Application of PIXE to the characterization of vitreous dacites from archaeolgical sites in the Atacama region in northern Chile

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Abstract

Geochemical characterization studies using PIXE were carried out on 21 vitreous dacite artifacts from early formative archaeological sites in the Atacama region, in northern Chile, and on 13 samples taken from two potential volcanic sources located within the region. Performing statistical analyses it was possible to obtain elemental concentration patterns for the archaeological samples of this material and match some of these artifacts with the geological source samples.
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1. Introduction

In northern Chile, since the work of Aldunate et al. and others [1–4], the upper Salado river Basin, the main tributary of the Loa River in the Atacama region, has been considered a nodal area in the macroregional interaction and exchange networks of the Formative Period (1300–500 BC). During this period, lithic resources were used to manufacture tools both from local as from distantly located sources. The local sources, mainly basalts, andesites, vitreous dacites and quartz were used for the manufacture of simple expedient tools. The non-local raw materials used for the production of stone tools, are mainly of two types: obsidian and siliceous sedimentary rocks. Studies in volcanic glass geochemistry are of great importance for understanding the sources of raw materials, as well as for inferring exchanges and group interactions in past societies. In South America this type of analysis started to be performed more systematically beginning in the early 1990s. Studies have been centered on obsidian analysis using mainly instrumental neutron activation analysis, (INAA) or energy dispersive X-ray fluorescence, (EDXRF). Most of these studies have been performed for Ecuadorian obsidian by the Berkeley group [5] and for obsidian from the Titicaca region in Bolivia by others [6–10]. Later, analyses began at the Missouri Research Reactor facilities for obsidian samples from Bolivia, Peru and Argentina [11–23]. In South America, particle induced X-ray emission (PIXE) analysis, to our knowledge, has only been performed previously for obsidian materials from Ecuador and Colombia, and in central Chile [24–27] using the facilities of the Centre de Recherche et de Restauration des Musées de France, the Australian Nuclear Science and Technology Organization, ANSTO, and the University of Chile, respectively. So far, other types of vitreous rocks from archaeological contexts in South America have never been analyzed by PIXE. Also, it looks like PIXE has been rarely used as a routine way of analysis of large numbers of archaeological materials, for which it is ideally suited due to its non-destructive analytical

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capabilities [25,27]. For the current research we used PIXE to characterize vitreous dacite samples both from archaeological and geological contexts, in order to ascribe archaeological artifacts to their geological source of origin. This information in conjunction with the analysis performed on other artifacts (ceramic and obsidian) should eventually allow us to confront Rees and De Souza hypothesis [4] relative to the use of local vs. non-local raw materials in the study area, during the Formative Period. On the basis of macroscopic characteristics such as rock type, color and shine and applying standard morphological lithic tool analysis, the authors have classified the raw materials used for tool manufacture at the sites. Based on this analysis, several rock types, vitreous dacite being one of them, were classed as being local. The present study is the first experiment-based attempt to indicate the provenance of the raw materials used, hoping that in the long run an extended study will provide important information to evaluate the percentage of local vs non-local resources in the study area.

2. Samples

By comparison with obsidian, other types of lithic material like dacites are far less well studied specially in relation with source characterization. Vitreous dacite, in accordance with the Peccerillo and Taylor diagram [29] is a volcanic glassy rock, high in SiO2 and relatively low in its K2O contents. As source material, this rock has been detected in our study area on the slopes of two volcanoes, Toconce and Paniri (Fig. 1).

On the slope of the Toconce volcano at 4300 m altitude, there is a small distinctive outcrop, which we called the Linzor source. It shows extensive quarrying and mainly primary reduction of boulders at the quarry for the manufacture of bifacial tool blanks, with little evidence of secondary reduction of the tool preforms [30]. At this quarry site, the dacite rock contains small plagioclase needles in a glassy matrix with fine magnetite disseminations [31].

