Preliminary Assessment of the REE Potential in the Woodford Shale
&
Overview of Cobalt Potential in Western Oklahoma's Stratiform Copper Deposits

Andrew Cullen / Big Hill Adventures

OUTLINE

PART 1 : Woodford Shale

Geochemistry & Usage of REEs
Review of REE Production
Overview of the Woodford Shale
Woodford Shale Phosphate Nodules
The Lawrence Uplift Prospect

PART 2 : Flowerpot Shale

Review of Global Cobalt Production
Geochemistry & Usage of Cobalt
Central African Copperbelt
70% of Global Cobalt Production
Oklahoma's Stratiform Cu Deposits
Cobalt Potential of Creta Mine

ACKNOWLEDGMENTS

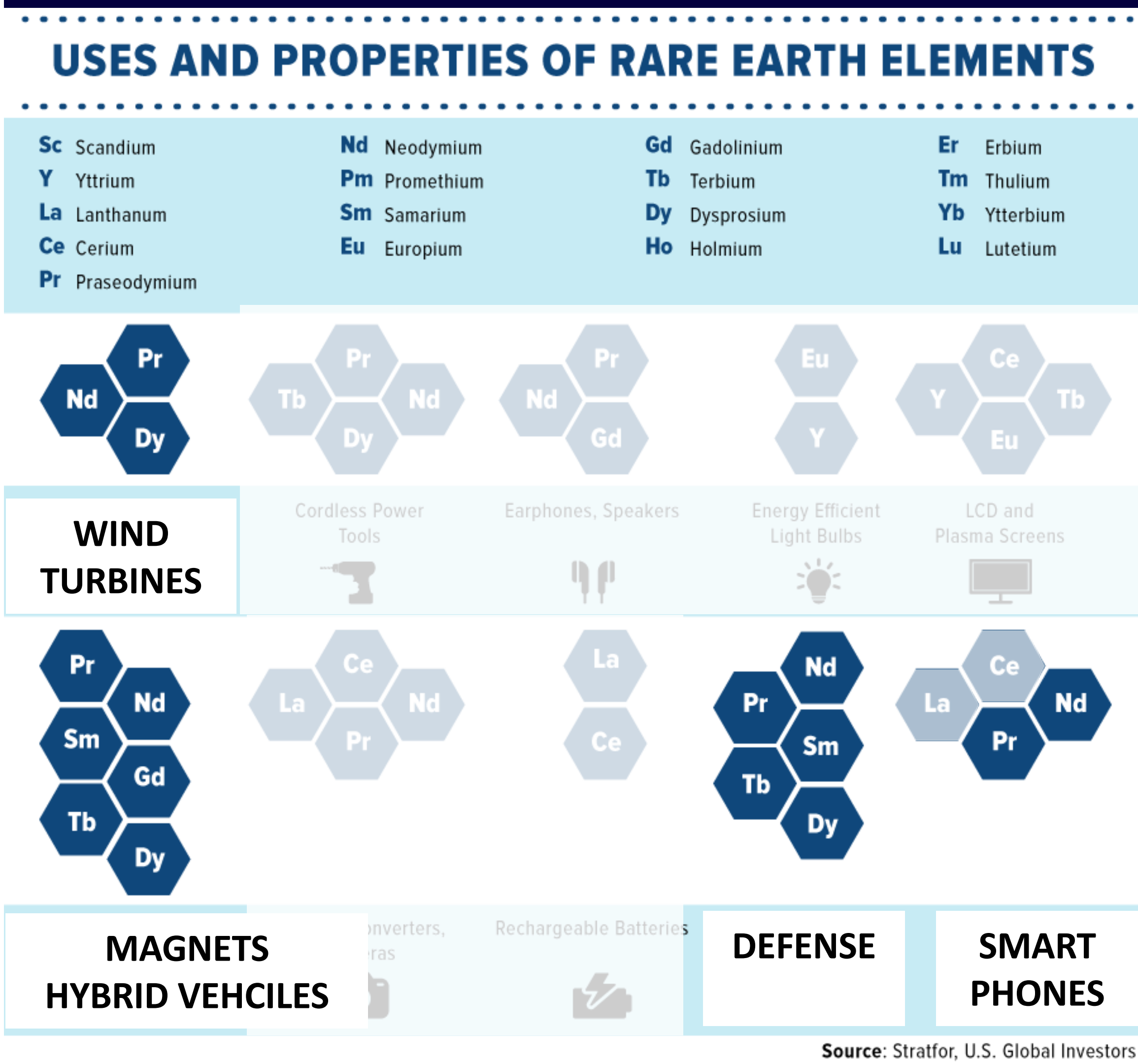
- Nick Hayman (OGS) for funding Woodford analytical work
- Carl Symcox (OGS) and David Hull (Practical Geoscience) for assistance in the field and guidance.

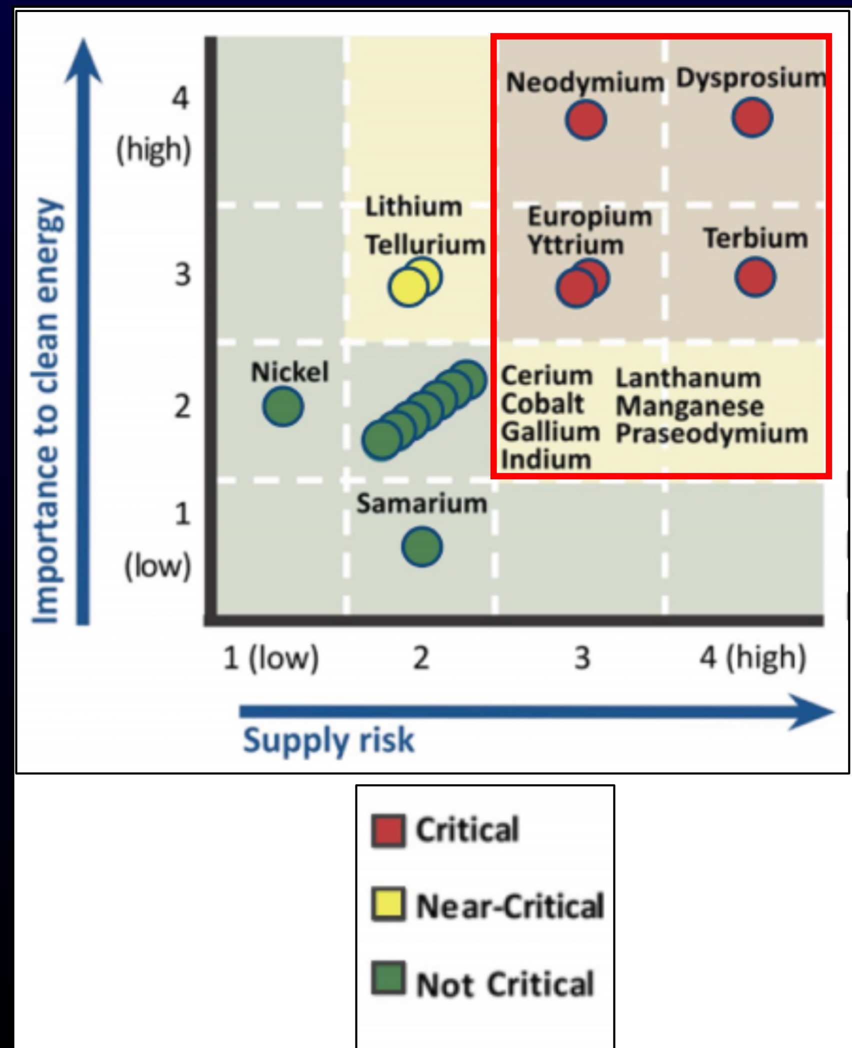
Rare Earth Element Potential of the Phosphate Nodules in the Woodford Shale

- Usage & Geochemistry of REEs
- Review of REE Production
- REE in Apatite
- Overview of the Woodford Shale
- Woodford Shale Phosphate Nodules
- The Lawrence Uplift Prospect

Usage of Rare Earth Elements

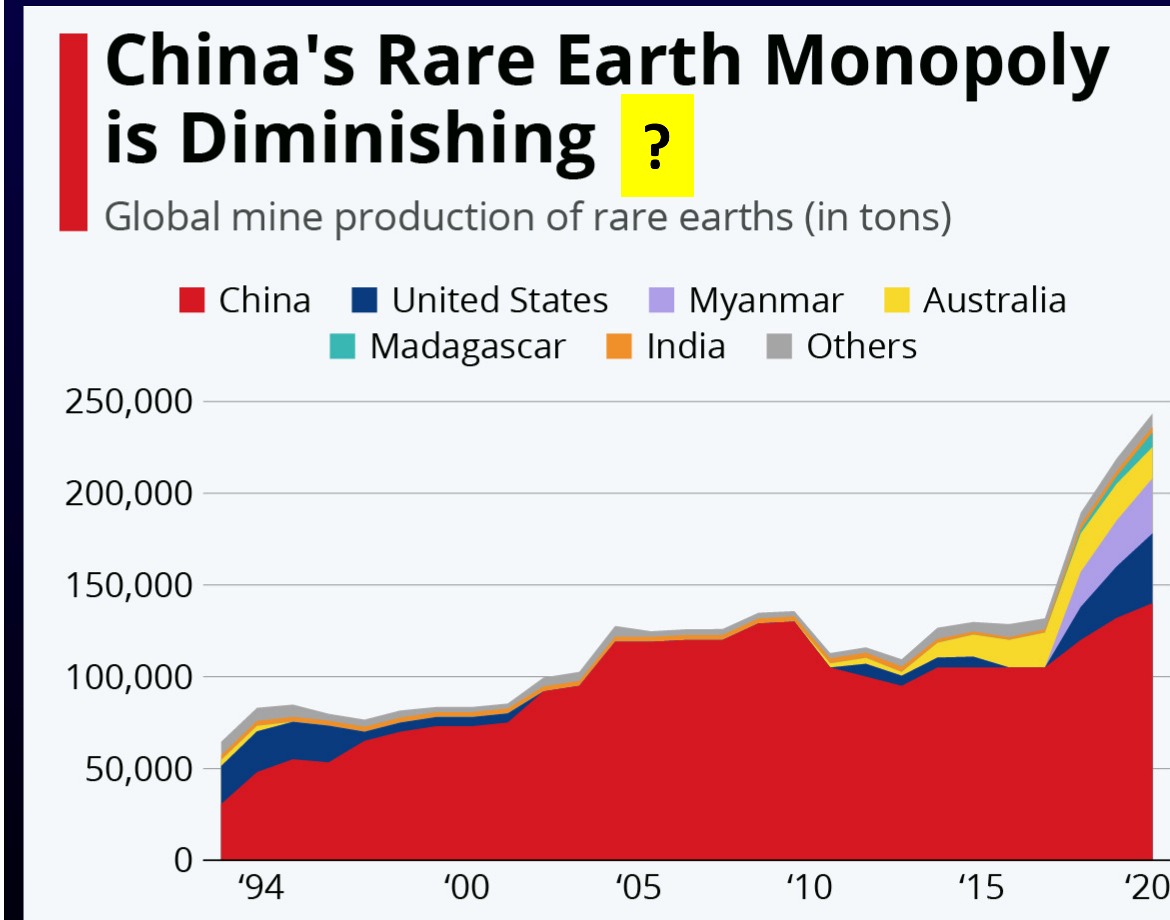
High Importance and Supply Chain Risk
Neodymium, Dysprosium, Terbium Praseodymium
Wind Turbine, High-end Magnets, Defense, Smartphones



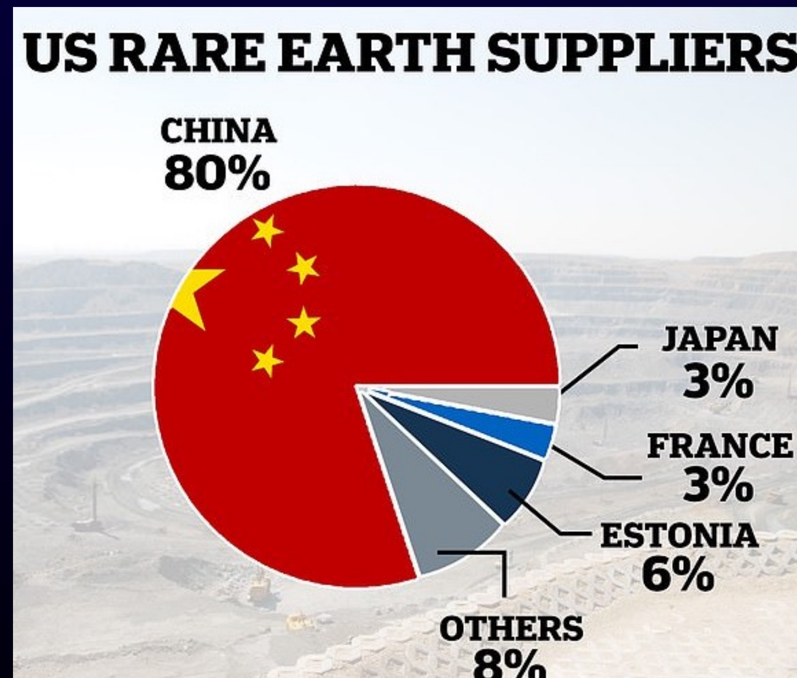


Supply Chain Issues & Threats to US

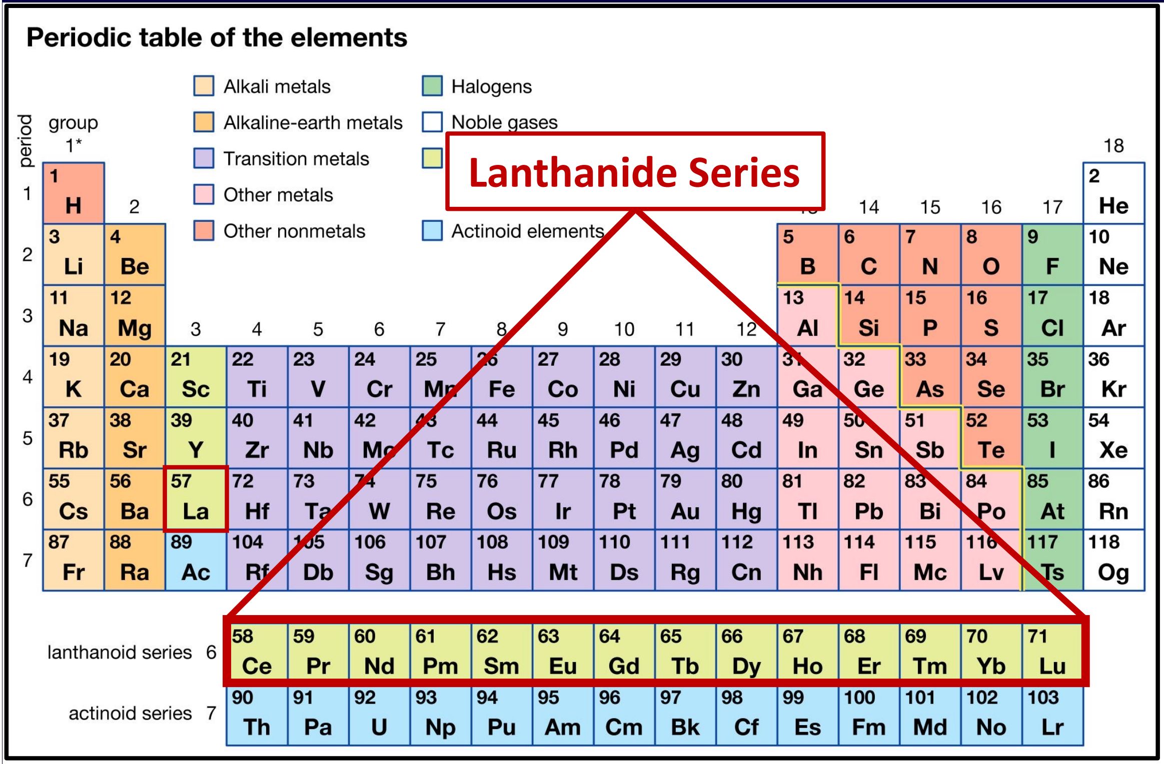
Mine production numbers are misleading.



