Comparison of the Elemental Geochemistry of the Arkansas Novaculite and the Boone Chert in their Type Regions, Arkansas

J. Philbrick
*University of Arkansas, Fayetteville, jphilbri@email.uark.edu*

E. Pollock
*University of Arkansas, Fayetteville*

A. Potra
*University of Arkansas, Fayetteville*

Follow this and additional works at: [http://scholarworks.uark.edu/jaas](http://scholarworks.uark.edu/jaas)

Part of the *Geochemistry Commons*, and the *Geology Commons*

**Recommended Citation**


Available at: [http://scholarworks.uark.edu/jaas/vol70/iss1/31](http://scholarworks.uark.edu/jaas/vol70/iss1/31)
Comparison of the Elemental Geochemistry of the Arkansas Novaculite and the Boone Chert in their Type Regions, Arkansas

J. Philbrick*, E. Pollock, and A. Potra

Department of Geosciences, University of Arkansas, Fayetteville, Ar 72701

*Correspondence: jphilbri@email.uark.edu

Running Title: Elemental Geochemistry of the Arkansas Novaculite and the Boone Chert in their Type Regions, Arkansas

Abstract

The name Arkansas Novaculite was proposed by A.H. Purdue, 1909 to replace the name Arkansas Stone assigned by L. S. Griswold, 1892, but deemed too generic, to an interval of Early Devonian-Early Mississippian, very fine-grained, even textured, siliceous sedimentary rock famous for use as whetstones. The interval is exposed along the margins of the Benton Uplift, south flank of the Ouachita Mountains, west-central Arkansas, where it reaches a maximum thickness of 243.8 m (800 ft). The Arkansas Novaculite comprises informal lower and upper members characterized by massive beds of nearly pure novaculite, separated by a shale-bearing middle member that spans the Devonian-Mississippian boundary. The formation represents deep water deposition below carbonate compensation depths, in contrast to contemporaneous chert-bearing intervals, such as the Early Mississippian Boone Formation in the southern Ozarks, with chert formed in shallower marine conditions, or as a replacement of associated limestone beds.

Source of the prodigious quantities of silica forming the Arkansas Novaculite has been controversial. Geochemical analyses, using both EDX and trace element analysis, were performed using mass spectrometry and have identified a significant contribution by both aluminum and potassium, which would seem to eliminate a biogenic origin and favor a volcanic source, perhaps related to an island arc system that formed during the Ouachita Orogeny as Laurasia collided with Gondwana. Trace element analysis also suggests that the Arkansas Novaculite and the chert in the Boone Formation may have both been formed from the same volcanic source.

Introduction

Deposition of the Arkansas Novaculite, named by Purdue (1909), began during the Early Devonian, possibly even Silurian (Lowe 1985), and continued through the Kinderhookian Series, Early Mississippian. It is bounded stratigraphically by gradational contacts between thick shale intervals referred to the Missouri Mountain Shale and Stanley Group at the base and top, respectively. The Arkansas Novaculite has been divided into numerous named members and submembers (Miser and Purdue 1929), but regional application of that nomenclature is questionable. This study examines the major and trace elements of informal lower, middle, and upper members of the formation, and did not differentiate between novaculite and chert. All Arkansas Novaculite samples were taken from the well-known Caddo Gap roadcut, located on the southern flank of the Benton Uplift, the structural core of the Ouachita Mountains in east-central Arkansas.

The source of the silica for both the Arkansas Novaculite and Boone chert has generated considerable debate, although there has been little comparison of the two intervals. Most studies of the Novaculite (Sholes and McBride 1975 is typical), and Boone and other chert-bearing intervals (see Hesse 1990 for a review) cite altered siliceous bioclastic remains, commonly sponge spicules, as the silica source. However, other proposed origins for the Novaculite silica include simultaneous dissolution of limestone and precipitation of silica (Rutley 1894, Derby and Banner 1898, Correns 1950), volcanic ash deposited in a sediment-starved basin (Goldstein and Hendricks 1953), and hydrothermal alteration of quartz sandstone (Owen 1860, Comstock 1888). Tarr (1926) hypothesized direct precipitation of silica as a colloidal sol derived from terrestrial erosion and transported to marine environments by rivers and streams for the Boone and other midcontinent chert.

