Compositional Analysis of Ceramics from Carriacou, Grenada, West Indies

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INTRODUCTION

A wide array of ceramics, mostly from Carriacou in the Lesser Antilles were analyzed by instrumental neutron activation analysis (INAA) at the University of Missouri Research Reactor Center (MURR). Scott M. Fitzpatrick submitted the fifty samples in this pilot study. The sample includes ceramic specimens from 8 sites in Carriacou (Lauriston, Sabazan, Jew Bay, Tyrell Bay, Great Bretache Bay, Dover, Grand Bay, and St. Louis) and the nearby island of Petite Martinique. The ceramic samples from Carriacou will address issues related to the compositional diversity of the island's ceramics to understand processes of ceramic production and exchange through time. The sample preparation and analytical techniques used at MURR and the analytical results of the compositional analysis are reported here.

SAMPLE PREPARATION

The ceramics were prepared for INAA using standard MURR procedures. Pieces of each sherd were burred with a silicon carbide burr to remove painted or slipped surfaces and adhering soil. The burred sherd samples were then washed with deionized water and allowed to dry in air. These were then crushed in an agate mortar to yield a fine powder. Where possible a portion of each specimen was retained, unpowdered, for the MURR archive of analyzed ceramic fabrics.

The powder samples were oven-dried at 100 degrees C for 24 hours. Portions of approximately 150 mg were weighed and placed in small polyvials used for short irradiations. At the same time, 200 mg of each sample were weighed into high-purity quartz vials used for long irradiations. Along with the unknown samples, reference standards of SRM-1633a (coal fly ash) and SRM-688 (basalt rock) were similarly prepared, as were quality control samples (e.g., standards treated as unknowns) of SRM-278 (obsidian rock) and Ohio Red Clay.

IRRADIATION AND GAMMA-RAY SPECTROSCOPY

Neutron activation analysis of ceramics at MURR, which consists of two irradiations and a total of three gamma counts, constitutes a superset of the procedures used at most other laboratories (Glascock 1992; Neff 1992, 2000). As discussed in detail by Glascock (1992), a short irradiation is carried out through the pneumatic tube irradiation system. Samples in the polyvials are sequentially irradiated, two at a time, for five seconds at a neutron flux of 8×10^{13} n cm^{-2} s^{-1}. The 720-second count yields gamma spectra containing peaks for nine short-lived elements aluminum (Al), barium (Ba), calcium (Ca), dysprosium (Dy), potassium (K), manganese (Mn), sodium (Na), titanium (Ti), and vanadium (V). The samples encapsulated in quartz vials are subjected to a 24-hour irradiation at a neutron flux of 5×10^{13} cm^{-2} s^{-1}. This long irradiation is analogous to the single irradiation utilized at most other laboratories. After the long irradiation, samples decay for seven days, and then are counted for 1800 seconds (the "middle count") on a high-resolution germanium detector coupled to an automatic sample changer. The middle count yields determinations of seven medium half-life elements, namely arsenic (As), lanthanum (La), lutetium (Lu), neodymium (Nd), samarium (Sm), uranium (U), and ytterbium (Yb). After an additional three- or four-week decay, a final count of 9,000 seconds is carried out on each sample. The latter measurement yields the following 17 long half-life elements: cerium (Ce), cobalt (Co), chromium (Cr), cesium (Cs), europium (Eu), iron (Fe), hafnium (Hf), nickel (Ni), rubidium (Rb), antimony

(Sb), scandium (Sc), strontium (Sr), tantalum (Ta), terbium (Tb), thorium (Th), zinc (Zn), and zirconium (Zr).

Elemental concentration data from the two irradiations and three counts (a total of 33 elements) were assembled into a single tabulation and stored in a dBASE III file along with descriptive information available for each sample.

QUANTITATIVE ANALYSIS OF THE CHEMICAL DATA

The analyses at MURR described above produced elemental concentration values for 33 elements in most of the analyzed samples. As is customary in ceramic provenance studies at MURR (Bishop and Neff 1989), the data were converted to base-10 logarithms of concentrations. Use of log concentrations instead of raw data compensates for differences in magnitude between major elements, such as iron, on one hand and trace elements, such as the rare earth or lanthanide elements, on the other hand. Transformation to base-10 logarithms also yields a more nearly normal distribution for many trace elements.