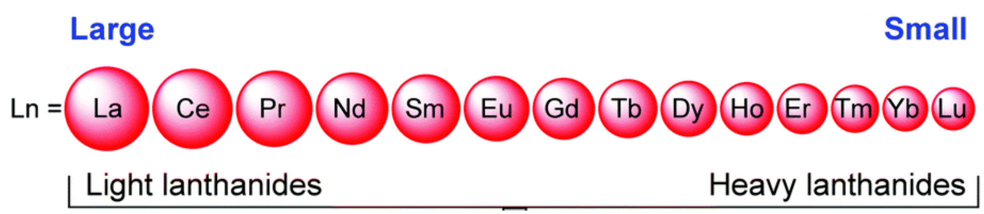
Ore concentrates from US and Australia are shipped to China for smelting and then exported.



Geochemistry and Mineralogy of Rare Earth Elements



- The lanthanide contraction keeps rare-earth ions about the same size.
- REE ions are generally have +3 oxidation state.
- Their chemical properties are similar with the result that at least small amounts of each one are usually present in every rare-earth mineral.
- This makes separation into high purity difficult



The 5d[1] and 6s[2] electron shells fill before the 4f [1-14] shell. As the inner 4f shell fills the ionic radius decreases.

There are ~ 10 REE-bearing minerals

Mineral	Formula
Allanite	(Ce,Ca,Y)2(Al,Fe3+)3(SiO4)3(OH)
Ancylite	**CeSr(CO3)2(OH)▪H2O**
Apatite	**Ca5(PO4)3(OH)(F,Cl)**
Bastnaesite	(Ce,La)(CO3)F
Euxenite	(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)2O6
Fergusonite	(Nd,Ce)(Nb,Ti)O4
Florencite	CeAl3(PO4)2(OH)6
Monazite (placer)	**(Ce,La,Nd,Th)PO4**
Parisite	Ca(Ce,La)2(CO3)3F2
Xenotime	YPO4

Apatite is the only common REE-bearing mineral formed in the sedimentary environment (precipitated from sea water)

REE in Apatite

There are 3 types of apatite that differ in their F, Cl, and OH content.
1) Chlorapatite 2) Fluorapatite 3) Hydroxyapatite

Substitution of other elements such as rare earth elements (REE), sodium, strontium and manganese the crystal lattice commonly occurs.

There are two processes of REE enrichment in apatite involving coupled substitutions

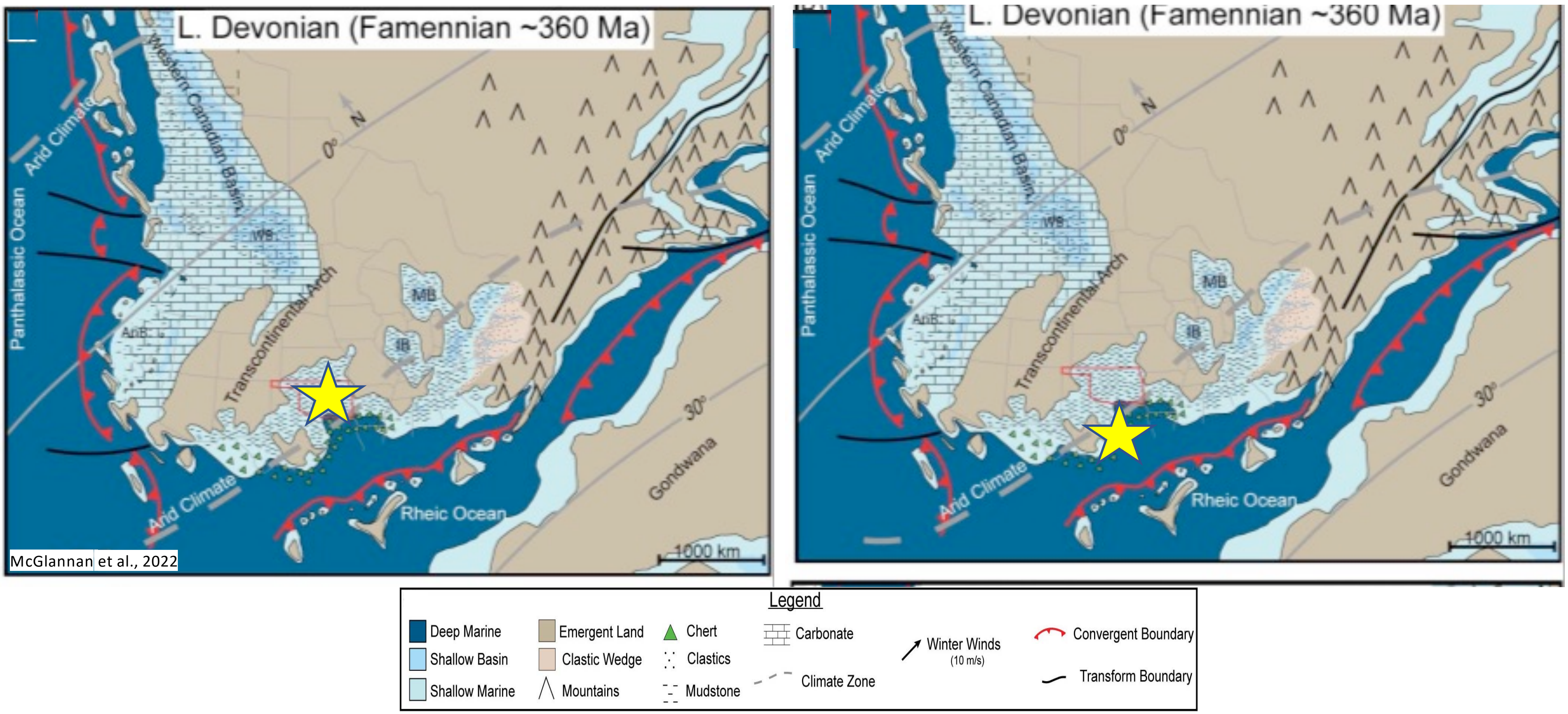
1) $REE^{3+} \Leftrightarrow Na^{+} + Ca^{2+}$
2) $REE^{3+} + Si^{4+} \Leftrightarrow P^{5+}$

Most global REE recovery is the by-product from other mining operations.

The separation of REEs from host (hard rock minerals) minerals is one of the most challenging processes in solvent extraction and generally involves multiple steps.

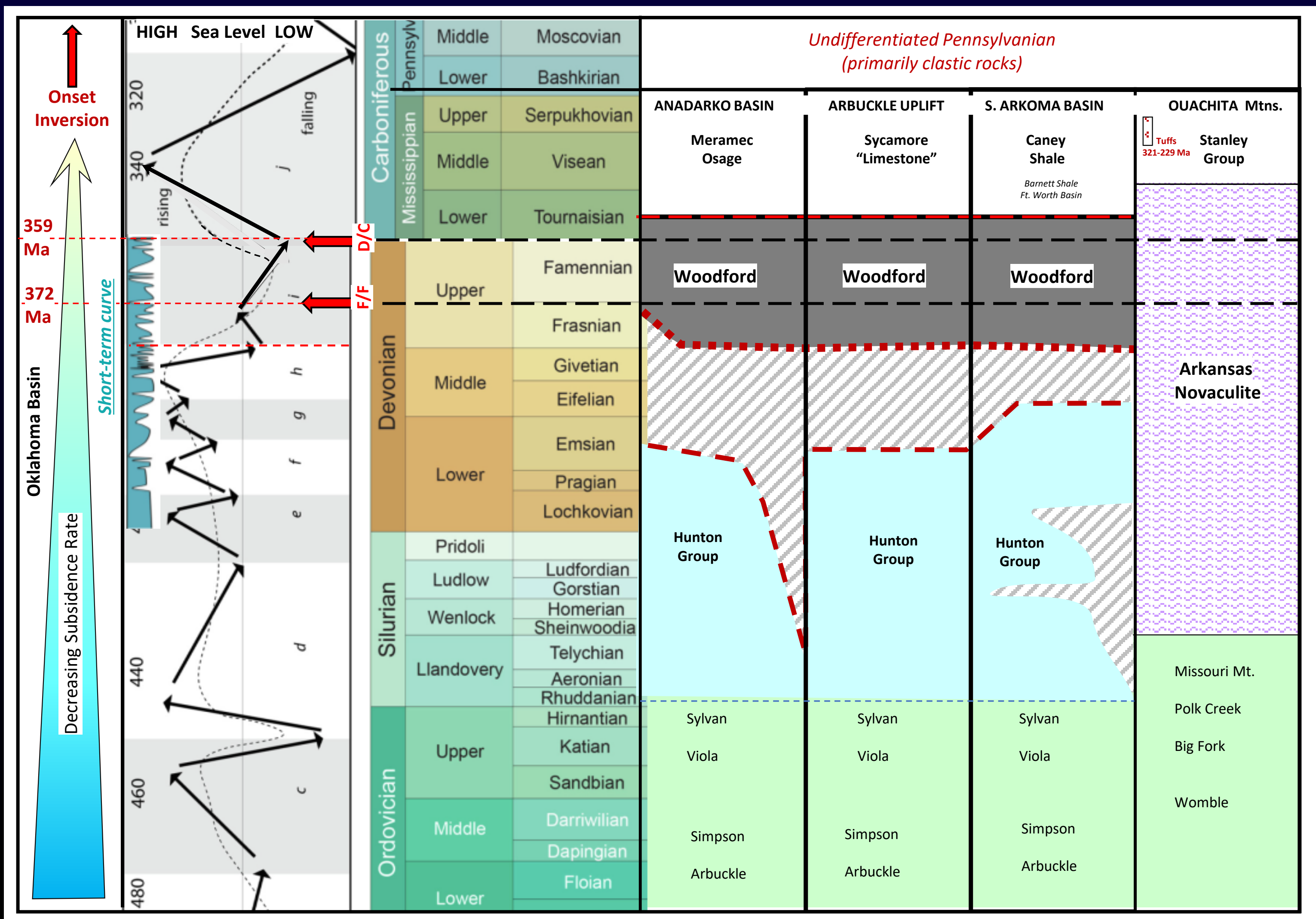
Recovery of REE from apatite by acid leaching and concentration as salts is a relatively well-established process with recoveries commonly exceeding 60%.

The Woodford Shale was deposited on a south-facing rifted margin on the subducting Laurentian plate during closure of the Rheic Sea



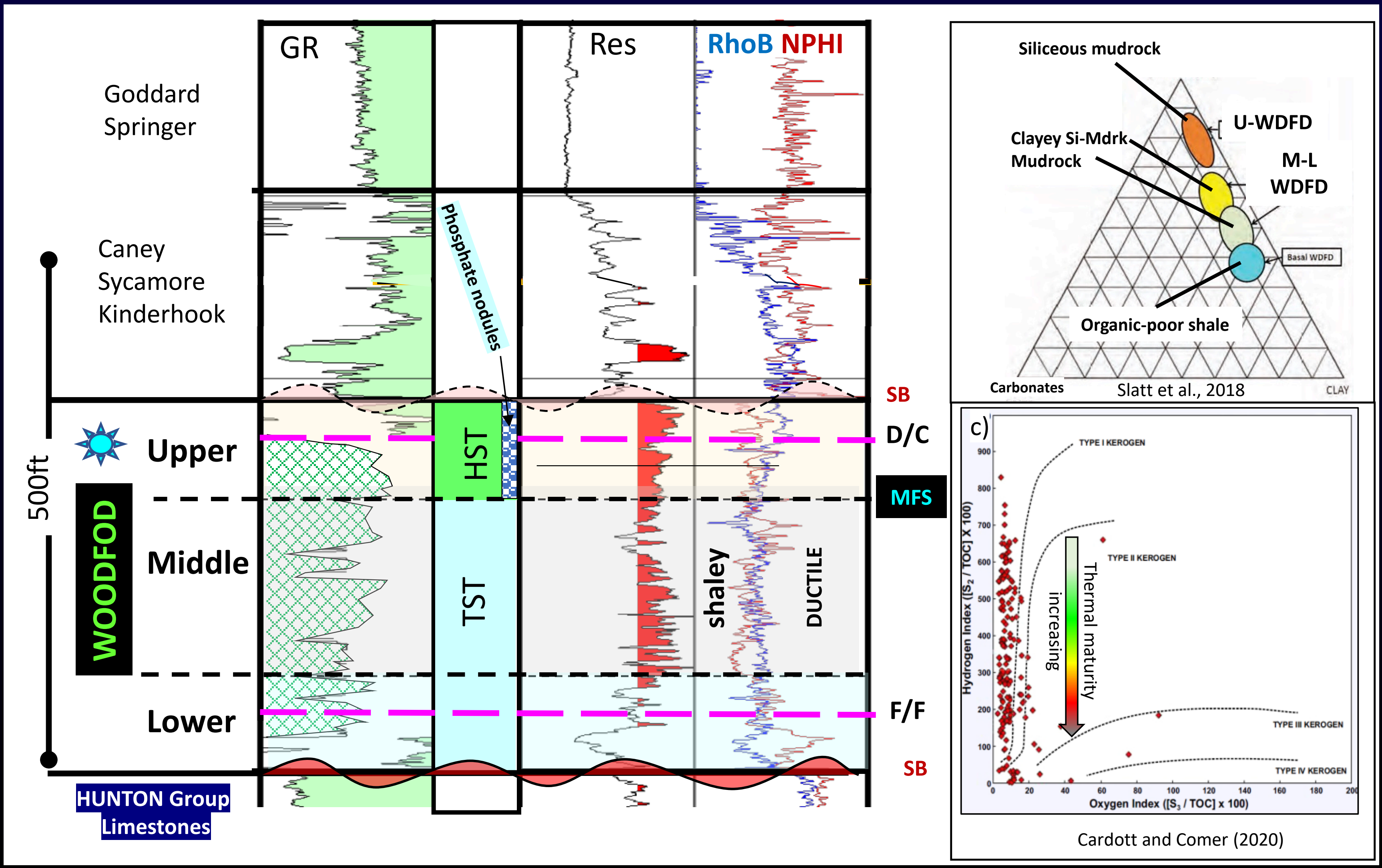
Overview of the Woodford Shale

- Late Devonian to Early Mississippian organic-rich siliceous mudrock and shale.
- Correlative with other North American black shales (e.g., Chattanooga, New Albany)
- Arkansas Novaculite is the correlative deepwater facies
- Deposition spans 2 mass extinctions (Frasnian-Famennian & Devonian-Carboniferous).
- Deposited during the rapid expansion of land plants.

