Chapter 6

Geochemistry: Neodymium Isotopes

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Seventy-one samples of metamorphosed volcanic rocks (dacite, andesite, and rhyolite) and metamorphosed volcaniclastic rocks (e.g., mudstones, siltstones, sandstones, and volcanic breccia) from archaeological quarry sites in North Carolina and nine samples of lithic artifacts from archaeological sites on Fort Bragg were analyzed for neodymium (Nd) isotope geochemistry. The isotopic ratios, corrected for radioactive decay of parent samarium (Sm), were used to develop a database for North Carolina quarry samples and to determine if artifacts could be sourced to individual geologic formations or quarries. This report summarizes the first attempt to source artifacts from Fort Bragg using Nd isotope geochemistry and is based on the method presented by Brady and Coleman (2000).

Background

Because interpretation of Nd isotope data in archaeological studies is somewhat unconventional, it is worthwhile to explain the theory behind the technique and differences between this analysis and more conventional approaches before presenting the results. Previous attempts to discriminate lithic artifact quarry sites have mainly focused on petrographic analysis and analysis of major-element compositions using a variety of techniques (Daniel and Butler 1991, 1996; Daniel 1994a). Both petrography and major-element concentrations are very useful for broad characterization of igneous rocks. However, these analyses can overlook important genetic differences between similar rock types. A volcanic rock of rhyolitic composition, for example, is defined mineralogically by the abundance of quartz, alkali feldspar, and plagioclase and is defined chemically by the proportions of major cations — silicon (Si), calcium (Ca), sodium (Na), aluminum (Al), iron (Fe), and magnesium (Mg). Magmas of rhyolitic composition, however, can be produced in different geological settings and by partial melting of different types of source rocks. Trace-element geochemical signatures and Nd-isotopic compositions are much more powerful tools by which modern geochemists are able to characterize and discriminate ancient volcanic rocks that formed in different geological settings and were derived from melting of different source rocks.

The isotope approach (Brady and Coleman 2000) is distinct from elemental approaches because geologic processes occurring in the earth's crust are incapable of fractionating *isotopes* of the "heavy elements" (e.g., Nd) from one another. Thus, if a magma with an isotopic ratio of $^{143}Nd/^{144}Nd = 0.5125$ is cooling and crystallizing, all of the minerals crystallizing from that magma will have the same ratio of $^{143}Nd/^{144}Nd = 0.5125$. Geologic processes do, however, segregate different *elements* (e.g., Sm from Nd). Thus, if the magma with $^{143}Nd/^{144}Nd = 0.5125$

has a Sm/Nd ratio of 0.25, minerals crystallizing from the magma will all have the same $^{143}Nd/^{144}Nd$ but could theoretically inherit a range of Sm/Nd from 0 to ∞. These relations can be plotted on a bivariate diagram, with Sm/Nd expressed in terms of isotopes of the elements (i.e., $^{147}Sm/^{144}Nd$) for reasons that will be apparent below (Figure 6.1). On this plot, the theoretical magma and its crystallizing minerals plot along a horizontal line ($m = 0$) with the same $^{143}Nd/^{144}Nd$ isotopic ratio but different Sm/Nd elemental ratios at the time of crystallization.

Herein lies the advantage of isotopic approaches over elemental approaches. If samples are taken from the crystallized magma the absolute Sm and Nd concentrations, and even the Sm/Nd ratio, can vary from sample to sample. The problem becomes less acute when large samples can be collected, but this is not always possible in archaeological studies. If isotopic ratios are compared, however, all samples, and even individual minerals within the samples, should have the same initial isotopic ratio.

The isotope approach can be applied as a sourcing tool only if the potential source rocks inherited different original Nd isotope ratios. The $^{143}Nd/^{144}Nd$ of rocks is variable because ^{147}Sm undergoes radioactive decay to ^{143}Nd with a half-life of 106 billion years ($\lambda = 6.54E^{-12}$). Thus, the ratio of $^{143}Nd/^{144}Nd$ in any magma source is dependent on $^{147}Sm/^{144}Nd$ and time and varies by geologic setting and age. This relation can be expressed as

$$^{143}Nd/^{144}Nd_{(now)} = (^{143}Nd/^{144}Nd_{(original)} + {}^{147}Sm/^{144}Nd_{(now)}) (\exp^{\lambda t} -1) \qquad (1).$$

This is the equation of a line in a bivariate plot of $^{143}Nd/^{144}Nd_{(now)}$ versus $^{147}Sm/^{144}Nd_{(now)}$ with the y-intercept equal to $^{143}Nd/^{144}Nd_{(original)}$ and the slope proportional to the age of the sample, t (hence the choice of axes in Figure 6.1).

