Rare Earth Elements in Sedimentary Phosphate: Solution to the Global REE Crisis?

ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

Pat McLaughlin

USGS
science for a changing world

Contributors

Jared Freiburg (ISGS)
Jay Zambito (Beloit College)
Charles Ver Straeten (NYGS)
Alex Bartholomew (SUNY New Paltz)
Drew Andrews (KGS)
Jed Day (IL State U.)
Mike Sell (Illinois State U.)
Erika Danielsen (OGS)
Jeff Trop (Bucknell U.)
Jeff Over (SUNY Geneseo)
Maria Mastalerz (IGWS)
Arkansas Geo. Survey
Oklahoma Geo. Survey
Matt Johnson (IGWS)

Poul (Emsbo)
Neil Griffis (USGS)
Ryan Clark (IGS)
Joe Devera (ISGS)
Carlton Brett (U. Cincinnati)
Gordon Baird (SUNY Fredonia)
Ron Clendening (TGS)
Katherine Tucker (IGWS)
Greg Cane (ISGS)
Dave Malone (IL State U.)
Damon

Thijs Vandenbroucke (U. Ghent, Belgium)
Jahan Ramezani (MIT)
Alyssa Bancroft (IGS)
Tim Paton (ISGS)
Cristiana Esteves (U. Ghent)
Kyle Ganz (MGS)
Bill Batten (WGNHS)
Carsyn Ames (WGNHS)
Jenna Lanman (IGWS)
Brian Witzke (IGS)
Heikki Bauert (Estonian GS)
Jared Thomas (ISGS)

Sedimentary phosphate REEs

Gondwana Research 27 (2015) 776–785

Contents lists available at ScienceDirect

Gondwana Research

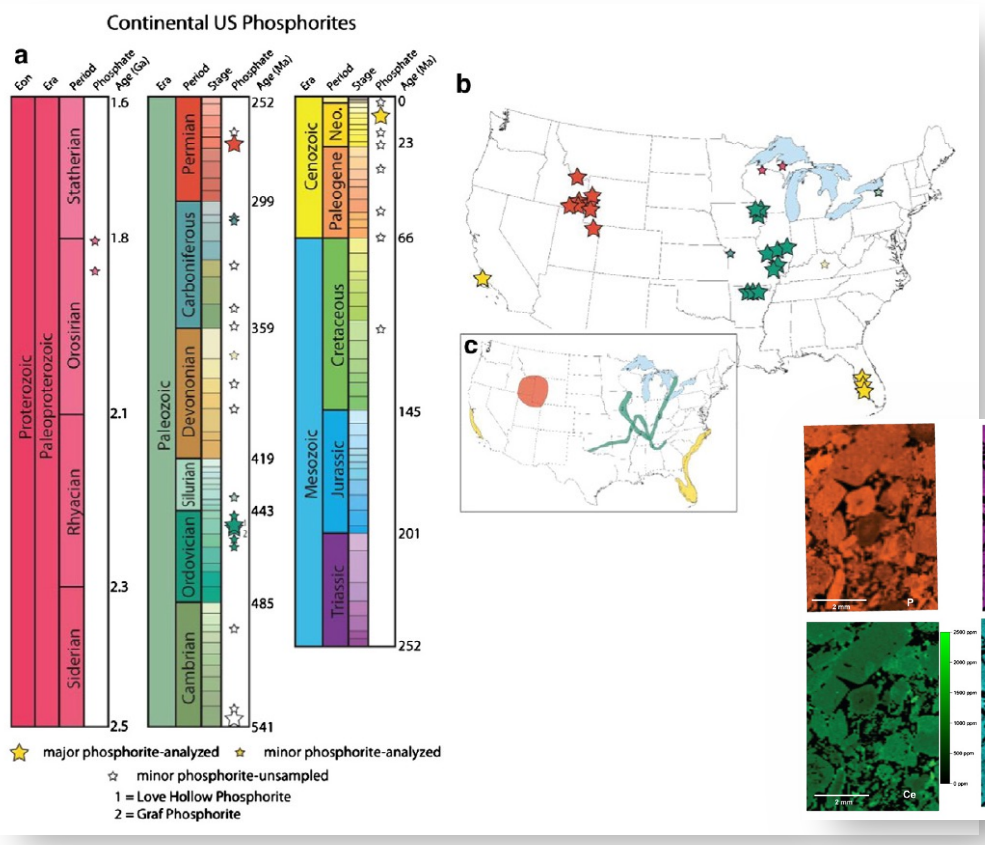
journal homepage: www.elsevier.com/locate/gr

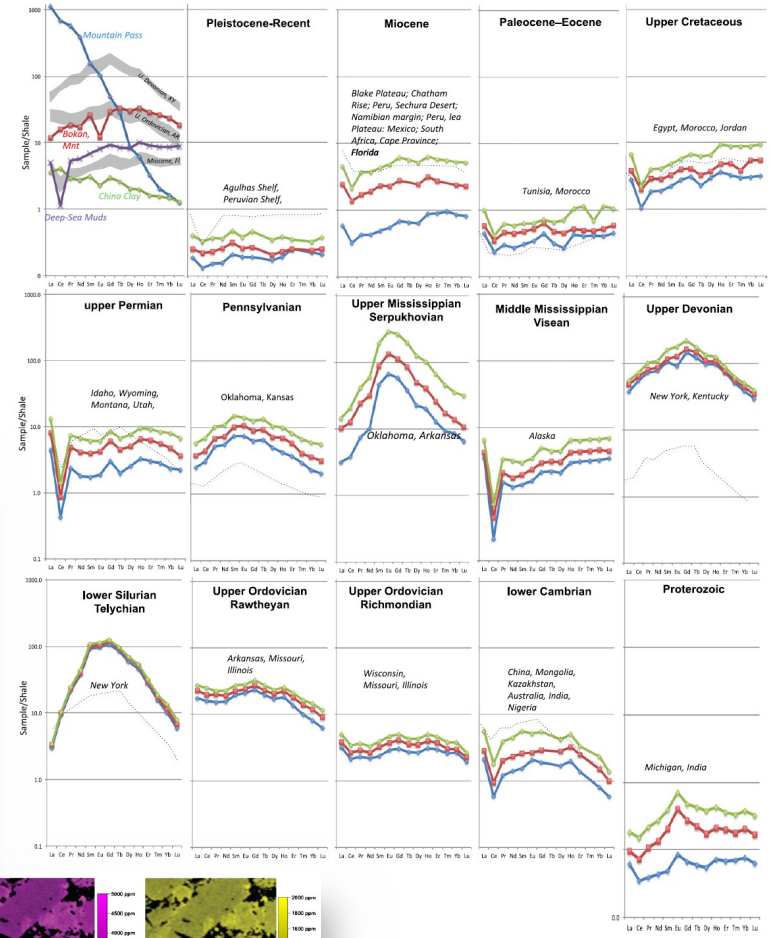
GR focus review

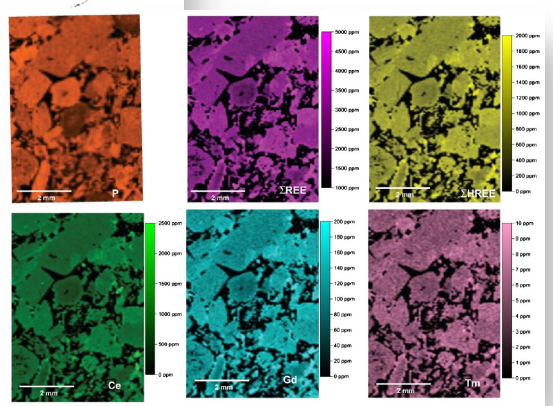
Rare earth elements in sedimentary phosphate deposits: Solution to the global REE crisis?

Poul Emsbo [a,*], Patrick I. McLaughlin [b], George N. Breit [a], Edward A. du Bray [a], Alan E. Koenig [a]

[a] U.S. Geological Survey, Box 25046, MS-973, Denver Federal Center, Denver, CO 80225, USA
[b] Wisconsin Geological and Natural History Survey, University of Wisconsin—Extension, 3817 Mineral Point Rd., Madison, WI 53705, USA







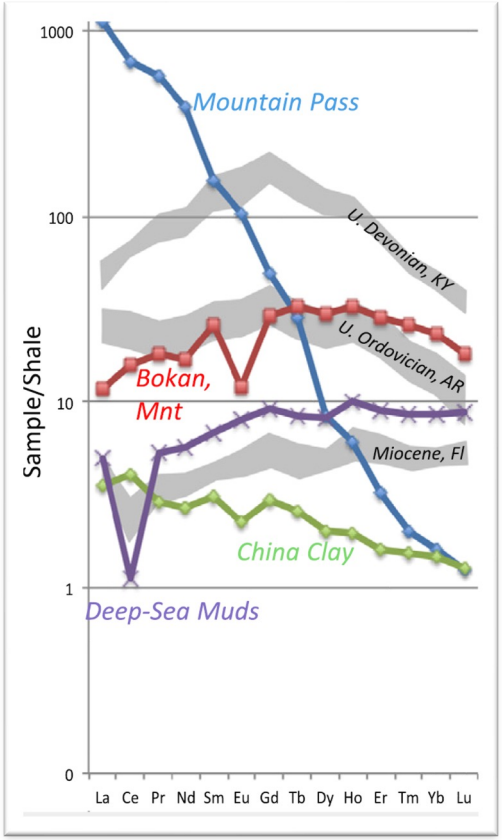
ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

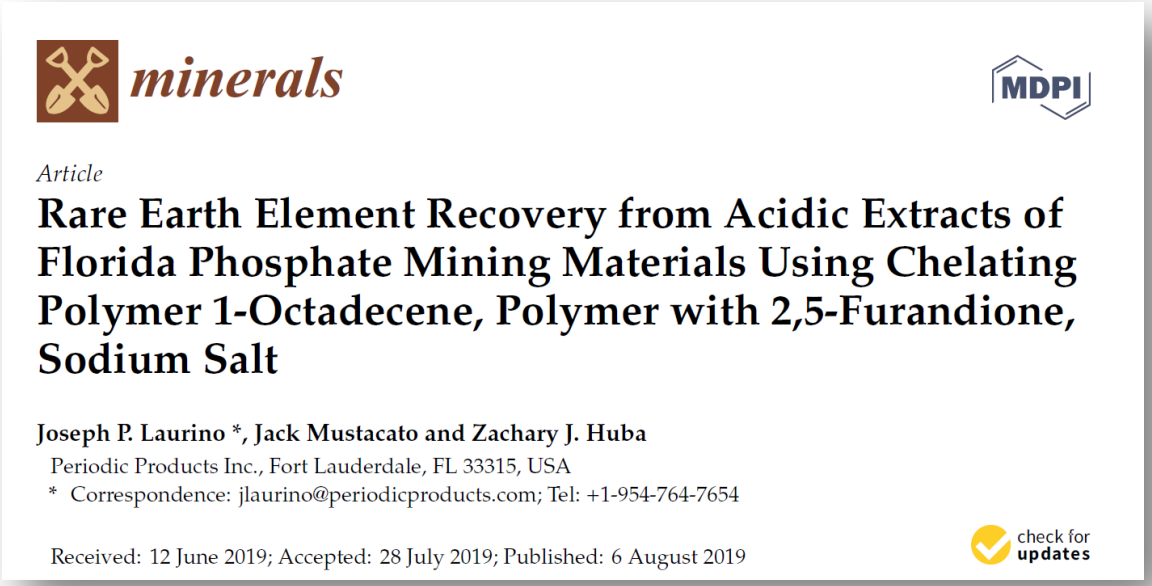
Florida Miocene-Pliocene phosphate and carbonates: *Hawthorne Group*

ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

REEs in Florida phosphate

- 85% of U.S. phosphate production
- 3% P beneficiated to 30% P
- 100% Francolite digestion with weak acid
- ΣREE 900 ppm
- ~50% of annual HREE demand put into solution but not recovered





minerals

MDPI

Article

Rare Earth Element Recovery from Acidic Extracts of Florida Phosphate Mining Materials Using Chelating Polymer 1-Octadecene, Polymer with 2,5-Furandione, Sodium Salt

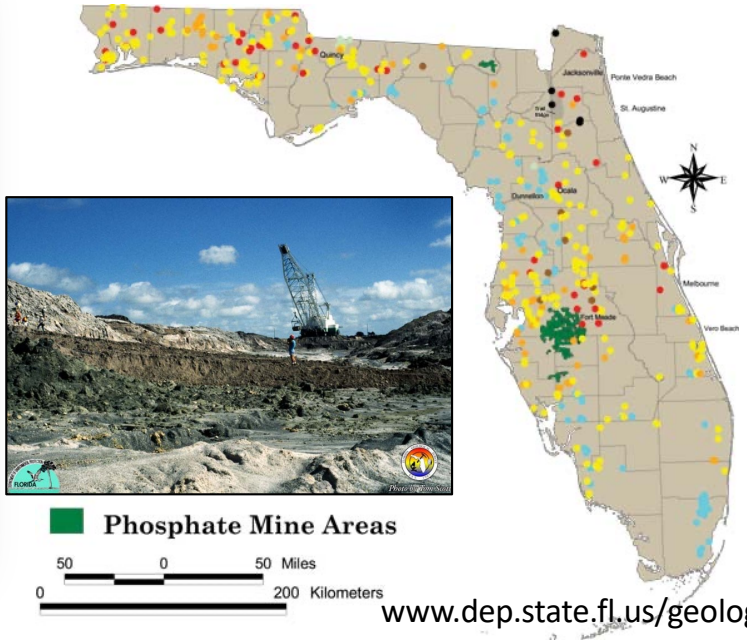
Joseph P. Laurino *, Jack Mustacato and Zachary J. Huba

Periodic Products Inc., Fort Lauderdale, FL 33315, USA

* Correspondence: jlaurino@periodicproducts.com; Tel: +1-954-764-7654

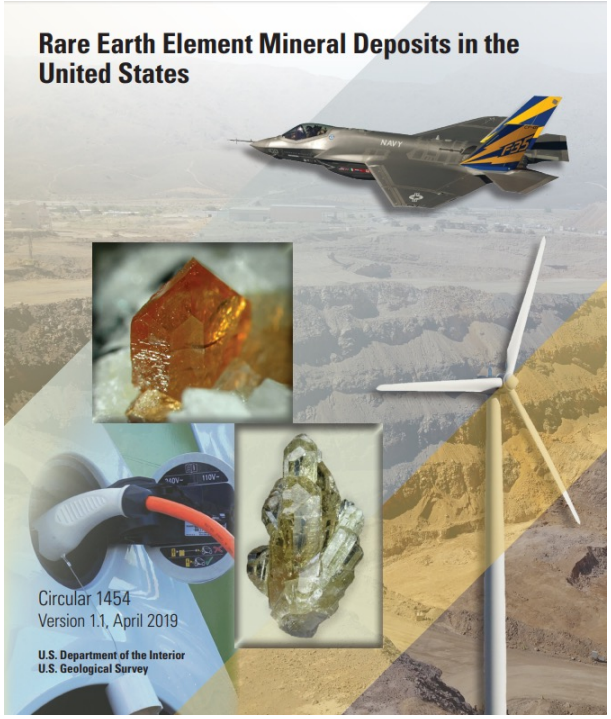
Received: 12 June 2019; Accepted: 28 July 2019; Published: 6 August 2019

