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A Geochemical Analysis of the Arkansas Novaculite and Comparison to the Siliceous Deposits of the Boone Formation

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by

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This thesis is approved for recommendation to the Graduate Council

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Abstract

Geochemical analyses of the Arkansas Novaculite, located within core structures of the Ouachita Mountains in west-central Arkansas, and penecontemporaneous chert of the lower Boone Formation, located atop the Springfield Plateau of southwest Missouri, northwest Arkansas, and northeast Oklahoma, have identified a significant concentration of both aluminum and potassium. This would seem to eliminate a biogenic origin and favor a volcanic source of the silica that comprises these units. Trace and rare earth element (REE) analysis also suggests that the Arkansas Novaculite and the chert in the lower Boone Formation may have both been formed from the same volcanic source.

The volcanic signatures of these two formations were compared to average elemental concentrations of continental, Aleutian, and boninite magmatic bodies. Both the Arkansas Novaculite and Boone Formation resemble a boninitic magmatic body in composition. Second order mantle melt needed to create this titanium depleted primitive andesitic body would have been generated as the Gondwana landmass approached the North American craton throughout the Devonian and Lower Mississippian periods, eventually closing the Ouachita Trough during the Ouachita Orogeny (Pennsylvanian).

Field samples of the Arkansas Novaculite were collected at Caddo Gap, Arkansas, while the Boone Formation was sampled across southwest Missouri and northwest Arkansas. Both the energy-dispersive X-ray and mass spectrometry analysis was performed at the University of Arkansas’ Nano-Bio Materials Characterization Facility and Department of Chemistry, respectively.

Acknowledgments

My first acknowledgment needs to be extended to my committee chair and mentor Dr. Walt Manger. Without his guidance and general Geology expertise this project would not have been possible. His ability to convey complex geological processes in a way that makes logical sense is unrivaled. His confidence in myself never wavered and was crucial in the success of this project.

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There is not enough space for me to fully express my gratitude towards Dr. Doy Zachry. He has always been willing to aid my academic career by offering insightful knowledge on any number of subjects. I have never left Dr. Zachry's office unsatisfied with an answer to a question or response to a request that I had. Almost as importantly he opened the door to my professional career during a time when numerous others are facing brick walls. For that I will always be grateful. The amount of students Dr. Zachry has influenced is hard to rival and is a testament to his contributions to the field of Geology not only as a researcher but as an educator and advisor.

I would like to thanks all my friends that allowed me to ramble about novaculite and chert geochemistry in order to make sense of the data in a geologic setting. My girlfriend, Emma

Hlavaty, stuck with me through this process, which was no easy task. Her and my dog Roxie were always there for me when I needed a little extra support and an escape from the grind of a thesis project.

Lastly without my family I would not have developed the desire to better myself through education. This was something that was always stressed to me growing up and after this process I appreciate the impact it had on my life.

Table of Content

1. Introduction

The main objective of this study is to identify the source of the silica for the Arkansas Novaculite and compare it to the chert of the coeval lower Boone Formation. A geochemical approach has been utilized to identify the source of the silica within the Arkansas Novaculite of the Ouachita Mountains region. The elemental composition throughout the entire section of the Arkansas Novaculite, and the Boone Formation was determined using energy-dispersive X-ray spectroscopy (EDX) and mass spectrometer analysis. EDX established the major element components, while the mass spectrometer data was used to analyze specific trace elements in an attempt to better establish the silica source.

The deposition of the Arkansas Novaculite spans approximately 60 million years. Deposition of this nearly pure siliceous unit began at the beginning of the Devonian and possibly even Silurian (Lowe, 1985), and continued through the early Mississippian Kinderhookian series, possibly Osagean (Shaulis *et al.*, 2012). It is bounded stratigraphically by a gradational contact between the shaley lithologies of the Missouri Mountain Shale and Stanley Group at the base and top, respectively. The Arkansas Novaculite has been divided into numerous members and submembers (Miser and Purdue, 1929). For this study, an informal three member classification will be utilized and described as the lower, middle, and upper members. The working definition for the formation in this study was a sedimentary, siliceous rock located stratigraphically between the Missouri Mountain Shale and Stanley Group representing at least Devonian through early Mississippian time. All Arkansas Novaculite samples were taken from Caddo Gap, Arkansas, located on the southern flank of the Benton Uplift, a core structural feature of the Ouachita Mountains.

The Arkansas Novaculite has been studied by not only geologists, but archeologists for its importance as the source of material for tools and weapons for Native Americans. Archeologists have tried to use geochemical analysis to source artifacts to known aboriginal quarries (Scarr, 2008). Geologists have studied the novaculite since it was formally named and described by Purdue (1909) and Miser (1917). Trace element analysis has been undertaken by several geologist (Cornish 1997; Doerr 2004; Scarr, 2008), but little work has been done to compare the results with the coeval chert bearing carbonate sequence of northwest Arkansas. The source of the silica for the Arkansas Novaculite and Boone Formation is also a subject of much debate. Sholes and McBride (1975) among others argue that the silica source is biogenic and that the ~300 meters of siliceous rock is the result of alteration of biologic siliceous remains. A less followed train of thought was presented by Rutley (1894), Derby (1898), and Correns (1950), who believed simultaneous dissolution of limestone and precipitation of silica were responsible for the novaculite. Beaty (1989) conceived the idea that the silica was released by hydrothermal activity related to plate tectonics. Another theory, proposed by Goldstein and Hendricks (1953), and the working hypothesis for this study, claims that volcanic ash deposited in a sediment-starved basin could have been altered to the novaculite we see today as it passed through the water column.

2. Geologic Setting

2.1 Southern Mid-Continent

The tri-state area of the Ozark Mountain Range encompasses portions of northwest Arkansas, northeast Oklahoma, and southwest Missouri. Within this geographical area parts of three geologic provinces are found: the Ozark Dome to the north, Cherokee Platform to the northwest, and the Arkoma Basin to the south, which marks the start of the Ouachita Mountain orogenic belt (Figure 1). The geology of the area is dominated by the Ozark Dome as a broad, asymmetrical, cratonic uplift. This uplift is cored by Precambrian granite and rhyolite that is exposed in the St. Francois region of southeast Missouri. Rocks of Cambrian to middle Pennsylvanian age make up greater than 150 meters of sedimentary section while dipping radially away from the core area. Regional dip along the southern portion of the Ozark Dome, known at the Springfield Plateau is typically less than 1° and averaging only 19′ (Chinn and Konig, 1973). Due to its cratonic setting this area is relatively structurally undeformed as compared to the Arkoma Basin and Ouachita Mountains to the south. However, a series of major normal faults run northeast-southwest with hanging wall movement towards the southeast.

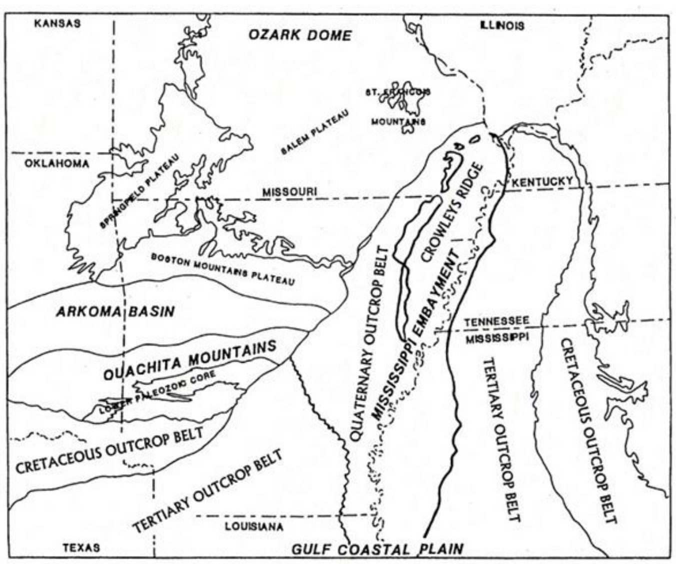

Figure 1:Geologic Provinces of Tri-State and adjacent areas. (Modified from Manger, Zachry and Garrigan, 1988)

Three broad plateau surfaces comprise the Ozark Dome and reflect the epeirogenic uplifts that have affected the craton (Fenneman, 1938). These platforms developed over time further away from the core area and decrease in current elevation due to erosion and differential resistance to weathering within the sedimentary section. In order from oldest and lowest elevation these plateaus are the Salem, Springfield, and Boston Mountains Plateaus (Figure 1). The Salem Plateau is comprised of Lower Ordovician limestones and dolomites. Due to these rocks being deposited during the highest covering of modern day land by seas this plateau has the largest aerial extent covering most of southern Missouri and adjacent northern Arkansas. The Springfield Plateau covers the tri-state area of southwest Missouri, northwest Arkansas, and northeast Oklahoma. It is capped by the limestone and chert of the Boone Formation and St. Joe Limestone. In the majority of location the Lower Mississipian strata rest unconformably on Ordovician rocks. Where the Silurian and Devonian record is preserved it is thin and only located in the Eureka Escarpment between the Salem and Springfield Plateaus. The Boston Mountain Plateau is, again, the youngest and highest topographical surface in northern Arkansas. It is formed by Upper Mississippian through Pennsylvanian rocks and is capped by the Atoka Formation.

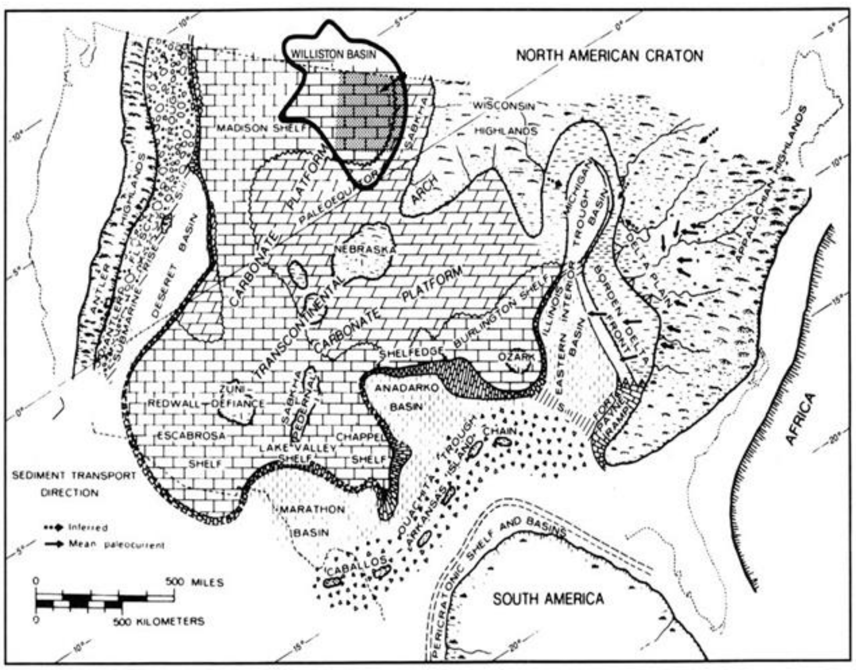

Figure 2: Lower Mississippian Paleogeography (from Gutschick and Sandberg, 1983)

These plateaus can also be described based on their geographical relationship to the carbonate production area during the late Paleozoic Era known as the Burlington Shelf (Figure 2). The core of the Ozark Dome as well as the Salem Plateau was located on the shelf throughout the time period while the Springfield and Boston Mountain Plateau deposits represent the deeper ramp setting and associated deposition via transportation of shelf carbonates.

2.2 Ouachita Mountains' Structural Features

The Ouachita Mountains are an east-west trending anticlinorium of Paleozoic rocks across west-central Arkansas and southeast Oklahoma. The structure is the result of a collisional-subduction orogeny between Laurasia and Gondwana during the late Paleozoic era (Lowe, 1975). The Quachitas are part of the frontal fold-thrust belt that is north vergent, excluding the core uplifts of the Benton and Broken Bow Uplifts, towards a midcontinent foreland basin, the Arkoma Basin (Arbenz, 1989). The strata of the Ouachita Mountains are dominated by deep-water facies, both initially starved basin and becoming clastic flysch sedimentation, in contrast to its shallower carbonate Appalachian equivalent, found in the Valley and Ridge Province (Arbenz, 1989). To the south and east of the exposers coastal plain sediments sit unconformably above the orogenic belt and obscure the connection in eastern Mississippi to the southwestward trends of the Appalachian Mountains (Lillie *et al.*, 1983).

The Ouachita orogenic belt has been subdivided into several provinces based on their structural styles (Figure 3**)**. These provinces include the Arkoma foreland basin, frontal embrocated zone, central thrust belt (north of the Benton-Broken Bow Uplift), and the Benton and Broken Bow Uplifts (Arbenz, 1989). To the north of the Arkoma Basin lies the Ozark Dome, which dominates the southern mid-continent and occupies the stable cratonic setting.

The Arkoma Basin is characterized by mildly compressed folds of southward thickening Carboniferous strata that flatten to the north as they near the stable Ozark Dome (Arbenz, 1989; Blythe, 1988). The basin trends east-west, from the Mississippi Embayment, across central Arkansas, and plunges south-west into south central Oklahoma (Housenecht and Kacena, 1983).

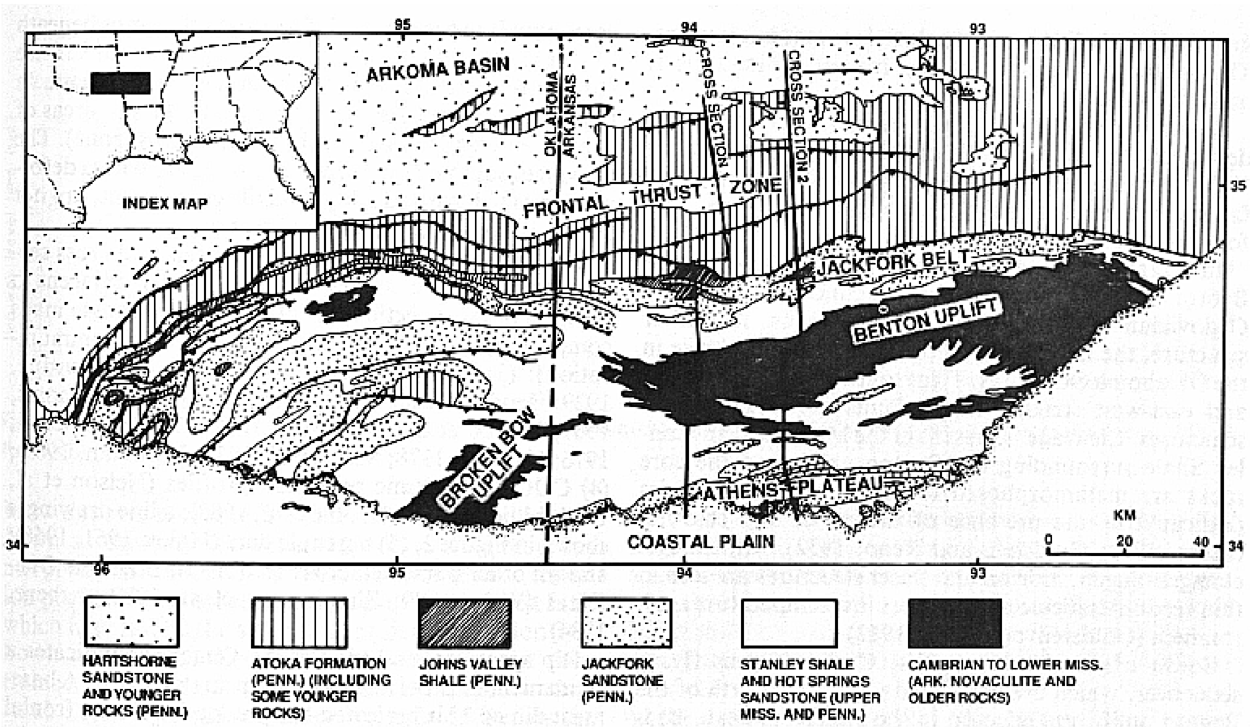

Figure 3: Structural provinces of the Ouachita fold belt and their associated rock units (from Blythe, 1988)

The structural boundary to the north in Arkansas is the Mulberrry fault, a southward dipping normal fault, and in Oklahoma, due to the die out of the Mulberry, near the stoppage of folds that consist of Desmoinesian coals in the intervening synclines. The transition from the Arkoma Basin to frontal imbricated zone, to the south, is well defined in Oklahoma, as the Choctaw fault, but is less clear in Arkansas and is arbitrarily drawn as the Ross Creek fault due to it being the next major thrust fault to the south (Arbenz, 1989).

The frontal imbricated zone is comprised of numerous, stacked, telescoping thrust sheets (Blythe, 1988). The boundary of this province is indicated by the first occurrence of thrust faults as one traverses southward (Lillie *et al*., 1983). These narrowly spaced thrust faults, where observed at the surface, appear very steep (45°-65°), but seismic surveys show they flatten at fairly shallow depth (Arbenz, 1989). These faults are also shown to commonly merge in the subsurface with one another (Arbenz, 1989). The outcropping section of this zone is most commonly the Atoka Formation. The southern boundary of the frontal imbricated zone is marked as the Ti fault of Oklahoma and the Y City fault of Arkansas (Arbenz, 1989; Blythe, 1988)

The Benton Uplift, Arkansas, and Broken Bow Uplift, Oklahoma, form the central core of the Ouachita Mountains. They are composed of highly deformed, early to middle Paleozoic units, and contain the most extensive outcroppings of Upper Cambrian to Mississippian rocks that were deposited before major uplift and clastic influences effected the area (Nielsen *et al.*, 1989). The oldest formation within these core structures is the Collier shale (Upper Cambrian), while the youngest is the Devonian to Mississippian Arkansas Novaculite. Regional metamorphism is seen within and adjacent to the Benton and Broken Bow Uplifts. The northeastern margin of the Benton and southern flank of the Broken Bow Uplift exhibit the highest metamorphism, while the central and southern Benton Uplift and northern Broken Bow uplift sit in a saddle of low temperatures (Nielsen *et al.*, 1989). The Benton and Broken Bow Uplifts experienced continual tectonic deformation from the first folding and faulting of the accretionary wedge growth to its eventual obduction onto the North American cratons southern margin (Keng, 2011).

