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Total vs. Partial Acid Digestion Methods for Trace Element Analysis in Archaeological Sediments

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Abstract: Trace element analysis of sediments from archaeological sites is a valuable method to investigate the anthropic impact and obtain information on the functions of different areas and changes in human activities. One of the most used and effective techniques to carry out this kind of analysis is inductively coupled plasma–mass spectrometry. This technique needs a previous dissolution of the sample by acid attack, but the development of the best method is still a discussed issue. In the present work, total and partial digestion methods were carried out in sediment samples of Cueva de la Cocina (Dos Aguas, Spain), and trace elements were measured and statistically compared. Major elements, soil organic matter amount, and pH data were used to evaluate the main drivers of trace element contents. The differences between the results from the two methods were highlighted. Total digestion is more effective for aluminosilicates and heavy minerals, although the partial digestion results suggested that, in most cases, the difference between the two methods is irrelevant for archaeological interpretations. Furthermore, in some cases, the total digestion of the mineral phases related to the geological contribution could mask the anthropic elemental signals.

Keywords: sediment analysis; trace elements; REE; ICP-MS; acid digestion; archaeology

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1. Introduction

In the last few years, sediment multielement analysis has become a valuable tool in the interpretation of archaeological stratigraphy. Indeed, especially when remains are scarce, the identification of chemical proxies allows evaluating the anthropic impact on the development of the strata and discriminating among activities carried out within a site, therefore marking the different functional areas and occupational changes from the diachronic point of view [1].

X-ray fluorescence spectroscopy (XRF) is a widely used technique to obtain major element concentrations in archaeological sediments, while the employment of portable X-ray fluorescence spectrometers (pXRF) is increasing due to the possibility of carrying out in situ analyses during archaeological fieldwork [2–4]. Among the major elements, phosphorous has traditionally been considered a marker of human activities [5], but the anthropic contribution to sediment formation can also be identified in anomalous trace element levels. For example, archaeological strata are often enriched in Zn and Cu [6–9], and recently, Gallello and colleagues have explored the possible contribution of rare-earth elements (REEs) as anthropic markers in several archaeological sites from Europe and Africa [10–14]. Since XRF is not the optimal choice for trace element analysis due to its high detection limits, inductively coupled plasma–mass spectrometry (ICP-MS), which allows the accurate and fast determination of several elemental concentrations down to a just few parts per billion [1], has been employed by several authors. However, in order to carry out ICP-MS sediment analysis, the samples must be previously dissolved by acid attack, and the best way to do it is discussed. Some researchers recommended mild acid extraction protocols [15–19], while others used partial [10–13,20–22] or total [7,23,24] acid digestion methods. According to those who employed sample total digestion, this treatment is necessary to completely destroy the sediment matrix and also bring the elements bound to the most recalcitrant species into the solution. On the other hand, the rationale behind the choice of less aggressive methods of digestion and mild acid extraction would be precisely to avoid the complete dissolution of all the mineralogical phases, which would increase the noise of the geologic signal overwhelming that related to the contribution of human activities on soil formation. Furthermore, total digestion is more time-consuming, implying several digestion steps and the use of reactives such as hydrofluoric acid, which are potentially harmful to the analyst.

The present paper shows the results of the chemical analysis carried out on sediments from the archaeological site of Cueva de la Cocina (Dos Aguas, Spain) aiming to compare the ICP-MS results of partial and total digestion acid attacks.