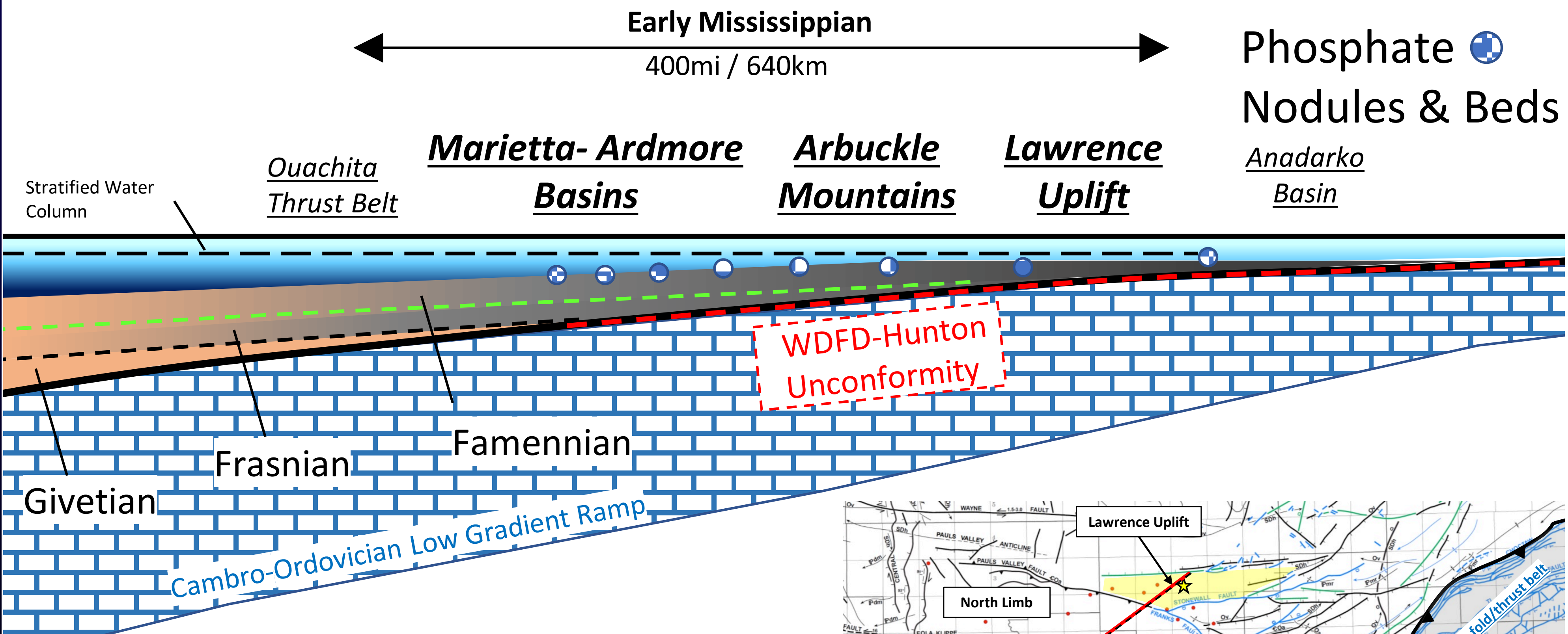


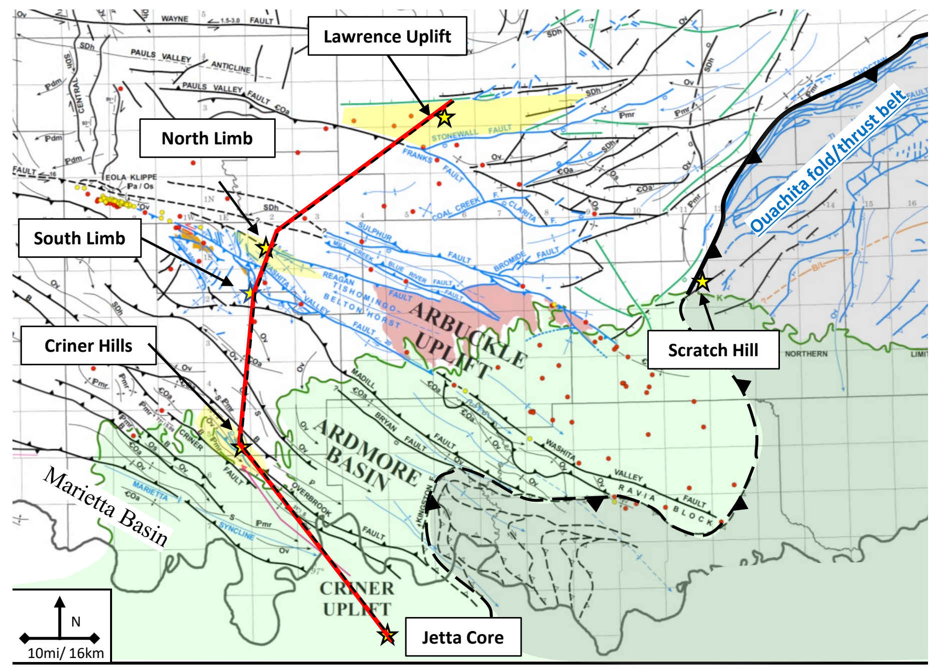
The Woodford Shale is world-class algal petroleum source rock.

- The Woodford is divided into Lower, Middle and Upper units that were deposited during a progressive rise and subsequent fall in global sea level.
- The Upper Woodford is rich in phosphate (apatite) nodules



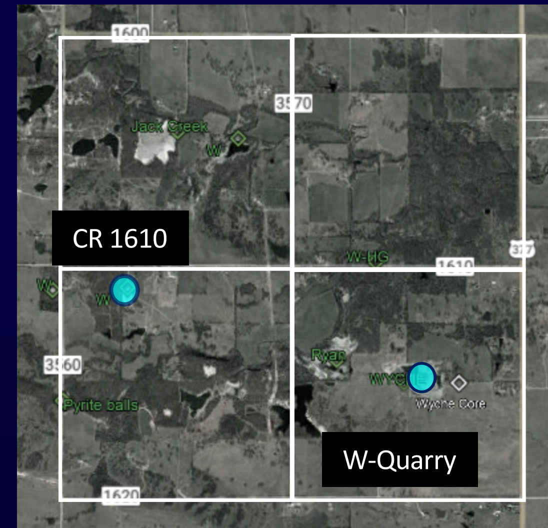
Woodford Phosphate Nodules: A basinward transect from the Lawrence Uplift through the Arbuckle Mountains to the Ardmore-Marietta Basins





In the earliest Mississippian Woodford phosphate nodules were deposited over a dip-oriented length of at least 300mi

Phosphate Nodules of the Lawrence Uplift (western Arkoma Basin)

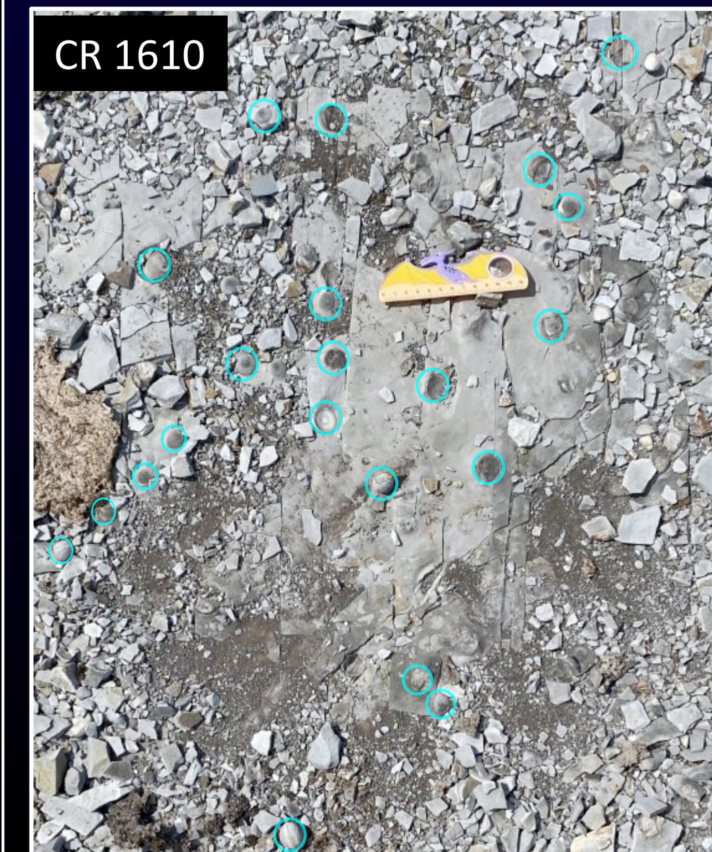


Wyche Quarry

Spherical to elliptical to wispy beds

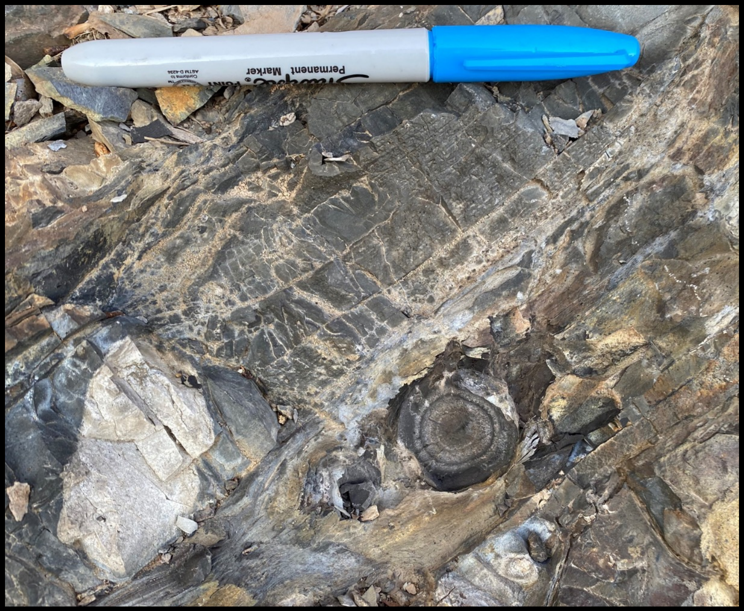
Spherical-concentric with pyrite compaction

Spherical-concentric



Phosphate nodules on the north and south limbs of Arbuckle Anticline

South limb- spherical nodules

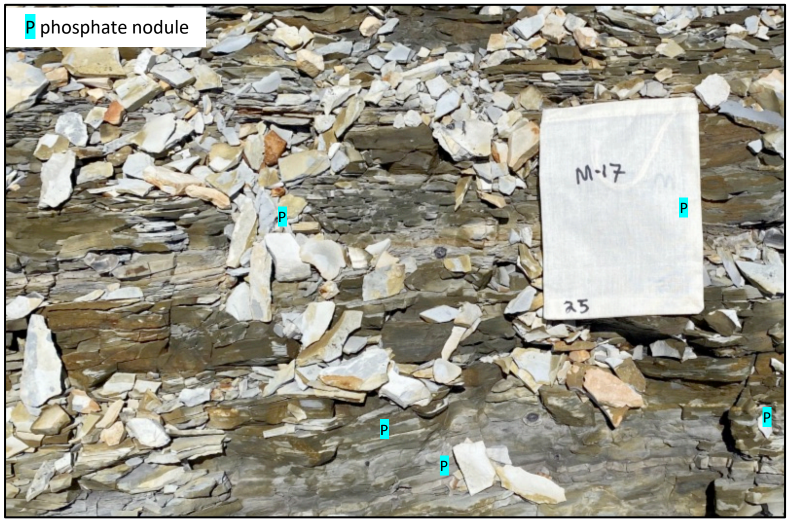


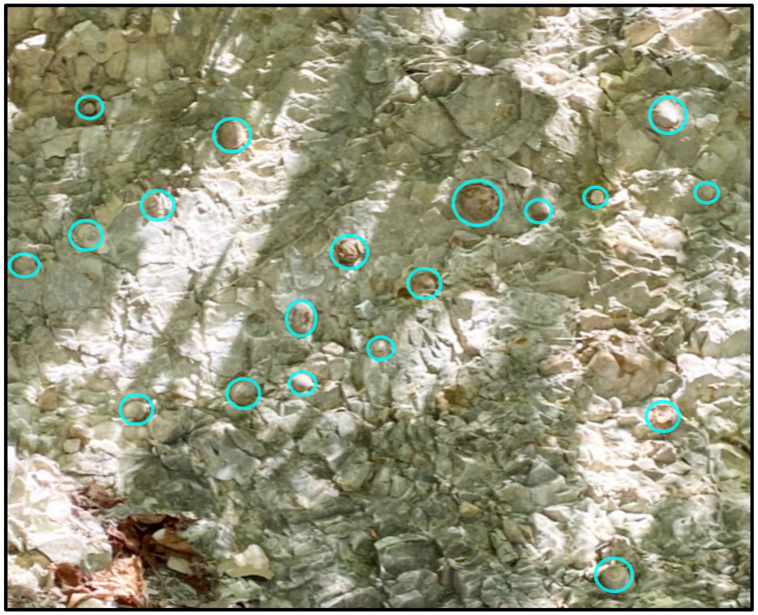
North limb- spherical to oblate nodules

Nodule lag deposit (?) at top Woodford disconformity

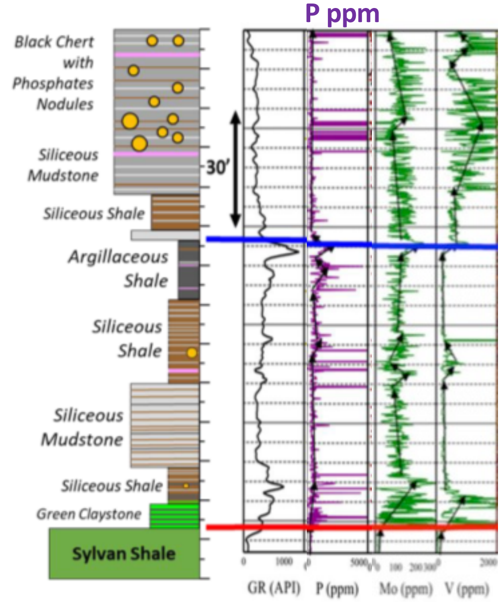
Phosphate nodules in the Ardmore and Marietta Basins

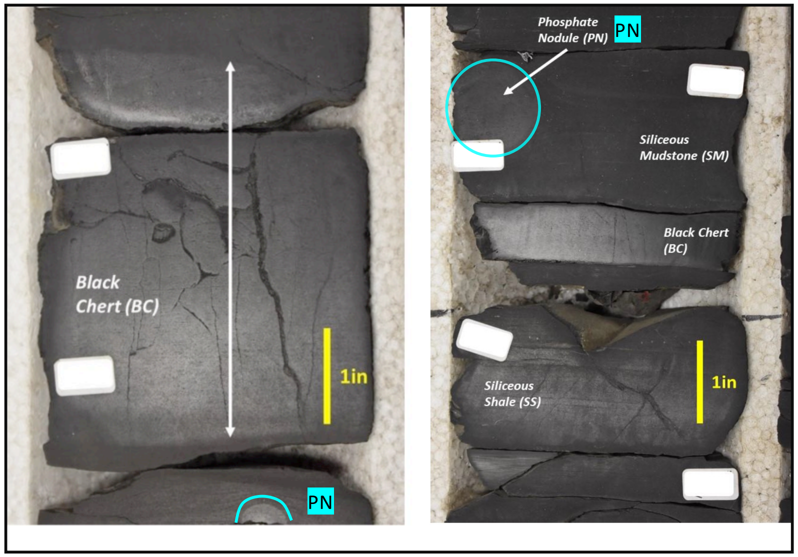
McAlister Cemetery Quarry / Criner Uplift, Ardmore Basin. Spherical nodules, some elliptical nodules





Jetta Operating Co. / Cored well, Grayson Co. TX Marietta Basin. Spherical nodules





Phosphate nodules in the Arkansas Novaculite at Scratch Hill, Atoka OK.

Formation of Woodford phosphate nodules: 3 studies* show the following:

- Carbonate-fluorapatite precipitated at or near seafloor under anoxic conditions.
- Phosphorus was release by anerobic decay of phytoplankton
- Nodules commonly contain radiolaria tests and sponge spicules
- Diverse morphologies and internal variations show distinct geographic trends.
-     Spherical, concentric, well-organized nodules are prevalent down-dip (I35-S McAlister Cemetery).
-     Oblate to elliptical nodules with little internal organization are more prevalent up-dip (I-35N).
- Dark concentric rings have higher metal (U, Zr) contents- possible redox changes.