2.3 Tectonic Evolution

The sequence of events responsible for the development of the Ouachita fold belt and its associated rock units span nearly 270 MY, from the opening of the paleo-Atlantic to the

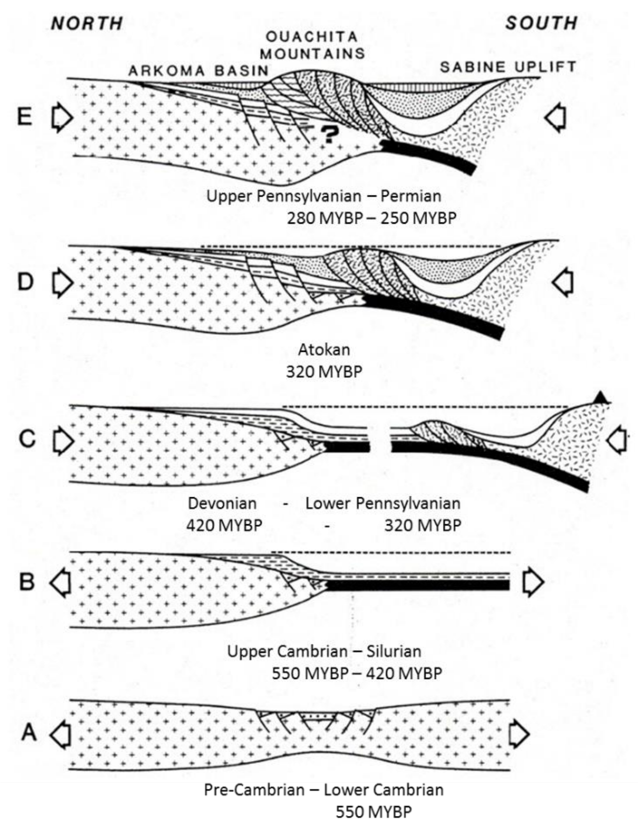

Figure 4: Tectonic History of the Ouachita region (modified from Houseknecht, 1986)

formation of the Pangea supercontinent (Figure 4). The tectonic belt now represented by the Appalachian and Ouachita mountain belts was the margin of an open seaway, the ancient Atlantic Ocean, throughout most of the Paleozoic Era (Lowe, 1975). The northern Appalachian region is understood in much more detail, and records the opening of the seaway during the late Precambrian to Middle Ordovician followed by contraction and the closing of that seaway from the Middle Ordovician through the Devonian (Bird and Dewey, 1970). Two major orogenic pulses were identified during the late Ordovician and late Devonian as the Taconic and Acadian orogenies, respectively (Lowe, 1975).

The southern Appalachian, northern Mississippi and western Tennessee, and Ouachita, west-central Arkansas, regions show a coeval spreading phase resulting in the North American craton being located at the equator and Gondwana near the South Pole (Lowe, 1975). Major compressional pulses corresponded with the Taconic, Acadian, and Pennsylvanian-Permian Alleghanian orogenies (Hatcher, 1972). Pre-Carboniferous tectonic evidence is rare due to the deposition of these units in an embayment along the southern margin of the North American craton, while the active volcanic and orogenic belt presumably would have followed a linear or arcuate trend from the Appalachians (Lowe, 1975). The Ouachita basin was situated between the extremely stable North American craton to the north and an active volcanic arc related to a convergent plate junction to the south (Figure 5; Lowe, 1975).

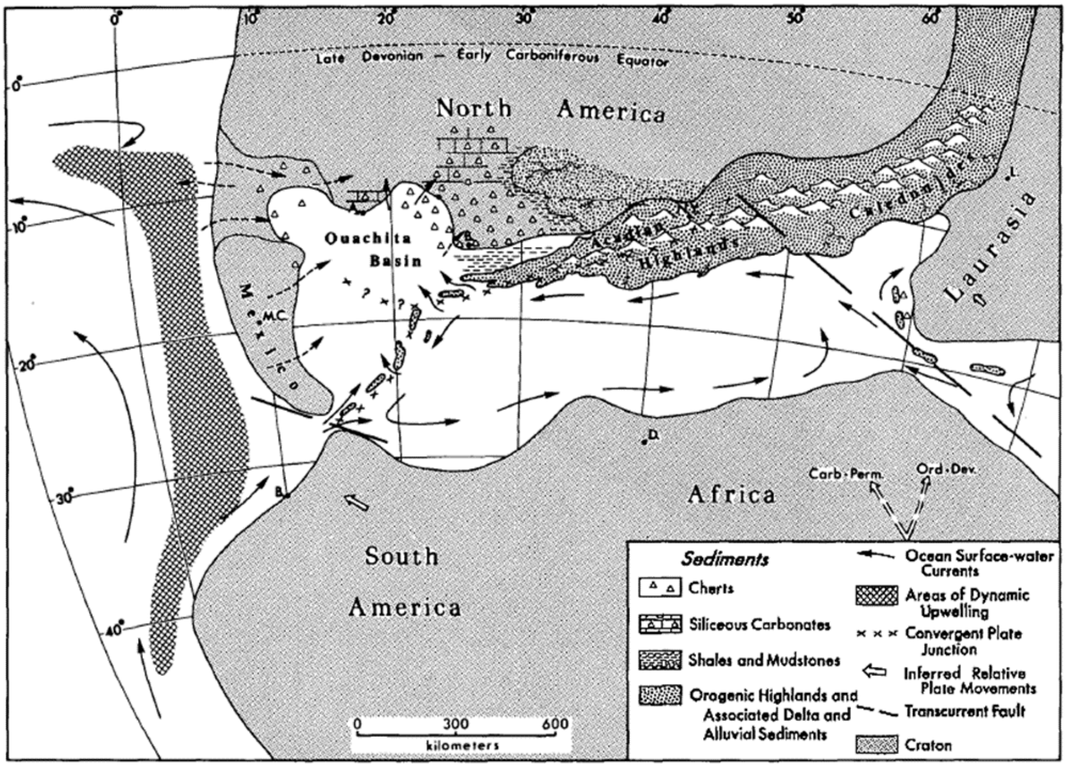

Figure 5: Late Devonian palegeography, paleotectonics, and sediment facies around the western paleo-Atlantic Ocean. Note north flowing wind and ocean currents (from Lowe, 1975)

Post-Arkansas Novaculite tectonics are characterized by orogenic uplift of the entire region supplying large amounts of terrigenous clastic sediment to the basin. This increase in detrital sediment suppressed pure silicate sedimentation especially in the deep water setting, but silica contribution by the active volcanic arc remained high as evidenced by replacement chert of the upper Boone Formation as well as tuff deposits within the Stanley Group (Manger, personal communication; Shaulis *et al.*, 2012). The Ouachita Mountains are the result of the stacking of mildly compressed thin thrust sheets (Arbenz, 1989). Deep seeded thrust faults such as the Y City and Ti Valley faults flatten quickly with depth and delineate the boundary between the central Ouachitas and the frontal zone of heavy deformation (Viele and Thomas, 1989; Arbenz, 1989).

Exposure of pre-orogenic strata is limited to four areas of the Ouachita Mountains: Black Knob Ridge, Potato Hills, Broken Bow Uplift, and Benton Uplift, with the oldest strata being limited to the Broken Bow and Benton Uplifts (Viele and Thomas, 1989). These two uplift reveal a much more complicated deformation history involving multiple phases. These phases are described by Viele and Thomas (1989) as follows: the first resulted in the folding and thrusting of pre-orogenic deep-water rocks onto the North American craton with the highest sheets containing the southern facies of the Arkansas Novaculite. The second phase backfolded the stacked nappes resulting in upright and overturned fold limbs, axial surfaces, and thrust faults toward the south. This upright character is observed throughout the Benton Uplift with the best example being the Caddo Gap outcrop with ~300 horizontal meters of vertically bedded southern facies Arkansas Novaculite. The third phase of deformation formed crenulation cleavage seen primarily in thin sections. This cleavage transects the limbs and cleavage formed during the second phase while also arching the planar elements, bedding, cleavage, and axial surfaces of the second phase.

Throughout the Arkansas Novaculite, regions of triple-point texture have been identified as being the result of thermal metamorphism (Keller *et al.*, 1985). This metamorphism is thought to be the result of Mesozoic intrusions, which out crop along the eastern flank of the Benton Uplift. Based on gravity signatures these intrusions extend far beyond the outcrop area and underlie a large portion of the Benton Uplift (Viele and Thomas, 1989). Metamorphism decreases towards the southwest within the Benton Uplift (Keller *et al.*, 1985). Within the Broken Bow uplift, metamorphism increases to the southwest, and in general for both uplifts, metamorphism is lower and more variable in relation to the metamorphic belt of east Texas (Viele and Thomas, 1989). Based on minerological analysis of quartz veins within the area, temperatures were less than 300°C while oxygen isotope ratios estimate temperatures of 140°C for samples taken ~100 meters from the igneous intrusion at Magnet Cove, Arkansas (Viele and Thomas, 1989; Keller *et al.*, 1985). However, this contact metamorphism interpretation does not provide a satisfactory explanation for the occurrence of triple-point texture within the Broken Bow Uplift as its area of highest alteration sits ~175 km from the nearest exposed igneous intrusion and alteration lowers in the direction of the intrusion.

2.4 Depositional History

The depositional history of the Ouachita trough follows a clear starved basin to flysch pattern. A distinct transition to silica deposition separates these depositional regimes and is reflected in the Ouachita Mountains as the Arkansas Novaculite. Each of these three sedimentation cycles will be discussed in more detail in the following section.

Morris (1974) contended that the entire Ouachita Phanerozoic sequence could be classified as flysch sedimentation. For the purposes of this study, the pre-Arkansas Novaculite strata are assigned to a starved basin regime. A starved basin regime is characterized by extremely fine grained sediment that settled out of suspension very slowly or were brought to the deep, tectonically stable trough by infrequent gravity and turbidity flows (Morris, 1974). The conditions resulted in shale intervals, designated the Collier Shale, Mazarn Shale, and Womble Shale, and a siliceous shale interval, the Bigfork Chert (in ascending order). Periods of sandstone deposition marked an increase in turbidity currents and a drop in sea levels that brought sandy shore zones basinward to the platform-slope edge to the north (Morris, 1974; Lowe, 1989). The regressive sequences are reflected by the Crystal Mountain Sandstone, Blakely Sandstone, and

Blaylock Sandstone. The depositional basin was an elongated, two-sided trough as evidenced by the paleocurrent and facies patterns described by Lowe (1985). The extremely limited sediment supply was primarily derived from the extremely stable North American Craton to the north. However, the Blaylock Sandstone and courser beds of the Womble Shale show mineralogical evidence of a southerly source (Lowe, 1989). The Blaylock Sandstone is the last major sandstone unit in the section before the Arkansas Novaculite. The southern sediment source is a key indication that the approaching Gondwana landmass was starting to influence the geology of the Laurasian southern margin. Once sediment reached the trough, it was transported primarily east to west along the axis of the basin (Lowe, 1989).

During the Ordovician through the early Mississippian, which includes both the starved basin clastic regime and the siliceous Arkansas Novaculite, the entire North American craton drifted toward the north (Lowe, 1975). The sediment sources were moving through the southern hemisphere dry belt, latitude 20°S to latitude 30° S, where the modern day deserts of Australia and southern Africa are located (Boucot *et al.*, 2013; Edgar and Cecil, 2003). The arid environment contributed to the lack of sediment supply and transport from the north to the deep-water deposition site (Edgar and Cecil, 2003). The sediment consisted primarily of detrital carbonates and medium, rounded quartz, characteristic of saltation transport in an arid environment (Edgar and Cecil, 2003).

The Arkansas Novaculite can be divided into a northern and southern facies as first described by Purdue and Miser (1923) based on the transition of chert and shale in the north to a pure siliceous deposit in the south. The southern facies is dominated by white, massive silica deposited in an area with virtually no clastic input (Lowe, 1975). The environment was altered during the deposition of the middle member which is generally similar to the northern facies

(Park and Croneis, 1969). The north to south transition from clastic to silica deposition reflects the lack of sediment input from the extremely stable craton to the north (Morris, 1974; Purdue and Miser, 1923; Lowe, 1975; 1977). Decrease clastic sedimentation is coupled with an increase in silica from a southern source as evidenced by the comparable thickness of the lower shale-and-chert subdivision at northern and southern facies exposures (Lowe, 1976). Paleocurrent studies of the middle member indicate a northerly source of sediment (Lowe, 1985). Morris (1974) and Lowe (1975) identify a convergent zone to the south of the Ouachita Trough producing volcanism that contributed significant amounts of silica to the Paleozoic ocean. The closing in the east of the Paleozoic Atlantic seaway allowed for the inflow of silica-rich upwelling waters from the Pacific to enter the trough further increasing silica levels (Lowe, 1975). Increase in silica occurred during a first order maximum flooding interval (early Osagean), allowing for the deposition of silica-rich carbonates and chert further onto the shelf (Manger, 2015; Lowe, 1975). The Arkansas Novaculite sits conformably over the Missouri Mountain Shale, and is succeeded by the Stanley Group with gradational contacts at numerous locations (Lowe, 1976**)**. However, some locations show an unconformable contact at the base and top of the Novaculite, which has led to some contention regarding the water depth during deposition. The overall lack of sediment influx coupled with the gradational contact at many locations have led to the acceptance that the Arkansas Novaculite was deposited in a deep marine setting with potential unconformable contacts representing a cessation in sedimentation as described by Lowe (1975) and Morris (1974) rather than subaerial erosion. The significant increase in clastic sedimentation within the middle member of the Arkansas Novaculite corresponds to a second order regressive cycle during the late Devonian (Manger, 2015). Falling sea levels shifted the clastic influence further to the south stopping the silicate regime. The chert-and-shale interval of the middle member does indicate there was still a strong silica supply, however, it was not able to deposit the pure, massive novaculite of the upper and lower members.

The post-Arkansas Novaculite depositional regime is assigned to the Stanley Group, Jackfork Group, Johns Valley Formation, and Atoka Formation. These units are attributed to classic, continual, flysch-style sedimentation (Lowe, 1985; Morris 1974, 1989; and Shaulis *et al.*, 2012 among numerous others). The flysch sequence consist of deep marine turbidity current deposits and contain almost no chert or novaculite within the Ouachita Mountains or adjacent regions (Morris, 1989).

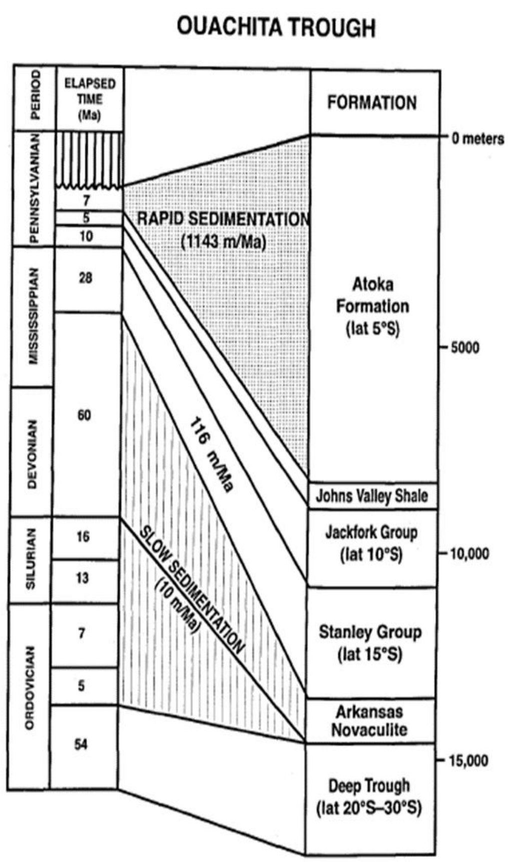

Figure 6: Sedimentation rates and thicknesses relationship of Ordo-Penn units of the Ouachita Mountains (from, Edgar & Cecil, 2003)

The Stanley Group of the Mississippian (Chesterian) strata marks the return of clastic sedimentation to the Ouachita region. At the beginning of the Stanley Group deposition, the system drifting northward, entered the tropical humid zone, which with an increasing sediment supply increased rates of deposition (Figure 6; Edgar & Cecil, 2003). The transition from a sediment starved trough to flysch sedimentation is described by Shaulis *et al.* (2012) using biostratigraphy and geochemistry of tuff deposits found in the Stanley Group. Conodonts near the base of the Stanley Group and the U-Pb ages of the four stratigraphically lowest tuffs, found in the bottom

500 m of the unit, suggest depositional rates until ~323 Ma were low, between 1-40 m/My. Following this slow period Shaulis *et al.* (2012) calculate a dramatic rise in rates to an average of ~800 m/My until the next tuff deposit. This high rate of deposition during the late Mississippian is comparable to that of the Atoka Formation proposed by Morris (1974), ~900 m/My, and is inferred to represent the beginning of significant flysch sedimentation. Due to the lack of absolute dating controls within the Pennsylvanian formations, Jackfork Group, Johns Valley Formation, and Atoka Formation, it is difficult to pinpoint the exact depositional rates, although it is clear based on biostratigraphic correlations that the rate was exceptionally high.

