

Reassessment of elemental concentration data of sediments from the western delta of the Nile River

Kostalena Michelaki,¹
Ronald G.V. Hancock²

¹School of Human Evolution and Social Change, Arizona State University, Cady Mall, Tempe, Arizona, USA; ²Department of Medical Physics and Applied Radiation Sciences and Department of Anthropology, McMaster University, Hamilton, Ontario, Canada

Abstract

The present study re-examines geochemical data produced by instrumental neutron activation analysis (INAA) of sixty-two fired clay sediment samples from the western Nile delta in Egypt. The goal is to assess the strengths and weaknesses of principal component analysis (PCA) and bivariate data splitting (BDS), two widely used data analysis methods, in successfully sorting differing sediment chemistries. Both PCA and BDS are performed using various data formats [*i.e.* original, calcium (Ca)-corrected, scandium (Sc)-normalized, or logarithmically (\log_{10}) transformed]. Both PCA and BDS are shown to sort differing chemistries well. While PCA has the advantage of speed, BDS has the advantage of providing specific chemical clarity and the opportunity to assess the degree of sand dilution more precisely. In PCA, the data format is semi-immaterial, while in BDS, different formats of the data may hinder, rather than enhance, data interpretation, depending on the questions being asked.

Introduction

It has often been proposed that, prior to the interpretation of elemental concentration data from ceramics, the original data should be modified by calcium carbonate correction (Steponaitis and Blackman, 1981), by scandium normalization (Topping and Mackenzie, 1988; Dias and Prudêncio, 2008), or by logarithmic (\log_{10}) transformation (Blomster *et al.*, 2005). There has also been some debate as to whether simple or sophisticated data analysis procedures should be employed in data analysis (Hancock *et al.*, 2008).

Here we reassess a small but complex set of data to see whether principal component analysis (PCA) or bivariate data splitting

(BDS) is the optimal method of data analysis. We also investigate whether the format of the data [*i.e.* original, calcium (Ca)-corrected, scandium (Sc)-normalized, or logarithmically (\log_{10}) transformed] influences the final data interpretation.

Materials and Methods

Sixty-two fired sediment samples from the northwestern Nile delta region of Egypt were analyzed for twenty-nine elements using instrumental neutron activation analysis (INAA) at SLOWPOKE-Toronto in 1986. The samples came from different depths at fifteen sampling locations in nine towns (Table 1). Three of the towns (El Zawia, Denshal, and Kafr Mesaed) were close to the Nile River and six were close to Alexandria (Abis, Shaikh, Yamaneia, Abo Qir, Mamora, and Hagar Nawateia) (Figure 1). All the samples were first fired at 600°C to eliminate their 2-22% organic contents without decomposing any calcium carbonate (CaCO_3) that might be present in each sample. In 1987, based only on very simple data analysis procedures, such as calcium- and silica-correcting the data in Ca-rich and/or silica-rich samples, it was proposed that all samples were composed of assorted mixtures of Nile alluvium, limestone, organic materials (fired out, and so determined by sample weight-loss), and sand (silica-rich minerals or quartz) (Hancock *et al.*, 1987). As a data analysis inter-comparison, here we are reassessing the original 1986 data using two approaches – PCA and BDS. PCA was chosen since it checks for patterning in the geochemical data considering the simultaneous contribution of a large number of measured elements. BDS was chosen since bivariate plots illustrate the basic geochemical relationships within the data. Strengths and weaknesses of each approach to data analysis are presented and compared below, along with the effect that the data format (original, Ca-corrected, Sc-normalized or logarithmically (\log_{10}) transformed) may have on the interpretation.

Results

Principal components analysis

PCA was run using the original concentration data (Figure 2a), Ca-corrected (Figure 2b), Sc-normalized (Figure 2c), and logarithmically transformed (\log_{10}) data (Figure 2d). In all plots, the high Ca samples were separated from the Nile alluvium samples, as were the sand-diluted samples. As Figure 2a,d shows, the original and the \log_{10} versions of the data

Correspondence: Kostalena Michelaki, School of Human Evolution and Social Change, Arizona State University, 900 S. Cady Mall, Tempe, Arizona, 85287-2402, USA.
Tel. +1.480.965.6170 - Fax: 01.480.965.7671.
E-mail: kmichela@asu.edu