check for updates

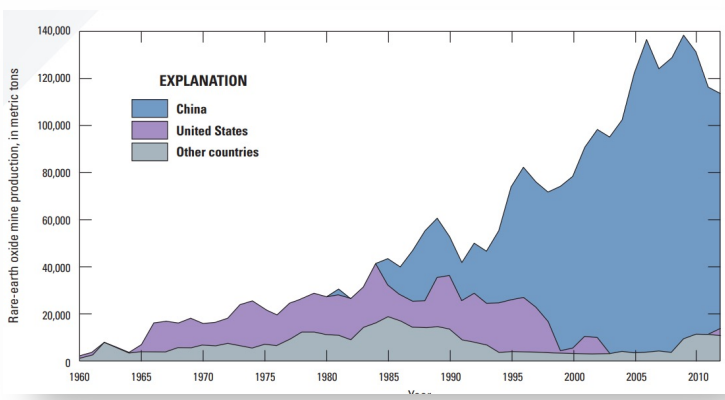


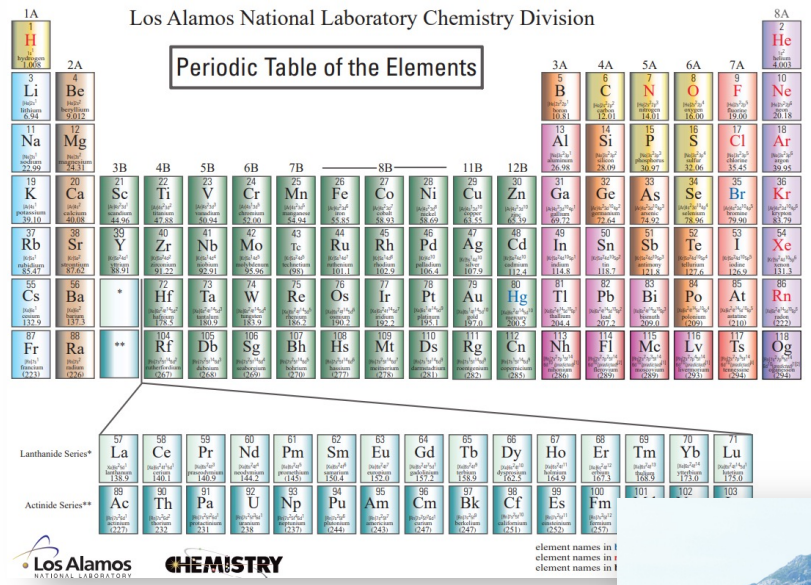
www.dep.state.fl.us/geology

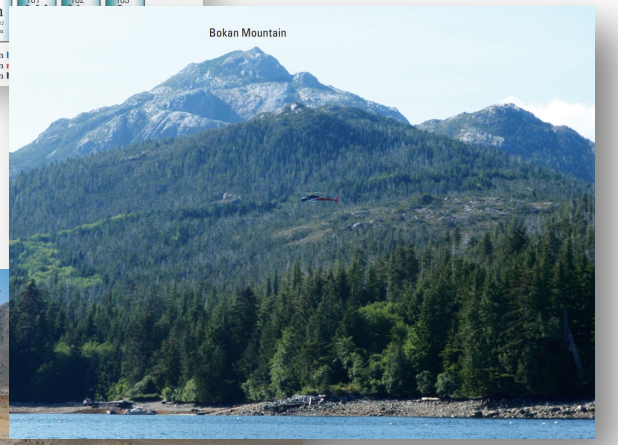
Earth Mapping Resources Initiative



By Bradley S. Van Gosen, Philip L. Verplanck, and Poul Emsbo

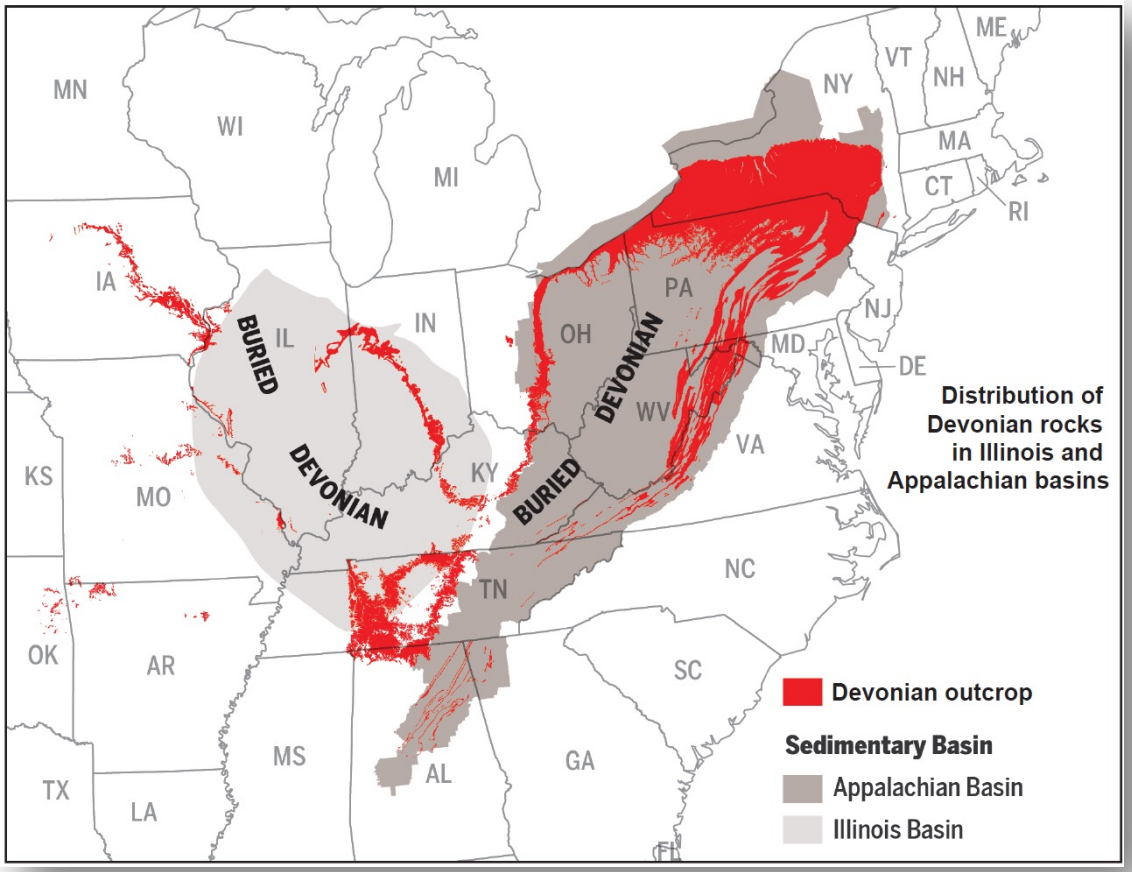






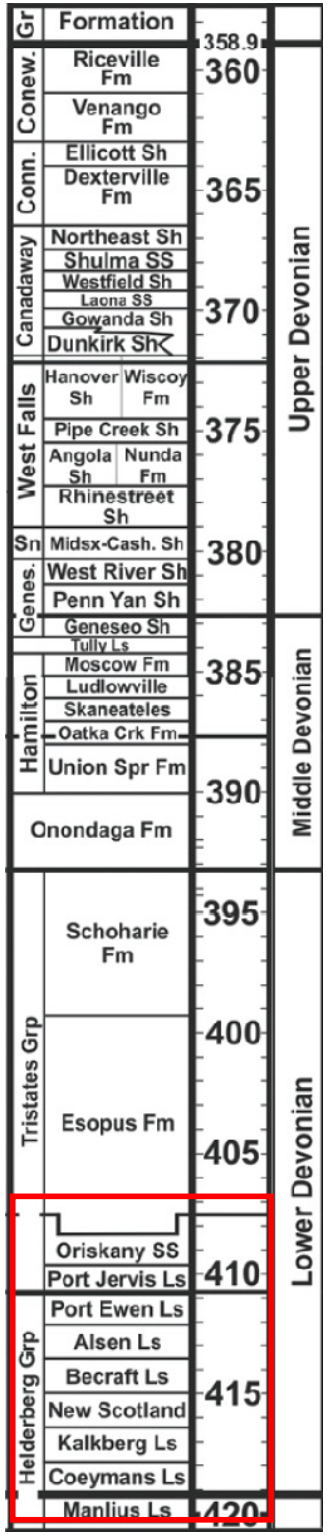
Earth MRI Phase II: **Geochemical Sampling (Appalachian Basin) and Regional Interpretation (Illinois and Appalachian Basins) of Devonian-Aged Rare Earth Element-Enriched Sedimentary Phosphatic Stratigraphic Units in the Central and Eastern United States**

- Appalachian Basin
  - New York
  - Pennsylvania
  - West Virginia
  - Ohio
  - Kentucky
- Illinois Basin
  - Indiana
  - Illinois
  - Kentucky
  - Tennessee
  - Iowa
  - Missouri
  - Arkansas
  - Oklahoma

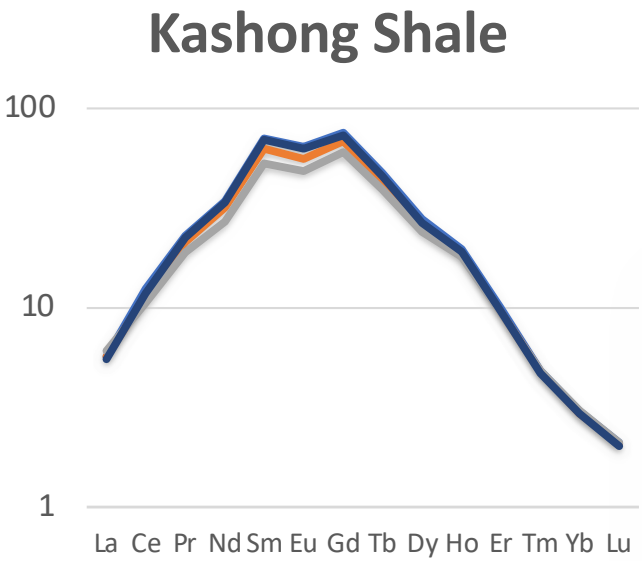


ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

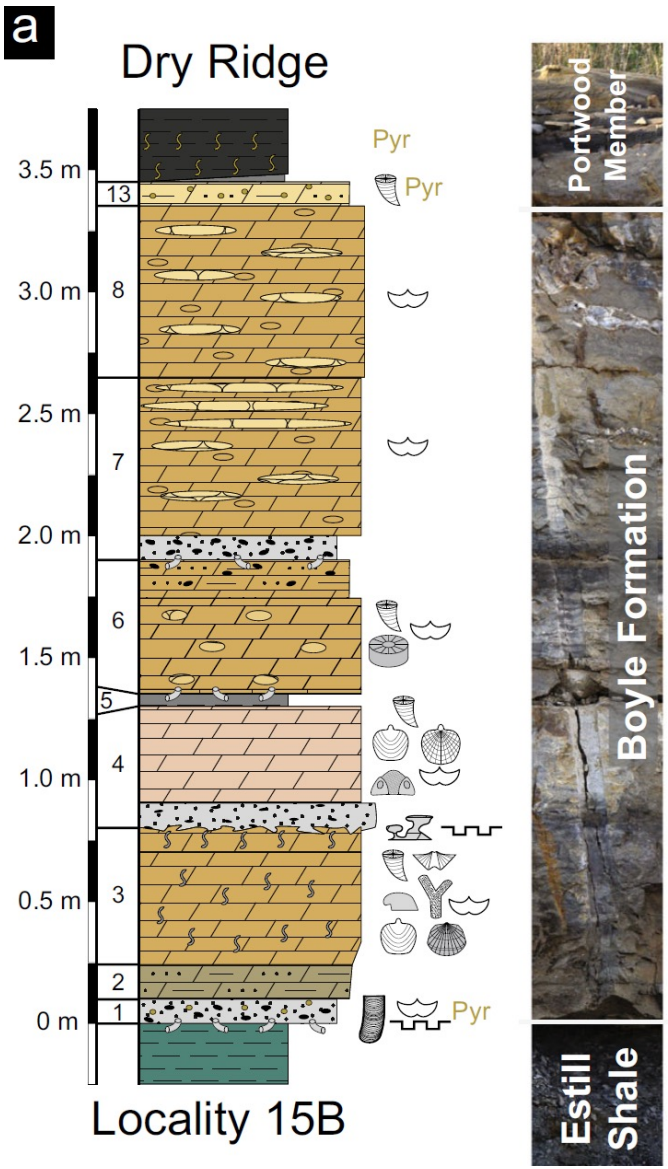
Devonian phosphorite, Appalachians: New York

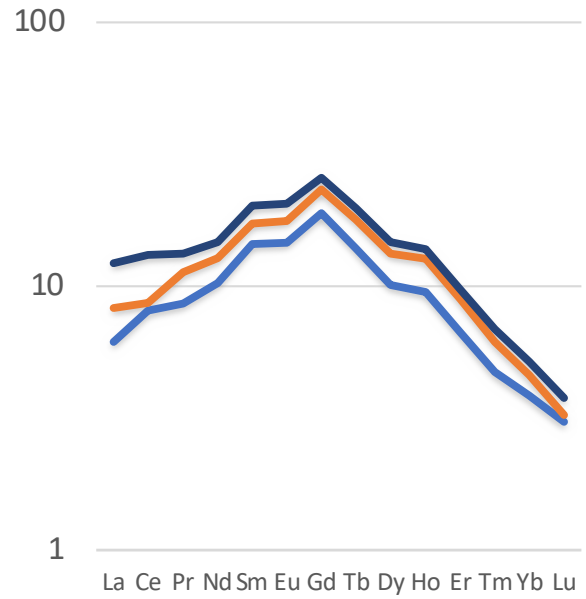


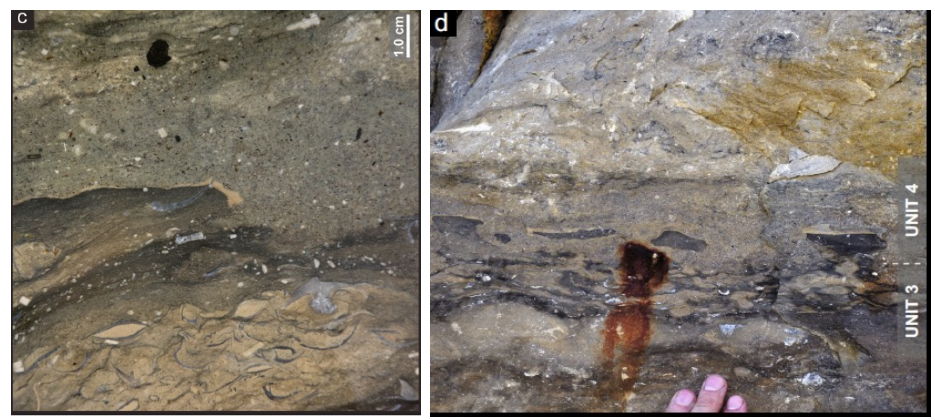
Devonian phosphorite, Appalachians: Collections



Midcontinent Devonian phosphorite: Kentucky



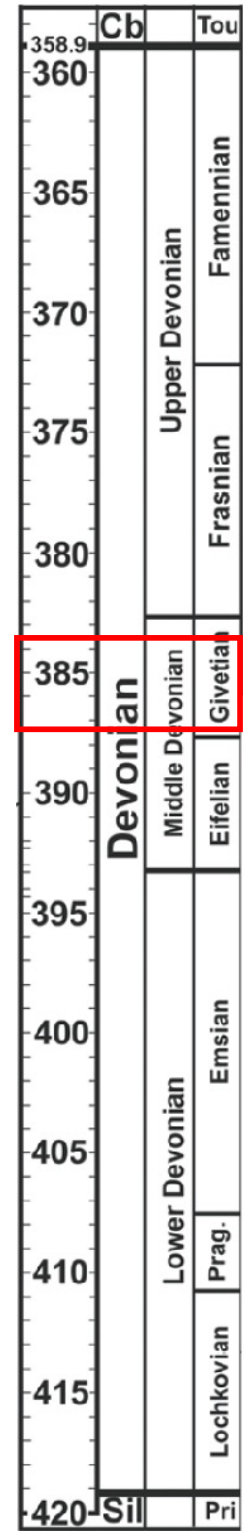




Palaeobiodiversity and Palaeoenvironments (2018) 98:331–368
https://doi.org/10.1007/s12549-018-0323-6
SENCKENBERG
CrossMark
ORIGINAL PAPER

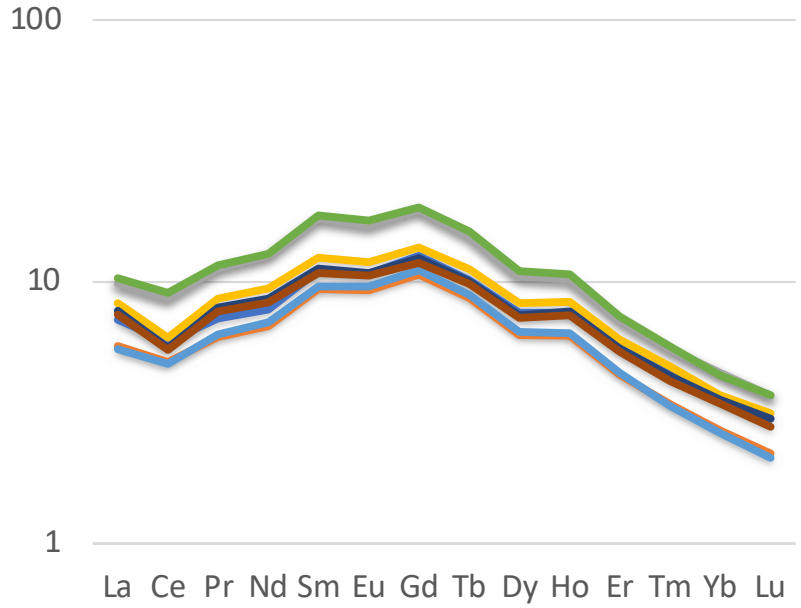
Litho-, bio-, and sequence stratigraphy of the Boyle-Portwood Succession (Middle Devonian, Central Kentucky, USA)

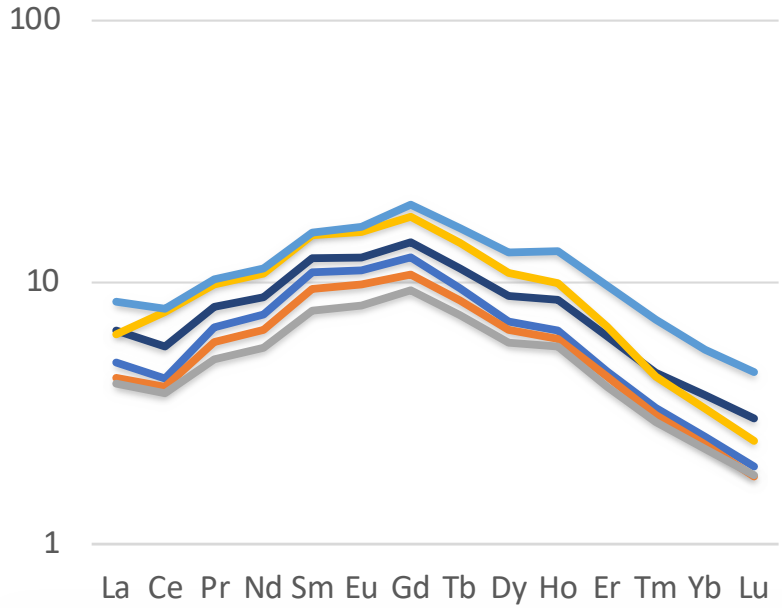
Carlton E. Brett[1] · James J. Zambito IV[2] · Gordon C. Baird[3] · Z. Sarah Aboussalam[4] · R. Thomas Becker[4] · Alexander J. Bartholomew[5]

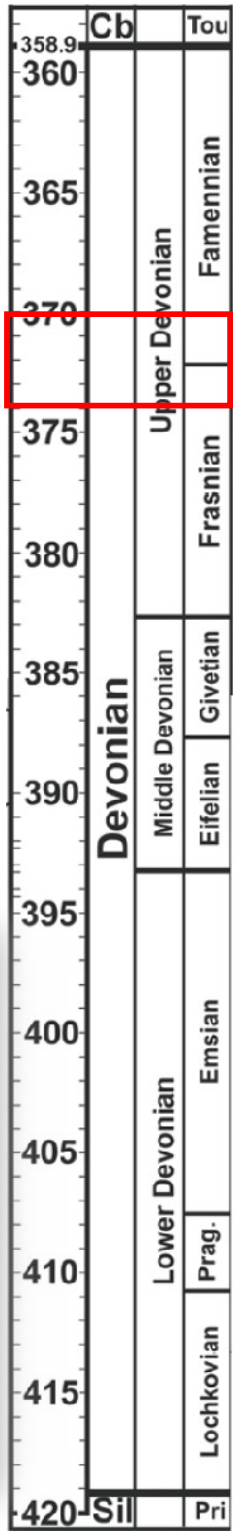


Midcontinent Devonian phosphorite:

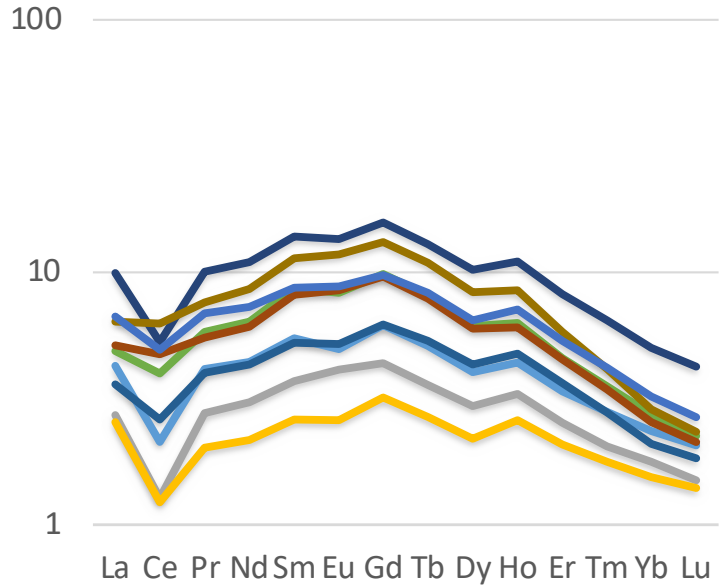
Tennessee

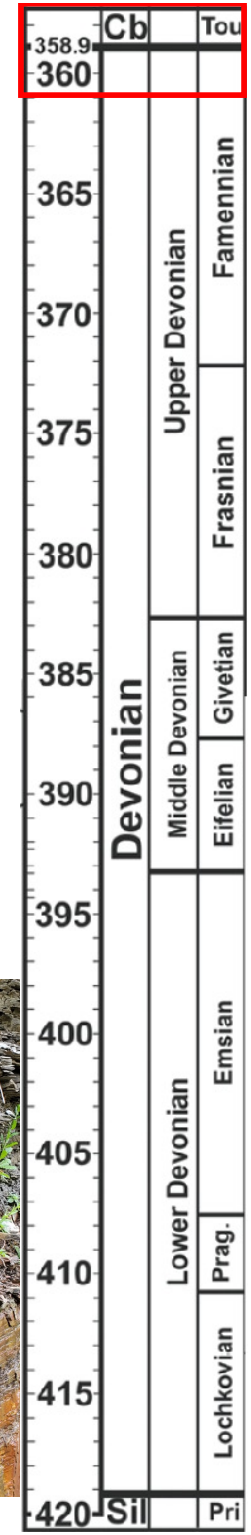




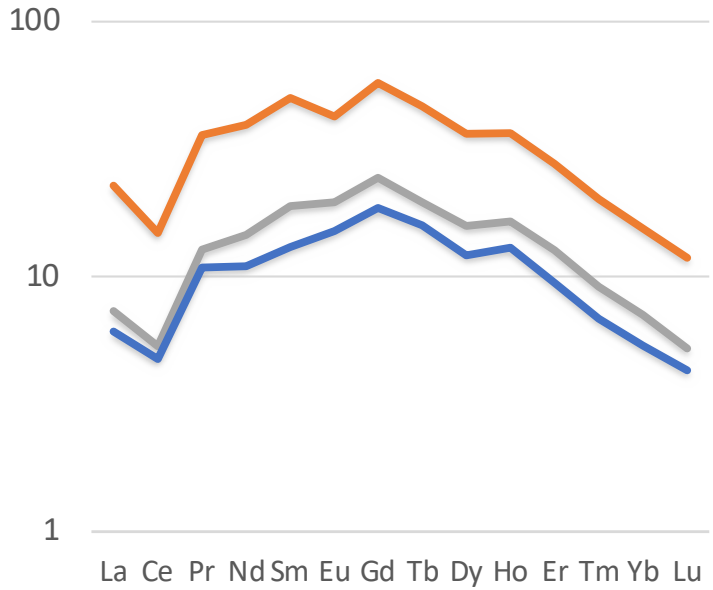


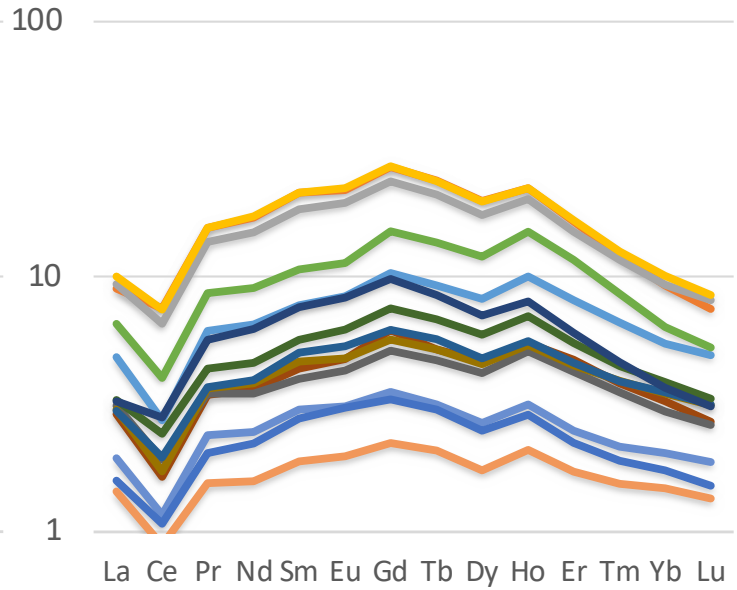
Midcontinent Devonian-Miss. phosphorite: Tennessee