The goal of quantitative analysis of the chemical data is to recognize compositionally homogeneous groups within the analytical database. Based on the "provenance postulate" (Weigand et al. 1977), such groups are assumed to represent geographically restricted sources or source zones. The location of sources or source zones may be inferred by comparing the unknown groups to knowns (source raw materials) or by indirect means. Such indirect means include the "criterion of abundance" (Bishop et al. 1982) or arguments based on geological and sedimentological characteristics (e.g., Steponaitis et al. 1996).

Initial hypotheses about source-related subgroups in the compositional data can be derived from non-compositional information (e.g., archaeological context, decorative attributes, etc.) or from application of pattern-recognition techniques to the chemical data. Principal components analysis (PCA) is one technique that can be used to recognize pattern (i.e., subgroups) in compositional data. PCA provides new reference axes that are arranged in decreasing order of variance subsumed. The data can be displayed on combinations of these new axes, just as they can be displayed relative to the original elemental concentration axes. PCA can be used in a pure pattern-recognition mode, i.e., to search for subgroups in an undifferentiated data set, or in a more evaluative mode, i.e., to assess the coherence of hypothetical groups suggested by other criteria (archaeological context, decoration, etc.). Generally, compositional differences between specimens can be expected to be larger for specimens in different groups than for specimens in the same group, and this implies that groups should be detectable as distinct areas of high point density on plots of the first few components.

One often exploited strength of PCA, discussed by Baxter (1992) and Neff (1994), is that it can be applied as a simultaneous R- and Q-mode technique, with both variables (elements) and objects (individual analyzed samples) displayed on the same set of principal component reference axes. The two-dimensional plot of element coordinates on the first two principal components is the best possible two-dimensional representation of the correlation or variance-covariance structure in the data. Small angles between vectors from the origin to variable coordinates indicate strong positive correlation; angles close to 90^{o} indicate no correlation; and angles close to 180^{o} indicate negative

correlation. Likewise, the plot of object coordinates is the best two-dimensional representation of Euclidean relations among the objects in log-concentration space (if the PCA was based on the variance-covariance matrix) or standardized log-concentration space (if the PCA was based on the correlation matrix). Displaying objects and variables on the same plots makes it possible to observe the contributions of specific elements to group separation and to the distinctive shapes of the various groups. Such a plot is called a "biplot" in reference to the simultaneous plotting of objects and variables. The variable interrelationships inferred from a biplot can be verified directly by inspection of bivariate elemental concentration plots (note that a bivariate plot of elemental concentrations is not a "biplot").

Whether a group is discriminated easily from other groups can be evaluated visually in two dimensions or statistically in multiple dimensions. A metric known as Mahalanobis distance (or generalized distance) makes it possible to describe the separation between groups or between individual points and groups on multiple dimensions. The Mahalanobis distance of a specimen from a group centroid (Bieber et al. 1976; Bishop and Neff 1989; Neff 2001; Harbottle 1976; Sayre 1975) is:

$$D^2_{y,X} = [y - \overline{X}]^t I_X [y - \overline{X}]$$

where y is 1 x m array of logged elemental concentrations for the individual point of interest, X is the n x m data matrix of logged concentrations for the group to which the point is being compared with $\overline{X}$ being its 1 x m centroid, and I_x is the inverse of the m x m variance-covariance matrix of group X. Because Mahalanobis distance takes into account variances and covariances in the multivariate group it is analogous to expressing distance from a univariate mean in standard deviation units. Like standard deviation units, Mahalanobis distances can be converted into probabilities of group membership for each individual specimen (e.g., Bieber et al. 1976; Harbottle 1976). For relatively small sample sizes, it is appropriate to base probabilities on Hotelling's T^2, which is a multivariate extension of the univariate Student's t.

