The Paleozoic Sedimentary Rocks of the Ouachita Mountains and Ozark region and their Genetic Relationship to the Mississippi Valley-Type Mineralization in the Southern Ozark Region: Insights from Radiogenic Pb Isotope and Trace Elements Studies

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1. Introduction

The Mississippi Valley-Type(MVT) deposits are epigenetic and stratabound Zn-Pb± fluorite±Barite deposits mainly hosted by carbonate platform sequences located on the flanks of sedimentary basins. It is widely recognized that the low temperature mineralizing fluids (70-200°C) were expelled from the adjacent foreland basin (Arkoma basin) in response to an orogenic event (Ouachita orogeny).

The nature of the orebodies ranges from massive replacement zones to open space fillings to disseminated clusters of crystals in intergranular pore space(Gregg and Shelton,2012).

Hypothesis: Though the ore genesis is still a debatable topic, it is believed that the sedimentary rocks, consisting mostly of organic-rich shales of the sedimentary basin, might have sourced the metals of the MVT deposits.

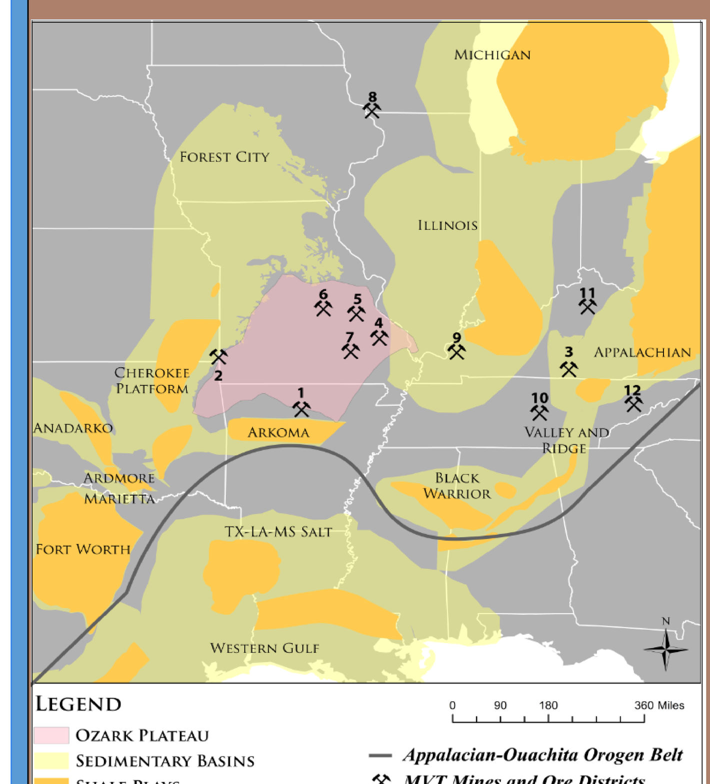


Fig. 1. Map of the US midcontinent region showing the location of sedimentary basins (pale yellow), Devonian-Mississippian shales (bright yellow), and major MVT mining districts and deposits (1 through 12): **(1) Northern Arkansas, (2) Tri-State,** (3) Burkesville deposit, (4) Old Lead Belt, (5) Southeast Missouri Barite, (6) Central Missouri Barite, (7) Viburnum Trend, (8) Upper Mississippi Valley, (9) Illinois-Kentucky Fluorspar, (10) Central Tennessee, (11) Central Kentucky, and (12) Eastern Tennessee. Modified from Garven et al. (1993). For drawing the basemap: https://www.eia.gov/maps/maps.htm; https://geology.com/energy/shale-gas/shale-gas-map-lg.jpg