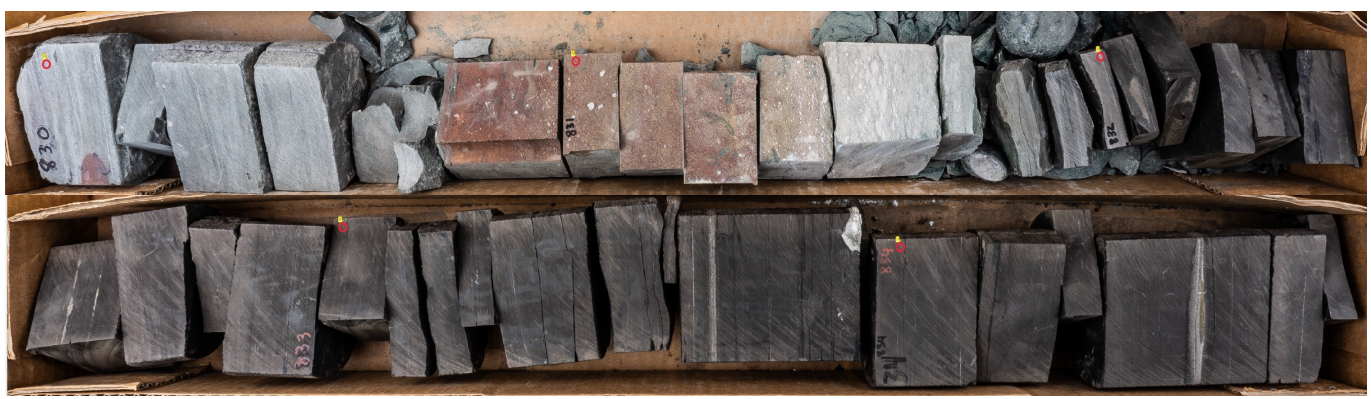


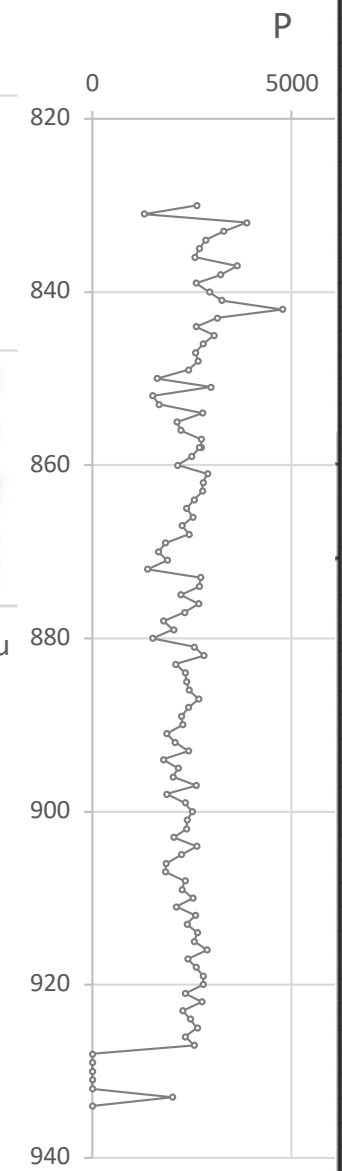


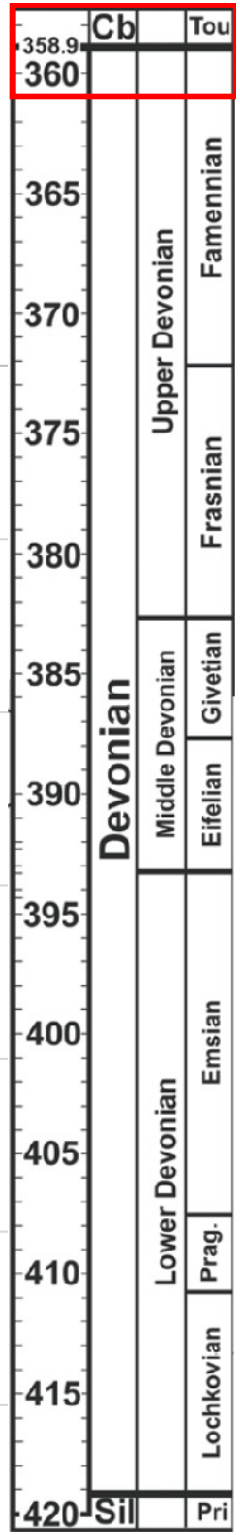
Midcontinent Devonian-Miss. phosphorite:
Kentucky + Indiana





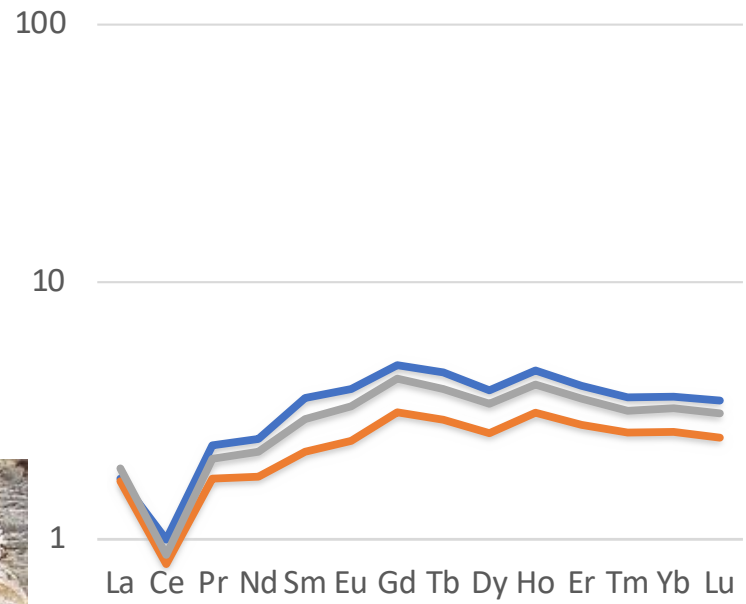


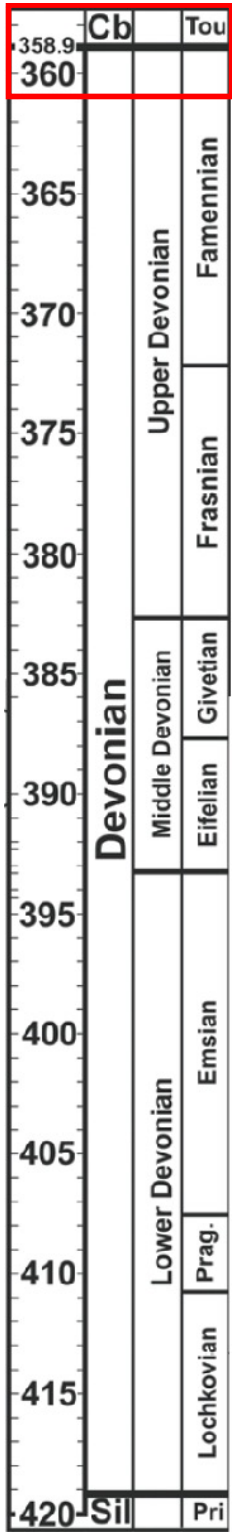




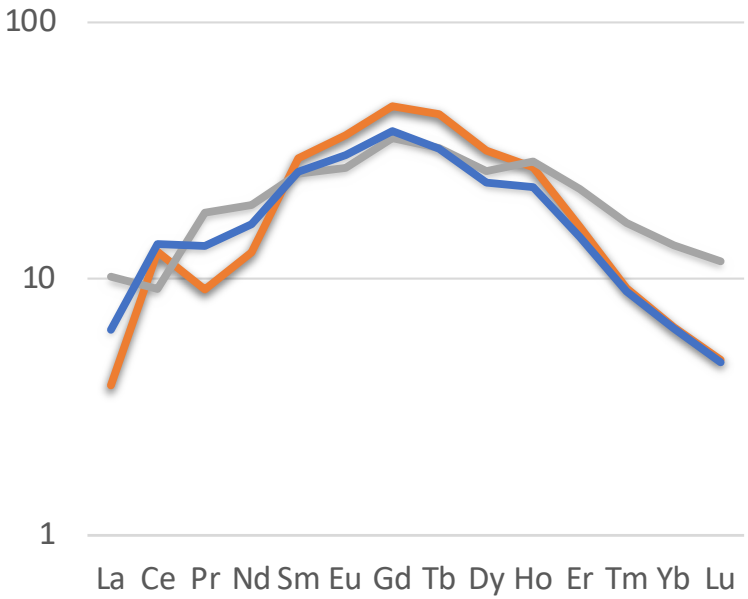
Midcontinent Devonian-Miss. phosphorite: Oklahoma

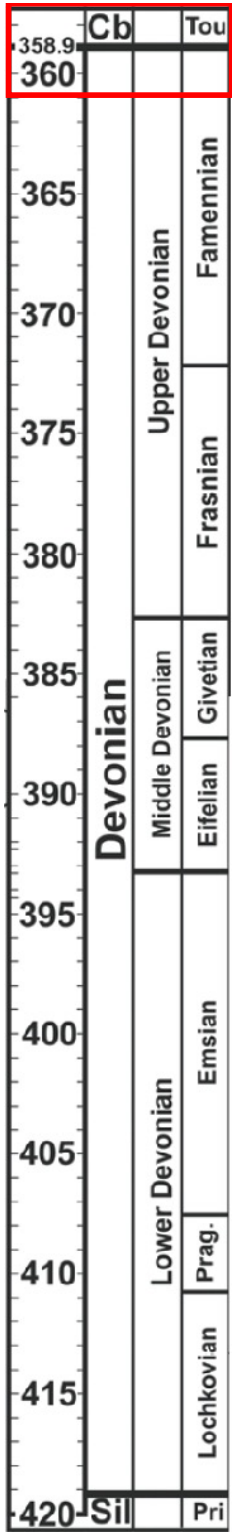
www.paleocurrents.com





Midcontinent Devonian-Miss. phosphorite: Illinois

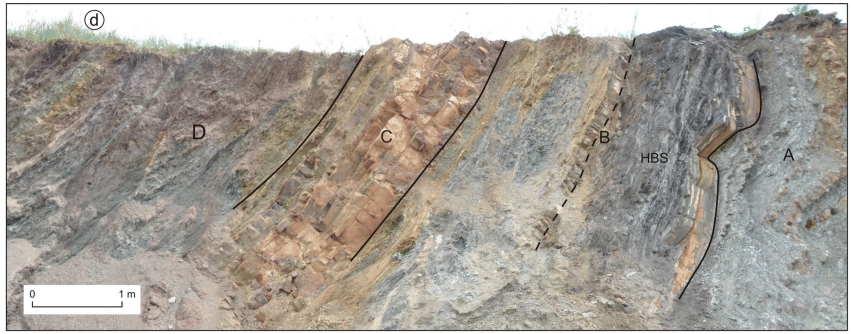




Association with Devonian oceanic anoxic events

Hangenberg Event

- Devonian-Mississippian boundary (359 Ma)
- 2nd largest extinction in Devonian
- Large carbon isotope excursion (+5 per mil)
- Widespread black shales-oceanic anoxia

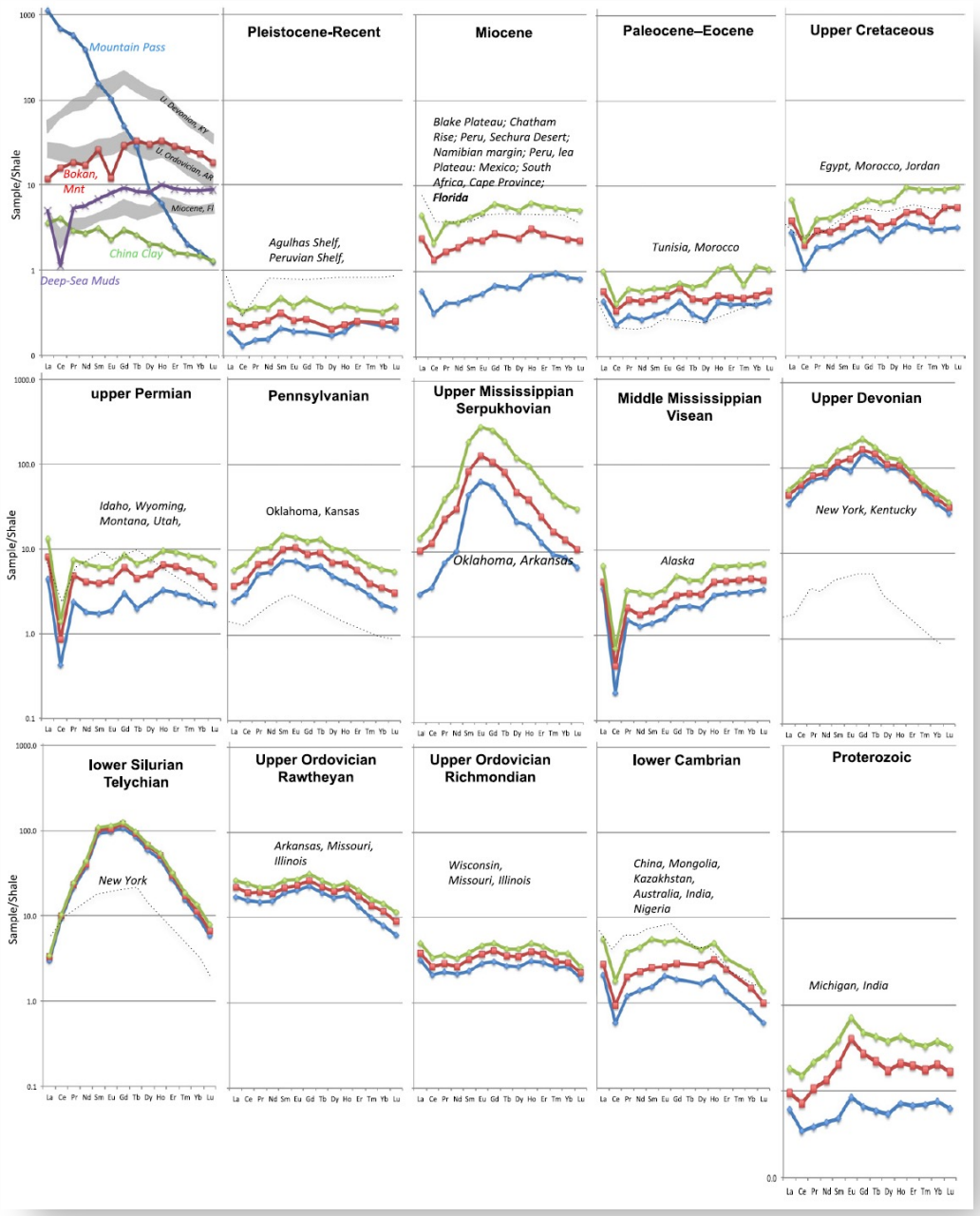


Hangenberg black shale, Kowala Quarry, Poland (Matyja et al., 2021)

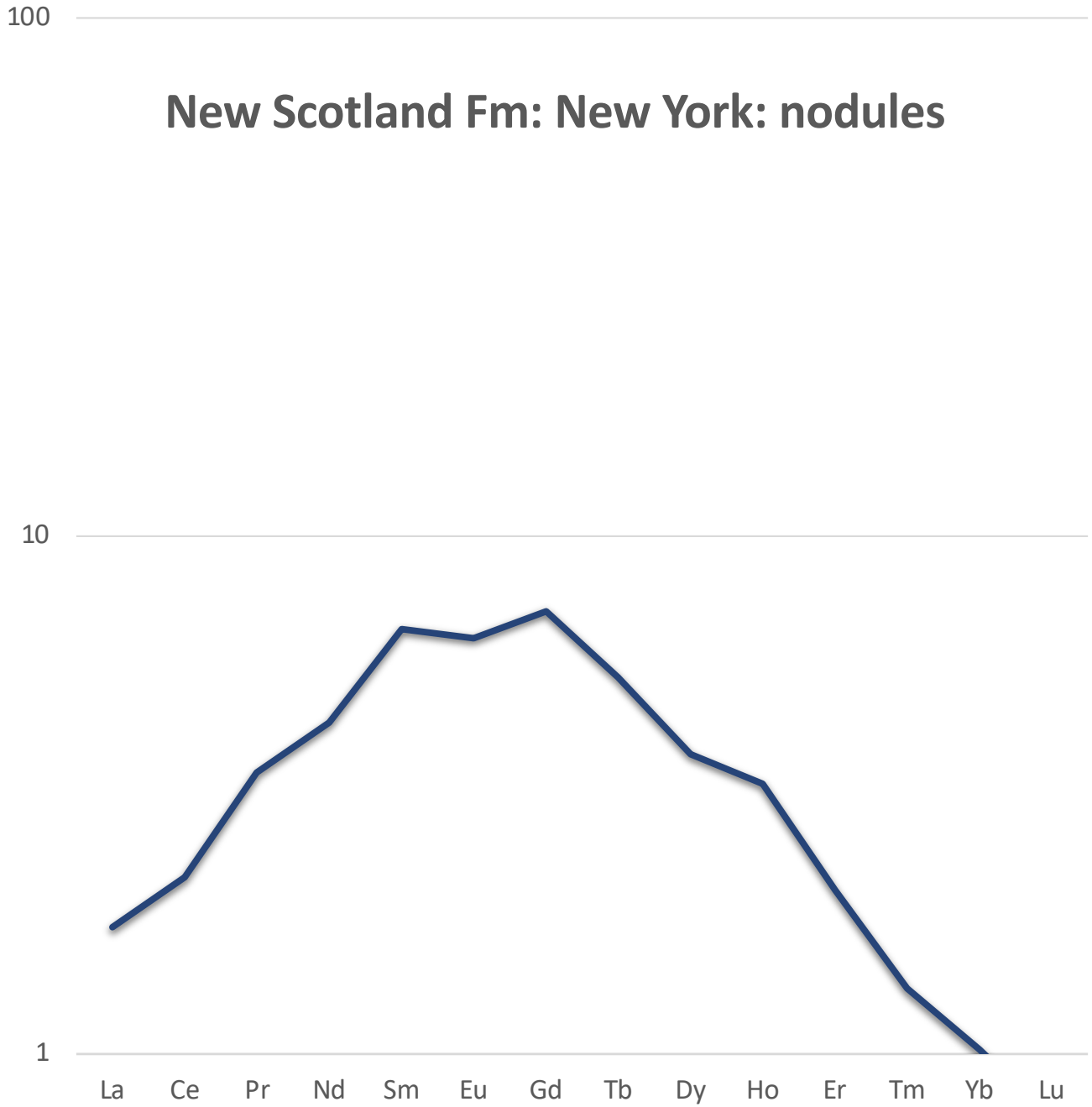
Kellwasser Event

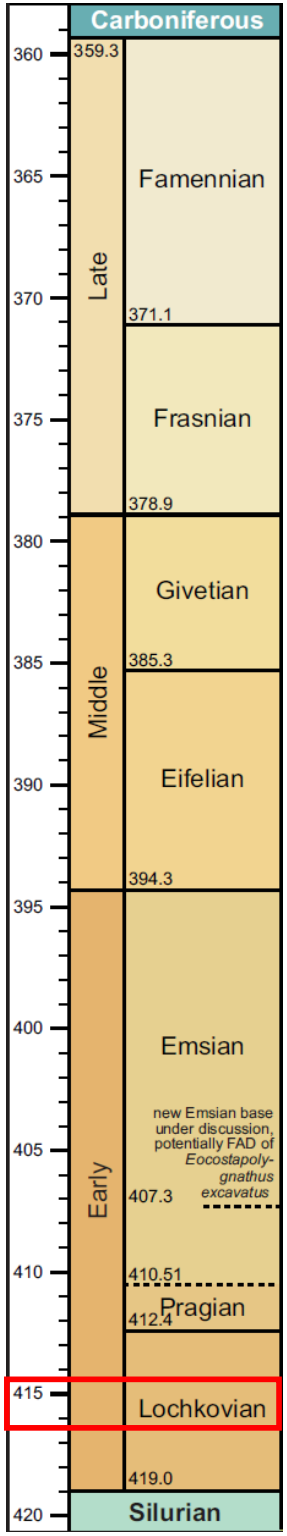
- Frasnian-Famennian boundary (372 Ma)
- One of top 5 largest mass extinction events
- Two pulses of oceanic anoxia