The sediment source of the Carboniferous flysch sequence was predominantly the southern Appalachian Mountain range located adjacent to the east of the remnant Ouachita ocean basin (Ingersoll *et al.*, 2003). However, as the basin sutured shut from east to west, terrigenous influxes occurred in both the north and south (Shaulis *et al.*, 2012). An extensive, long lasting, east-west trending fan complex developed from turbidity currents transportated sediment to the basin floor. The Stanley Group is comprised mainly of elongate fans developing over a gentle slope with broad, shallow channels. As rapid deposition continued into the Morrowan, represented by the Jackfork Formation, a drop in sea levels exposed the northern shelf and allowed for craton derived quartz sand to be deposited as thick sandstone beds (Morris, 1974; 1989). These beds also contain thick olistostrome deposits, mainly along the basin margins, as a result of debris flows and slope failures possibly caused by an increase in seismic activity as the Gondwana plate drew further north (Morris, 1974; 1989). Moving westward down the trough axis, the number of sand beds increased, while the thickness of each individual bed decreased. The sediment flow direction also converged from various point sources to the south, east, and north and a built an abyssal plain subsea fan complex extending east to west (Morris, 1974). The

Atoka Formation marks the last unit of Carboniferous sedimentation before the depositional system is uplifted by the suturing of Laurasia and Gondwana. Estimates by Morris (1989) put a maximum thickness of 8,500 m at the time of deposition of the Atoka Formation along the northern margin of the depositional basin. The axis of the trough shifts northward, yet westward flow of turbidity currents continued associated with the highest rates of deposition. Enough sediment was supplied to the trough in such a relatively short amount of time that the accommodation space nearly filled. This led to late Atokan sedimentation as south building deltaic complexes with sediment from across the eastern part of the North American continent (Morris, 1974).

3. Lithostratigraphy

3.1 Tri-State Area

The Lower Mississippian transgressive-regressive sequence is represented by the St. Joe and Boone Formations in Northern Arkansas (Figure 7). This succession reflects the down ramp deposition of carbonates sourced from the Burlington Shelf of located in current southern Missouri. This ramp developed along the southern margin of the North American Craton and today forms the Springfield Plateau.

Nomenclature for these units is complicated due to "state-line faults" between

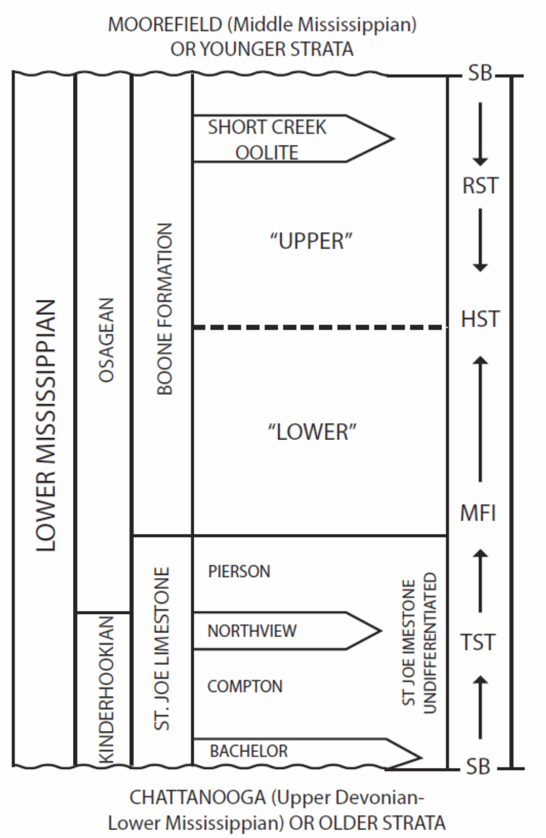

Figure 7: Stratigraphic column of NW Arkansas with associated sequence intervals

Oklahoma, Arkansas, and Missouri. The names St. Joe and Boone were taken from exposures in northern Arkansas and are the oldest, valid lithostratigraphic designations for their respective intervals. The name St. Joe was originally proposed for the basal, chert-free limestone member of the Boone Formation (Hopkins, 1893; Girty, 1915) with a type location near St. Joe, Searcy County, Arkansas (Thompson and Fellows, 1970). The Missouri nomenclature divides the equivalent units into four formations, the Bachelor, Compton, Northview, and Pierson in ascending order. This discrepancy in nomenclature does not exist for this basal Mississippian strata in Oklahoma. The Boone Formation of northern Arkansas facies similar difficulties in reference to continuity of nomenclature in the tri-state area. It was originally named by Branner (1891) with a type locality in Boone County, Arkansas. Again, this is the oldest valid designation of the chert bearing interval of the Lower Mississippian succession in the southern Ozarks. The Missouri statigraphic section divides this interval into, in ascending order, the Reeds Spring, Elsey, and Burlington-Keokuk formations while in Oklahoma we see the Reeds Spring followed directly by the Keokuk. The lack of terminology agreement between these three geologically and geographically connected states has led to difficulties in correlating exact thicknesses and aerial extent of these units.

The St. Joe Limestone is deposited across an unconformity surface and represents deposition in rising sea levels. The lowest member, Bachelor, represents the last orthoquartzites in the northern Arkansas succession, demonstrating that Lower Mississippian strata blanketed the region, and eliminating the ability to rework older units until the Mississippian-Pennsylvanian boundary. Following the Bachelor are two thin-bedded, crinozoan packtone and wackestone members, Compton and Pierson, separated by a thin siltstone or shale Northview member. The carbonate rocks are composed primarily of crinozoan detrital material as well as lime mud from green algae (Manger *et al.*, 1988). This material was deposited by grain flows from the Burlington Shelf in the north down the southward facing ramp. The limestone is massively bedded with abrupt, flat tops and do not show grading of the detrital material. Isopachous maps show the aerial extent and distinct lobate depositional patterns distinctive of down ramp sediment movement (Handford and Manger, 1990). The lithology of the unit becomes more mud-rich up-section consistent with deepening seas. It is inferred that the zero line on the isopachous map reflects the approach of carbonate compensation depths and the onset of the chert bearing carbonates of the Boone Formation. This would make the down ramp Boone Formation at least partially coeval with the up ramp, chert free St. Joe Limestone. The maximum thickness of the St. Joe as an entire formation is no more than 35 meters in the upper ramp setting. It also condenses in a down ramp setting to a meter in Penters, Arkansas. (Manger *et al.*, 1988).

The Boone Formation of northwest Arkansas reaches 125 meters in the southern Ozarks (Giles, 1935). This represents a large increase in carbonate production across the Burlingston Shelf and its preservation across its adjacent ramps. The contact between the St. Joe and Boone is determined based on the transition from crinozoan packstone to carbonate mudstones and calcisiltites, which also corresponds to the first development of dark, nodular, generally void of macrofossils, chert. This contact is transitional and does not represent either a biostratigraphic break or lower order sequence boundary. In Arkansas, the formation is divided into informal lower and upper members based on chert development. The lower Boone is characterized by penecontemporaneous chert whereas the upper Boone chert is a replacement feature that follows bedding planes, preserves the original limestone fabric, is fossiliferous, and white in color. The upper Boone also contains a significantly larger portion of crinozoan detrital. The transition as well as the section becoming more grain dominated up-section reflects the regressive sequence drawing seas and shelf basinward.

3.2 Definition of "Arkansas Novaculite"

The Arkansas Novaculite as a formation, and the term novaculite, have been defined by several people in several ways. The formation name of "Arkansas Novaculite" was formally introduced by Griswold (1892), who used the term in a petrographic connotation to refer to cherts in both the currently assigned Arkansas Novaculite and the underlying Big Fork Chert (Lowe, 1989). This work was followed by Purdue (1909), who narrowed the application of the term to the siliceous unit between the Missouri Mountain Shale, below, and the Stanley Group, above (Lowe 1977, 1989). Miser and Purdue (1929) defined the formation in the following statement:

> *"The Arkansas Novaculite consists predominantly of novaculite with subordinate though considerable amounts of shale and Conglomerate.*
>
> *Novaculite as it is found in the Ouachita Mountains of Arkansas and Oklahoma is a gritty, fine-grained, homogenous, highly siliceous rock, possessing a conchoidal of subconchoidal fracture and being translucent on thin edges."*

Schoolcraft (1819) referred to the mineral novaculite at Hot Springs introducing it in the Ouachita Mountains. Tarr (1938) differed in his definition of the term novaculite as "A very dense, even-textured, light colored, cryptocrystalline siliceous rock; similar to chert but characterized by a dominance of quartz rather than chalcedony." (Goldstein, 1959). King (1937) differentiates novaculite from chert based on its white color, uniform grain size, lack of laminations, and somewhat porous texture, when observed in hand samples (Goldstein, 1959). Use of the novaculite term has been inconsistent (Sholes and McBride, 1975). The Arkansas Novaculite was named for its lithologic character fitting both Tarr and King's qualifications for the term novaculite, and its outcrops being located along the flanks of the Benton Uplift of the Ouachita Mountains in west central Arkansas. The current subdivision of a lower novaculite member, middle chert and shale member, and upper novaculite member was proposed by Miser in 1917 (Lowe, 1989).

3.3 Type Area

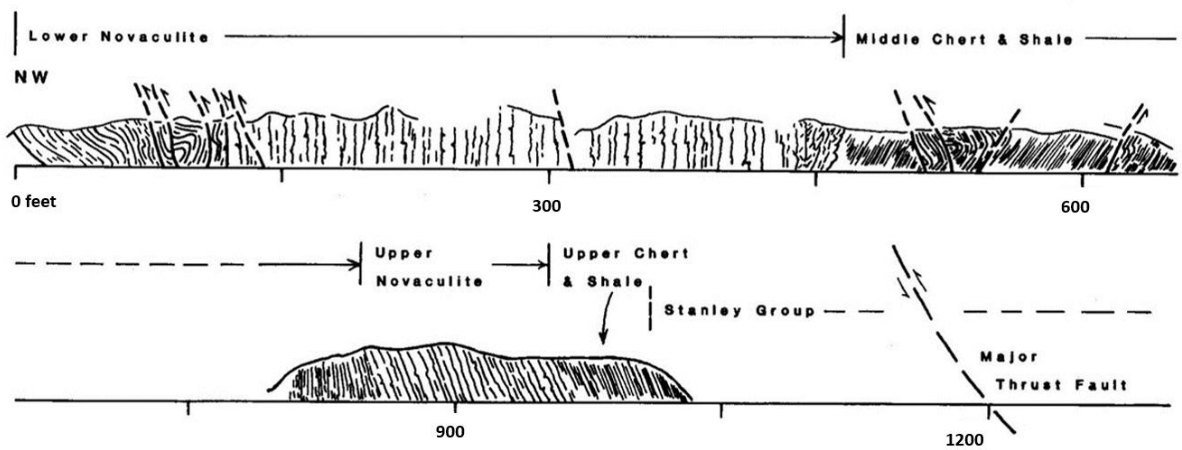

Figure 8: Simplified cross section of the Caddo Gap exposure of Arkansas Novaculite. This figure was completed prior to highway construction, which altered the length but not the surface of the exposed sequence. (modified from Zimmerman and Ford, 1988)

The accepted type area (no formal type section has been designated) for the Arkansas Novaculite is within the Benton Uplift, south of Hot Springs, Arkansas. The southern flank holds the best exposures for field study. The most heavily visited and studied exposure is located at Caddo Gap, Arkansas, along State Highway 8, approximately 80 km southwest of Hot Springs. The road cut exposes roughly 300 m of vertical to near vertical beds (Figure 8). South from Gaddo Gap, toward Glenwood, Arkansas, the thick Carboniferous flysch sequence of the Stanley Group-Atoka Formation is encountered. Conversely, traveling north along State Highway 8 toward Norman, Arkansas, the starved basin sequence from the Ordovician to Silurian, Collier Shale through Missouri Mountain Shale, are exposed. The Novaculite is also partially exposed in parts of far eastern Oklahoma within the Broken Bow Uplift, Potato Hills, and Black Knob Ridge structures (Figure 9). This east-west trending outcrop pattern is indicative of the large anticlinorium structure created by the northward thrusting of pre-orogenic rocks onto the North American margin.

3.4 Lithology

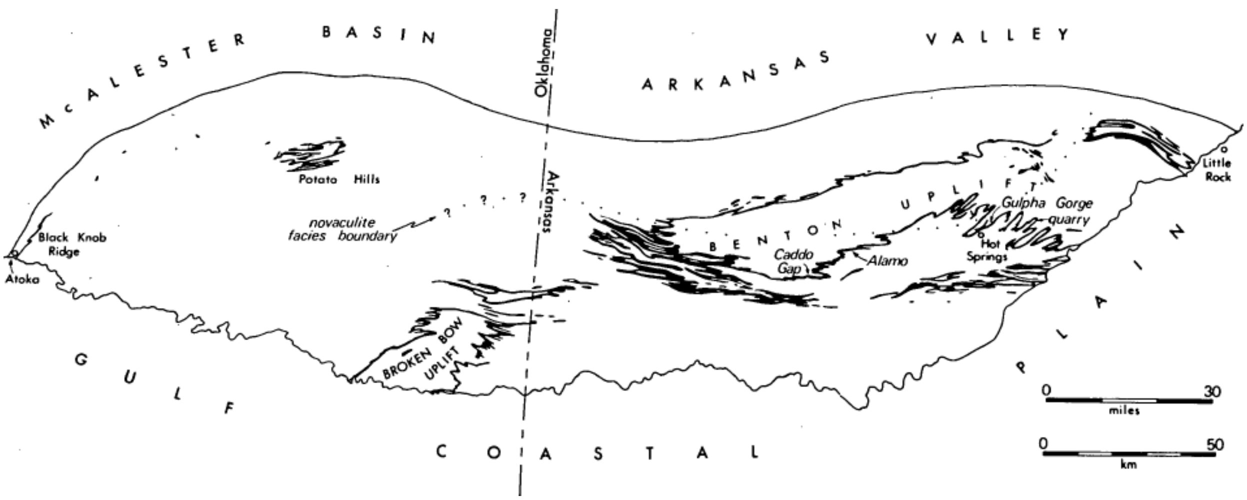

Figure 9: Outcrop map of the Arkansas Novaculite across west-central Arkansas and eastern Oklahoma (from Lowe, 1976)

Although there is no formal designation as such, the lithology of the Arkansas Novaculite should be referred to as two distinct, northern and southern, facies described originally by Miser and Purdue (1929) (Figure 9). Lowe (1977) applied the term northern facies to describe the black chert, shale, sandstone, siltstone, and chert and shale pebble conglomerate and breccia of the northern exposures. Following Lowe (1977) the term northern facies in relation to the Arkansas Novaculite is used in this study to describe the same lithologic character. The term southern facies of the Arkansas Novaculite also follows Lowe (1977) for the better known southern exposures of white novaculite.

The northern facies can be divided additionally into western and eastern classifications. The western exposures are generally thinly bedded, black, clay-rich cherts interbedded with black and green claystones and siltstones. Coarser grains are found predominantly in thin beds of breccia near the top of the Novaculite (Lowe, 1977). Exposures of the northern facies north and northeast of Hot Springs lie in a structurally complex regime making stratigraphic correlations difficult to resolve. The interval described by Lowe (1977) that represents the Arkansas Novaculite in other localities is characterized by shale, massive chert and shale chip breccias that can be multiple meters thick, as well as quartz sandstone and siltstone. Significantly less research has been applied to the northern facies because of poor exposers and structural complexity.

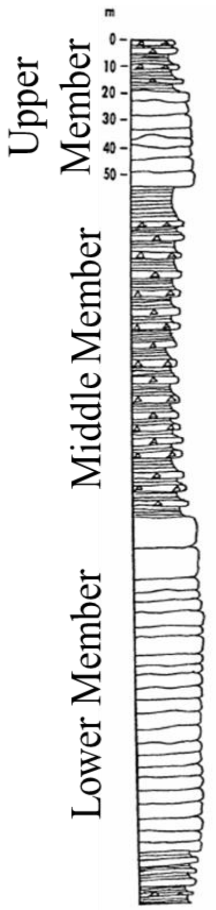

Figure 10: Simplified stratigraphic column of the Arkansas Novaculite, southern facies (modified from Sholes & McBride, 1975)

The southern facies, characterized by the massively bedded white novaculite, is much more commonly thought of as the Arkansas Novaculite. As mentioned previously, the facies is divided into three members (Miser, 1917), and is broadly characterized as a lower member of novaculite, middle member of chert and shale, and upper member of novaculite (Figure 10). Each member is discussed in more detail in the following paragraphs.

Both the upper and lower contacts of the Arkansas Novaculite exhibit gradational boundaries with the shale formations that bound it. This relationship creates interbedded chert and shale sequences, which Sholes and McBride (1975) distinguish as distinct, subdivisions to the established lower, middle, and upper intervals. Gradational contacts indicate the progressive transition from clastic-dominated sedimentation to silicate accumulation in an extremely low energy environment. Further subdivisions were proposed by Lowe (1976) in his study of nonglacial varves, at the Caddo Gap road cut, for the lower member. These include (ascending order) the lower chert-and-shale, calcareous novaculite, translucent novaculite, massive novaculite, and breccia subdivision. The middle member is subdivided by Lowe (1989) into three divisions: a lower bedded black chert and shale, ~50-70 m thick; a middle shale, ~14 m thick; and an upper chert and shale interval, ~20 m thick. The upper member is predominately white or light gray, highly weathered novaculite (Lowe, 1989). The member was deposited with higher proportions of carbonate than its lower member counterpart resulting in a more porous weathered products. At some localities the upper member is tripolitic due to this carbonate leaching (Cornish, 1997). Eastern exposures located in the Broken Bow uplift contain beds of pure crystalline calcite (Lowe, 1989).

