Asmosia 5: Interdisciplinary Studies on Ancient Stone, J. J. Herrmann, Jr., N. Herz & R. Newman (eds)
Archetype Publications Ltd., London, 2002, ISBN: 1-873132-08-5

Source tracing marble: trace element analysis with inductively coupled plasma–mass spectrometry

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Abstract Before modern chemistry provided tools for characterizing materials by chemical or isotopic signature, most provenance studies depended on subjective studies of artistic style. It has often been pointed out that it is the development of modern analytic techniques that has given us the ability to make scientifically repeatable statements about the sources of marble artifacts. In particular, several studies have used analysis of trace element concentrations to characterize marble artifacts and attribute them to their source quarries. In this paper we describe measurements made in order to evaluate the viability of using inductively coupled plasma–mass spectrometry (ICP–MS) to measure trace elements in marble scrape samples. We report on analyses of chip samples from two different quarries on the island of Paros and scrape samples from archaeological artifacts. In addition we examine and evaluate previously published comparative data and discuss the repeatability of trace chemical characterization measurements.

HISTORICAL INTRODUCTION

The earliest attempts to apply a scientific method to marble identification seem to have been during the mid-19th century (Herz, 1985) and had nothing to do with analytic chemistry. It is well known that in 1890 the geologist G.R. Lepsius published a treatise called *Griechische Marmorstudien* giving a description of marbles from different quarries in the Aegean (Lepsius, 1890). He based these descriptions partly on visual inspection of hand samples (color, smell of newly broken surface, degree of crystallization, etc.), but he also applied the then recently developed technique of thin-section petrography, which consists of examination in polarized light under an ordinary optical transmission microscope of a polished stone chip that is thin enough to transmit light. This technique, which is still in use today, often allows identification of the mineral components of rocks. Lepsius's identifications of artifacts seem to have been widely accepted, and his techniques were emulated by the archaeological and art historical community. It has even been argued that *Griechische Marmorstudien* "has been the bible on Greek marble for classical archaeologists for a century" (Moltesen *et al.*, 1992: 277). Almost from the beginning, however, there was criticism of his results, or rather of the lack of discrimination with which they were applied. The American geologist H.S. Washington, for instance, pointed out in 1898 several instances in which artifacts had been given two different, contradictory provenances in equally positive terms by different art historians (Washington, 1898). We will see that this lack of repeatability in provenance studies is still with us.

Although some of the principles employed were available earlier, it was not until the 1930s that spectrographic techniques for measuring trace elements (constituents of concentration less than 0.01%) became relevant to archaeology (Budd *et al.*, 1996; Young *et al.*, in press). Optical emission spectroscopy (OES) was soon followed by atomic absorption spectroscopy (AAS), nuclear activation analysis (NAA), the electron microprobe (EMP), proton-induced X-ray emission (PIXE), X-ray fluorescence (XRF), inductively coupled plasma spectroscopy (ICPS), inductively coupled plasma atomic emission spectroscopy (ICP–AES) and inductively coupled plasma–mass spectrometry (ICP–MS).

It was in the 1960s that elemental and isotopic techniques seem first to have been applied to marble provenance studies. The earliest attempt at trace element analysis was in 1965, when Rybach and Nissen used neutron activation analysis to measure marbles for sodium and manganese. In 1972, Craig and Craig used mass spectrometry to measure isotope ratios of carbon and oxygen in ten samples of marble from the Mediterranean. In 1975, Conforto *et al.* applied AES and XRF to analysis of a larger suite of elements. In 1980, Germann *et al.* applied AAS to chemical analysis of marbles, and in 1983, Cordischi *et al.* used Mn^{2+} electron spin resonance. Cathodoluminescence was applied in 1989 (Barbin *et al.*, 1992), ICP-AES was used for chemical characterization in 1992 (Jongste *et al.*), and LREE/HREE and La/Yb ratios were used in 1995 (Meloni *et al.*).

The most successful individual technique of discriminating marbles has been measurement of carbon and oxygen isotopic ratios by mass spectrometry (Craig and Craig, 1972; Manfra *et al.*, 1975; Herz, 1985, 1987; Germann *et* *al.*, 1980; van der Merwe *et al.*, 1995; and many more). But it has been convincingly argued that "a single method of analysis, such as light stable isotope measurements, is not particularly effective as a means for tracing marble quarry sources" (van der Merwe *et al.*, 1995: 195). Instead, studies that integrate several methods seem to have had the greatest success. Despite different methods of sampling and chemical analysis, there seems to be consensus that there is promise of future success from trace element analysis of marble, especially if trace data are combined with data from other sources such as oxygen and carbon isotope ratios, petrography, and cathodoluminescence. Another common difficulty facing investigators has been the statistical treatment of data. No combination of three or fewer discriminatory variables has been discovered, so multivariate statistical methods are needed in order to analyze the data fully.

Some studies (e.g. van der Merwe *et al.*, 1995) have focused on an ad hoc approach that attempts to look at all available data on a given group of artifacts so as to determine probable or definite provenances for certain artifacts by a process of elimination. This ad hoc approach, however, does not offer increased returns as the scale of our quarry data increases so there has been increasing emphasis (e.g. Matthews, 1997) on establishing a universal database of marble analyses. Advocates of this approach imply that the routine and systematic provenance determination will be possible if a sufficiently large and accurate database of marble analyses can be created. In that case, a less expensive and more widely applicable method of measuring trace element concentrations would substantially contribute to classical marble provenance studies. We initiated this study in the hope that ICP–MS could provide such a method.