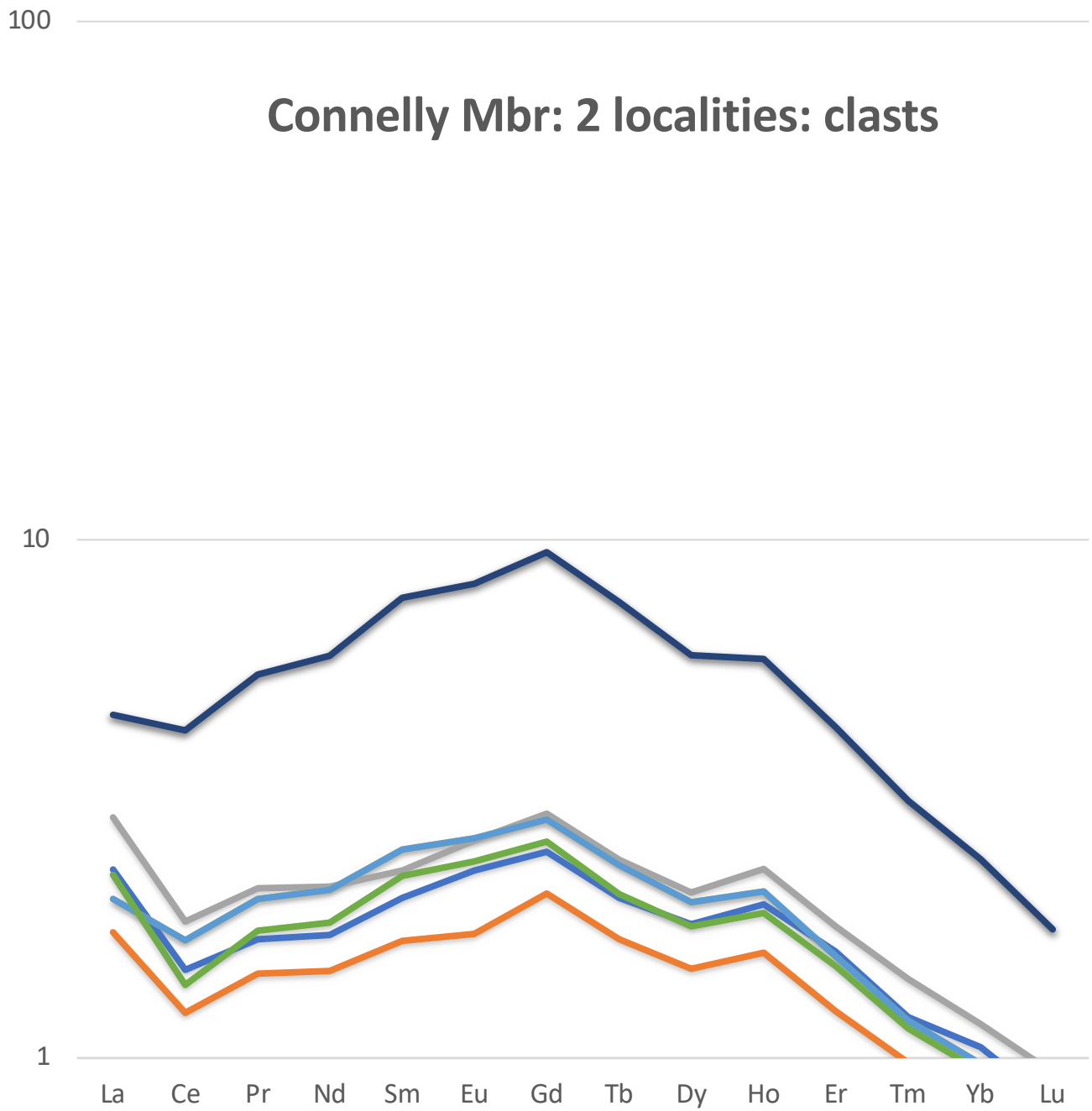
Secular change in phosphate REEs

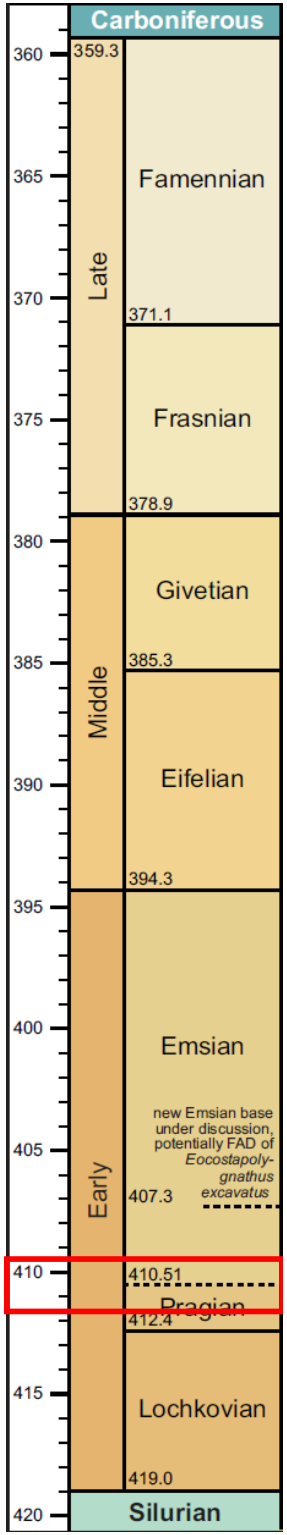


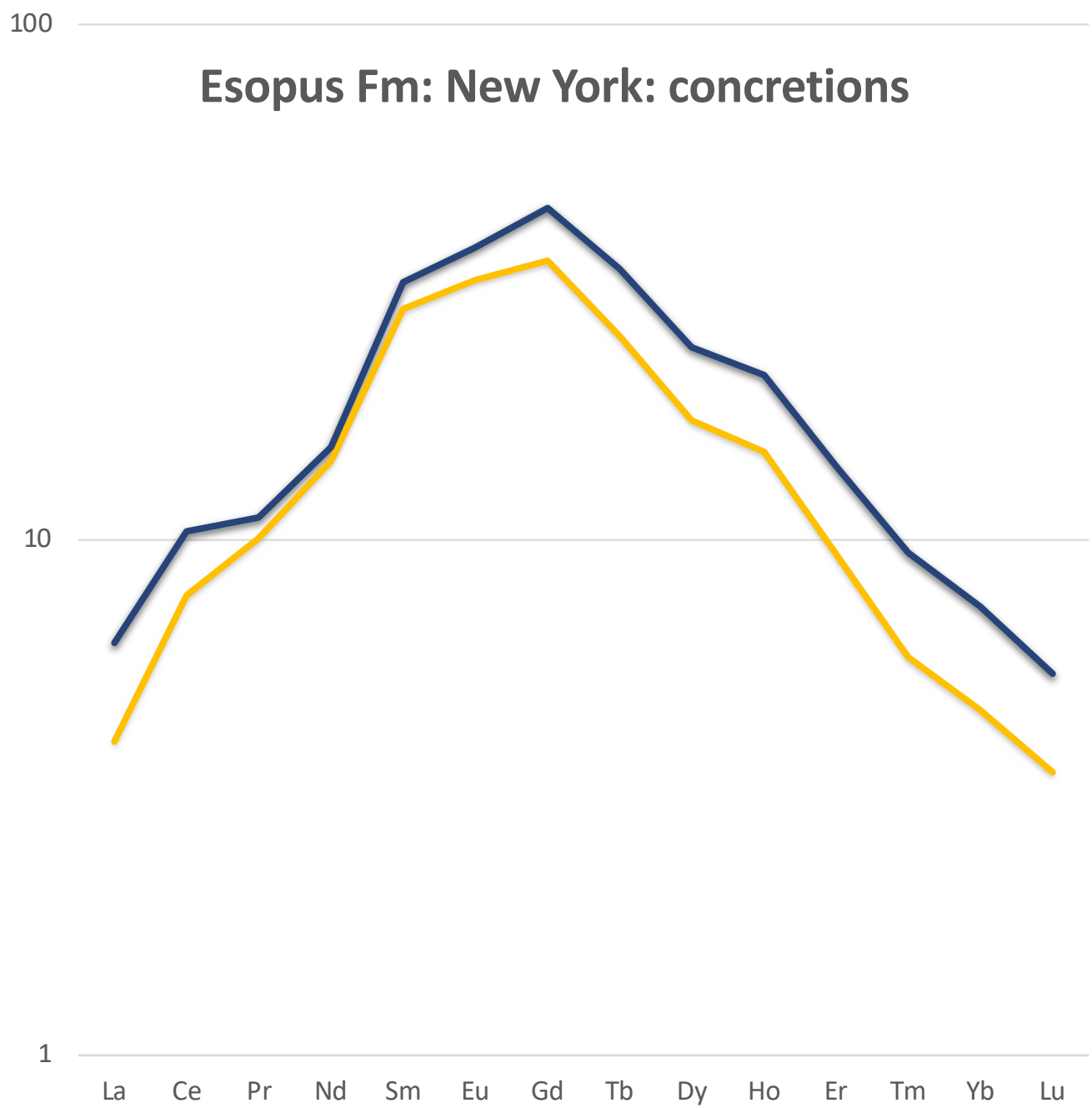
ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

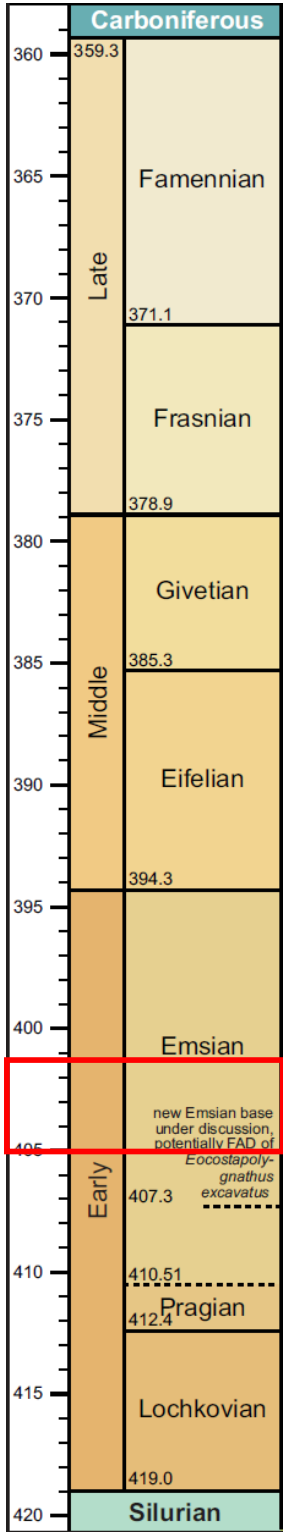

New Scotland Fm: New York: nodules
100
10
1
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

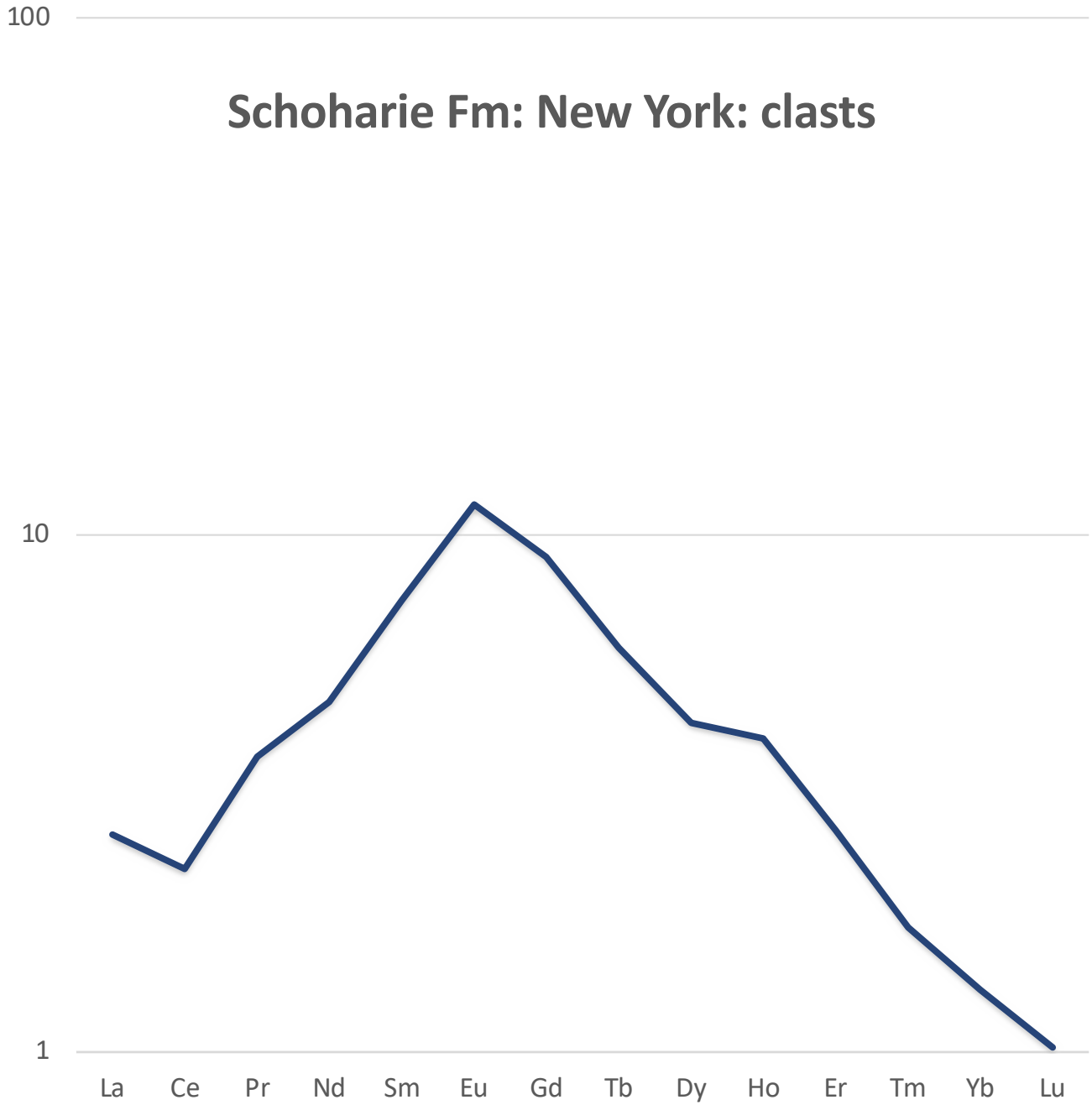

Carboniferous
360
365
370
375
380
385
390
395
400
405
410
415
420
359.3
Late
Famennian
371.1
Frasnian
378.9
Middle
Givetian
385.3
Eifelian
394.3
Early
Emsian
new Emsian base under discussion, potentially FAD of Eocostapoly-gnathus excavatus
407.3
410.51
Pragian
412.4
Lochkovian
419.0
Silurian

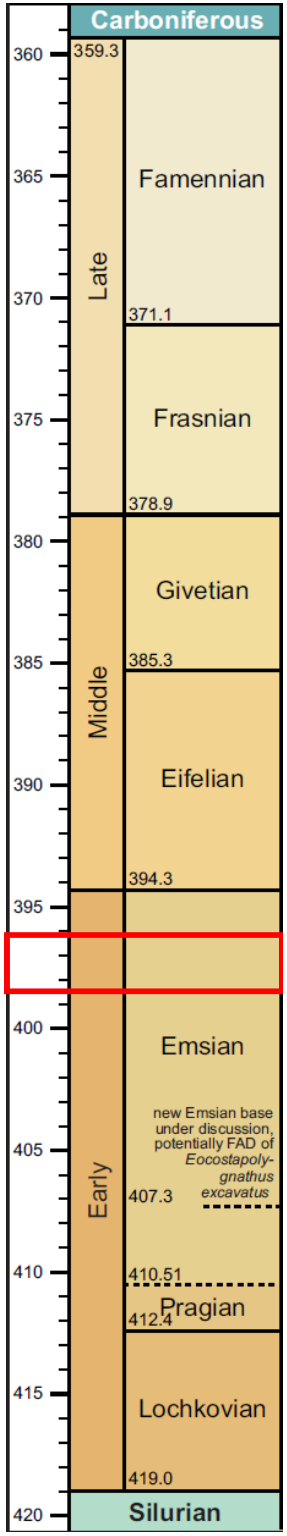

Connelly Mbr: 2 localities: clasts
100
10
1
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

