Samarium-Neodymium Isotope and Trace-Element Analysis of Metavolcanic Rocks from the Vicinity of Fort Bragg, North Carolina: A Pilot Study of Artifact Source Quarry Discrimination

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Introduction

Fifty rock samples, of either metamorphosed volcanic flows (dacite, andesite, and rhyolite) or metamorphosed volcanic-sedimentary detritus of similar composition (e.g., mudstones of water-lain ash), were selected from archaeological quarry sites in south-central North Carolina (Fig. 1). Twenty-two sites are cataloged with the North Carolina Office of State Archaeology (Table 1) and two sites have not yet received official site numbers. Each site is identified as a potential raw-material source quarry for prehistoric Native American artifacts found on Ft. Bragg. The sites are grouped into eight quarry clusters based on geographic proximity (Fig. 1). One quarry cluster (Uwharries 1) was sampled extensively to test for smaller-scale variability within a quarry group, and samples from this group are sub-divided based on geological map unit (Fig. 2).

This report documents the results of a pilot study conducted to test methods of geochemical and isotopic discrimination, or "fingerprinting", of the prehistoric quarry sites. Such fingerprints could be used as a highly sensitive tool for tracing Native Peoples' trading and travel routes in the southeastern United States.

Background

The present study of lithic sources in south-central North Carolina is the outgrowth of more than a decade of multi-disciplinary collaboration between archaeology researchers at Ft. Bragg, University of North Carolina - Chapel Hill, Eastern Carolina University and geologists affiliated with both University of North Carolina - Chapel Hill and North Carolina State University. In addition, the Archaeometry Laboratory at the University of Missouri Research Reactor Center (MURR) was contracted to conduct instrumental neutron activation analysis (INAA) of the lithic samples.

Petrography (the rock textures and mineral contents as seen in thin sections examined under a microscope) and major-element concentrations are very useful for broad characterization of igneous rocks. However these analyses might 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 - Si, Ca, Na, Al, Fe, and 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. Previous attempts to discriminate lithic artifact quarry sites have focused mainly on petrographic analysis and on analysis of major-element compositions using a variety of analytical techniques (Daniel and Butler, 1991; 1996; Daniel, 1994). However, these studies have been, to a degree, inconclusive and a recent Nd-isotope study in Massachusetts has shown some promise (Brady and Coleman, 2000).

With the exception of radioactive ^{147}Sm and its daughter, radiogenic ^{143}Nd, the isotopic compositions of Sm and Nd are constant in nature because all of the isotopes of Nd are either stable or have very long half-lives; only ^{147}Sm has a half-life (1.06E^{11} years) of geologically suitable duration. Therefore, the present-day ^{143}Nd/^{144}Nd ratio is a time-integrated measure of the original ^{143}Nd/^{144}Nd ratio, which is inherited from the source rock, and the original Sm/Nd ratio of a magma, which is affected by the type of crystal-liquid fractionation processes operating in different geological settings.

Sample Selection, Preparation, and Analytical Methods

The lithic samples are sherds and rock fragments derived from locally exposed bedrock and collected from known quarry sites (Fig. 1). The sample selection process was conducted in collaboration between archaeology and geology researchers in order to ensure samples were suitable for both cultural and geological analysis. Most samples were selected from the collection housed at the Research Laboratory of Archaeology, University of North Carolina - Chapel Hill. Some samples were also collected during the course of several field excursions attended by the principle researchers.

Samples were photographed, and assigned a basic hand-sample description. The rock was sawed into three pieces. One piece was returned to the RLA collection for reference. A roughly 1" x 1.5" x 0.5" piece was sent to Dr. Skip Stoddard at North Carolina State University for detailed petrographic analysis. Any weathered surfaces or hydrothermal alteration zones along fractures were removed and the remainder of the sample was crushed to fine-gravel consistency using a jaw crusher. The crushed pieces were pulverized to a fine powder in an aluminum-oxide shatter box. The powder was split into two vials, one of which was sent to MURR for INAA analysis and the second was retained at the Department of Geological Sciences, University of North Carolina - Chapel Hill for Sm-Nd isotopic analysis.

For Sm-Nd isotopic analysis, approximately 200 mg of sample powder is dissolved with an HF/HNO_3 mixture in pre-cleaned teflon high pressure dissolution vessels, to which is added a mixed ^{147}Sm-^{150}Nd tracer solution. Complete dissolution and equilibration of spike is achieved after 7 days at approximately 180°C. Conversion from fluoride to chloride solution is achieved by drying the HF solution on a hot plate in a clean air environment and re-dissolution in 6M HCl. Separation of bulk REE group elements follows standard cation exchange procedures. Rare-earth element separation is achieved by reverse-phase chromatography using 2-methyllactic acid on cation exchange resin. Analytical procedural contamination is less than 500 pg for Sm and Nd, which is negligible considering the Sm and Nd concentrations of analyzed samples.

