

ASSESSING CERAMIC COMPOSITIONAL DATA: A COMPARISON OF TOTAL REFLECTION X-RAY FLUORESCENCE AND INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS ON LATE IRON AGE SPANISH CELTIBERIAN CERAMICS*

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A solid-phase, non-chemical processing protocol was recently developed as a means of chemically characterizing archaeological ceramics by total reflection X-ray fluorescence (TXRF). Following this methodology, TXRF can provide semi-quantitative determinations for 18 elements with comparable levels of precision and accuracy for the majority of them in comparison with a clay reference material analysed by instrumental neutron activation (INAA). In order critically to assess the analytical capabilities of TXRF, a large sample set of Late Iron Age Spanish Celtiberian ceramics and modern clays was analysed both by TXRF and INAA. Semi-quantitative chemical data provided by TXRF and quantitative data provided by INAA were subjected to commonly used multivariate statistical methods as a way of evaluating the ability of the new technique to discriminate among different compositional groups. The comparison of the two data sets shows no significant discrepancies, thereby allowing support for the same archaeological interpretation. These results suggest that TXRF has potential applicability for compositional characterization of archaeological ceramics, providing data that are useful for provenance studies.

KEYWORDS: CENTRAL SPAIN, LATE IRON AGE, CELTIBERIAN PERIOD, TOTAL REFLECTION X-RAY FLUORESCENCE, INSTRUMENTAL NEUTRON ACTIVATION, INTERCOMPARISON, CERAMIC COMPOSITIONAL ANALYSIS, PROVENANCE

INTRODUCTION

A basic aim of compositional characterization of archaeological ceramics is to isolate ceramic groups of similar chemical profiles and statistically to test the validity of those groups. The emerging compositional patterns can be further evaluated through comparison with typological and/or mineralogical data and used to address different aspects of ancient ceramic production and distribution.

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To meet the above objectives, a battery of instrumental techniques has been used throughout the past three decades. These include atomic absorption spectrometry (AAS), X-ray fluorescence (XRF), instrumental neutron activation analysis (INAA) and, more recently, inductively coupled plasma atomic emission spectrography (ICP–AES) and inductively coupled plasma mass spectrometry (ICP–MS) (see, e.g., Schneider 1993; Shingleton *et al.* 1994; Hatcher *et al.* 1995; Mirti *et al.* 1995). The technique most often used has been INAA, primarily because of its ability to provide the required levels of precision and accuracy, large sample throughput and simultaneous elemental determinations. A limitation of this method, however, stems from the need to have access to a suitable nuclear reactor for sample irradiation.

Regardless of the specific technique used, both precision and accuracy play a significant role in compositional studies. The more precise and accurate the bulk chemical determinations provided by a given technique, the better is the chance of making more plausible and refined inferences on production and distribution of archaeological ceramic materials. Accordingly, development of new analytical methods requires standardization of elemental determinations in order to assure the reproducibility and comparability of results (Bishop *et al.* 1990).

Since the appearance of the first commercial units in early 1989, the use of the relatively new technique of TXRF has increased in several scientific fields. Although the technique has produced high-quality data, especially from liquid and forensic samples (see, e.g., Prange 1989; Aiginger 1991; Kregsamer 1991; Tölg and Klockenkämper 1993), prior to the present research it had not been used in archaeological studies. Distinct advantages of TXRF are low sample preparation costs and precise, simultaneous, multi-elemental determinations for those elements with atomic number higher than 12. In contrast with traditional X-ray fluorescence (XRF), it also offers the advantage of minimizing matrix effects.

In order critically to assess the analytical capabilities and resolution of TXRF for the compositional analysis of archaeological ceramics, a large sample of Celtiberian potsherds and modern clays was analysed both by total reflection X-ray fluorescence (TXRF) and by instrumental neutron activation analysis (INAA). A comparison of these data sets provides a basis from which to evaluate the application of TXRF. In addition, the availability of mineralogical information provided further understanding of the results derived from each technique. In our approach, therefore, the evaluation of TXRF as a reliable and alternative compositional method for ceramic analysis required that general trends in the TXRF data should parallel results provided by INAA. This paper reports the work undertaken to compare the techniques. The results show that, with some exceptions, samples analysed by INAA were assigned into the same compositional groups previously suggested by TXRF data. Chemical patterns of both data sets, in concordance with textural and mineralogical data, suggest that some of these groups represent different paste recipes rather than different raw material sources. Yet, more importantly, both techniques were able to recover the same range of information, from which one can infer distinct manipulations of the raw clay. These results lead us to propose that TXRF has potential applicability for multi-elemental characterization of ancient ceramics, providing data useful for provenance studies and, consequently, for archaeological interpretations.

ARCHAEOLOGICAL BACKGROUND OF THE SAMPLE SET

The Celtiberian period (approximately the last four centuries BC) is the final chronological phase of Late Iron Age in central Spain prior to the arrival of the Romans. It is mainly associated with the emergence of towns and the first widespread appearance of wheel-made pottery. The

Upper Duero Valley is one of the settings where this period is better known. The valley is a Tertiary basin formed by the erosion of soft clay and marl sediments, mostly of Miocene origin, and punctuated by small outcrops of Jurassic and Cretaceous origins (Bachiller and Sancho 1990, 8–10). The Upper Duero Valley is almost entirely confined within the current administrative province of Soria (Fig. 1).

Recent systematic archaeological surveys (see, e.g., Jimeno and Arlegui 1995) have recovered evidence for the development of an important settlement pattern during the late second and first centuries BC. This pattern, which occupies most of the agricultural land, has been explained in terms of an effective Romanization of the Celtiberian inhabitants of the communities in the region (Romero 1992). Numancia was the most important walled town in this area (Fig. 1, site 1). With an almost continuous occupation since, at least, the end of the third century BC until imperial times, the site has long been a subject of interest for scholars. According to classical written sources, the Celtiberian inhabitants were involved in an epic struggle with Roman invaders, who, after a long siege, preferred to die rather than surrender the town (the town fell in 133 BC). Such action and history converted the site into a nationalistic symbol that has endured even up to the present day.

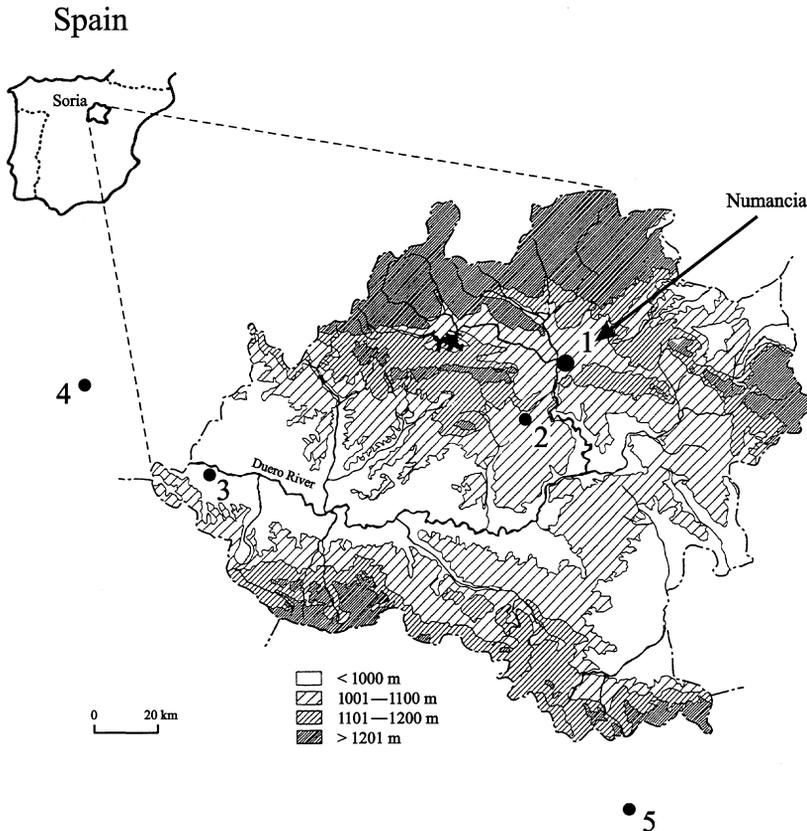


Figure 1 A map of the Upper Duero Valley showing sites mentioned in the text. 1, The town of Numancia; 2, Izana; 3, Langa de Duero; 4, El Pradillo; 5, El Palomar.

Because of the town's historical prominence, Numancia has been the focus of several periods of excavation since the second half of the nineteenth century (e.g., 1860–1866, 1905–1923, 1963 and 1970–1971), which have unearthed almost half of the ancient town (around 6 ha). Following a period of relative inactivity, a new project was undertaken in 1990 that attempted to coordinate conservation, research and education activities better to understand the historical context in which the development of Numancia took place. As part of this project, integrated compositional and mineralogical research was initiated to address questions related to production and distribution of the recovered ceramic remains (García-Heras 1998, forthcoming).

The foremost Numantian-style ceramic is dominated by a wheel-thrown red/orange plain or decorated serving ware, most often with a wide range of black-painted geometric and/or figurative motives. Lesser quantities of serving grey wares and cooking black wares are also present (García-Heras 1998, 59–66), as well as polychrome serving vessels decorated with black, red and white pigments (García-Heras and Vendrell-Saz 2000).

The investigation of instrumental TXRF as a characterization method for ceramics was designed, first, to identify compositional groups and determine their probable provenance and, second, to identify potential interactions both within and outside the region. The former objective might suggest different raw material sources or production units, whereas the latter could provide evidence for determining whether ceramics with similar decorative designs found outside the Upper Duero Valley represent an incipient trade or exchange, as commonly presumed, or merely shared interregional style.