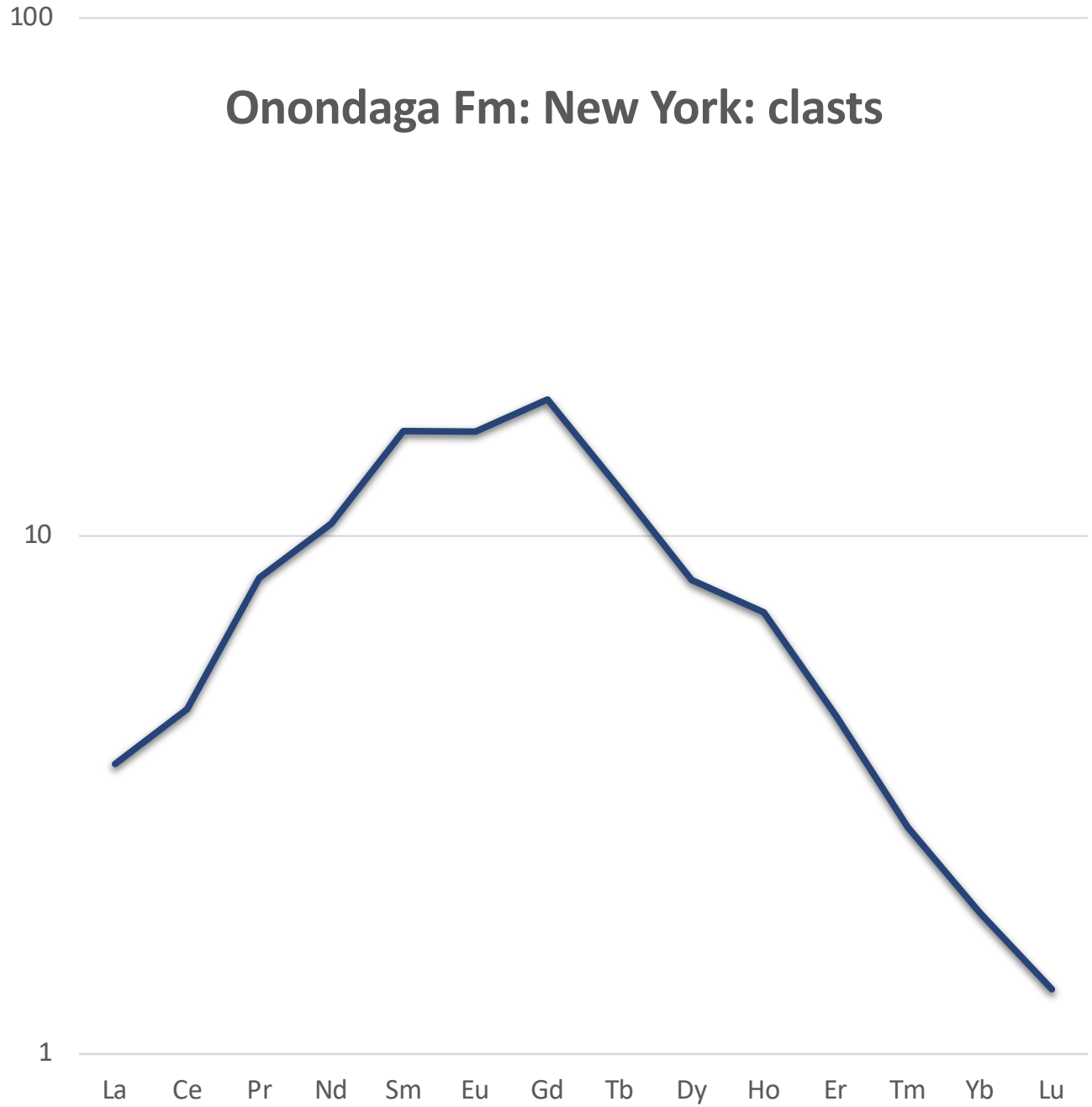

Carboniferous
360
365
370
375
380
385
390
395
400
405
410
415
420
359.3
Late
Famennian
371.1
Frasnian
378.9
Middle
Givetian
385.3
Eifelian
394.3
Early
Emsian
new Emsian base under discussion, potentially FAD of Eocostapoly-gnathus excavatus
407.3
410.51
Pragian
412.4
Lochkovian
419.0
Silurian

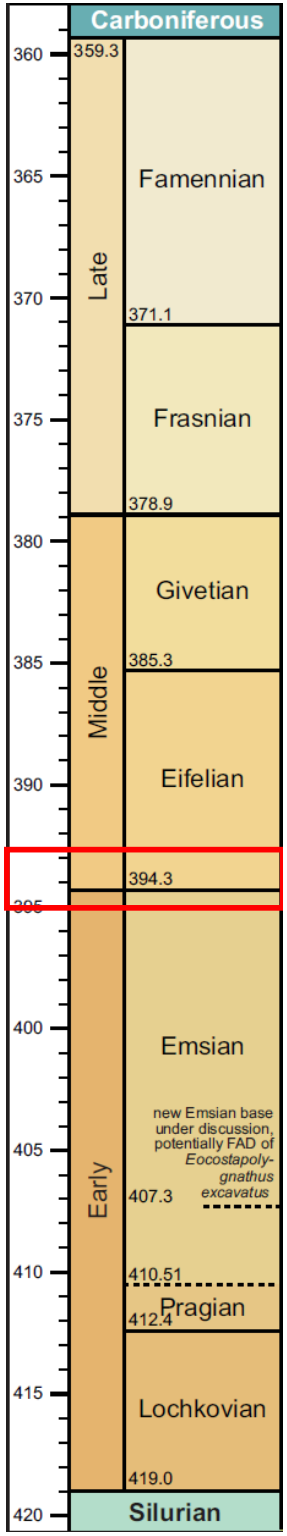

Esopus Fm: New York: concretions
100
10
1
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

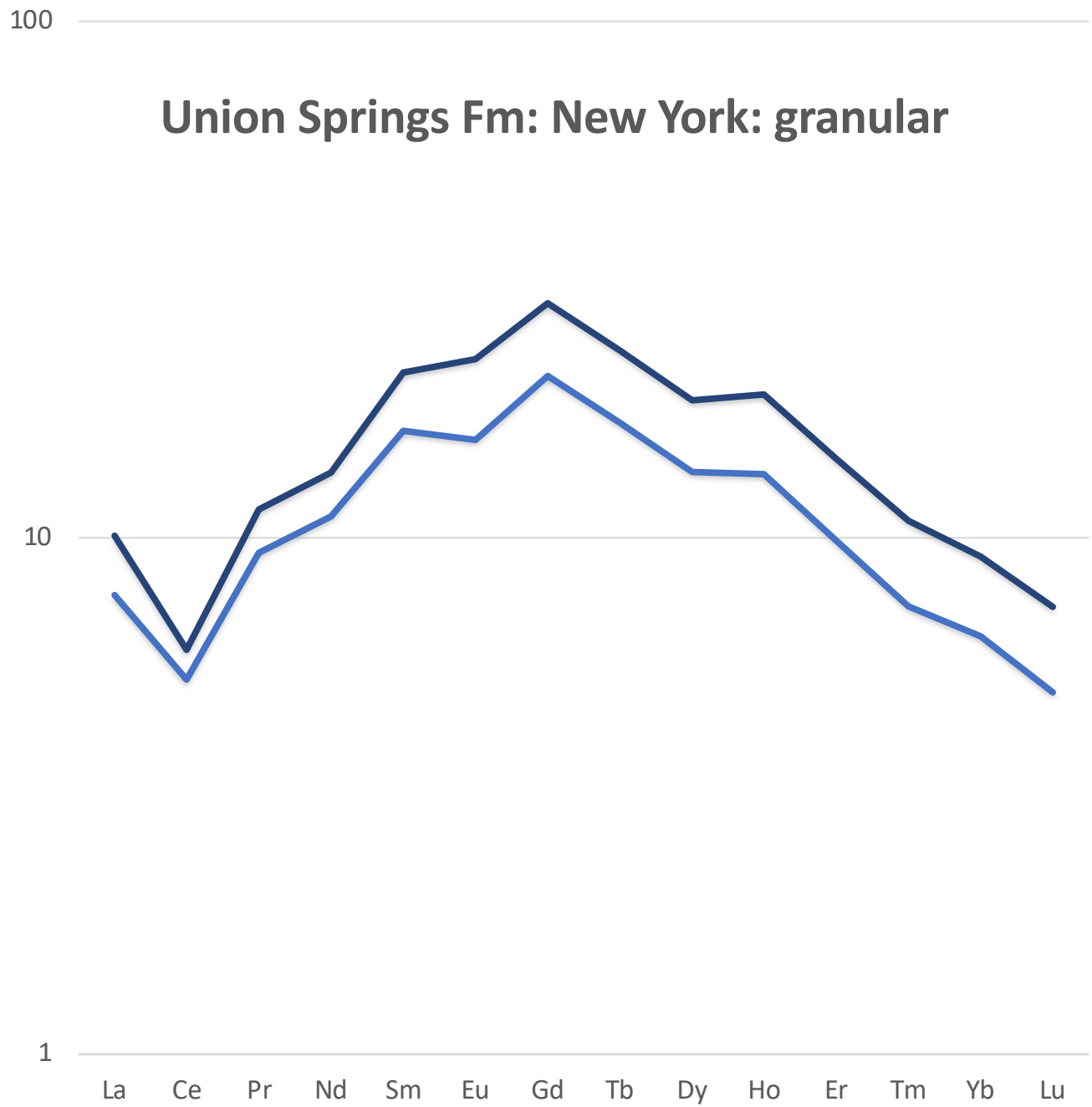

Carboniferous
360
365
370
375
380
385
390
395
400
405
410
415
420
359.3
Late
Famennian
371.1
Frasnian
378.9
Middle
Givetian
385.3
Eifelian
394.3
Early
Emsian
new Emsian base under discussion, potentially FAD of
Eocostapoly-gnathus excavatus
407.3
410.51
Pragian
412.4
Lochkovian
419.0
Silurian

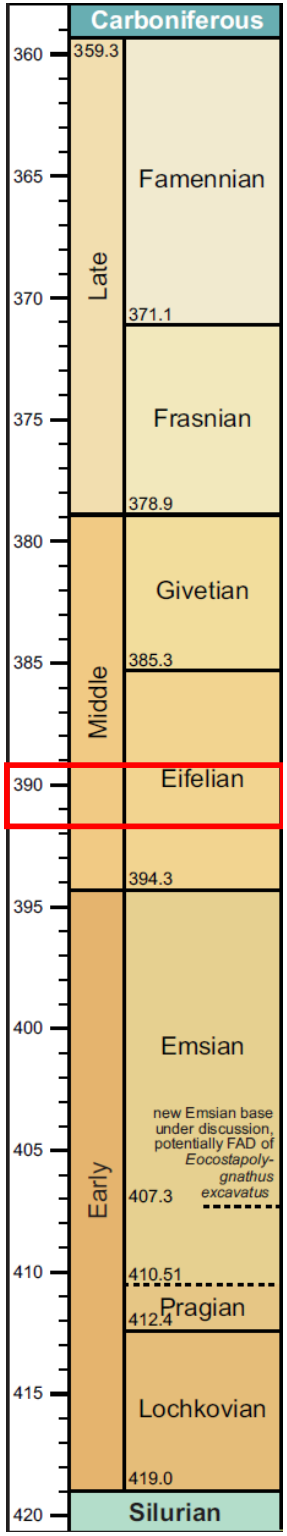

Schoharie Fm: New York: clasts
100
10
1
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

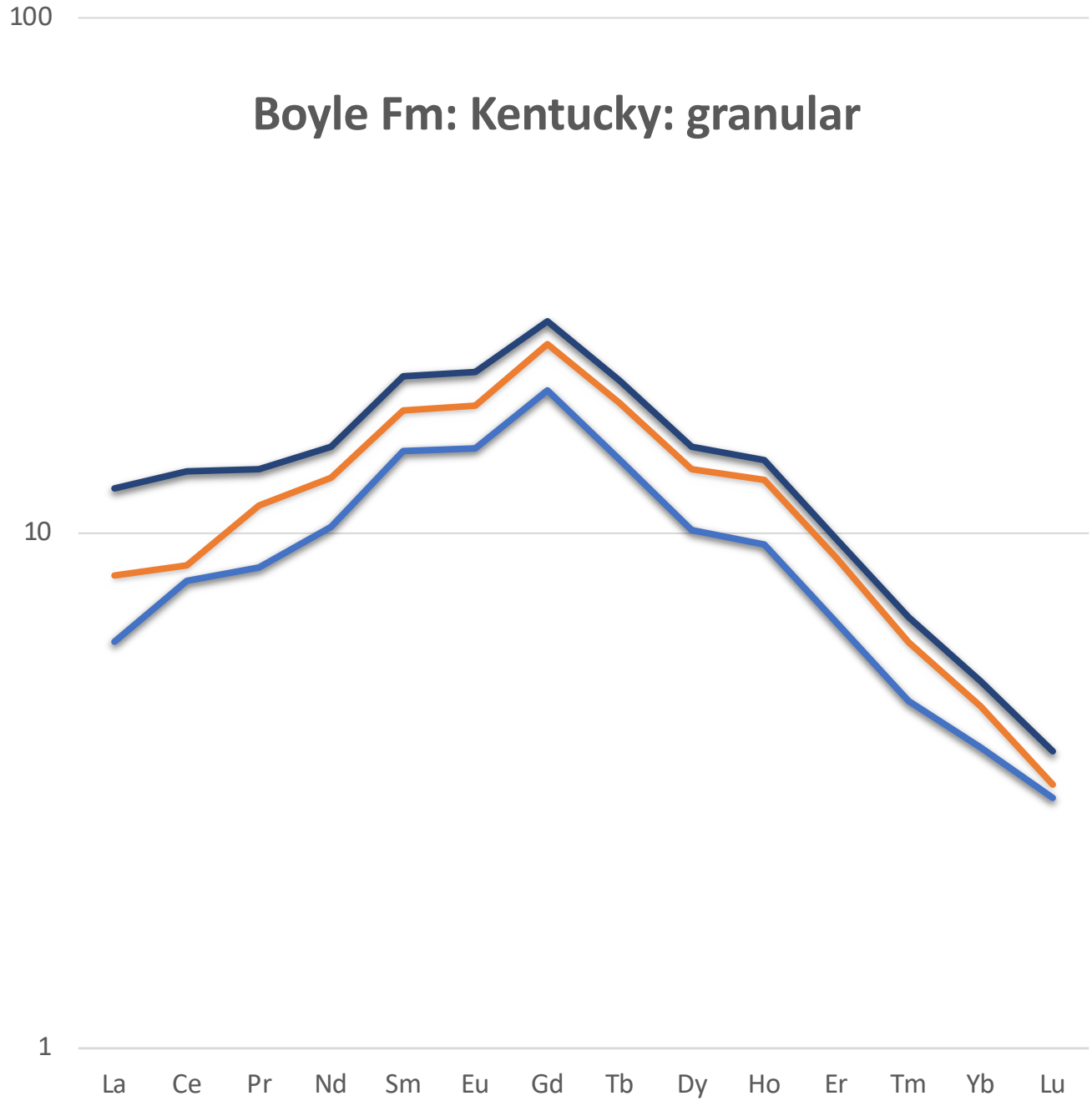

Carboniferous
360
365
370
375
380
385
390
395
400
405
410
415
420
359.3
Late
Famennian
371.1
Frasnian
378.9
Middle
Givetian
385.3
Eifelian
394.3
Early
Emsian
new Emsian base under discussion, potentially FAD of Eocostapoly-gnathus excavatus
407.3
410.51
Pragian
412.4
Lochkovian
419.0
Silurian

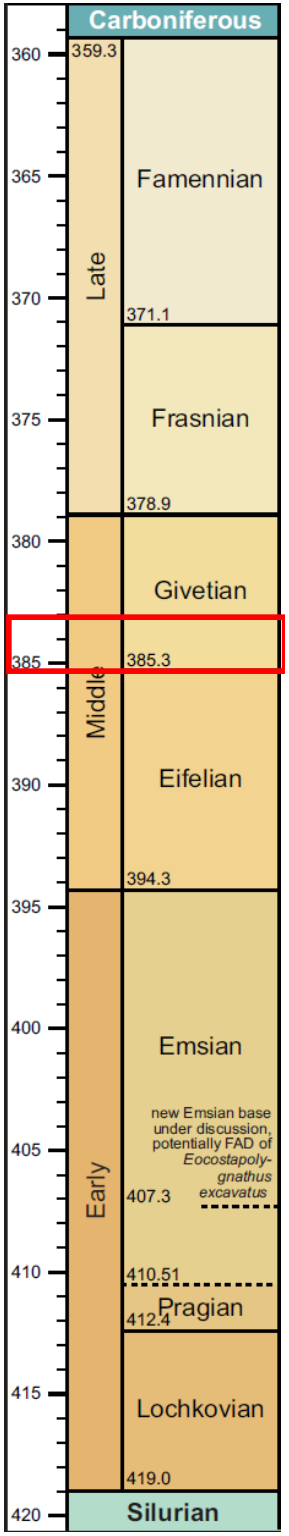

Onondaga Fm: New York: clasts
100
10
1
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu


Carboniferous
360
365
370
375
380
385
390
395
400
405
410
415
420
359.3
Late
Famennian
371.1
Frasnian
378.9
Middle
Givetian
385.3
Eifelian
394.3
Early
Emsian
new Emsian base under discussion, potentially FAD of Eocostapoly-gnathus excavatus
407.3
410.51
Pragian
412.4
Lochkovian
419.0
Silurian

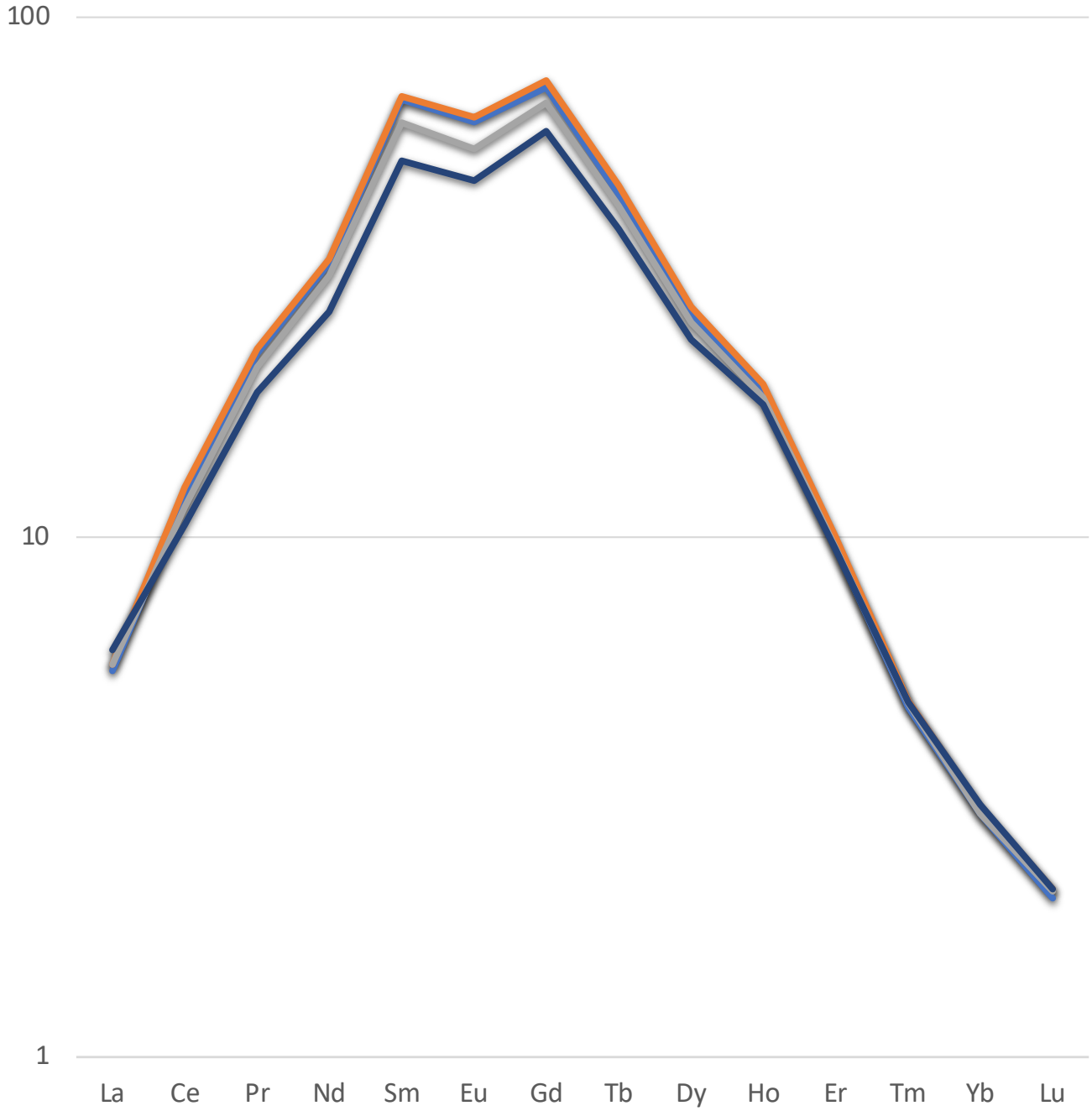

Union Springs Fm: New York: granular
100
10
1
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