Within the lower and upper members of the Arkansas Novaculite, sedimentary structures are rare (Lowe, 1977). Although limited, cross-laminations, varves, and in fewer numbers burrows have been observed (Lowe, 1976). Where cross-laminations are found it is mainly located in the sandstones of the chert-and-shale subdivisions and within one bed of the upper member (Lowe, 1977). The relatively common varves of the lower member are also observed in the middle and upper members and were described in great detail by Lowe (1976). They can be separated into two types: terrigenous and calcareous. Both types are extremely fine, parallel laminations separated by 0.5 mm to 1 cm of pure novaculite. Terrigenous varves are almost exclusively found in the chert-and-shale subdivision as well as the translucent novaculite. They represent thin layers of chert with an increased amount of terrigenous detrital quartz grains. Lowe (1976) also outlines the spatial relationship of these terrigenous varves to the boundary between the detrital dominated northern facies and the nearly silica pure southern facies. This relationship coupled with the equal thicknesses of the chert-and-shale subdivision located at the northern, shale-rich, Gulpha Gorge exposure and southern, chert-rich, Caddo Gap exposure help indicate that not only did the influx of terrigenous material decrease along a southerly trend but silica accumulation increased (Lowe, 1976). The lithologic relationship supports the idea of a southerly source for the nonterrrigenous silica (Morris, 1974). Calcareous varves are found within both the calcareous novaculite and massive novaculite subdivisions. The calcareous laminations are identified by the increase in silt and very fine sand-sized carbonate rhombohedra. These rhombs rarely form a continuous carbonate layer, but are separated by novaculite and lack evidence of carbonate enrichment by diagenetic processes.

The grain population found in the Arkansas Novaculite is overwhelmingly dominated by cryptocrystalline quartz (Keller *et al.*, 1985; Lowe, 1977). However, the individual members and subdivisions of the formation each contain identifiable detrital grains that fall within four principle groups: detrital quartz, detrital carbonate, intraformational clasts, and organic particles (Lowe, 1977). The detrital quartz is found in two distinct grain sizes; a fine, angular, sand and silt sized population is found randomly throughout the massive white novaculite, but forms less than 1% of the novaculite in all sections examined by Lowe (1977) and the other a quartz population consisting of medium to coarse, well rounded grains. Where these grains are concentrated, they form the terrigenous varves described by Lowe (1976). The texturally mature grains occur in thin beds within the bottom 20 m of the lower member and are commonly cross-laminated and silica cemented. Lowe (1977) described them as being texturally and compositionally identical to the shelf deposits of the St. Peter Sandstone to the north and possibly indicating sediment transport by turbidity currents from the shelf to the deep basin. The carbonate grains are very fine sand and silt size euhedra. Detrital carbonates have not been found in the massive novaculite but they have been identified in the bases of graded beds of the middle member and chert and shale chip breccia at the top of the upper member. A general increase in carbonate up section is also observed, as described previously for the relatively calcareous-rich upper member and can be partially attributed to the northward drift of the depositional center towards the warmer waters of the equatorial region. Intraformational clasts are again most prevalent in the coarse-grained units of the middle member. Clasts of white novaculite are rare; most are made of black, organic or siliceous shale. Organic particles include siliceous spheres, spherical ghosts and abundant siliceous sponge spicules within the white novaculite. The organic mudstones and black chert of the middle member and northern facies include siliceous spheres, sponge spicules, and nonsiliceous spore capsules (Lowe, 1977). In the middle member, coarser bases of the graded beds preserve conodonts (Cooper, 1931).

Based on scanning electron micrograph studies, a range of textures have been documented within the novaculite of the Ouachita Mountain fold belt of Arkansas and Oklahoma ranging from cryptocrystalline, anhedral quartz with an average diameter <1 μm to coarse, polygonal triple-point, euhedral quartz with a diameter of 100 μm or more (Keller *et al.*, 1985). A regional trend of coarser grains and triple-point texture are plotted across the Ouachita fold belt by Keller *et al.* (1985) showing the parallel relationship to the structural core and areas of igneous intrusions. Polygonal, triple-point texture was described by Spry (1969) as the result of thermal metamorphism of chert-novaculite.

3.5 Depositional Dynamics

The deposition of sediment in the Ouachita trough follows a starved basin to flysch sedimentation pattern. Morris (1974) contended that the entire Ordovician through Carboniferous sequence can be considered flysch, but by its most widely accepted definition only the

Carboniferous strata (Stanley Group-Atoka Formation) should be considered flysch sequences. The Arkansas Novaculite, like the Ordovician and Silurian units below, represents a starved basin, yet the massive white novaculite must be explained as a change in some aspect of the environment. As described previously, the terrigenous varves of the Arkansas Novaculites lower member can be traced laterally with the boarder of the clastic-rich northern facies and silica-rich southern facies. This is direct evidence toward the decrease in clastic sedimentation moving southward into the basin. Lowe (1976) described the similar thickness of the shale-and-chert subdivision of the lower member between two locations with distinctly different major components. Caddo Gap, located along the southern flank of the Benton Uplift unquestionably within the southern facies area, yet exhibits the same thickness as the Gulpha Gorge exposure, located in the northern facies zone. The lithologic ratio evidence supports the thought that sedimentation of silica increased to the south to keep pace with the clastic sedimentation to the north. The relationship is explained by a silica source being located to the south of the depositional center (Lowe, 1976). During the time of Arkansas Novaculite deposition there was a volcanic arc system located south of the Ouachita Trough (Morris, 1974; Lowe, 1975) that could have provided much of the primary silica to the ocean through subsea volcanic vents and volcanic rock or pyroclastic debris alteration (Lowe, 1975).

Lowe (1975) outlines four key tectonic characteristics that effected silica sedimentation in the region. The first was the stability of the North American craton in combination with frequent cover by broad shallow seas that restricted clastic influx to the basin. This effect was increased during transgressive cycles. The second tectonic influence that effected deposition was the drastic increase in oceanic silica concentration due to the active volcanism to the south. A volcanic arc system would have provided a nearly continuous silica supply through north and westward flowing surface waters that funneled into the embayment of the North American craton. As the Gondwana land mass approached from the south and the seaway was sutured from east to west, the surface water circulation would have been disrupted leading to Lowe's third influence, an inflow of silica rich waters from upwelling in the Pacific Ocean. The last influence on silica sedimentation in the area was the occurrence of major transgressive sequences during this time frame. Silica cement as well as nodular and bedded chert is found throughout the shelf sequences of Devonian through Lower Mississippian age, notably the Boone Formation of northwest Arkansas which was deposited at the same time as the upper member of the Arkansas Novaculite. Sloss (1963) identified the Kaskaskian transgression during the late Devonian and Early Mississippian, which would have allowed the flow of the same silica rich waters that sourced the Arkansas Novaculite to reach the shelf environments.

3.6 Age and Correlation

It is widely accepted that the precise age of the Arkansas Novaculite is difficult to determine and is only poorly constrained (Lowe, 1989; Park and Croneis, 1969; Sholes, 1977). The accepted age ranges from Early Devonian through Early Mississippian (Kinderhookian, possibly Osagean). The Devonian-Mississippian boundary at Caddo Gap lies 8.5 m below the top of the middle member and the 48 m below this horizon is Late Devonian (Haas, 1951). A limited fossil assemblage within the Missouri Mountain Shale, stratigraphically below the Arkansas Novaculite, results in a loose determination that the lower member is early Devonian possibly latest Silurian (Lowe, 1989). Age of Missouri Mountain Shale is primarily determined from the underlying Blaylock Sandstone reliably dated as Lower Silurian based on a graptolite assemblage (Park and Croneis, 1969). The Stanley Group sits conformably over the Arkansas Novaculite at Caddo Gap indicated by its gradational contact in many locations (Ethington *et al.*

1989). The accepted age of the Stanley Group is Mississippian based on biostratigraphic correlations, however, pinpointing the stage is much more difficult as many of the fossil assemblages are recovered from exotic blocks of fossiliferous limestone (Park and Croneis, 1969). Absolute dating of tuff deposits in the lower part of the Stanley Group put the average age of the lowest tuff, Chickasaw Creek, at 320.7 ± 2.5 Ma (late Chesterian – early Morrowan; Shaulis *et al.*, 2012). With these ages of sedimentation, the Arkansas Novaculite must have been deposited over a period of approximately 63 Ma from the early Devonian through early Mississippian.

The Arkansas Novaculite can be correlated with the Caballos Novaculite formation of the west Texas Marathon region both in time of deposition and lithology (Park and Croneis, 1969). The correlation chart proposed by Ethington and others (1989) breaks down the regional correlations between the Ouachita and Marathon orogens. The Caballos Novaculite has a zone of conodonts in its lower chert beds, similar to those of the gradational contact between the Arkansas Novaculite and Missouri Mountain Shale, which are dated to the Devonian Age (Park and Croneis, 1969). The Caballos upper novaculite and chert members are assumed to be the same age as those of the Arkansas Novaculite (Park and Croneis, 1969). For both formations, the lower member is thought to be of similar age to the Camden Chert of western Tennessee (Wilson and Majewske, 1960). Both the Arkansas and Caballos Novaculite are overlain by Mississippian clastics of the Stanley Group and Tesnus, respectively (Park and Croneis, 1969). Each of the novaculites represent deep sea environments with little to no clastic influx. The dramatic increase in oceanic silica can be seen not only in the thick sequence of novaculite and chert in each formation, but also in the shallower platform and slope deposits of the Ozark Region of Arkansas and southern Missouri. The Boone Formation contains an informal lower member rich in penecontemporaneous black chert that was deposited at approximately the same time as the upper member of the novaculite formations (Ethington *et al.*, 1989). The occurrence of carbonate deposits along the continental slope north of the depositional system of the Arkansas Novaculite could have also contributed to the higher amounts of carbonates in the upper member of the Arkansas Novaculite. At least, it is a lithologic indicator that the regional area was entering warmer waters as proposed by Edgar and Cecil (2003).

4. Sequence History

Despite the differing depositional environments for the Boone and Arkansas Novaculite, ramp and deep sea respectively, the fluctuations in sea levels across the North American craton played a very influential role for both units. The Kaskaskia sequences as proposed by Sloss (1963) represents the first-order cycle the starts near the base of the Devonian and continues until the Mississippian-Pennsylvanian boundary (Figure 11). The two second-order Kaskaskian cycles play a major role in the depositional dynamics affecting the Arkansas Novaculite. The transgressive cycle occurred during deposition of the lower novaculite member. This craton submergence pushed the shelf further away from the deep sea setting of the Arkansas Novaculite restricting detrital influx allowing for the development of the nearly pure novaculite that characterizes the lower member (Lowe, 1976). Not only was the stable craton not shedding sediment but the sediment that was being added to the basin was being trapped by rising seas close to the shore line (Lowe, 1975). The second order regression seen during the Upper Devonian (Sloss, 1963) correlates with the transition to a more terrigenous clastic influenced

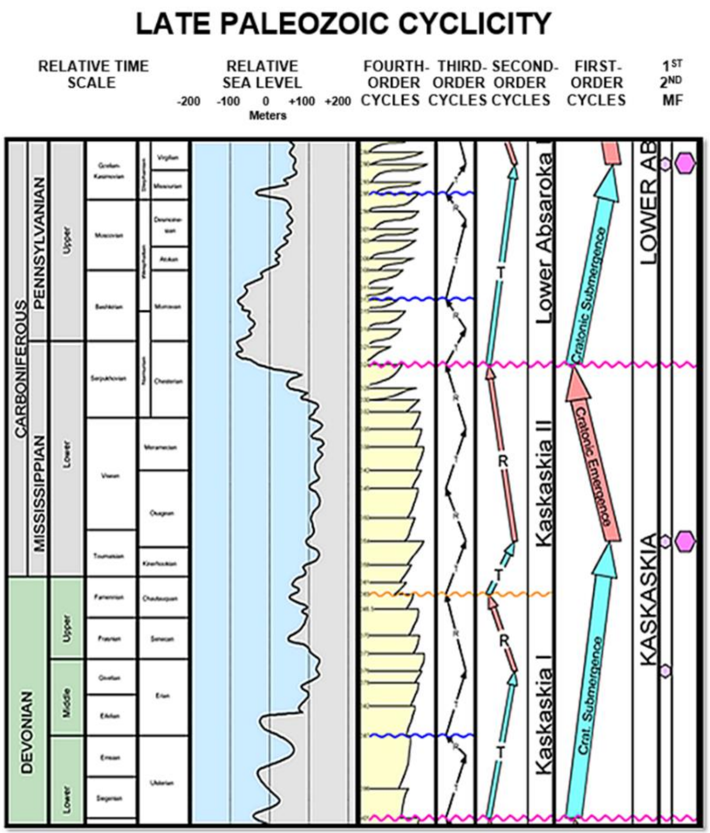

Figure 11: Devonian through Carboniferous sea level fluctuations (from Waite, 2000)

middle novaculite member. The interbedded shales of the middle member were brought out to the deep basin from the exposed shelf by the retreating seas. Sediment starved pure novaculite development but the enormous amounts of silica in the system still allowed for the development of silicate rocks presumably during much higher order cycles and ended with the type 1 unconformity at the base of the Mississippian (Sloss, 1963). The Kaskaskia II cycle saw the relatively short return of transgressive seas across the craton during the Kinderhookian and beginning of the Osagean Series (Sloss, 1963). In response the upper novaculite member, again characterized by a more pure siliceous rock, was deposited in the deep waters. The transgressive seas were responsible for the development of the Burlington Shelf and accompanying ramp setting represented by the Boone Formation (Lane, 1978). The boundary between the lower and upper members of the Boone, the transition from penecontemporaneous chert to diagenetic groundwater replacement chert, sits at the transition from a second order maximum flooding interval (MFI) to a regressive tract.

5. Methods

5.1 Sampling

Samples were collected at the Caddo Gap road cut along Highway 27 in Arkansas (Figure 12). This location was chosen based on its accepted representation of the southern facies of the Arkansas Novaculite and the exposure of nearly 300 m of vertical to near vertical beds. This location exposes significant portions of all three members. It is located along the southern flank of the Benton Uplift.

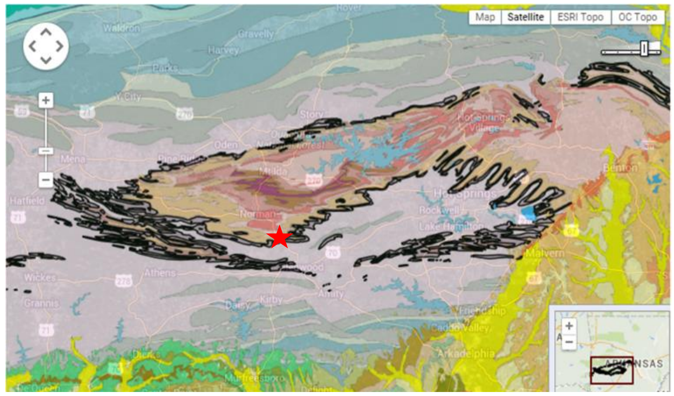

Figure 12: Geologic map of the Benton Uplift. Arkansas Novaculite is oulined in black. Star marks location of the Caddo Gap exposure (from geology.arkansas.gov)

Samples were collected at 10 ft. intervals from the exposed base of the outcrop to the top, where the occurrence of the Stanley Group is inferred based on the presence of a scoured gulley by a minor tributary to the Fivemile Creek that runs below the road. In places where structural deformation is seen, intense tight folding of the massive bedding, samples were taken at an interval inferred to be 10 ft. upward in the section.

Samples for geochemical analysis were selected based upon several criteria. First, the entire interval needed to be represented. However, degradation of the middle member exposure at the sampling site prevented the acquisition of field samples from this interval. This was accepted practice due to the terrigenous clastic influence on this interval and the associated effects these clays would have on the geochemistry of the chert. Second, geochemical analysis was targeted to compare the numerous colors and unique variations within each member and then apply those findings to the formation as a whole. Third, the size and condition of the hand sample was taken into account. Due to the type of geochemical approaches utilized for this study, a sample large enough to yield one gram of unweathered material for rare earth elements (REE) analysis as well as several small chips for imaging and major element analysis was taken at each sampling point.

5.2 Sample Preperation

Hand samples were taken from the field and washed using deionized water to remove surface debris. These samples were then allowed to air dry before samples were selected for further geochemical analysis. Once samples for geochemical study were selected they were slabbed using a miter saw attached with a diamond edged blade. Three cuts were made on each sample in order to self-contaminate the blade. The third slab was then washed with double distilled water to remove any possible contamination from the saw table and again allowed to air dry. Once dry, the slabs were individually wrapped for breaking into small flakes and pieces suitable for powdering within a rock crusher. Several small flakes were removed during this step for EDX analysis as well. The inner coating of the rock crusher used was composed of an aluminum-traced ceramic to prevent contamination of trace elements found in many metals. Once powdered samples were stored in leached containers within a class 100 clean lab to protect against contamination.

5.3 Sample Digestion

Powdered samples were dissolved using the MARS 5 microwave digestion system from CEM Corporation. Digestion was accomplished following the sand digestion method provided by CEM. This utilized HF (5 mL), HCL (2 mL), and HNO_3 (3 mL), along with high temperatures (200 °C) and sustained for 15 minutes to breakdown the extremely resistant silicate structure.

Following digestion, the acids were neutralized using a 4% by volume boric acid solution in compliance with the HF Neutralization method, again provided by CEM. The neutralized samples were then subjected to a 10x dilution before trace element analysis was performed using the iCAP Q ICP-Mass Spectrometer (Thermo Scientific, Brenon, Germany).