Cueva de la Cocina is a cave located in the inner part of the Valencian Community (Figure 1), being a pivotal site for the presence of Mesolithic levels, linked to the last hunter–gatherer populations of the Iberian Peninsula, up to the Bronze Age strata [25,26]. A detailed study of the geological and sedimentological characteristics of Cueva de la Cocina and their links with its surroundings was previously carried out by Fumanal [27,28]. From a geological point of view, Cueva de la Cocina is a cavity excavated in Late Cretaceous limestone levels by the combination of chemical lixiviation and fluvial mechanical erosion, filled by the sediments carried along the La Ventana ravine. Sedimentary parent materials can be identified from the Early to Late Cretaceous levels outcropping in the area, which include carbonate rocks (limestones and marlstones), as well as sandstones and sandy/clayish sediments. The studied area is part of the first Holocene sedimentary sequence. The analyses carried out by Fumanal [27,28], highlighted the alkalinity of the environment, pointing out the presence of a decalcified and archaeologically sterile layer of reddish clay below the levels of human occupation, which are, instead, rich in organic matter and carbonates (about 50% of the fraction), while silt and clay range between 20% and 35%, due to both anthropic activities and environmental condition changes. A recent study by Gallello et al. [14] dealt with the analysis of the sediment of this cave, aiming to investigate the chemical markers of the different human activities carried out during the different occupation phases of Cueva de la Cocina and focusing especially on the behavior of rare-earth elements (REEs). The analyses, obtained employing a partial digestion method, revealed peculiar elemental markers and REE patterns able to discriminate between natural sediments and anthropic strata, and among different human activities in the latter (hunter–gatherer or pastoral activities). The sediment datasets obtained from the present work were analyzed by pXRF and ICP-MS for major, minor, and trace element concentrations. Furthermore, pH and soil organic matter (SOM) were also measured. Concerning ICP-MS analysis, as previously mentioned, each sediment sample was prepared by both partial and total digestion.

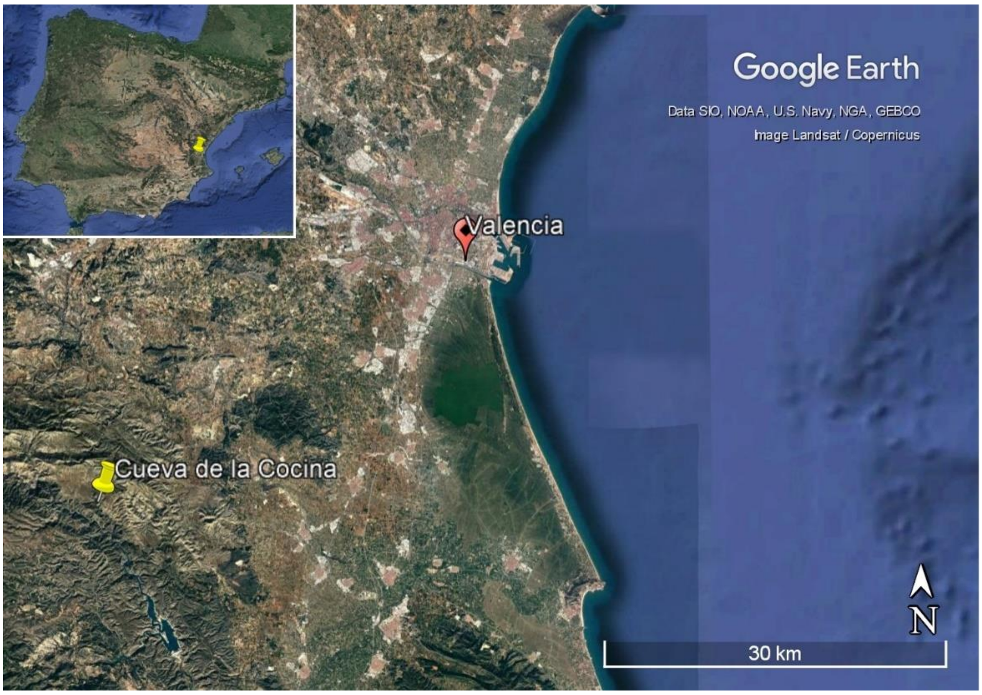

Figure 1. Location of Cueva de la Cocina.

2. Materials and Methods

2.1. The Sediments

Thirty-nine samples (Table 1) were collected from three cross-sections of Area S4, which is close to the cave entrance and was excavated during fieldwork in 2017 and 2018 [29].

Table 1. Collected samples and sediment types.