Returning to the theoretical magma in Figure 6.1, as time passes, samples and minerals with high $^{147}Sm/^{144}Nd$ will show a relatively rapid increase in $^{143}Nd/^{144}Nd$ and samples and minerals with low $^{147}Sm/^{144}Nd$ will show a relatively slow increase in $^{143}Nd/^{144}Nd$. At any time, however, the samples will all fall on a line with a slope

$$m = (\exp^{\lambda t} -1) \qquad (2)$$

and by rearranging

$$t = \ln(m + 1) / \lambda \qquad (3).$$

Therefore, assuming the $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ ratios can be measured and the *geologic* age of the sample (t) can be estimated, it is possible to calculate $^{143}Nd/^{144}Nd_{(original)}$, which should be the same for any geologic sample or artifact collected from the same volcanic rock.

A few final points regarding the utility of the Sm/Nd isotopic approach are important to summarize. First, the present-day isotopic ratios ($^{143}Nd/^{144}Nd_{(now)}$ and $^{147}Sm/^{144}Nd_{(now)}$) are potentially (and likely) useless for comparison depending on the scale of variation of Sm/Nd and the geologic age of the sample. More useful is the *initial* $^{143}Nd/^{144}Nd$ ($^{143}Nd/^{144}Nd_{(original)}$) at the time of magma or lava crystallization. Initial ratios are better geological discriminants because they are indicative of distinct geological processes and magma sources. Calculation of $^{143}Nd/^{144}Nd_{(original)}$ requires that the ^{143}Nd that has accumulated due to the decay of ^{147}Sm be stripped out of the measured, present-day $^{143}Nd/^{144}Nd$ ratio. This requires knowledge of the amount of time that has passed since crystallization.

Second, as a consequence of the foregoing process, the *geologic* age of the sample must be known. Accumulation of ^{143}Nd through the decay of ^{147}Sm occurs independently of collecting a sample and/or fashioning it into a tool. Because dating rocks is a costly and time-consuming
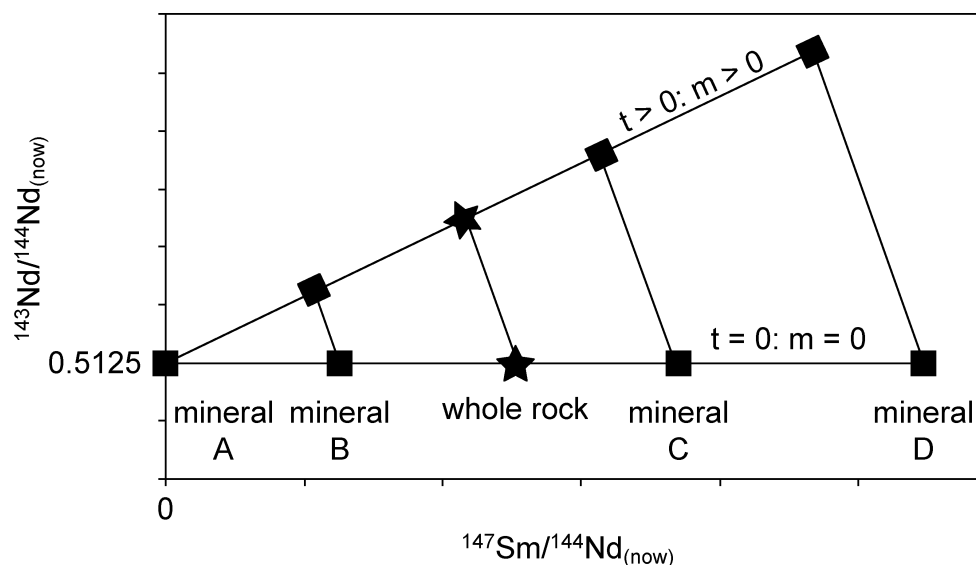
Figure 6.1. Conventional Sm/Nd isochron diagram. Samples from a single magma will have identical $^{143}Nd/^{144}Nd$ and variable $^{147}Sm/^{144}Nd$ at the time of crystallization. Through time, however, these ratios will change ($^{143}Nd/^{144}Nd$ will increase and $^{147}Sm/^{144}Nd$ will decrease) as the result of decay of parent isotope ^{147}Sm to daughter ^{143}Nd. If the geologic age of a sample collected today is known, the effects of decay can be corrected for and initial isotope ratios can be compared. Samples of a single rock (a homogeneous quarry) should have identical $^{143}Nd/^{144}Nd_{(initial)}$ despite having variable concentrations of Sm and Nd and variable Sm/Nd ratios that may be introduced through sampling bias caused by necessarily small samples of artifacts.