The sample set analysed in this comparison study consisted of 121 ceramic and eight modern clay samples acquired from five excavated archaeological sites. Of the 121 sherds, 83 were from Numancia. These samples were selected after the whole ceramic assemblage, dated to the late second and first centuries BC, was studied, sorted and classified into fabric categories using a binocular microscope. The specimens were selected to encompass the variability of vessel shape and decoration, and to represent the range of fabrics. To explore interactions, both within and outside the Upper Duero Valley, 38 additional sherds from four other locations were also analysed: 17 from Izana (Soria province), five from Langa de Duero (Soria), 11 from El Pradillo (Burgos), and five from El Palomar (Guadalajara). Figure 1 shows the locations of these sites.

Samples from Izana (Fig. 1, site 2) were selected to determine whether pottery from Numancia was intraregionally distributed. Izana is a secondary centre (a walled village) dating from the late second to the first century BC. Fieldwork undertaken in the 1920s recovered a ceramic assemblage that is very similar to that found in Numancia, except for the absence of polychrome decorations (see Taracena 1927). Langa de Duero (Fig. 1, site 3) is a non-walled small town, dated to the late first century BC. This site yielded some of the few sherds of polychrome vessels recovered either within or outside the Upper Duero Valley (García-Heras 1998, 17–22). They were included in the analysis to determine whether polychrome ceramics came from Numancia or were locally produced. To explore outside interactions, Numantian-style samples were selected from two additional sites. El Pradillo (Fig. 1, site 4) is a burial site located at the head of the Middle Duero Valley. It is a Celtiberian necropolis used during the last four centuries BC, from which an assemblage of graves dated to the first century BC were excavated (Moreda and Nuño 1990). El Palomar (Fig. 1, site 5) is a hillfort located in the Upper Tajo Valley and occupied, along with earlier and later phases, during the last two centuries BC (Arenas 1999).

Modern clay deposits were explored and seven samples were taken from different outcrops within the 5 km catchment area of Numancia, as well as one in the vicinity of Izana. Several briquettes from each clay sample were prepared in the laboratory and fired in an electric kiln under

an oxidizing atmosphere¹ at temperatures of 700 °C, 800 °C, 900 °C and 1000 °C. Those unfired and those fired to 900 °C, however, were eventually chosen, as this encompasses the range of firing temperatures for the archaeological ceramics (García-Heras 1998, 90–1). The total sample set for the present study consisted of 137 samples: 121 sherds and 16 clay briquettes.

METHODS

TXRF analytical procedure

The angle of incidence of the primary X-ray beam in conventional XRF is about 45°. In comparison, the angle of incidence for TXRF is about 4 min of arc, which thereby produces a substantial improvement in the peak : background ratio. To exploit this advantage and to minimize corrections for matrix absorption, the sample is deposited on a flat carrier to achieve a thin-film geometry (Prange 1989, 438). This condition can be achieved as long as the deposited sample complies with the following three requirements: (1) chemical homogeneity, in order to avoid selective sedimentation of micro-particles as a result of their density; (2) average particle sizes of less than 10 µm; and (3) homogeneous distribution of particles deposited as a mono-particle layer (García-Heras *et al.* 1997, 1004).

A non-chemical processing protocol for ceramics has been developed to provide the optimum sample for analysis (García-Heras *et al.* 1997; García-Heras 1998). This protocol involves (1) the homogenization of the whole sample by a grinding process using a vibration micropulverizer with ball and base of agate; (2) suspension of the fine-ground mixture in high-purity water; (3) ultrasonic disaggregation of the suspension; and (4) immediate deposition of an aliquot of that suspension in a flat carrier where the high-purity water is evaporated by vacuum. Following this protocol, TXRF can provide semi-quantitative determinations, expressed as weight% versus Fe, for the following 18 elements: As, Nd, Cr, Hf, Ni, Rb, Sr, Zn, Al, Ba, Ca, K, Mn, Ti, V, Cu, Ga and Y. A more detailed description of the protocol, as well as an estimate of precision (or reproducibility) and accuracy based on the replicate analysis of the Ohio Red Clay-2 reference material, can be found in García-Heras *et al.* (1997, 1006–7). Table 1 shows the descriptive statistics for that reference material measured at the Missouri University Research Reactor (MURR) and the SCMRE facility maintained at National Institute of Standards and Technology (NIST) for the range of elements analysed by TXRF. Measurements have been normalized versus Fe in order to make them comparable with those provided by TXRF. On the right side of Table 1, the column labeled 'routine' shows measurements of the reference material undertaken in each batch of 15 or 20 samples during the analysis of the full sample set as a check on internal analytical precision. In general, TXRF provides comparable levels of precision and accuracy for at least 15 elements.

As a further development of the technique, fully quantitative analysis of archaeological ceramics was recently explored. As a result, a chemical processing, liquid-phase protocol has been developed. Using this protocol, which involves both microwave oven acid lixiviation and Fe selective extraction processes, TXRF can provide quantitative determinations for

¹ Samples were processed by soaking clay for 5 h, followed by sieving with a 120-mesh sieve, and then spreading it out to dry. From this, briquettes were made. After a drying period of 10 days at room temperature, they were fired. The firing was performed with an annealing period of 3 h, during which the temperature was raised by 50 °C every half hour up to 300 °C. In a second stage, the temperature was raised by 100 °C every 10 min up to the maximum range. In each case, the maximum temperature was only maintained for 15 min.

Table 1 Descriptive statistics for Ohio Red Clay-2 of INAA and TXRF measurements

Element	INAA (MURR) (n = 20) Mean ± sd	CV	INAA (NIST) (n = 124) Mean ± sd	CV	TXRF (protocol) (n = 5) Mean ± sd	CV	TXRF (routine) (n = 7) Mean ± sd	CV
As	0.028 ± 0.002	7.1	0.031 ± 0.002	5.6	0.041 ± 0.002	4.9	0.044 ± 0.002	4.5
Nd	0.09 ± 0.01	11.1	0.101 ± 0.017	17.3	0.06 ± 0.02	33.3	0.06 ± 0.02	33.3
Cr	0.18 ± 0.01	5.5	0.18 ± 0.007	3.7	0.18 ± 0.01	5.5	0.18 ± 0.01	5.5
Hf	0.015 ± 0.001	6.6	0.015 ± 0.0005	3.3	0.013 ± 0.007	53.8	0.009 ± 0.002	22.2
Ni	0.14 ± 0.03	21.4	n.d.	–	0.44 ± 0.01	2.3	0.15 ± 0.003	2
Rb	0.36 ± 0.02	5.5	0.41 ± 0.033	8.1	0.35 ± 0.004	1.1	0.37 ± 0.01	2.7
Sr	0.05 ± 0.06	120	n.d.	–	0.13 ± 0.004	3	0.14 ± 0.005	3.6
Zn	0.18 ± 0.02	11.1	0.19 ± 0.027	14.3	0.28 ± 0.03	10.7	.20 ± .01	5
Al	185 ± 6	3.2	n.d.	–	151 ± 30	19.9	152 ± 5	3.3
Ba	1.2 ± 0.3	25	1.33 ± 0.13	9.8	1.34 ± 0.07	5.2	0.73 ± 0.2	27.4
Ca	3.0 ± 0.4	13.3	n.d.	–	2.81 ± 0.04	1.4	3.5 ± 0.3	8.6
K	64 ± 16	25	66 ± 3.1	4.7	69 ± 1	1.4	70 ± 2	2.8
Mn	0.51 ± 0.01	2	n.d.	–	0.5 ± 0.01	2	0.4 ± 0.01	25
Ti	11.9 ± 0.6	5	n.d.	–	12.3 ± 0.2	1.6	11.6 ± 0.2	1.7
V	0.39 ± 0.01	2.5	n.d.	–	0.49 ± 0.02	4.1	0.38 ± 0.02	5.1
Cu	n.d.	–	n.d.	–	0.04 ± 0.01	25	0.03 ± 0.0004	13.3
Ga	n.d.	–	n.d.	–	0.05 ± 0.002	4	0.051 ± 0.001	2
Y	n.d.	–	n.d.	–	0.08 ± 0.01	12.5	0.08 ± 0.007	8.7

Values expressed as wt% versus Fe; CV, coefficient of variation in per cent; n.d., not determined.

24 elements with comparable levels of precision and accuracy on the same check material mentioned above (García-Heras *et al.* 1998; Fernández-Ruiz *et al.* 1999).²

The analysis by TXRF was performed using a Seifert Extra-II spectrometer equipped with two 2 kW fine-focus tubes of Mo and W working at 30 mA and 50 kV, and a 80 mm² active area Si(Li) detector with a 157 eV resolution at 5.9 keV. The peripheral electronic system was a pulsed optical feedback preamplifier, a Wilkinson type analogue–digital converter (ADC) of 100 MHz and a pulsed processor with dead time correction and pile-up rejection (Link Systems Ltd). Spectra were acquired for 2000 s. Samples were taken by means of a steel drill with diamond powder electrolytically deposited on the cut area, a technique especially designed for this research (García-Heras 1998, 40–1).

INAA analytical procedure

Instrumental neutron activation analysis was undertaken at the SCMRE facility maintained at National Institute of Standards and Technology (NIST, Gaithersburg, Maryland, USA). In this study, the following 27 elements were routinely quantified: Na, K, Ca, Sc, Cr, Fe, Co, Zn, As, Rb, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Th, U, W and Ga. Samples were irradiated for 4 h at a flux of 7.7×10^{13} n cm⁻² s⁻¹. Each sample was counted twice using a germanium detector. The first count was after a 6-day decay and the second after at least a

² The instrumental TXRF employed in this research is different from the new high-precision method of conventional XRF analysis recently reported by Adan-Bayewitz *et al.* (1999).