Isotopic analyses are performed on a VG Sector 54 magnetic sector, thermal ionization mass spectrometer with eight Faraday collectors operating in dynamic-multicollector mode. Typical ^{144}Nd beam intensities are 5.0E^{-12} to 2.5E^{-11} volts relative to a 10E^{-11} ohm resistor. Accuracy is assessed by replicate analyses of the Ames, La Jolla Nd, and JNdi-1 standards. Long-term means of the Ames and La Jolla standards are ^{143}Nd/^{144}Nd = 0.512143 ± 0.000009 and 0.511850 ± 0.000008 (all errors in this report are 1σ absolute unless otherwise stated), respectively. The JNdi-1 isotopic standard was monitored throughout the period of sample analysis and yielded ^{143}Nd/^{144}Nd = 0.512110 ± 0.000009. The accepted value for this standard is 0.512116 ± 0.000008, calibrated relative to La Jolla = 0.511858. Neodymium isotopic compositions are normalized to ^{146}Nd/^{144}Nd = 0.7219 using an exponential fractionation law. Internal run precision for the critical isotopic composition measurement, ^{143}Nd/^{144}Nd, is better than ± 0.000005, absolute. Samarium isotopic compositions are normalized to ^{149}Sm/^{152}Sm = 0.51685 using a linear fractionation law. Internal run precision for the critical element concentration measurement, ^{147}Sm/^{152}Sm is better than ± 0.00001, absolute. Total uncertainties in isotopic ratios are the quadratic sum of individual sample measurement errors, uncertainties in spike weight and concentration, sample weight, and the reproducibility of standards. These sources of error are assumed to be completely uncorrelated. Correlation of errors reduces the magnitude of each error source, and therefore the quoted total errors are maxima.

Results

The Sm-Nd isotopic data are plotted on diagrams of ^{147}Sm/^{144}Nd versus ^{143}Nd/^{144}Nd (Figs. 3, 4). Three quarry groups form distinct trends or clusters. The group Uwharries 1 forms a broadly linear array at intermediate values of ^{147}Sm/^{144}Nd and ^{143}Nd/^{144}Nd (Fig. 3). Much higher ^{147}Sm/^{144}Nd along that same trend characterizes the Cape Fear group. Chatham 1 samples form a trend with distinctly low ^{143}Nd/^{144}Nd. Chatham groups 2 and 3 cluster tightly together on Figure 3, but other trace element characteristics (see below) can clearly delineate these groups. The other quarry groups tend to overlap indistinguishably.

Within the Uwharries 1 group some clear Sm-Nd isotopic distinctions can be correlated with geological map unit (Figs. 2, 4). Samples from Horse Trough Mountain (Unit CpCut; all unit designations follow Stromquist and Henderson, 1985) anchor the low end and samples from Wolf Den Mountain (Unit Ccmr) cluster tightly at the high ^{147}Sm/^{144}Nd -^{143}Nd/^{144}Nd end of the Uwharries 1 trend. One sample from farther north (HD-31) does not fall within the Ccmr cluster and appears to characteristics more similar to those of Morrow Mountain samples. It is unclear whether this is a mapping error or real variation with the Ccmr unit. Samples from throughout unit Ccmb cluster just below the Wolf Den samples. Within unit Ctr, the Morrow Mountain samples appear to be distinct from the Shingle Trap samples. Samples from the Ct unit scatter between the Morrow Mountain and Shingle Trap samples, probably a result of this unit composing mainly volcaniclastic siltstones, sedimentary rocks that may inherit mixed isotopic signatures from their eroded sources.

Differentiated volcanic suites commonly produce linear arrays similar to that of Uwharries 1. If these samples represent an ancient differentiated volcanic suite - that is if each sample is derived from the same source region and inherited the same initial ^{143}Nd/^{144}Nd ratio but different concentrations of Sm (i.e., different Sm/Nd ratios) - then the slope of this array will be proportional to the time since crystallization, or the geologic age of the suite, and the Y-axis intercept will be the initial ^{143}Nd/^{144}Nd ratio at the time of crystallization. A line fit through the Uwharries 1 group yields an age of 891 Ma, and an initial ratio of 0.511715. However, it is likely that both numbers reflect the time-integrated effects of geological events in the source rocks prior to melting and eruption of the volcanic rocks because U-Pb zircon crystallization ages indicated that the geologic ages of the units in this region are between about 540 Ma and 580 Ma (Wright and Seiders, 1980; Mueller et al., 1996; Ingle, 1999). A rhyolite sample collected from bedrock at the top of Morrow Mountain (site 31RD18, sample equivalent to HD-20) yielded a U-Pb zircon crystallization age of 569 ± 4 Ma (B.V. Miller, unpublished data). The slope of the four samples from Shingle Trap, considered independently, indicate an 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", which was actually collected from Shingle Trap Mountain)

Thorium concentrations are plotted against Eu* in Figure 4. Thorium is a highly incompatible element, meaning that lavas rich in Th were derived either from the earliest melts to come out of a source rock or from the latest melts from a crystallizing magma body. Europium is a rare-earth element that substitutes for Ca in plagioclase. Depletion in Eu, relative to geochemically similar Sm and Gd (the magnitude of the difference is Eu*), indicates fractionation of plagioclase during progressive crystallization of the magmatic source of the lavas. The Th-Eu* diagram (Fig. 4) clearly delineates the Chatham quarry groups. Chatham 2 has distinctly low Eu* and Chatham 1 has high Th concentrations.