2. ABSTRACT

Mississippi Valley Type (MVT) lead-zinc deposits are epigenetic ore deposits hosted mainly in dolostone and limestone. Accounting for 24 % of the worldwide Pb and Zn (Pb-Zn) resources, the Mississippi Valley-Types Pb-Zn deposits comprise the largest recognized concentration of Pb in North America in the Ozark region. Scattering Pb and/or Zn deposits in North America encompass, among others, the well-known Tri-State, Central Missouri and Northern Arkansas districts located north of the Arkoma basin and the Ouachita fold-thrust belt. The genetic model for the Ozark MVT ore formation is still a matter of hot debate among scholars. Nevertheless, it is generally believed that the mineralization is connected to the Pennsylvanian-Permian Ouachita orogeny, which triggered a South-North topographic gradient flow of basinal brines, leaching metal rich sediments en route. The objective of the research is twofold. First, to ascertain whether the organic-rich shales and sandstones from the study area (Ouachita Mountains, the Arkoma Basin, and the Ozark Region) provided metals during the mineralization event, which was coeval with the Ouachita orogeny. Second, to assess the depositional environment of the potential source rocks, which will shed light on their ability to sequester metals. The Pb isotope compositions of the ores (sphalerite) have been compared to their associated sedimentary rocks (Collier, Mazarn, and Polk Creek, Womble, Fayetteville, Stanley and Chattanooga shales and Jackfork Sandstone) and metal sources have been evaluated. In addition, the role of environmental deposition of sedimentary rocks to sequester adequate amounts of metals has been appraised using redox sensitive trace elements (U, V, Mo, Cr, etc.). Pb isotope compositions of whole rocks and leachates, and their associated ores from the Northern Arkansas and Tri-State districts, indicate a mixing model of fluids sourced from high and less radiogenic rocks, with the Chattanooga rock samples being the most prominent source rocks. Paleoredox proxies indicate deposition m under suboxic to anoxic conditions, which are favorable for metal enrichment. However, oxic conditions are also indicated by other geochemical proxies, suggesting possible additional factors such as the organic matter production ,the rates of sediment accumulation, the post depositional alteration processes associated with diagenesis and low-grade metamorphism during the Ouachita orogeny.

2. Geological Setting

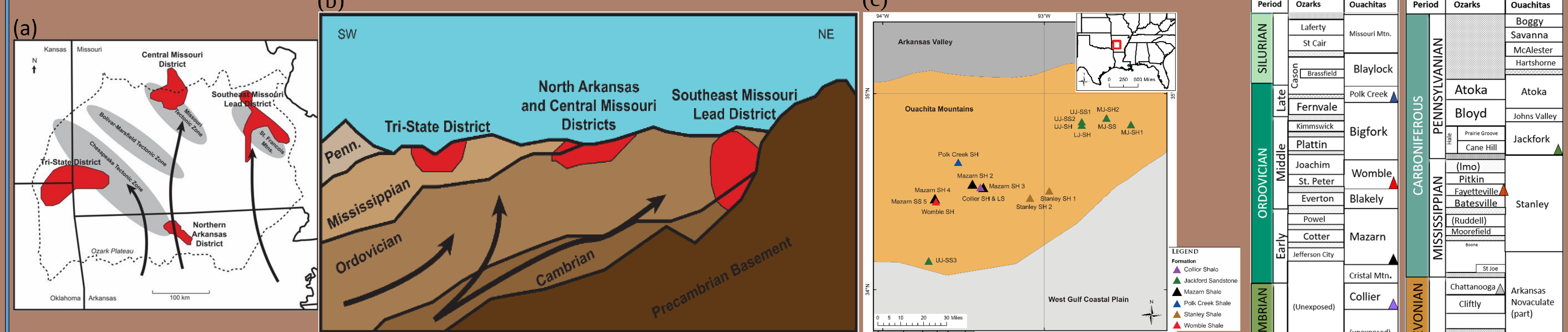


Fig. 2. **a**. Geologic sketch maps showing the location of major MVT ore districts of the Ozark region **b**. Cross section showing brine migration(in arrows) during MVT mineralization event(Reprinted from Lopaka L.,2000) **c.** Location of rock samples in the Ouachita Mountains. **d.** Illustrate the stratigraphic position of the rock samples in the stratigraphic section of the Ozarks and Ouachitas (Retrieved from http://www.geology.ar.gov/geology/stratigraphy.htm)

