

THE UTILIZATION OF RARE EARTH ELEMENT CONCENTRATIONS FOR THE CHARACTERIZATION OF SOAPSTONE QUARRIES

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INTRODUCTION

The use of trace elements to characterize certain lithic and ceramic artifacts is well established. In most provenance studies of this type numerous artifacts are analyzed for a variety of minor and trace elements. The results are examined in order to group those artifacts having similar compositions. The assumption is made that the same raw material was used to manufacture those objects which are of similar composition. This type of investigation has been greatly aided by the development of computer programs designed for pattern recognition. Such programs are not only valuable for the management of large amounts of data, but they do help establish the statistical significance of this grouping of artifacts (e.g. Jurs and Isenhour 1975, de Bruin *et al.* 1972).

An alternative approach can be used for some types of artifacts. When there is a limited source of raw materials and this source can be found then the artifacts can be matched to materials from these sources (Allen *et al.* 1975). Soapstone was a resource with limited availability and the rare earth elements (REE) have proven to be particularly valuable in the characterization of soapstone quarries and artifacts (Allen and Pennell 1978). Matching artifacts to the source of the raw materials can reveal the patterns of resource procurement that existed in prehistoric times. However, misinterpretation and error can result from improper collection or selection of samples. Since 'raw materials' are geological specimens from a geological formation, the archaeologist must know enough about geology to select materials which would have been suitable for use by prehistoric man. In some cases the 'quarry' area may be easily identified by evidence of prehistoric manufacturing or by its proximity to a known archaeological site.

Soapstone is a general term used to describe metamorphic rocks which are composed primarily of talc (hydrous magnesium silicate) but which may contain varying quantities of chlorite, amphibole, and carbonate minerals. These talcose rocks were formed by metamorphism. The behaviour of trace elements during the formation of soapstone by metamorphic reactions in a serpentinite body was investigated (Williams 1977). This study indicated that the concentrations of the rare earth elements (as well as other trace elements) showed relatively little variation through the soapstone body even though the mineralogy (talc, antigorite, chlorite, and tremolite) varied considerably. There were samples near the edge of the alteration zone which did not fit into this pattern and had far higher concentrations. Analysis

of a number of soapstone formations, has supported the idea that soapstone from a particular geological formation has trace element concentrations which are independent of the exact mineralogy as long as the sample does not come from near the margins of the reaction zone. Analysis of these geological samples has also shown that soapstone from different geological formations could be distinguished on the basis of the REE distributions (Rogers 1981, Pennell 1977). There has been one major problem with the attempts to match soapstone artifacts to their source quarries on the basis of trace element concentrations and this has been the lack of geological samples from all possible soapstone quarries. When an artifact is analyzed which has a REE distribution pattern similar to a quarry it has been difficult to match them in a reliable way without knowing how much and what kind of variation in the trace elements is characteristic of the particular geological formation.

The problems with the identification of soapstone quarries became most acute in the study of soapstone utilization along the Labrador coast where artifacts from various locations, representing Indian and Eskimo cultures spanning a 4000 year period, have been analyzed (Rogers 1981, Allen *et al.* 1978).

MATERIALS AND METHODS

Sample description

An effort was made to identify soapstone outcrops and collect enough material in order to characterize the geological formation. One quarry sampled was at Peabody Point (figure 1) in Seven Island Bay near the northern tip of Labrador. Large numbers of debitage samples were also collected from nearby Komaktorvik. Further south along the coast a quarry on Rose Island in Saglek Bay (7 samples) and one at Cape Nuvotannak (21 samples) were visited and sampled. Even further south along the coast (south of Hopedale) a large group (28 samples)

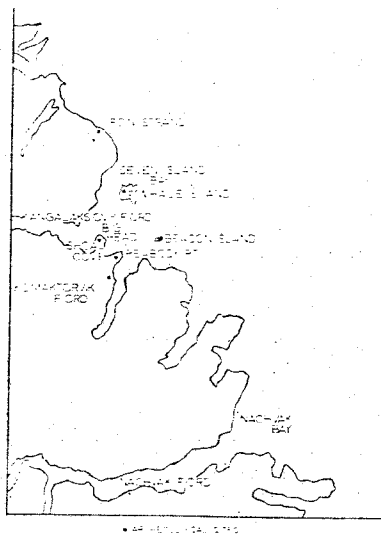


Figure 1 Map of the northeastern coast of Labrador showing the region around Seven Island Bay

of geological samples were collected at the McNeill outcrop in the Bay of Islands. In addition to the geological materials, fragments of soapstone lamps and bowls and debitage were collected at archaeological sites in the region of each suspected quarry.