With small groups, Mahalanobis distance-based probabilities of group membership may fluctuate dramatically depending on whether or not each specimen is assumed to be a member of the group to which it is being compared. Harbottle (1976) calls this phenomenon "stretchability" in reference to the tendency of an included specimen to stretch the group in the direction of its own location in the elemental concentration space. This problem can be circumvented by cross-validation (or "jackknifing"), that is, by removing each specimen from its presumed group before calculating its own probability of membership (Baxter 1994; Leese and Main 1994). This is a conservative approach to group evaluation that sometimes excludes true group members. All probabilities discussed below are cross-validated.

In the present case, all but one of the groups is smaller than the total number of variates, and this places a further constraint on use of Mahalanobis distance. With more variates than objects, the group variance-covariance matrix is singular thus rendering calculation of I_x (and D^2 itself) impossible. Dimensionality of the groups therefore must be reduced somehow. One approach to dimensionality reduction would be to eliminate elements considered irrelevant or redundant. The problem with this approach is that the investigator's preconceptions about which elements should best discriminate sources may not be valid; it also squanders one of the major strengths of INAA,

namely its capability to determine a large number of elements simultaneously. An alternative approach to dimensionality reduction, used here, is to calculate Mahalanobis distances not with log concentrations but with scores on principal components extracted from the variance-covariance or correlation matrix of the complete data set. This approach entails only the assumption, entirely reasonable in light of the above discussion of PCA, that most group-separating differences should be visible on the largest several components. Unless a data set is highly complex, with numerous distinct groups, using enough components to subsume 90% of total variance in the data may be expected to yield Mahalanobis distances that approximate Mahalanobis distances in the full elemental concentration space.

RESULTS & CONCLUSION

Exploratory data analyses were conducted on the thirty-three elemental abundance measurements before identifying compositional groups. We decided to drop the elemental concentrations of nickel from subsequent analyses because of its low detection limits. A two-group structure was identified in the ceramic specimens: Group 1 (n=30) and Group 2 (n=16). The compositional groups can be graphically represented in principal component space (Figures 1–2) and in elemental space (Figures 3). Statistical tests based on Mahalanobis distance-derived probabilities using eight principal components were conducted subsuming 90.7% of the total variance; see Table 1) to support the graphical representation of the group structure (Figures 1–3). A cut-off of 1% was generally used to refine the membership of Groups 1 and 2, however, exceptions were made based on the graphical representation of the data. Ten specimens (18%) could not be assigned to any of the identified compositional groups (Figures 2–3; Table 4). It is highly probable that analyzing more samples compositional groups could be identified more clearly in the Carriacou ceramic assemblage. Determining whether the identified compositional groups refer to local or exotic sources will require the submission of raw clay samples for chemical analysis or the mineralogical analysis of raw clay samples and ceramics from the island.

Chemical characteristics for the compositional groups are represented in Figure 1. Relative to Group 2, Group 1 clearly has elevated concentrations of antimony, dysprosium, and ytterbium. Antimony is a semi-metal whereas the other two are rare earth elements. Group 2, on the other hand, is enriched in two rare earth elements, an actinide, and a transition metal, that is cerium, lanthanum, thorium, and tantalum when compared to Group 1. Without more information, if the ceramics were locally made, it would appear at this stage to signify two distinct clay sources, possibly related to the two main geological zones (fossiliferous limestone vs. volcanic lava flows) mentioned in your proposal,

Given the small sample size and our unfamiliarity with your sampling strategy, only tentative statements can be made about the relationship between the provenience of the sherds and their group assignments (see Table 5). Interestingly, the Grand Bay site has almost equal amounts of both compositional types. Another possibly significant observation is that only Group 1 ceramics were collected from the sites of Dover, Lauriston and Sabazan while Jew Bay only has compositional Group 2 ceramics.

In sum, this study has identified two distinct ceramic compositional groups. Possible tendencies or associations between the chemical compositions of the sherds and their site provenience were

found. The submission of more samples from these contexts could further test these identified patterns as well as delineate more groups (seven of the ten unassigned samples clearly have no affinity with the two compositional groups) and subgroups.