Sample	Type	Sample	Type	Sample	Type
S4a1	Disturbed	S4b6	Disturbed	S4d3	Archaeological
S4a2	Disturbed	S4b7	Disturbed	S4d4	Archaeological
S4a3	Disturbed	S4b8	Disturbed	S4d5	Archaeological
S4a4	Disturbed	S4c1	Natural	S4d6	Archaeological
S4a5	Disturbed	S4c2	Natural	S4e1	Disturbed
S4a6	Disturbed	S4c3	Archaeological	S4e2	Disturbed
S4a7	Disturbed	S4c4	Archaeological	S4e3	Disturbed
S4a8	Disturbed	S4c5	Archaeological	S4e4	Disturbed
S4b1	Disturbed	S4c6	Archaeological	S4f1	Disturbed
S4b2	Disturbed	S4c7	Archaeological	S4f2	Disturbed
S4b3	Disturbed	S4c8	Archaeological	S4f3	Disturbed
S4b4	Disturbed	S4d1	Archaeological	S4f4	Disturbed
S4b5	Disturbed	S4d2	Archaeological	S4f5	Disturbed

According to the remains found during the excavation, the study of the area revealed the presence of natural (no signs of anthropic activities) and archaeological strata (presence of remains marking anthropic activities), as well as disturbed levels linked to recent works (mixed remains including contemporary remains). The surface of the sampled cross-sections was scraped with a trowel to remove the most exposed surface; then, about 20 g of sediments were collected with a laboratory spoon from different points along five columns, in other words, along five vertical lines (a, b, c, d, e, f) from the bottom of the cross-section (e.g., from S4a1) and going up along an ideal vertical line (e.g., up to S4a8). Each sample of the column is distant around 5–10 cm from the previous one. Natural, archaeological, and disturbed levels were identified in this cross-section. The other columns ("e" and "f") are characterized by disturbed levels. The results of the analyses from columns "a" to "d" were previously published [14]; however, samples from two more columns were added, and an extended discussion on the differences between the two digestion methods was provided. The pictures of the area and the localization of the sampling points are shown in the supplementary online materials (Figures S1 and S2).

2.2. Analytical Techniques

All the samples were powdered and homogenized by agate mortar and pestle prior to the analyses.

The powdered samples were analyzed by an S1 TITAN pXRF spectrometer (Bruker, Kennewick, Washington, USA) to obtain Al, Si, P, K, Ca, Ti, Fe, and Zr concentrations.

In order to carry out the ICP-MS analysis, two samples were prepared for each sediment employing two different acid digestion methods. A 0.15 g amount of each sediment was used for acid attack with aqua regia, obtaining a partial digestion, while multiple acid attacks using HCl, HNO3, and HF were carried out for the total digestion of the same amount of sediment. The concentrations of Ba, Bi, Cd, Cr, Co, Cu, Pb, Li, Mn, Mo, Ni, Sr, Tl, V, Zn, and REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, including Sc and Y) were measured with an ELAN DRC II ICP-MS (Perkin Elmer, Waltham, MA, USA).

A certified reference material (NIM-GBW07408 Soil) was used for the control of the analytical results.

SOM was measured by oxidation with $K_2Cr_2O_7$, as indicated by Radojevic and Bashkin [30], and pH was analyzed in a soil/distilled water (1:2) extract with a MicropH2000 pH-meter (Crison, Alella, Spain).

More details on the analytical methods employed and the quality control of the analytical results can be found in Gallello et al. [14].

2.3. Data Analysis

Multivariate statistical analysis and data visualization were carried out in R (version: 4.1.2 [31]). Principal component analysis (PCA) was used to explore a large data set by reducing the variables and observing the main tendencies. Z-score standardization was performed prior to PCA.

3. Results and Discussion

3.1. Trace Elements

The analytical results and some data processing are shown in the supplementary online materials (Table S1 and Figure S3 for pXRF results, SOM amount, and pH; Table S2 and Figure S4 for trace elements concentrations; and Table S3 for Sc, Y, and REE concentrations, ratios, and Ce and Eu anomalies).

In order to explore the whole dataset and the relationship among the different variables in the multivariate space, PCA was used. The results of the PCA carried out on the whole set of elements are shown in Figure 2. The first three PCs explain 86% of the overall variance.