Summary and Conclusions

The Nd isotopic composition of rock samples from quarry sites can clearly discriminate the Uwharrie 1, Cape Fear, Chatham 1 groups. The Person, Durham, Chatham 2 and 3, and Uwharries 2 groups cluster together on the $^{147}Sm/^{144}Nd$ versus $^{143}Nd/^{144}Nd$ diagram, but the potential exists for further delineation of these groups if individual sites can be re-classified according to geologic map unit instead of geographic proximity. Other geochemical signatures can help to further characterize and discriminate between these groups. The Nd isotopic composition of samples from sites within the more extensively sampled Uwharries 1 group show good distinction that corresponds to geological map unit.

This pilot study demonstrates the strengths, and a few weaknesses, in Nd isotope and trace-element characterization or "fingerprinting" of prehistoric quarry sites. Taken as a whole, these techniques provide a power tool for constraining possible source locations of Native American lithic artifacts.

Future Work and Recommendations

Other geochemistry-based discrimination may be possible using both raw materials from quarry sites and artifacts, but a complete geochemical analysis will require data from all of the major elements (particularly Si and Mg). Geochemically important trace elements not analyzed by INAA include Nb, Ti, Y, and the full suite of rare-earth elements. If the principle researchers agree that the tools of geology and geochemistry provide the best approach to artifact-sourcing and discrimination studies, then I recommend that the conventional geochemical techniques be used - major element concentrations by X-ray fluorescence (XRF), trace-element concentrations by induced-couple plasma mass spectrometery (ICPMS), and isotopic compositions by isotope-dilution thermal-ionization mass spectrometry (ID-TIMS).

It is my recommendation that a "Phase 2" pilot study be conducted as a test of chemical and isotopic variability within real artifacts collected from Fort Bragg. This will provide an indication of the usefulness of these techniques for correlating and discriminating artifacts with/from quarry sites.

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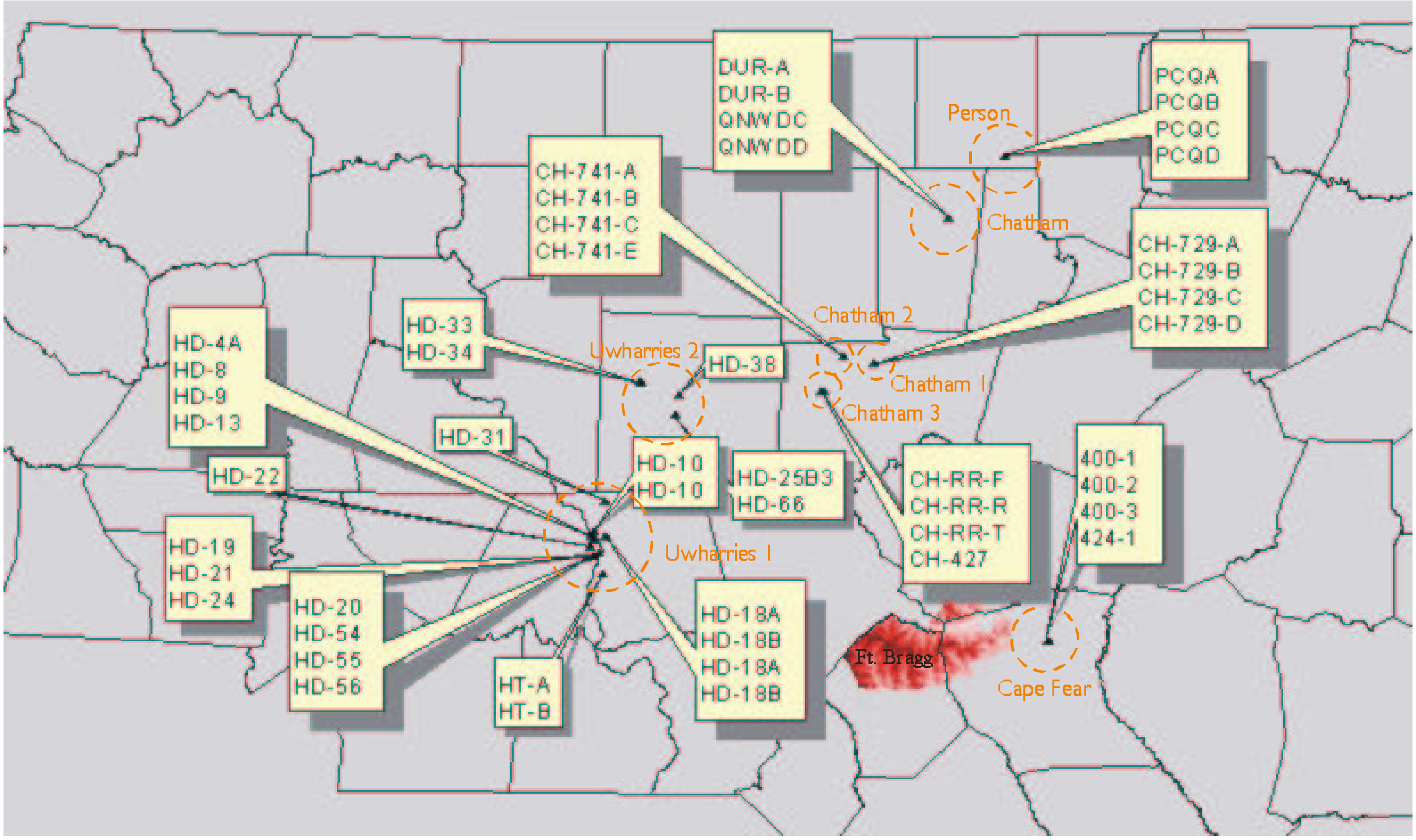