The Paniri source rock is found at two places on the volcanic slope. At the so called Paniri upper source at 4500 m altitude on the eastern slope of Paniri volcano, the raw material appears in the form of small boulders (of about 50–80 cm in diameter) on a shoulder of the volcanic slope. Some primary flaking and initial reduction stages for tool manufacture can be observed around the boulders, but since there are no final tools or other evidence of their manufacture at this place, it seems that most of the later reduction was performed at somewhat lower altitudes. Samples for analysis were taken here from several different boulders. Vitreous dacite is also found on the southern side of the volcano at the base of the cone, and was denoted as "Paniri lower source". Archaeological samples analyzed come from five archaeological sites located no more than 20 km from the Paniri volcano and about 25 km in direct line from the Linzor source. One site (Alero Derrumbado) is close to the Linzor source. The tools manufactured with the vitreous dacite are mostly large bifacial tools and dart points.

For this pilot study, in total 34 samples were chosen for analysis. Of these, 21 correspond to archaeological artifacts (denoted by Axx), and the remainder are samples from the geological sources, five from the Linzor source, three from the "Paniri upper source" and five from the "Paniri lower source" (all source samples labeled as Zxx).

3. Experimental

The PIXE analytical technique has been implemented at the Nuclear Physics Laboratory of the University of Chile in Santiago, Chile. Proton beams are provided by the Van de Graaff accelerator, KN3750 built by High Voltage Engineering. Sample irradiation takes place in a vacuum measuring chamber mounted on a dedicated beam line. A Canberra Si(Li) cryogenic detector Model 7300 having 220 eV FWHM resolution at 5.9 keV collects the induced X-rays. At the beam spot the sample surface makes an angle of 45° with respect to the incident beam. X rays from the sample pass to the detector which is located in the open air at 1 mm distance from the window chamber made of 6.3 μm thick Mylar film. The detector encompasses a solid angle $\Delta\Omega/4\pi$ equal to $(2.8 \pm 0.3) \times 10^{-4}$ and is located 68 mm from the sample. Standard electronic circuitry was used for pulse shaping optimization and collection by an ORTEC PC MCA Model Trump-8k. The spectroscopic system was energy calibrated with a ^{241}Am source. For the present work, 2.2 MeV proton beams were used with typical beam currents in the range of 0.1–0.5 nA up to a total charge of 0.1 μC. Additional information on the laboratory facilities is given elsewhere [32].

The special characteristics of the materials analyzed in this work, such as irregular shapes, and thickness of a few millimeters, forced for manual positioning of each sample in the chamber. Since the sample material is non-conductive, the use of an indirect method to measure the electric charge is used. The total charge deposited by the beam on the samples, was determined by the simultaneous irradiation of the sample and a Mylar film coated with cobalt ordered from Micromatter Inc. located at 2 mm in front of the sample. In an X-ray spectrum the net number of counts of the Co characteristic K lines was associated to the charge deposited on the sample during the irradiation time. The total charge is determined from a calibration function obtained previously, between the total number of cobalt counts in the film, and the total charge measured by a Faraday cup. Details of this method are given elsewhere [33].