CURRENT TECHNIQUES OF TRACE CHEMICAL ANALYSIS

From the 1930s through the 1980s, the standard method of chemical analysis for most archaeological specimens was OES, which allowed analysis of most sample matrices (pottery, obsidian, faience, metals) for trace elements down to the parts per thousand (per mil) and high parts per million (ppm) range. This has now been mostly replaced by AAS, which provides better precision and lower detection limits on samples that can be dissolved in acid (Young *et al.*, in press). Since a separate measurement has to be made for each element measured with these instruments, these techniques are extremely cumbersome for analysis of many elements. XRF, EMP, and a less-prevalent technique PIXE, though they are extremely important analytical techniques, measure elemental concentrations on the surface of an object and thus are inappropriate when dealing with the heterogeneous, weathered surface usually found in archaeological artifacts. A possible way of avoiding this is to grind a volume sample into a homogenous powder and then analyze it by XRF. This has provided excellent results in the ppm range and allows simultaneous measurement of a large suite of elements (often as many as several dozen). Since its development in the mid-1940s, however, NAA, where available, has been the preferred method of multi-element analysis (Hughes, 1991). It requires a relatively small sample (usually about 100 mg) and in theory can operate non-destructively (it is effectively destructive when dealing with analyses of marble because a sample must be taken from the artifact in question and the samples remain radioactive for months or years). More importantly, it provides concentration information for virtually all the elements (excepting lead, silicon, gold, and a few others) down to the parts per billion (ppb) level. Unfortunately, it requires the use of a nuclear reactor and is therefore extremely expensive, often costing more than $200 per sample. At that price, it is hardly preferable to thermal ionization or spark source mass spectrometry (TIMS and SSMS, respectively), ultra-accurate mass spectrometry techniques used by geologists for measuring isotope ratios, with detection limits in the parts per trillion (ppt) range and extremely high precision.

Since the 1980s, mass spectrometers that ionize a liquid sample in a torch of argon plasma have become increasingly important to archaeologists because they reliably provide ppm concentration data for virtually all the elements. There are three main variants with slightly different limitations and capabilities: ICPS, ICP–AES, ICP–MS. The last of these, and the most recent development, provides the widest range of elemental concentrations (unmeasurable elements vary with the acid matrix in which the samples are dissolved; only H, He, C, N, O, Ne, and Ar are theoretically indeterminable) at the best accuracies and precisions (for standards, 1–3% error with detection limits between 1 ppb and 50 ppt) (Young *et al.*, in press). A recent incarnation, the magnetic sector, multiple collector ICP–MS (Plasma P54) can match the precision of traditional TIMS isotopic measurements at a tenth of the cost per sample.

NAA, the standard technique for getting multi-element concentration data at low trace levels (fractions of a ppm), requires that samples be drilled or chipped from the artifacts being analyzed, and it is relatively expensive per sample. It is often these practical factors that limit our ability to analyze marble artifacts accurately and easily. Since ICP–MS can potentially detect concentrations lower than 1 ppb, it can be used to measure trace elements in very small samples scraped from clean surfaces. Thus, if ICP–MS can be used to measure elemental concentrations in marble scrape samples obtained with practically non-destructive sampling, the results obtained may be comparable to those produced by more traditional methods of multi-element analysis such as NAA and XRF and obtainable at a quarter the cost. Because the sampling technique is virtually non-destructive, it will also be applicable to a much wider range of artifacts.

ANALYTICAL PROCEDURES

The samples available for this study were 13 chips of marble and 4 scrape samples recently collected from Paros quarries, and 13 scrape samples from sculptures in the Museum of Fine Arts, Boston and the Harvard University Art Museums, which had been collected for a previous study of light stable isotope ratios (van der Merwe *et al.*, 1995). All samples were clear white marble; detailed examination of the hand specimens was not made.

Because there was no established laboratory protocol for trace element measurements of marble samples by ICP–MS, preliminary measurements were made of four samples from the same piece of marble (Paros 1.78.5) from the Paros 1 quarry in order to determine the best method of acid digestion, amount of sample dilution necessary, and what elements were measurable. Two chips (CN and CB) from Paros 1.78.5 were washed with agitation for 40 seconds in 25% HNO_3 and then rinsed twice in distilled H_2O and dried. Since this method of washing visibly reduced the size of the chips, it is not anticipated that there was any contamination remaining from the sampling procedure, though differential leaching of more soluble elements in the washing process may have taken place. Although all chips were removed from freshly broken marble surfaces with a cold chisel and hammer, it was not possible to make more than one measurement at different depths from the cortex of each sample. Therefore, if contamination from ground water penetrated to a depth greater than several millimeters, some erroneous signals may have been present. Measurements were not made to evaluate the significance of this potential source of contamination. CN and a scrape sample also from Paros 1.78.5 (SN) were dissolved in 10 ml of Optima grade HNO_3 in a volumetric flask and then diluted to 250 ml with H_2O. CB and a second scrape sample from Paros 1.78.5 (SB) were dissolved in 5 ml HNO_3 and 5 ml HCl and similarly diluted. These four samples along with reagent blanks were run for semi-quantitative data on the Fisons VG PlasmaQuad II/s ICP-MS at the Department of Geology and Geophysics of the University of Hawaii.

As the results from these preliminary measurements were intended for internal comparison only, the instrument count rates were not calibrated and cannot be reported as concentration data. These semi-quantitative data indicated that digestion by nitric acid was slightly preferable to digestion by hydrochloric and that the REEs were in very low concentrations. In order to attempt to collect REE data, the final dilution protocol was modified. As with the preliminary samples, the chips were washed in 25% HNO_3 for 40 seconds and rinsed twice. They were then powdered in an agate mortar, and samples of about 10 mg were weighed out into volumetric flasks. At the same time, each of the scrape samples was weighed and put into a volumetric flask. In order to determine whether there were significant amounts of clay minerals in the samples, they were initially dissolved in 2 ml of 5% glacial acetic acid (CH_3COOH), which would dissolve the calcite but leave any incorporated silicates practically unaffected. None of the samples showed any visible particulate matter remaining out of solution after three days, at which time the samples were evaporated to near dryness (under 0.5 ml) without boiling (to avoid vaporizing volatile elements). Finally, 10 ml of Optima grade HNO_3 was added to each volumetric flask, and the samples were diluted to 50 ml with H_2O. In addition to the reagent blank that was prepared along with the other samples (BLK1), a second blank (BLK2) was prepared with 10 ml of HNO_3 and 40 ml of H_2O in order to assure that the dissolution in acetic acid was not adding impurity to the samples. The samples were again run on the PlasmaQuad II/s at the University of Hawaii for the elements Na, Sc, V, Cr, Mn, Fe, Co, Zn, As, Sb, Cs, Ba, Hf, Pb, Th, U, and the REEs. Since the two blanks were virtually identical, indicating that contamination from the acetic acid was insignificant, the concentrations reported for BLK1 were subtracted from the reported data, and BLK2 was ignored.