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generated the clearest group separations, while the Sc-normalized data (Figure 2c) generated adequate differences. The Ca-corrected data (Figure 2b) generated the least clear differences. For the original data and \log_{10} data plots (Figure 2a,d), PC1 was pulled negatively by the carbonate forming elements [Ca and strontium (Sr)], along with antimony (Sb), arsenic (As), and uranium (U), and was stretched positively by the silicate forming elements [*e.g.* aluminum (Al), iron (Fe), vanadium (V), Sc, and the rare earth elements (REEs)]. On the other hand, PC2 was pulled negatively by sodium (Na), barium (Ba), chromium (Cr), hafnium (Hf), cobalt (Co), and V, and was stretched positively by U, Sb, Ca, As, Sr, and caesium (Cs). It has been clearly established that in some cases the elements included in a PCA can hinder the recognition of existing chemical groupings (Michelaki and Hancock, 2011). Because of this, we subjected our original data to PCAs with progressively

fewer elements, eliminating elements of similar chemistry that could be expected to be well correlated, so that each periodic group was represented by progressively fewer elements. Our selections were as follows:

- 29 elements: Al, Ca, Dy, Mn, Ti, Na, V, As, La, Sb, Sm, U, Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, Lu, Nd, Rb, Sc, Sr, Ta, Tb, Th, Yb
- 20 elements: Al, Ca, Na, V, La, Sm, U, Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sc, Sr, Ta, Th, Yb
- 10 elements: Al, Ca, Sr, Sc, Fe, Na, La, Eu, Yb, Rb
- 5 elements: Al, Ca, Sc, Na, La

The chemical groupings remained the same, no matter how many elements were included in the PCA. In Figure 2e we present the PC1 vs PC2 plot when ten elements were included. In comparison to Figure 2a it is clear that sample sorting was not affected by the numbers of elements used.

As suggested by Baxter (1999), once the very high Ca (Abo Qir) samples were clearly separated, we removed them and subjected the remaining samples to PCA again (Figure 2f).

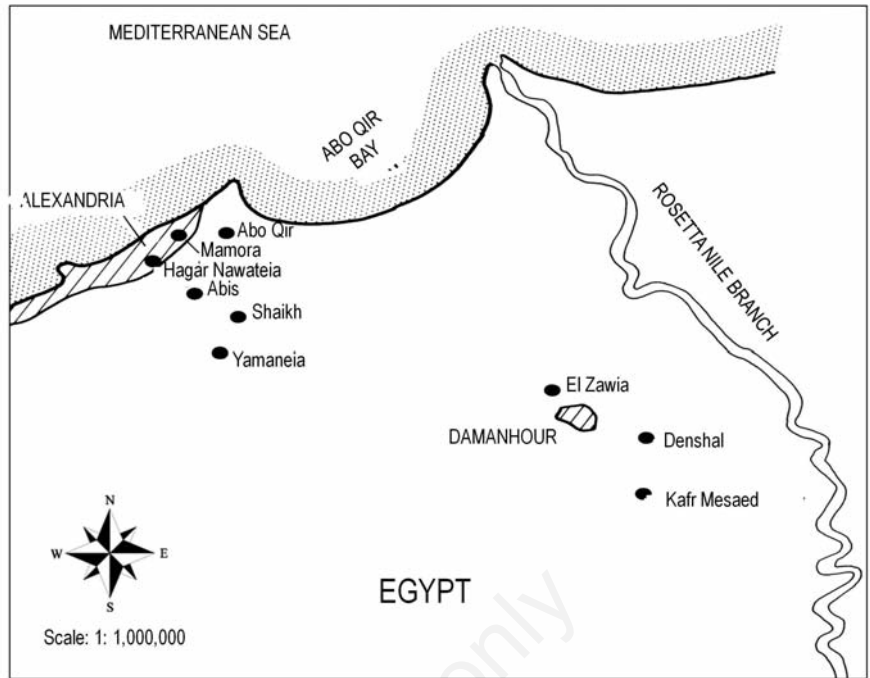


Figure 1. Map showing the locations from where the study samples were collected.