Natural cobalt in these vitreous dacite samples was not detected by PIXE in irradiations performed in similar conditions, but without the Micromatter film. In a previous analytical study using PIXE/PIGME on Chilean obsidian by one the authors, [27] no Co was detected. Measurements performed by INAA on obsidian from the same region [16]
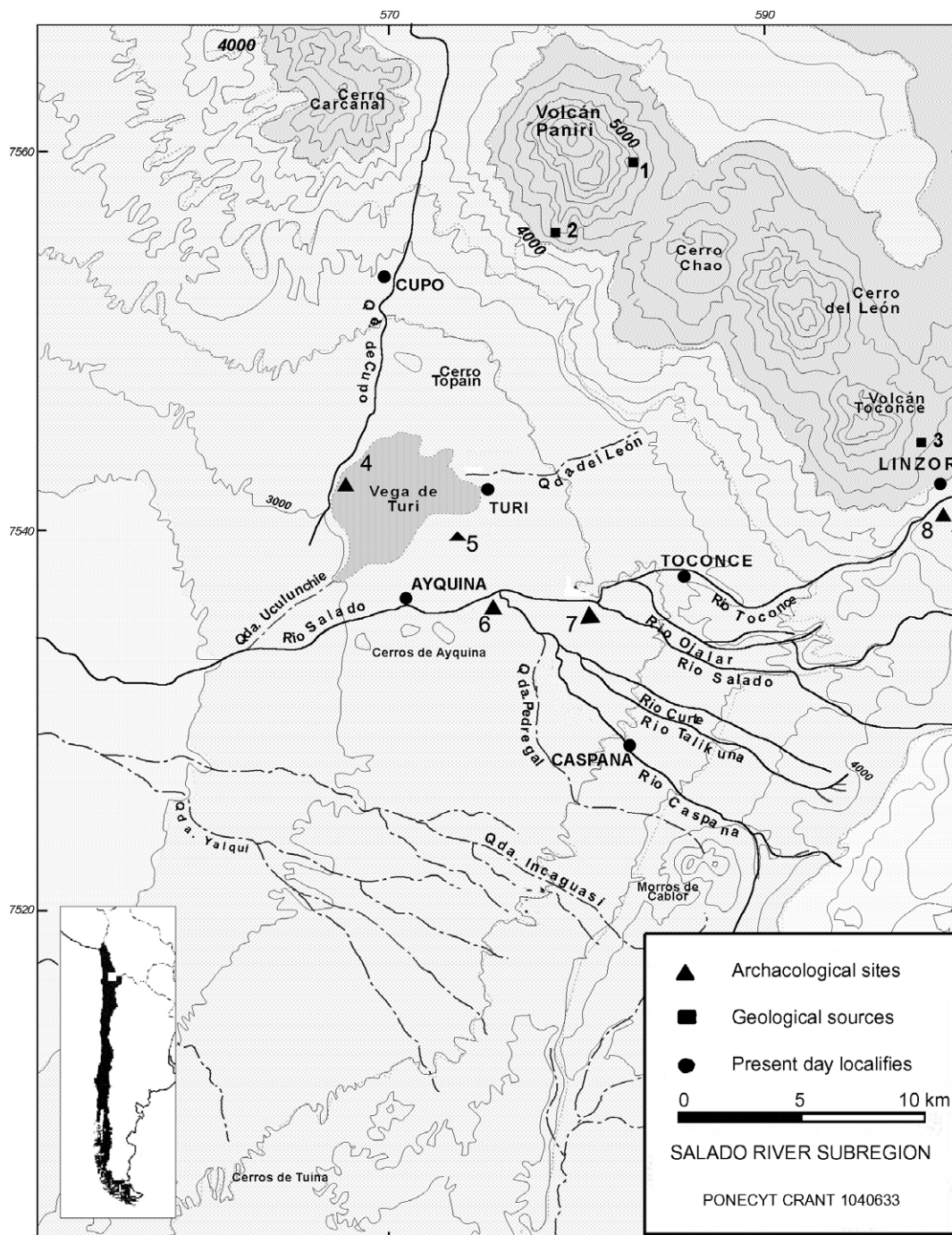
Fig. 1. Location of geological sources and archaeological sites in the Salado river basin in the Atacama Region, northern Chile. Geologic sources 1. Paniri upper source, 2. Paniri lower source 3. Linzor, source. Archaeological sites: 4. El Otro Sitio 5. Los Morros III 6. Confluencia 7. Alero Toconce 8. Alero Derrumbado.

show that the concentration of this element in this rather similar material, is less than 1.0 ppm.

The peak resolution in our system does not allow a separation between the Co Kα and the Fe Kβ lines and therefore an overlap between these lines is produced. Nevertheless, the evaluation of iron concentration was not affected because the Fe Kα line was used for this purpose. Secondary fluorescence does not affect the determina-tion of elemental concentration mainly because the ratio of intensities of cobalt K X-rays and the proton beam are around $1:10^8$ and even though their respective K-shell ionization cross sections are in the ratio $10^2:1$ approximately, [34] the primary fluorescence by protons is dominant.

In each run a special standard was irradiated under the same experimental conditions as the samples to be ana-lyzed, thus providing parameters for the determination of

Table 1
Elemental concentrations for Laguna del Maule standard

Element	Concentration [ppm]	% Fit error	LOD [ppm]
Al	67800	10.7	7300
Si	358000	4.4	5350
P	–	–	6310
Cl	3270	10.6	390
K	37800	1.5	210
Ca	5990	4.3	380
Ti	1600	11.6	180
Mn	641	18.5	130
Fe	8970	3.2	260

elemental concentrations. This standard had been previously prepared from a piece of obsidian rock collected by one of the authors (A.S.), from an obsidian source located at the Maule Lake in the Chilean central Andean region. This source was chosen because samples from it have been fully analyzed previously at independent laboratories using different methods (see Table 1). This procedure is currently applied in other laboratories [35,36].