5.4 EDX Methods

Small flakes, approximately 0.5 cm^2, of each sample undergoing trace element analysis were taken from the slabbed samples prior to powdering. These flakes were then broken into smaller pieces with an emphasis on exposing a fresh surface for analysis. Samples were placed on carbon tape to adhere to the microscope stage and then sputter coated with gold. EDX was utilized to understand the major element composition. This was accomplished using a FEI Nova Nanolab 200 Dual-Beam microscope.

An EDX analytical method on was the inclusion of gold and carbon in the analyzed spectrum. Gold was a sample preparation addition for better imaging and electron beam focus and should not have been included when analyzing for sample geochemistry. The carbon anomaly was determined to be, at least in part, from the carbon tape that adhered the sample to the sample stand within the instrument and again influenced the weight percentages for some of the samples (Dr. Benamara, Personal Communication). The inclusion of these elements into the spectrum subdued the weight percentages found in this study.

5.5 ICP Methods

Samples were analyzed using a Thermo ICap Q quadrapole mass spectrometer. The ICP-MS was run in KED mode (kinetic energy discrimination) and Helium as a collision gas to reduce interferences. Samples were standardized using the external quantification and a multi element standard (SPEX high purity standards). The ICP conditions were:

Parameter Values
Peristaltic pump speed 40rpm
Nebulizer PFA-ST
Interface cones Nickel
RF Power 1550 W
Cool gas flow 14 L/min
Auxiliary gas flow 0.8 L/min
Nebulizer gas flow 1.06 L/min
Injector Type; ID Quartz; 2.5 mm

6. Results

EDX analysis (Tables 1 & 2) of the Arkansas Novaculite and lower Boone chert reveals elevated levels of aluminum. Elevated aluminum (Al) levels were found throughout the sampling for both units, usually ranging between 0.35 wt % and 2.0 wt %. Two samples of Arkansas Novaculite that were not representative of the massive white novaculite, samples 50A and 50B, showed even more elevated levels of Al. Additional elements that showed anomalous spikes in the EDX spectrum were magnesium (Mg), sodium (Na), iron (Fe), calcium (Ca) and potassium (K). The weight percentage of these elements, when present, ranged from 0.02 wt % to 0.91 wt %.

Trace element and REE concentrations (Tables 3 & 4) were collected on both Arkansas Novaculite (19 samples, 1 duplicate) and the Boone Formation (7 samples). Average trace element concentrations of the Arkansas Novaculite ranged from 0.19 ppm (Thallium, Tl) to 983.40 ppm (K), while average REE concentrations fell in a much narrower range, 0.21 ppm (thulium, Tm) to 15.94 ppm (cerium, Ce). The Boone Formation had a range of trace element concentrations of 0.00 ppm (Cd and Cs, caesium) to 776.50 ppm (K). REE concentrations from the seven Boone formation samples analyzed in this study range from 0.00 ppm (europium, Eu; holmium, Ho; thulium, Tm; lutetium, Lu) to 3.52 (Ce). It should be noted that one REE, terbium (Tb), plotted as a severe positive anomaly throughout the Arkansas Novaculite and Boone Formation samples (210.96 and 64.23, respectively) and these values of 0.00 ppm are inferred based on negative readings by the ICP-MS. This result was not considered valid and was attributed to machine error during analysis. It was not included in trend analysis or used in comparisons to previous studies. Geochemical data was normalized to the values of average primitive arc andesites of continental and intra-oceanic magmatic arcs (Aleutian) compiled by Kelemen *et al.* (2003) in order to attempt to draw a conclusion regarding the kind of volcanic source contributing the silica to the Ouachita Basin and its northern shelf and ramp settings. Kelemen *et al.* (2003), collected geochemical data from various public sources as well as their own research to form a comprehensive analysis of the composition of subduction related magmatic bodies. The study defined andesites as igneous rocks that formed from magmatic compositions with >54 wt. % SiO_2. The majority of normalized values regardless of arc type plotted between 10 and 0.1 on a log scale (Figures 13-16). As a generality, the normalized values for the Aleutian arc consistently plotted higher than the continental arc. A average normalization of the Arkansas Novaculite and Boone Formation data to MORB geochemical data compiled by Hofmann (1988) was also performed with values for REE's again having a narrower range (Arkansas Novaculite: 3.50, erbium, to 14.80, lanthanum; Boone Formation: 0.12, ytterbium, Yb, to 5.48, lanthanum) than the trace elements (Figures 17 and 18). Trace element values within the Arkansas Novaculite normalized to MORB averaged a range of 148.66 (U) to 0.004 (nickel, Ni).

7. Discussion

The presence of Al, K, and Fe in relatively high concentrations, found by EDX analysis within both Boone and Novaculite samples indicates a volcanic contribution of the vast amounts of silica that comprises these formations. EDX analysis of these was needed due to the high levels of aluminum present in a majority of the samples. This analysis was consistent with findings by Fallacaro and Cortez (2000) and Fallacaro (2001), 2 wt % for Al and 0.22 wt %-0.60 wt % for K, of sand-size volcanic composite grains found within insoluble residues of the Boone Formation. Extremely limited testing of Boone Formation insoluble residue was explored by this study and found elevated levels of titanium (Ti) within the sample (0.64 wt %-0.82 wt %). TiO_2 weight percentages were reported by Pollock (1987) in a study of Ordovician chert located in northwestern Maine to range between 0.03 and 0.57 for chert with a minor volcanic influence and 0.1-1.29 for chert that exhibited more prolific contributions from a volcanic source. Stratigraphy, paleogeographic constraints, and geochemistry supports the hypothesis that a volcanic arc was contributing siliceous material to the depositional site of the Boone Formation.

Paleogeographic reconstructions by Morris (1974) and Lowe (1975) present two differing interpretations of the convergent boundary located to the south of the Novaculite and Boone Formation depositional sites. Lowe (1975) hypothesizes a volcanic island arc system to the south of the Ouachita Basin and adjacent ramp-shelf settings, with surface wind and ocean currents pushing pyroclastic debris northward. Morris (1974) places a microcontinent to the south of the basin with a developing volcanic arc system. Geochemical data in this study were normalized to REE concentration averages of both continental and Aleutian magmatic arcs as presented by Kelemen *et al.* (2003). The Arkansas Novaculite and Boone Formation chert were both undersaturated in REE in comparison to those magmatic arcs. When analyzing the normalized

Arkansas Novaculite data for uranium (U), clear segregation of two groups of samples stand out. Samples CG50A-CG69 plot as clearly oversaturated with respect to magmatic arc values, 1.61-8.47 and 3.08-16.22 for continental arcs and Aleutian arcs, respectively. This is higher than the values for all the other samples, which show a maximum value of 0.65 normalized to continental arcs and 1.24 to Aleutian arcs. When comparing concentration values of different samples within the formation very little crossover between elements, i.e. if a sample has the lowest concentration of Thorium (Th) it will also have the lowest concentration of many other elements. This relationship coupled with the general lack of enrichment of most trace elements and REE's is interpreted to be due to the lack of clay incorporated into both the Arkansas Novaculite and Boone Formation chert. Most of the REE's in siliceous deposits are found in the incorporated clay sediment and the concentration of REE's in quartz is usually very low (Cullers *et al.*, 1979). The Arkansas Novaculite, as stated previously, has a very low percentage of grains other than cryptocrystalline quartz. However, the U enriched group (samples CG50A-CG69), relative to the average magmatic arcs, is comprised of samples of extremely dark coloring, which could be attributed to a larger proportion of clay minerals explaining the overall enrichment of all elements in the analyzed suite relative to the other samples.

The lack of clay minerals within the majority of the Arkansas Novaculite does raise an interesting question. Where did the igneous mineral assemblages associated with the volcanic eruptions that sourced the silica end up? It is the conclusion of this study that they were transported by the northward flowing wind and surface oceanic currents as suggested by Lowe (1975), and contributed to the chert and shale-rich northern facies of the Arkansas Novaculite. Using modern oceans as an analog for the velocity and depth of influence the clay sized grains, settling through the water column at a rate of 11.8-15.8 m/day (Whitehouse *et al.*, 1958), could be transported ~2,200 km before they were no longer being carried by waters affected by the surface currents. This would easily be a far enough distance to remove the clay from the depositional area of the Arkansas Novaculites southern facies. Volcanic glass (amorphous silica) has long been reported to undergo devitrification and produce opaline silica and cristobalite (Wise *et al.*, 1972), which have been described as the predecessor unstable isomers to quartz in the maturation succession of SiO_2 (Ernst and Calvert, 1969).

When analyzing the comparison of the Arkansas Novaculite and Boone Formation geochemical data to MORB data collected by Hoffman (1988) the resulting spider diagrams (Figure 17) showed similar trends along the REE's (La-Lu) as MORB normalized spider diagrams of Sun and McDonough (1989) who were studying oceanic island arcs. Not only was the trend similar (flat), the values were similar (between 3 and 7). The trace elements do not align as closely. Sun and McDonough (1989) report strong positive anomlies in K, which is the opposite findings of this study. However, K still plots above one in the MORB normalized spider diagram. The trace element Pb correlates quantitatively between the two studies. Both studies show a strong positive anomaly in Pb with respect to MORB averages. These relationships support the conclusion that a magmatic arc contributed material to the Ouachita Basin but again, does not indicate what kind of arc it was.

Trace element and REE concentrations found in the Arkansas Novaculite compare favorably to volcanically sourced chert within the Nicoya Complex of Costa Rica analyzed by Hein *et al.* (1983). In particular the average values found within the Nicoya Complex for Co (3.38 ppm), La (15.8 ppm), Be (1.14 ppm), Cr (15.1 ppm), and Pb (8.1 ppm) are analogous to average values for the Arkansas Novaculite, Co (4.62 ppm), La (9.09 ppm), Be (3.08 ppm), Cr (16.26 ppm), and Pb (11.36 ppm).

Elevated levels of Al and to a lesser extent Fe, Na and K support the conclusion that a source inherently rich in these elements played a major role in the siliceous sedimentation. Analysis of early diagenesis of chert and chemical fractionation by Murray (1994) provide evidence that Al, Fe and REE are immobile into or out of the silicate crystalline framework and K is only moderately mobile. Al, Fe, and K are element indicators in chert for volcanic inputs (Murray, 1994; Hein *et al.,* 1981), which would have influenced the Paleozoic oceans during the time of Arkansas Novaculite and Boone Formation deposition (Lowe, 1975).

When comparing the geochemistry of siliceous deposits in the Arkansas Novaculite and Boone Formation, the Novaculite is more enriched in trace elements and REE. This is consistent with the conclusions of Murray (1994) that exposure time to seawater influences the chemistry of chert and that as sedimentation rates increase the amount of REE's incorporated from the seawater decreases. This water would have been enriched in REE's due to the volcanic activity to the south. The dramatic increase in sedimentation rates seen during the formation of the Boone Formation would have quickly buried the penecontemporaneous chert, which originally developed below the sediment water interface, and initiated lithification and dewatering of the surrounding sediment. However, two indicators of a volcanic influence align closely between the Arkansas Novaculite and Boone Formation, Al and K. The general trends of the normalized data (consistent values across the suite of elements except the relative enrichment in uranium and lead, and depletion of nickel relative to the other elements analyzed) are consistent for both formations as well. These relationships are key to the conclusion that the Arkansas Novaculite and the siliceous deposits of the Boone Formation represent silica sedimentation from a similar volcanic source.

8. Future Work

This geochemical study of the Arkansas Novaculite with a comparison to the siliceous deposits within the Lower Mississippian carbonate units of northwest Arkansas was the first of its kind to be applied to these two sequences. As is the case with many first, there is much room for growth and development in the proceeding versions. This study laid the primitive ground work for future studies to incorporate isotope geochemistry and additional comparisons to siliceous strata, not only in Arkansas, but across the southern mid-continent and west Texas.

The use of radioisotope ratios in identifying the source of igneous products has been utilized by many researchers. Specifically Sr, Nd, and Pb isotope ratios can be utilized to identify the products of Aleutian and continental arcs (Faure, 2013; King *et al.*, 2007; among numerous others). Isotopic analysis would not only clarify some of the conclusions of this study but also add a new perspective to the debate on the source of the silica.

An important expansion of this study would be to compare the geochemical findings to more coeval siliceous units across the southern mid-continent. Chert rich units located in Tennessee (Camden chert), Arkansas (Penters chert), and Oklahoma (Pinetop chert) are all considered Lower to Middle Devonian in age (Hass, 1951) and would be viable for geochemical comparisons to not only the Arkansas Novaculite but the penecontemporaneous chert of the Boone Formation. The most interesting comparison would be to the Caballos Formation of west Texas. This coeval unit shows similar mineralogical traits to that of the Arkansas Novaculite and is presumed to come from the same source (Park and Croneis, 1969). However, like the Arkansas Novaculite and chert within the Boone Formation it is widely speculated in the literature that this formation is sourced from biogenic silica. It is the speculation of this author that the same volcanism contributing silica to the Arkansas Novaculite and Boone Formation would also be influencing the Caballos.

8. Tables

Arkansas Novaculite EDX Values (wt %)

	CG2				CG8				CG13		CG18		CG23					
	EDX1	EDX2	EDX3	EDX4	EDX1	EDX2	EDX3	EDX4	EDX1	EDX2	EDX1	EDX2	EDX1	EDX2	EDX3	EDX4	EDX5	EDX6
O	49.68	47.59	46.42	60.72	40.76	38.56	38.96	39.13	51.47	49.83	54.70	62.44	45.02	63.19	46.47	53.28	55.57	50.69
Si	41.85	41.44	39.51	42.03	40.21	40.20	38.00	37.79	38.56	35.68	34.72	44.28	35.88	43.07	38.25	43.98	43.65	44.49
Al	1.94	1.67	1.71	1.90	0.64	0.44	0.35	0.49	0.48	0.27	12.18	0.58	0.22	0.43	0.38	0.37	0.36	0.33
K	0.81	0.71	0.67	0.74	0.20	0.09	0.11	0.23	0.12	0.11	0.09	0.15	0.11	0.08	0.10	0.05	0.08	0.07
C					0.00	5.35	3.58	0.00	12.46	3.22	0.00	0.00	2.25	3.65	5.32	4.54	2.72	4.61
Au	0.40	0.34	0.64	0.42	2.56	2.65	2.09	2.45	1.49	1.35	1.07	2.31	1.85	2.28	1.83	2.36	2.02	2.36
Mg						0.07	0.01	0.01	0.06	0.00	0.34	0.17	0.00	0.21	0.05	0.13	0.14	0.11
Na											0.54	0.22	0.00	0.40	0.09	0.22	0.30	0.23
Fe																		
Ti	0.10	0.07	0.11	0.12														
Total	94.78	91.82	89.06	105.93	84.37	87.36	83.10	80.10	104.64	90.46	103.64	110.15	85.33	113.31	92.49	104.93	104.84	102.89

	CG26			CG35		CG39				CG45		CG50A				CG50B	
	EDX1	EDX2	EDX3	EDX1	EDX2	EDX1	EDX2	EDX3	EDX4	EDX1	EDX2	EDX1	EDX2	EDX3	EDX4	EDX1	EDX2
O	47.47	45.26	33.84	46.37	49.89	44.11	39.17	45.88	42.85	55.60	50.99	45.69	38.26	39.87	46.47	42.45	34.31
Si	52.40	50.81	43.79	48.14	43.55	39.34	44.67	43.16	41.80	45.79	41.60	30.91	29.04	26.30	31.03	37.00	32.59
Al	0.59	0.50	0.42	0.44	0.37	1.43	0.36	0.39	0.32	0.36	0.26	7.08	3.98	4.15	6.14	4.08	2.71
K	0.05	0.07	0.09	0.08	0.08	0.09	0.12	0.14	0.09	0.16	0.06	2.69	2.18	1.94	2.14	1.74	1.09
C						0.00	4.06	7.07	4.93	0.00							
Au	0.90	0.95	1.13	0.66	0.73	1.43	1.80	1.85	0.46	0.80	0.93	0.65	0.53	0.66	0.50	1.17	0.57
Mg						0.11	0.05	0.08	0.01								
Na																	
Fe			3.75														
Ti																	
Total	101.41	97.59	83.02	95.69	94.62	86.51	90.23	98.57	90.46	102.71	93.84	87.02	73.99	72.92	86.28	86.44	71.27

Table 1: EDX values collected on various Arkansas Novaculite samples. Samples are listed in stratigraphically ascending order.

Arkansas Novaculite EDX Values (wt %)

	CG67			CG77					CG82	CG85		CG86			
	EDX1	EDX2	EDX3	EDX1	EDX2	EDX3	EDX4	EDX5	EDX1	EDX1	EDX2	EDX1	EDX2	EDX3	EDX4
O	43.84	40.86	43.31	53.11	54.51	43.23	53.99	44.11	52.36	58.17	53.04	38.46	70.82	63.92	63.36
Si	38.76	36.22	37.40	47.43	44.74	45.31	44.05	39.64	41.74	42.23	33.09	27.34	19.65	35.96	42.16
Al	1.37	0.94	1.35	0.38	0.36	0.46	0.40	0.23	0.52	0.34	0.11	0.83	0.37	0.43	0.77
K	0.91	0.55	0.55	0.14	0.14	0.22	0.15	0.11	0.10	0.11	0.13	0.14	0.10	0.14	0.15
C				0.00	0.00	3.58	0.00	3.41		3.20	3.24	2.29	10.16	0.72	0.00
Au	0.53	0.20	0.50	0.39	0.39	1.01	1.27	1.43	0.24	1.22	1.14	0.99	1.21	1.27	0.84
Mg					0.28	0.12	0.22			0.18	0.00	0.39	4.08	0.82	0.29
Na					0.45	0.12	0.32					0.22	0.44	0.52	0.61
Fe												18.70	1.60	0.46	
Ti															
total	85.41	78.77	83.11	101.45	100.87	94.05	100.40	88.93	94.96	105.45	90.75	89.36	108.43	104.24	108.18

Table 1 (Continued): EDX values collected on various Arkansas Novaculite samples. Samples are listed in stratigraphically ascending order.