Sodium pervades aqueous reagents, so the data for Na are considered suspect when the samples are in solution and, though Na was measured, it is not included in the graphs of our data. Similarly Ba is not acid soluble and was excluded from the graphs. The Fe concentrations are calculated from the minor nuclide ^{54}Fe because the ^{56}Fe count is contaminated by the compound ArO, which has the same mass. Fe data have been left in the data, but their numerical values should be treated with caution. Because the concentrations of REEs in the samples were near the instrument's detection limit, the REE data were not chondrite-normalized and should not be considered numerically significant, but merely indicative of presence or absence.

DATA ANALYSIS

An initial inspection of our data showed that As was above blank levels only in one artifact. This may be a legitimate datum, or it may represent contamination of the sample, but as As was below detection limits in any of the quarry samples, it is not of use for attributive purposes and it was eliminated from the data set. The elemental concentration data from all samples are tabulated in Appendix A and plotted on a logarithmic mountain chart (Fig. 1) to give a visual idea of the spread of the data. It can be seen that the overall variation in transition element concentrations is not great. The tight grouping also suggests that neither contamination of the scrape samples nor leaching of soluble elements during the washing of the chip samples was a problem. The presentation gives a reasonable intuitive sense of the amount of variation in the transition element data, and it demonstrates that simple inspection of it will not give distinct groupings for the quarries. It is possible, however, for statistical groups to reveal patterns in the data that are not evident to visual inspection. The greater spread of the REE data indicates that REE concentrations may be more useful as a discriminatory variable.

In Figure 2, the quarry average values have been plotted with $\pm\sigma$ error bars to indicate where discrimination between the quarries may be possible. As the transition metal data for the two quarries are coincident, there is no expectation of reliable resolution. The REEs, however, show markedly higher LREE concentrations in samples from Paros 2 than in those from Paros 1; this is probably due to higher clay-mineral content in the Paros 2 samples and is potentially a useful discriminatory variable. On this basis, it could be argued that artifact samples APS, AQS, ARS, ATS, AUS, AVS, AZS, AAAS, and AABS are more liable to have come from Paros 2, while ASS, AWS, AXS, and AYS are more likely to be from Paros 1, provided of course that they are independently known to be from one of the Paros quarries.

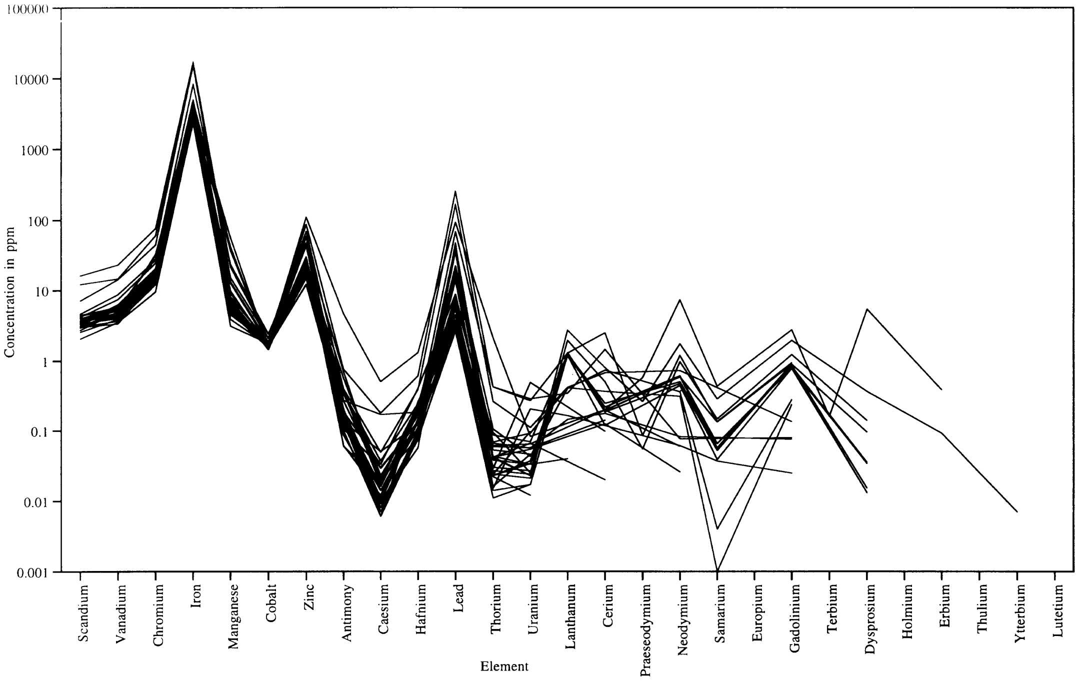


Figure 1 Elemental concentrations in all samples. Graphical representation in the form of a log-linear mountain chart of the data accumulated by this study. It is easy to see that all the samples measured follow the same general pattern of trace elemental concentrations. Note that because values of zero do not plot on a logarithmic scale, in Figures 1–3, concentration values should not be taken from the lines (which merely serve to identify the different series) but only from cusps.