Figure 1- Location of samples and quarry groups

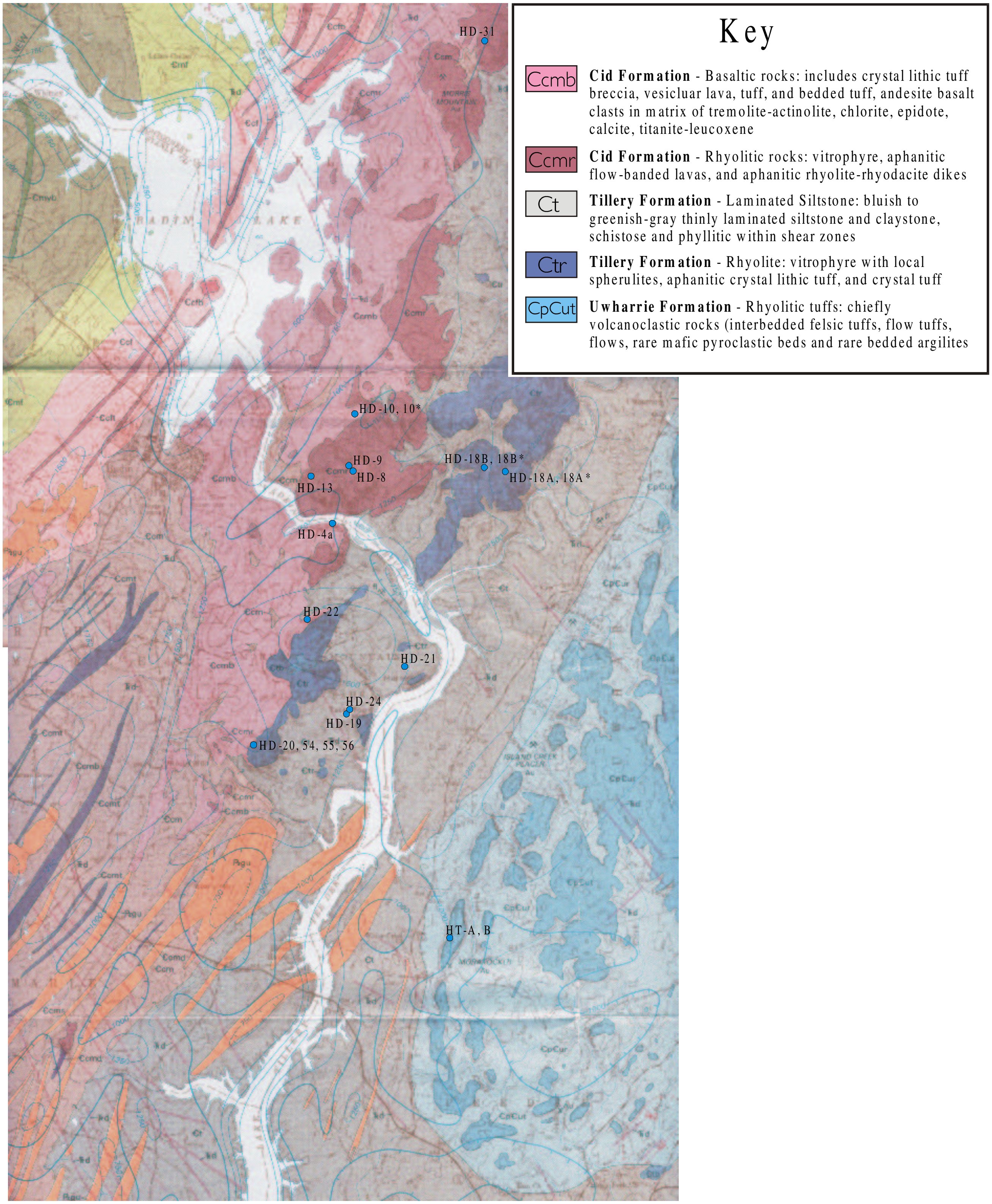

Figure 2 - Geologic map units and sample locations for group Uwharries 1

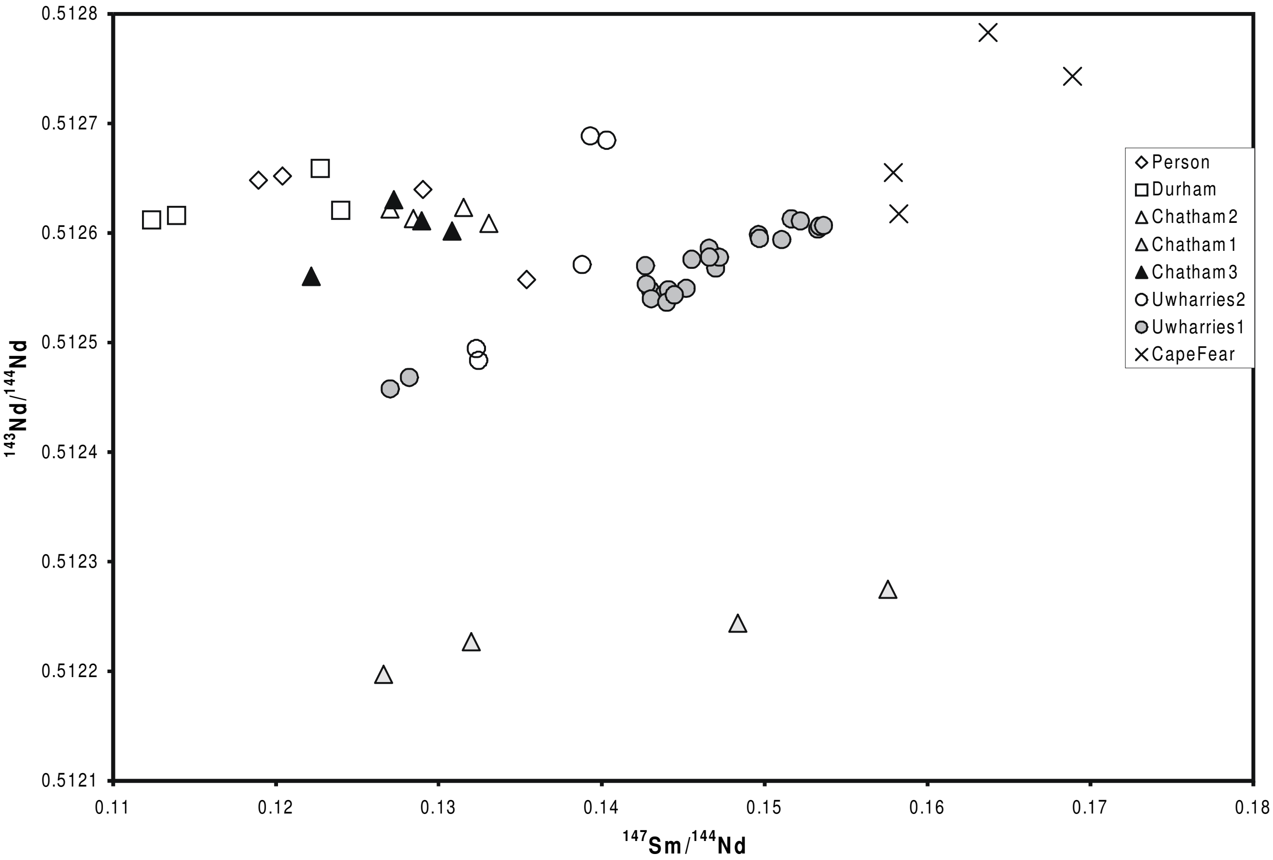

Figure 3 - Nd isotopic compositon of all samples, categorized according to quarry group.