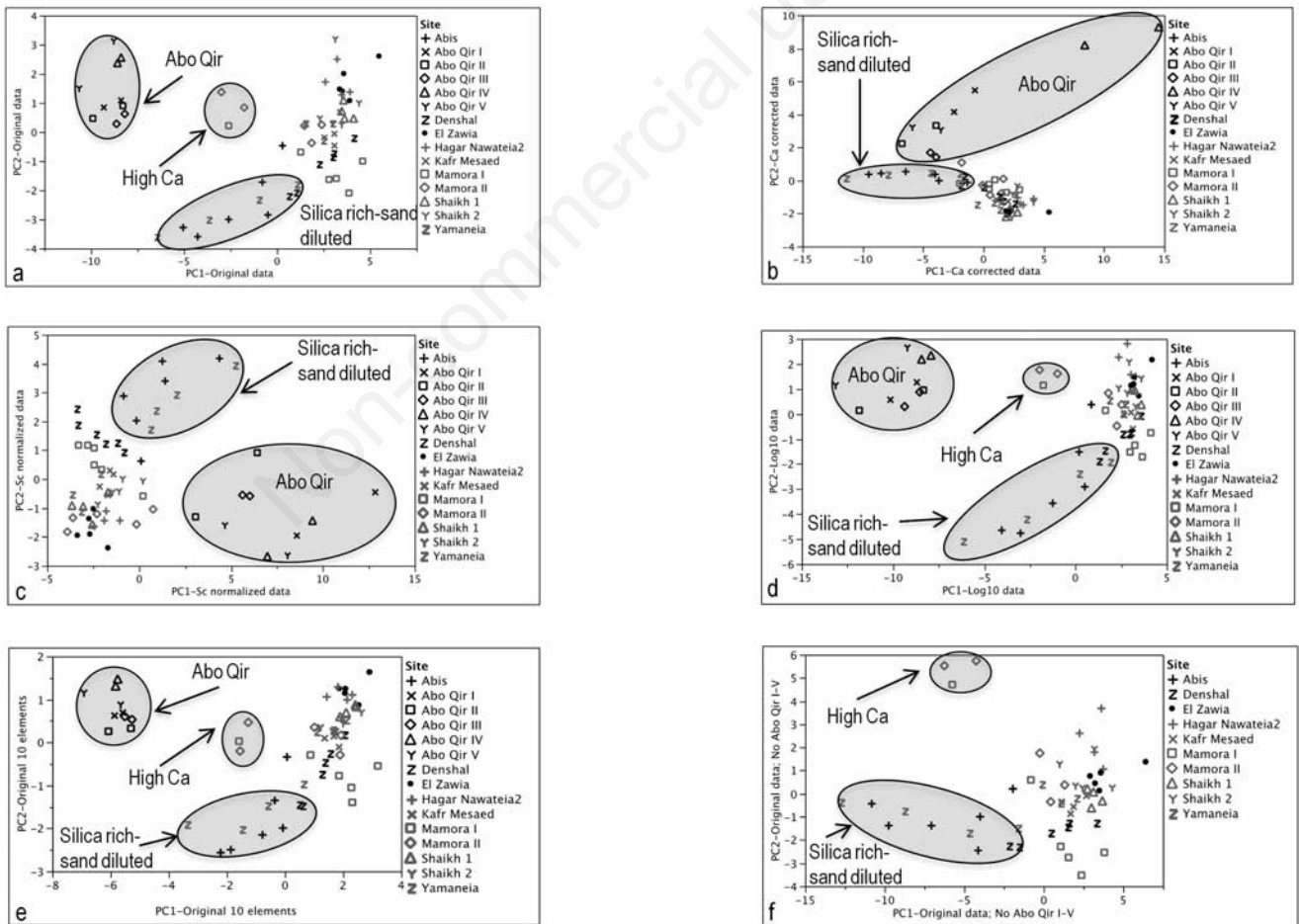


Figure 2. Principal component analysis: a) all samples, original data, all elements; b) all samples, Ca-corrected data, all elements; c) all samples, Sc-normalized data, all elements; d) all samples, log10 data, all elements; e) all samples, original data, 10 elements - Al, Ca, Sr, Sc, Fe, Na, La, Eu, Yb, and Rb; f) all samples, except Abo Qir I-V, original data, all elements.