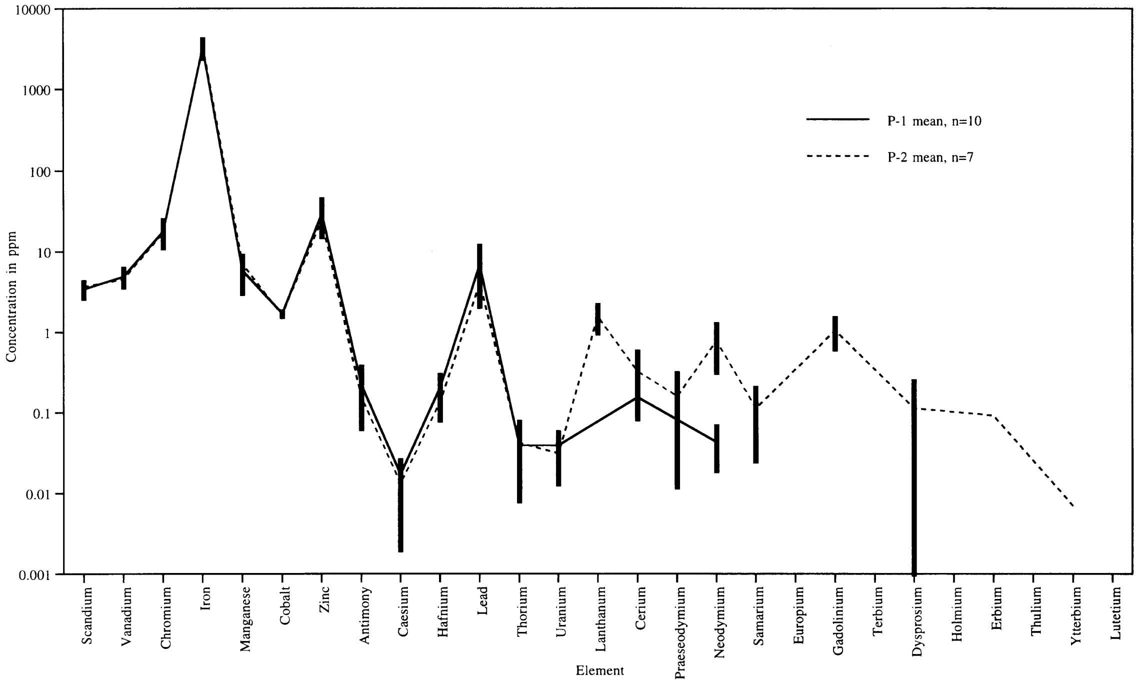
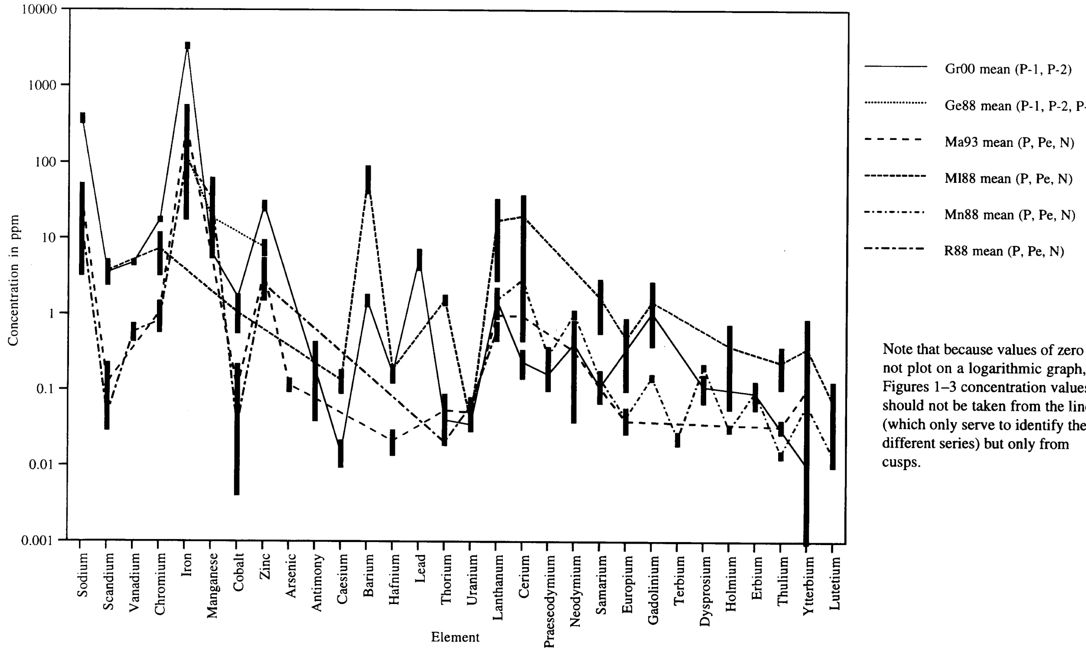


Figure 2 Paros 1 and Paros 2 quarry sample averages. Mean concentrations of the quarry samples (i.e. the samples of known provenance). Samples from the two quarries show similar concentrations of transition elements, but Paros 2 samples show traces of more of the rare earths. Note that the rare earth elements were present in such low concentrations in all samples that they should be taken only to imply presence or absence, not numerical values. Error bars are ±σ.



Note that because values of zero do not plot on a logarithmic graph, in Figures 1–3 concentration values should not be taken from the lines (which only serve to identify the different series) but only from cusps.

Figure 3 Mean concentrations of samples from Paros, Penteli, and Naxos, keyed by laboratory. Mean concentrations of measurements made by each laboratory. Where two or more error bars (which are ±σ) are in a vertical line and do not overlap (e.g. Hafnium), this indicates that the data produced for all quarries by one laboratory are inconsistent with those produced by another laboratory.

Since this study is concerned with methodological development rather than determining the source of particular artifacts, this line of argument has not been pursued; we merely note that there does seem to be systematic variation in the LREE concentrations of samples from the two quarries.

It was naturally impossible to evaluate the absolute accuracy of our data without comparison to previous measurements, so we compared our results to the published data from Germann *et al.* (1988), Mandi *et al.* (1995), Mello *et al.* (1988), Meloni *et al.* (1988; 1995), and Roos *et al.* (1988) (See Appendix B.). Because of the difficulty of calibrating PIXE measurements to obtain numerical concentration data, the PIXE measurements reported in Margolis and Showers (1988) are reported as parts per 1000 parts calcium in the sample. Calcium, which constitutes about 48% by weight of a marble sample, was not measured in this study because it was a major constituent of the samples and would have overloaded the ICP–MS detectors. Therefore the measurements made in this study cannot be normalized to calcium content and are not directly comparable with the data in Margolis and Showers (1988). Matthews (1997) also contains comparable data, which were not considered.

Initial inspection showed not only that our data were inconsistent with published measurements from Paros quarries, but also that the published data varied by orders of magnitude. Therefore we decided to include data from the quarries of Penteli and Naxos to see whether the inconsistency was limited to Paros quarries. In Figure 3, the average elemental concentrations measured by each laboratory are shown along with associated ±σ error bars. Note that these are averages of samples from *all three quarries* (except in the case of the present study and Germann *et al.*, 1988, which did not measure samples from Penteli) and that Mello *et al.* (1998) and Meloni *et al.* (1998) provide the same measurements (with only rounding error present). Two or more error bars in a vertical line indicate inconsistencies between the studies. Because the standard errors calculated for Figure 3 are based on very low sample numbers and are therefore not statistically valid, Figures 4 to 7 provide more detailed pairwise comparisons of some of the published studies. In each case, the shapes indicate the quarries (square = Paros,

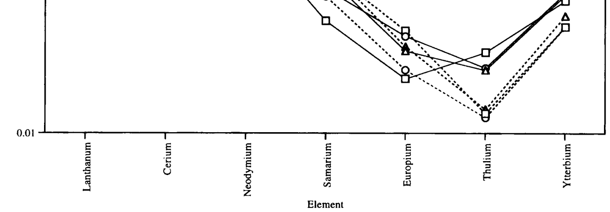


Figure 4 Pairwise comparison of Mandi *et al.*, 1995 and Meloni *et al.*, 1995.