	MORPHOLOGY	Locality A - Abundant C - Common S - Scarce	WSP= MCQ	Other Features
Type A	Circular, concentric, well-defined rings	WSP (A)	Higher concentrations of uranium in dark bands and consistent, symmetrical trendology of metal distribution	Well-preserved radiolarions
Type B	Elongate, well-defined rings (continuous)	WSP (A) I35N (S)	Higher concentrations of uranium in dark bands and consistent, symmetrical trendology of metal distrib- Higher concentrations	Well-preserved radiolarions
Type C	Elongate, poorly-defined, discontinuous rings	I35N (A) WSP (S)	Lower concentration of uranium, but uranium remains most concentrated in darker bands	Delicate structures are poorly preserved
Type D	Elongate, rings are absent	I35N (C) WSP (S)	Uranium concentration is low compared to Types A and B; similar trends in certain metals exist, but symmetrical pattern is absent	Delicate structures are poorly preserved
Type E	Circular, poorly-defined to absent rings	WSP (S)	Difficult to analyze because structure is not obvious	Not thin-sectioned

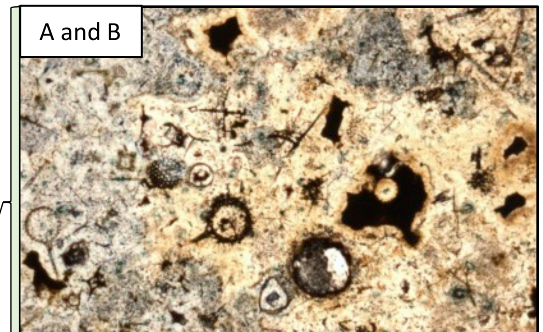


Figure 11. Plane-polarized light photomicrograph of a Type A nodule showing diverse communities of well-preserved radiolarians [WSPR3-F].

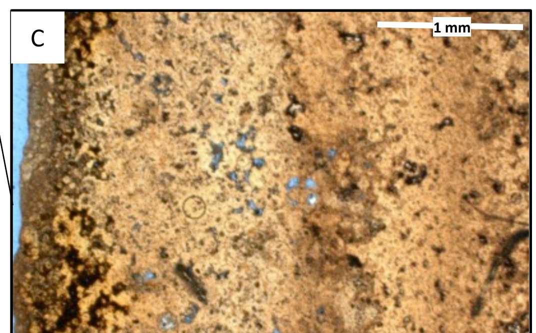
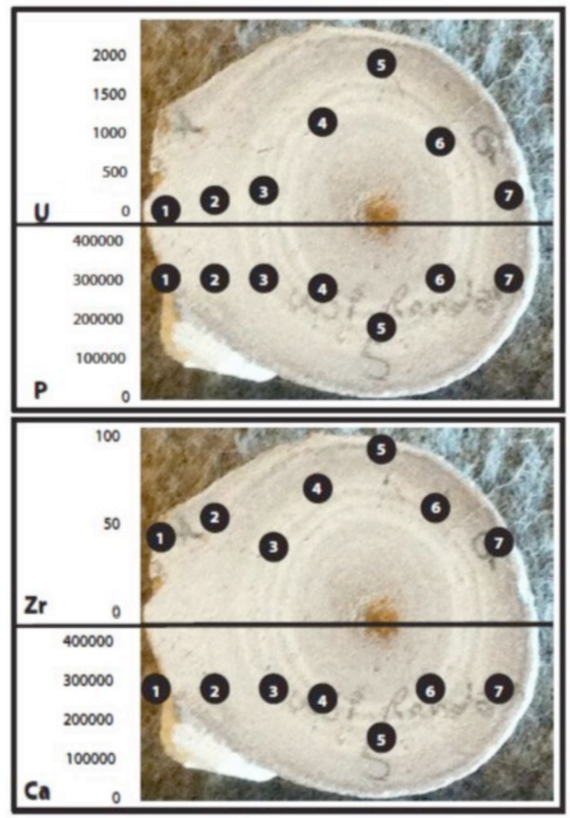


Figure 12 PPL photomicrograph type C nodule. Preservation of radiolarian skeletons is poor with moldic radiolarian porosity [Sample I35NR-1].

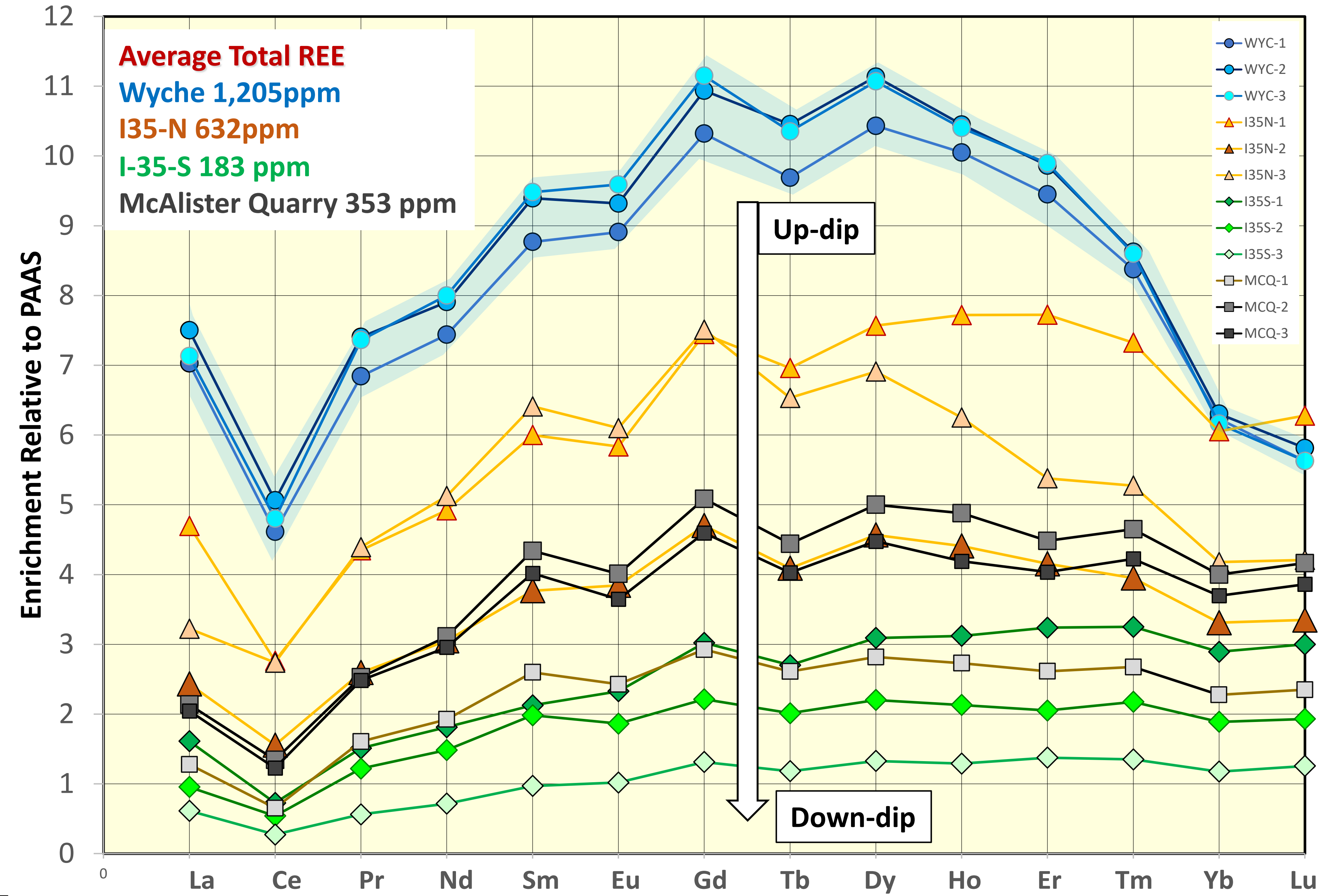


XRF elemental comparisons (ppm) between uranium, phosphorous, zircon and calcium in nodule Type A.WSP-5 (MCQ).

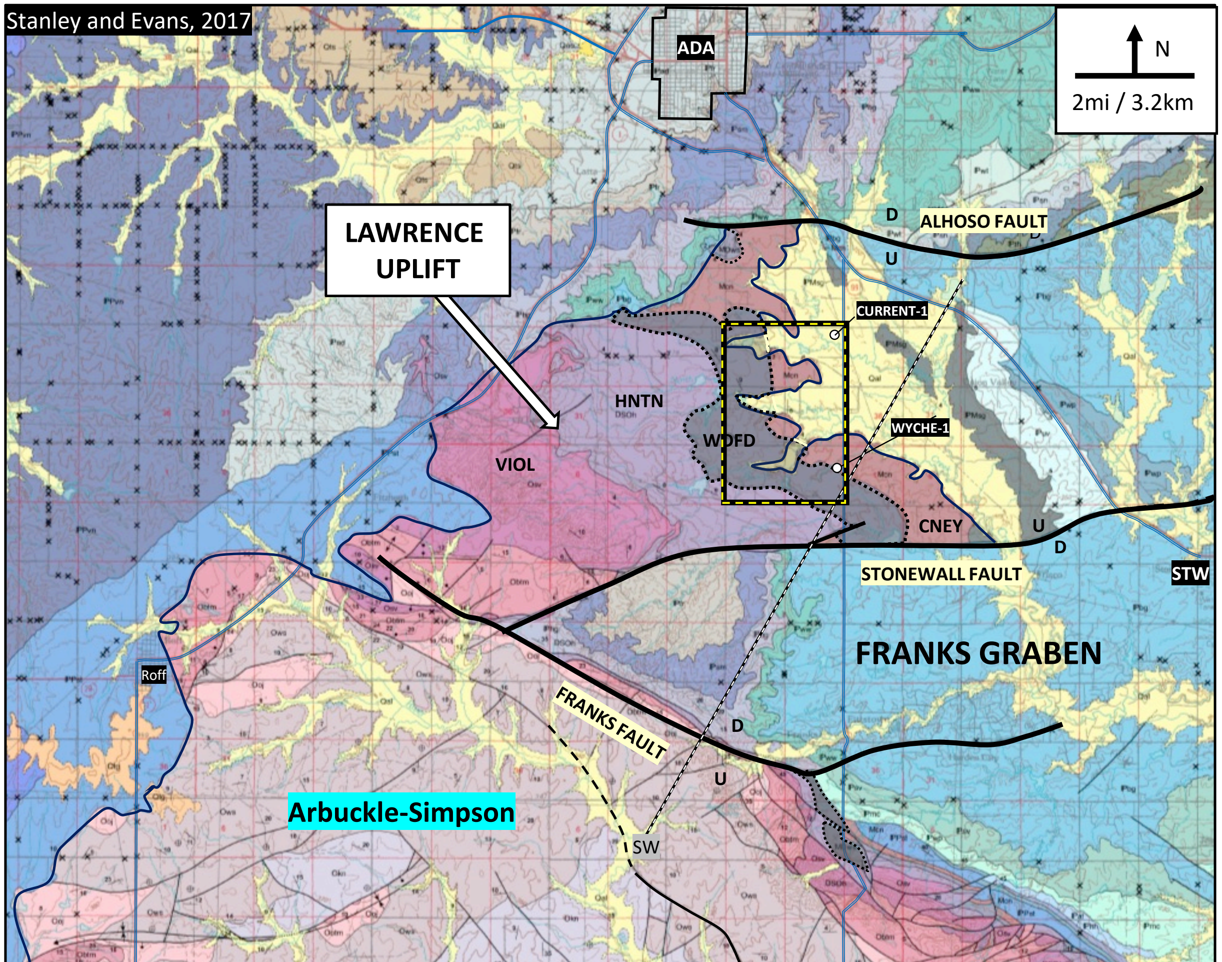
* Siy,1987; Kirkland et al., 1992; Boardman, 2012

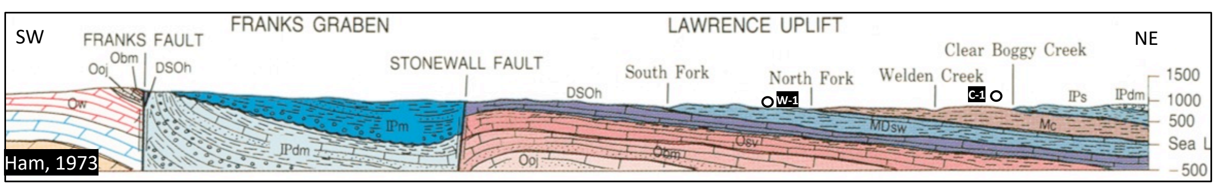
REEs in phosphate nodules

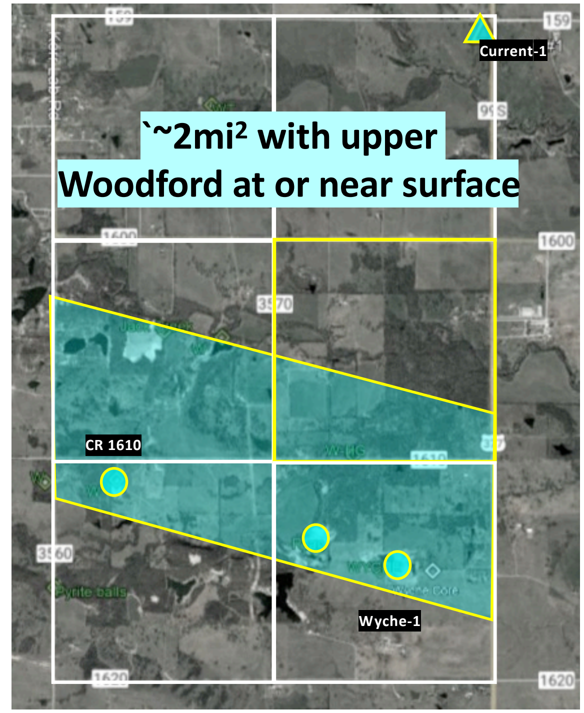
Wyche nodules are strongly enriched. I35-N modestly enriched. Data indicate basinward decrease in REE enrichment

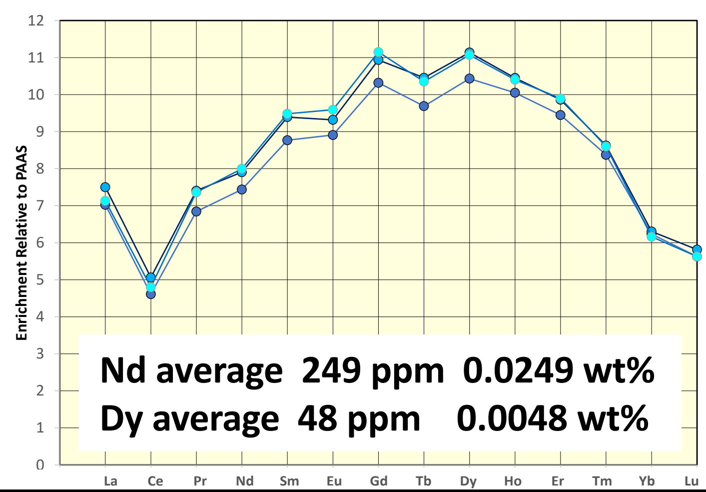


Lawrence Uplift REE Prospect: 1) Strong REE enrichment in PNs 2) Simple structure very low dip 3) Large area with minimal overburden 4) Active Woodford Quarry