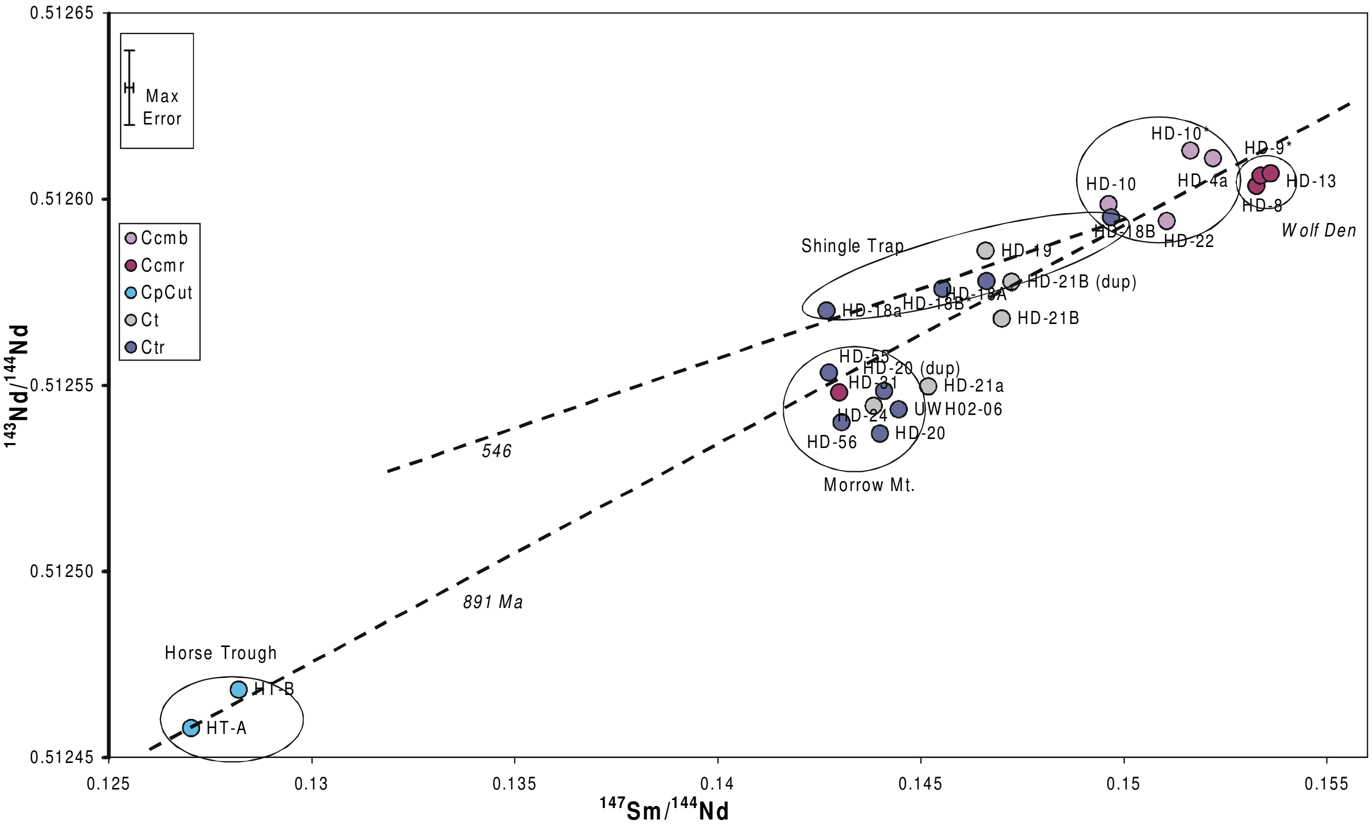

Figure 4 - Nd isotopic composition of samples from group Uwharries 1, categorized according to map unit (see Fig. 2).