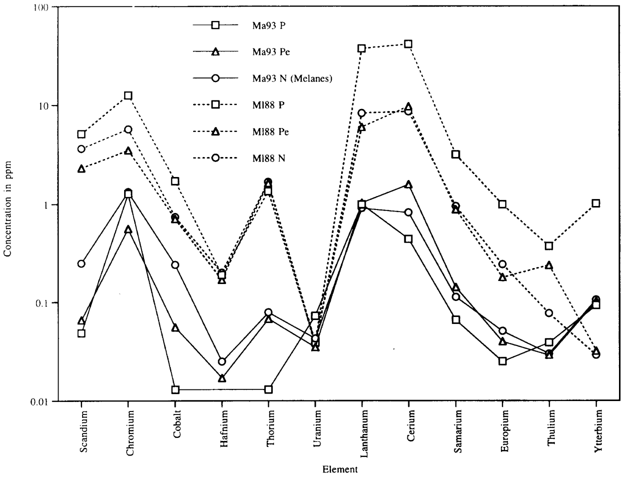


Figure 5 Pairwise comparison of Mandi *et al.*, 1995 and Mello *et al.*, 1988.

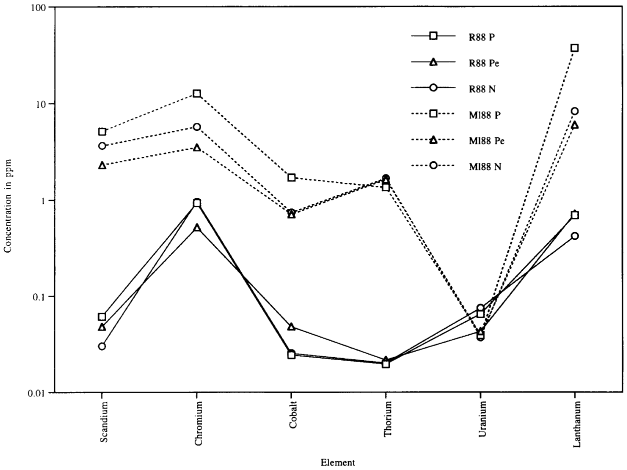


Figure 6 Pairwise comparison of Roos *et al.*, 1988 and Mello *et al.*, 1988.

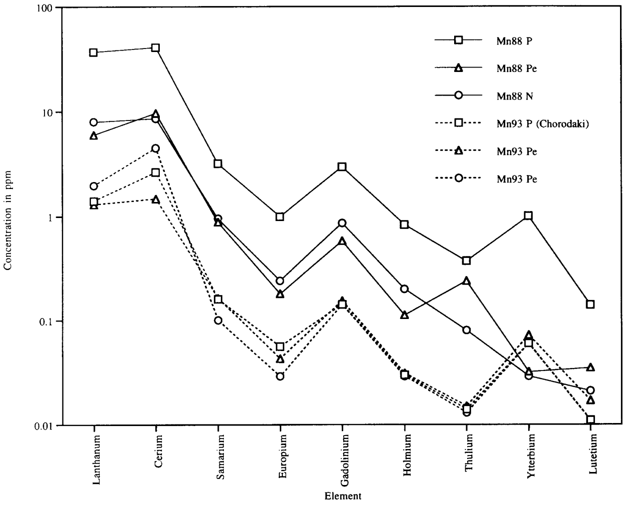


Figure 7 Pairwise comparison of Meloni *et al.*, 1988 and Meloni *et al.*, 1995.

triangle = Penteli, circle = Naxos), and the line type (solid or dashed) discriminates the studies being compared. Thus, if consistent data are produced, *the shapes must group together.* It is extremely disappointing to find that the only natural groupings that are evident – and they are very evident – are correlations between results obtained in each laboratory or by each study. Differences between laboratories, even between two laboratories using the same techniques, are greater by orders of magnitude than variation in all samples, regardless of quarry, from a single laboratory.

CONCLUSIONS

If we considered the measurements made for this study in isolation, the results are encouraging, but not conclusive: though little can be said from the trace metal data about the provenance of the artifacts tested, the LREEs are present in higher concentrations in the Paros 2 samples, allowing possible discrimination between the Paros 1 and 2 quarries, if other possibilities are eliminated by, for instance, light stable isotope analysis. From the data obtained, it would be reasonable to hope that statistical tools operating on larger or more precise data sets than the one produced for this study might produce good provenance information even without the application of other techniques. A large database of quarry data, multivariate statistics, and an almost unlimited number of potentially discriminatory variables give promise of further progress. If trace element data alone are not discriminatory, they may help to resolve ambiguities in other methods of characterization such as light stable isotope analysis and petrography. This is the sanguine conclusion reached by many previous trace chemistry studies, and it would be a reasonable conclusion if only the data produced by this study were examined.

Our examination of previously published data, however, reveals serious difficulties with comparison of data from different laboratories. Not only is there little correlation between the data obtained in this study by ICP–MS and published NAA or AAS measurements (not a surprising result in the application of a new analytical technique to a problem), but also the published NAA and AAS data are not internally consistent. The assumptions behind marble provenance studies include the hypotheses that within-quarry variation is statistically smaller than between-quarry variation and the presupposition that laboratories are making accurate and repeatable measurements of the trace element concentrations in marble samples. The presence of greater variation among laboratories than within the

Pairwise comparisons show the detailed differences between studies that cannot be seen in Figure 3. Data for Paros are represented with a square; for Penteli with a triangle, and for Naxos with a circle. Thus if laboratory results are comparable, the shapes – representing quarries – must group together. As can be seen from the charts, it is the line qualities (solid or dotted) – representing the individual studies done – that form distinct groups. Remember also that these are logarithmic graphs, so the concentrations of, for instance, scandium (regardless of quarry) measured by Roos *et al.* and Mello *et al.* (Fig. 6) differ by nearly two orders of magnitude.