Analytical methods

All samples were analyzed by instrumental neutron activation analysis (INAA) following procedures similar to those described elsewhere (Allen *et al.* 1975, Allen *et al.* 1978). For this work a soapstone standard was prepared from a large sample soapstone block (5 kg) from the Albemarle-Nelson County quarries in Virginia. This material was ground, homogenized, sampled, and analyzed using several U.S.G.S. standard rocks and aqueous standards for the REE.

Samples were counted three to ten days after irradiation to determine short half-life elements and then thirty days after irradiation for those with long half-lives. In many cases, the REE concentrations were very low, and approached the limits of our sensitivity. Only ten of the REE are routinely analyzed. The others are either obscured by interfering peaks from other elements or are of insufficient intensity to be measured effectively. On the basis of our knowledge of REE behavior in geochemical systems it is felt that accurate analysis of La, Sm, Eu, Gd, and Yb or Lu is sufficient to define the REE distribution pattern. Problems in the analysis of Gd were of greatest consequence because the character of the REE distribution patterns is very dependent upon the Gd concentration. Ta has been identified as a consistent interference in the detection of Gd especially when the Gd concentrations are low. Three γ -ray peaks are detectable for Tb although two are susceptible to interferences so the Tb concentrations can help to define the trend in the REE pattern near the Gd and can be used in the case of poor Gd detection. A number of other trace elements including Cr, Fe, Co, and Sc are always measured while some elements, As, Sb, Hf and Ta are often measured although they are not always present in detectable concentrations.

REE DISTRIBUTION CURVES

The REE are a unique family of fourteen elements since the geochemistry of this group of elements is determined by the sizes of the trivalent (+3) ions. There is a relatively smooth decrease in size of the trivalent REE ions with (lanthanum being the largest) increasing atomic number which is called the Lanthanide Contraction. Since the size of the REE ion determines the ease with which it can substitute in minerals the REE elements show a smooth trend in the concentrations found in rocks when the results are shown as a function of atomic number. Before making such a plot, the concentration of each rare earth element is divided by the measured concentration of that element in chondritic meteorites. This normalization gives distribution patterns which are representative of the terrestrial geochemical processes since the REE concentrations in these meteorites are considered to be representative of the undifferentiated material from which the earth was made (Haskin *et al.* 1966). This is also necessary since elemental abundances exhibit an odd-even effect and elements with paired protons (even atomic numbers) have greater nuclear stability and hence are more abundant than the element with one proton more. Normalization removes this artifact of nucleosynthesis and allows one to observe the separation of the REE from each other due to the geochemical processes which lead to the formation of the rock.

RESULTS AND DISCUSSION

The geological samples from Peabody Point give a good indication of the care that must be taken in the interpretation of the REE data from a soapstone quarry. The characteristic REE distribution patterns for Peabody Point samples are shown in figure 2. The REE concentrations are all very low compared to igneous rocks with 6 of the 10 samples showing patterns like *A* and *C* and the other 4 are like *B*. The variability in absolute concentrations for samples with patterns like *A* is indicated by comparing this sample (with the lowest concentration) with sample *C* (the highest). The main difference in the REE patterns *A* and *B* is in the concentrations of the heavier elements (Lu end). The significance of these differences in REE distributions can only be understood by considering the geochemical factors which effect the REE concentrations in rocks. During various geological processes trace elements can substitute for major elements in the crystal lattice of a mineral. The degree to which these impurities can substitute in a particular mineral lattice depends upon how nearly the charge and radius of the ion matches the lattice dimensions (referred to as Goldschmidt's rule, Goldschmidt