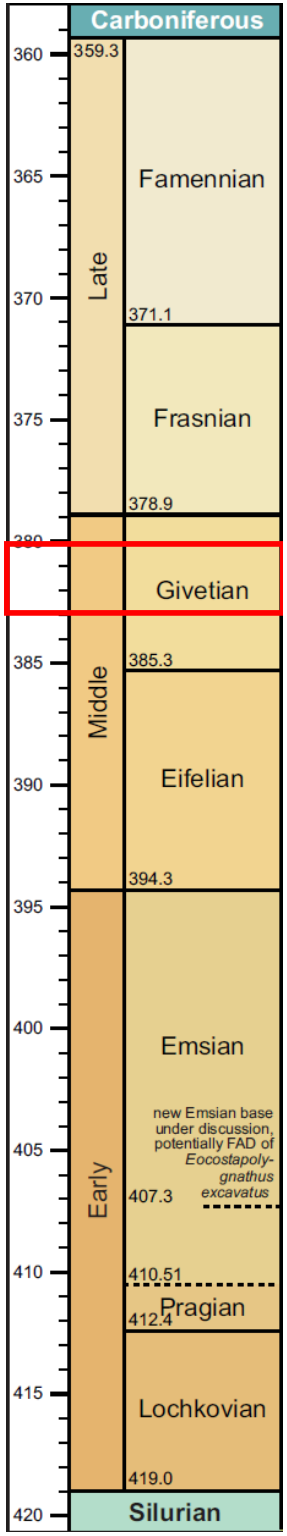

Carboniferous
360
365
370
375
380
385
390
395
400
405
410
415
420
359.3
Late
Famennian
371.1
Frasnian
378.9
Middle
Givetian
385.3
Eifelian
394.3
Early
Emsian
new Emsian base under discussion, potentially FAD of Eocostapoly-gnathus excavatus
407.3
410.51
Pragian
412.4
Lochkovian
419.0
Silurian

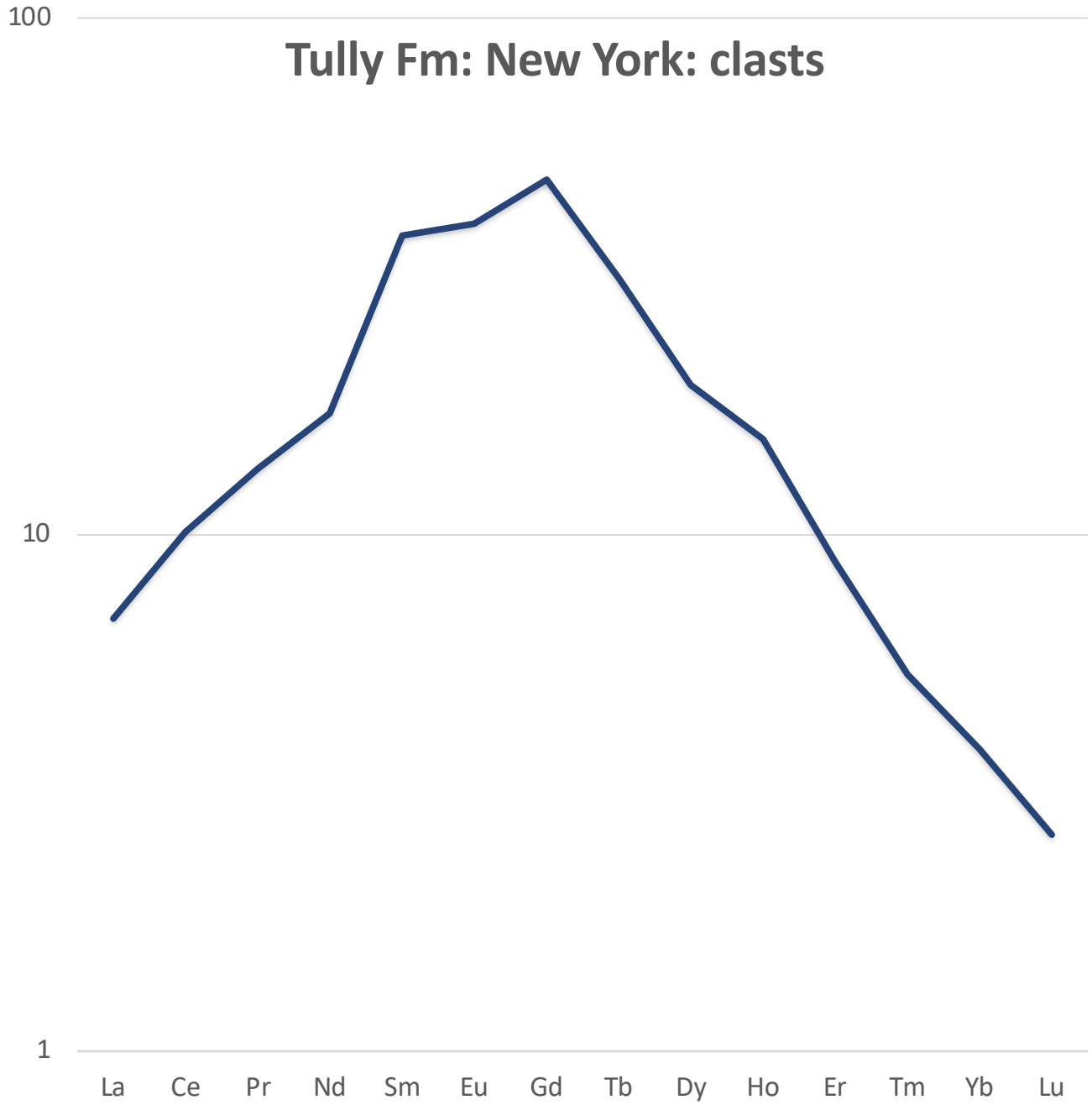

Boyle Fm: Kentucky: granular
100
10
1
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

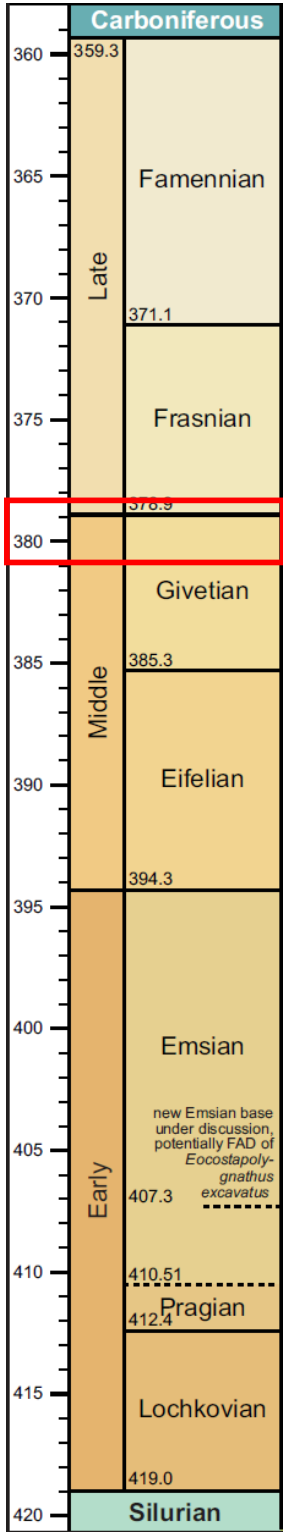

Carboniferous
360
365
370
375
380
385
390
395
400
405
410
415
420
359.3
Late
Famennian
371.1
Frasnian
378.9
Middle
Givetian
385.3
Eifelian
394.3
Early
Emsian
new Emsian base under discussion, potentially FAD of Eocostapoly-gnathus excavatus
407.3
410.51
Pragian
412.4
Lochkovian
419.0
Silurian

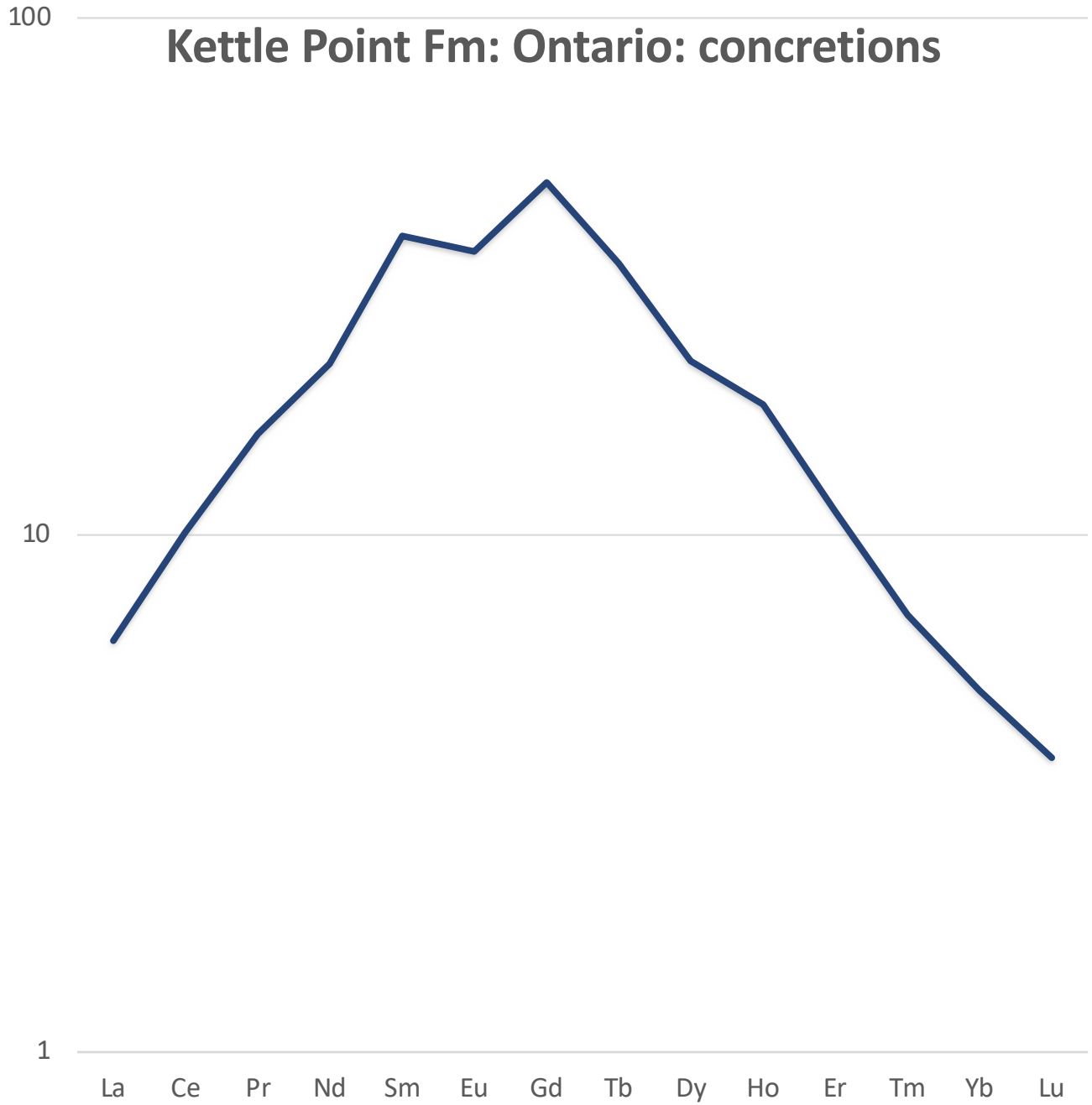
Kashong Mbr: New York: nodules

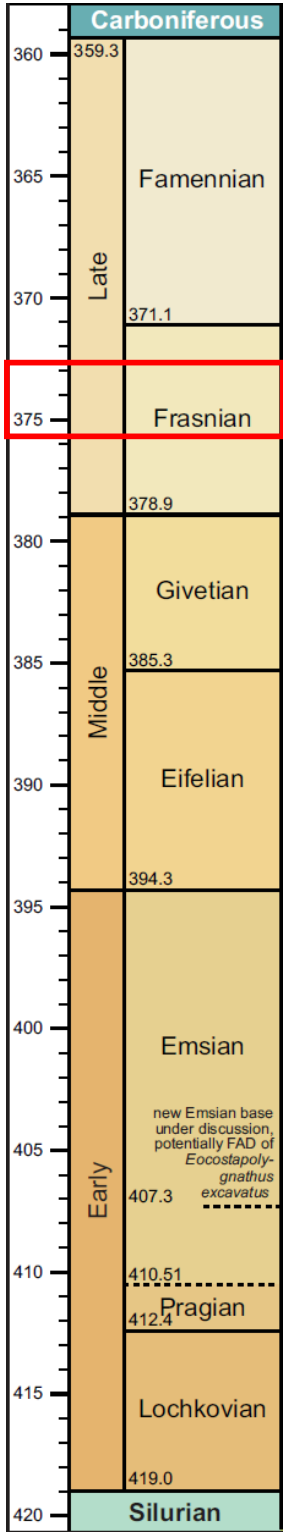


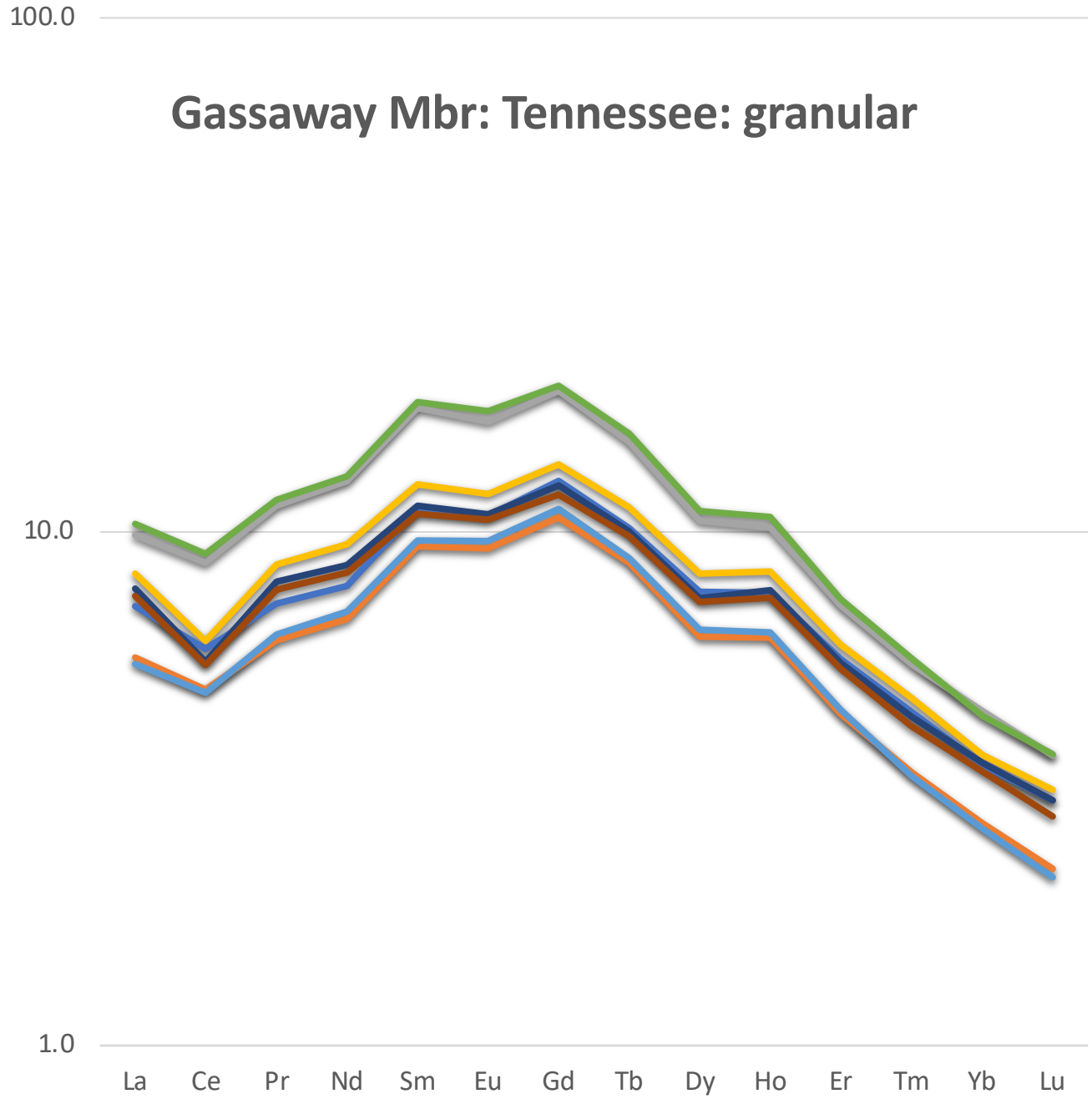


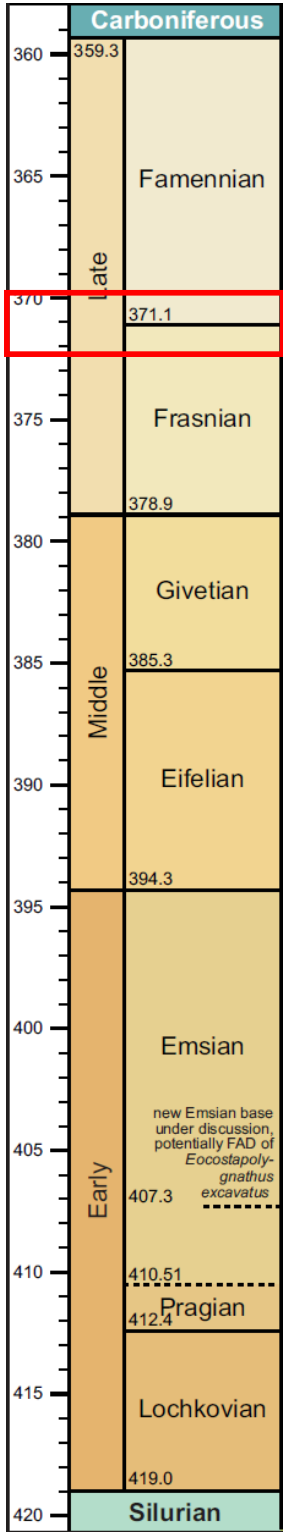

Tully Fm: New York: clasts
100
10
1
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

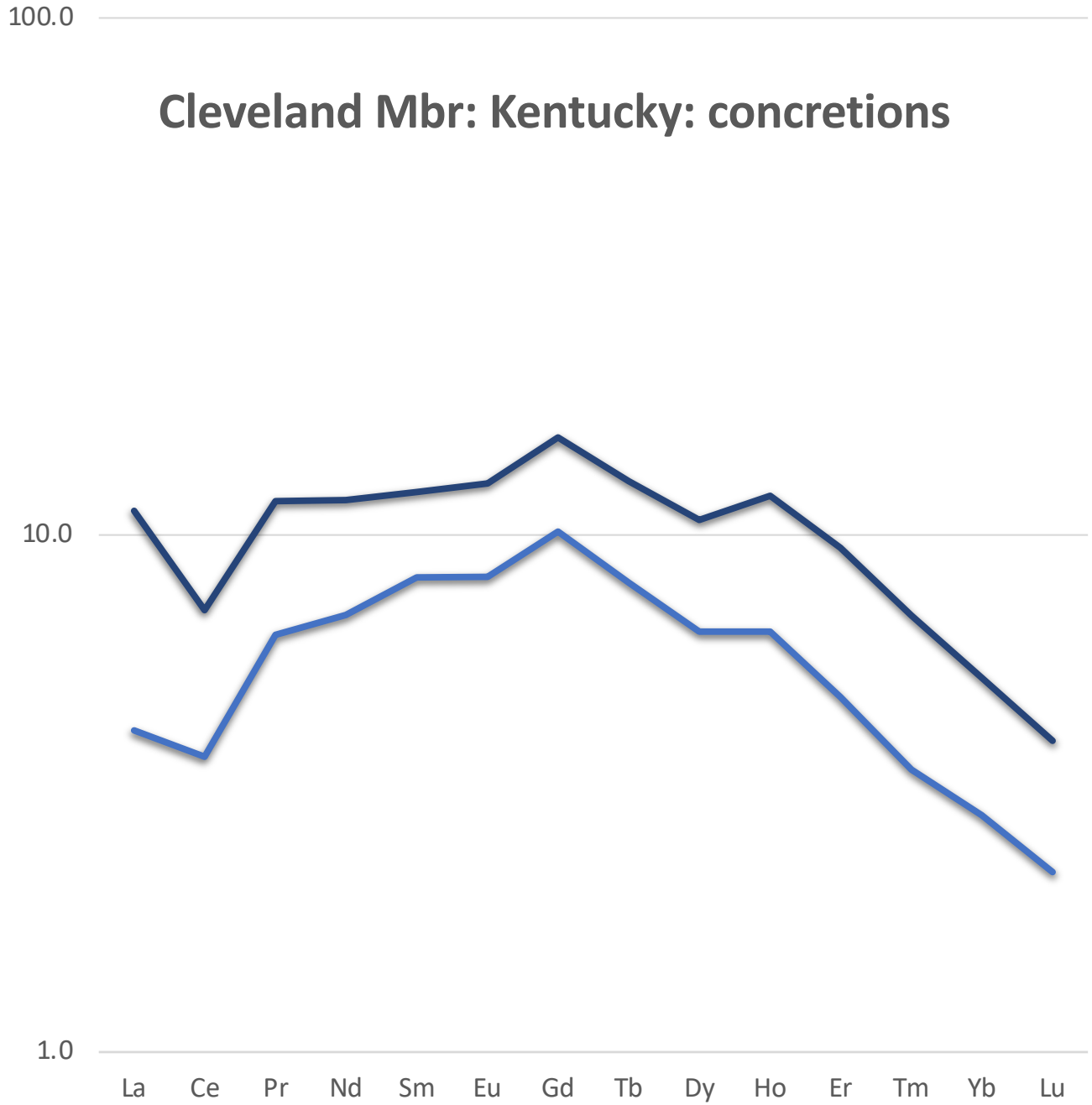

Carboniferous
360
365
370
375
380
385
390
395
400
405
410
415
420
359.3
Late
Famennian
371.1
Frasnian
Middle
Givetian
385.3
Eifelian
394.3
Early
Emsian
new Emsian base under discussion, potentially FAD of Eocostapoly-gnathus excavatus
407.3
410.51
Pragian
412.4
Lochkovian
419.0
Silurian