As expected, the separation of the Nile alluvium samples from the remaining high Ca and the Si-rich samples appears to be clearer than when the very high Ca samples were included in the analyzed data set (Figure 2a).

PCA, therefore, rapidly resolved the most calcareous samples from the rest, and also sorted what turned out to be the silica-diluted samples from the rest, regardless of the data format.

Bivariate data splitting

The BDS approach was conducted on the original data set, on Ca-corrected data, and on Sc-normalised data. It led to the same level of sample sorting as was achieved by PCA, with what looks to be a clear connection to the variable chemistries of the samples studied, and confirmation of the conclusions of the original 1987 report (Hancock *et al.*, 1987). In each of the following figures, *x* represent Ca-rich sam-

ples; *y* represent Nile alluvium; and *z* are the silica-rich samples. Figure 3a shows that Ca and Sr are reasonably well correlated, indicating that aragonitic limestone was the source of the additional Ca in the samples (Sheppard *et al.*, 2008). In Figure 3b, the plot of Ca *vs* Sc

shows essentially the same features as the PCA plots displayed in Figure 3a,d,e, confirming the chemical interpretations made for these figures. Figure 3c, a scattergram of Sc *vs* hafnium (Hf), indicates that the silica-rich samples contain slight excesses of Hf, an ele-

Table 1. Sample locations and depths.

Town	Samples	Depth (cm)
Abo Qir	01-10	0-15; 15-30
Mamora	11-21	0-15; 15-30; 30-45; 45-60; 60-75
Hagar Nawateia	22-25	0-15; 15-30; 30-60; 60-75
Abis	26-31	0-15; 15-30; 30-45; 45-60; 60-75; 75-90
Shaikh	32-40	0-15; 15-30; 30-45; 45-60; 60-75
Yamaneia	41-47	0-15; 15-30; 30-45; 45-60; 60-75; 75-90; 90-105
El Zawia	48-52	0-15; 15-30; 30-45; 45-60; 60-75
Denshal	53-58	0-15; 15-30; 30-45; 45-60; 60-75; 75-90
Kafr Mesaed	59-62	0-15; 15-30; 30-45; 45-60

