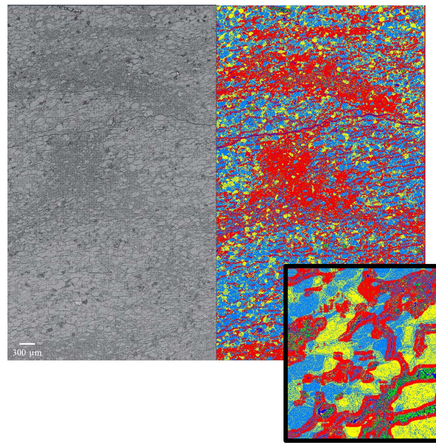
Consistent with XRD results, under BSE imaging, Bob's Ridge sandstone was characterized by an abundance of quartz and glauconite grains.





2D BSE image montage

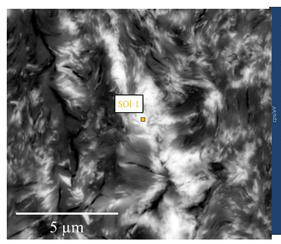
Advanced image processing, included phase segmentation and quantification, was accomplished using **PerGeos** software. For a given area (30.91mm²), the areal extent of glauconite and clay matrix is approximately equal, at **36% and 41%,** respectively. Quartz, the other major constituent, makes up 19% in this instance. Such areal estimations are useful in highlighting the abundance of glauconite grains and the surrounding matrix. High-density minerals include zircon and titanium oxides were also observed under SEM-EDS.

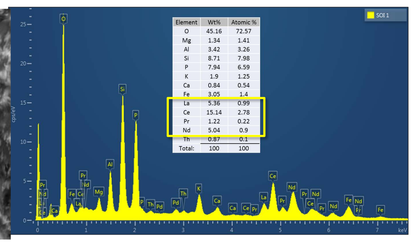


	Area (mm²)	%
Pores	0.83	3%
Clay Matrix	11.1	36%
Quartz	5.72	19%
Glauconite	12.5	41%
High-Density Minerals	0.50	2%
Total	30.6	100%

REE phosphate minerals

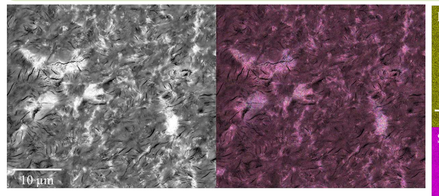
Within the glauconite grains are inclusions of small (nano- to micro-) scale, dense minerals. SEM-EDS analysis disclose a **phosphate mineral phase with detectable amounts of REEs, particularly the light REEs**. EDS analyses yield a generalized formula of (La, Ce, Nd, Pr)PO_4.

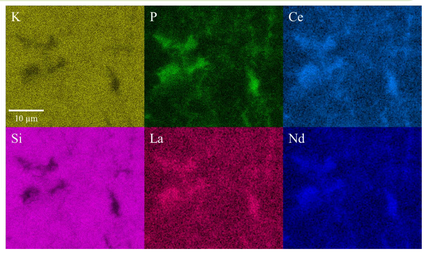




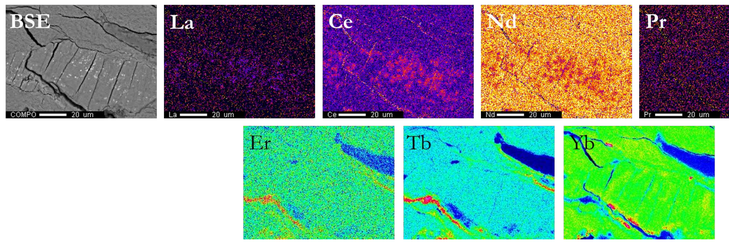
Elemental Mapping of REE phosphates

Elemental mapping by SEM-EDS shows the distribution of P plus La, Ce, and Nd within these high-density mineral phases.



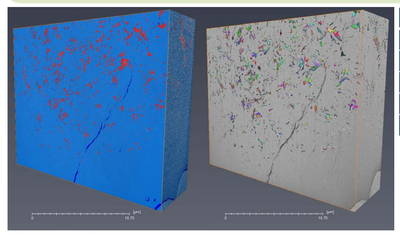


Elemental mapping by EPMA WDS confirms the distribution of the light REEs (La, Ce) in these nano- to micro- scale phosphate minerals (top row of figure below). Qualitative EDS mapping of Er, Tb, and Yb show disseminated occurrences in the glauconitic fabric (bottom row of figure below).



3D volume reconstructions

Multiple (3) sites used for 3D reconstructions of volumetric phases via FIB-SEM for a total volume of 11535 µm³. REE-bearing phosphates accounted for 8% of the total volume analyzed.



	Volume (µm³)	%	Area (µm²)	%
Pores	130	1%	11577	10%
Matrix	9735	84%	57501	50%
REE-phosphates	895	8%	29860	26%
Fe-phosphates	774	7%	15728	14%
Total	11535	100%	114666	100%

Conclusions

- REE-PO_4 observed as nano-/micro-mineral inclusions in glauconite grains
- LREEs associated with these nano/micro- phosphate minerals
- Heavy REEs observed in surrounding clay (glauconite) matrix
- Important consequences for potential extractability of REEs (i.e., as discrete phosphate mineral phases) and interpretations of diagenetic history

Acknowledgements

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