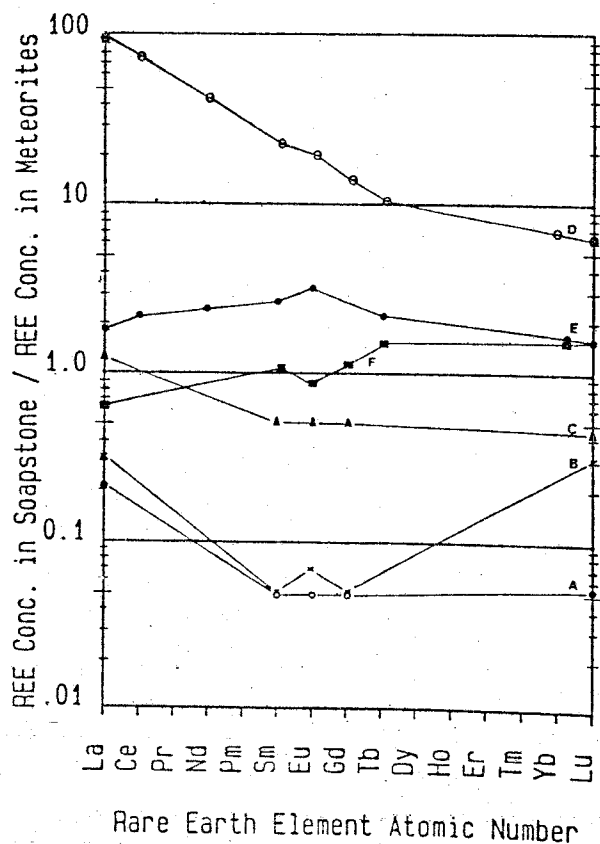


Figure 2 Geological samples, Peabody Point, Newfoundland. Major REE patterns, (A, B, C) representative of soapstone from Peabody Point, Newfoundland. (D) hard serpentinite, not soapstone, (E) talc sample with chlorite crystals, (F) prevalent REE pattern for some debitage samples that resembles Outcrop in Newfoundland.

1954). Since the ionic radius of the + 3 REE ions varies, the REE ions will be separated (differentiated) from each other on the basis of their ability to fit into a mineral lattice. The results of such separations are shown graphically by the plots like figure 2. In a rock these patterns represent a mixture of several minerals and may be the result of several geological events each of which changes the REE distributions. There are at least some cases where the REE pattern is more important in characterizing the material than the absolute concentrations. One such case is when large portions of the total REE impurities are located in a minor mineral which is distributed inhomogeneously through the rocks in a particular geological body. In soapstone there are several minerals which appear to fractionate the REE in a similar manner, but there are variations in the absolute amounts of REE which are accepted in each type of mineral lattice. Thus mixtures of these minerals would have similar patterns while varying in absolute concentrations. Our experience with numerous soapstone quarries has led us to the conclusion that the considerable variation in magnitude of the absolute concentrations (*A* and *C* in figure 2) is typical when the REE concentrations are very low (below those found in chondritic meteorites).

In order to facilitate comparisons, one can take all the results for samples which are characteristic of an outcrop and devise a composite pattern based upon averaging the logs of each REE concentration. By noting the variation in absolute abundances it is possible to look for artifacts with similar patterns and falling within the range observed for the 'quarry'. In addition to the two types of patterns characteristic of this quarry, there were also several samples which were collected as soapstone but upon examination proved to be serpentinite, a metamorphic rock often found associated with soapstone deposits. The pattern (*D* in figure 2) of the REE distributions and the absolute concentrations are very different from the soapstone. What is more important is to avoid including materials which are not soapstone (and which would not have been utilized by prehistoric man) with the materials used to characterize the quarry. Another sample from Peabody Point contained long, light green crystals of chlorite and the REE pattern (*E* in figure 2) was significantly different from the other 10 soapstone samples. An analysis of the green crystals themselves showed that pattern *E* was characteristic of this chlorite. While chlorite is present in some of the other Peabody Point samples, it occurs as much smaller grains. The geological setting from which sample *E* was collected is not known, but there were some analogous samples with large chlorite crystals found in the region nearer the margin of the metamorphic reaction zone in a soapstone body in California (Williams 1977). The higher concentrations of REE near the margin of the reaction zone was interpreted to be the result of a deposition of trace elements derived from the more metamorphosed talc rich zone. If trace element rich rocks are a general characteristic of materials from the edge of metamorphic reaction zones, then care must be taken to collect sufficient samples in order to recognize these materials which have the higher concentrations.

The 28 geological samples from the Bay of Islands fall within the range shown bracketed by samples *A* and *B* in figure 3. These samples give some indication of how much variation in actual REE concentrations is found in soapstone from a particular geological formation when the concentrations are greater than found in meteorites.