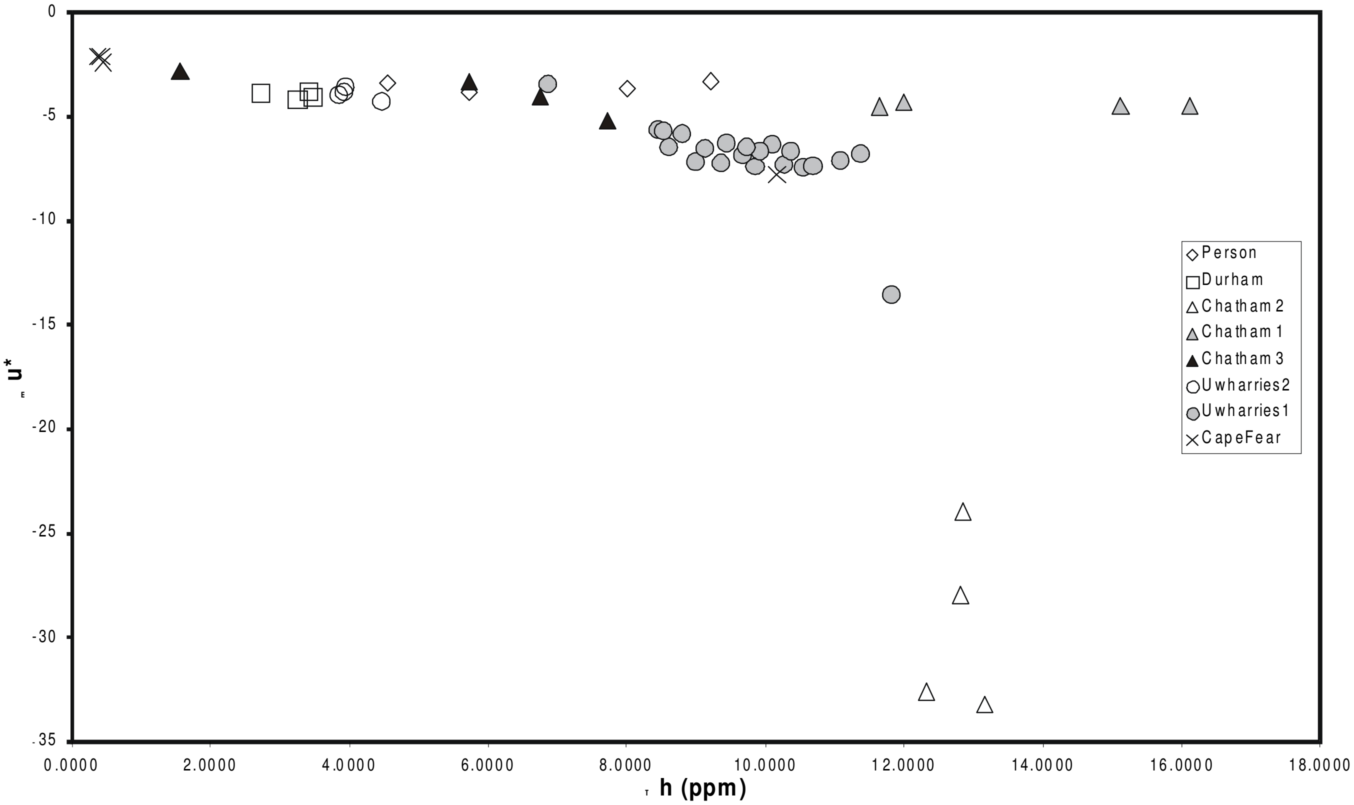

Figure 5 - Plot of two geochemical indicator elements. Eu* is the relative depletion of Eu compared to the geochemically similar elements Gd and Sm (see text for description and discussion).

Table 1 - Sm-Nd isotopic composition of samples from lithic quarry sites.