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FIGURES

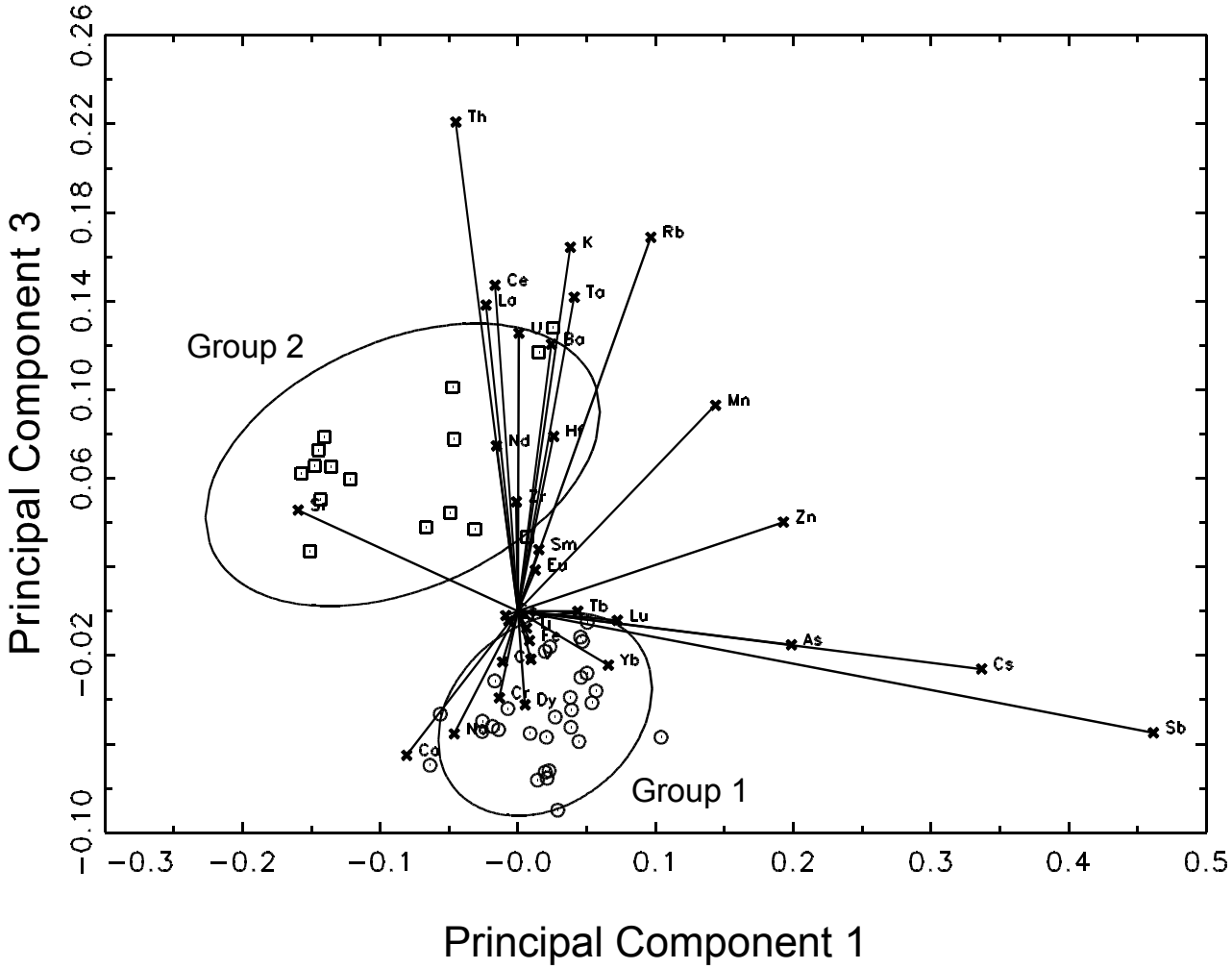


Figure 1: Bivariate plot of principal components 1 and 3 displaying two compositional groups. Ellipses represent 90% confidence level for membership in the groups. Vectors denote elemental influences on the ceramic data. Unassigned specimens are not shown.