The PC1 vs. PC2 samples/scores plot (Figure 2a) shows that the samples from the two digestion methods have similar scores, suggesting that, taking into account the overall set of samples, the differences are not significant for many elements. However, if the different types of sediments (archaeological, disturbed, and natural) are taken into account, total digestion samples have higher PC1 scores than those prepared with aqua regia for natural and archaeological sediments. On the other hand, disturbed samples are scattered in the plot, both on the PC1 and the PC2 axes. Most of the variables are positively correlated with PC1 (Figure 2c), indicating that higher scores correspond to higher elemental concentrations. The samples from the two digestion processes form two different clusters on the PC3 axis. Indeed, most samples from aqua regia digestion have positive PC3 scores, while those processed by total digestion have negative scores. As can be observed in

Figure 2e, the most influential variables are Ba, Li, Sr, and Tl in the negative direction and Y and Co in the positive direction.

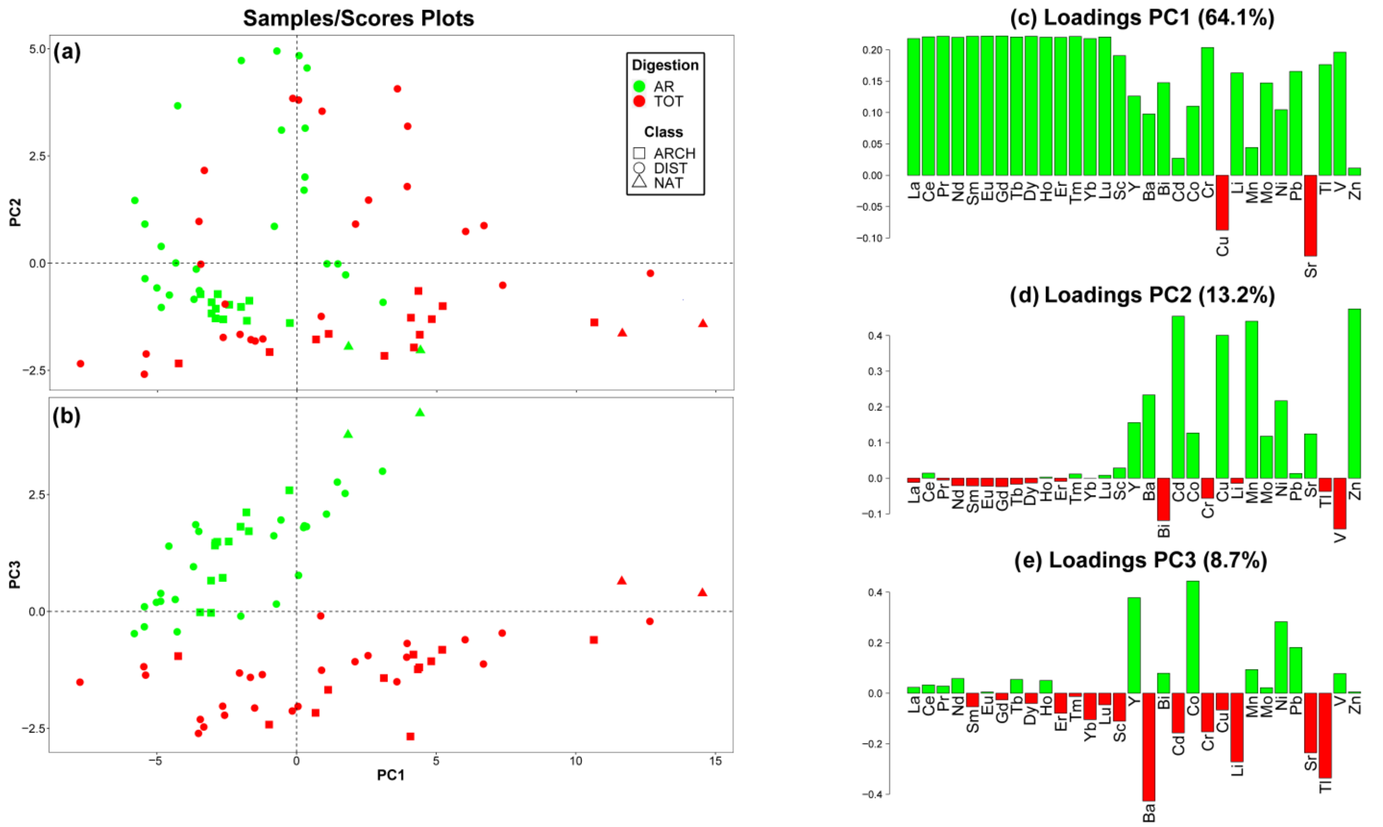

Figure 2. Samples/scores plots for PC1 vs. PC2 (**a**) and PC1 vs. PC3 (**b**); loading plots for PC1 (**c**), PC2 (**d**), and PC3 (**e**). AR: aqua regia; TOT: total digestion; ARCH: archaeological; DIST: disturbed; NAT: natural.

It is worth comparing strata from the different types for some of the analyzed trace elements (Figure S4). Total digestion allowed obtaining relevantly higher concentrations for some trace elements in archaeological (Cr, Li, Pb, Tl) and natural (Bi, Cr, Li, Mo, Ni, Pb, Sr, Tl, V) levels due to the effective sediment matrix dissolution. However, the relationship among the different types seems to be minimally affected by the used digestion method for these elements. Concerning the anthropic markers identified in the previous work (Ba, Cd, Cu, Mn, Zn) [14], as can be observed, the concentrations for the three types obtained by total digestion are relevantly higher than those of partial digestion for Ba and Cd, although for disturbed