Geologic Setting

Paleozoic Area of Arkansas

The Paleozoic area of Arkansas comprises three...
geologic provinces, from north to south: the south flank of the Ozark Dome, Arkoma Basin and Ouachita Mountain orogenic belt (Figure 1). The Ozark Dome is a broad, asymmetrical, cratonic uplift cored by Precambrian granite and rhyolite, with Upper Cambrian to Middle Pennsylvanian strata dipping radially away from the core area. The area lacks structural complexity, compared to the Arkoma Basin and Ouachita Mountains. A series of in echelon normal faults striking northeast-southwest and downthrown to the southeast extends across the southern Ozarks, and the regional dip averages only 19' (Chinn and Konig 1973). Three broad plateau surfaces reflect periodic epeirogenic uplifts. From oldest and lowest elevation, these are the Salem, Springfield, and Boston Mountains Plateaus. The Salem Plateau comprises Lower Ordovician limestones and dolomites with the largest aerial extent in the region. The Springfield Plateau forms the Eureka Springs Escarpment, and is capped by limestone and chert of the Lower Mississippian St. Joe Limestone and Boone Formation. The Boston Mountain Escarpment and its Plateau are the youngest and highest surface in the Paleozoic area of Arkansas formed by Upper Mississippian through Middle Pennsylvanian (Atokan) strata.

The Ouachita Mountains are an east-west trending anticlinorium of Paleozoic rocks extending across west-central Arkansas into southeast Oklahoma. The Ouachita orogenic belt has been subdivided into the Arkoma foreland basin, separating the Ozarks and Ouachitas, the frontal imbricated zone, central thrust belt, and the Benton and Broken Bow Uplifts (Arbenz 1989). The frontal fold-thrust belt of the Ouachitas is north vergent, excluding the cores of the Benton and Broken Bow Uplifts, and forms the southern margin of the Arkoma foreland basin (Arbenz 1989). Strata forming the Ouachita Mountains are dominated by deep-water facies, beginning as a starved basin from the Late Cambrian through the Early Mississippian followed by flysch sedimentation characterizing the Upper Mississippian through Middle Pennsylvanian (Arbenz 1989). The structure is the result of a collisional-subductional orogeny between Laurasia and Gondwana during the late Paleozoic era (Lowe 1975).

Lithostratigraphy and Sequence Stratigraphy

**Tri-State Area**

This study focuses on the Lower Mississippian transgressive-regressive sequence represented by the St. Joe (Hopkins 1893) and Boone (Branner 1891) Formations in northern Arkansas, particularly penecontemporaneous chert in the lower Boone. This succession reflects transportation of carbonates sourced from the Burlington Shelf, in what is now Missouri, which were deposited frequently as condensed intervals down ramp in northern Arkansas. This ramp developed extensively along the southern margin of the North American Craton. 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 proposed (Hopkins 1893) as the basal, chert-free limestone member of the thicker, potentially >121.9m (400ft), chert-bearing Boone Formation (Giles 1935).

The Lower Mississippian St. Joe-Boone interval represents a single, third-order, transgressive-regressive, eustatic cycle. It is a portion of the first-order Kaskaskia sequence recognized by Sloss (1963) that extended from the Early Devonian to the Mississippian-Pennsylvanian boundary, and has been subdivided into second-order Kaskaskia I and Kaskaskia II Cycles (Witzke and Bunker 1996). The Kaskaskia I second-order cycle began in the Early Devonian and extended to the Devonian-Mississippian boundary, while the Kaskaskia II second-order cycle encompassed the entire Mississippian. The Early Mississippian third-order cycle includes the Kinderhookian-Osagean interval (Witzke and Bunker 1996), which comprises the St. Joe-Boone carbonates in northern Arkansas. Initial transgression of this third-order cycle is represented by the St. Joe interval, which spans the Kinderhookian-Osagean boundary. Maximum flooding occurred in the lower Boone, while high-stand and regression encompass the upper Boone.
Formation (Manger and Shelby 2000).