measurements made by any individual laboratory – regardless of quarry – casts doubt on one or both of these premises. After three decades of effort and many thousands of dollars of investment in trace element marble provenance studies, there is still unexplained variation in measurements that cannot vary significantly if the theoretical assumptions behind the measurements made are correct. More generally, provenance studies of marble artifacts have faced methodological criticism for over a hundred years and current publications do not comment on obvious inconsistencies in the published data. If there is to be any possibility of establishing such a database of trace chemical analyses of Mediterranean marbles as Matthews (1997) and others have suggested, standards of absolute accuracy as well as analytical precision must be stated and met. Otherwise, trace elemental analysis must be restricted to small-scale, ad hoc studies and the hopes of routine characterization by reference to a cumulative database: *requiescant in pace.*

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APPENDIX A: SAMPLE LIST AND KEY TO ABBREVIATIONS

Key to abbreviations

Gr00	Green *et al.* (2000) ICP–MS (this study)
Ge88	Germann *et al.* (1988) AAS
Ma95	Mandi *et al.* (1995) NAA
Ml88	Mello *et al.* (1988) NAA
Mn88	Meloni *et al.* (1988) NAA
Mn95	Meloni *et al.* (1995) NAA
R88	Roos *et al.* (1988) NAA, AAS
P	Paros
P-1	Paros 1
P-2	Paros 2
P-3	Paros 3
Pe	Penteli
N	Naxos

Sample list

Sample name	Mass in mg	Quarry sample accession number*	Lab no. from van der Merwe *et al.* (1995)	Museum accession number†
1A	10.69	78.1		
1B	10.49	78.2		
1C	10.68	78.5		
1CS	5.92	78.5		
1D	11.03	78.8		
1DS	8.98	78.8		
1E	7.49	78.13		
1FS	7.55	78.26		
1G	7.15			
1H	6.36			
2IS	5.69			
2J	6.21			
2K	8.52			
2L	7.34			
2M	10.33			
2N	7.14			
2O	8.57			
APS	7.25		HI-353	Sackler 1977.216.2185
AQS	7.64		HI-356	Sackler 1988.459
ARS	5.74		HI-711	MFA 00.311
ASS	8.29		HI-719	MFA 03.751
ATS	1.52		HI-720	MFA 03.754
AUS	7.21		HI-726	MFA 16.62
AVS	1.57		HI-729	MFA19.318
AWS	9.44		HI-745	MFA 1979.556
AXS	7.77		HI-753	MFA 22.593
AYS	3.05		HI-754	MFA 23.1
AZS	5.61		HI-755	MFA 30.543
AAAS	6.77		HI-757	MFA 34.113
AABS	1.59		HI-775	MFA 99.338

*from the private collection of J. J. Herrmann. †from the Museum of Fine Arts, Boston (MFA) and the Harvard University Art Museums. A final "S" in the sample name indicates a scrape sample. An initial "1" indicates a quarry sample from the Paros-1 quarry. An initial "2" indicates a quarry sample from the Paros-2 quarry. An initial "A" indicates an artifact.

APPENDIX B: ICP-MS DATA

APPENDIX B: ICP-MS CONCENTRATION DATA IN PPM; BLANK SUBTRACTED													
Element	1A	1B	1C	1CS	1D	1DS	1E	1FS	1G	1H	2IS	2J	2K
Scandium	2.550	3.102	3.013	4.206	2.050	3.640	3.745	3.715	3.949	4.458	4.330	3.289	4.039
Vanadium	3.899	4.860	3.344	7.461	3.507	4.776	5.179	4.729	5.456	5.741	5.562	4.176	4.589
Chromium	12.114	14.082	14.188	24.400	9.494	32.651	17.014	17.667	17.573	19.432	28.575	15.354	16.570
Iron	2413.457	2604.397	2431.988	4921.037	2372.991	3115.148	3597.287	3439.926	3616.409	3790.287	4533.600	4088.361	3030.095
Manganese	4.763	4.500	4.688	12.721	3.895	8.104	5.993	3.106	5.302	5.144	9.209	5.873	6.321
Cobalt	1.774	1.806	1.715	1.731	1.674	1.827	1.695	1.762	1.644	1.582	1.693	1.701	1.664
Zinc	43.163	47.025	25.056	56.887	18.810	23.349	20.629	22.655	17.066	20.202	27.489	29.865	29.237
Antimony	0.195	0.060	0.061	0.187	0.165	0.566	0.267	0.171	0.165	0.358	0.350	0.119	0.086
Caesium	0.006	0.019	0.012	0.033	0.014	0.023	0.021	0.016	0.007	0.017	0.037	0.014	0.010
Hafnium	0.258	0.228	0.202	0.401	0.107	0.166	0.230	0.198	0.083	0.171	0.241	0.137	0.147
Lead	3.236	3.748	3.092	8.761	4.451	8.008	19.113	5.782	5.469	6.709	7.093	5.720	2.949
Thorium	0.042	0.042	0.030	0.053	0.023	0.059	0.061	0.041	0.016	0.022	0.086	0.043	0.023
Uranium	0.023	0.054	0.027	0.046	0.034	0.057	0.064	0.023	0.046	0.012	0.069	0.033	0.037
Lanthanum	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	1.255	1.193	1.309
Cerium	BBL	0.124	BBL	BBL	BBL	0.141	0.197	BBL	BBL	BBL	0.246	0.119	0.195
Praeseodymium	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL
Neodymium	BBL	0.026	BBL	BBL	BBL	BBL	0.060	BBL	BBL	BBL	0.499	0.444	0.591
Samarium	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	0.057	0.039	0.057
Europium	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL
Gadolinium	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	0.895	0.775	0.823
Terbium	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL
Dysprosium	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	0.013	0.035
Holmium	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL
Erbium	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL
Thulium	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL
Ytterbium	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL
Lutetium	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL
		BBL=below blank level											