30-day decay. The analytical parameters and check standards used are described in more detail elsewhere (Blackman 1984, 23–5; 1986). INAA was carried out on the same samples obtained using the drill mentioned earlier, except for 16 sherds for which insufficient sample remained after the analysis by TXRF. The latter specimens were resampled using another type of drill, which occasionally induces Co and W contamination in the samples. For that reason, Co and W were eliminated from the data set.

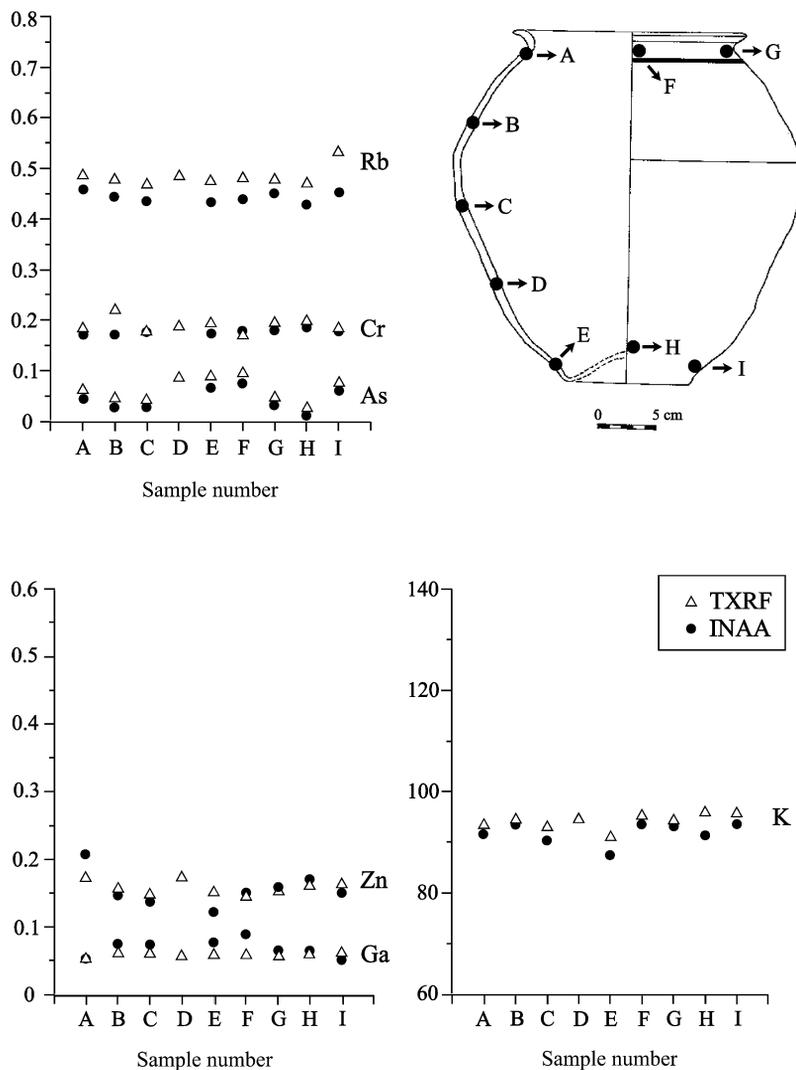


Figure 2 Locations and comparison determinations of the samples taken from the profile of a Celtiberian full vessel for the error assessment test. Sample D was not analysed by INAA because there was an insufficient quantity of sample available. Values expressed as wt% versus Fe.

RESULTS AND DISCUSSION³*Error assessment*

Before starting the numerical analysis of the entire sample set derived from both techniques, an error assessment test (see, e.g., Henrickson and Blackman 1992) was carried out to verify the reproducibility and representativeness for the type of low-fired ceramics considered in this paper. Figure 2 shows concentrations obtained by TXRF and INAA for those elements in common on a set of nine samples taken from the profile wall of a Celtiberian full vessel recovered in the El Palomar settlement site (García-Heras 1998, 52–6). INAA determinations were normalized to weight% versus Fe to make them comparable with those provided by TXRF.

Good agreement was observed for the paired determinations. The samples exhibited the same patterns of variability in data for both analytical techniques. The results, therefore, show that TXRF provides a high level of reproducibility. They also suggest that it is possible to use a single bulk sample as representative of the whole sherd in the analysis of this type of ceramics.

TXRF data analysis

Values derived from determinations made by TXRF were submitted to three numerical procedures: cluster analysis, principal components analysis and canonical discriminant analysis

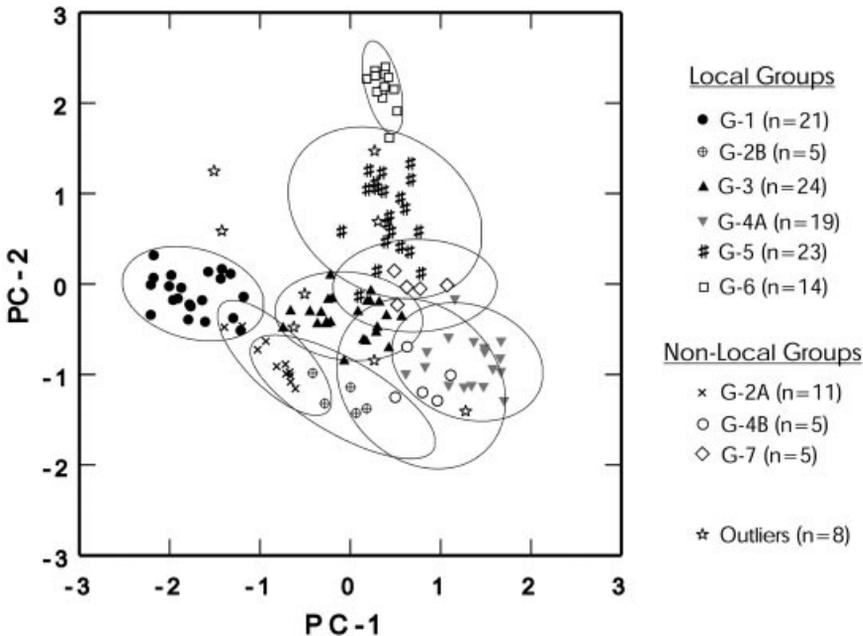


Figure 3 The first two components plot derived from principal components analysis of the TXRF data ($n = 135$). The ellipses represent the 90% confidence level for membership in each group.

³ The concentration data on which the following analyses are based are not presented here due to space limitations, but are available upon request from the senior author.

Table 2 Component loadings derived from principal components analysis of the TXRF data

	PC-1	PC-2	PC-3	PC-4	PC-5	PC-6
As	-0.099	0.038	0.169	-0.158	0.090	-0.013
Cr	0.015	0.117	0.023	-0.018	0.007	0.013
Ni	-0.019	0.141	0.012	0.024	0.022	0.016
Rb	0.033	0.135	0.029	0.001	0.020	0.006
Sr	-0.056	0.117	0.084	-0.008	0.059	-0.007
Zn	-0.002	0.212	-0.028	0.049	0.017	0.090
Al	0.004	0.137	0.027	-0.020	0.004	0.008
Ba	-0.076	0.192	0.022	0.039	0.008	-0.142
Ca	-0.624	-0.011	0.086	-0.044	-0.032	0.020
K	0.026	0.133	0.026	0.010	0.021	-0.033
Mn	-0.247	0.011	-0.167	0.155	0.025	-0.001
Ti	0.006	0.159	0.013	0.002	0.014	0.020
V	0.040	0.114	0.016	-0.005	-0.001	0.015
Cu	0.006	0.188	-0.104	-0.049	-0.149	-0.010
Ga	0.051	0.143	-0.008	-0.023	-0.018	0.005
Y	-0.001	0.165	0.037	0.001	0.015	0.027
Eigenvalue	0.476	0.307	0.088	0.059	0.038	0.032
Variance (%)	44.5	28.7	8.2	5.5	3.5	3.0

including the calculation of Mahalanobis distances. Bivariate plots were employed to display the structure of the groups in a reduced dimensional space. The relative concentrations were transformed into log base 10 values to compensate for large magnitudes of difference between major and trace elements (Bishop and Neff 1989, 63). Nd and Hf were eliminated from the data set because of some missing values that resulted from their concentrations being close to or below the detection limits of TXRF (García-Heras *et al.* 1997, 1006). Consequently, statistical analysis of the TXRF data was carried out using 16 elemental variables.

TXRF chemical data were first subjected to cluster analysis using the centroid clustering method on a matrix of Euclidean distances. The resulting dendrogram showed that the majority of the samples were classified into nine primary groups, linked at different levels of similarity, with a few unassigned individuals. A principal components analysis, based on a variance-covariance matrix, shows the same general structure. The compositional distinctiveness of the nine groups is illustrated in Figure 3, which shows sample scores and group membership (as suggested by the cluster analysis) with respect to the two first components, summarizing 73.2% of the total variation in the data. Relative concentrations of Ca and Mn on the one hand, and Rb, V and K on the other, are key variables that reveal the greatest separation among the groups. Table 2 presents the component loadings obtained for the six first components. Inferred local groups are composed of both ceramic and clay samples from the town of Numancia and the secondary site of Izana, while non-local ones are composed of ceramic samples from sites located outside the core region. Means, standard deviations and coefficients of variation for these groups are presented in Appendix A.