**Ouachita Mountains**

The name Arkansas Novaculite as a lithostratigraphic name was proposed by Purdue (1909), to replace the name Arkansas Stone assigned by Griswold (1892), as a lithologic term that also included the Middle-Late Ordovician Big Fork Chert. Lithologies of the Arkansas Novaculite can be divided into northern and southern facies described originally by Miser and Purdue (1929). Lowe (1977) applied the term northern facies to describe the black chert, shale, sandstone, siltstone, and chert-shale pebble conglomerate and breccia of the northern exposures. The southern facies of Lowe (1977) comprises the better known distribution of the massively bedded, white novaculite, which is more commonly thought of as the Arkansas Novaculite lithostratigraphic entity. The southern facies was divided into three unnamed members (Miser 1917), described as the lower and upper novaculite members, separated by a middle member of chert and shale. Further subdivisions were proposed by Lowe (1976) at the Caddo Gap road cut, sampled for this study, that include (ascending order) the lower chert-and-shale, calcareous novaculite, translucent novaculite, massive novaculite, and breccia subdivision. The middle member was 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 upper member includes enough calcium carbonate that it develops porosity from weathering, which has been exploited for tripoli (Cornish 1997).

The two second-order Kaskaskian cycles also play a major role in the depositional dynamics affecting the Arkansas Novaculite. The transgressive cycle represented in the lower novaculite member caused craton margin submergence that limited detrital influx by trapping it close to shore producing nearly pure novaculite in a deep sea setting (Lowe 1976). A second order regression seen during the Upper Devonian produced the middle novaculite member, with interbedded shales brought into the deep basin from the exposed shelf by the retreating seas. This terrigenous influx suppressed pure novaculite deposition, but enough silica remained in the system to produce chert. The Kaskaskia II cycle produced a return of transgressive seas across the craton during the Kinderhookian and beginning of the Osagean Series (Sloss 1963). Consequently, the upper novaculite member represents a return to siliceous rock deposition, but with a carbonate contribution as a deeper water setting returned.

**Geochemistry of the Arkansas Novaculite and Lower Boone Chert**

**Sample Collection, Preparation, and Analysis**

Arkansas Novaculite samples were collected at the Caddo Gap road cut along Highway 27 through nearly 274.3 m (900 ft) of vertical to near vertical beds of the southern facies. Samples were collected at 3.05m (10 ft) intervals from the exposed base of the outcrop to the top exposure at the presumed contact with the Stanley Group. Weathering of the middle member prevented the acquisition of field samples from that interval. Samples of the penecontemporaneous chert of the Boone Formation were collected from the Bella Vista road cut along the off-ramp, where I-49 joins U.S Highway 71B on the south side of Bella Vista, Arkansas.

Samples from both intervals were taken from the field, washed using deionized water, and allowed to air dry. Samples for geochemical study 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. Dry slabs were wrapped individually, and broken into small flakes and pieces suitable for powdering with a rock crusher, and for EDX analysis.

Powdered samples were dissolved using a MARS 5 (CEM Corp., Matthews, NC) microwave digestion system. Approximately 0.5g of sampled material was placed in a 55ml digestion vessel. Digestion utilized concentrated acids: HNO3 (3ml), HCl (2ml), and HF (5ml). Samples were ramped to 200° C and held for 15 minutes. Following digestion, the acids were neutralized using a 4% by volume boric acid solution in compliance with the HF neutralization method. The neutralized samples were then subjected to a 10x dilution before trace element analysis was performed using the iCAP Q ICP-Mass Spectrometer. The elemental suite chosen for this study was based on the Kelemen, Hanghøj, and Greene (2003) study of subduction-related magmatic arcs.

Small flakes of each sample undergoing trace element analysis were taken from the slabbed samples prior to powdering, and broken into smaller pieces with an emphasis on exposing a fresh surface for analysis.
Table 1: Average concentration of trace elements and rare earth elements (REE) for the Arkansas Novaculite, its enriched and depleted U groups, and the Boone Formation.