APPENDIX B, CON'T													
Element	2L	2M	2N	2O	APS	AQS	ARS	ASS	ATS	AUS	AVS	AWS	AXS
Scandium	3.570	3.024	3.993	3.380	3.641	3.318	3.419	3.009	16.064	3.607	12.147	2.936	3.107
Vanadium	4.578	3.638	5.664	3.982	4.529	5.353	6.263	4.888	23.172	5.597	14.709	4.899	4.470
Chromium	16.179	12.215	18.466	13.290	16.730	15.881	20.291	15.066	76.272	16.357	60.271	14.394	13.610
Iron	3402.612	2550.824	3499.248	2964.634	3462.468	3277.011	4476.524	3055.921	17008.573	3545.816	16627.413	2989.393	3012.364
Manganese	5.599	6.782	9.872	5.547	6.157	7.371	36.686	6.353	21.719	4.895	13.225	38.071	7.498
Cobalt	1.569	1.652	1.552	1.623	1.562	1.596	1.690	1.537	2.088	1.529	1.842	1.599	1.429
Zinc	20.842	24.608	21.087	16.029	15.491	22.127	58.677	28.644	86.908	23.024	109.276	12.120	25.406
Antimony	0.100	0.126	0.155	0.135	0.196	0.127	0.106	0.206	0.759	0.333	4.672	0.150	0.387
Caesium	0.006	0.008	0.011	0.006	0.014	0.010	0.030	0.009	0.179	0.029	0.501	0.009	0.020
Hafnium	0.102	0.099	0.132	0.078	0.110	0.057	0.130	0.091	0.602	0.134	1.308	0.074	0.078
Lead	3.067	3.351	3.476	2.666	13.993	47.274	22.085	35.336	252.861	16.334	92.506	3.146	20.282
Thorium	0.014	0.094	0.024	0.011	0.027	0.015	0.105	0.024	0.420	0.066	2.123	0.029	0.038
Uranium	0.017	0.025	0.021	0.017	0.024	0.204	0.043	0.096	0.284	0.056	0.082	0.490	0.033
Lanthanum	1.190	2.719	1.964	1.297	1.298	0.163	0.402	BBL	0.342	0.144	BBL	0.000	0.040
Cerium	0.217	0.795	0.501	0.197	0.184	BBL	0.728	BBL	1.451	0.176	0.200	0.097	BBL
Praeseodymium	BBL	0.262	0.055	BBL	BBL	BBL	BBL	BBL	BBL	BBL	0.571	BBL	BBL
Neodymium	0.609	1.756	0.964	0.587	0.469	0.061	0.358	BBL	0.076	0.082	7.339	BBL	BBL
Samarium	0.065	0.285	0.147	0.133	0.052	0.037	0.004	BBL	BBL	BBL	0.431	BBL	BBL
Europium	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL
Gadolinium	0.788	1.960	1.223	0.891	0.853	0.025	0.276	BBL	0.079	0.075	2.759	BBL	BBL
Terbium	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	0.160	BBL	BBL
Dysprosium	0.034	0.361	0.140	0.095	0.015	BBL	BBL	BBL	BBL	BBL	5.412	BBL	BBL
Holmium	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL
Erbium	BBL	0.092	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	0.383	BBL	BBL
Thulium	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL
Ytterbium	BBL	0.007	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL
Lutetium	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL	BBL
		BBL=below blank level											

APPENDIX B, CON'T								
Element	AYS	AZS	AAAS	AABS	P-1 mean	σ, n=10	P-2 mean	σ, n=7
Scandium	4.618	2.711	3.436	7.105	3.443	0.754	3.661	0.471
Vanadium	8.781	4.983	6.096	14.290	4.895	1.205	4.598	0.769
Chromium	27.013	16.165	17.258	44.205	17.861	6.630	17.236	5.415
Iron	8250.801	4687.992	3863.357	15085.585	3230.293	812.705	3438.482	683.844
Manganese	23.456	41.816	56.040	15.190	5.821	2.765	7.029	1.778
Cobalt	2.420	1.542	1.562	2.111	1.721	0.075	1.636	0.058
Zinc	42.517	15.069	44.238	68.637	29.484	14.073	24.165	5.102
Antimony	0.707	0.135	0.271	0.398	0.219	0.150	0.153	0.090
Caesium	0.018	0.050	0.170	0.049	0.017	0.008	0.013	0.011
Hafnium	0.128	0.122	0.183	0.385	0.204	0.088	0.134	0.053
Lead	43.023	16.751	68.219	164.476	6.837	4.726	4.046	1.681
Thorium	0.042	0.068	0.423	0.261	0.039	0.016	0.042	0.034
Uranium	0.066	0.092	0.266	0.111	0.039	0.017	0.031	0.018
Lanthanum	BBL	0.412	1.283	0.418	BBL	—	1.561	0.578
Cerium	0.020	0.361	2.497	0.673	0.154	0.038	0.324	0.240
Praeseodymium	BBL	BBL	0.085	BBL	BBL	—	0.158	0.146
Neodymium	BBL	0.309	1.199	0.719	0.043	0.024	0.778	0.462
Samarium	BBL	0.001	0.134	BBL	BBL	—	0.112	0.087
Europium	BBL	BBL	BBL	BBL	BBL	—	BBL	—
Gadolinium	BBL	0.236	0.939	0.134	BBL	—	1.051	0.429
Terbium	BBL	BBL	BBL	BBL	BBL	—	BBL	—
Dysprosium	BBL	BBL	BBL	BBL	BBL	—	0.113	0.130
Holmium	BBL	BBL	BBL	BBL	BBL	—	BBL	—
Erbium	BBL	BBL	BBL	BBL	BBL	—	0.092	—
Thulium	BBL	BBL	BBL	BBL	BBL	—	BBL	—
Ytterbium	BBL	BBL	BBL	BBL	BBL	—	0.007	—
Lutetium	BBL	BBL	BBL	BBL	BBL	—	BBL	—
		BBL=below blank level						