Local group G-1 contains all of the sampled calcareous clays (four from Numancia and a single one from Izana) as well as all the domestic black ceramic samples. The latter were also from Numancia and Izana, and are characterized by containing large amounts of intentionally

added monocrystalline calcite, as determined by petrographic analysis (García-Heras 1998, 70–1; forthcoming). Individual specimens making up this group occur low on the first component as a result of their high relative concentrations of Ca and Mn (Fig. 3). In fact, this group shows the highest concentrations for both elements (see Appendix A). Interestingly, no consistent patterns of increase or decrease of elements dependent on processing were found in any of the five calcareous clays, since those fired at 900 °C do not cluster apart from samples dried at room temperature (cf., Cogswell *et al.* 1996).

Non-local group G-2A is composed exclusively of samples from the burial site of El Pradillo, which is located in the Middle Duero Valley. They plot near G-1 as a result of its high relative values of Ca (Fig. 3; Appendix A). These results are in agreement with mineralogical data, since only the samples from this group have calcareous matrices (García-Heras 1998, 70–1; forthcoming).

Local group G-2B only contains five samples: four non-calcareous clay briquettes from Numancia and a single domestic black ceramic sample from Izana with no added calcite (Fig. 3). These clays do not show a strong tendency for elemental patterns to either increase or decrease with firing. This small group contains too few samples to estimate multivariate group parameters. Using discriminant analysis, members of this group were rejected from inclusion in any of the other groups. Its validity as a meaningful compositional group, however, remains in question.

Local groups G-3 and G-4A are composed principally of serving red and domestic black ceramic samples, the latter with no added calcite. The groups lying at the centre of the Figure 3 plot reflect moderate concentrations of Rb, K, Ti and V (see Appendix A). These groups also contain four samples of grey ceramics. Samples from the town of Numancia and the secondary site of Izana are included in both of them. In spite of its small size (five specimens), non-local group G-4B is formed exclusively by having samples from the site of El Palomar. It differs from G-4A by having higher relative concentrations of Sr (see Appendix A).

Two well separated local groups (G-5 and G-6), containing specimens from Numancia only, are represented by samples having the highest relative values of Rb, Al, Ti and K. Located towards the upper part of Figure 3, both groups show strong compositional homogeneity, as evidenced by low coefficients of variation for these mentioned elements (see Appendix A). Group G-5 contains the majority of the grey ceramic samples analysed in this study, as well as the lighter red/orange sherds. In contrast, group G-6 is almost entirely composed of ceramics carrying polychrome decorations on light orange or near white sherds. Ceramics from these two groups were probably manufactured from kaolinitic clays that fire from white to light orange in an oxidizing atmosphere and which have a higher Al : Rb ratio than those containing mainly illites (Rice 1987, 45–50)—a situation in accord with microstructural data provided by scanning electron microscopy (García-Heras 1998, 114–19). Nevertheless, one clay sample taken near Numancia and identified as kaolin could not be assigned to either of these two groups. It appears to be compositionally different and was subsequently removed from the statistical analyses. For this reason, those figures depicting statistical information only show a sample set composed of 135 specimens.

Finally, the inferred non-local group G-7 consists of five samples (Fig. 3). Only three of the five polychrome sherds taken from Langa de Duero are classified into this group. The other two samples include one from Numancia and another from Izana. Due the small size of this compositional group, it is difficult to know whether it is a 'real' group or several close-lying outliers in 16-dimensional space. The impression of the samples being outliers, however, is strengthened by the fact that both have higher concentrations of Rb, K and Cu, and lower

concentrations of Al, Ca, Ti and Ga in comparison with the three samples from Langa de Duero. Due to this fact, only the three samples of Langa de Duero have been included in the calculations shown in Appendix A.

A total of eight samples remain unassigned (Fig. 3). They appear to be outliers of the nine groups. Thus, a single calcareous sample diverges from the other samples of group G-1 because it exhibits lower relative concentrations of Ca. Two other outliers fail to plot reasonably close to the samples of groups G-3 and G-5, respectively. Both show extremely high relative values of Cu and As that could be related to some contamination processes that occurred during burial. The five remaining outliers were all identified by mineralogical techniques as having unique over-firing features such as areas of vitrification or neoformed high-temperature phases. The two polychrome samples from Langa de Duero, which were not classified into group G-7, are in this category.

The distinctiveness of these compositional groups was subsequently evaluated by discriminant analysis. In general, results from this analysis are in agreement with those previously obtained. Most of the members of each compositional group showed acceptable levels of confidence, usually higher than 95%, for integration into its group.

In summary, numerical analysis of the TXRF data indicates the existence of chemically distinct compositional groups, demonstrating that different raw materials or different production units are present in the ceramic assemblage from the town of Numancia. These raw materials are compositionally compatible with modern clay samples recovered from survey in the area. Numantian-style ceramics from outside the Upper Duero, however, show a different chemical profile, suggesting that they were not distributed outside this region. Ceramic samples from Numancia and the secondary site of Izana failed to show any compositional differences.

INAA data analysis

The resulting data were submitted to principal components and canonical discriminant analysis with calculation of Mahalanobis distances. Cluster analysis seemed to be unnecessary, since previous TXRF data showed that different groups did exist. Concentrations derived from INAA were transformed, like those from TXRF, into log base 10 values to compensate as well for large magnitudes of difference between major and trace elements.

The first step in the numerical analysis of the INAA data attempted to identify the compositional structure previously provided by TXRF. Ideally, as long as one uses highly precise methods for the same elements, the compositional vectors characterizing the samples in the n -dimensional space should not be affected as a consequence of the analytical method employed. In this particular case, however, the assumption is weakened, since the methods do not provide determinations for the same suite of elements.

Previous compositional groups, as suggested by TXRF, were tested initially by plotting them on principal components axes, using different combinations of elements determined with the lowest analytical errors. Figure 4 shows sample scores and group membership with respect to the two first components, which summarize 76.3% of the total variation in the entire data set. This analysis was based on a variance-covariance matrix using the 11 elements with the lowest coefficients of variation (always less than 5%): namely, K, Sc, Cr, Fe, Cs, La, Ce, Sm, Eu, Hf and Th. Nine different groups are present, and 12 outliers are now shown. Concentrations of K, Cs, Eu, Cr, Fe, Sm and Ce are primarily responsible for separating the groups. Table 3 shows component loadings obtained for the six first components. As before in the TXRF data, the inferred local groups are composed of both ceramic and clay samples from the town of

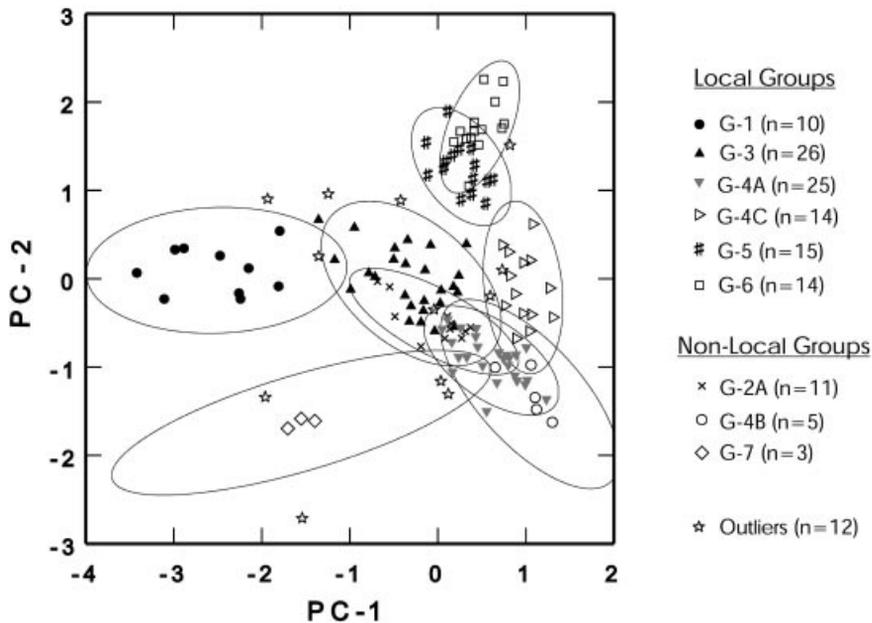


Figure 4 The first two components plot derived from principal components analysis of the INAA data ($n = 135$). The ellipses represent the 90% confidence level for membership in each group.

Numancia and the secondary site of Izana, while non-local groups are composed of ceramic samples from sites located outside the core region. Means, standard deviations and coefficients of variation are presented in Appendix B.

Broadly speaking, the INAA data analysis reveals the same general structure previously obtained with the TXRF set, but with two minor differences. The first difference is that the previous G-2B group found by TXRF has lost its appearance of cohesiveness. Most of its

Table 3 Component loadings derived from principal components analysis of the INAA data

	PC-1	PC-2	PC-3	PC-4	PC-5	PC-6
K	0.116	-0.033	0.003	-0.058	0.057	0.005
Sc	0.089	-0.026	0.010	-0.015	-0.021	-0.023
Cr	0.091	-0.026	0.001	-0.010	-0.025	-0.033
Fe	0.058	-0.125	-0.044	0.056	0.014	0.003
Cs	0.111	-0.049	0.043	-0.011	-0.041	0.034
La	0.086	0.040	-0.013	0.013	0.001	0.002
Ce	0.085	0.042	-0.004	0.016	0.016	-0.005
Sm	0.084	0.059	-0.035	0.008	-0.002	0.011
Eu	0.099	0.068	-0.047	0.002	-0.016	0.006
Hf	0.053	0.038	0.070	0.051	0.024	-0.002
Th	0.071	0.007	-0.027	0.011	0.003	-0.011
Eigenvalue	0.085	0.033	0.013	0.010	0.007	0.003
Variance (%)	54.7	21.6	8.5	6.6	4.7	2.0

members now appear as unassigned outliers. The second difference is that a new compositional subgroup has been identified: G-4C. This new subgroup is composed of 14 specimens and is primarily separated by the pattern of rare earth element concentrations. Table 4 summarizes the comparison between groups provided by each technique. Figure 5 graphically displays INAA local and non-local groups showing previous classification of the samples. Figure 6 depicts, in addition, the number of samples that have changed groups and their new location.