samples, the distributions overlap due to the high variance. On the other hand, the levels for Cu, Mn, and Zn obtained by the different digestion methods are quite similar in the three types. Furthermore, if the total digestion results are taken into account, it must be noticed that the enrichment of Ba, Cd, and Zn in archaeological strata compared to natural strata is not evident.

These data suggest that the complete digestion of aluminosilicates, by using HF, is higher at natural levels, as indicated by major element profiles (Figure S3), possibly masking the formation of human fingerprints in soil by enhancing the geologic contribution in some anthropic markers (Ba, Cd, and Zn) and, consequently, making difficult the distinction between natural and archaeological layers. On the other hand, for other anthropic markers (Cu and Mn), the digestion method shows to be almost irrelevant for the interpretation of the stratigraphy.

3.2. Rare-Earth Elements (REEs)

The study of REEs as anthropic markers was the main aim of Gallello et al. (2021) [14], and the effect of the digestion method on this group of elements deserves a deeper insight.

The results of the PCA using only REEs, Sc, and Y can be visualized in Figure 3. The first two PCs explain 96.8% of the overall variance. As can be observed in the samples/scores plot (Figure 3a), total digestion and aqua regia samples can be discriminated taking into account both PC1 and PC2 axes. If we take into account the different types, natural samples show higher PC1 and lower PC2 scores than archaeological samples, while disturbed samples are scattered on both axes. PC1 is positively correlated with all the variables (Figure 3b), while PC2 shows an intense negative correlation with yttrium concentration and a certain degree of fractionation since light REEs (LREEs: from La to Nd) have negative coefficients, and most medium REEs (MREEs: from Sm to Ho) and heavy REEs (HREEs: from Er to Lu) have positive coefficients (Figure 3c). It is evident that samples from total digestion have a higher variance on both axes than aqua regia samples.