<table>
<thead>
<tr>
<th>Trace Element and REE Average Concentration Values (ppm)</th>
<th>Be</th>
<th>Al</th>
<th>K</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Ga</th>
<th>As</th>
<th>Rb</th>
<th>Cd</th>
<th>Cs</th>
<th>La</th>
<th>Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>Novaculite Average</td>
<td>3.08</td>
<td>9333.94</td>
<td>983.40</td>
<td>69.04</td>
<td>16.26</td>
<td>111.23</td>
<td>4.62</td>
<td>9.35</td>
<td>22.19</td>
<td>14.77</td>
<td>4.51</td>
<td>3.75</td>
<td>17.60</td>
<td>0.12</td>
<td>1.72</td>
<td>9.09</td>
<td>15.94</td>
</tr>
<tr>
<td>Novaculite Average 50-69</td>
<td>4.25</td>
<td>24344.69</td>
<td>2295.15</td>
<td>164.17</td>
<td>40.72</td>
<td>47.76</td>
<td>4.60</td>
<td>20.27</td>
<td>47.22</td>
<td>25.41</td>
<td>10.11</td>
<td>7.75</td>
<td>43.72</td>
<td>0.24</td>
<td>4.16</td>
<td>16.61</td>
<td>29.25</td>
</tr>
<tr>
<td>Novaculite Average others</td>
<td>2.44</td>
<td>6279.59</td>
<td>277.08</td>
<td>1.77</td>
<td>3.09</td>
<td>145.40</td>
<td>4.62</td>
<td>3.47</td>
<td>8.71</td>
<td>9.04</td>
<td>1.50</td>
<td>1.56</td>
<td>3.53</td>
<td>0.05</td>
<td>0.41</td>
<td>5.03</td>
<td>8.78</td>
</tr>
<tr>
<td>Boone Averages</td>
<td>1.83</td>
<td>10526.91</td>
<td>776.50</td>
<td>3.74</td>
<td>5.16</td>
<td>79.07</td>
<td>2.73</td>
<td>3.28</td>
<td>1.74</td>
<td>5.84</td>
<td>1.22</td>
<td>-</td>
<td>-</td>
<td>3.37</td>
<td>3.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pr</td>
<td>Nd</td>
<td>Sm</td>
<td>Eu</td>
<td>Gd</td>
<td>Tb</td>
<td>Dy</td>
<td>Ho</td>
<td>Er</td>
<td>Tm</td>
<td>Yb</td>
<td>Lu</td>
<td>Hg</td>
<td>Tl</td>
<td>Pb</td>
<td>Th</td>
<td>U</td>
<td></td>
</tr>
<tr>
<td>--------------------------------------------------------</td>
<td>----</td>
<td>----</td>
<td>---</td>
<td>---</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td>2.66</td>
<td>9.46</td>
<td>1.50</td>
<td>0.59</td>
<td>2.41</td>
<td>210.96</td>
<td>2.50</td>
<td>0.52</td>
<td>1.46</td>
<td>0.21</td>
<td>1.37</td>
<td>0.23</td>
<td>0.02</td>
<td>0.19</td>
<td>11.36</td>
<td>2.28</td>
<td>3.02</td>
<td></td>
</tr>
<tr>
<td>5.19</td>
<td>18.28</td>
<td>2.93</td>
<td>1.15</td>
<td>4.56</td>
<td>388.04</td>
<td>4.42</td>
<td>0.90</td>
<td>2.51</td>
<td>0.37</td>
<td>2.45</td>
<td>0.41</td>
<td>0.06</td>
<td>0.45</td>
<td>22.12</td>
<td>4.70</td>
<td>7.46</td>
<td></td>
</tr>
<tr>
<td>1.29</td>
<td>4.71</td>
<td>0.74</td>
<td>0.29</td>
<td>1.25</td>
<td>116.68</td>
<td>1.47</td>
<td>0.32</td>
<td>0.89</td>
<td>0.13</td>
<td>0.79</td>
<td>0.13</td>
<td>0.00</td>
<td>0.05</td>
<td>5.57</td>
<td>0.98</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>0.49</td>
<td>2.96</td>
<td>0.31</td>
<td>-</td>
<td>0.35</td>
<td>64.23</td>
<td>0.31</td>
<td>-</td>
<td>0.10</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
<td>0.00</td>
<td>0.05</td>
<td>2.40</td>
<td>0.10</td>
<td>0.42</td>
<td></td>
</tr>
</tbody>
</table>

Samples were placed on carbon tape to adhere to the microscope stage, sputter coated with gold and examined by EDX using a FEI Nova Nanolab 200 Dual-Beam microscope.