Results from the Johannes Point quarry shows how too small a sample set can be misleading. Initially only 3 samples were analyzed and resulted in the two REE patterns shown in Figure 4. Based on only three samples, two (figure 4, curve *A* and *B*) had similar patterns while one sample (curve *C*) was higher in absolute concentration and had a greater partitioning of the elements between La and Eu. While there was a question about how characteristic curve *C* was,

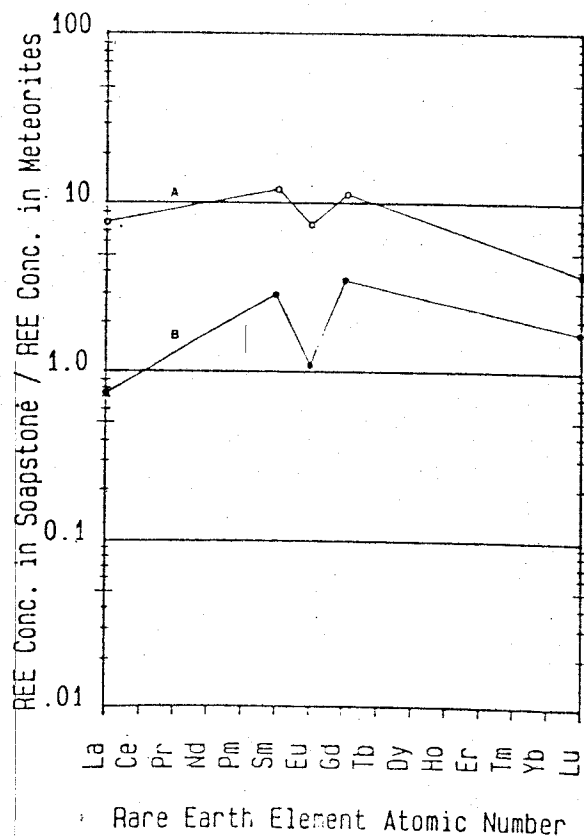


Figure 3 Geological samples, Bay of Islands, Newfoundland. A total of 28 samples of soapstone from this quarry had REE patterns which fell between samples A and B.

the analysis of four additional samples looked like curve D and showed that this was indeed characteristic of the soapstone from Johannes Point. Only a careful geological examination of the area could give a good explanation of why these two patterns are found.

Further evidence for the need of extensive sampling of a suspected quarry region is shown by two other relatively large sample sets. Over 80% of the 21 geological samples from Cape Nuvotannak fall within the range between curves A and B of figure 5. Those Cape Nuvotannak samples which did not fall within the range (between A and B) of absolute concentrations that seems to be most characteristic of the quarry had concentrations more like curve C. The significant difference in the patterns is the degree of partitioning between the larger (La) and smaller (Lu) ions and not the absolute concentrations.

The necessity of careful examination of a small set of quarry samples is shown by the material from Saglek. Four of the seven were good soft talc soapstone and gave matching REE patterns (figure 5, curve D). The other 3 samples were much harder (probably unusable for producing bowls), were composed primarily of serpentinite, and had higher REE concentrations with large negative Eu anomalies. By comparison with our previous geochemical studies we interpret one sample as unaltered country rock, while two were

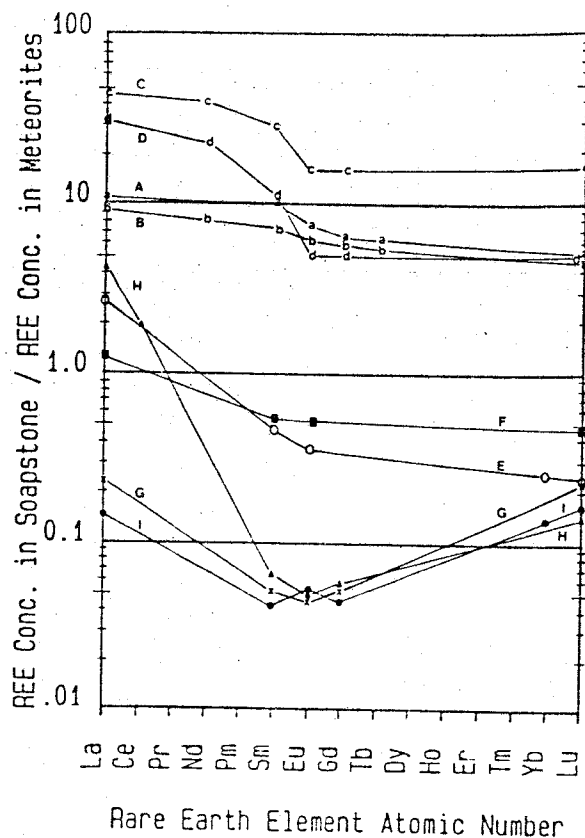


Figure 4 Geological samples, Johannes Point, Newfoundland. (A, B, C) Curves from initial analysis of Johannes Point samples. (D) typical curves for five soapstone samples from Johannes Point. (E and G) curves are representative of 68% of the debitage from Komaktorvik while (F) is the REE pattern for soapstone from the nearby Peabody Point Quarry. Sample H is debitage while sample I is a soapstone bowl fragment found at Komaktorvik.

partly altered and may come from near the margin of the reaction zone (Allen and Pennell 1978).