Sample	Group	Map Unit*	site number	northing	easting	Nd (ppm)	Sm (ppm)	$\frac{^{147}Sm}{^{144}Nd}$	$\frac{^{143}Nd}{^{144}Nd}$	Eu*	description
PCQA	Person		31PR115	4015567	688965	35.88	6.89	0.1189	0.512648	-3.303569	green metamudstone (?
PCQB	Person		31PR115	4015567	688965	39.27	8.59	0.1354	0.512558	-3.834032	aphyric dark gray fel
PCQC	Person		31PR115	4015567	688965	26.45	5.15	0.1204	0.512652	-3.624191	green felsite
PCQD	Person		31PR115	4015567	688965	17.49	3.65	0.1290	0.512640	-3.390610	metamudstone/metasilt
DUR-A	Durham		31DH703	3999181	684723	16.21	3.25	0.1240	0.512621	-3.830788	dk green fragmental r
DUR-B	Durham		31DH703	3999181	684723	22.98	4.56	0.1227	0.512659	-3.758368	dk gray aphyric felsi
QNWDC	Durham		31DH703	3999181	684723	28.06	5.09	0.1123	0.512612	-4.046046	gray aphyric felsite
QNWDD	Durham		31DH703	3999181	684723	28.56	5.26	0.1139	0.512616	-4.163232	pale green felsite
CH-741-A	Chatham2		31CH741	3964340	647964	59.43	12.63	0.1315	0.512623	-23.962455	purple spherulitic fe
CH-741-B	Chatham2		31CH741	3964340	647964	60.39	12.39	0.1270	0.512622	-32.596648	purple felsic breccia
CH-741-C	Chatham2		31CH741	3964340	647964	61.08	12.67	0.1284	0.512613	-33.186396	dark gray aphanite
CH-741-E	Chatham2		31CH741	3964340	647964	59.06	12.70	0.1331	0.512609	-27.962570	dark purple/black bre
CH-729-A	Chatham1		31CH729	3962302	655654	23.10	5.54	0.1484	0.512244	-4.525956	felsic aphanite/mudst
CH-729-B	Chatham1		31CH729	3962302	655654	42.17	8.99	0.1320	0.512227	-4.499450	laminated metamudston
CH-729-C	Chatham1		31CH729	3962302	655654	33.67	6.89	0.1266	0.512197	-4.294033	laminated metamudston
CH-729-D	Chatham1		31CH729	3962302	655654	58.27	14.83	0.1576	0.512275	-4.494651	felsic metasandstone
CH-427	Chatham3		31CH427	3955164	641835	19.99	4.11	0.1272	0.512630	-4.054436	v fine metasandst/sil
CH-RR-F	Chatham3		none	3955002	642790	23.99	5.07	0.1308	0.512601	-3.340972	dark gray lam. metamu
CH-RR-R	Chatham3		none	3955233	642626	22.19	4.62	0.1289	0.512611	-5.196515	plag +/- qtz phyric d
CH-RR-T	Chatham3		none	3955282	642442	36.04	7.11	0.1222	0.512560	-2.833110	fine green felsic tuf
HD-25b3	Uwharries2		31RD37	3949435	604806	19.53	4.18	0.1324	0.512484		felsic tuff and brecc
HD-25b-3 (dup)	Uwharries2					19.37	4.14	0.1323	0.512495	-4.054035	
HD-33	Uwharries2		31RD854/1201	3957254	596221	23.41	5.27	0.1393	0.512689	-3.533010	felsic tuff and brecc
HD-34	Uwharries2		31RD855/1202	3957764	595700	23.05	5.22	0.1403	0.512685	-3.811229	felsic tuff and brecc
HD-38	Uwharries2		none	3954018	605863					-3.918138	felsic tuff and brecc
HD-66	Uwharries2		31RD37	3949435	604806	20.25	4.54	0.1388	0.512571	-4.243016	felsic tuff and brecc
HD-10	Uwharries1	Ccmb	31MG117	3919205	584222	32.42	7.84	0.1496	0.512599	-6.811603	plag-phyric rhyolite
HD-22	Uwharries1	Ccmb	31ST67	3915034	583325	24.37	5.95	0.1511	0.512594	-7.202471	plag-qtz phyric rhyol