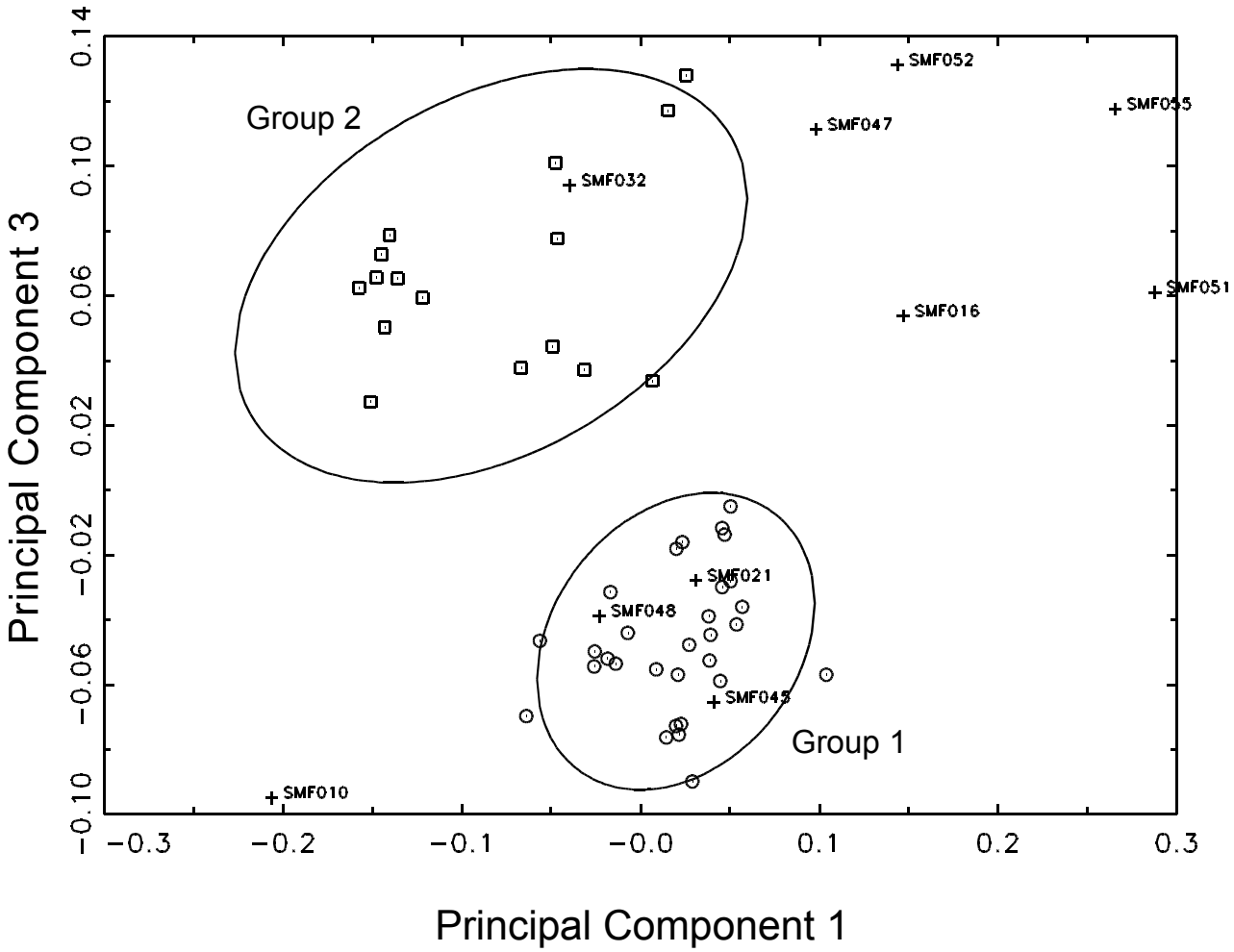


Figure 2: Bivariate plot of principal components 1 and 3 displaying the two compositional groups and labeled unassigned specimens (+). Ellipses represent 90% confidence level for membership in the groups.