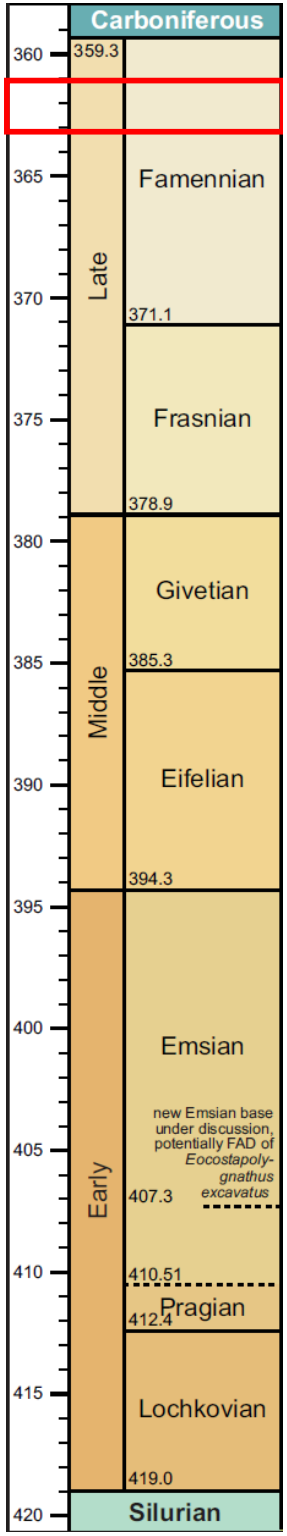

Kettle Point Fm: Ontario: concretions
100
10
1
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu


Carboniferous
360
365
370
375
380
385
390
395
400
405
410
415
420
359.3
Late
Famennian
371.1
Frasnian
378.9
Middle
Givetian
385.3
Eifelian
394.3
Early
Emsian
new Emsian base under discussion, potentially FAD of Eocostapoly-gnathus excavatus
407.3
410.51
Pragian
412.4
Lochkovian
419.0
Silurian

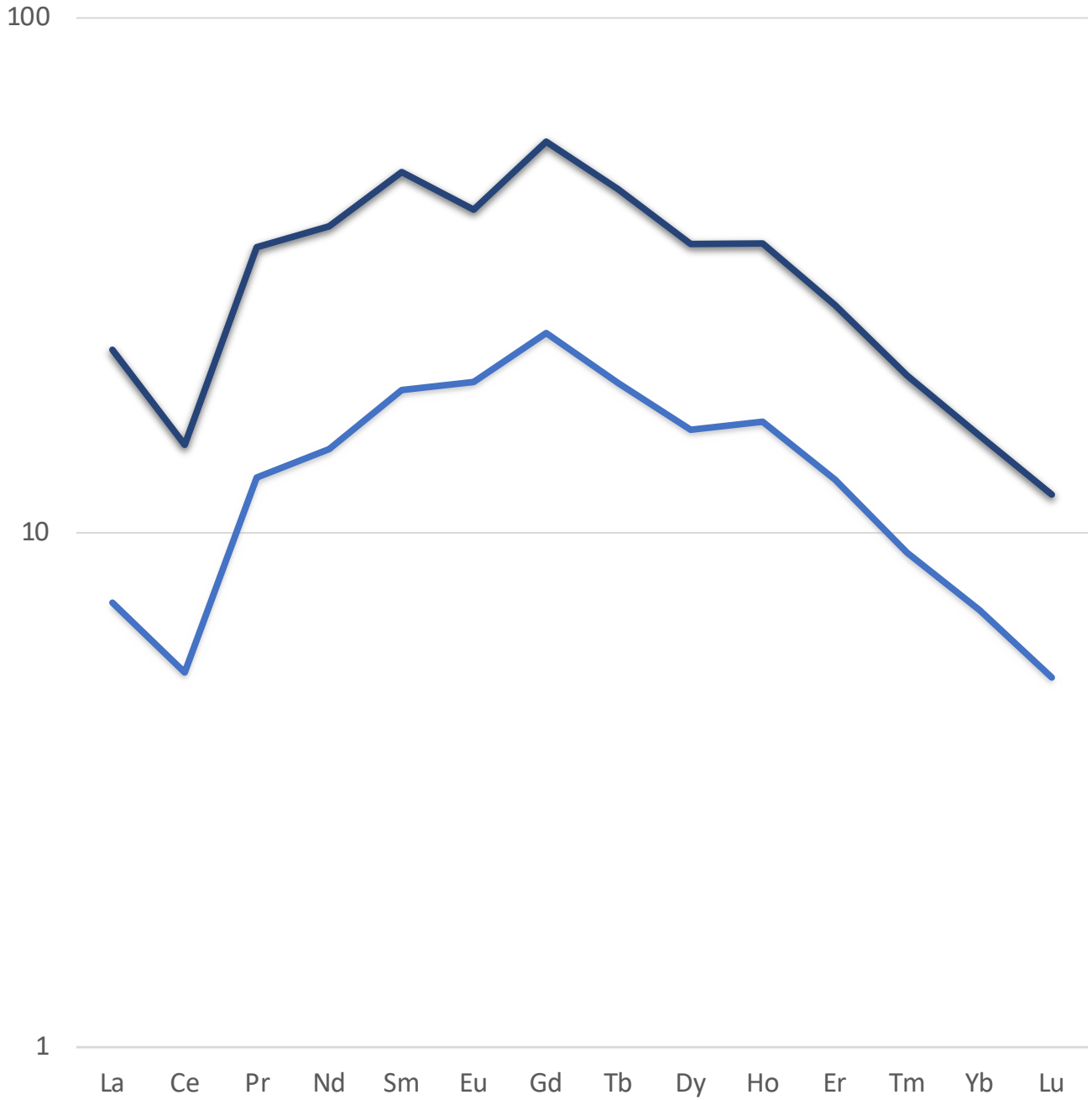

Gassaway Mbr: Tennessee: granular
100.0
10.0
1.0
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

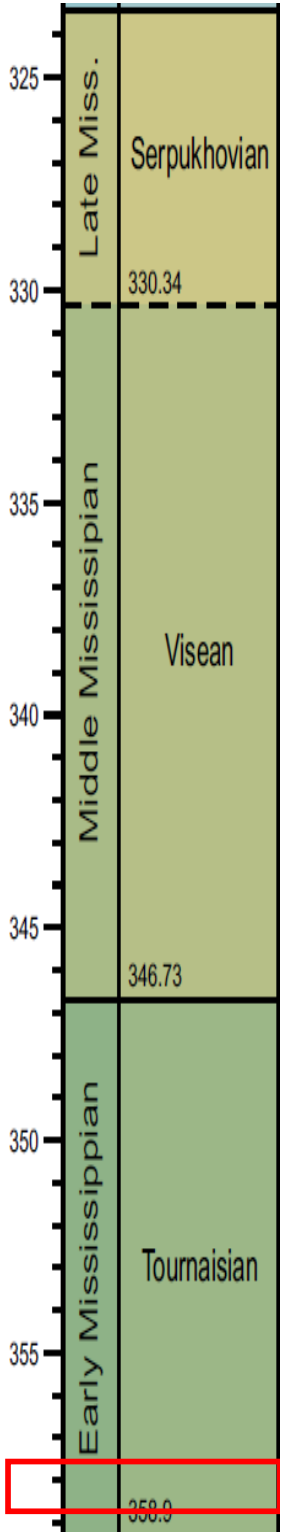

Carboniferous
360
365
370
375
380
385
390
395
400
405
410
415
420
359.3
Late
Famennian
371.1
Frasnian
378.9
Middle
Givetian
385.3
Eifelian
394.3
Early
Emsian
new Emsian base under discussion, potentially FAD of Eocostapoly-gnathus excavatus
407.3
410.51
Pragian
412.4
Lochkovian
419.0
Silurian


Cleveland Mbr: Kentucky: concretions
100.0
10.0
1.0
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu


Carboniferous
360
359.3
365
Famennian
370
371.1
375
Frasnian
378.9
380
Givetian
385
385.3
390
Eifelian
394.3
395
400
Emsian
405
new Emsian base under discussion, potentially FAD of Eocostapoly-gnathus excavatus
407.3
410
410.51
Pragian
412.4
415
Lochkovian
419.0
420
Silurian
Late
Middle
Early

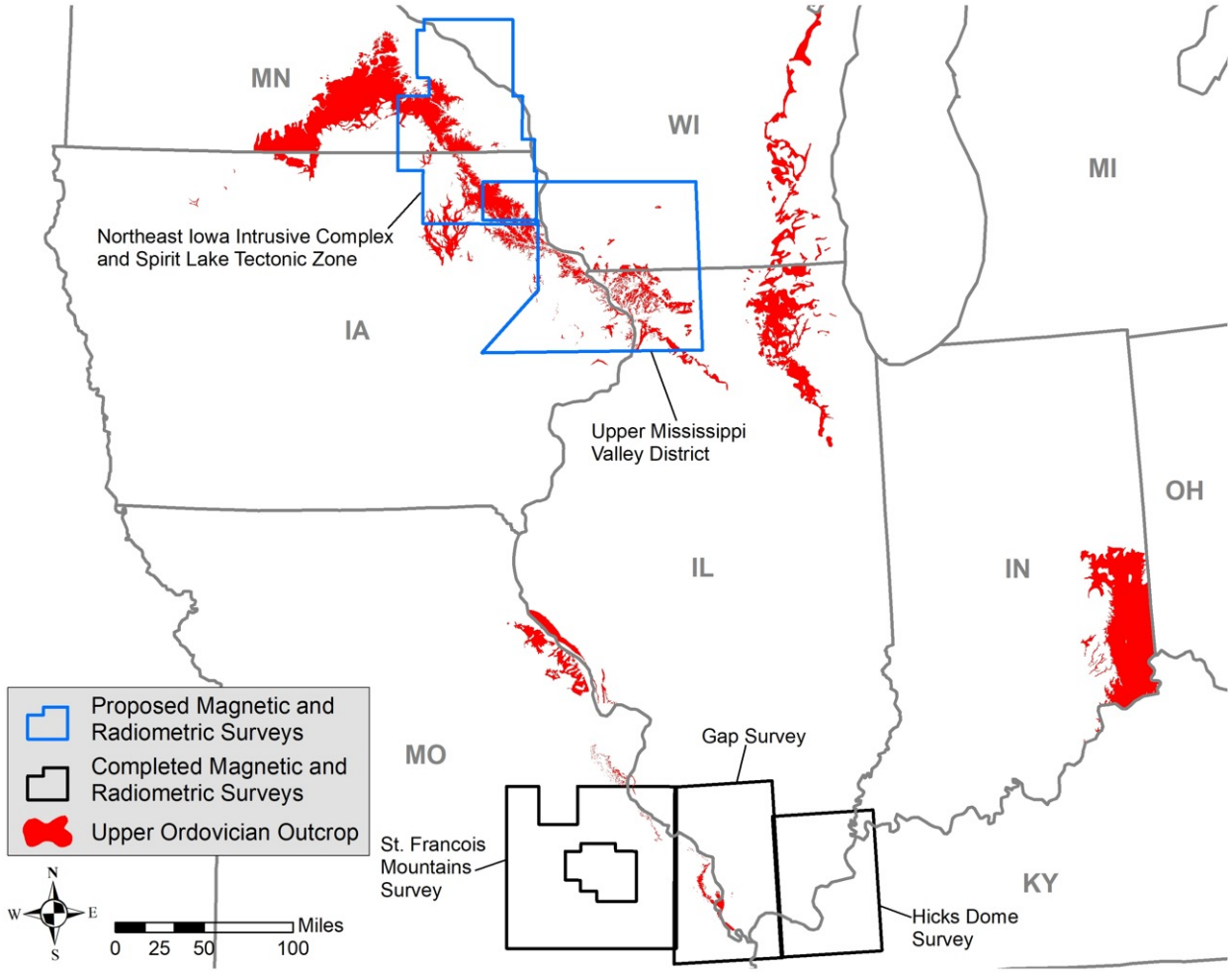
Falling Run Bed: Indiana: concretions



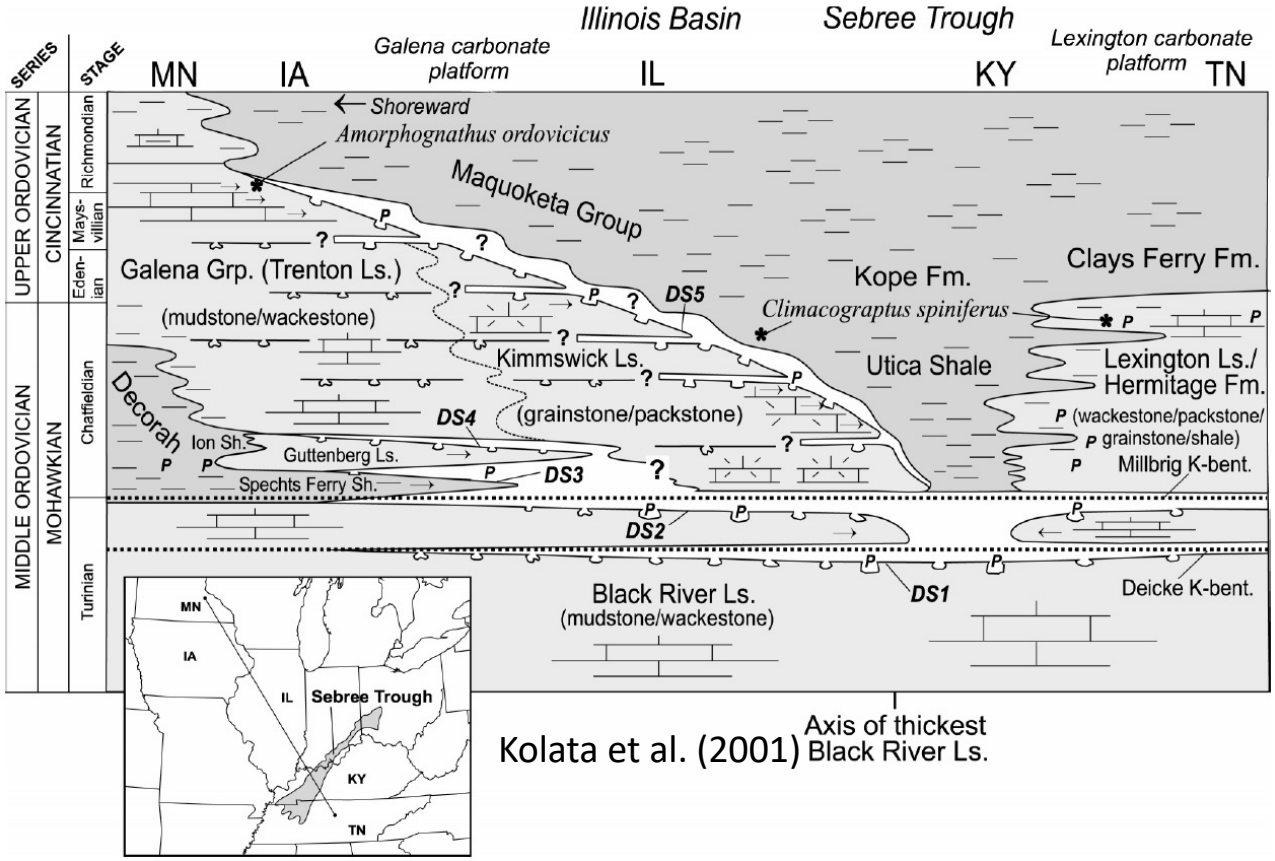


Earth Mapping Resources Initiative:

Geochemical Reconnaissance of Ordovician-aged Rare Earth Element-Enriched Sedimentary Phosphate in the Central United States



Regional stratigraphic framework



Kolata et al. (2001)

Midcontinent Ordovician phosphorite:

Graf, Iowa

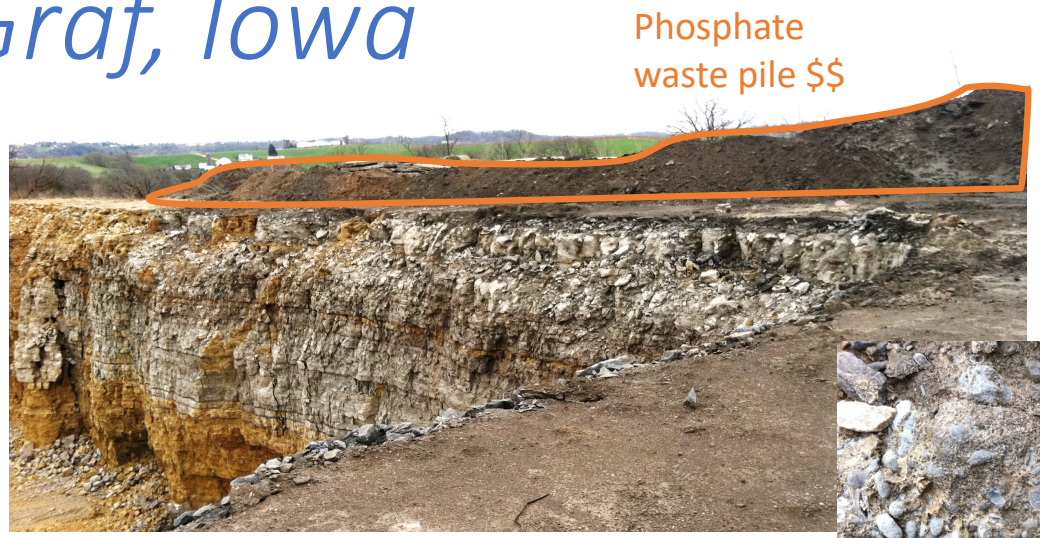
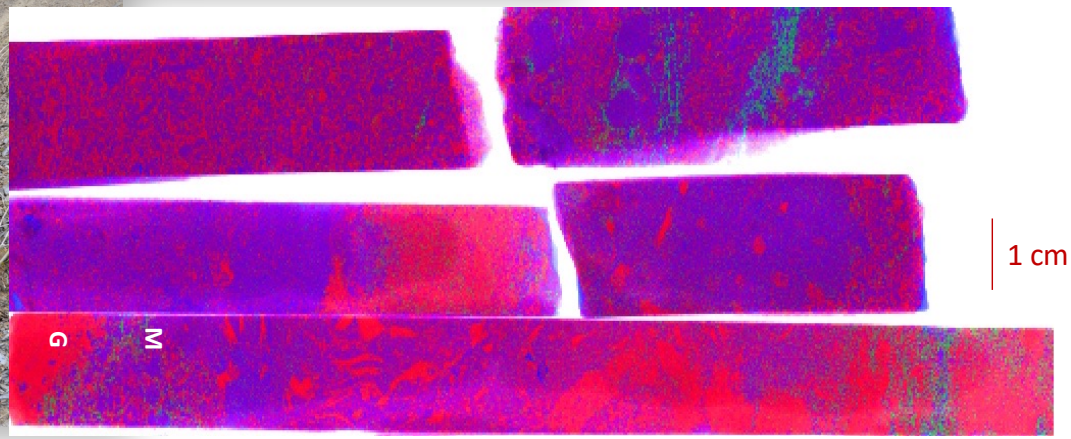