3.Objectives and Methods

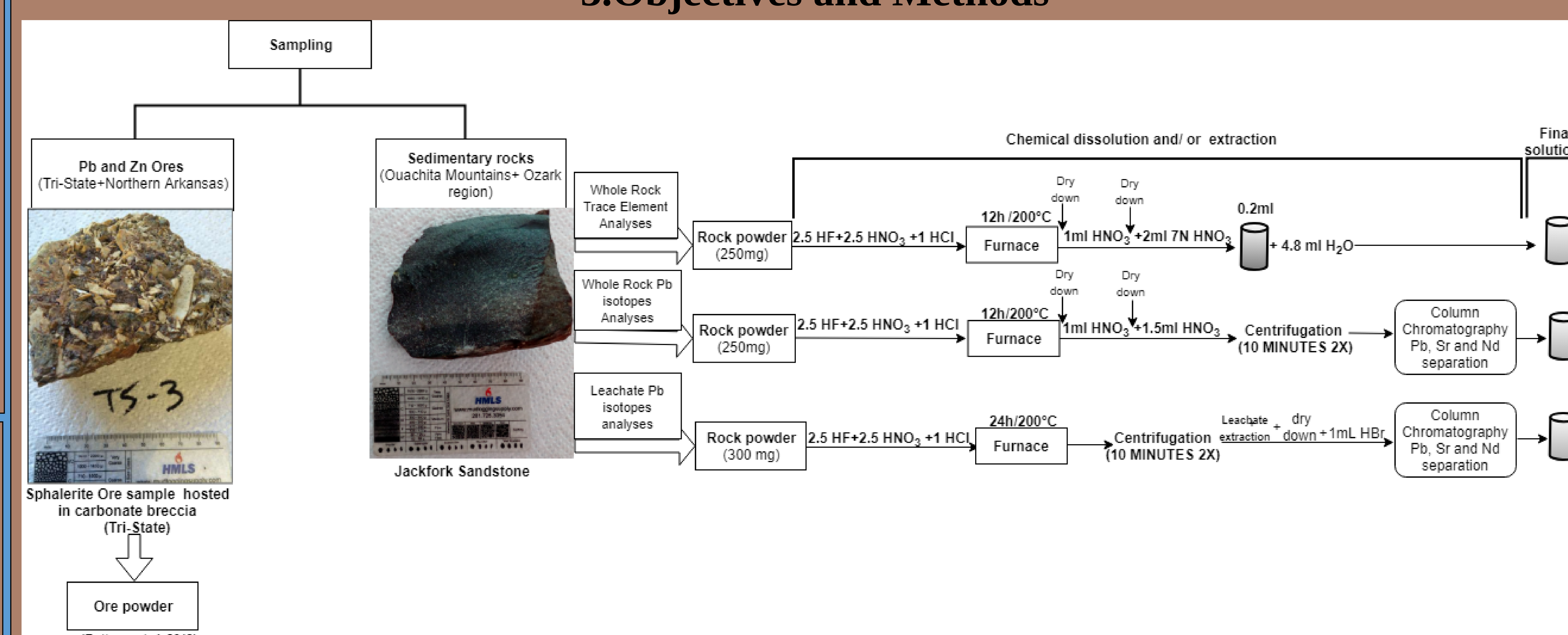
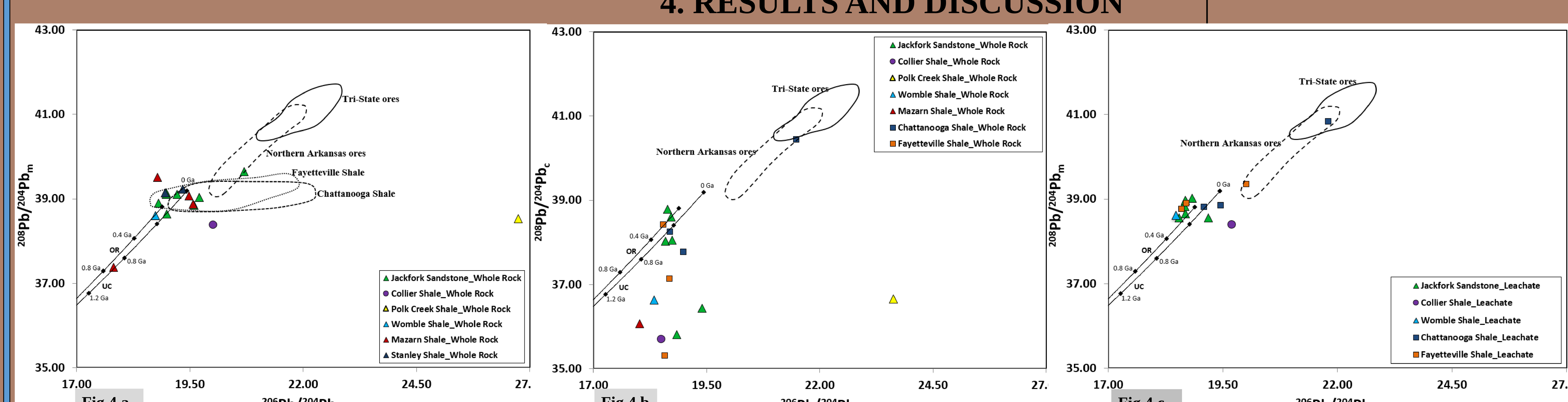


Fig.3 Flow sheet showing analytical processes of rock samples. Trace Element concentrations were obtained from the a Thermo Scientific iCAP Q ICP-MS. Whole rock Pb isotope ratios and leachate Pb isotope ratios were obtained from the Nu Plasma multi-collector ICP-MS.