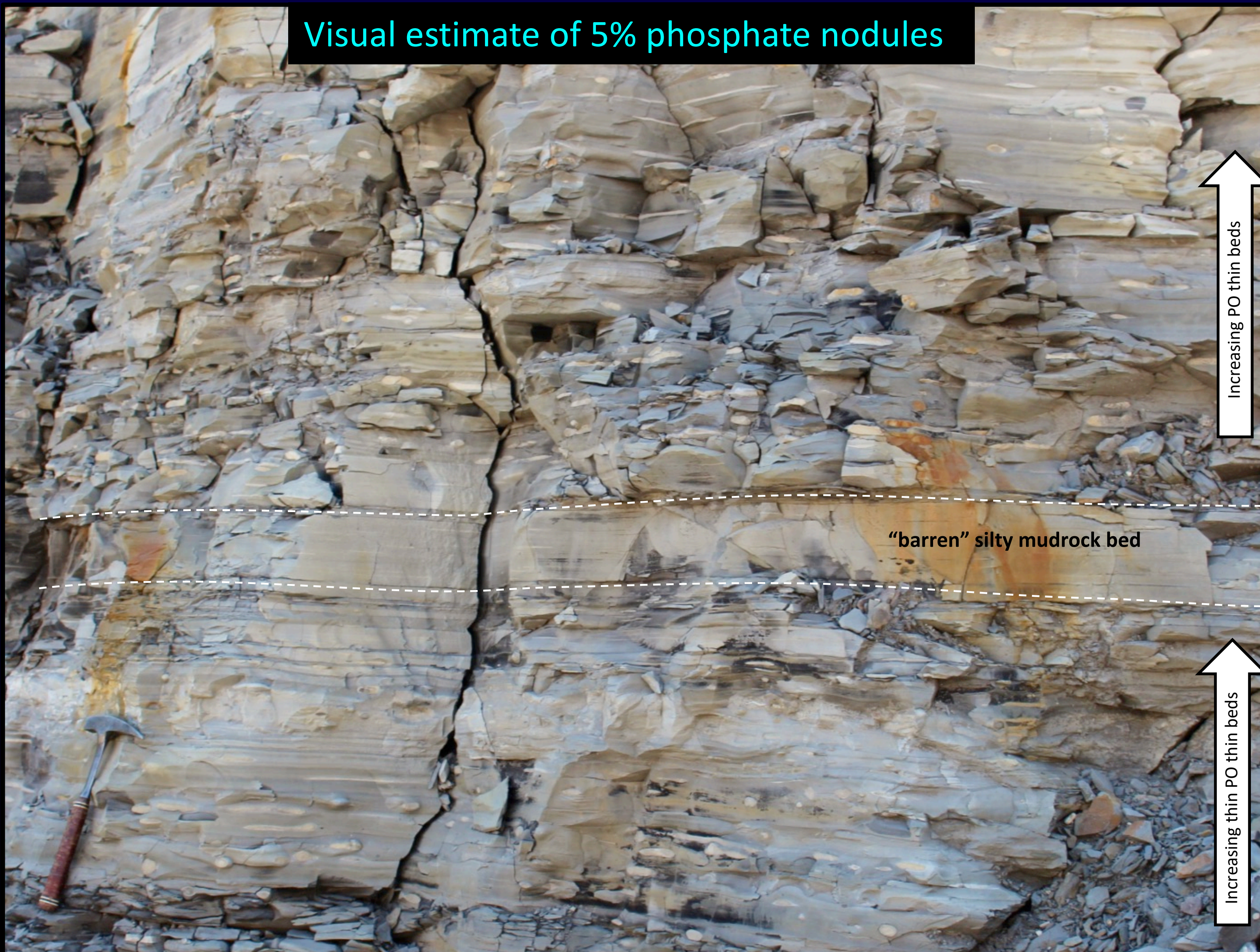




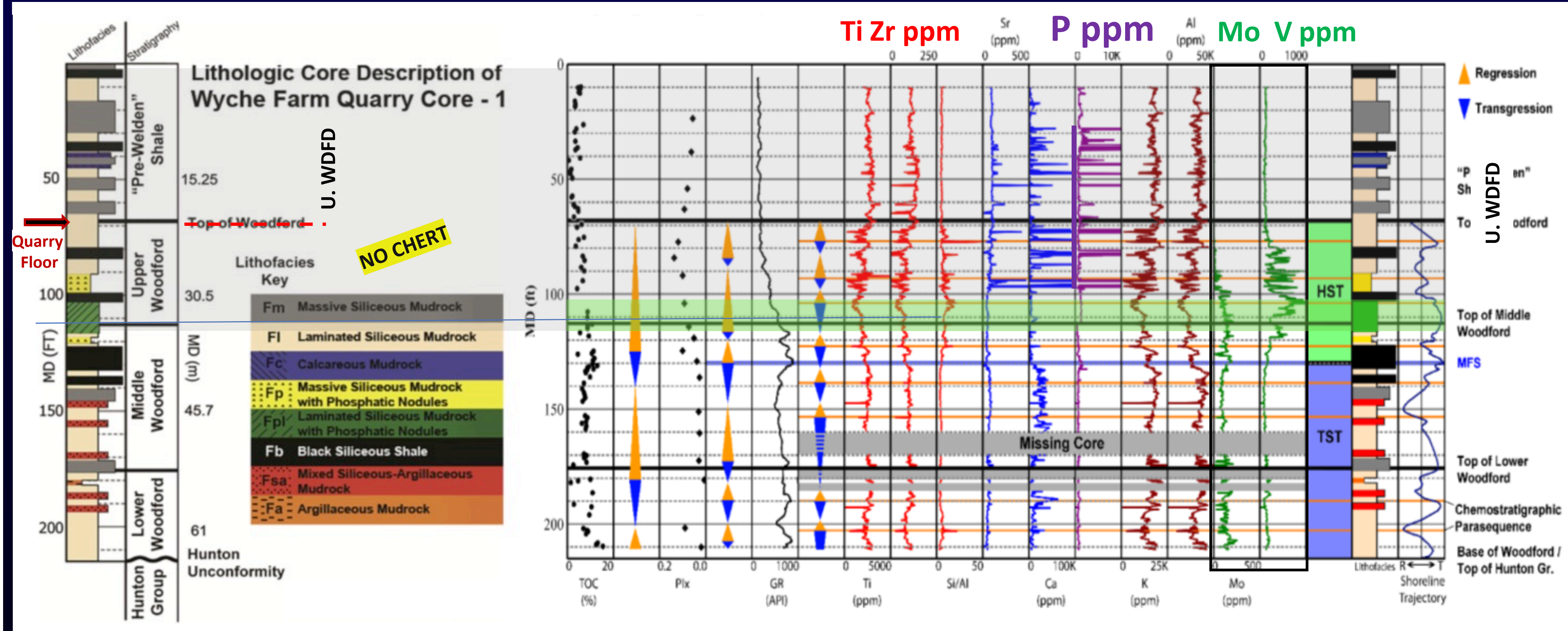




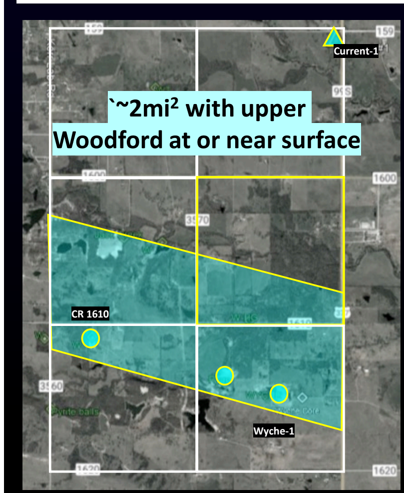
Lawrence Uplift: REE Potential Phosphate Nodules in the Woodford Shale



Core XRF elemental data indicate 21m of phosphate nodules. Surface geology indicates ~1280 acres w/ shallow overburden.



from Turner et al., 2016 Chemostratigraphic, palynostratigraphic, and sequence stratigraphic analysis of the Woodford Shale, Wyche Farm Quarry, Pontotoc County, Oklahoma, SEG Interpretations.



"Of particular significance to REE exploration, however, is the consistency of REE abundances within individual time horizons and that these may identify time periods, like the Late Mississippian, **Devonian**, and Ordovician, that were favorable for the formation of phosphorites with high-REE abundances." (Emsbo et al., 2015)

CONCLUSIONS

1. Woodford phosphate nodules show spatial changes in REE enrichment.
2. Up-dip area appears more enriched in REE.
3. The Lawrence Uplift shows the strongest enrichment in RREs.
4. Simple structure and minimal overburden are favorable for strip mining.
5. Further appraisal work is underway to consider commerciality.

Key References

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PART 2 : Cobalt Potential of the Flowerpot Shale, Jackson Co. OK*

- Review of Global Cobalt Production
- Geochemistry & Usage of Cobalt
- Central African Copperbelt
  - 70% of Global Cobalt Production
- Oklahoma's Stratiform Cu Deposits
- Cobalt Potential of Creta Mine

Cobalt Global Production and Reserves

Top 10 Countries	Prod. metric tons/yr	Global %	Reserves	Type
D.R. Congo	**120,000**	**71%**	**3,500,000**	**Stratiform Copper**
Russia	7,600	4%	250,000	Hydrothermal mafic host
Australia	5,600	3%	1,200,000	Lateric nickel deposits
Philippines	4,500	3%	280,000	Lateric nickel deposits
Canada	4,300	3%	250,000	By-product Ni production
Cuba	3,900	2%	500,000	Lateric nickel deposits
Papua New Guinea	3,000	2%	51,000	Lateric nickel deposits
Magagascar	2,500	1%	150,000	Lateric nickel deposits
Morocco	2,300	1%	14,000	Epithermal sulfide
China	2,200	1%	80,000	Magmatic massive sulfide
Rest of World	14,530		6,275,000	
World Total	170,000		7,100,000	*USGS estimates*
USA	650	0.4%	69,000	

4 Modes of occurrence

1. Sediment hosted, sulfate-reduction in shallow marine setting (0.1 to 0.4%)
2. Hydrothermal alteration of host rock (0.1%)
3. Magmatic sulfide – immiscible phase (0.1%)
4. Nickle-bearing laterites on ultramafic rocks (0.05 to 0.15%)

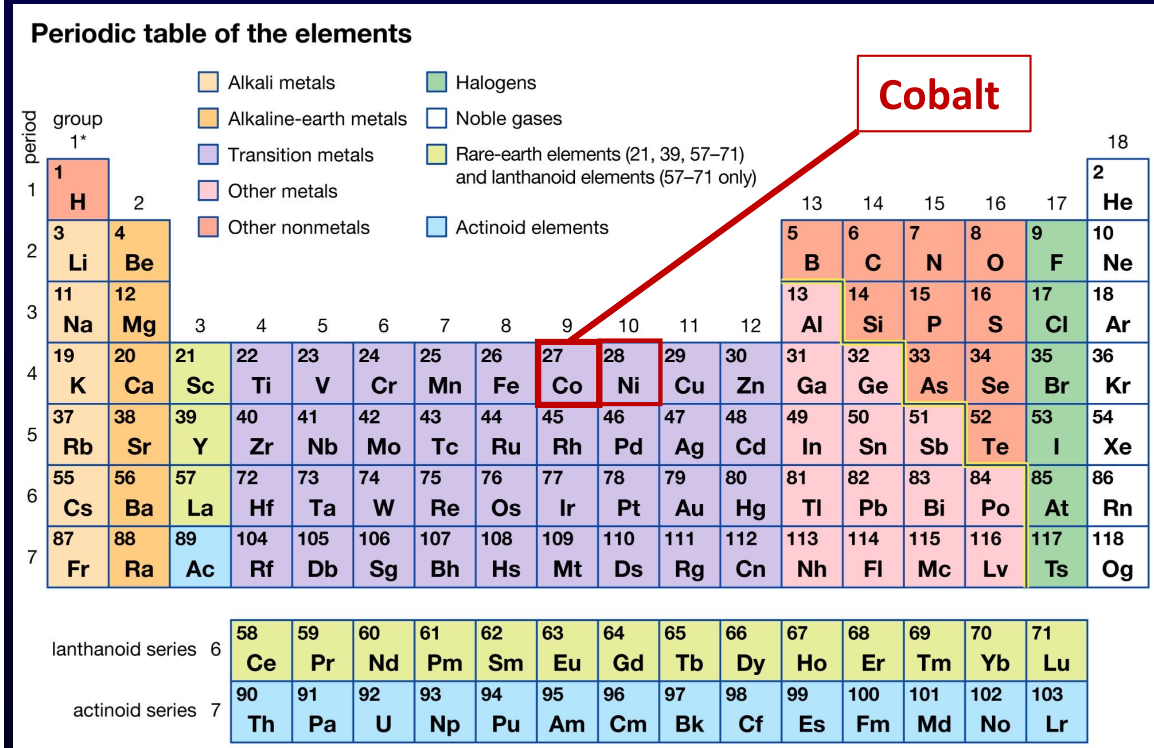
Manganese seabed nodules (2.5%). Not currently economic

- **Cobalt is a "critical mineral" defined as a non-fuel material essential to the economic or national security of the U.S. and which has a supply chain vulnerable to disruption.**
- **Although nickel-bearing laterites and ultramafic igneous rocks are the most common hosts.**
- **Stratiform copper deposits in Central Africa account 71% of global cobalt production.**

The Flowerpot Shale in western Oklahoma hosts stratiform copper deposits.

The talk considers the cobalt of the Flowerpot Shale in the Creta Mine, Jackson Co. OK.

Geochemistry and Uses of Cobalt

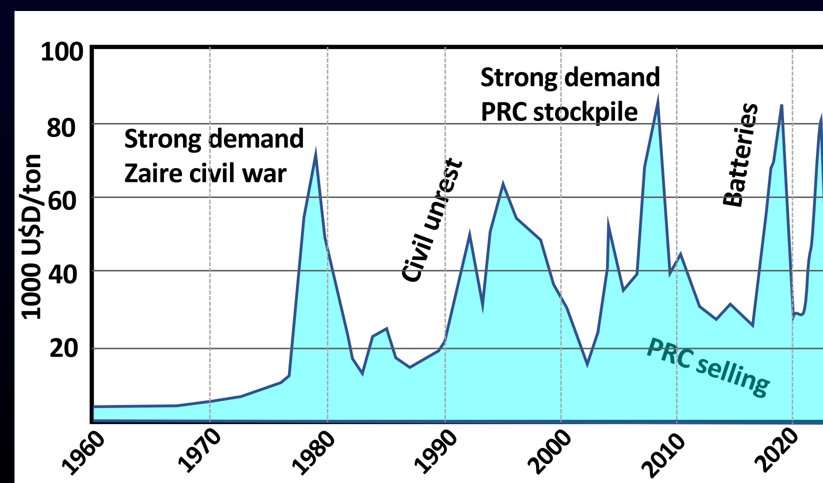


Cobalt, like nickel, is a transition metal that almost exclusively occurs in alloys of with iron and sulfur.

Cobalt-bearing ores occur in nickel-bearing laterites, hydrothermal massive sulfides, and copper-bearing red beds.

Cobalt ores must be smelted to produce usable metal.

- Since 2005 480% swings in price
- Demand, civil unrest, dumping COVID



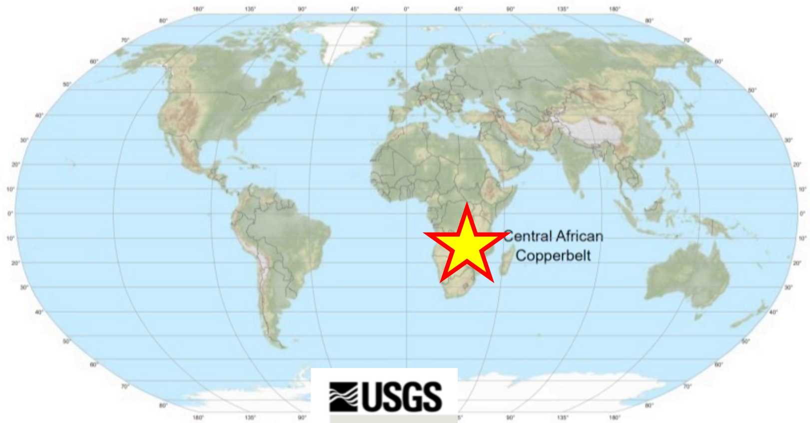
Current spot price ~$52,000/ton

- Lithium-ion batteries in EVs. Demand for will keep rising as the shift toward "clean technologies" continues.
- Metal alloys for turbines & prosthetic limbs
- Also used as a catalyst and in pigments & coloring

Cobalt Potential of the Flowerpot Shale

- Review of Global Cobalt Production
- Geochemistry & Usage of Cobalt
- **Central African Copperbelt**
  - **70% of Global Cobalt Production**
- Oklahoma's Stratiform Cu Deposits
- Cobalt Potential of Creta Mine

The Central African Copperbelt, CACB, ★ is the only sedimentary rock-hosted stratiform copper district that contains economic cobalt resources.