Boone Formation EDX Values (wt %)

	Comp2				P2			P10			BV14						ER1		
	EDX1	EDX2	EDX3	EDX4	EDX1	EDX2	EDX3	EDX1	EDX2	EDX3	EDX1	EDX2	EDX3	EDX4	EDX5	EDX6	EDX1	EDX2	EDX3
O	49.54	59.16	62.86	46.17	51.73	56.45	45.72	67.59	71.12	58.61	44.11	32.66	48.52	56.76	47.67	44.64	52.26	51.91	
Si	36.40	43.29	48.01	32.05	37.14	41.33	31.42	44.83	44.37	42.54	47.84	35.21	47.65	40.58	44.49	45.09	48.95	41.09	
Al	0.89	0.66	0.82	0.34	1.08	1.23	0.65	0.75	0.78	0.65	0.32	0.12	0.43	0.37	0.35	0.31	0.38	0.30	0.46
K	0.32	0.02	0.20	0.17	0.21	0.22	0.20	0.00	0.00	0.00	0.04	0.00	0.04	0.02	0.06	0.00	0.08	0.00	0.05
C	0.00	10.11	9.04	6.57		0.00	2.52	6.43	7.98	0.00									
Au	0.35	0.89	0.28	0.24		2.21	1.74	0.76	0.72	0.66	0.50	0.68	0.64	0.55	0.52	0.52	0.69	0.55	2.30
Mg	0.09	0.15	0.29	0.00	0.65	0.83	0.37	0.24	0.20	0.20									
Na					0.40	0.46		0.40	0.42	0.32									
Fe	0.36	0.00	0.13	0.06	0.61	0.46		0.00	0.05	1.91	0.05	0.06							
Sn	0.25	0.02	0.90	0.06				0.00	0.04							0.69			
Ti	0.05	0.10	0.02	0.00				0.00	0.03										
S	0.00	0.10	0.16	0.00				0.00	0.03	1.99									
Bi	0.00		1.94	0.00				0.00	0.00										
Bi		0.00		0.00				0.00	0.00		1.90	1.56	1.86	3.10	2.16	1.76	3.99	3.69	12.24
Ca					0.54	0.74					0.03	0.41	0.03	8.54	0.31	0.00	1.39	6.55	7.04
V																			
Total	88.25	114.50	124.65	85.66	92.36	103.93	82.62	121.00	125.74	106.88	94.79	70.70	99.17	109.92	95.56	93.01	107.74	104.09	22.09

Table 2: EDX values collected on various Boone Formation samples. Samples are listed in stratigraphically ascending order.

Boone Formation EDX Values (wt %)

	ER4					PV3_230								PV3_insols			
	EDX1	EDX2	EDX3	EDX4	EDX5	EDX1	EDX2	EDX3	EDX4	EDX5	EDX6	EDX7	EDX8	EDX1	EDX2	EDX3	EDX4
O	61.45	25.83	47.59	48.63	49.86	47.46	56.09	48.69	41.14	32.11	50.74	52.18	56.21	61.45	63.09	52.98	51.89
Si	42.05	39.44	39.59	40.04	42.37	33.73	26.73	36.69	19.82	39.63	31.39	16.14	24.30	11.67	39.54	24.65	28.18
Al	0.57	0.02	0.22	0.45	0.53	1.31	9.51	0.96	7.30	1.28	1.12	6.26	11.08	6.95	1.18	12.46	11.81
K	0.00	0.00	0.04	0.05	0.05	0.80	4.39	0.45	6.06	0.68	0.88	3.99	4.75	2.95	0.33	5.25	4.86
C	9.21	1.83	2.39	4.09	4.94						7.63	29.02	11.53	82.68	13.33	8.81	8.21
Au	0.72	0.11	0.71	0.69	0.85	0.45	0.33	0.46	0.50	0.41		0.29	0.51	0.34	0.47	0.34	0.36
Mg	0.16	0.00	0.03	0.00	0.07		1.60	0.08	2.75	0.08	0.09	0.97	1.50	1.06	0.34	1.77	1.52
Na	0.32	0.00	0.06	0.04	0.06									0.44	0.50	0.66	0.63
Fe	0.07					1.18	4.15	0.76	3.83	9.14	0.67	1.49	5.57	1.95	1.53	3.51	3.61
Sn		0.98				0.78	0.41	0.64	0.36	0.29	0.94	0.38	0.27		0.64	0.30	0.38
Ti	0.00						0.88						0.70	0.56	0.06	0.77	0.79
S						1.03	1.23	0.53			0.51	0.43	1.04	0.27	1.35	0.45	1.10
Bi	0.00					1.36	1.72	1.76	2.41	1.14	1.50		1.55		1.14	1.54	1.95
Bi			0.00	0.00	0.00							0.94					
Ca						0.16	0.06										
V							0.09									0.06	0.06
Total	114.55	68.21	90.63	93.99	98.73	88.26	107.19	91.02	84.17	84.76	95.47	112.09	119.01	170.32	123.50	113.55	115.35

Table 2 (Continued): EDX values collected on various Boone Formation samples. Samples are listed in stratigraphically ascending order.

Arkansas Novaculite Trace Element and REE Concentrations (ppm)

	Be	Al	K	V	Cr	Mn	Co	Ni	Cu	Zn	Ga	As	Rb	Cd	Cs	La	Ce
CG2	1.97	6360.26	353.48	1.87	4.40	366.53	2.16	3.27	22.14	9.04	1.88	2.81	4.69	0.06	0.70	5.50	12.00
CG6	1.79	6223.77	759.41	4.03	3.52	73.17	2.78	4.75	14.22	6.54	2.60	0.65	11.88	0.01	1.73	6.93	20.63
CG8	1.68	4336.52	326.84	4.36	2.44	7.40	1.23	1.29	3.32	5.40	1.07	0.95	4.50	0.03	0.65	2.81	7.96
CG13	2.02	2850.14	127.28	-0.29	1.06	1.77	1.14	0.73	1.97	3.21	0.70	0.84	1.54	0.02	0.11	3.35	5.75
CG13*	3.05	5475.64	253.18	0.66	1.81	3.08	1.74	1.21	3.00	6.67	1.10	1.38	2.30	0.02	0.14	4.20	7.09
CG18	3.86	10682.90	239.25	3.09	4.52	429.78	33.57	10.16	35.65	17.94	2.53	2.48	2.39	0.09	0.21	11.53	13.84
CG23	1.39	1862.89	50.19	-1.29	0.70	1.29	0.84	0.56	1.31	2.39	0.45	0.51	0.75	0.02	0.07	1.51	2.52
CG26	2.15	3526.10	179.81	0.53	2.09	2.29	1.34	0.99	1.79	3.50	0.78	0.53	2.44	0.02	0.19	3.29	4.34
CG35	2.41	6436.34	152.02	-0.02	3.07	3.83	1.82	7.38	4.85	11.93	1.16	2.02	1.69	0.04	0.19	3.05	3.89
CG39	2.81	9583.65	304.69	2.67	4.39	6.42	2.09	2.93	6.41	7.82	2.16	2.26	2.91	0.08	0.24	5.10	6.59
CG50A	5.79	34386.06	4012.91	184.64	86.15	21.43	2.82	22.70	102.38	26.91	16.76	4.02	75.29	0.10	6.60	34.82	49.61
CG50B	6.32	49650.63	5383.33	305.86	78.46	29.99	2.99	8.22	27.89	17.01	23.52	5.49	99.55	0.14	8.53	25.24	55.83
CG52	3.51	19114.58	862.42	144.35	18.47	17.07	2.66	21.64	53.17	16.64	6.35	10.25	13.90	0.18	1.37	10.25	17.62
CG60	3.66	12619.05	865.01	149.95	20.07	46.62	4.62	23.27	41.84	12.34	4.71	9.26	16.36	0.16	1.62	8.05	16.01
CG66	4.07	14808.28	768.75	75.15	15.78	20.90	3.49	16.67	23.55	14.94	4.53	10.44	12.86	0.17	1.21	5.65	11.09
CG67	2.74	16492.12	1861.50	121.41	31.05	107.34	6.55	21.26	23.18	17.81	7.01	7.65	45.89	0.26	6.16	18.46	27.92
CG69	3.70	23342.14	2312.15	167.81	35.07	90.95	9.08	28.08	58.57	72.26	7.92	7.18	42.24	0.65	3.66	13.83	26.65
CG77	3.23	4880.46	58.55	0.07	3.00	3.16	3.83	1.45	3.86	6.49	0.75	0.95	0.63	0.05	0.06	1.14	1.71
CG85	3.49	13036.45	178.36	0.20	4.00	7.26	4.47	3.25	5.90	10.80	2.15	3.12	1.48	0.15	0.12	9.29	12.21
CG86	1.90	6379.57	618.94	7.07	5.14	984.27	3.09	7.13	8.81	25.73	2.11	1.75	8.65	0.06	0.87	7.70	15.64
Average	**3.08**	**12602.38**	**983.40**	**58.61**	**16.26**	**111.23**	**4.62**	**9.35**	**22.19**	**14.77**	**4.51**	**3.73**	**17.60**	**0.12**	**1.72**	**9.09**	**15.94**

*Table 3: Trace Element and REE Concentration values of Arkansas Novaculite samples. * Denotes duplicate sample for quality control. Samples are listed in stratigraphically ascending order.*

Arkansas Novaculite Trace Element and REE Concentrations (ppm)

	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Tl	Pb	Th	U
CG2	1.39	4.88	0.72	0.29	1.11	98.87	1.20	0.25	0.72	0.11	0.74	0.13	0.05	7.97	1.48	0.75
CG6	2.10	7.55	1.26	0.48	1.92	169.49	1.88	0.36	0.95	0.14	0.84	0.13	0.10	5.70	1.91	0.69
CG8	0.77	2.58	0.40	0.16	0.57	51.31	0.59	0.12	0.35	0.06	0.42	0.08	0.13	6.19	1.49	0.75
CG13	0.90	3.30	0.51	0.20	0.94	90.20	1.15	0.24	0.67	0.09	0.51	0.08	0.03	3.47	0.48	0.49
CG13*	1.08	4.07	0.59	0.24	1.09	103.44	1.29	0.28	0.75	0.10	0.58	0.09	0.02	3.68	0.47	0.49
CG18	2.48	8.54	1.10	0.37	1.40	112.21	1.31	0.26	0.72	0.11	0.71	0.12	0.09	8.99	1.41	0.80
CG23	0.45	1.76	0.28	0.12	0.50	41.31	0.48	0.10	0.28	0.04	0.25	0.04	0.05	2.28	0.41	0.36
CG26	0.82	3.09	0.43	0.16	0.67	54.64	0.59	0.11	0.29	0.04	0.26	0.04	0.03	2.43	0.60	0.36
CG35	0.69	2.37	0.31	0.11	0.44	36.97	0.43	0.09	0.27	0.04	0.30	0.05	0.03	6.02	0.64	0.48
CG39	1.12	3.79	0.57	0.21	1.02	102.80	1.46	0.37	1.12	0.18	1.11	0.18	0.04	7.53	0.96	0.71
CG50A	9.84	36.25	6.15	2.52	10.15	834.73	9.15	1.80	4.69	0.67	4.20	0.68	0.55	28.66	7.70	6.20
CG50B	11.29	39.64	6.50	2.54	10.38	868.71	9.82	1.99	5.42	0.80	5.15	0.86	0.60	33.19	9.87	8.43
CG52	2.64	9.04	1.35	0.50	2.00	179.13	2.22	0.48	1.52	0.25	1.81	0.32	0.40	19.79	2.17	6.19
CG60	2.15	7.16	1.08	0.39	1.45	129.87	1.55	0.34	1.03	0.17	1.18	0.21	0.43	18.31	2.24	11.19
CG66	1.36	4.27	0.57	0.21	0.80	73.26	0.95	0.22	0.74	0.13	0.91	0.17	0.25	16.92	1.90	13.30
CG67	5.38	19.15	2.95	1.14	4.29	360.52	4.14	0.83	2.29	0.33	2.12	0.35	0.41	18.17	4.80	2.52
CG69	3.66	12.42	1.87	0.73	2.85	256.09	3.09	0.65	1.89	0.28	1.75	0.30	0.52	19.82	4.23	4.42
CG77	0.39	2.09	0.78	0.47	2.86	354.33	5.42	1.32	3.60	0.48	2.66	0.38	0.02	2.28	0.39	0.66
CG85	2.63	10.05	1.50	0.51	1.92	160.17	1.86	0.39	1.22	0.19	1.30	0.22	0.01	8.60	1.22	1.01
CG86	2.01	7.12	1.12	0.44	1.75	141.10	1.46	0.26	0.65	0.10	0.56	0.10	0.09	7.21	1.26	0.55
Average	**2.66**	**9.46**	**1.50**	**0.59**	**2.41**	**210.96**	**2.50**	**0.52**	**1.46**	**0.21**	**1.37**	**0.23**	**0.19**	**11.36**	**2.28**	**3.02**

*Table 3 (Continued): Trace Element and REE Concentration values of Arkansas Novaculite samples. * Denotes duplicate sample for quality control. Samples are listed in stratigraphically ascending order.*

Boone Formation Trace Element and REE Concentrations (ppm)

	Be	Al	K	V	Cr	Mn	Co	Ni	Cu	Zn	Ga	As	Rb	Cd
Comp2	1.84	8658.99	1605.68	5.37	3.93	84.57	8.13	9.06	2.35	0.54	1.29	1.55	7.92	-0.28
P2	1.65	7535.98	952.70	6.12	4.76	46.83	2.97	5.55	1.50	4.00	0.75	0.52	4.37	-0.22
P10	1.06	6052.72	483.18	1.75	2.57	13.17	1.45	2.40	0.28	0.94	0.51	0.28	1.97	-0.24
BV1	1.91	5987.44	210.76	1.18	3.02	54.89	1.37	1.28	0.42	5.09	0.57	0.68	0.58	-0.22
BV7	2.08	6286.73	634.86	5.63	10.39	166.11	1.56	1.05	0.97	19.75	0.91	0.58	2.40	0.03
BV14	2.02	7524.45	643.42	4.31	5.02	124.64	1.71	1.19	3.52	5.55	1.11	0.39	2.52	-0.05
ER1	2.22	31642.07	904.93	1.81	6.44	63.27	1.92	2.46	3.18	4.99	3.38	1.06	2.70	0.17
Average	**1.83**	**10526.91**	**776.50**	**3.74**	**5.16**	**79.07**	**2.73**	**3.28**	**1.74**	**5.84**	**1.22**	**0.72**	**3.21**	**-0.11**

	Cs	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Comp2	0.17	1.81	2.86	0.21	1.82	0.09	-0.21	0.11	40.39	0.08	-0.22	-0.05	-0.28	-0.07
P2	0.01	2.42	3.17	0.35	2.36	0.22	-0.21	0.23	52.09	0.16	-0.21	-0.01	-0.28	-0.05
P10	-0.12	0.83	1.25	-0.05	0.71	-0.12	-0.28	-0.12	18.61	-0.13	-0.27	-0.17	-0.30	-0.16
BV1	-0.28	2.48	2.72	0.34	2.36	0.22	-0.21	0.25	57.09	0.25	-0.19	0.04	-0.27	-0.03
BV7	-0.20	6.83	4.55	1.10	5.66	0.81	-0.03	0.96	120.68	0.84	-0.06	0.38	-0.23	0.16
BV14	-0.19	4.59	3.60	0.70	3.91	0.50	-0.14	0.52	80.43	0.45	-0.15	0.16	-0.26	0.07
ER1	-0.19	4.61	6.50	0.77	3.91	0.48	-0.15	0.49	80.29	0.49	-0.13	0.33	-0.22	0.44
Average	**-0.12**	**3.37**	**3.52**	**0.49**	**2.96**	**0.31**	**-0.18**	**0.35**	**64.23**	**0.31**	**-0.18**	**0.10**	**-0.26**	**0.05**

Table 4: Trace Element and REE Concentration values of Boone Formation samples. Samples are listed in stratigraphically ascending order.

Boone Formation Trace Element and REE Concentrations (ppm)

	Lu	Hg	Tl	Pb	Th	U
Comp2	-0.27	0.00	0.10	3.00	0.18	0.15
P2	-0.27	0.00	0.05	3.45	0.19	0.22
P10	-0.29	0.00	0.09	2.55	0.06	0.27
BV1	-0.27	0.00	0.01	1.16	-0.02	0.10
BV7	-0.24	0.00	0.03	1.76	-0.32	0.80
BV14	-0.25	0.00	0.03	1.53	-0.06	0.28
ER1	-0.17	0.00	0.03	3.37	0.66	1.14
Average	**-0.25**	**0.00**	**0.05**	**2.40**	**0.10**	**0.42**

Table 4 (Continued): Trace Element and REE Concentration values of Boone Formation samples. Samples are listed in stratigraphically ascending order.