APPENDIX C: COMPARATIVE DATA

APPENDIX C: COMPARATIVE DATA													
	Green (2000)				Germann et al. (1988)				Mandi et al. (1995)			Mello et al. (1988)	
	n=10	σ	n=7	σ	n=12	n=42	n=20	n=27					σ
Element	Gr00 P-1	Gr00 P-1	Gr00 P-2	Gr00 P-2	Ge88 P-1	Ge88 P-2	Ge88 P-3	Ge88 N	Ma93 P	Ma93 Pe	Ma93 N	Ml88 P	Ml88 P
Scandium	3.44	0.75	3.66	0.47	ND	ND	ND	ND	0.049	0.066	0.25	5.16	0.04
Vanadium	4.90	1.20	4.60	0.77	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chromium	17.86	6.63	17.24	5.42	ND	ND	ND	ND	1.27	0.56	1.33	12.63	0.25
Iron	3230.29	812.71	3438.48	683.84	50	105	170	170	35	280	584	ND	ND
Manganese	5.82	2.77	7.03	1.78	10.5	14	13	37	ND	ND	ND	ND	ND
Cobalt	1.72	0.08	1.64	0.06	ND	ND	ND	ND	0.013	0.056	0.242	1.71	0.11
Zinc	29.48	14.07	24.17	5.10	6.5	7	7	10	2	2.7	5.8	ND	ND
Antimony	0.22	0.15	0.15	0.09	ND	ND	ND	ND	ND	ND	ND	0.12	0.01
Caesium	0.02	0.01	0.01	0.01	ND	ND	ND	ND	ND	ND	ND	0.159	0.053
Hafnium	0.20	0.09	0.13	0.05	ND	ND	ND	ND	ND	0.017	0.025	0.19	0
Lead	6.84	4.73	4.05	1.68	ND	ND	ND	ND	ND	ND	ND	ND	ND
Thorium	0.04	0.02	0.04	0.03	ND	ND	ND	ND	0.013	0.068	0.079	1.346	0.032
Uranium	0.04	0.02	0.03	0.02	ND	ND	ND	ND	0.073	0.035	0.043	0.039	0.004
Lanthanum	BBL	BBL	1.56	0.58	ND	ND	ND	ND	0.99	1.03	0.908	37.3	5
Cerium	0.15	0.04	0.32	0.24	ND	ND	ND	ND	0.44	1.58	0.82	41.23	1.95
Praeseodymium	BBL	BBL	0.16	0.15	ND	ND	ND	ND	ND	ND	ND	ND	ND
Neodymium	0.04	0.02	0.78	0.46	ND	ND	ND	ND	0.31	0.29	0.38	ND	ND
Samarium	BBL	BBL	0.11	0.09	ND	ND	ND	ND	0.066	0.142	0.113	3.18	0.35
Europium	BBL	BBL	BBL	BBL	ND	ND	ND	ND	0.025	0.04	0.051	0.99	0.034
Gadolinium	BBL	BBL	1.05	0.43	ND	ND	ND	ND	ND	ND	ND	2.97	0.01
Terbium	BBL	BBL	BBL	BBL	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dysprosium	BBL	BBL	0.11	0.13	ND	ND	ND	ND	ND	ND	ND	ND	ND
Holmium	BBL	BBL	BBL	BBL	ND	ND	ND	ND	ND	ND	ND	0.826	0.015
Erbium	BBL	BBL	0.09	BBL	ND	ND	ND	ND	ND	ND	ND	ND	ND
Thulium	BBL	BBL	BBL	BBL	ND	ND	ND	ND	0.039	0.029	0.03	0.373	0.015
Ytterbium	BBL	BBL	0.01	BBL	ND	ND	ND	ND	0.093	0.102	0.106	1.006	0.02
Lutetium	BBL	BBL	BBL	BBL	ND	ND	ND	ND	ND	ND	ND	0.143	0.011
	BBL=below blank level			ND=no datum									

APPENDIX C, CON'T													
					Meloni et al. (1988)			Meloni et al. (1995)			Roos et al. (1988)		
		σ		σ							n=22	n=24	n=12
Element	Ml88 Pe	Ml88 Pe	Ml88 N	Ml88 N	Mn88 P	Mn88 Pe	Mn88 N	Mn93 P	Mn93 Pe	Mn93 N	R88 P	R88 Pe	R88 N
Scandium	2.32	0.11	3.65	0.22	5.16	2.3	3.6	ND	ND	ND	0.0612	0.0481	0.0302
Vanadium	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.62	0.42	0.71
Chromium	3.52	0.29	5.75	0.17	12.6	3.5	5.7	ND	ND	ND	0.93	0.52	0.96
Iron	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	41.6	240	49.5
Manganese	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	6	68	24.8
Cobalt	0.71	0.04	0.74	0.01	1.7	0.71	0.74	ND	ND	ND	0.0244	0.0481	0.0255
Zinc	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.91	3.73	1.84
Antimony	0.07	0.01	0.48	0.05	0.12	0.07	0.48	ND	ND	ND	ND	ND	ND
Caesium	0.078	0.012	0.162	0.025	0.16	0.08	0.16	ND	ND	ND	ND	ND	ND
Hafnium	0.17	0	0.2	0.01	0.19	0.17	0.2	ND	ND	ND	ND	ND	ND
Lead	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Thorium	1.634	0.215	1.68	0.132	1.35	1.6	1.7	ND	ND	ND	0.0196	0.0217	0.0202
Uranium	0.039	0.004	0.037	0.003	0.039	0.039	0.037	ND	ND	ND	0.065	0.0428	0.075
Lanthanum	6	0.3	8.3	1.8	37	6	8	1.4	1.3	1.97	0.69	0.72	0.42
Cerium	9.7	0.92	8.61	0.61	41	9.7	8.6	2.65	1.473	4.51	ND	ND	ND
Praeseodymium	ND	ND	ND	ND	ND	ND	ND	0.261	0.201	0.371	ND	ND	ND
Neodymium	ND	ND	ND	ND	ND	ND	ND	0.94	0.983	1.1	ND	ND	ND
Samarium	0.88	0.05	0.95	0.02	3.2	0.88	0.95	0.16	0.163	0.1	ND	ND	ND
Europium	0.179	0.012	0.243	0.021	0.99	0.18	0.24	0.056	0.043	0.029	ND	ND	ND
Gadolinium	0.577	0.026	0.864	0.026	2.97	0.58	0.86	0.142	0.154	0.142	ND	ND	ND
Terbium	ND	ND	ND	ND	ND	ND	ND	0.023	0.019	0.027	ND	ND	ND
Dysprosium	ND	ND	ND	ND	ND	ND	ND	0.193	0.204	0.21	ND	ND	ND
Holmium	0.112	0.005	0.196	0.036	0.83	0.112	0.2	0.03	0.031	0.029	ND	ND	ND
Erbium	ND	ND	ND	ND	ND	ND	ND	0.094	0.098	0.089	ND	ND	ND
Thulium	0.239	0.006	0.077	0.011	0.37	0.239	0.08	0.014	0.015	0.013	ND	ND	ND
Ytterbium	0.032	0.004	0.029	0.003	1	0.032	0.029	0.06	0.072	0.06	ND	ND	ND
Lutetium	0.035	0.006	0.021	0.001	0.14	0.035	0.021	0.011	0.017	0.011	ND	ND	ND
	BBL=below blank level			ND=no datum									