Modified from Slack and others, in press.

The CACB is composed of two separate sub-belts

- ❑ The **Congo Copperbelt-** hosted by Neoproterozoic carbonate-rich evaporitic rocks
- ❑ The **Zambian Copperbelt-** hosted in slightly younger rift facies siliciclastic rocks.

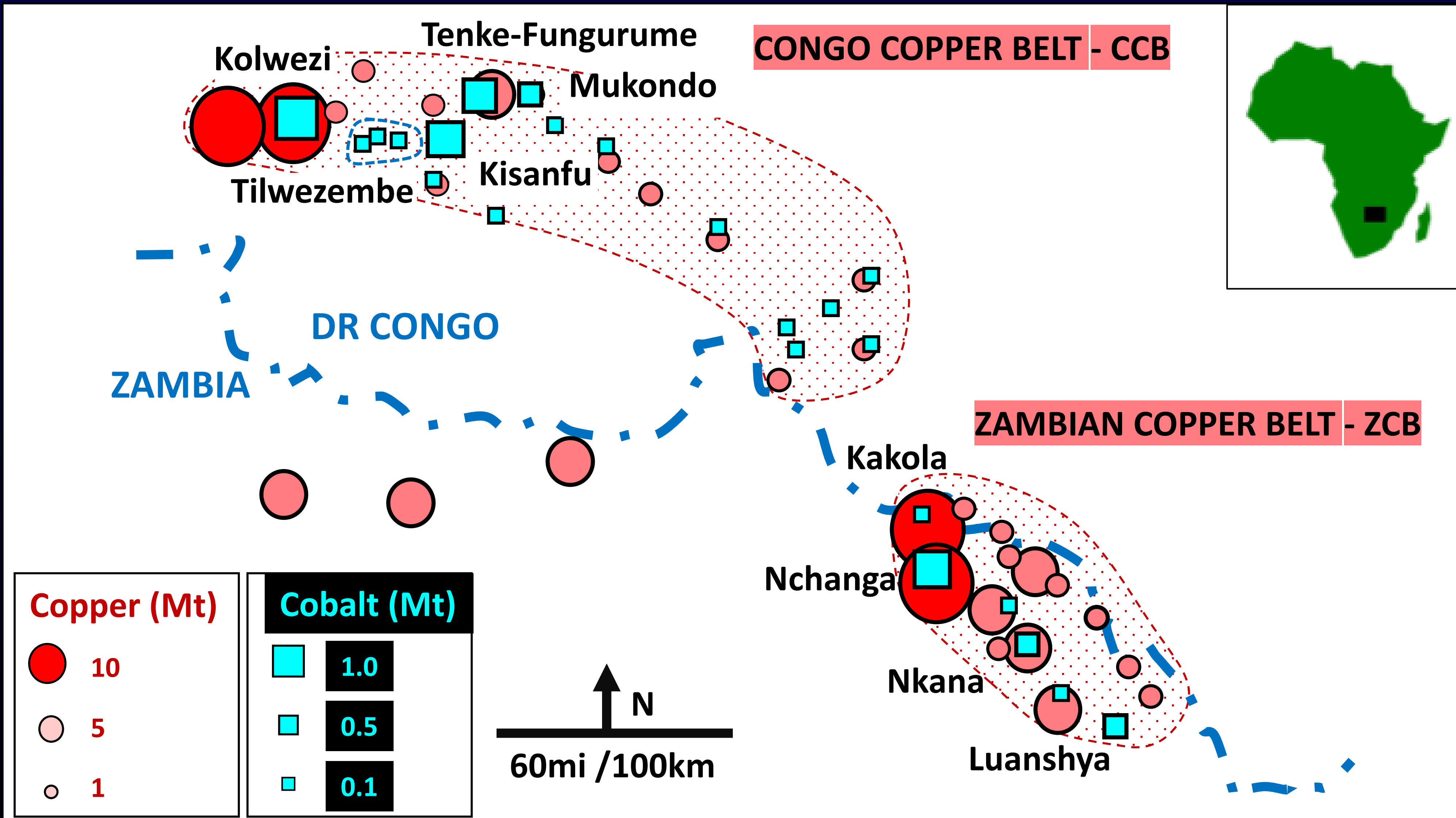
- **Complex multi-stage ore-paragenesis involves replacement of early formed pyrite.**
- **Pyrite sulfur isotopes indicate crystallization is related to bacterial sulfate reduction.**

Cobalt grades > 0.6%
Sufficient to support primay production

Kisanfu	1.1%	★
Mukondo	0.7%	★
Tilwezembe	0.6%	★
Nchanga	0.4%	
Kolwezi	0.4%	
Tenke	0.3%	
Luanshya	0.2%	
Nkana	0.1%	

Carrollite ($CuCo_2S_4$,)
primary cobalt ore

Congo and Zambian Copperbelts

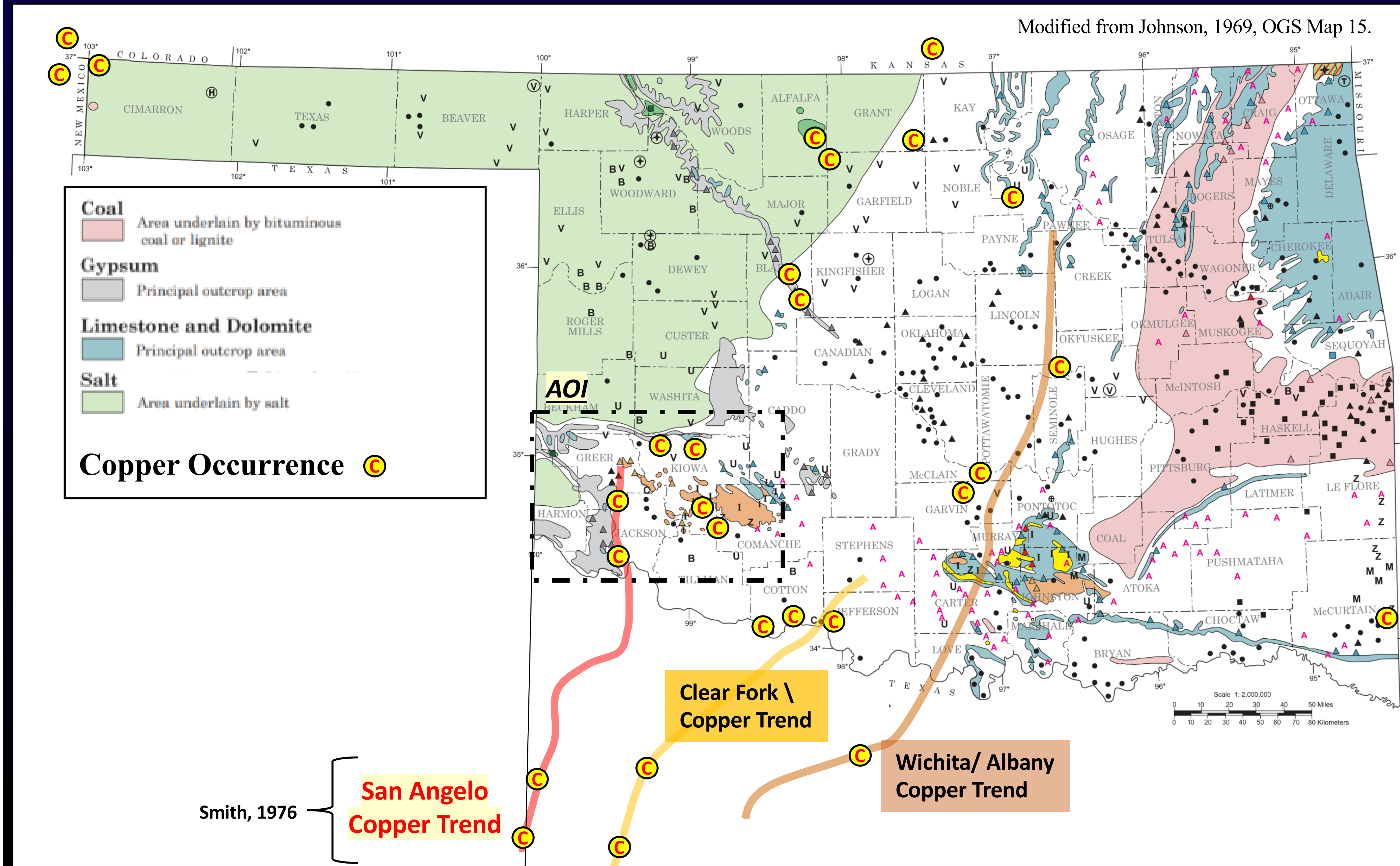


- The CCB has more copper deposits, but fewer giants (40% of endowment).
- Cobalt does not always accompany copper.
- The CCB has a much richer cobalt endowment.
- Cobalt in the ZCB is restricted to the western side- associated with mafic intrusions.

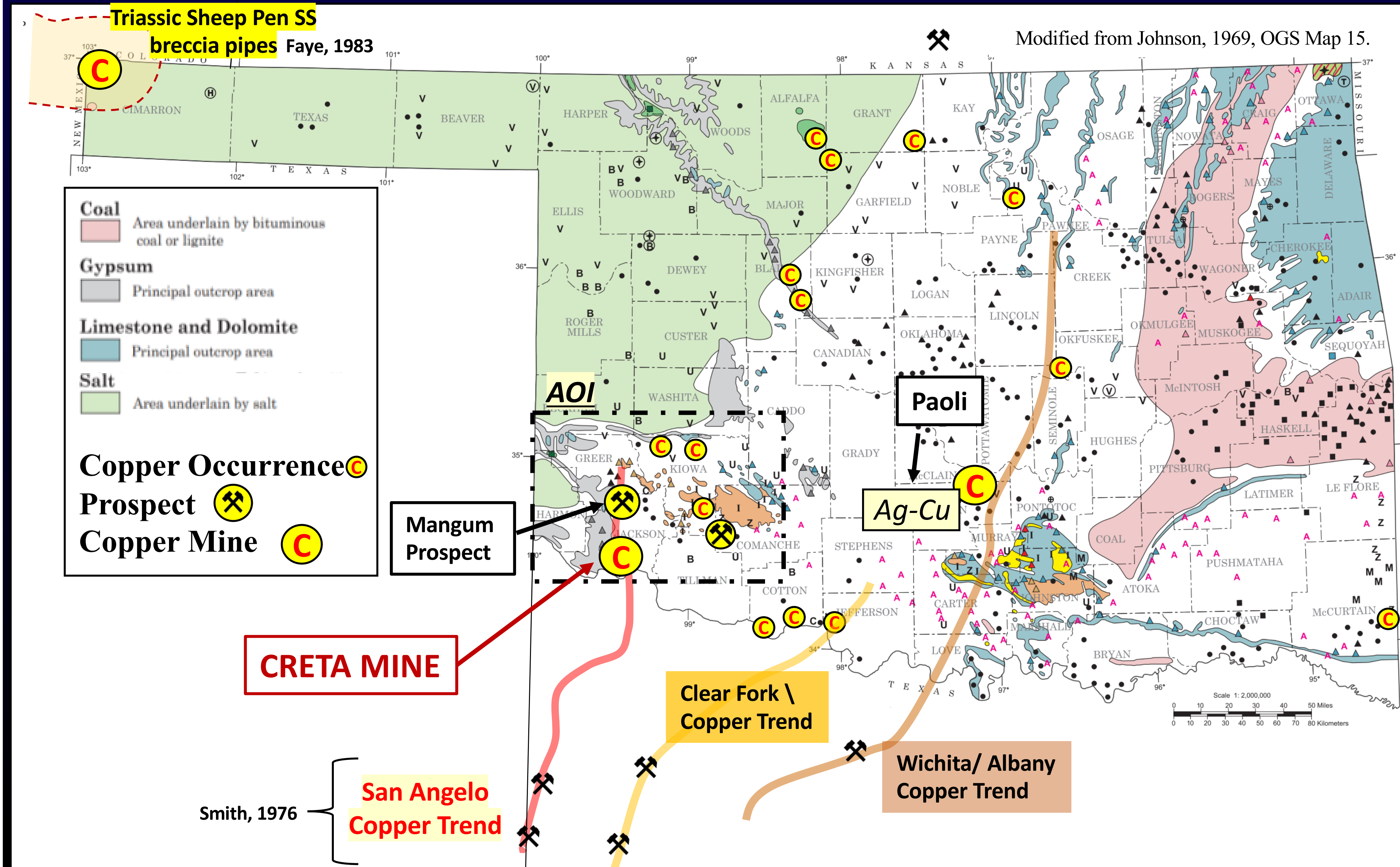
Review of Global Cobalt Production
Geochemistry and Uses of Cobalt
Central African Copperbelt – World's Largest Cobalt Production
Oklahoma's Stratiform Copper Deposits
Cobalt Potential in Western Oklahoma's Stratiform Copper Deposits

Chalcocite-bearing shale from Creta Mine.
Photo courtesy of Ken Johnson

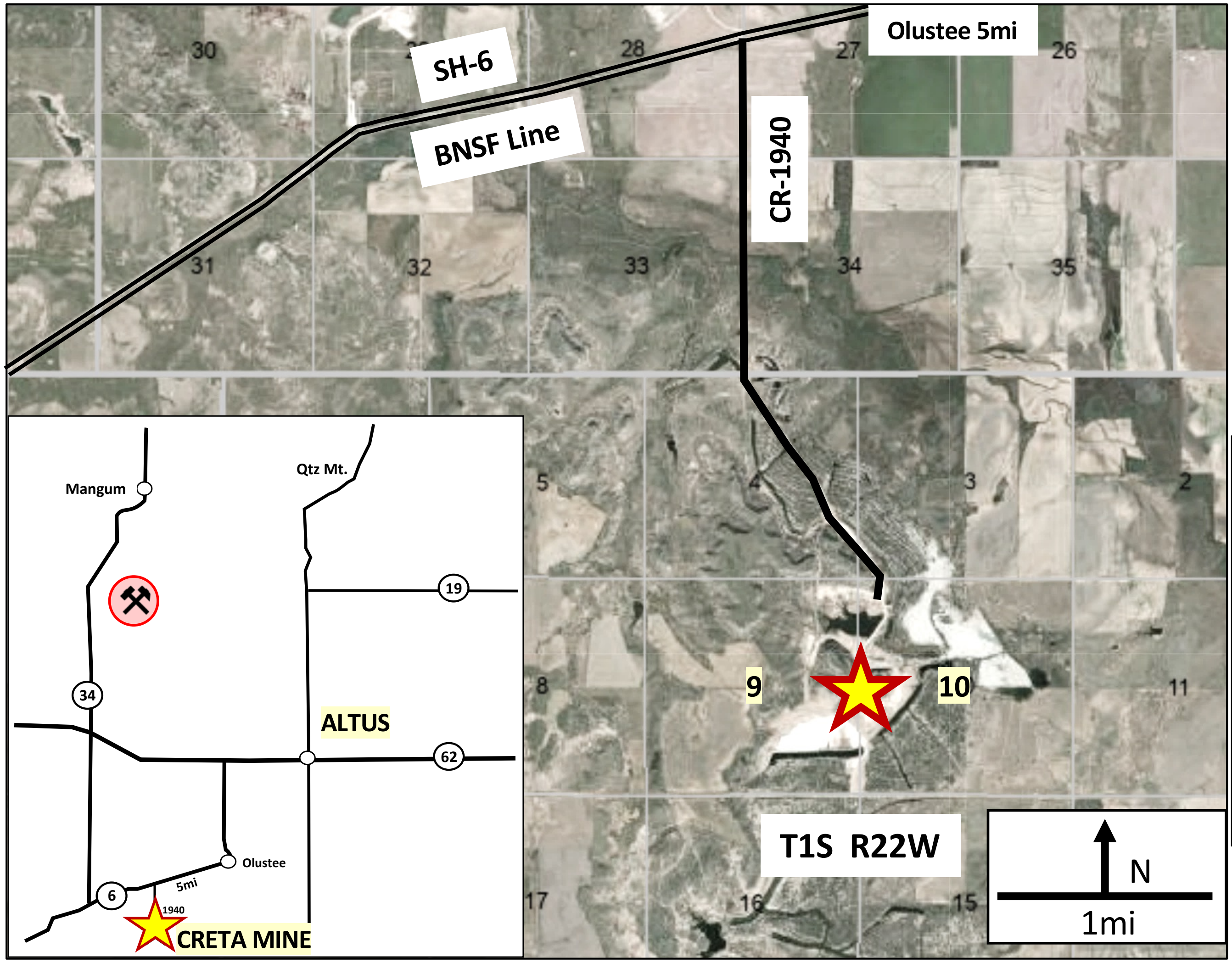
Cu-bearing Permo-Triassic sediments in Oklahoma & adjacent states are widespread Chalcocite [Cu_2S] & Malachite [$Cu_2CO_3(OH)_2$] are the most common minerals. Copper mineralization occurs in distinct trends extending from Texas.