Based upon the analysis of the quarry specimens from Laborador, it is clear that a geologist should collect or examine samples. In the case of soapstone it is often enough to determine the hardness of the rock. Utilization of soapstone in earlier cultures required that it be reasonably carvable and people were probably quite discriminating in their choice of raw materials. At some soapstone quarries partially carved preforms or indentations where soapstone was taken give clear evidence of an actual quarry and shows the type of rock that was used. Another source of information may be the debitage left from the manufacture of lithic objects. Ethnographic evidence indicates that the initial steps in the manufacturing are carried out at or near the quarry (e.g. Fitzhugh 1976). In the case of soapstone one would expect that a large amount of debitage with the same trace element 'fingerprint', could be used to characterize a nearby soapstone quarry. Since this does represent the quality of material that was actually being used, the selecting of proper geological samples for analysis is already accomplished.

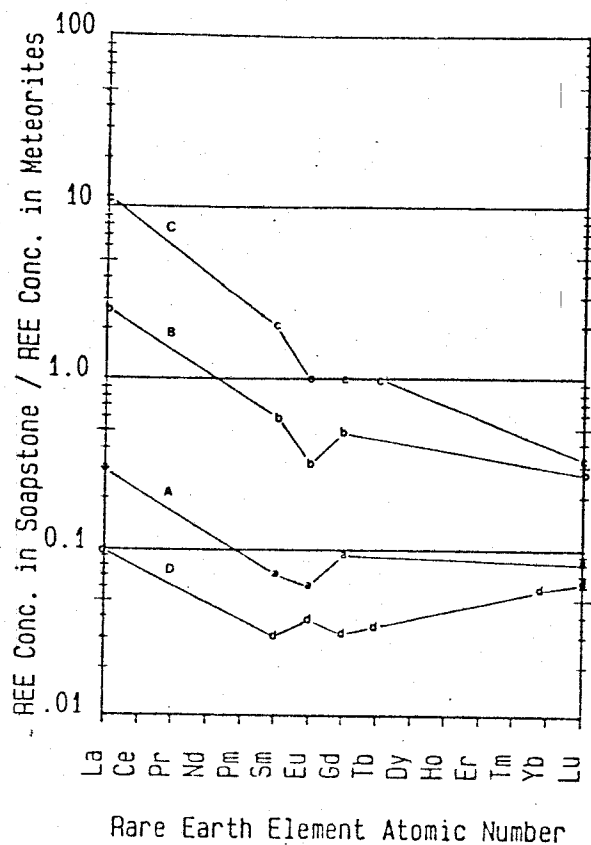


Figure 5 Geological samples, Cape Nuvotanniak and Saglek, Newfoundland. 17 Cape Nuvotanniak samples fall between curves A and B but several had patterns like curve C. Sample D is from Saglek Quarry.

An archaeological site at Komaktorvik (figure 1) near Peabody Point allowed this concept to be tested.

The debitage analyzed from Komaktorvik exhibited three basic REE distribution patterns. The first type, curve *E* in figure 4, is clearly related to the major pattern associated with the Peabody Point quarry (curve *F*). Over 21% of the debitage samples match this pattern and were presumably from the nearby Peabody Point quarry. Another 47% of the debitage (curve *G*) also matches soapstone from Peabody Point, (curve *B*, figure 2). This result is particularly interesting because Komaktorvik debitage was analyzed before the samples from the Peabody Point quarry. The debitage showed that a major outcrop, existed in the Komaktorvik area. Indeed, further sampling and analysis of geological samples from Peabody Point revealed the source of the material with this characteristic REE pattern.