HD-10*	Uwharries1	Ccmb	31MG117	3919205	584222	29.98	7.35	0.1516	0.512613	-6.291353	plag-phyric rhyolite
HD4a	Uwharries1	Ccmb	none	3916984	583805	30.93	7.61	0.1522	0.512611	-5.768285	plag-phyric rhyolite
HD-31	Uwharries1	Ccmr	31MG641	3926914	586797	27.56	6.37	0.1430	0.512548	-3.401680	plag-phyric rhyolite
HD-8	Uwharries1	Ccmr	31MG639	3918064	584215	28.93	7.16	0.1533	0.512604	-5.595110	plag-phyric rhyolite
HD-9*	Uwharries1	Ccmr	31MG639	3918154	584125	27.06	6.70	0.1534	0.512606	-6.445993	plag-phyric rhyolite
HD-13	Uwharries1	Ccmr	31MG640	3917943	583375	27.95	6.94	0.1536	0.512607	-5.632539	plag-phyric rhyolite
HT-A	Uwharries1	CpCut	*31MG378,31	3908577	586311	24.89	5.11	0.1270	0.512458	-7.140960	plag-qtz phyric felsi
HT-B	Uwharries1	CpCut	*31MG378,31	3908577	586311	25.30	5.24	0.1282	0.512468	-6.517990	plag-phyric felsite
HD-24	Uwharries1	Ct	31ST64	3913131	584180	26.71	6.21	0.1438	0.512544	-7.416400	aphyric rhyolite
HD21a	Uwharries1	Ct				22.73	5.33	0.1452	0.512550		
HD-19	Uwharries1	Ct	31ST68	3913174	584185	37.51	8.88	0.1466	0.512586	-13.477832	plag-qtz phyric rhyol
HD21b	Uwharries1	Ct				32.04	7.61	0.1470	0.512568		
HD21b (dup)	Uwharries1	Ct				31.91	7.59	0.1472	0.512578		
HD-21	Uwharries1	Ct	31ST66	3914094	585325					-7.362399	plag-qtz phyric rhyol
HD-20 (dup)	Uwharries1	Ctr				30.70	7.15	0.1441	0.512548		
HD-18a	Uwharries1	Ctr	31MG554	3918069	587355	35.15	8.10	0.1427	0.512570	-6.241311	plag-qtz phyric rhyol
HD-55	Uwharries1	Ctr	31ST18	3912457	582233	26.56	6.12	0.1427	0.512553	-7.261928	aphyric rhyolite
HD-56	Uwharries1	Ctr	31ST18	3912457	582233	28.08	6.49	0.1430	0.512540	-7.321101	aphyric rhyolite
HD20	Uwharries1	Ctr	31RD18	3912457	582233	31.24	7.27	0.1440	0.512537	-6.772672	aphyric rhyolite
UWH02-06	Uwharries1	Ctr				26.78	6.25	0.1445	0.512544		
HD-18B*	Uwharries1	Ctr	31MG554	3918158	586937	27.91	6.56	0.1455	0.512576	-6.601610	plag-qtz phyric rhyol
HD-18A*	Uwharries1	Ctr	31MG554	3918069	587355	29.90	7.08	0.1466	0.512578	-6.637916	plag-qtz phyric rhyol
HD-18b	Uwharries1	Ctr	31MG554	3918158	586937	36.92	8.93	0.1497	0.512595	-6.409012	plag-qtz phyric rhyol
HD-54	Uwharries1	Ctr	31ST18	3912457	582233					-7.079123	aphyric rhyolite
400-1	CapeFear		31CD400	3891155	700233	15.10	3.99	0.1637	0.512783	-7.762961	white musc + gar apli
400-2	CapeFear		31CD400	3891155	700233	20.48	5.22	0.1579	0.512655	-2.099447	dk green metass/hornf
400-3	CapeFear		31CD400	3891155	700233	13.40	3.42	0.1582	0.512618	-2.394173	greenstone or metasan
424-1	CapeFear		31CD424	3891125	700463	12.89	3.52	0.1689	0.512743	-2.127175	v fine greenstone (?)
HD57b						31.52	8.83	0.1733	0.512520		
HD41b						29.78	5.92	0.1231	0.512581		
HD57a						38.71	9.09	0.1454	0.512575		
HD57b (dup)						31.10	8.74	0.1740	0.512541		
HD-41a						24.66	6.25	0.1570	0.512589		

* Map units based on Stromquist & Henderson (1985)