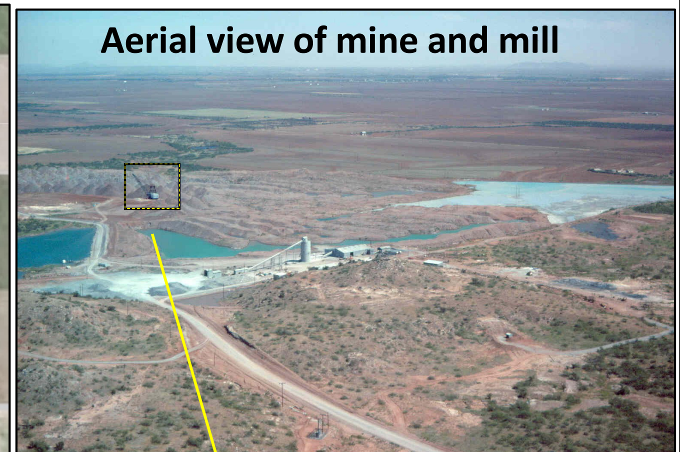


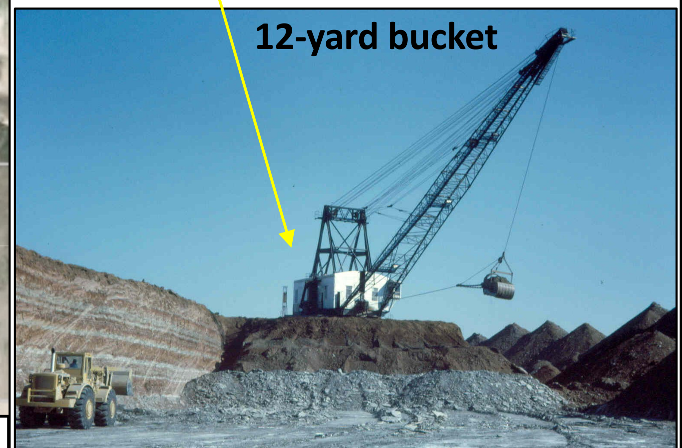
Cimarron County – copper, silver, minor gold, brecciated sandstone & pipes.
Paoli- silver-copper, roll front deposit in sandstone (Avg. 4.7 oz/ton silver Cu/Ag 40:1)
Only the Creta deposit (Jackson Co.) was mined strictly for copper (Avg. 2.3% Cu)



The Creta Mine: Jackson County OK (14mi / 21km SW of Altus)



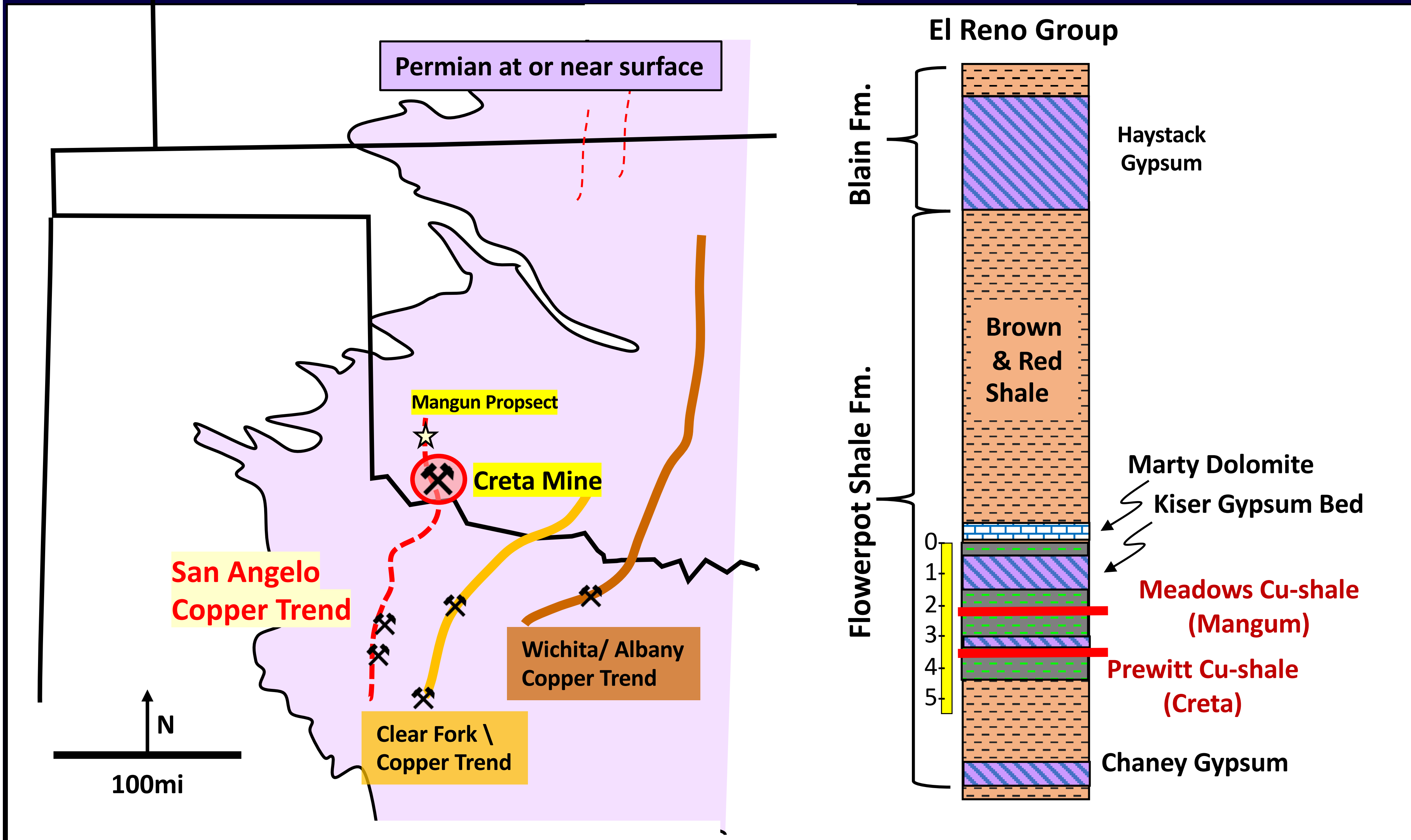




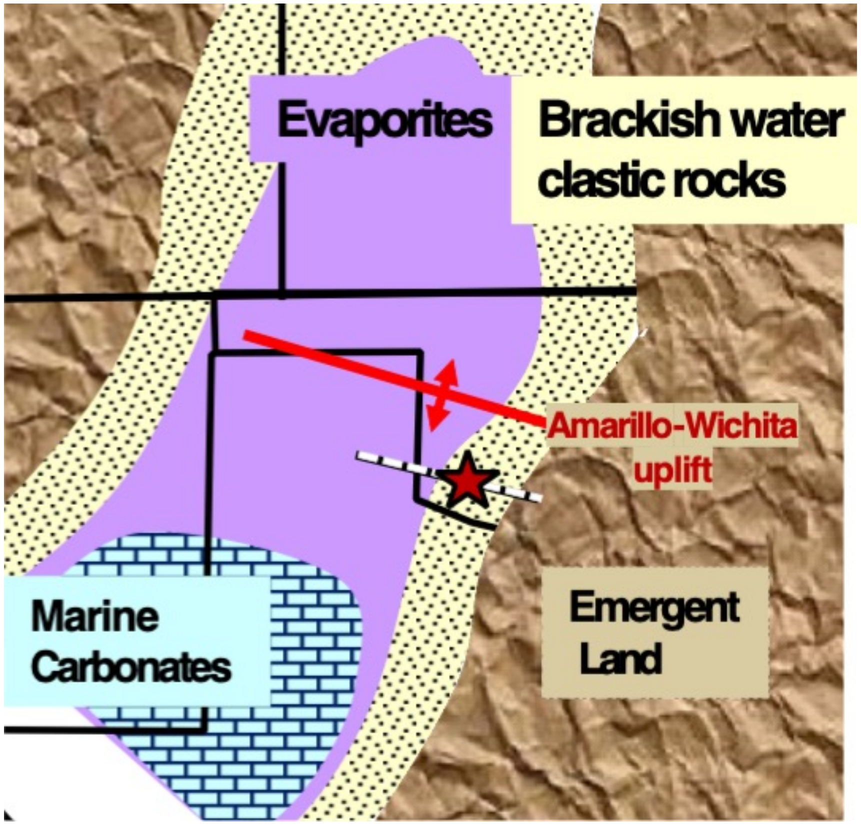
Photos courtesy of Ken Johnson

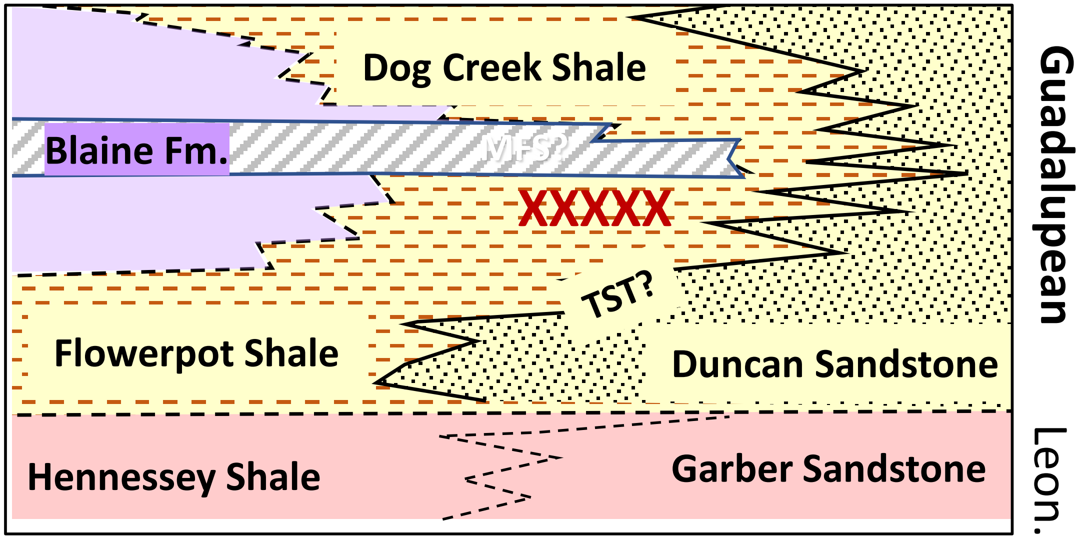
- **The Creta Mine was operated by Eagle Picher from 1964 to 1975.**
- **1.9 million tons of copper ore was strip mined from a thin copper-bearing shale.**
- **On-site mill with concentrates railroaded to El Paso (515mi) to ASARCO smelter**
- ***The Mangum deposit (15mi /25km) north of Creta has never been developed***

The Creta and Mangum deposits occur in the San Angelo Copper trend. Ores are hosted in the lower Flowerpot Shale below the Marty Dolomite.



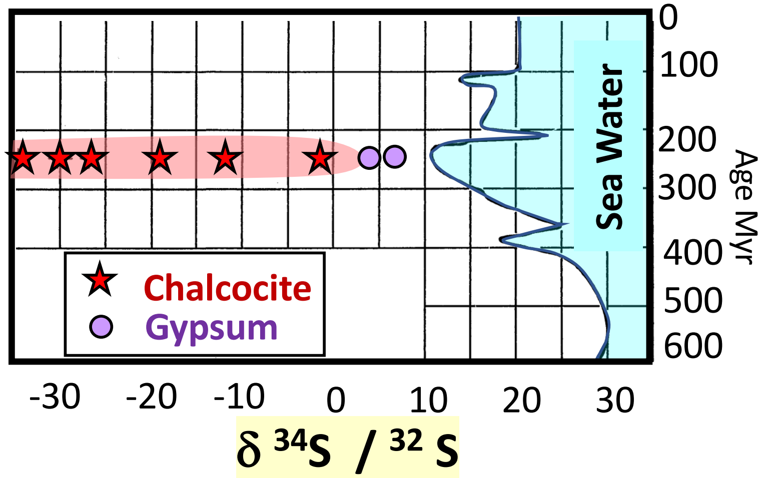
The Flowerpot Shale of Permian (Guadalupean) age was deposited in brackish water in a restricted marine embayment on the east side of the Permian Basin.





Prewitt Cu-shale XXXX
Chalcocite is primary ore.