- Analyze sphalerite ores from the Tri-State and Northern Arkansas MVT districts
- Analyze shales and sandstone lithologies from the Ouachita Mountains and Ozark region

- Comparative study of the Pb isotope signatures of ores and the associated sedimentary rocks to constrain the possible sources of metals
- Whole-rock trace element concentration analysis to determine the initial Pb isotope ratios (age of mineralization)
- Leaching experiments to better assess the contribution in Pb isotope composition from leached sedimentary rock by hydrothermal fluids (Chiaradia and Fontboté,2003)
- Separation of Pb from other metals following the method outlined by Pin et al. (2014)

4. RESULTS AND DISCUSSION



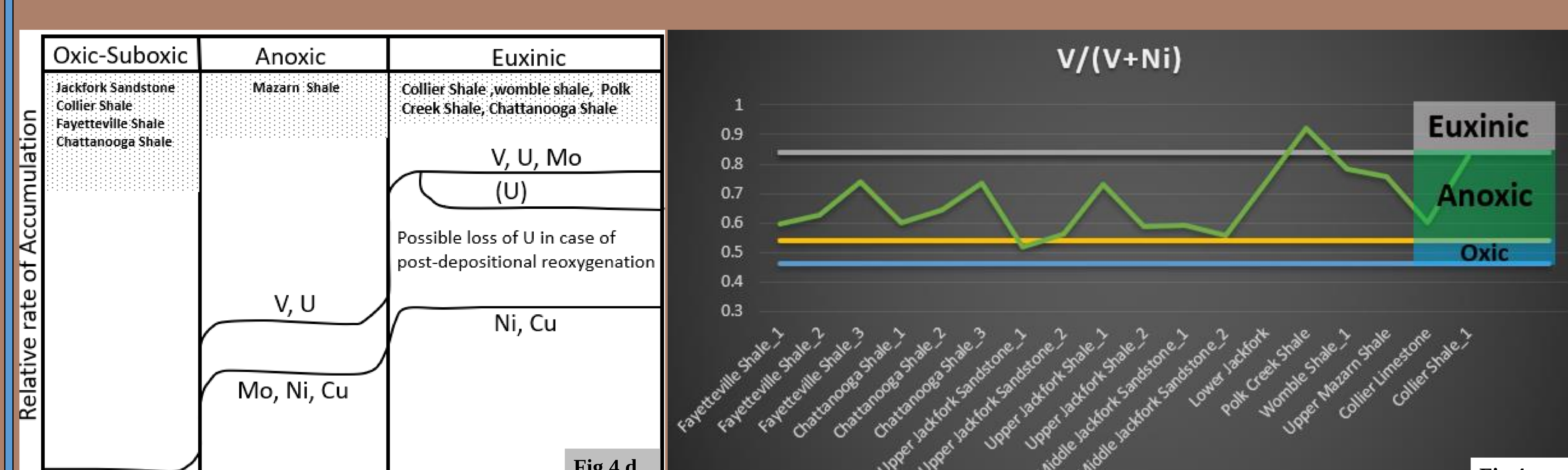


Fig.4.a Thorogenic diagram of Pb isotope compositions of ores of N. Arkansas ,Tri-State MVT districts and whole rock(4.a), initial(4.b) and leachate(4.c) Pb isotope compositions of potential source rocks from the Ouachitas and the Ozarks. Fig.4.d Constraint of paleoredox conditions Fig.4.e Reconstruction of paleoredox conditions from V/(V+Ni) ratio

-Major Pb and or Zn contributions might have been provided by the Chattanooga Shales, the Fayetteville shales and the Jackfork sandstones.

-Geochemical proxies (fig.4.d and fig.4e) show that rock samples were deposited from oxic to anoxic and euxinic conditions implying the first order control of the primary production of organic matter on the formation and preservation of organic carbon rich sediments which were also favorable sinks for metals(Pb, Zn, Cu, Mo, Ni…)

-The sinking and sourcing functions of organic rich sediments from the Ouachita Mountains and Ozark region might have played a critical role in sourcing metals to the Northern Arkansas and Tri-State MVT districts.

5. References

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