9. Graphs

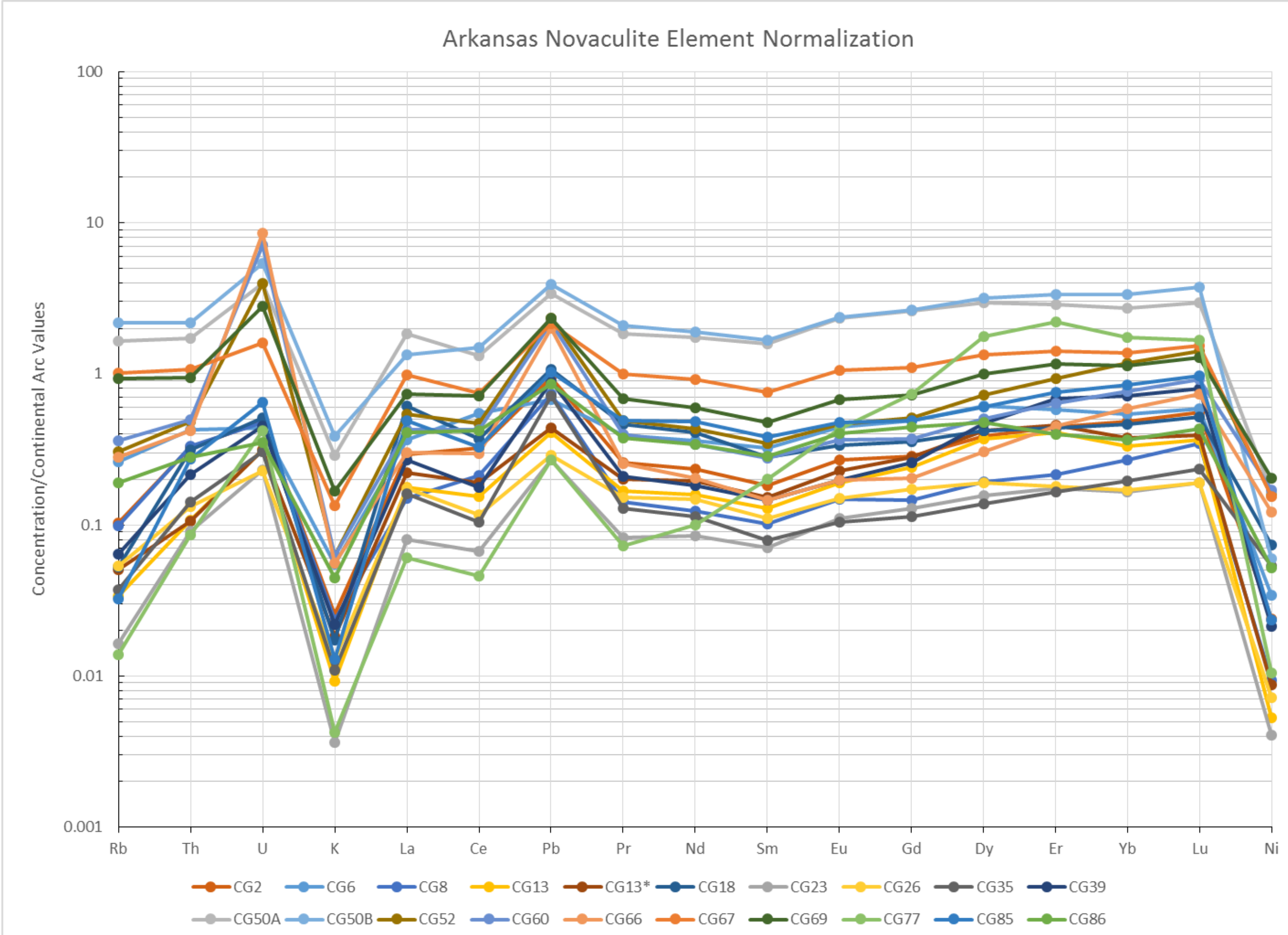

*Figure 13: Arkansas Novaculite trace element and REE concentrations normalized to average Continental arc andesite. * Denotes sample duplicated for quality control*

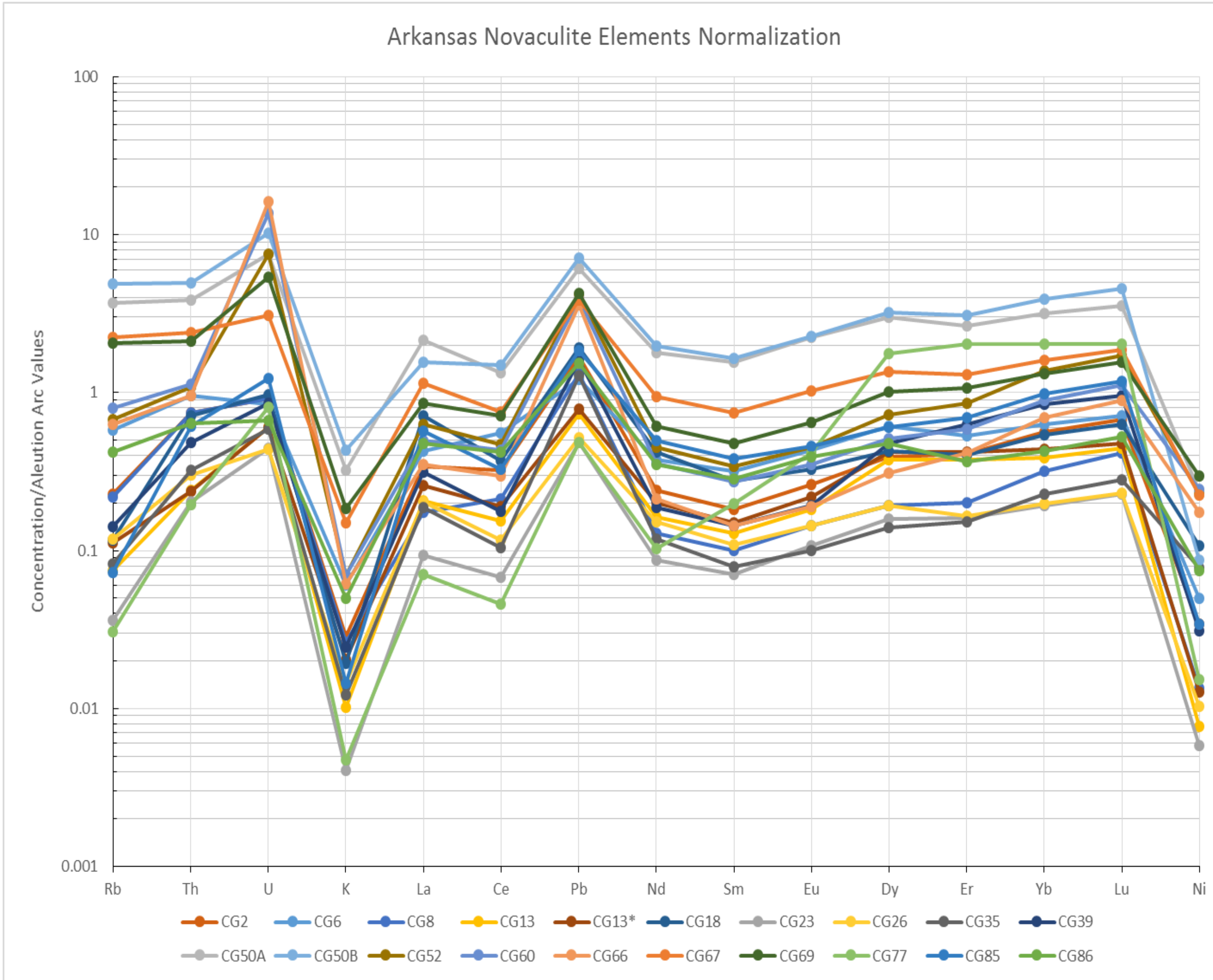

*Figure 14: Arkansas Novaculite trace element and REE concentrations normalized to average Aleutian arc andesite. * Denotes sample duplicated for quality control*

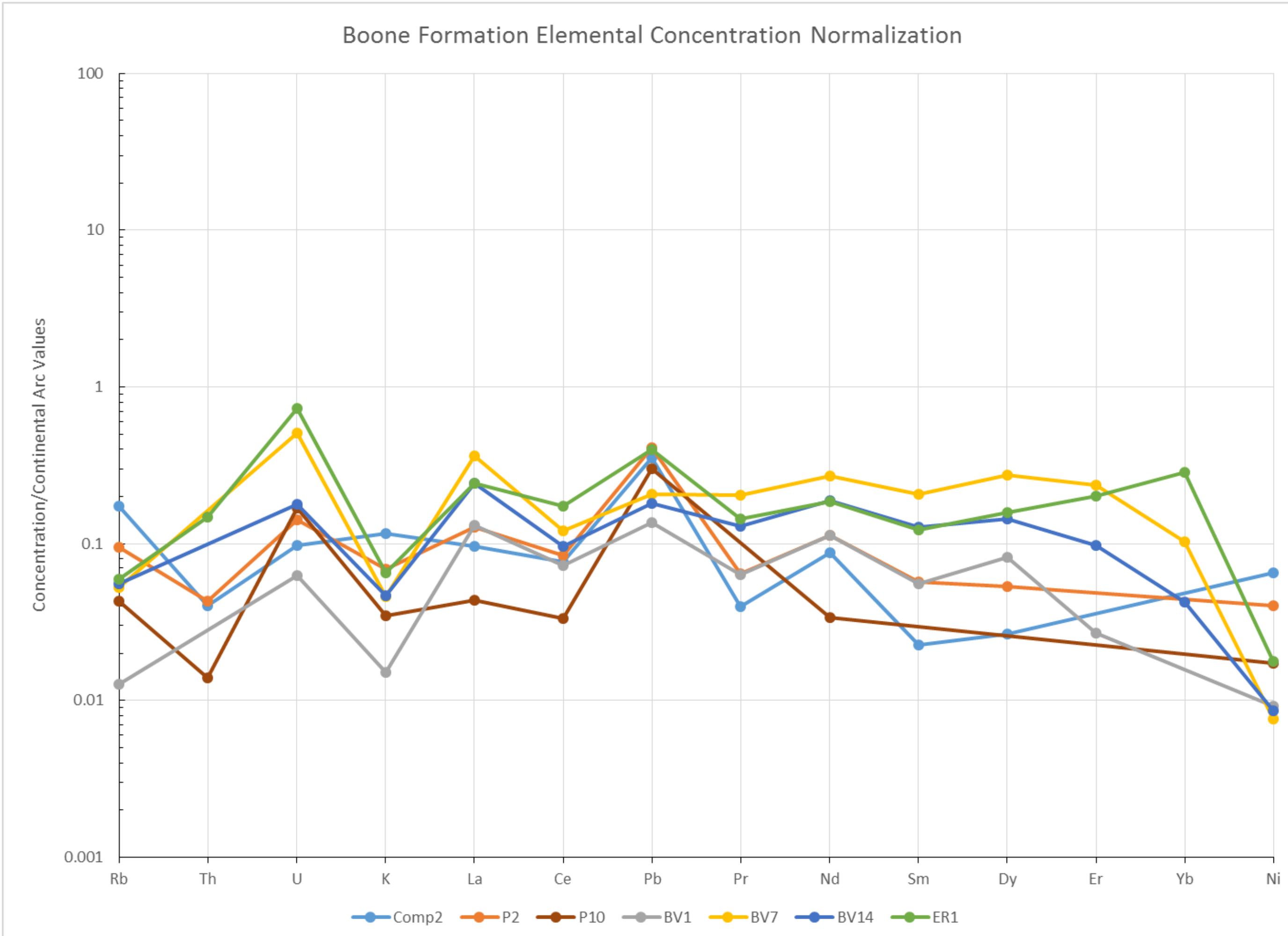

Figure 15: Boone Formation trace element and REE concentrations normalized to average continental arc andesite

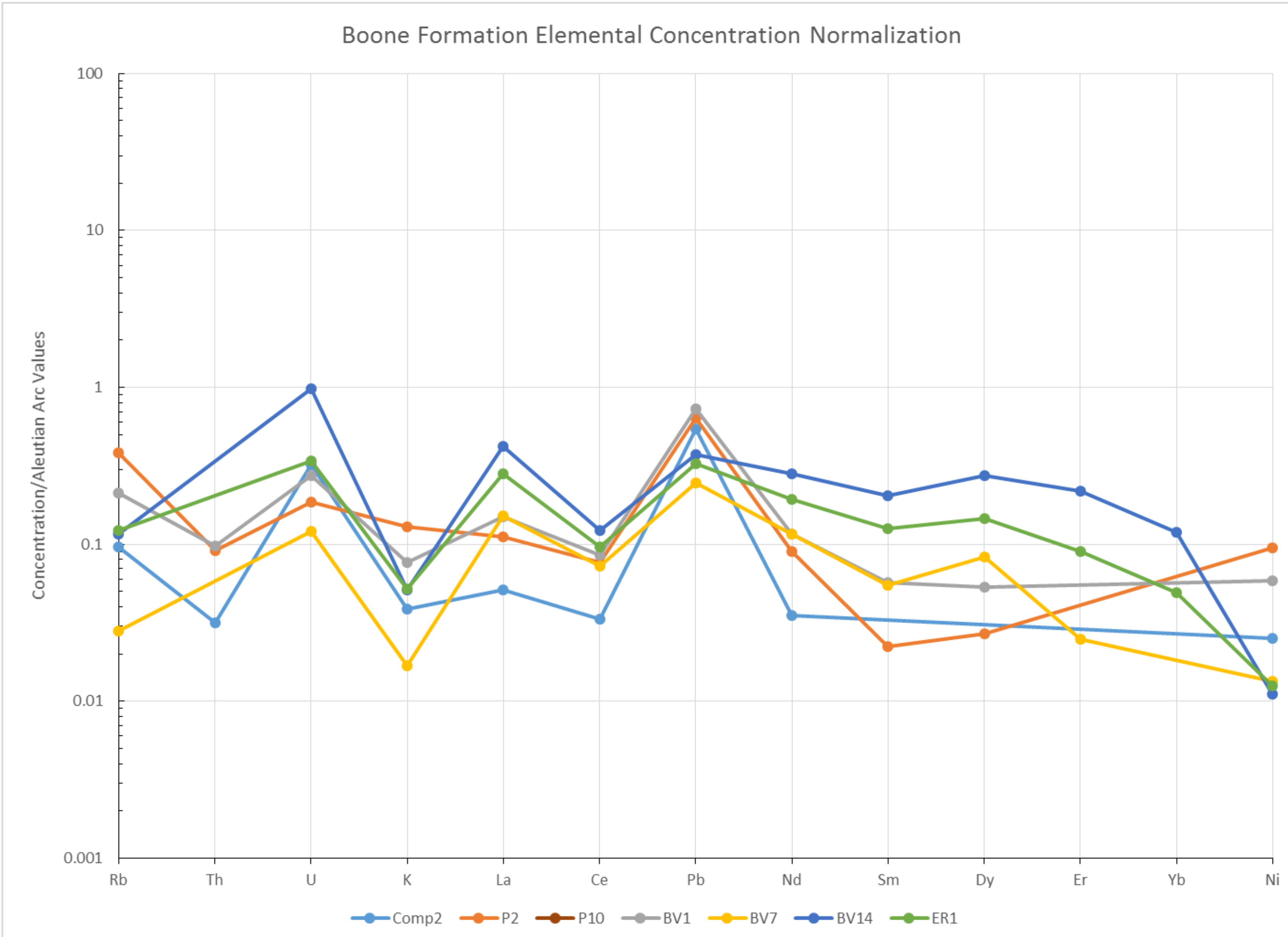

Figure 16: Boone Formation trace element and REE concentrations normalized to average Aleutian arc andesite

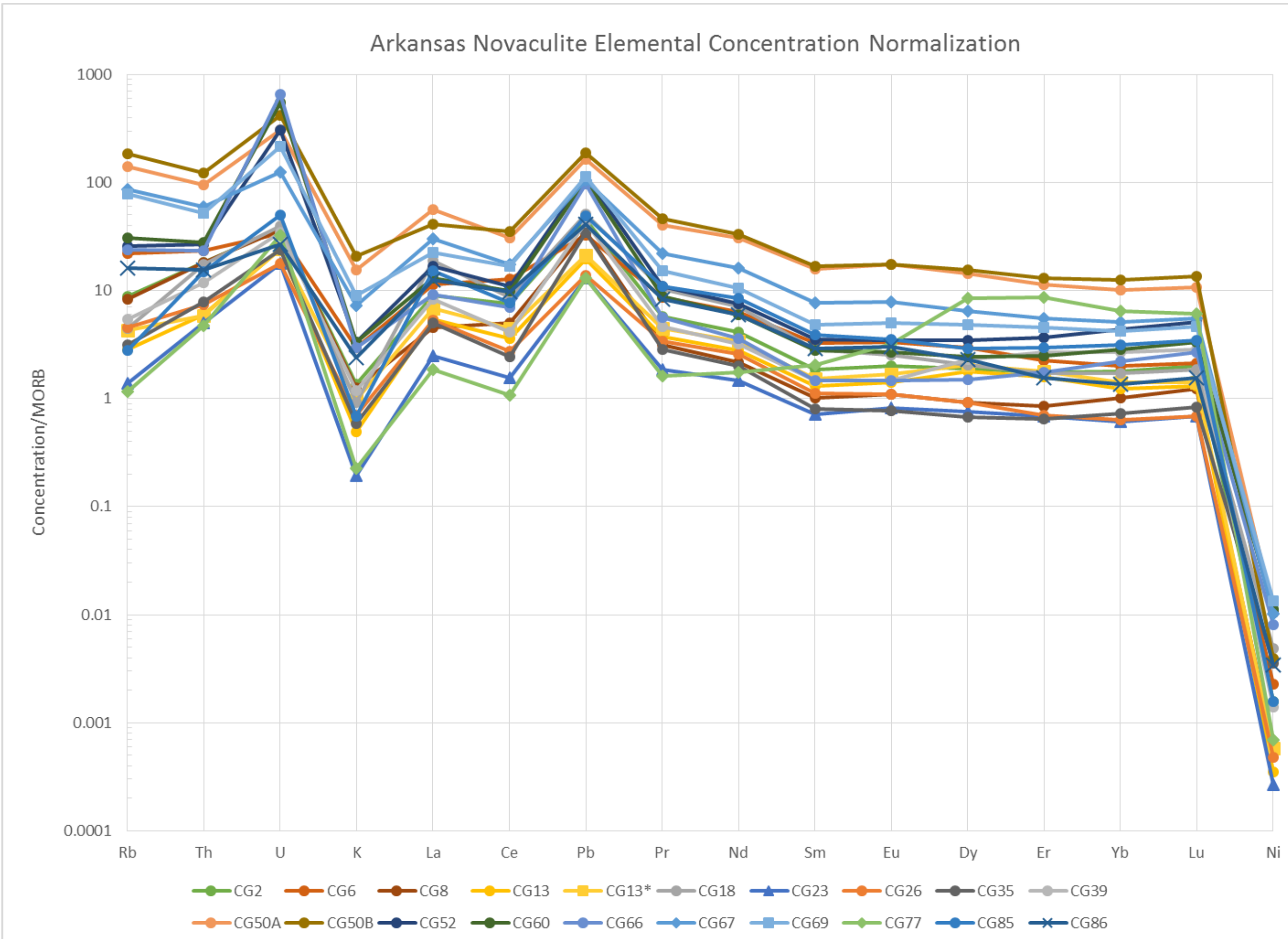

Figure 17: Arkansas Novaculite trace and REE concentration normalized to average MORB