endeavor, the geologic age is commonly estimated with only a minor effect on the accuracy of $^{143}Nd/^{144}Nd_{(original)}$. Since the geologic age of an artifact cannot be estimated through geological correlation and reasoning, its $^{143}Nd/^{144}Nd_{(original)}$ must be calculated using the age of each quarry to which it is being compared.

Third, the technique depends on the assumption that $^{143}Nd/^{144}Nd_{(original)}$ of an outcrop is homogeneous. The necessity of this assumption poses two potential problems relevant to this study. First, heterogeneous outcrops with variable rock types cannot be used unless all rock types are sampled and direct comparisons of artifacts to specific rock types are made. Second, sedimentary rocks must be approached with caution as they are aggregates of different rocks and minerals from different sources with (almost certainly) variable $^{143}Nd/^{144}Nd_{(original)}$. An important corollary is that metamorphosed rocks (with igneous or sedimentary protoliths) can be used if $^{143}Nd/^{144}Nd$ is homogenized during metamorphism (although this would need to be independently verified).

Fourth, the Sm/Nd approach has a distinct advantage over other isotopic and elemental approaches in that Sm and Nd are both rare-earth elements and therefore behave very similarly during post-magmatic processes. Thus, the technique is relatively impervious to alteration of samples and artifacts. Secondary alteration likely impacts the absolute concentrations of most elements (including Sm and Nd), but it is unlikely to significantly impact Sm/Nd and will certainly not impact $^{143}Nd/^{144}Nd$. Consequently, unlike other isotopic systems (e.g., rubidium/strontium [Rb/Sr]) and elemental data, the Sm/Nd system can "see through" all but the worst alteration.

Results

The quarry zones form distinct trends or clusters on the conventional Sm/Nd isochron diagram (Figure 6.2; Appendix G). Most samples from the Uwharries form a broadly linear array that spans much of the total range of $^{147}Sm/^{144}Nd_{(now)}$, although two Uwharries Asheboro samples fall off this trend at significantly higher $^{143}Nd/^{144}Nd_{(now)}$ (FBL021 and FBL022). Most Cumberland County samples lie along the same trend defined by the Uwharries samples, but at higher $^{147}Sm/^{144}Nd_{(now)}$, and one sample from Cumberland County (FBL070) plots with the two Uwharries Asheboro outliers. Chatham Pittsboro samples form a trend with distinctly low $^{143}Nd/^{144}Nd_{(now)}$, although there is one outlier at higher $^{143}Nd/^{144}Nd_{(now)}$ (FBL056). Chatham Silk Hope and Chatham Siler City samples cluster tightly together. Durham and Person County samples also overlap significantly, and together with the Chatham Silk Hope and Chatham Siler City samples they define a trend at nearly constant $^{143}Nd/^{144}Nd_{(now)}$ over a range of $^{147}Sm/^{144}Nd_{(now)}$. The Orange County samples define a tight cluster distinct from other quarries.

Within the Uwharrie Mountains, some clear Sm-Nd isotopic distinctions can be correlated with geological formation and quarry zone (Figure 6.2). Generally speaking, samples from the Uwharrie Formation (Uwharries Southeastern and Asheboro zones) anchor the low end of the linear trend, samples from the Cid Formation (Uwharries Western zone) comprise the high end, and samples from the Tillery Formation (Uwharries Asheboro, Southern, and Eastern zones) fall in the middle. With a few exceptions, samples from individual quarry zones tend to form distinct clusters on the graph. Whether the exceptions result from mapping errors or real variation within the formations is unclear. Of all the quarry zones within the Uwharries, Uwharries Asheboro seems to show the greatest variation.