Using INAA, local group G-1 is now exclusively composed of the black domestic ceramic samples either from Numancia or Izana, in which large amounts of intentionally added monocrySTALLINE calcite was identified. Individuals from this group are well represented on the left side of Figure 4 as a result of their low concentrations of K, Cs, Fe and rare earth elements (e.g., La, Ce and Sm). Based on discriminant analysis, each of the 10 samples retained their integration to the group at the 99% confidence level. As the concentration of Ca has not been taken into consideration in the principal components analysis, because it contained some missing values, calcareous clay samples have been now assigned to former group G-3 (this also occurred with TXRF data when Ca was eliminated from the statistical treatment). Added calcite can act as a diluent, depressing the concentrations of most elements (see, e.g., Neff *et al.* 1989, 68; Cogswell *et al.* 1998; see also Appendix B). This group, with its calcareous nature, therefore appears to be created by human intervention to produce another compositional group most likely from the same raw materials as group G-3; the background matrices of both look very similar in thin section (see discussion below).

Non-local group G-2A, composed of those samples from the burial site of El Pradillo, retains its previous membership (Figs. 4 and 5). As mentioned above, former local group G-2B disappears. The four non-calcareous clay samples remain as unassigned outliers, while the single domestic black ceramic sample from Izana with no added calcite is now assigned to local group G-4A (see Table 4).

In the centre portion of Figure 4, sample scores reflect a compositional continuum that seems difficult to partition into discrete groupings. Although former groups G-3 and G-4A, and new group G-4C, appear to overlap on the first two components, they are quite distinct in elemental concentration space. Based on calculations of Mahalanobis distances, the individual specimens assigned to each group cluster tightly around each group centroid. Low coefficients of variation for rare earth elements and Th document strong homogeneity for these groups (see Appendix B). As a further test to assess the distinction between them, canonical discriminant analysis was undertaken. Such analysis seeks to identify the dimensions of maximal separation between groups (Bishop and Neff 1989, 68). This distinction is readily visible in Figure 7. The three groups contain samples from the town of Numancia and the secondary site of Izana, constituted principally of serving red or grey and domestic black ceramics with no added calcite. Nevertheless, as Figure 6 and Table 4 show, they reveal the main differences as were found in the TXRF groups. Group G-3 now contains four of the five calcareous clay samples, as well as three former outliers including the single calcareous sample, one over-fired sherd, and one of the samples in which high relative values of Cu and As were detected by TXRF. It loses nine samples, which relocate into group G-4A. On the other hand, group G-4A gives seven samples to the new association G-4C, while gaining 13 samples, primarily from former group G-3.

Non-local group G-4B, whose small size also made it impossible to estimate individual probabilities of belonging to the group, is still formed by the five samples from the site of El Palomar (Figs. 4 and 5). It now differs from G-4A and G-4C groups by higher concentrations of Fe and Cs. Low coefficients of variation for the rare earth elements Hf and Th reflect a relative degree of compositional homogeneity (see Appendix B).

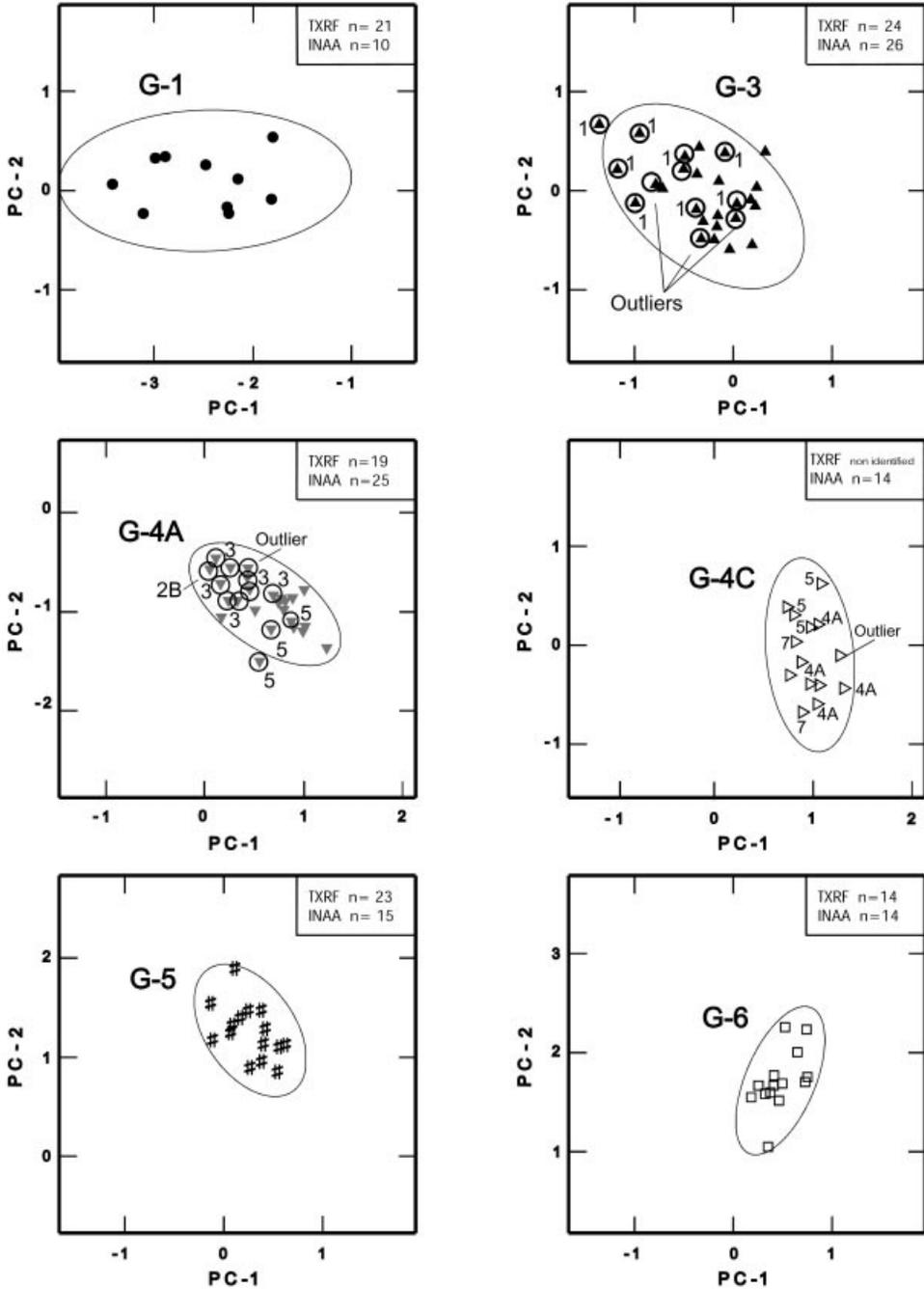


Figure 5 Single local and non-local INAA groups as projected on principal components 1 and 2 in Figure 5, showing the previous classification of the samples provided by TXRF. The circled and numbered points represent those samples classified into other groups by TXRF, except in new group G-4C in which, obviously, all samples were classified into other groups.

