RARE EARTH ANALYSIS OF CHERTS OF THE TRI-STATE AREA (OHIO, PENNSYLVANIA, WEST VIRGINIA)

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Abstract
In an effort to distinguish fresh-water and marine cherts of the lower, middle and upper Pennsylvanian (Pottsville through Dunkard) strata of Ohio, Pennsylvania, and West Virginia, rare earth element fractions of 14 samples from six discrete stratigraphic units were analyzed using a direct current plasma emission spectrometer. It was hoped not only that relative percentages of rare earth elements could be used to distinguish marine cherts of the lower strata of the stratigraphic section from stratigraphically higher fresh-water cherts but also that rare earth composition could be used to identify the stratigraphic and possibly the geographic source of cherts utilized by prehistoric inhabitants of the region.

Results indicate no distinct differences or general trends in relative composition that are consistently related to geography or stratigraphy; however, comparison of the relative rare earth composition of these cherts is useful in identifying and sourcing some materials used prehistorically. Specifically, lithic material from the Late Woodland Monongahela Saddle and Middle Woodland Bluebird sites, Marshall Co., West Virginia, misidentified as Brush Creek chert (which occurs no closer than ca. 100 km. to the southwest of these sites), is confidently identified as local bedded chert from the Upper Washington limestone of the Dunkard Group, outcropping only a few km distant.

Methodological limitations include cost, requisite sample size (ca. 2 g), and large variation in composition within the same rock stratigraphic unit. Nonetheless, the procedure is a useful adjunct in sourcing and distinguishing some Paleozoic cherts of economic value to prehistoric inhabitants of the midwestern United States.

Introduction
Upper Paleozoic strata of the Tri-State area (Ohio, Pennsylvania, West Virginia) include no fewer than twelve rock-stratigraphic units that contain significant amounts of flint or chert utilized to varying extent by prehistoric inhabitants of the region. In ascending stratigraphic order, these are: Kanawha Flint, Boggs Limestone, Lower Mercer Limestone, Upper Mercer Limestone, Zaleski Flint, Vanport Limestone, Brush Creek Limestone, Cambridge Limestone, Fishspot Limestone, Waynesburg (“Uniontown”) Limestone, and Washington Limestone. These units span a marine/freshwater transition from the lowermost Pottsville Group to the uppermost Dunkard Group, the last marine rocks appearing about halfway through the rock column, at the horizon of the Cambridge Limestone (Conemaugh Group). Morgan (1929) and Stout and Schoenlaub (1945) provide a general if somewhat dated geologic framework for the study.

Lateral distribution of the siliceous deposits in any given unit varies considerably, and several isolated deposits of the same stratigraphic unit have sometimes been given distinct informal names; e.g., Flint Ridge Flint and Plum Run Flint both represent the Vanport Limestone, while Hughes River Flint of northern West Virginia occurs in the same stratigraphic unit as the Brush Creek Flint of southeastern Ohio. Higher in the rock column, differences in stratigraphic nomenclature create some confusion; in the case of the Waynesburg limestone, which in Pennsylvania has been recognized as the Uniontown Limestone (Eisert, 1974) and the occurrence of fresh-water chert in the Washington Limestone has been given the local geographic name of Ten Mile chert.

The discovery of significant deposits of flint and chert in non marine strata of the Monongahela and Dunkard groups of western Pennsylvania (Eisert, 1974) and eastern Ohio and West Virginia (Murphy, 1916) invites the question of whether such non-marine cherts can be distinguished from similar appearing marine cherts found lower in the rock column. Chert debitage analysis in the Tri-State area has heretofore been almost entirely based upon lithology and general appearance (Fogelman, 1983; DeRegnaucourt and Georgiady, 1998). While various methods of chemical analysis of cherts in southeastern Ohio have been used with some success in distinguishing cherts and inferring provenance or outcrop source (Foradas, 1994), no one to our knowledge has looked specifically at the heavier rare-earth elements. It was hypothesized that while the source area for all these detrital rocks was from the Appalachian highland to the east, local variations in sedimentation might result in distinctive suites and recognizable patterns of the relatively inert rare earth elements and that these patterns might be used to infer geographic area of specific chert artefacts or debitage found on archaeological sites.

Methodology
Approximately 2 g of finely powdered chert sample was dissolved in 10 ml. of concentrated HF acid. After drying and redissolving in weak HCl, the sample was loaded onto 20x1 cm columns of AG50xw8 cation exchange resin. The rare earth element fraction was separated using a combination of HCl and HNO3 acids. Rare earth analyses were performed using a direct current plasma emission spectrometer (Beckman Spectraspan V) on a 2 ml analytical solution containing 1000 ppm K+ as an ionization buffer. Concentrations were normalized using an external standard (BHV01, Kilhuean basalt) measured during the same run.

Sample
The relative “marineness” of a given rock stratigraphic unit, while variable geographically, was determined by the presence/absence and relative abundances of marine fossils (brachiopod shells, sponge spicules, etc.). The invertebrate paleontology of these units is sufficiently well known to corroborate the vertical transition from marine to non-marine environments noted by earlier paleontologists, with the last truly marine rocks occurring in the middle portion of the Conemaugh Group (Stout, 1931). Stout and Schoenlaub (1945) failed to recognize the localized occurrence of high quality chert resources in the fresh-water limestone of the higher strata (Monongahela, Dunkard groups) of the Tri-State area, and little attention has been paid to these sources since their discovery by Eisert (1974) and Murphy (1976).