EDX analysis of the Arkansas Novaculite and lower Boone chert reveals elevated levels of aluminum that can only be explained by derivation of the material from an igneous source. Elevated aluminum levels were found throughout the sampling for both units, usually ranging between 0.35 wt % and 2.0 wt %. Two samples of Arkansas Novaculite (50A and 50B) that were not representative of the massive white novaculite also exhibited elevated levels of aluminum (Al). This is attributed to their incorporation of aluminum silicate clay minerals producing their dark black and light gray colors respectively. 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 ranged from 0.02 wt % to 0.72 wt %. However, these weight percentages are suppressed by the inclusion of gold from the coating for EDX in the analyzed spectrum. Trace element and REE data (Table 1) were normalized to the values of average primitive arc andesite of continental and Aleutian arc types compiled by Kelemen et al. (2003) in order to verify which kind of volcanic source was contributing the silica to the Ouachita Basin and its northern shelf and ramp settings. Kelemen et al. (2003) compiled geochemical data from various public sources as well as their own research in order to form a comprehensive analysis of the composition of subduction related magmatic bodies. The study defined andesite as magmatic compositions with >54 wt. % SiO₂. The majority of normalized values regardless of arc type plotted between 10 and 0.1 on a log scale (Figure 2).

Discussion

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) proposed a volcanic island arc system with surface wind and ocean currents pushing pyroclastic debris north into the Ouachita Basin. Morris (1974) placed a microcontinent to the south of the basin. With these two interpretations in mind, the geochemical data obtained in this study were normalized to REE concentration averages of both continental and Aleutian magmatic arc systems as

![Figure 2: Elemental concentrations normalized by average continental and Aleutian values.](http://scholarworks.uark.edu/jaas/vol70/iss1/31)
analyzed by Hein et al. Chert within the Nicoya Complex of Costa Rica compare favorably to volcanically sourced REE concentrations found in the Arkansas Novaculite. 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), La (15.8), Be (1.14), Cr (15.1), and Pb (8.1) are analogous to average values for the Arkansas Novaculite, Co (4.62), La (9.09), Be (3.08), Cr (16.26), and Pb (11.36).

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) provides evidence that Al, Fe and REEs are immobile into or out of the silicate crystalline framework. These two elements as well as potassium are an indicator of volcanic contributions (Murray 1994, Hein et al. 1981), which would have been present in the Paleozoic ocean during the time of deposition for these formations (Lowe 1975).

When comparing the geochemistry of siliceous deposits in the Arkansas Novaculite and Boone Formation, it is clear that the Novaculite is much more enriched in trace elements and REEs. 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 REEs incorporated from the seawater decreases. This water would have been enriched in REEs by the volcanic activity to the south. The dramatic increase in sedimentation rates during deposition of the Boone Formation would have quickly buried the penecontemporaneous chert, which originally developed below the sediment water interface, and initiate lithification and dewatering of the surrounding sediment. Two indicators of a volcanic influence align, 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 penecontemporaneous chert of the Boone Formation represent silica sedimentation from a similar volcanic source.

Acknowledgments

Thanks to my co-workers in the Lower Mississippian Research Group in the Department of Geosciences – Julie Cains, Sean Kincade, Forrest McFarlin, and advisor Dr. Walter Manger - for their help and support in seeing this paper to completion. The Department of Geosciences defrayed the page charges for this paper.

Literature Cited


Elemental Geochemistry of the Arkansas Novaculite and the Boone Chert in their Type Regions, Arkansas