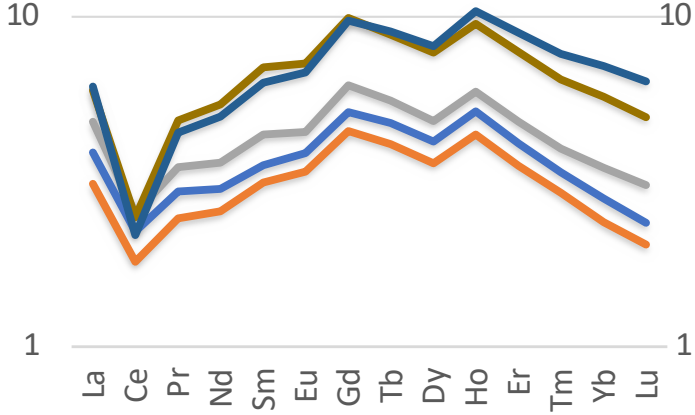
Photo credit: B.J. Witzke



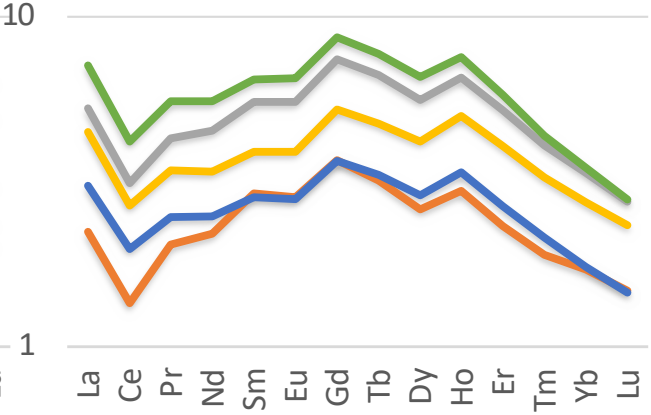
Red = Ca | Green = Al | Blue = P

Ordovician phosphorite: *IA-WI-IL*

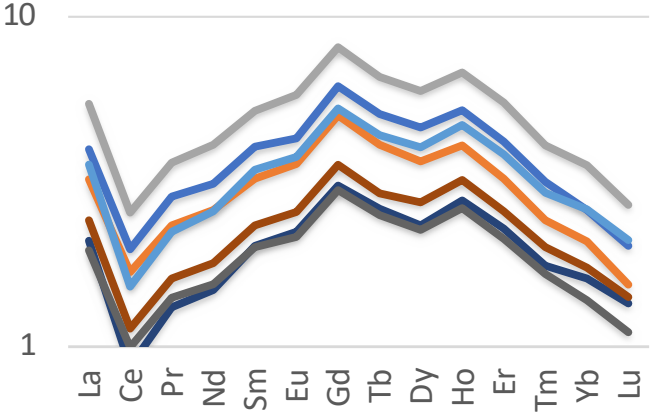
Browns Bottom Quarry
Dubuque, IA



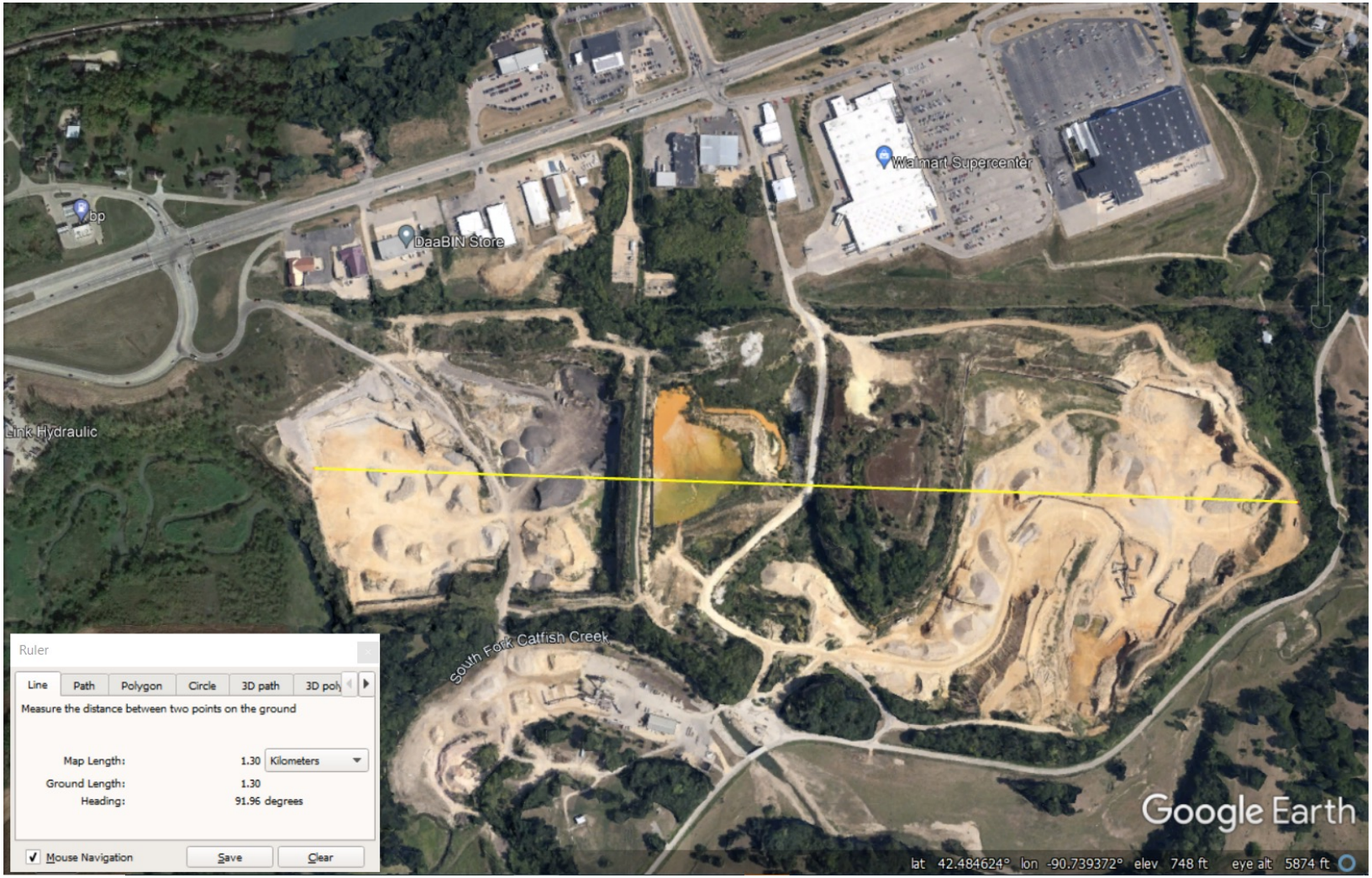
Mt. Carol Quarry
Mt. Carol, IL



Minooka Park core
Milwaukee, WI

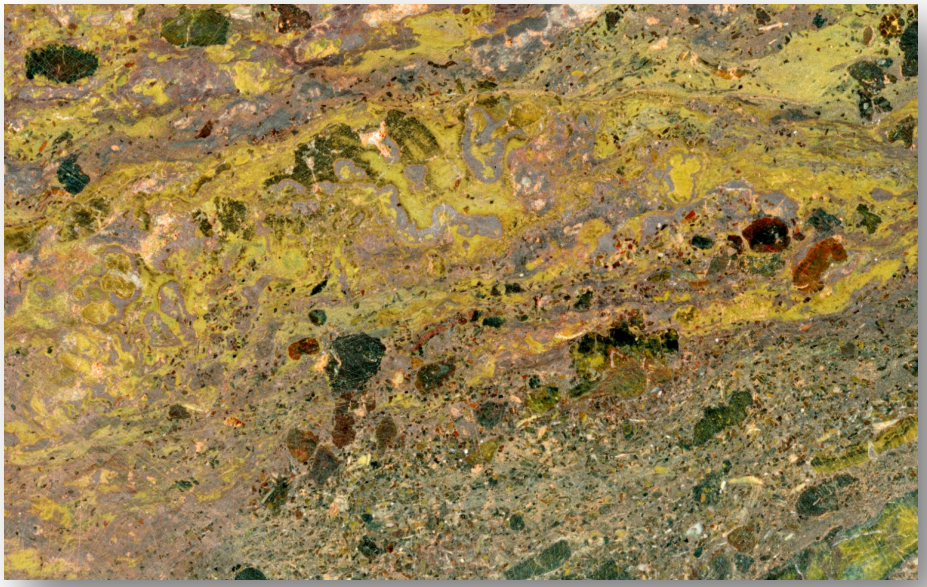


Midcontinent Ordovician phosphorite: *Graf, Iowa*

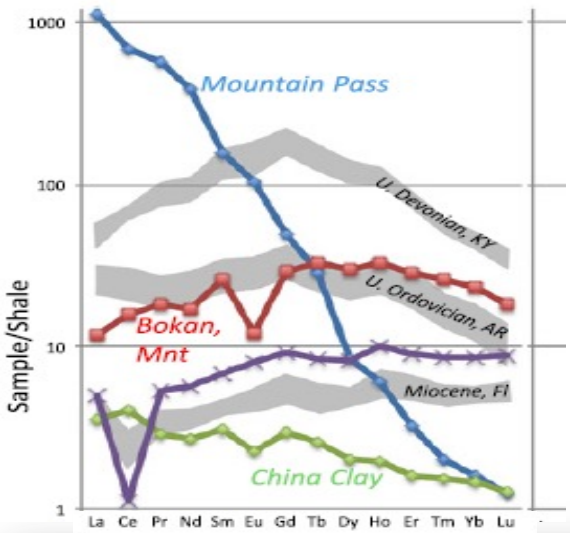


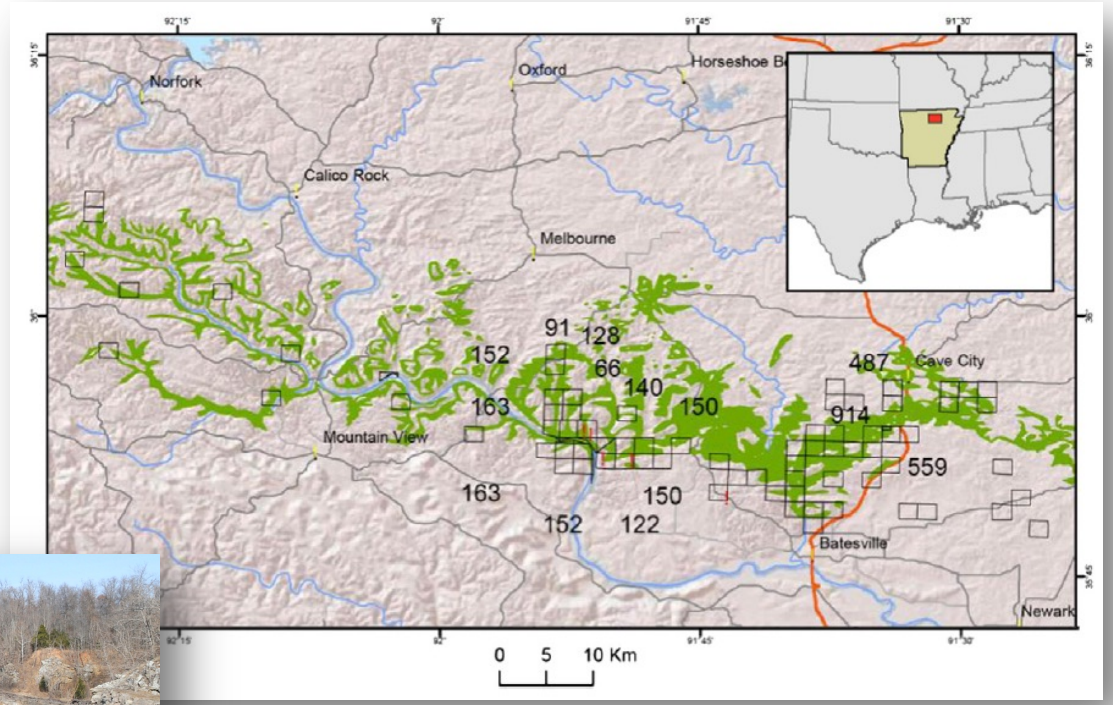
Brown's Quarry in southwestern Dubuque, Iowa ΣHREE >50% Bokan Mnt

Midcontinent Ordovician phosphorite:
Love Hollow, Arkansas



Midcontinent Ordovician phosphorite:
Love Hollow, Arkansas





ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

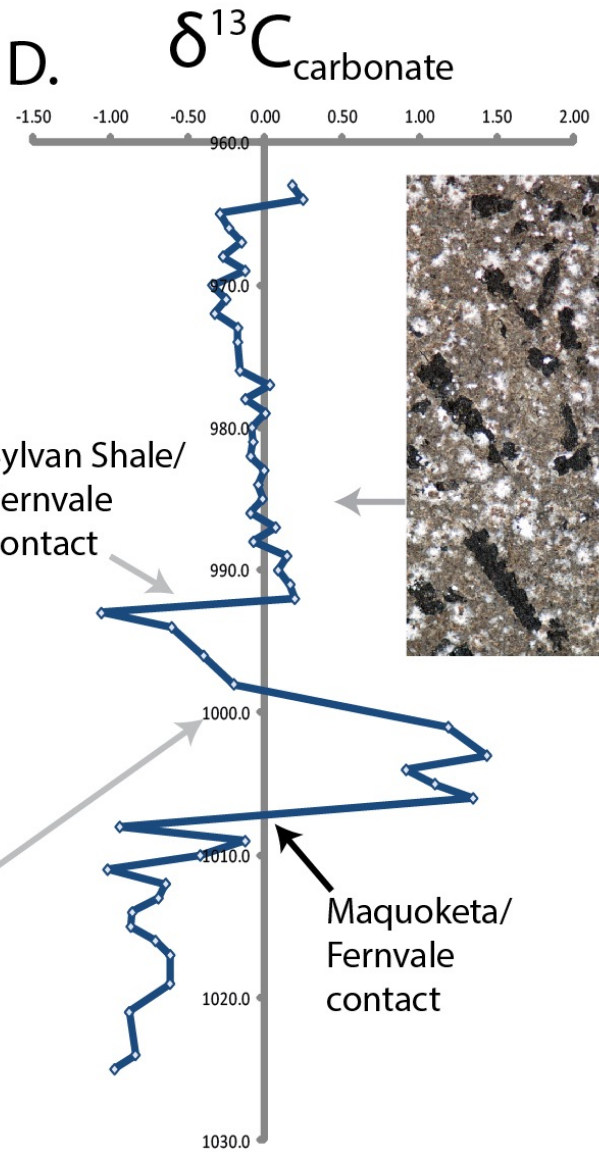
Midcontinent Ordovician phosphorite:
Love Hollow, Illinois

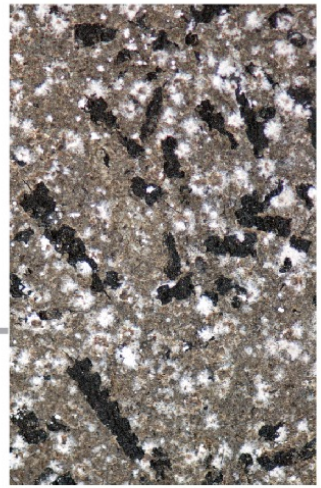
Tuscola, Illinois

paleokarst infill

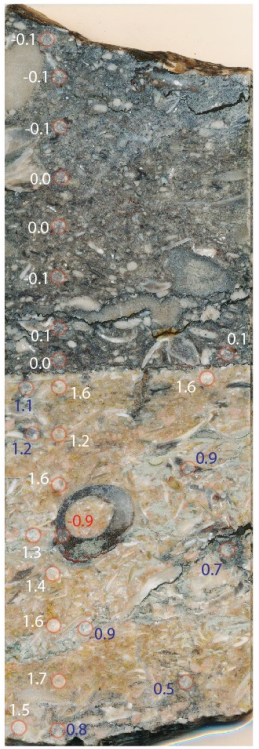
Maquoketa/ Fernvale contact

Fernvale

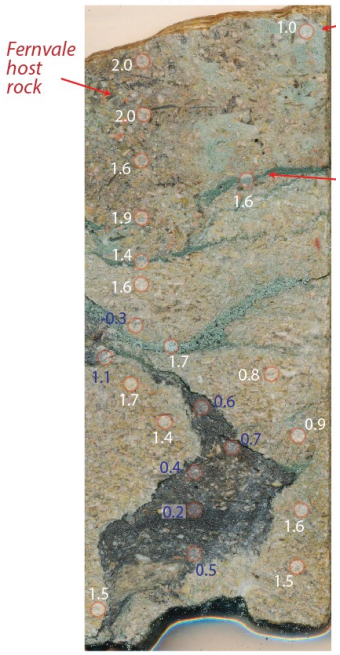




VG999

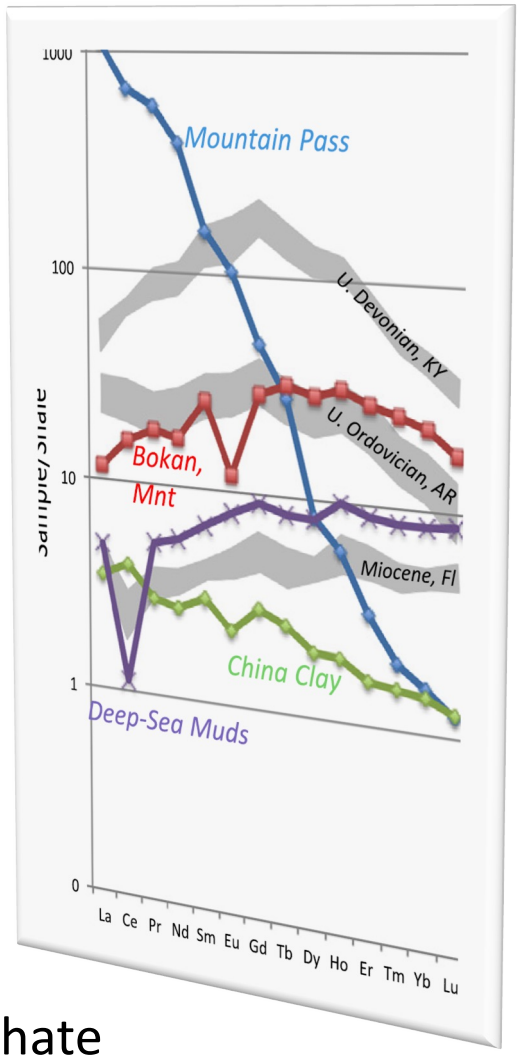


VG1007



Summary

- Devonian phosphate REEs
  - Inventoried cores and outcrops over eastern US
  - Documented secular changes
  - Identified highly prospective intervals
  - More work geo-framework locating “thicks”



- Ordovician phosphate REEs
  - Project still ramping up, runs until Sept. 2024
  - Many samples already analyzed
  - Concentrations similar Florida and Phosphoria phosphate
  - Advanced geo-framework for predicting thicks
  - Coordinated with PhD biostrat project
  - Fledgling geochronology effort underway
  - Regional chemostratigraphy ramping up