Artifacts from Fort Bragg show significant variability in both $^{143}Nd/^{144}Nd_{(now)}$ and $^{147}Sm/^{144}Nd_{(now)}$ (Figure 6.2). Two artifacts yield results along the relatively flat data array defined by samples from Chatham, Cumberland, Durham, Orange and Person Counties. Two artifacts have isotopic ratios within the array defined by quarries within the Uwharries. Together, the artifacts lie along a poorly defined trend with a much steeper slope than arrays defined by quarry samples.

Age of the Quarries

The crystallization ages of the rocks from the quarries must be reasonably well known in order to compare initial isotopic ratios with the artifacts. The crystallization age of the rocks from the Uwharries is known to be between 540 and 580 million years ago (Ma) based on U-Pb zircon geochronology (Wright and Seiders 1980; Mueller et al. 1996; Ingle 1999). A single rhyolite sample collected by one of us (BVM) from bedrock at the top of Morrow Mountain (equivalent to FBL015) yielded a U-Pb zircon crystallization age of 569 ± 4 Ma. Samples from Chatham, Durham, Orange, and Person Counties are derived from rocks in the Virgilina sequence, which consistently yields ages of approximately 600 Ma (Wortman et al. 2000). Samples from Cumberland County were collected from river gravels; thus, it is impossible to assign a precise geologic age with confidence. Fortunately, because the samples have similar Sm/Nd, and because the half-life of ^{147}Sm is so long (106 billion years), correction of all the Nd isotopic data to initial ratios between 500 and 700 Ma yields similar results. Consequently, we compare initial ratios at 550 Ma.

Age information for the quarries may also be obtained from the Sm/Nd data by solving equation (3) if the samples are geologically related and shared a common initial $^{143}Nd/^{144}Nd$. For
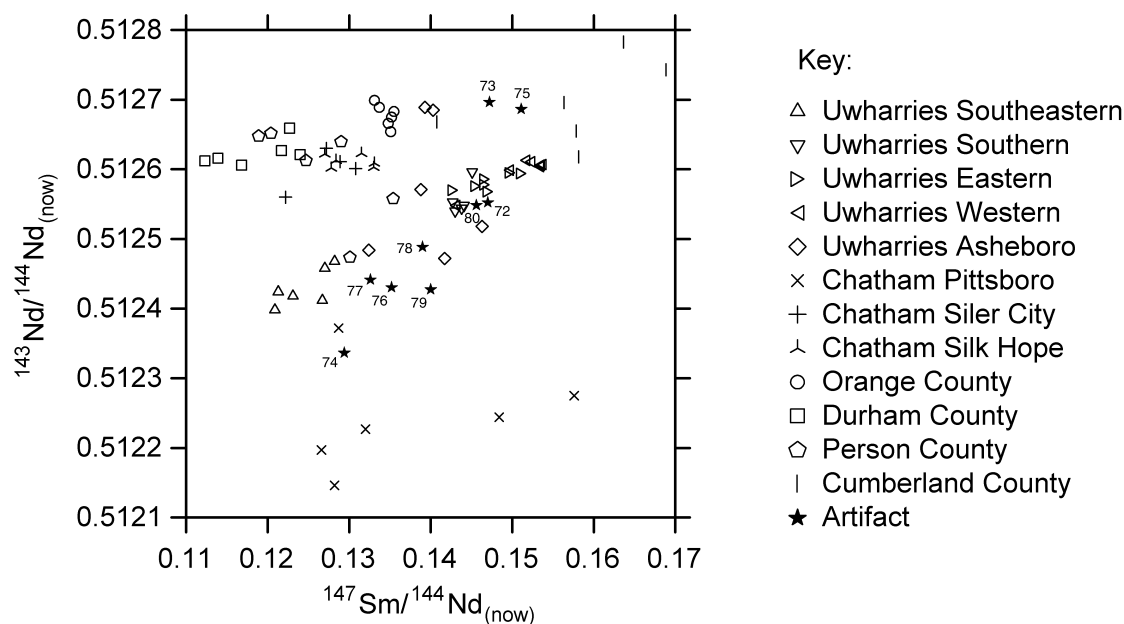
Figure 6.2. Conventional isochron diagram showing isotope ratio plots for quarry and artifact samples. Samples from the Uwharries form a fairly consistent sloping array. Although artifacts are anchored within the array at high $^{147}Sm/^{144}Nd$, they deviate from the trend with decreasing $^{147}Sm/^{144}Nd$. Individual artifacts are labeled with their FBL-number suffixes.