Focusing on the specific question of distinguishing marine and nonmarine samples, we initially included several older (Silurian and Devonian) samples from Ohio. Overlap in the resultant patterns was so great as to suggest that no recognizable distinctions could be observed between marine cherts of the Cincinnati Arch region, platform, the nearshore marine cherts of the Appalachian margin, and the non-marine cherts of the younger Monongahela and Dunkard rocks.

Cost limitations permitted us to analyze only 14 samples, and data on the older Bisher chert (Silurian) and Prout Chert (Devonian) are not included in this paper. General locations of the samples that were analyzed may be inferred from the map in Fig. 1 and the headings used in Figs. 2-4.
More detailed location information is available from the senior author.

Results
Although data presented in Fig. 2 might suggest that the nearshore marine Kanawha Black Flint contains a distinctively greater amount of all rare earth elements, this is probably due simply to a comparatively greater amount of included detrital material. Foradas (1994) provided a similar explanation for trends in marine cherts analyzed from southeastern Ohio. The apparent distinctiveness of the Kanawha data does not hold when compared to those derived from other marine units (Fig. 3).

The data derived from various marine samples for the most part exhibit generally similar trends or patterns. The depressed Eu values and Gd highs are ubiquitous, for example. On the other hand, the strikingly high amount of Yb in the Plum Run (Vanport) sample may be significant. While a local facies of the Vanport Limestone, the Plum Run also appears to be distinguishable by the presence of an unusually high amount of barium (Foradas 1994: 157). Additional Plum Run samples should be analyzed to test these apparent distinctions. Given the small sample size, the somewhat different trends exhibited by Upper Mercer samples from Coshocton and Perry Co., Ohio, outcrops (Fig. 3) may be significant or may simply reflect the range in rare earth element composition within a single stratigraphic unit. Only additional analyses will clarify this point.

Application
Although results of the initial analyses failed to provide a means for generally distinguishing marine and non-marine cherts, the method does have some promise in identifying specific chert sources. It has been applied successfully to a particular archaeological problem involving Brush Creek (Hughes River) and Washington (Ten Mile) cherts of the northern West Virginia Panhandle.

Church and McDaniel (1992) and Stevenson (1992) report upon excavation and mitigation of the Middle Woodland Saddle Site (46 Mr 95) and the Late Woodland Bluebird Site (46 Mr 6), both located along Dunkard Fork of Wheeling Creek near the eastern border of West Virginia. Despite the occurrence of local fresh-water chert in the Washington Formation (Dunkard) along the headwaters of Dunkard Fork and within a few km of these sites, both investigators attribute large percentages (>50%) of the artifact and debitage material from these sites to outcrops of "Hughes River flint" (Brush Creek chert) that occur approximately 100 km to the southwest (Fig. 1). This identification appears to be based upon general lithic similarity of the two materials, which are drab cherts varying from olive to tan to gray and even black in color and for the most part lacking conspicuous fossil inclusions. (Although Brush Creek outcrops in southeastern Ohio generally contain megasopic fossils, this is not always the case with the Brush Creek in its more southern exposures along the Burning Springs Anticline of West Virginia.) These authors appear unaware of the presence of similar-appearing chert in nearby outcrops of Washington limestone (locally known as "Ten Mile chert") as well as in the form alluvial material derived from these outcrops, and it is believed that some of their "Ohio River Pebble" chert may be misidentified fragments of Washington chert with river-worn cortex. This opinion is based upon examination of material recovered from the Saddle Site and examined by the senior author at the West Virginia Division of Culture and History. Local archaeologists are also in agreement that the "Hughes River chert" of Church and McDaniel (1992) and Stevenson (1992) is in actuality locally available Washington or "Ten Mile" chert.

To test this hypothesis, a sample of Hughes River chert from Wirt Co., West Virginia, was analyzed, as well as a sample of "Hughes River chert" and a water-worn sample presumably identified previously as "Pebble chert" from the Saddle site, the latter two samples provided by Patrick D. Trader, West Virginia Cultural and Historical Center. The results, as shown in Fig. 4, seem conclusive. While graphs of the relative abundance of rare earth elements are very similar for the Washington limestone sample and both samples from the Saddle site, proportions for the Brush Creek (Hughes River) sample are substantially elevated.

Conclusions
Rare earth analysis of a small number of upper Paleozoic (Pennsylvanian) chert samples from eastern Ohio, southwestern Pennsylvania, and the northern West Virginia Panhandle failed to reveal any general distribution patterns that might be used to distinguish younger, nonmarine cherts from earlier cherts developed in a marine environment. There is some evidence that outcrop-specific chert samples may in some instances be "fingerprinted" by the relative amount of specific elements, but this suggestion requires additional testing. In one application to an archaeological problem, the technique has proven successful in correcting a misidentified chert resource in the northern West Virginia Panhandle, and it is expected that similar applications to specific sourcing problems may also prove successful.

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Note
This paper was originally presented as a poster session at the 2000 International Symposium on Archaeometry (Murphy and Morton 2000) but has not been published previously.

References
Figure 1. Generalized outcrop areas for upper Paleozoic cherts in the Tri-State Area, 1929, revised. (B would now be called Obryan).

1. Plum Run (Vanport)
2. Upper Mercer
3. Fishpot
4. Waynesburg (Uniontown)
5. Flint Ridge (Vanport)
6. Ten Mile (Washington)
7. Zaleski
8. Vanport
9. Brush Creek
10. Hughes River (Brush Creek)
11. Kanawha
Figure 2. Relative amounts of rare earth elements in near-shore marine Kanawha Flint and three fresh-water cherts.

Figure 3. Relative amounts of rare earth elements in four marine cherts.

Figure 4. Comparison of Wirt Co. Hughes River chert with Washington chert and "Hughes River" and "Pebble Chert" samples from the Saddle Site (46 Mr95).