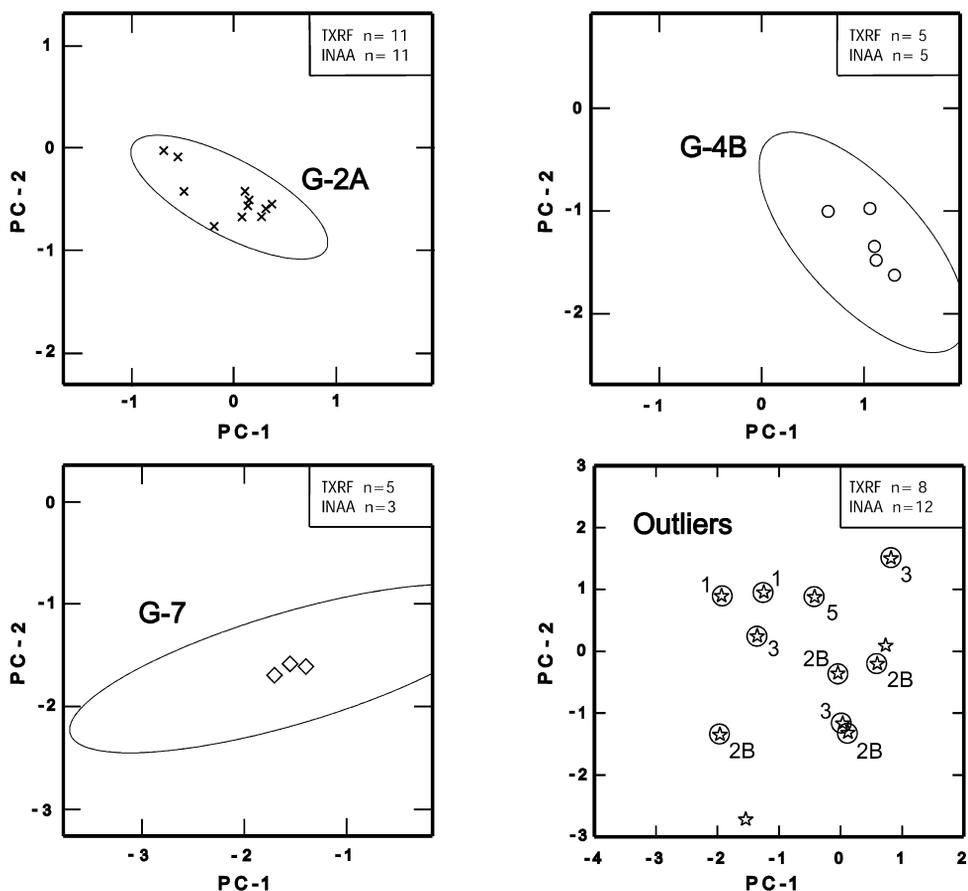


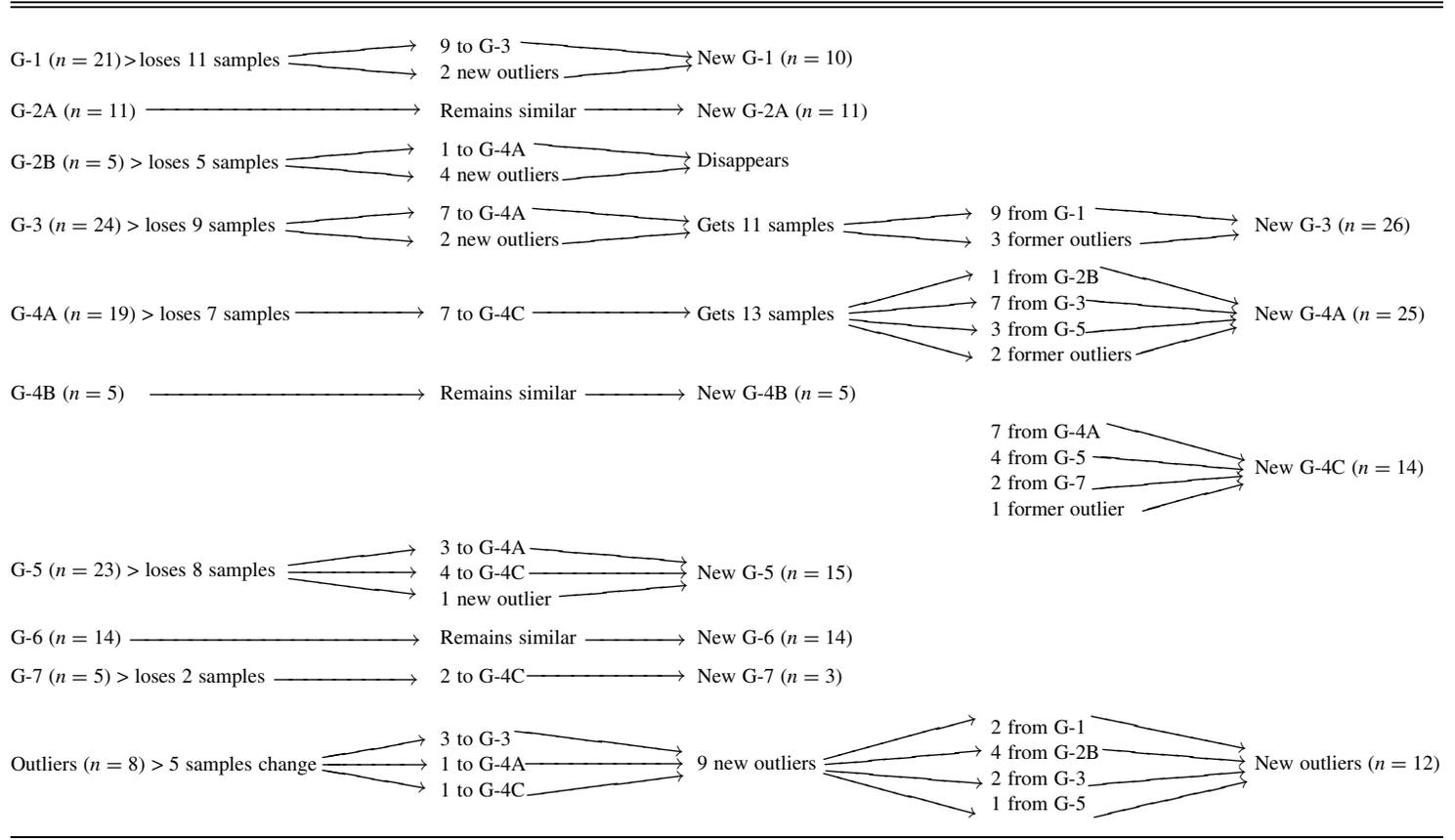
Figure 5 continued

Inferred local groups G-5 and G-6, well discriminated by TXRF data, barely exhibit any significant change. The latter remains similar to such an extent that its samples retain their membership to the group at the 99% confidence level (see Table 4). Both groups, which are chemically quite close on Figure 4 projections, are most clearly differentiated by means of the bivariate plot of Figure 8 based on concentrations of Cr and Fe transition metals.

Finally, the same group of three of the five polychrome sherds taken from Langa de Duero is again classified into the smallest group G-7 (Figs. 4 and 5). These three samples vary significantly in the content of intermediate rare earths Sm and Eu and Th with respect to the local group G-6, which is composed of most of the polychrome ceramics from Numancia (see Appendix B). This observation strongly suggests that two different clay sources were used in the manufacture of these ceramics and supports the idea of non-local provenance for group G-7. In addition, two other samples previously clustered with this group have been now classified into new group G-4C (see Table 4).

Twelve samples remain unassigned (Figs. 4 and 6). As before with the TXRF data, most appear to be outliers of the nine groups, although three individuals coincide with those previously unassigned by TXRF. The two remaining polychrome sherds from Langa de

Table 4 Summary of comparison between TXRF groups (left) and INAA groups (right) ($n = 135$)



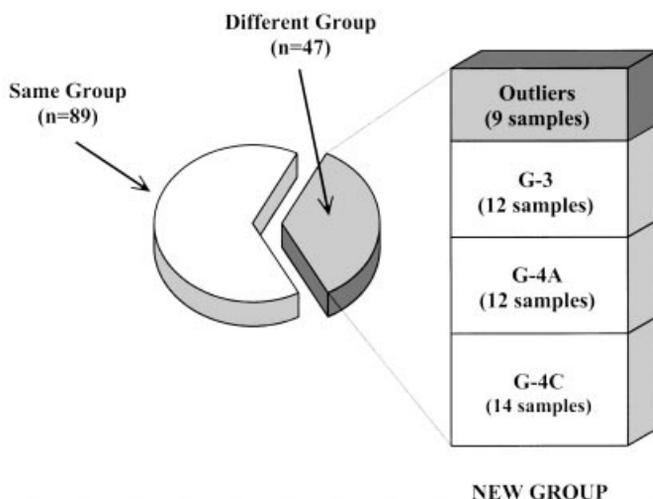


Figure 6 The sample set structure after INAA results.

Duero are not classified with group G-7. They consist of the non-calcareous clay briquettes from the disappearing group G-2B, as well as one single calcareous clay with extremely variable concentrations of Cr, Fe and Rb, and one domestic black ceramic sample with lesser amounts of added calcite, as revealed by petrographic analysis (see Table 4). In conjunction with TXRF data, neither the calcareous nor the non-calcareous clay samples show patterns of elemental increase or decrease as a result of firing.

Despite minor variations discussed above, numerical analyses of the INAA data are consistent with the structure found in the TXRF data set. Nevertheless, TXRF is not able to reach

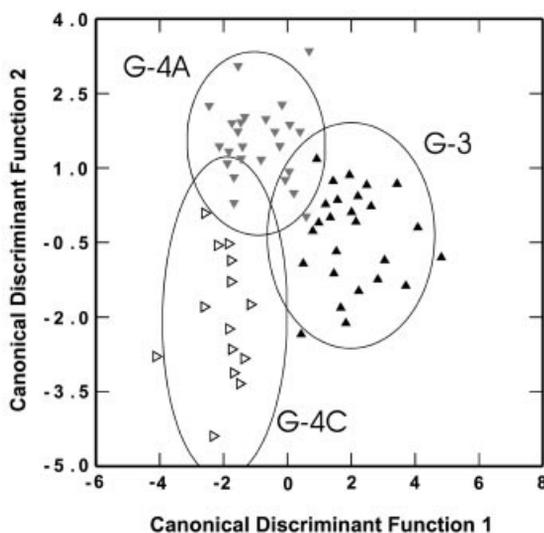


Figure 7 A canonical scores plot differentiating local groups G-3, G-4A and G-4C. The ellipses represent the 90% confidence level for membership in each group.