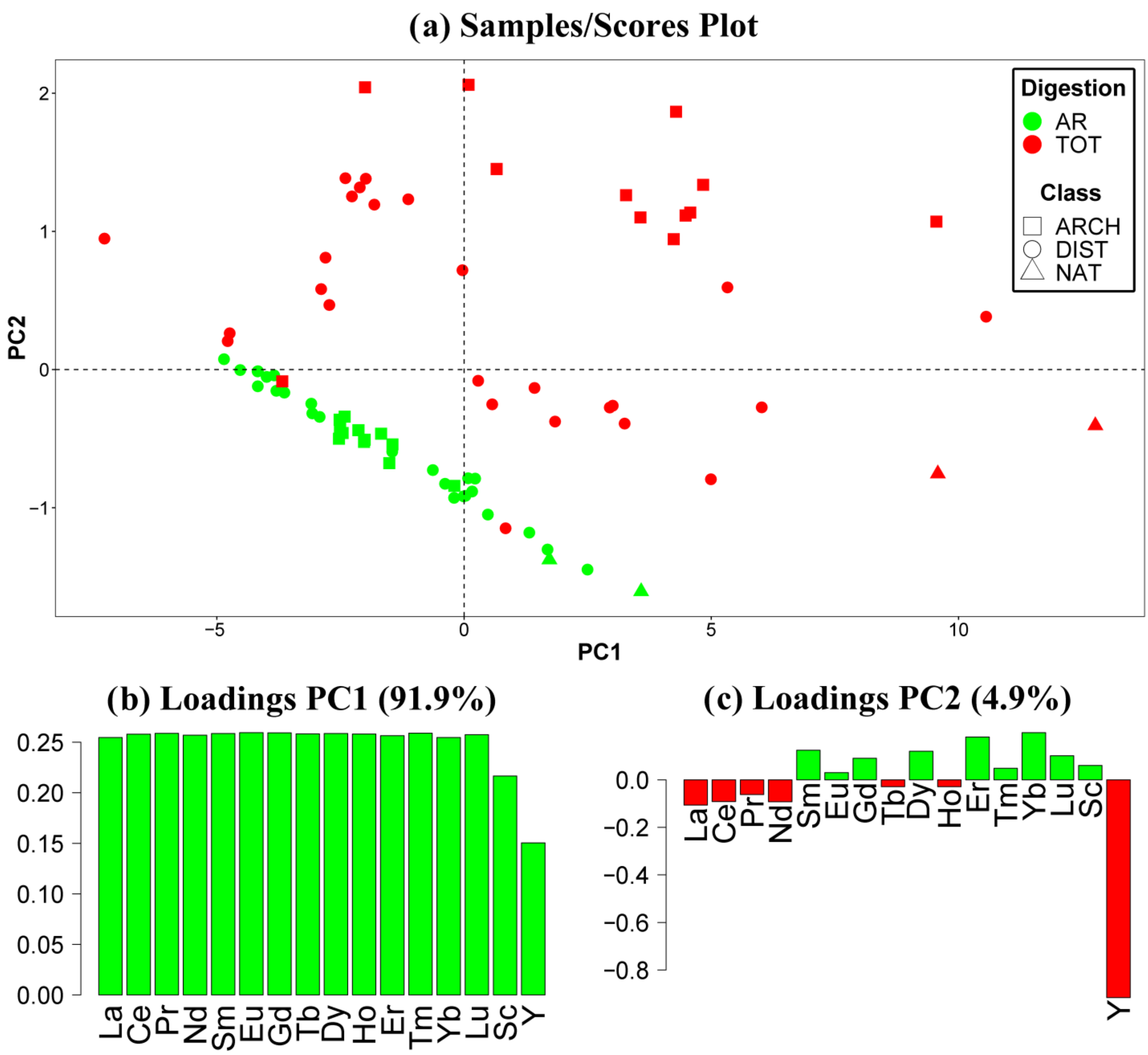

Figure 3. Samples/scores plots for PC1 vs. PC2 (**a**) and loading plots for PC1 (**b**) and PC2 (**c**). AR: aqua regia; TOT: total digestion; ARCH: archaeological; DIST: disturbed; NAT: natural.

Figure 4 shows REE, Sc, and Y concentrations and fractionation parameters for the three types according to the digestion method.