example, most samples from the Uwharries appear to fall along a linear sloping array in Figure 6.2. However, regression of a line through the Sm/Nd data yields a slope corresponding to a geologically unreasonable age of nearly 900 Ma. Closer inspection of data from a single quarry locality at Shingle Trap Mountain (FBL001-FBL004) yields a Sm/Nd age of 546 Ma, which is very close to the 538 ± 6 Ma crystallization age reported by Ingle (1999; her "Morrow Mountain rhyolite" was actually collected from Shingle Trap Mountain). These trends from the Uwharries imply that magmas were isotopically homogeneous locally, but overall reflect mixing of magma sources. This results in samples from the Uwharries having initial isotopic ratios from 0.51195 to 0.51207.

With the exceptions of one Chatham Pittsboro sample (FBL056), two Person County samples (FBL044, FBL068), and the Cumberland County samples, the remaining quarries define relatively small ranges in isotopic ratios at 550 Ma that are distinct from the initial ratios of the Uwharries.

Although it is tempting to attach significance to the fairly coherent linear trend defined by the artifacts, there is no a priori reason to believe that the samples have any geologic relation. Therefore, the apparent trend is likely meaningless. The artifacts correct back to initial $^{143}Nd/^{144}Nd$ between 0.51187 and 0.51218 at 550 Ma (Appendix G).

Matching Artifacts to Quarries

Comparison of isotopic ratios at 550 Ma reveals significant overlap between the artifacts and quarries within the Uwharries (Appendix G). One sample from Chatham Pittsboro (FBL056) has a $^{143}Nd/^{144}Nd_{(550\,Ma)}$ ratio that comes close to samples from the Uwharries and is quite distinct from other Chatham Pittsboro samples. Whereas other Chatham Pittsboro samples were

collected from outcrop, FBL056 was collected from float at the quarry and showed clear evidence for working. This raises the possibility that the sample was in fact transported from the Uwharries — perhaps it was abandoned at the quarry site thousands of years ago, or perhaps it is a piece of modern construction trash. Yet it is equally possible that this variation is characteristic of the metasedimentary rocks in the Virgilina sequence, of which the Chatham Pittsboro quarries are a part. Similarly, two samples from Person County (FBL044, FBL068) have Uwharrie-like isotope ratios, but again these are metasedimentary rocks, which seem to exhibit much more isotopic variation than the metavolcanics from any given locality.

To help identify potential matches between quarries and artifacts, $^{143}Nd/^{144}Nd_{(550\ Ma)}$ is plotted against ratios of immobile elements (i.e., elements not readily impacted by alteration, such as lanthanum/lutetium [La/Lu] and tantalum/ytterbium [Ta/Yb]; Figures 6.3-6.4). Note that the artifact samples have trace element ratios very similar to quarries that the Nd isotope ratios exclude as possible sources. For example, most artifacts have La/Lu (Figure 6.3) and Ta/Yb (Figure 6.4) ratios similar to quarry samples from Chatham, Durham, Orange and Person Counties, but with few exceptions the Nd isotopic data exclude these localities as sources.

Using a combination of isotopic and immobile element ratios, several fairly reliable matches between artifacts and quarries can be made. Two artifacts (FBL072, FBL080) consistently match Uwharries Southern samples collected from Morrow Mountain and Tater Top Mountain and Uwharries Eastern sample FBL006 collected from Sugarloaf Mountain. Two additional artifacts (FBL077 and FBL078) are consistent matches for the Uwharries Southeastern samples collected from Lick Mountain. The petrographic description of FBL078 also matches the Lick Mountain quarries quite well, but petrographic data tentatively identify FBL077 as being derived from a metasedimentary rock. Therefore, the isotopic correlation of FBL077 with Lick Mountain volcanic rocks is either fortuitous (emphasizing the importance of a multidisciplinary approach to this exercise), or the artifact was derived from a very closely related volcaniclastic rock. Artifact FBL076 is described as petrographically similar to FBL077, and there is significant overlap in the initial Nd isotopic ratio of these two artifacts and samples from Lick Mountain and the Uwharries Asheboro zone. The trace element ratios of FBL076, however, are significantly different from those of FBL077 and both quarry localities. This may indicate that the artifact was derived from an unidentified quarry in immature metasedimentary rock that is closely related to the Lick Mountain and Uwharries Asheboro volcanic rocks.