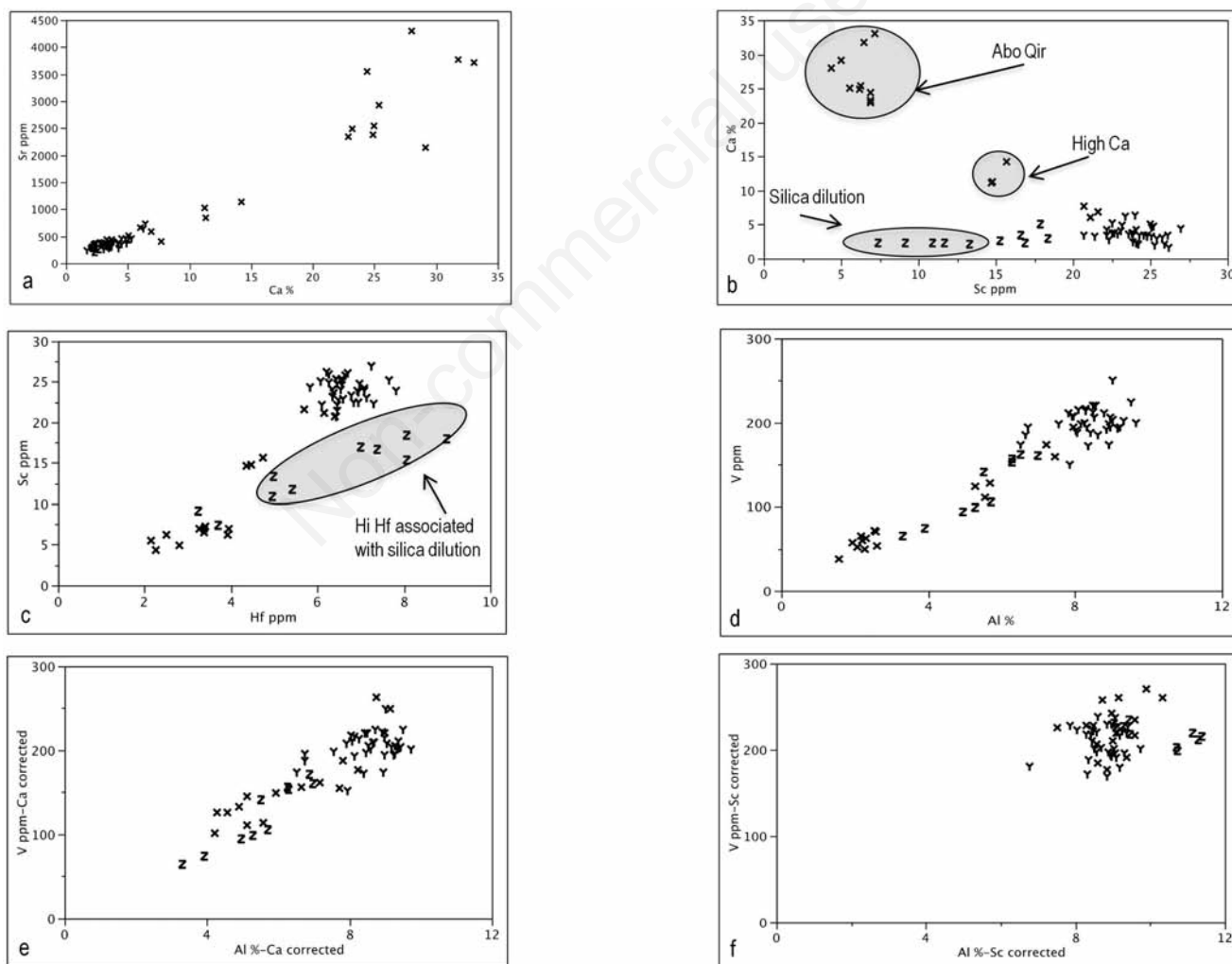


Figure 3. Bivariate data splitting. Scattergrams of: a) Sr *vs* Ca, original data; b) Ca *vs* Sc, original data; c) Sc *vs* Hf, original data; d) V *vs* Al, original data; e) V *vs* Al, Ca-corrected data; f) V *vs* Al, Sc-normalized data.

ment sometimes associated with zircon-rich sands. Scattergrams were made of V vs Al for the original data (Figure 3d), for the Ca-corrected data (Figure 3e), and for the Sc-normalized data (Figure 3f). The theoretical advantage of Sc-normalization over Ca-correction is that the former corrects for both carbonate and silica dilutions, while the latter corrects only for carbonate dilutions. These figures show successive reductions of the data scatter as one approaches what appear to be the concentrations of these two elements in Nile alluvium (Figure 3f). The potential usefulness of Sc-normalization of data is that samples not made of Nile alluvium should be clearly separable from those made of Nile alluvium, based on the relative concentrations of V and Al.

Discussion

PCA and BDS both work well in sorting differing chemistries of fired clay sediment samples from the western Nile delta. PCA has the advantage of speed, while BDS has the advantage of providing specific chemical clarity and the opportunity to assess the degree of sand dilution more precisely. A problem with the Sc-normalization approach is that, while it may be used to unequivocally establish the source sediment material, the individual, locally-characteristic, dilution effects are lost. As far as the Ca-correction approach is concerned, source sediment materials are only partially established. In each case, characteristic material information is lost. Thus, both Sc-normalization and Ca-correction should always be run in conjunction with the original, or \log_{10} trans-

formed, analytical data. Relative to the original analytical data, the use of \log_{10} transformed data did not enhance the separation of different sample types in this data set. When it comes to the specific clay sediment samples from the western Nile delta, Nile alluvium sediment was found at Kafr Mesaed, Denshal, El Zawia, Shaikh (with some additional limestone), Hagar Nawateia (with some extra limestone), above the 45 cm level at Yamaneia, and below the 30 cm level at Mamora. Limestone-diluted Nile alluvium was found above the 30 cm level (maximum depth sampled) at Abu Qir, and above 45-60 cm at Mamora. Silica-diluted Nile alluvium was found at Abis and below the 45 cm level at Yamaneia.

Conclusions

To conclude, if ceramics were made from sediments from any depth at any of the towns studied, their chemistries should match those represented in this paper. As such, the specific or general locations of the sources of these ceramics could easily be established. Whether this possibility translates into similar location sourcing for ancient ceramics made from Nile alluvium of this geographical region is yet to be established.

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