The homogeneity of the elemental contents in dacite material was studied by irradiating slabs of dacite at six or more points by a proton beam collimated to around 5 mm^2. Results indicated that, at least for the elements determined by PIXE, the elemental concentrations were similar within 5–10%.

4. Results and discussions

PIXE allowed the identification of 13 elements; nine through the K lines, Al, Si, S, Cl, K, Ca, Ti, Mn, and Fe,

and four through the L lines, Sr, Y, Zr, Ba. A typical spectrum is shown in Fig. 2. The spectra were fitted with functions generated with the GUPIXWIN code (version 1.2) [37] obtaining the net number of counts in each peak for the determination of elemental concentrations. Elemental concentrations [ppm] for the K lines are given in Table 2.

Bivariate plots were used for initial data exploration in order to investigate the capacity of the method to discriminate between the known sources (Fig. 3). The source material showed intrasource chemical variability, however the two main sources, Linzor and Paniri, could be separated.

Looking for meaningful groupings within the available data we performed several standard multivariate statistical tests, such bivariate plots using elements concentrations, element ratios, linear combinations of these, and cluster analysis, with statistical package STATISTICA (version 6.0). Cluster analysis performed with the ratios of Al/(K + Ca), Ti/(K + Ca), Fe/(K + Ca), was used in order to group samples into classes. The resulting dendrogram is shown in Fig. 4. This allowed adscription of the archaeological artifacts to one of the geological sources.

Results from the dendrogram indicate that the archaeological sample A47 unquestionably was manufactured from material from the Linzor source. Samples A48, A62, A63 and A73 form a subgroup chemically more closely related to the Paniri source; however this group includes a source sample (Z06) from Linzor, suggesting that these artifacts are most probably manufactured from rock from the Linzor source. This is a reasonable assumption at least for samples A62 and A63, since the archaeological site where these samples come from is no more than 6 km in straight line from the Linzor source. All
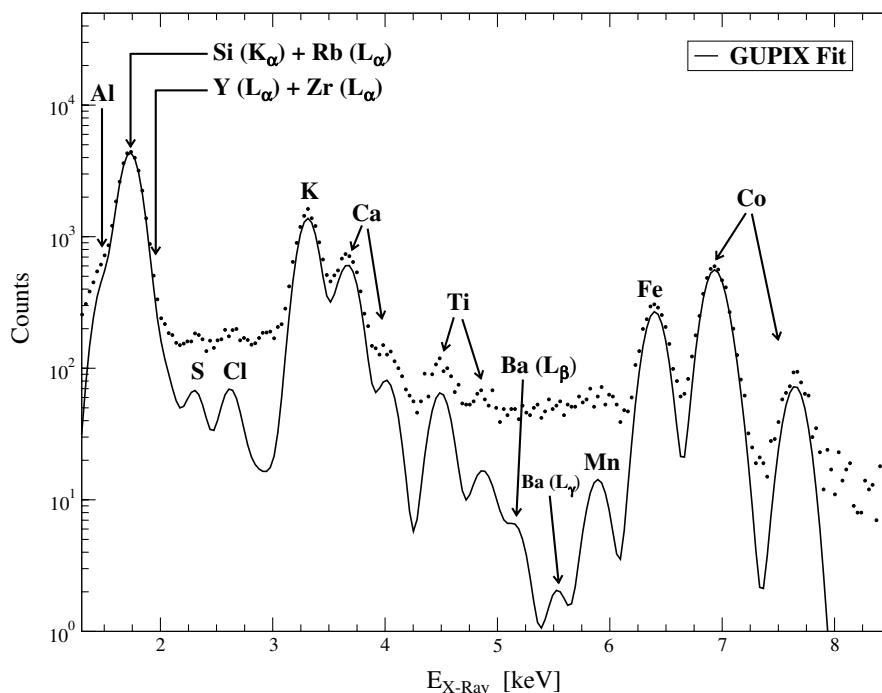

Fig. 2. Spectrum for sample Z04 from a dacite sample from the Linzor source, northern Chile. L lines were used to improve the fitting.