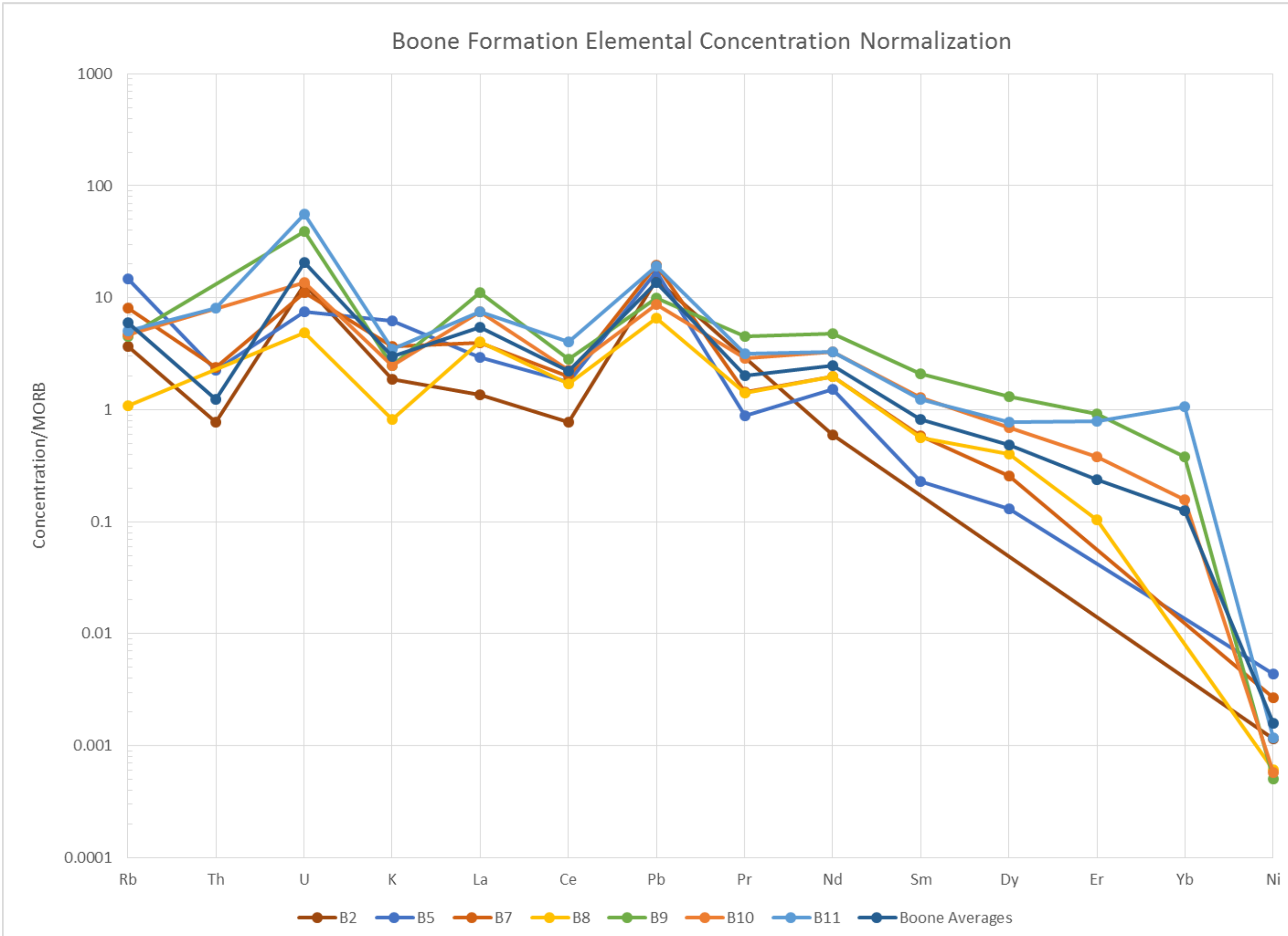

Figure 18: Boone Formation trace and REE concentration normalized to average MORB

10. References

Arbenz, J. K. (1989). Ouachita thrust belt and Arkoma basin. In *The Appalachian-Ouachita orogen in the United States* (pp. 621-634). Boulder, Colorado: Geological Society of America.

Bird, J. M., & Dewey, J. F. (1970). Lithosphere plate-continental margin tectonics and the evolution of the Appalachian orogen. *Geological society of America Bulletin, 81*, 1031-1060.

Blythe, A. E., & Phipps, A. S. (1988). Structural Profiles of Ouachita Mountains, Western Arkansas. *AAPG Bulletin*, pp. 810-819.

Boucot, A. J., Chen, X., & Scotese, C. R. (2013). *Phanerozoic Paleoclimate: An Atlas of Lithologic Indicators of Climate.* Society for Sedimentary Geology.

Cecil, N. T., & Edgar, C. B. (2003). Influence of Climate on Deep-Water Clastic Sedimentation: Application of a Modern Model, Peru-Chile Trough, to an Ancient System, Ouachita Trough. *Climate Controls on Stratigraphy*, 185-191.

Cornish, C. S. (1997). Trace Element and Isotope Geochemisty of the Laminated Facies of the Lower Member of the Arkansas Novaculite, Benton Uplift, Arkansas. *Unpublished MS Thesis*. Stephen F. Austin Unversity 157 p.

Correns, C. W. (1950). Zur geochemie der diagenese. *Geochimica et Cosmochimica Acta*, 49-54.

Cullers, R. C. (1979). Rare-earths in size fractions and sedimentary rocks of Pennsylvanian-Permian age from the mid-continent of the USA. *Geochimica et Cosmochimica Acta, 43*(8), 1285-1301.

Derby, O. A., & Branner, J. C. (1898). On the Origin of Certain Siliceous Rocks. *The Journal of Geology*, 366-371.

Doerr, E. L. (2004). *Trace Element Evidence of a Volcanic Source for Lower Mississippian Chert and Novaculite, Southern Midcontinent.* Honor's Thesis, Univeristy of Arkansas, Fayettevile, Ar.

Ernst, W. G., & Calvert, S. E. (1969). An experimental study of the recrystalization of porcellanite and its bearing on the origin of some bedded chert. *American Journal of Science, 267*(A), 114-133.

Ethington, R. L., Finney, S. C., & Repetski, J. E. (1989). Biostratigraphy of the Paleozoic rocks of the Ouachita orogen, Arkansas, Oklahoma, west Texas. In R. D. Hatcher, *The Geology of North America, Volume F-2, The Appalachian-Ouachita Orogen in the United States* (pp. 563-574). Boulder, Colorado: The Geological Society of America.

Fallacaro, A. (2001). Insoluble Residue Analysis of the Boone Formation (Mississippian), Northern Arkansas: Insights into the Origins of its chert and Regolith. 39 p. Unpublished Honors thesis, University of Arkansas.

Fallacaro, A., & Cortez, E. B. (2000). Implications of Volcanic Ash in Sand-Size Insoluble Fraction , Boone Formation (Mississippian-Osagean), Northwestern Arkansas (abs.). *Abstracts with Programs, 32*(3), A-9.

Faure, G. (2013). *Origin of igneous rocks: the isotopic evidence.* Springer Science & Buisness Media.

Goldstein, A. J. (1959). Cherts and Novaculites of Ouachita Facies. *Society of Economic Paleontologist and Mineralogist Special Publication 7*, 135-149.

Goldstein, A., & Hendricks, T. A. (1953). Siliceous sediments of Ouachita facies in Oklahoma. *Geological Society of America Bulletin*, 421-442.

Griswold, L. S. (1892). *Whetstones and Novaculite of Arkansas.* Arkansas Geological Survey.

Haas, W. H. (1951). Age of Arkansas Novaculite. *American Association of Petroleum Bulletin, 35*, 2526-2541.

Hatcher, R. D. (1972). Development model for the southern Appalachians. *Geological Society of America Bulletin, 83*, 2735-2760.

Hein, J. R. (1983). Petrology and Geochemistry of Cretaceous and Paleogene Chert From Western Costa Rica. In A. Iijima, J. R. Hein, & R. Siever, *Siliceous Deposits in the Pacific Region* (pp. 148-174). Amsterdam, Netherlands: Elsevier Scientific Publishing Company.

Hofman, A. W. (1988). Chemical differentiation of the Earth: the relationship between mantle. *Earth and Planetary Science Letters, 90*, 297-314.

Houseknecht, D. W., & Kacena, J. A. (1983). Tectonic and sedimentary evolution of the Arkoma foreland Basin. In *Tectonic-sedimentary evolution of the Arkoma basin: SEPM Midcontinent Section Guidebook 1* (pp. 3-33).

Ingersol, R. V. (2003). Remnant-ocean submarine fans: largest sedimentary systems on Earth. In a. A. M. A. Chan, *Extreme Depositional Environments: Mega End Members in Geologic Time* (pp. 191-208). Geologic Society of America.

Ingersol, R. V., Dickinson, W. R., & Graham, S. A. (2003). Remnant-ocean submarine fans: largest sedimentary systems on Earth. In A. W. Archer, & M. A. Chan, *Extreme Depositional Environments: Mega End Members in Geologic Time* (pp. 191-208).

Kelemen, P. B., Hangøj, K., & Greene, A. R. (2003). One View of the Geochemistry of Subduction-related Magmatic Arcs, with an Emphasis on Primitive Andesite and Lower Crust. In *Treatise on Geochemistry* (pp. 593-659). Oxford: Elsevier.

Keller, W. D., Stone, C. G., & Hoersch, A. L. (1985). Textures of Paleozoic chert and novaculite in the Ouachita Mountains of Arkansas and Oklahoma and their geological significance. *Geological Society of America Bulletin, 96*, 1353-1363.

King, P. B. (1937). Geology of the Marathon region, Texas. *U.S. Geological Survey Professional Paper 187*, 1-148.

King, R. L., Bebout, G. E., Grove, M., Moriguti, T., & Nakamura, E. (2007). Boron and lead isotope signatures of subduction-zone mélange. *Geochemical Geology, 239*, 305-322.

King, R. L., Bebout, G. E., Grove, M., Moriguti, T., & Nakamura, E. (2007). Boron and lead isotope signatures of subduction-zone mélange formation: hybridization and fractionation along the slab–mantle interface beneath volcanic arcs. *Chemical Geology, 239*(3), 305-322.

Lillie, R. J., Nelson, K. D., Voogd, B. D., Brewer, J. A., Oliver, J. E., Brown, L. D., . . . Viele, G. W. (1983). Crustal Structure of Ouachita Mountains, Arkansas: A Model Based on Integration of COCORP Reflection Profiles and Regional Geophysical Data. *AAPG Bulletin, 67*(6), 907-931.

Lowe, D. R. (1975). Regional Controls on Silica Sedimentation in the Ouachita System. *Geological Society of America Bulletin, 86*, 1123-1127.

Lowe, D. R. (1976). Nonglacial Varves in Lower Member of Arkansas Novaculite (Devonian), Arkansas and Oklahoma. *The American Association of Petroleum Geologist Bulletin, 60*(12), 2103-2116.

Lowe, D. R. (1977). The Arkansas Novaculite: Some aspects of its physical sedimentation. In S. C. G., *Symposium on the geology of the Ouachita Mountains, Volume I* (pp. 132-138). Arkansas Geological Commission.

Lowe, D. R. (1985, November). Ouachita trough: Part of a Cambrian failed rift system. *Geology, 13*, 790-793.

Lowe, D. R. (1989). Pre-orogenic stratigraphy, sedimentology, and depositional setting, Ouachita Mountains. In R. D. Hatcher, *The Geology of North America, Volume F-2, The Appalachian-Ouachita Orogen in the United States* (pp. 575-590). Boulder, Colorado: The Geological Society of America.

Manger, W. L. (2015). *An Introduction to the Lower Mississippian (Kinderhookian-Osagean) Geology of the Tri-State Region, Southern Ozarks.*

Miser, H. D. (1917). Manganese deposits of the Caddo Gap and DeQueen quadrangles, Arkansas. *U.S. Geological Survey Bulletin 660-C*, 59-122.

Miser, H. D., & Purdue, A. H. (1929). Geology of the McQueen and Caddo Gap quadreangles, Arkansas. *U.S. Geological Survey Bulletin 808*.

Morris, R. C. (1974). Sedimentary and Tectonic History of the Ouachita Mountains. *The Society of Economic Paleontologist and Mineralogist: Tectonics and Sedimentation Special Publication 22*, 120-142.

Morris, R. C. (1989). Stratigraphy and sedimentary history of post-Arkansas Novaculite Carboniferous rocks of the Ouachita Mountains. In W. A. R. D. Hatcher Jr. (Ed.), *The Geology of North America, Volume F-2, The Appalachian-Ouachita Orogen in the United States* (pp. 591-602). Boulder, Colorado: The Geological Society of America.

Murray, R. W. (1994). Chemical criteria to identify the depositional environment of chert: general principles and applications. *Sedimentary Geology, 90*, 213-232.

Park, D. E., & Croneis, C. (1969). Origin of Caballos and Arkansas Novaculite Formations. *The American Association of Petroleum Geologist Bulletin, 53*, 94-111.

Pollock, S. G. (1987). Chert Formation in an Ordovician Volcanic Arc. *Journal of Sedimentary Petrology, 57*(1), 75-87.

Purdue, A. H. (1909). The slates of Arkansas. *U.S. Geological Survey Bulletin 430*, 317-334.

Purdue, A. H., & Miser, H. D. (1923). Hot Springs Folio, Arkansas. *U.S. Geological Survey Folio 215*.

Rutley, F. (1984). On the origin of certain novaculites and quartzites. *Geological Society of London Quarterly Journal*, 391-392.

Scarr, K. D. (2008). *Trace Element Studies of the Arkansas Novaculite.* Master's Thesis, University of Arkansas, Fayetteville, Ar.

Schoolcraft, H. R. (1819). *A view of the lead mines of Missouri: including some observations on the mineralogy, geology, geography, antiquities, and soil, climate, population, and productions of Missouri and Arkansaw, and other sections of the western country.* Charles Wiley & Co.

Shaulis, B. J., Lapen, T. J., Casey, J. F., & Reid, D. R. (2012). Timing and Rates of Flysch Sedimentation in the Stanley Group, Ouachita Mountains. *Journal of Sedimentary Research, 82*, 833-840. doi:10.2110

Sholes, M. A. (1977). Arkansas Novaculite Stratigraphy. In C. G. Stone, *Symposium on the geology of the Ouachita Mountains, Volume I* (pp. 139-145).

Sholes, M., & McBride, E. F. (1975). Arkansas Novaculite. In *A Guidebook to the Sedimentology of Paleozoic Flysch and Associated Deposits, Ouachita Mountains - Arkoma Basin, Oklahoma* (pp. 69-87).

Sloss, L. L. (1963). Sequences in the cratonic interior of North America. *Geological Society of America Bulletin, 74*, 93-113.

Spry, A. (1969). Metamorphic Textures: New York. *Oxford Press*.

Sun, S., & McDonough, W. F. (1989). Chemical and isotopic systematics of oceanic basalts:implications for mantle composition and processes. In A. D. Saunders, & M. J. Norry (Eds.), *Magmatism in the Ocean Basins* (pp. 313-345). Geological Society Special Publications 42.

Tarr, W. A. (1938). Terminology of the chemical siliceous sediments. *Common Sedimentation for 1937-1938, National Research Counci*, 8-27.

Viele, G. W., & Thomas, W. A. (1989). Tectonic synthesis of Ouachita orogenic belt. In R. D. Hatcher, & W. A. Thomas, *The Appalachian-Ouachita Orogen in the United States* (Vols. F-2, pp. 695-728). Boulder, Ca: The Geological Society of America.

Wilson, J. L., & Majewske, O. P. (1960). Conjectured middle Paleozoic history of central and West Texas. *Texas University Bulletin 6017*, 65-68.

Zimmerman, J., & Ford, J. T. (1988). Lower Stanley Shale nad Arkansas Novaculite, western Mararn Basin and Caddo Gap, Ouachita Mountains, Arkansas. *Geological Society of America Centennial Field Guid - South Central Section* (pp. 267-272). Geological Society of America.