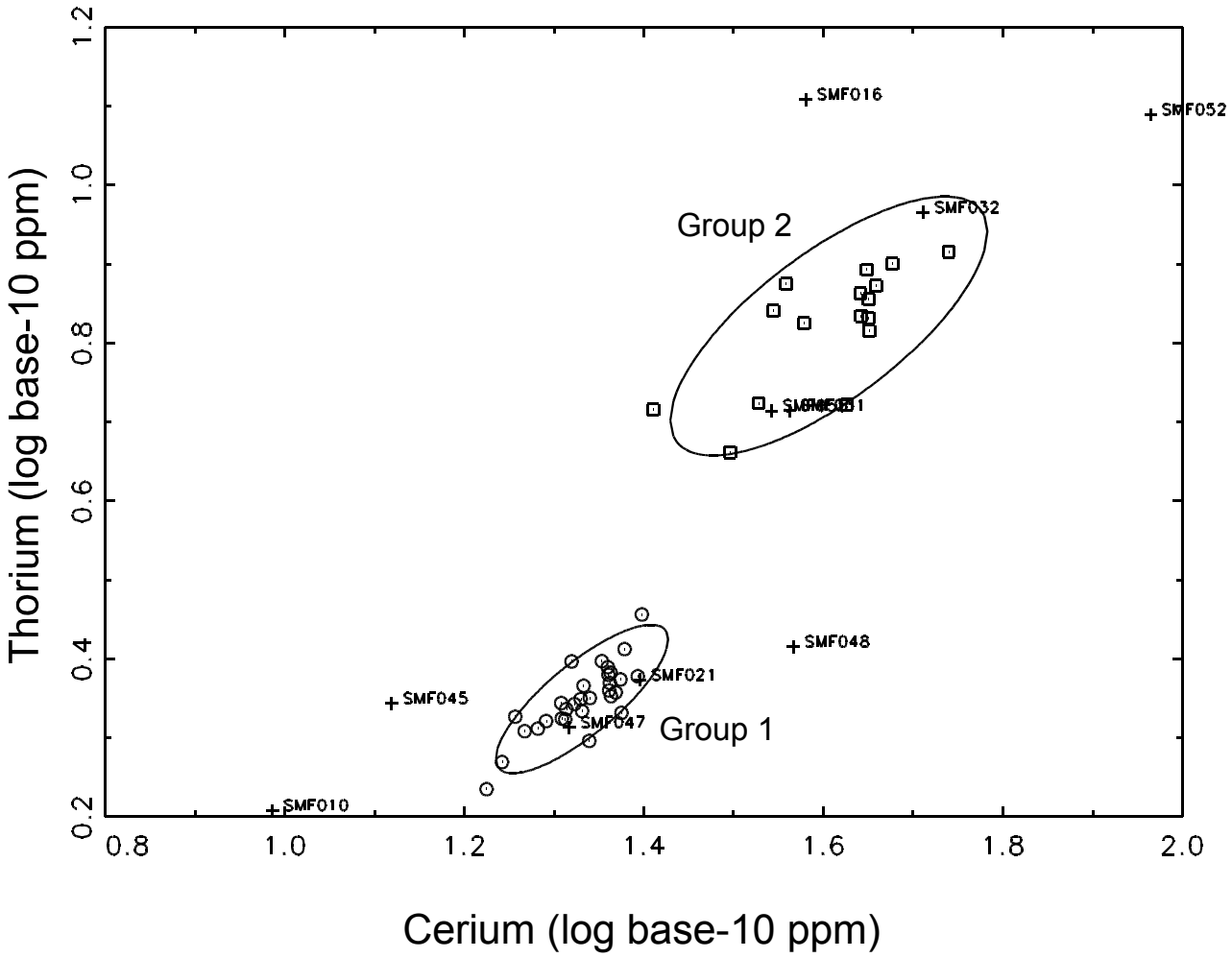


Figure 3: Bivariate plot of base-10 logged cerium and thorium concentrations showing the chemical distinctiveness of the two compositional groups Ellipses represent 90% confidence level for membership in the groups. Unclassified samples (+) are labeled.