Two additional artifacts (FBL073, FBL075) are good geochemical matches for the Uwharries Asheboro quarries at Caraway (FBL021) and Tater Head (FBL022) Mountains. However, artifact FBL073 was positively identified as derived from Orange County on the basis of petrographic data. There is also a good isotopic match between Orange County quarries and FBL073, but the trace element ratios are a poor fit. One possible explanation for this poor fit is the difference in alteration between Orange County quarry samples and the artifact (as described in Chapter 4): despite remarkable similarity in petrography, the artifact was significantly less altered. As described above, alteration would impact trace element ratios without impacting isotopic compositions, possibly offering an explanation for the discrepancy. As a result of the excellent match in isotopic ratios and petrography, we tentatively correlate FBL073 with the Orange County quarries.

Two final artifacts (FBL074, FBL079) have isotopic ratios lower than those from the Uwharries samples. Chatham Pittsboro sample FBL056 provides the closest match for these artifacts, but it is a better match for FBL079 on the La/Lu plot and for FBL074 on the Ta/Yb plot, suggesting that the match is not particularly robust.
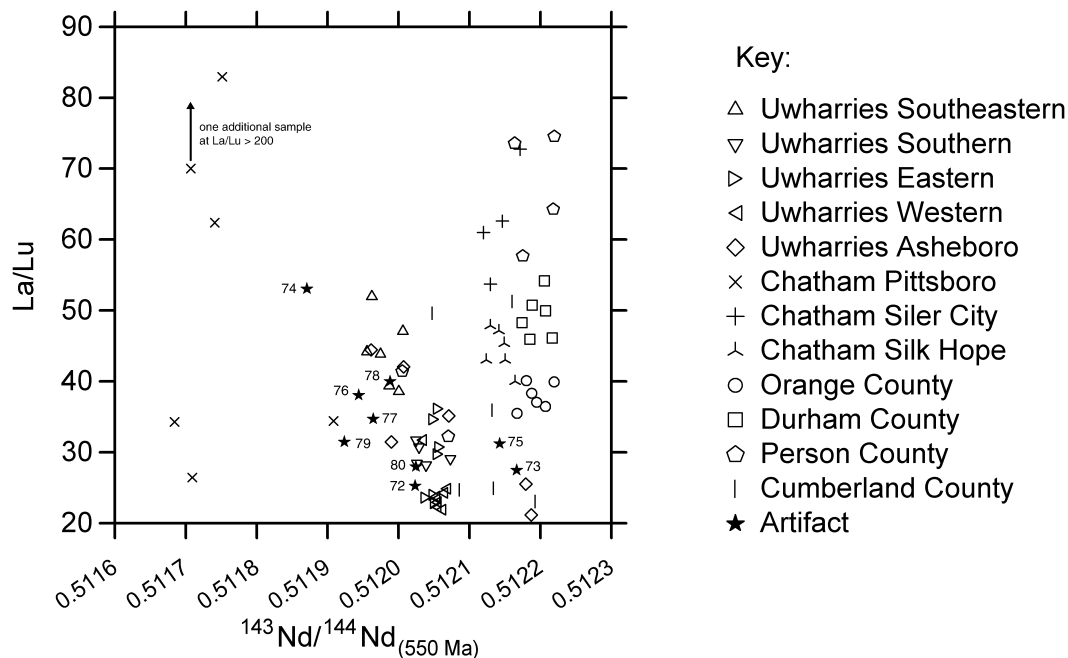
Figure 6.3. Isotope and trace element ratio plot for quarry and artifact samples showing Nd isotopes calculated at 550 Ma (the nominal age of rocks in the Uwharries) versus La/Lu. La/Lu provides an index of magmatic differentiation (more evolved magmas and sedimentary rocks have higher La/Lu) and is fairly insensitive to alteration. Individual artifacts are labeled with their FBL-number suffixes.
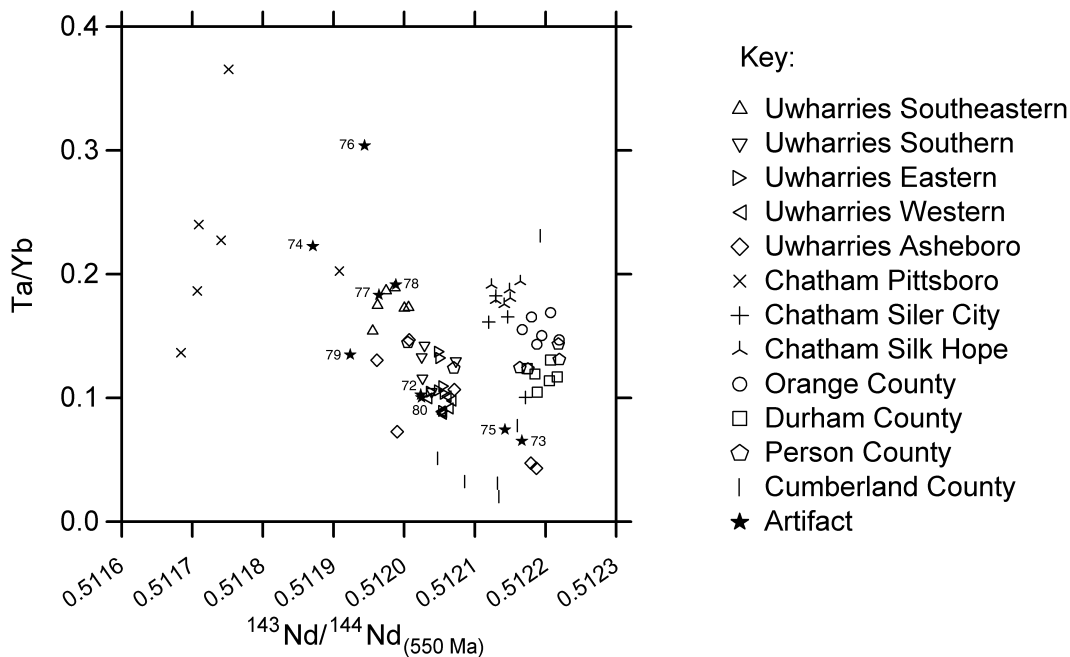