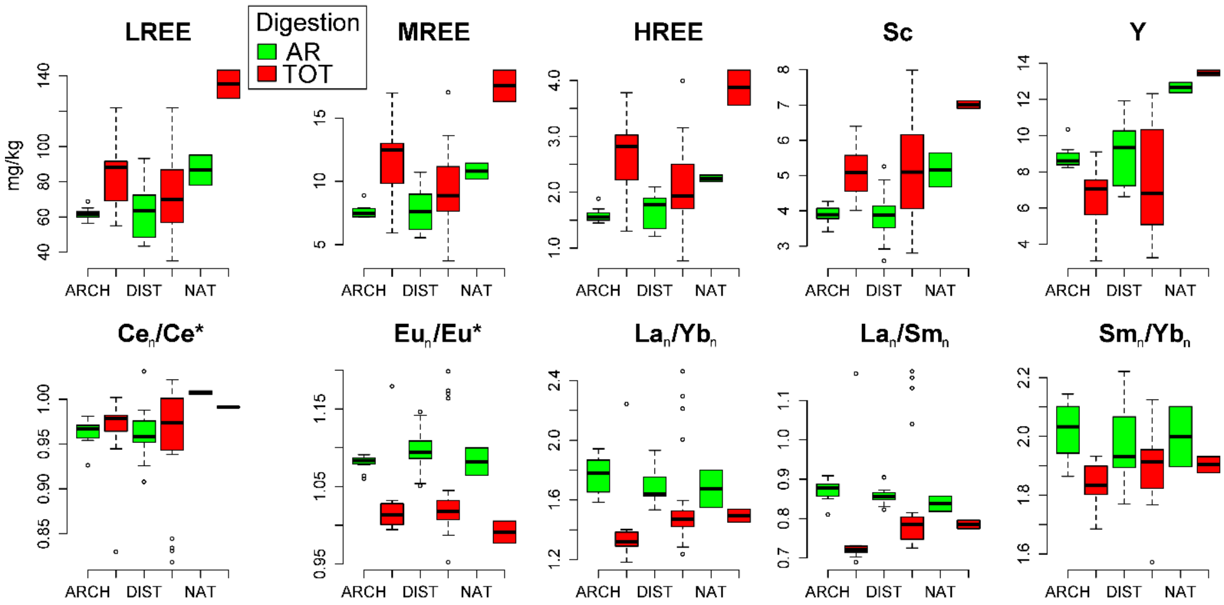

Figure 4. Boxplots for LREE, MREE, and HREE sums, Sc and Y concentrations expressed in mg/kg, and calculated ratios (see notes in Tables S4 and S5) of the fractionation parameters. AR: aqua regia; TOT: total digestion; ARCH: archaeological; DIST: disturbed; NAT: natural.

As can be observed, concentrations of LREEs, MREEs, and HREEs are higher for total digestion in archaeological and natural types, while for disturbed samples, the results are less clear and, possibly, the differences are not significant. Total digestion samples from the three types show also a higher variance for the elements taken into account, as suggested also by the PCA results. Anyway, for both digestion methods, the archaeological samples are depleted in REEs compared to natural samples, probably due to the higher presence of clay minerals in the latter type of sediment [32], as suggested by major elements patterns (Figure S3). Scandium behaves exactly like REEs. On the other hand, Y levels for partial digestion are slightly higher for archaeological and disturbed samples and slightly higher for natural samples than those for total digestion, although in this case, the relationship among the three types is not affected. As regards REE fractionation, Gallello et al. (2021) [14] showed that anthropic activity levels were characterized by a lower Ce_n/Ce^* anomaly related to the depletion of Ce compared to other lanthanides. These levels are enriched in P (Figure S3), and authigenic phosphate minerals often show negative Ce anomalies [33]. Since phosphorous enrichment is usually observed in anthropogenic sediments [5], more intense negative Ce anomalies could be a proxy of human activities. On the other hand, natural levels have higher Ce_n/Ce^* ratios. While this fact is clearly shown by the results obtained by partial digestion, it is less evident in the results of total digestion. The digestion of silicate minerals could also have masked the positive Eu anomalies, which are more intense in aqua regia samples than in total digestion samples. Indeed, some organic acids such as humic and fulvic acids can complex europium, leading to Eu enrichment over other neighboring lanthanides [34], while, except for feldspars, most silicate minerals do not display this anomaly [32]. Anyway, in both cases, the difference between archaeological and natural layers is not so evident. Finally, concerning LREE, MREE, and REE fractionation, expressed by the ratios La_n/Yb_n (LREE/HREE), La_n/Sm_n (LREE/MREE), and Sm_n/Yb_n (MREE/HREE), enrichment of both LREEs and MREEs over HREEs, as well as depletion of LREEs compared to MREEs, has been preserved for both digestion methods. However, although the relationship among the different types of sediments was conserved, lower ratio values were obtained by total digestion than by partial digestion, at least for La_n/Yb_n