TABLES

Table 1. Principal Components Analysis of 56 specimens. Simultaneous R-Q Factor Analysis Based on Variance-Covariance Matrix

PC	Eigenvalue	%Variance	Cum. %Var.
1	0.4868	32.4368	32.4368
2	0.3097	20.6338	53.0705
3	0.2395	15.9603	69.0308
4	0.0938	6.2468	75.2776
5	0.0754	5.0249	80.3025
6	0.0605	4.0321	84.3346
7	0.0500	3.3312	87.6658
8	0.0457	3.0464	90.7122
9	0.0252	1.6769	92.3891
10	0.0233	1.5510	93.9401
11	0.0181	1.2067	95.1468
12	0.0159	1.0570	96.2038
13	0.0114	0.7624	96.9661
14	0.0105	0.6986	97.6647
15	0.0081	0.5397	98.2044
16	0.0059	0.3947	98.5992
17	0.0046	0.3039	98.9031
18	0.0035	0.2359	99.1390
19	0.0034	0.2275	99.3665
20	0.0021	0.1366	99.5032
21	0.0019	0.1241	99.6272
22	0.0012	0.0796	99.7068
23	0.0011	0.0712	99.7780
24	0.0009	0.0633	99.8413
25	0.0006	0.0409	99.8822
26	0.0005	0.0337	99.9159
27	0.0004	0.0277	99.9436
28	0.0003	0.0183	99.9619
29	0.0002	0.0140	99.9759
30	0.0002	0.0115	99.9873
31	0.0001	0.0088	99.9961
32	0.0001	0.0039	100.0000

Table 2. Mahalanobis distance calculated probabilities and posterior classification for compositional Group 1 members. Eight principal components were used. Probabilities are jackknifed for specimens included in each group.

ID. NO.	Group 1	Group 2
SMF001	84.322	2.143
SMF005	88.743	1.224
SMF006	94.633	2.335
SMF007	17.885	0.104
SMF008	35.883	0.523
SMF009	28.550	0.694
SMF017	53.663	3.327
SMF020	44.278	3.244
SMF022	99.172	1.422
SMF023	14.475	0.303
SMF027	52.882	2.843
SMF028	74.355	0.244
SMF029	96.047	0.777
SMF030	19.257	0.117
SMF031	77.422	0.950
SMF033	28.140	3.970
SMF034	4.634	0.914
SMF035	35.558	2.375
SMF037	48.573	1.747
SMF038	7.878	0.328
SMF039	25.094	0.466
SMF040	86.945	1.037
SMF041	53.455	0.349
SMF042	2.478	0.533
SMF043	90.214	0.463
SMF044	10.815	0.020
SMF046	51.148	1.051
SMF049	26.230	1.004
SMF053	47.917	0.091
SMF054	82.972	2.220

Table 3. Mahalanobis distance calculated probabilities and posterior classification for compositional Group 2 members. Eight principal components were used. Probabilities are jackknifed for specimens included in each group.

ID. NO.	Group 1	Group 2
SMF002	0.000	78.209
SMF003	0.000	55.485
SMF004	0.000	87.512
SMF011	0.000	26.309
SMF012	0.000	97.785
SMF013	0.000	16.903
SMF014	0.000	47.163
SMF015	0.000	70.300
SMF018	0.000	59.265
SMF019	0.000	4.147
SMF024	0.000	81.479
SMF025	0.000	84.574
SMF026	0.000	31.292
SMF036	0.000	37.114
SMF050	0.000	1.010
SMF056	0.000	31.923

Table 4. Mahalanobis distance calculated probabilities and posterior classification for unassigned members into compositional Groups 1 and 2. Eight principal components are used.

ID. NO.	Group 1	Group 2
SMF010	0.000	0.000
SMF016	0.000	0.001
SMF021	40.016	8.913
SMF032	0.000	0.168
SMF045	0.148	0.540
SMF047	0.000	0.000
SMF048	0.002	0.166
SMF051	0.000	0.001
SMF052	0.000	0.000
SMF055	0.000	0.839

Table 5. Compositional Group Assignments and Site Provenience

Site	Group 1	Group 2	Unassigned
Dover	1	0	0
Grand Bay	9	11	3
Jew Bay	0	2	0
Lauriston	5	0	0
Sabazan	5	0	0
Sparrow Bay	5	1	4
St. Louis	0	0	1
Tyrrel Bay	2	1	1
Petite Martinique	3	1	1
Total	30	16	10

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