The third type of debitage (figure 4*H*) is only somewhat different from the Peabody quarry pattern. The major difference is the partitioning of the lighter REE (La, Ce, Nd). There seems to be a gradation with several debitage samples falling between curves *H* and *G* (which represents the primary Peabody pattern). Similar trends were observed for a series of outcrops in Maryland and Northern Virginia (Pennell 1977) so the material represented by curve *H* may be

from another nearby-outcrop which has not been sampled. Other debitage which matched the geological samples from Peabody Point came from neighboring sites in the Seven Islands Bay area (Peabody Point, Big Head, Beacon Island, Shoal Cove, Whale Island and Iron Strand in figure 1). One particular debitage sample from the Peabody Point site was matched to the Peabody quarry in an unusual way. The sample appeared to be composed largely of chlorite crystals and in fact its pattern matched the chlorite crystal pattern seen in the Peabody quarry samples.

Thus, of all the debitage from this area, about 78% of it originated from the nearest known outcrop, at Peabody Point. The remaining material could be from local outcrops which have not been sampled or more distant sources could be represented by material from the reworking and repairing of finished vessels brought from other locations. It is also important to consider that some of the debitage may not have been soapstone which was very talcose, soft and light in color. These were harder, darker materials which were probably not as carvable and had higher REE concentrations. This could represent material discarded from or chipped off the more usable sections of a soapstone block. Some of the debitage samples from the Komaktorvik area, however, could be soapstone from non-local sources.

The debitage sample represented by curve *F* (figure 2) is different from other Peabody Point materials as it has a positive slope between La and Sm. A similar pattern has been found for geological samples from an outcrop located on the northern coast of the island of Newfoundland. This would indicate a considerable distance from transportation, but until other outcrops are found which have this pattern this is the only source of this soapstone fragment that we can suggest. Artifacts have been found with this same pattern. We can not rule out the existence of another quarry with this positive La-Sm slope feature in the northern Labrador area.

CONCLUSIONS

Establishing the characteristics and variability of a particular geological formation is necessary before attempting to match artifacts. The most valuable approach is a careful geological and geochemical study, but this is impractical for each quarry. Therefore extensive sampling along with some sample selection is the next best approach. Finally it does appear the analysis of debitage can give the characteristics of the nearby sources of raw materials, but the results may be confused by material from other areas as well. Once an average or characteristic pattern (or patterns) is established for a quarry, the patterns for a particular artifact can be visually compared (matched) to the quarry patterns. If the patterns match, but the absolute abundance differs, then one must look at the extent of such variations found in the quarry samples. This may be useful for small groups of samples, but for extensive provenance studies a method must be found to determine the 'goodness of fit' for single samples when matched with a collection of known samples. Here pattern recognition programs are of great value since the quarry samples can be used as 'learning sets'.

Since the geochemistry of the REE suggests that the relative distributions (patterns) are probably even more characteristic of a geological formation than the absolute abundances, the normal approach of using trace element concentrations in the pattern recognition program may not be adequate. We have taken the approach that the pattern can be represented by such features as the slope of a line between the log of the chondrite normalized La concentration ($\log [La]_n$) and $\log [Sm]_n$ as a function of atomic number. This slope represents the fractionation that occurs as a function of ionic radius from 1.14 Å (La) to 1.00 Å (Sm). The slope from

$\log [\text{Gd}]_n$ to $\log [\text{Lu}]_n$ is another important feature which reflects the partitioning of ions between 0.97 Å (Gd) and 0.85 Å (Lu). A third feature is the Eu anomaly (size and direction) which can be measured as the difference between the actual concentration and that predicted by averaging the log of the normalized Sm and Gd concentrations. The final characteristic is the absolute value of the concentration of one of the elements, and this is the factor which shows the greatest variation in the learning set. Using this approach does give artifact matches and a statistical measure of how well the sample agrees with the quarry. A detailed analysis of patterns of soapstone procurement will be the subject of future papers, however some results of the analysis of artifacts are worth mentioning here. Approximately 48% of the artifacts from the Seven Islands Bay area matched the Peabody Point quarry patterns. This includes 90% of the artifacts from habitation sites at Peabody Point. The artifacts which did not match these quarry patterns did have REE distribution patterns which had also been observed for some of the debitage. A new REE pattern was seen for a group of artifacts from the Middle Dorset period and the nearest quarry showing the same pattern is at the Bay of Islands. The possible changes in the quarry utilization from culture to culture and period to period are of great significance. Proof of such changes can only come from careful scientifically based provenance studies of resource materials. An understanding of geochemical processes helps establish the significance of trace element differences in natural materials.

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