Table 2
Element concentrations expressed in ppm for all samples

Code	Site of collection	Al	Si	K	Ca	Ti	Fe
A47	Los Morros III	1.68E + 04	2.49E + 04	2.31E + 03	1.30E + 03	2.10E + 02	2.12E + 03
A48	Los Morros III	6.60E + 04	2.40E + 05	2.83E + 04	9.00E + 03	1.50E + 03	1.12E + 04
A50	Los Morros III	8.56E + 04	3.35E + 05	4.92E + 04	1.78E + 04	2.76E + 03	1.82E + 04
A52	Alero Toconce	6.03E + 04	2.15E + 05	2.97E + 04	8.46E + 03	1.34E + 03	8.71E + 03
A53	Alero Toconce	5.36E + 04	3.61E + 05	3.51E + 04	9.02E + 03	1.51E + 03	8.44E + 03
A54	Alero Toconce	6.93E + 04	2.27E + 05	6.01E + 04	1.40E + 04	1.75E + 03	1.39E + 04
A55	El otro sitio	7.26E + 04	3.50E + 05	3.67E + 04	9.45E + 03	2.22E + 03	7.98E + 03
A57	El otro sitio	6.37E + 04	3.47E + 05	6.56E + 04	1.69E + 04	4.00E + 03	1.33E + 04
A58	El otro sitio	7.82E + 04	3.56E + 05	4.05E + 04	1.01E + 04	2.37E + 03	8.45E + 03
A59	El otro sitio	7.82E + 04	3.56E + 05	4.05E + 04	1.11E + 04	3.18E + 03	9.90E + 03
A60	El otro sitio	5.53E + 04	3.55E + 05	6.34E + 04	1.63E + 04	4.73E + 03	1.69E + 04
A61	Confluencia	7.07E + 04	3.30E + 05	4.12E + 04	2.44E + 04	2.41E + 03	2.43E + 04
A62	Alero derrumbado	9.25E + 04	3.16E + 05	3.65E + 04	9.89E + 03	9.10E + 02	7.31E + 03
A63	Alero derrumbado	4.83E + 04	2.39E + 05	2.24E + 04	6.52E + 03	1.07E + 03	8.67E + 03
A68	Los Morros III	6.10E + 04	3.03E + 05	3.37E + 04	8.44E + 03	1.05E + 03	7.76E + 03
A69	Los Morros III	5.32E + 04	3.27E + 05	3.23E + 04	8.53E + 03	1.01E + 03	8.94E + 03
A70	Los Morros III	5.41E + 04	2.66E + 05	2.82E + 04	8.84E + 03	1.89E + 03	1.03E + 04
A71	Los Morros III	5.49E + 04	2.82E + 05	3.82E + 04	7.16E + 03	1.17E + 03	7.59E + 03
A72	Los Morros III	9.47E + 03	4.57E + 04	6.22E + 03	3.00E + 03	5.96E + 02	7.23E + 03
A73	Los Morros III	4.40E + 04	2.19E + 05	1.87E + 04	5.83E + 03	8.12E + 02	6.76E + 03
A74	Los Morros III	7.90E + 04	2.77E + 05	2.55E + 04	3.22E + 04	4.82E + 03	3.57E + 04
Z04	Linzor	5.23E + 04	1.60E + 05	1.50E + 04	4.17E + 03	6.05E + 02	6.63E + 03
Z05	Linzor	7.03E + 04	2.49E + 05	1.65E + 04	4.14E + 03	3.97E + 02	6.72E + 03
Z06	Linzor	5.53E + 04	2.81E + 05	2.40E + 04	6.67E + 03	8.63E + 02	6.00E + 03
Z07	Linzor	5.44E + 04	2.36E + 05	1.40E + 04	3.34E + 03	8.30E + 02	5.92E + 03
Z09	Linzor	3.71E + 04	9.23E + 04	5.52E + 03	1.98E + 03	2.46E + 02	2.87E + 03
Z027L	Paniri lower	6.34E + 04	3.12E + 05	3.77E + 04	1.27E + 04	1.96E + 03	1.66E + 04
Z040u	Paniri upper	8.55E + 04	3.43E + 05	3.54E + 04	1.79E + 04	3.33E + 03	2.06E + 04
Z041u	Paniri upper	6.64E + 04	2.88E + 05	3.99E + 04	1.79E + 04	3.00E + 03	1.92E + 04
Z043u	Paniri upper	4.59E + 04	1.90E + 05	2.71E + 04	1.44E + 04	2.60E + 03	1.87E + 04
Z046L	Paniri lower	5.10E + 04	2.77E + 05	2.72E + 04	8.69E + 03	1.77E + 03	1.05E + 04
Z047L	Paniri lower	7.03E + 04	3.53E + 05	3.63E + 04	1.08E + 04	1.59E + 03	9.45E + 03
Z049L	Paniri lower	6.05E + 04	2.77E + 05	2.95E + 04	1.09E + 04	2.33E + 03	1.53E + 04
Z051L	Paniri lower	3.75E + 04	1.78E + 05	2.39E + 04	7.58E + 03	1.23E + 03	1.02E + 04