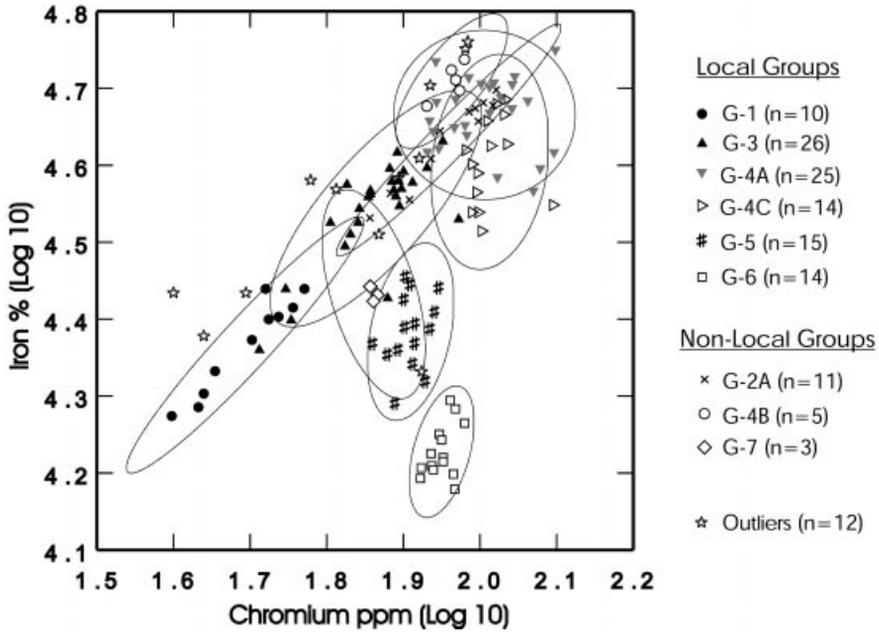


Figure 8 A bivariate plot of the Cr and Fe concentrations plotted as log base 10 values of compositional groups determined by INAA ($n = 135$). The ellipses represent the 90% confidence level for membership in each group.

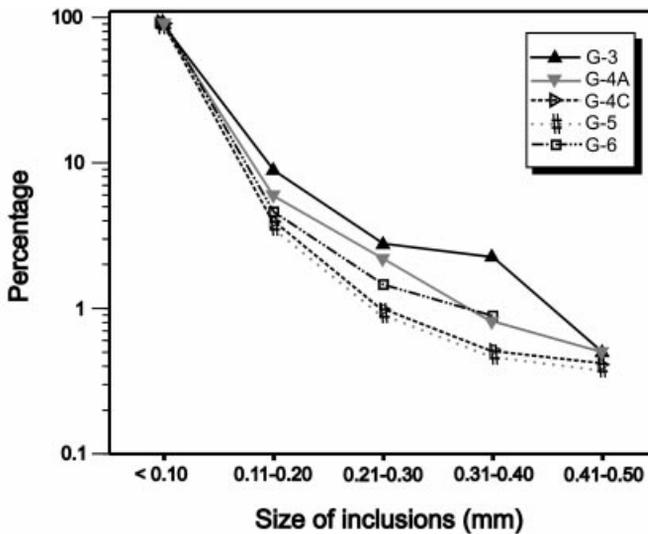


Figure 9 A grain sorting plot derived from modal analysis made by point counting procedures ($n = 150$).

the same level of resolution, since the solid sample method does not allow the analysis of rare earth elements. Previous interpretation, however, does not need to be modified. Evidence provided by INAA also supports the argument that different raw materials or different production units are present in the ceramic assemblage from the town of Numancia.

Indeed, the separation shown by the Cr and Fe transition metals plot of Figure 8 is a strong indication that the clays used in local groups G-3, G-4A and G-4C are from a different source than those used in local groups G-5 and G-6, in which most of the grey and polychrome ceramics are associated. However, gradual enrichment of alkali elements such as Rb and Cs, or rare earth elements such as La, Ce, Sm and Eu, in groups G-3, G-4A and G-4C, suggests that these three compositional groups represent different paste recipes (from one or more units/workshops of production) rather than three different raw material sources (see Appendix B). Patterns of grain sorting in samples from these groups provide additional evidence for that argument. One can see from Figure 9 that as the percentage of the fine fraction increases, so too does the concentration of rare earth elements (see, among others, Blackman 1992). Since no significant mineralogical differences were found among them, G-4A and G-4C groups seem to be variants produced by levigation of the same clay: the group G-3. On the other hand, the group G-1 tempered with large amounts of monocrystalline calcite appears to have been created by human alteration of the clay used for manufacturing group G-3.

INAA determinations reveal the compositional similarities among data for three of the seven modern clay samples taken within the catchment area of Numancia, as well as that of the sample taken in the vicinity of the secondary site of Izana. This is due, at least in part, to the rare earth element concentrations. However, the four clay samples show higher concentrations of Ca than those exhibited by ceramics belonging to group G-3. The high variability of this element in clay deposits has already been noted (see, e.g., Mommsen *et al.* 1992).

When examining the INAA results, a final point to emphasize is that three of the TXRF unassigned outliers, with unique over-firing features (see above discussion), are now classified into the G-3 and G-4A chemical groups. Since, to date, only low-fired ($\leq 900^\circ\text{C}$) ceramic and check standard samples have been analysed by TXRF, it is suspected that the solid-phase methodology would be sensitive to firing temperature and, consequently, to the development of associated glassy microstructures. This minor weakness needs to be further investigated (García-Heras *et al.* 1998; Fernández-Ruiz *et al.* 1999).

Based upon studies of decorative designs, it was generally accepted that Numantian-style pottery found outside the Upper Duero Valley was the consequence of an incipient interregional trade or exchange. The results provided by both techniques described in this paper contradict this assumption, since Numantian-style ceramics recovered from outside the region show chemical compositions that are distinct from those of Numancia. This finding strongly suggests that they were manufactured outside the region, providing evidence of a shared style rather than a pattern of interregional trade or exchange. There are samples from the secondary site of Izana in five of the seven local groups. Given the evidence found to date, samples from the town of Numancia or that of Izana lie within a theoretical non-resolution space in which it is not possible compositionally to differentiate the production from these sites.

The presence of distinct compositional groups, indicating the use of the different raw materials or production units represented, has important implications for the general discussion of the Celtiberian period in the Upper Duero Valley. Although no production remains are known from the town of Numancia, compositional patterns suggest the existence of one or more workshops manufacturing ceramics throughout the first century BC (García-Heras forthcoming).

The question of whether ceramics were produced at Numancia or Izana at different times or at the same time awaits further research.

CONCLUSIONS

Comparative results presented in this paper demonstrate the ability of TXRF to distinguish among ceramic groups of different compositional nature. The general chemical structure revealed in the TXRF data paralleled that found by INAA. The results suggest that TXRF has potential applicability for multi-elemental characterization of archaeological ceramics, providing data useful for provenance studies and, consequently, for archaeological interpretations. Some advantages of this technique are the relative ease of sample preparation (the sample is prepared without any chemical processing), accessibility (a nuclear facility is not needed) and the short period of time until results are obtained (approximately 2 h for the full process). However, because of the different levels of resolution, the INAA results in conjunction with available mineralogical data served further to refine compositional groupings and outliers derived from TXRF determinations, and were complementary in improving the understanding of the archaeologically oriented sample set.

Although TXRF seems to be a valid alternative to other well-known techniques, it is clear that more research is needed. An overall evaluation of TXRF and its quantitative analytical capabilities has led us to expect new advances in the near future.

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APPENDIX A
Means, standard deviations and coefficients of variation for TXRF groups

Group	As	Cr	Ni	Rb	Sr	Zn	Al	Ba	Ca	K	Mn	Ti	V	Cu	Ga	Y
<i>Local groups</i>																
G-1 (n = 21)																
Mean	0.118	0.237	0.110	0.535	0.354	0.367	224.5	2.437	506.7	84.8	1.426	12.9	0.193	0.057	0.060	0.093
sd	0.038	0.034	0.010	0.068	0.071	0.247	34.0	1.004	288.7	14.6	0.475	1.8	0.035	0.013	0.007	0.022
CV	31.7	14.1	9.1	12.8	19.9	67.4	15.1	41.2	57.0	17.2	33.3	13.9	18.0	23.2	12.2	23.6
G-2B (n = 5)																
Mean	0.148	0.188	0.094	0.349	0.132	0.202	181.5	0.599	42.2	42.1	0.609	6.3	0.187	0.060	0.059	0.079
sd	0.008	0.001	0.010	0.012	0.014	0.009	12.9	0.154	19.9	2.7	0.067	1.1	0.014	0.004	0.001	0.050
CV	5.4	0.7	10.3	3.4	10.4	4.7	7.1	25.7	47.1	6.4	11.1	17.5	7.7	7.0	2.6	63.3
G-3 (n = 24)																
Mean	0.081	0.215	0.098	0.540	0.259	0.273	206.1	1.779	35.8	87.9	0.941	11.4	0.207	0.064	0.069	0.069
sd	0.027	0.022	0.013	0.056	0.067	0.042	20.3	0.666	27.6	14.2	0.603	1.2	0.037	0.022	0.007	0.016
CV	32.8	10.4	13.0	10.3	26.0	15.4	9.8	37.5	77.1	16.1	64.1	10.5	17.9	34.5	10.4	23.5
G-4A (n = 19)																
Mean	0.045	0.222	0.085	0.545	0.177	0.202	186.2	0.964	7.2	78.5	0.204	9.6	0.221	0.040	0.065	0.080
sd	0.014	0.020	0.018	0.046	0.054	0.047	11.8	0.264	3.8	6.6	0.112	1.2	0.023	0.011	0.003	0.031
CV	31.7	9.1	21.5	8.4	30.8	23.1	6.3	27.3	52.8	8.4	54.9	12.5	10.2	27.3	5.0	39.1
G-5 (n = 23)																
Mean	0.084	0.335	0.150	0.823	0.363	0.551	289.6	2.033	15.4	116.2	0.531	19.8	0.327	0.094	0.099	0.128
sd	0.037	0.044	0.023	0.109	0.114	0.201	39.2	0.654	2.1	12.6	0.326	4.3	0.067	0.037	0.015	0.037
CV	44.6	13.2	15.1	13.2	31.3	36.5	13.5	32.2	13.6	10.8	61.4	21.7	20.4	39.7	14.8	28.5
G-6 (n = 14)																
Mean	0.093	0.515	0.224	1.315	0.569	0.854	561.8	4.047	22.5	185.4	0.358	27.9	0.453	0.144	0.188	0.219
sd	0.054	0.049	0.028	0.133	0.073	0.322	77.5	1.166	4.2	21.4	0.083	3.1	0.068	0.024	0.019	0.043
CV	58.4	9.6	12.7	10.1	12.8	37.7	13.8	28.8	18.7	11.5	23.2	11.1	15.0	16.5	10.0	19.7
<i>Non-local groups</i>																
G-2A (n = 11)																
Mean	0.092	0.228	0.094	0.484	0.349	0.218	209.8	0.893	165.4	58.0	0.508	10.1	0.214	0.046	0.063	0.068
sd	0.013	0.023	0.012	0.051	0.071	0.017	12.9	0.446	69.8	6.7	0.085	1.1	0.049	0.008	0.005	0.006
CV	14.4	10.0	13.0	10.5	20.3	8.0	6.1	49.9	42.2	11.5	16.7	10.9	23.1	16.5	8.1	9.0
G-4B (n = 5)																
Mean	0.046	0.200	0.074	0.486	0.517	0.154	162.4	1.034	10.6	90.7	0.347	8.3	0.184	0.019	0.057	0.052
sd	0.014	0.016	0.011	0.009	0.071	0.016	6.0	0.138	4.9	6.3	0.090	0.8	0.033	0.004	0.004	0.008
CV	30.6	7.8	15.2	1.8	13.8	10.7	3.7	13.3	46.2	6.9	26.1	9.6	18.2	20.1	6.9	15.7
G-7 (n = 5)																
Mean	0.047	0.288	0.042	0.492	0.288	0.535	314.4	0.969	21.4	73.0	0.246	18.0	0.291	0.098	0.108	0.084
sd	0.008	0.024	0.003	0.005	0.020	0.321	9.6	0.159	2.0	2.4	0.010	0.4	0.071	0.012	0.006	0.019
CV	16.9	8.3	5.9	0.0	6.9	59.9	3.0	16.4	9.3	3.3	3.9	2.2	24.6	12.4	5.1	22.4