and La_n/Sm_n. The effectiveness of total acid digestion on aluminosilicates and on heavy minerals, especially Ti- and Zr-bearing types, which are present in higher amounts in natural strata (Figure S3), could explain this fact. Indeed, the REE adsorption rate by some types of clay minerals increases with atomic mass, facilitating the complexation of heavier REEs [35], and heavy minerals usually have HREE impurities [32]. A slightly higher amount of LREEs over HREEs and MREE observed in natural strata compared to archaeological strata was also observed in the results by aqua regia along each single column and could be caused by REE fractionation due to accumulation and leaching release from upper to lower levels by organic matter, and phosphate and carbonate minerals, which are present in higher amounts in the upper archaeological levels (Figure S3) [14].

Finally, the comparison between the REE results from the total and partial digestion methods is consistent with that of the other trace elements and suggests that, in the case of Cueva de la Cocina, the use of total digestion is irrelevant, at best, for the archaeological interpretation of the multielement analysis results.

4. Conclusions

The comparison of the results obtained by processing sediments from Cueva de la Cocina through partial and total digestion allowed evaluating the effectiveness of the two digestion methods in the study of the anthropic impact and could also be a useful indicator for carrying out analogous works in similar environments.

As expected, the total digestion method gave higher concentrations of most of the trace elements compared to partial digestion. However, although it allows obtaining elemental levels that are closer to those of the bulk sample, in most cases, the relationship between the elemental concentrations of natural and archaeological levels is conserved. Furthermore, in some cases, the difference between archaeological and geological strata is more evident by partial than by total digestion, possibly due to the increasing noise of geogenic signals caused by the total dissolution of aluminosilicates and heavy minerals. Rare-earth elements seem to follow the same pattern, showing higher concentrations in the samples processed by total digestion than partial one. In particular, the differences observed in the fractionation parameters (i.e., slightly higher Ce_n/Ce^* ratio, lower positive anomalies, increased concentrations of heavier REEs compared to lighter REEs) are consistent with a more effective dissolution of aluminosilicates and heavy minerals, whose complete digestion could increase the signals from the geological contribution, masking the anthropic signals.

In conclusion, the obtained results showed that the use of a total digestion protocol is mostly irrelevant for carrying out the study of the anthropogenic impact on sediment formation along the stratigraphic sequence of Cueva de la Cocina, suggesting that the use of partial digestion could be a better choice in this kind of environment and for these aims, being not only less time-consuming and risky for the analyst than total digestion but also providing results that are also possibly more suitable for archaeological research.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min12060685/s1. Figure S1: Cueva de la Cocina map (modified from García-Puchol et al., 2018. [25]); Figure S2: 3D model of area S4 and localisation of sampling points (modified from García-Puchol et al., 2018. [25] and Gallello et al., 2021. [14]); Figure S3: Boxplots for pXRF results, SOM amount and pH; Figure S4: Boxplots for trace elements concentrations (AR: *aqua regia*; TOT: total digestion; ARCH: archaeologic; DIST: disturbed; NAT: natural); Table S1: Major elements, Zr and soil organic matter (SOM) amounts, and pH; Table S2: Trace elements concentrations for *acqua regia* digestion expressed as mg/kg; Table S3: Trace elements concentrations for total digestion expressed as mg/kg; Table S4: REE concentrations expressed as mg kg^{-1} and REE fractionation parameters obtained by *aqua regia* digestion; Table S5: REE concentrations expressed as mg kg^{-1} and REE fractionation parameters obtained by total acid digestion.

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