Samples marked as Axx are form archaeological site contexts, while samples marked Zxx are from the geologic sources.
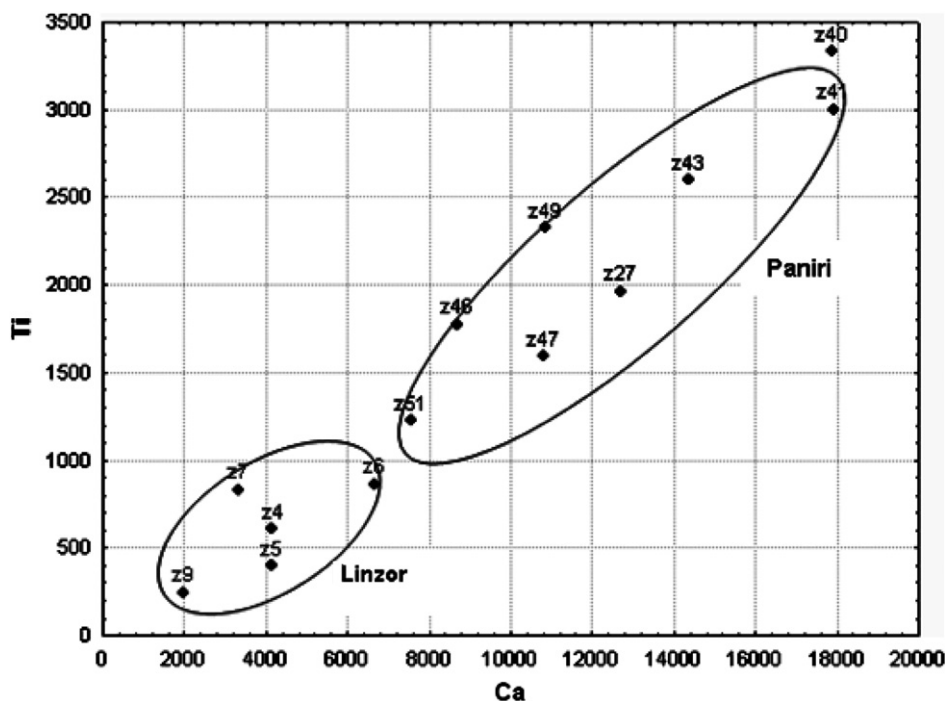

Fig. 3. Bivariate plot for all source samples using Ti and Ca concentrations expressed in ppm.