Values expressed as wt% versus Fe; sd, standard deviation; CV, coefficient of variation in per cent.

APPENDIX B

Means, standard deviations, and coefficients of variations for INAA groups

Group	Na (%)	K (%)	Ca (%)	Sc	Cr	Fe (%)	Zn	As	Rb	Sb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Hf	Ta	Th	U
<i>Local groups</i>																								
G-1 (n = 10)																								
Mean	0.2	2.0	18.9	8.4	49.8	2.3	54.6	11.9	117.6	1.2	8.9	829.0	26.4	53.6	21.9	5.3	0.0	0.6	1.9	0.3	3.6	1.0	9.0	2.3
sd	0.3	1.0	5.4	1.01	6.6	0.3	11.4	3.0	16.1	0.2	0.9	232.06	3.5	7.0	3.8	0.8	0.1	0.1	0.3	0.05	0.6	0.1	1.2	0.3
CV	113.1	49.2	28.3	12.0	13.2	14.2	20.9	25.2	13.7	19.0	10.6	28.0	13.2	13.1	17.5	14.8	13.5	18.7	15.2	15.3	17.1	12.0	13.0	14.5
G-3 (n = 26)																								
Mean	0.3	2.8		12.4	73.4	3.5	98.7	18.4	181.5	2.1	15.4	737.8	39.8	82.3	34.0	7.7	1.3	0.9	2.9	0.5	6.7	1.5	13.8	3.4
sd	0.3	0.4		1.5	9.8	0.5	52.0	9.5	28.6	0.5	2.1	311.0	3.5	8.3	3.8	0.7	0.1	0.09	0.3	0.049	1.1	0.2	1.3	0.7
CV	106.4	16.0		11.9	13.3	14.1	52.7	51.4	15.8	25.2	13.9	42.1	8.7	10.0	11.2	8.6	10.2	10.5	11.2	10.4	16.2	13.3	9.8	21.5
G-4A (n = 25)																								
Mean	0.3	3.8		17.1	102.0	4.7	87.6	14.3	242.3	2.7	22.1	703.1	43.6	86.3	37.3	8.0	1.4	0.9	3.1	0.5	5.9	1.7	15.7	3.6
sd	0.1	0.6		1.6	12.2	0.5	20.9	10.5	31.4	0.9	4.1	192.9	3.5	6.9	4.6	0.6	0.2	0.1	0.3	0.045	0.8	0.2	0.9	1.6
CV	42.0	14.7		9.2	11.9	10.8	23.9	73.5	12.9	31.5	18.6	27.4	8.0	8.0	12.4	7.2	11.3	14.4	9.1	9.4	14.1	9.7	5.9	45.4
G-4C (n = 14)																								
Mean	0.3	3.6		17.1	103.3	4.1	130.1	24.8	250.1	2.6	22.0	724.6	50.7	102.0	45.7	9.6	1.7	1.1	3.8	0.6	7.2	1.8	16.9	4.0
sd	0.1	0.4		1.3	7.9	0.5	66.2	49.4	22.3	0.6	1.7	205.9	3.4	8.3	5.9	0.7	0.1	0.2	0.4	0.067	0.8	0.2	0.7	1.4
CV	43.0	10.5		7.5	7.6	13.0	50.9	199.2	8.9	22.6	7.5	28.4	6.7	8.1	13.0	7.1	7.1	14.1	9.9	11.7	11.0	11.1	3.9	36.4
G-5 (n = 15)																								
Mean	0.2	2.6		13.6	81.3	2.4	140.6	7.0	206.4	2.1	16.8	601.9	50.9	104.1	44.6	9.4	1.7	1.1	4.1	.6	8.7	1.9	16.2	4.2
sd	0.022	0.4		0.9	4.3	0.3	29.0	3.2	16.1	0.2	1.2	123.02	2.9	3.8	4.4	0.6	0.1	0.2	0.4	0.047	0.8	0.1	0.4	0.6
CV	13.2	15.9		6.3	5.3	10.8	20.6	46.6	7.8	11.0	7.4	20.4	5.6	3.6	9.9	6.2	4.6	13.3	8.7	7.9	9.7	5.5	2.4	15.0
G-6 (n = 14)																								
Mean	0.2	3.0		15.4	89.2	1.7	124.1	8.3	218.2	1.7	19.5	808.7	50.9	99.3	49.7	10.8	2.1	1.2	3.8	0.6	6.3	1.8	16.1	5.8
sd	0.067	0.2		0.5	3.5	0.1	46.8	4.5	14.9	0.3	0.7	183.9	1.5	7.9	8.7	1.4	0.3	0.2	0.3	0.058	0.2	0.1	0.6	2.5
CV	30.5	5.8		3.5	4.0	8.2	37.7	54.6	6.8	16.6	3.7	22.7	3.0	7.9	17.4	12.7	15.2	16.6	7.9	10.1	3.5	6.0	3.7	43.9
<i>Non-local groups</i>																								
G-2A (n = 11)																								
Mean	0.1	2.5	7.7	14.8	91.7	4.3	78.5	28.6	184.9	2.2	16.4	553.0	41.9	86.2	36.4	8.1	1.4	0.9	2.7	0.4	4.6	1.6	13.9	2.7
sd	0.01	0.2	2.2	1.4	11.5	0.6	15.6	11.0	19.0	0.2	1.7	108.4	2.9	6.5	6.0	0.6	0.1	0.2	0.1	0.055	0.3	0.1	1.0	0.4
CV	11.6	9.4	28.9	9.5	12.6	12.9	19.9	38.3	10.3	10.7	10.7	19.6	6.9	7.5	16.4	7.8	8.9	17.9	5.0	12.4	5.6	7.9	7.0	16.3
G-4B (n = 5)																								
Mean	0.2	4.6		17.0	91.9	5.1	83.8	15.0	230.4	3.2	39.2	744.2	45.9	92.6	39.0	8.5	1.4	0.9	3.0	0.5	5.6	1.5	16.0	3.4
sd	0.064	1.8		0.8	4.0	0.3	18.7	7.3	20.3	0.5	17.3	83.6	1.2	1.8	5.9	0.4	0.054	0.1	0.3	0.057	0.4	0.082	0.5	0.7
CV	29.8	39.7		4.5	4.5	5.3	22.3	48.4	8.8	16.4	44.0	11.2	2.7	2.0	15.1	5.1	3.7	7.7	9.2	12.1	7.7	5.3	3.1	19.8
G-7 (n = 3)																								
Mean	0.2	2.0		14.1	72.7	2.7	122.0	11.5	127.3	0.9	21.1	461.0	23.0	43.4	14.6	3.7	0.5	0.5	2.8	0.4	7.3	2.1	14.6	3.4
sd	0.01	0.2		0.3	0.8	0.06	155.0	2.9	4.6	0.2	0.2	98.7	0.8	2.1	0.6	0.1	0.025	0.078	0.2	0.017	0.3	0.062	0.4	0.3
CV	6.2	8.9		2.2	1.1	2.2	127.1	25.2	3.6	23.7	0.7	21.4	3.4	4.8	3.9	3.5	4.7	14.8	6.3	4.0	4.2	2.9	2.7	8.8

Values expressed in parts per million, except for those Na, K, Ca and Fe, which are in per cent; sd, standard deviation; CV, coefficient of variation in per cent.