Figure 6.4. Isotope and trace element ratio plot for quarry and artifact samples showing Nd isotopes calculated at 550 Ma (the nominal age of rocks in the Uwharries) versus Ta/Yb. The Ta/Yb ratio was chosen because both elements are considered "immobile," and their ratio should be fairly resistant to metamorphism and alteration. Individual artifacts are labeled with their FBL-number suffixes.

Summary and Conclusions

Several of the artifacts from Fort Bragg can be sourced with some confidence to locations within the Uwharrie Mountains, and a single artifact is likely derived from Orange County. The remainder of the artifacts variably share petrographic and trace element affinities with samples from the Uwharries and most other quarries, but in initial Nd isotopic composition overlap only with samples from the Uwharries and one sample each from the Chatham Pittsboro and Person County zones. The close match of at least one, and possibly two, artifacts fashioned from metasedimentary rocks with elemental and isotopic data for volcanic rocks in the Uwharrie Mountains suggests a search for quarries within immature sedimentary rocks in the region may yield sources for these artifacts. There is also a suggestion in the quarry isotopic data that suitable sources may be located in the Chatham Pittsboro and Person County zones. Specifically, a closer investigation for variable rock types within the quarries from which FBL056 and FBL068 were collected seems warranted.

The multidisciplinary approach presented here demonstrates that no single data type (petrographic, elemental, or isotopic) can be relied upon to provide unique results. The isotopic approach described in this chapter has the distinct advantages, however, of (*a*) being independent of sample bias introduced by extremely limited sample sizes common in archaeological analysis, and (*b*) being able to distinguish common volcanic rocks that often share closely similar petrographic and geochemical signatures.

Acknowledgments