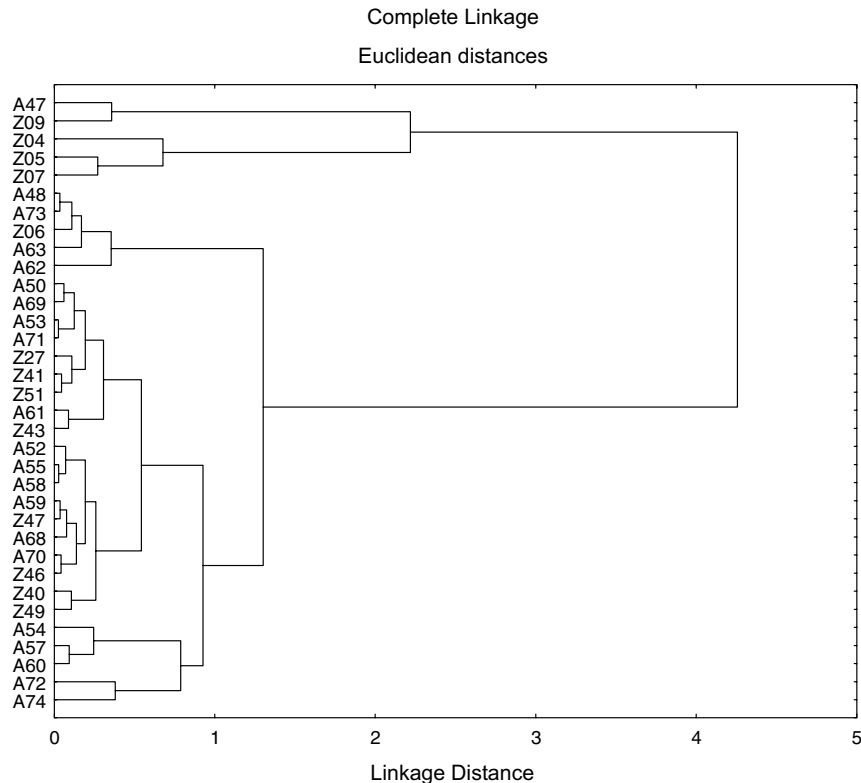Complete Linkage

Euclidean distances

Fig. 4. Cluster analysis (complete linkage, Euclidean distance) of 34 cases: 21 archaeological samples, and 13 source samples using elemental concentrations ratios Al/(K + Ca), Ti/(K + Ca), Fe/(K + Ca).

remaining archaeological samples can be assigned to the Paniri source. The cluster however does not allow distinguishing between the two localities at the Paniri volcano itself.

5. Conclusions

The application of PIXE to samples of volcanic vitreous dacite has shown the capability of this non-destructive analytical method to distinguish between geological sources of this material. Most samples could be assigned to either one of the sources identified during the course of this work. Only a small number of cases arose doubts, which could be resolved by complementing PIXE with another technique such as EDXRF, thus increasing the number of high Z-elements observed. Especially relevant are those trace elements such as Rb, Sr, Zr, Nb, and Y which have been shown to be important for source discrimination in volcanic glasses, such as obsidian [24,28,38]. However, our current PIXE equipment, does not allow detection of high Z-elements.

Archaeologically we can deduce from the present results that to the prehistoric population that lived around the Vega de Turi in the Upper Salado river basin, the Linzor source appears to be of less importance than the Paniri source. This can be verified by the fact that the provenance of 76% of the samples analyzed in this study has been assigned to the Paniri source through the cluster analysis shown in Fig. 4. The archaeological sites, where these samples come from, are located between 15 and 20 km south of the Paniri lower source area and about 25 km from the Linzor source. Both the upper Paniri source and the Linzor source are located at substantially higher altitudes (over 4000 m above sea level). The lower Paniri source can be reached by foot in an easy one day walk over fairly flat terrain. However getting to the Paniri upper source involves a steep one day walk over an uneven rocky landscape and ascending from 3000 to 4500 m above sea level. Even if distance to the source is measured in direct line, the access to Linzor is more complicated due to the topography of the area. In the case of the Linzor source, access on foot is a one or two day walk ascending from 3000 m to 4300 m above sea level. Distance to the source does seem to be factor in the choice of the raw material at some sites, as has been observed for the two samples, A62 and A63, located at the site Alero Derrumbado (N° 8 in Fig. 1) near the Linzor source. At another archaeological site, Los Morros III (N° 6 in Fig. 1), it is interesting to note that 30% of the samples analyzed come from Linzor while the other 70% was obtained from Paniri.

Finally, the non destructive capacity of PIXE to perform elemental analysis on vitreous rocks other than obsidian, like the archaeological artifacts of this work, opens a wide field for future applications to provenance studies. We have shown that PIXE used on unmodified vitreous dacite has the capacity for discriminating between source groups and to assign archaeological artifacts to either one of the sources. Up to now, all previous PIXE analysis

has been performed exclusively on obsidian. The degree of success obtained in this study, is a strong motivation to improve the present instrumental capacity so as to be able to include the high-Z and light elements such as Na and F in future studies. It is also necessary to increase the number of samples of the sources in order to better understand intra source variability and survey the area for the presence of additional sources of this material.

Acknowledgments

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