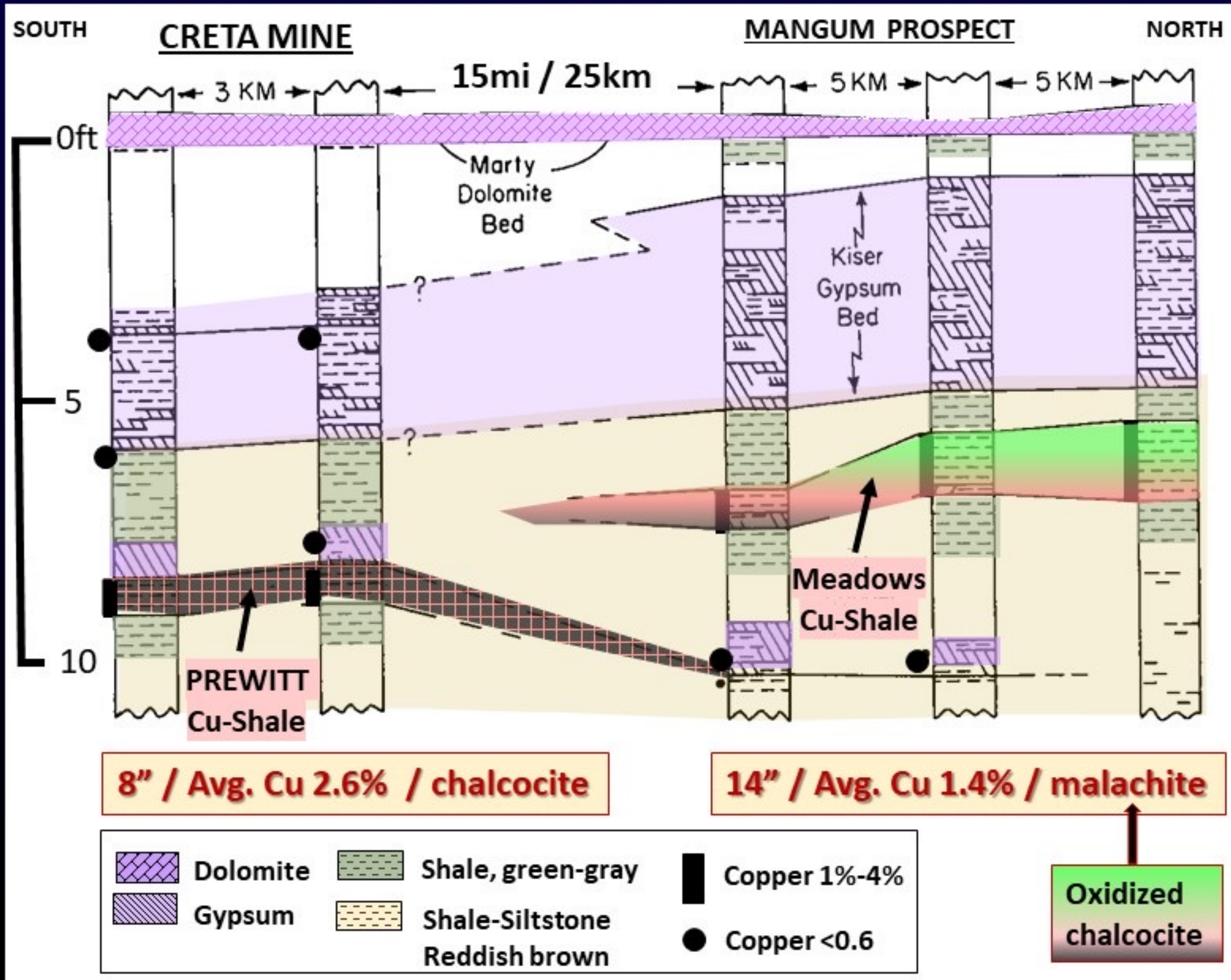
1. Disseminated grains
2. Replacement of pyrite*
3. Replacement of spores



Sulfur isotopes indicate that:

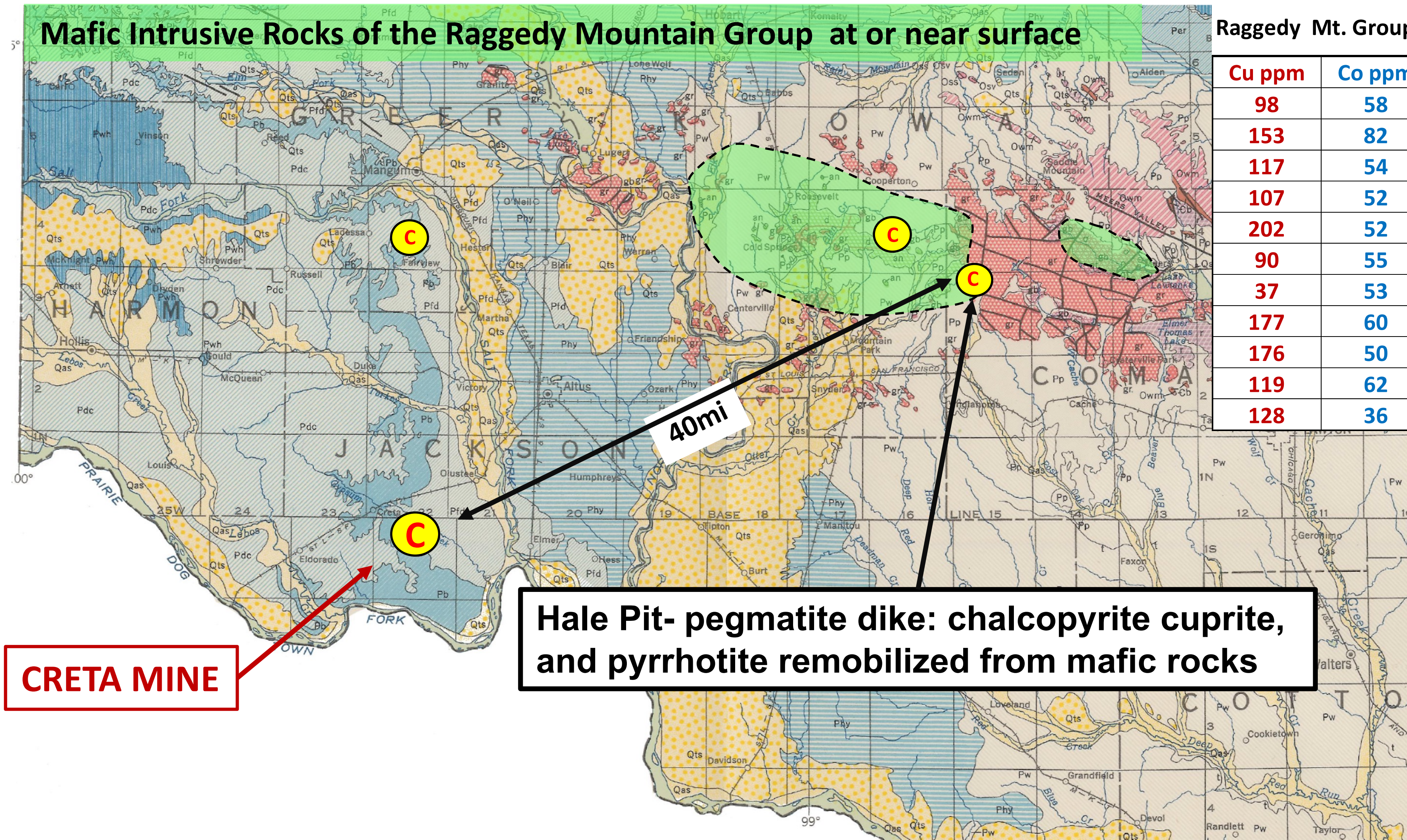
1. Chalcocite was formed by bacterial sulfate reduction
2. Gypsum was precipitated from Permian seawater

The Creta and Mangum deposits occur in 2 different shale units, Prewitt & Meadows
The Meadows deposit near Mangum is thicker but is oxidized and ~1/2 the grade.



Copper in the Creta Mine ores was probably sourced from the mafic-ultramafic intrusive rocks of the Cambrian-age Raggedy Mountain Group.

Recall cobalt in the Zambian CB is associated with mafic intrusions



Raggedy Mt. Group

Cu ppm	Co ppm	Cu/Co
98	58	1.7
153	82	1.9
117	54	2.2
107	52	2.1
202	52	3.9
90	55	1.6
37	53	0.7
177	60	3.0
176	50	3.5
119	62	1.9
128	36	3.5

Geochemistry and Uses of Cobalt

Review of Global Cobalt Production

Central African Copperbelt – World's Largest Cobalt Production

Geology of Western Oklahoma's Stratiform Copper Deposits

Cobalt Potential in Western Oklahoma's Stratiform Copper Deposits

Key Analyses from Creta and Mangum Deposits*

CRETA wt %	Cu-Shales	Gray shales	Red shales	Maroon shales	Avg Shale
Quartz	**19.2**	25.7	24.7	29.8	26.73
Gypsum	**15.7**	10.2	5	1.6	5.60
Illite	**47.9**	51.6	47.3	56.4	51.77
Chlorite	**16.7**	11.8	23	12	15.60
Chalcocite	**3.00**	**1**	**0**	**0**	**0.33**
CuO	**3.17**	1.26	0.16	0.15	0.52
TOC	**1.29**	1.48	0.99	1.83	1.43
Ag ppm	**26**	41.5	23	41.5	35.33
Pb ppm	**97**	55.5	28	16.5	33.33
V ppm	**93.9**	113	106	130.9	116.6
CuO ppm	**31700**	12600	1600	1500	5233
Co ppm	**19.6**	19.5	30	24.7	24.73
Ni ppm	**48**	48.5	31.7	45.8	42
		Average shale gray-red-maroon			

MANGUM wt %	Cu- Shales	Gray shales	Red shales	Maroon shales	Avg Shale
Quartz	**27.0**	26.2	26.9	23.6	25.57
Gypsum	**13.2**	13	16.3	17.4	15.57
Illite	**48.5**	47.9	43.6	45.7	45.73
Chlorite	**8.80**	11.2	12.4	1.9	8.50
Malachite	**1.70**	**1.7**	**0.1**	**0**	**0.60**
CuO	**2.59**	**1.29**	**1.29**	**0.19**	**1.03**
TOC	**1.75**	1.71	1.69	1.45	1.62
Ag ppm	**31**	34.7	25.9	33.1	31.23
Pb ppm	**87.8**	52	21.1	19.3	30.80
V ppm	**124**	119.3	107.3	115	113.87
CuO	**25900**	12900	1800	1900	5533.0
Co ppm	**24**	**19.1**	**18.6**	**18**	**18.57**
Ni ppm	**55.3**	51.2	38.5	44	44.57
		Average shale gray-red-maroon			

*** from Lockwood, 1972 1976**

Africa	Co
Kisanfu	1.1%
Mukondo	0.7%
Tilwezembe	0.6%
Nchanga	0.4%
Kolwezi	0.4%
Tenke	0.3%
Luanshya	0.2%

CRETA	Cu-Shales	Gray shales	Red shales	Maroon shales
Co wt%	0.0020	0.0020	0.0030	0.0025

MANGUM	Cu-Shales	Gray shales	Red shales	Maroon shales
Co wt%	0.0024	0.00191	0.0019	0.0018

Neither Creta nor Mangum have ore grade cobalt.
It's not even close.

Creta and Mangum Enrichment Factors

Enrichment factors represent normalization the average of the gray, red, and maroon shales of each respective area.

Creta Mine				
Enrichment >1	Cu Shale/ Avg	Gray/ Avg.	Red / Avg.	Maroon / Avg.
Ag	0.74	1.17	0.65	1.17
Pb	2.91	1.67	0.84	0.50
V	0.81	0.97	0.91	1.12
Co	0.79	0.79	1.21	1.00
Ni	1.14	1.15	0.75	1.09

Creta copper shales are depleted in cobalt, vanadium and silver.

Only the red shales show cobalt enrichment.

Mangum Prospect				
Enrichment >1	Cu shale/ Avg	Gray/ Avg.	Red / Avg.	Maroon / Avg.
Ag	0.99	1.11	0.83	1.06
Pb	2.85	1.69	0.69	0.63
V	1.09	1.05	0.94	1.01
Co	1.29	1.03	1.05	0.97
Ni	1.24	1.15	0.86	0.99

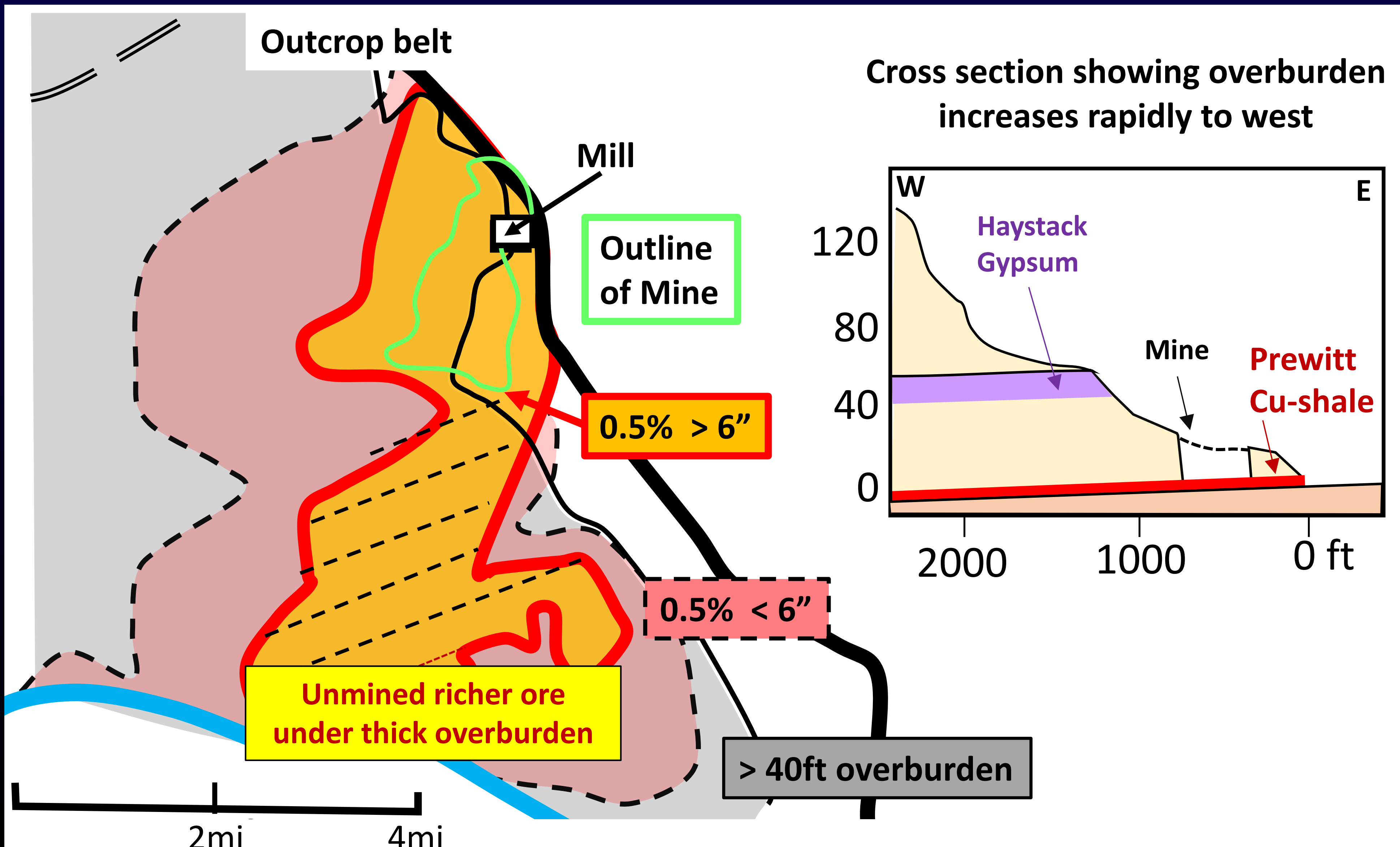
Mangum copper shales- enriched in cobalt, vanadium, but slightly depleted in silver.

The gray shales are enriched in all elements.
The red shales have slight cobalt enrichment.

- The Creta Mine shut down in 1975 owing to low copper prices and increased smelting costs from pollution regulations.
- Although lacking cobalt potential, the current copper price is now 670% higher. Is it worth considering re-opening the Creta Mine for copper?

SUMMARY

- Geological studies have defined isopach of ore grade cutoffs and overburden.
- These data are sufficient for an assessment of commerciality.
- The richest ore with thinnest overburden has already been mine.



CONCLUSIONS

Creta holds NO cobalt potential.

Thicker overburden is a negative factors, but

Creta might have remaining commercial copper ore at current copper prices.

The abandoned Creta mine still holds mysteries.

Who built the Creta Cannon and why?

One-eyed, One Barrel'd, Flyin' Purple Pumpkin Chucker

Defending our southern border from Redbacks.

Thank You

SPECIAL ACKNOWLEDGMENT

Dr. Ken Johnson

Oklahoma Geological Foundation: Living Legend Award, 2015

More than 60 years of sustained research on Oklahoma's geology with an emphasis on the Permian System and he's still publishing and teaching.

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