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# Provenance of obsidian artifacts from the Natural Protected Area Laguna del Diamante (Mendoza, Province Argentina) and upper Maipo valley (Chile) by LA-ICP-MS method

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ABSTRACT

By means of inductively Coupled Plasma Mass Spectrometry associated with Laser Ablation (LA-ICP-MS) we analyzed several obsidian artifacts from the Natural Protected Area Laguna del Diamante (Mendoza, Argentina) and upper Maipo valley (Chile). This analytical method, almost non-destructive, is a powerful tool for the determination of trace elements and is very useful in characterizing and determining the provenance of obsidian fragments of archeological interest, although care must be taken to avoid or account for heterogeneities within obsidian such as microcrysts.

In the macro-region of study, two types of sources can be differentiated on the basis of their primary location: high-altitude sources emplaced in the Andes range (≥2500 m a.s.l.) including Laguna del Diamante, Laguna del Maule, and Las Cargas sources; and low-altitude (≤1500 m a.s.l.) extra-Andean sources situated on the eastern plains: Cerro Huenul and El Peceño. In addition, while the primary location of Arroyo Paramillos source is currently unknown, we consider it as a sub source of Laguna del Diamante, since its wide archaeological distribution has a main core within Laguna del Diamante area and in the upper Maipo River basin. Considering this pattern, the assignation of provenances presented here improves the basis for assessing the use of high Andean environments from both sides of the mountain range. In addition, we will also improve the geochemical discrimination between the two sources Arroyo Paramillos and Las Cargas that based on only previous XRF analysis are chemically overlapping, leading to an incorrect interpretation of their pattern of archaeological distribution. The better characterization of the obsidian sources of the Laguna del Diamante and neighboring regions allows discussions of mobility, exchange, and human use of this lithic resource in the highland of central western Argentina - central Chile.



## 1. Introduction

In recent years, studies of trace elements on obsidian, using different geochemical methods, have been carried out with the intention of solving different archaeological problems of central western Argentina and central Chile (Seelenfreund et al., 1996; Durán et al., 2004, 2012; De Francesco et al., 2006; Giesso et al., 2011). Several obsidian sources (Fig. 1) have been discovered and characterized chemically, and their spatial distribution, intensity and changes of their use over time have begun to be defined. Among the results obtained, it was surprising the dearth of obsidian from the Laguna del Diamante sources in the archaeological sites from the Andean highlands, eastern lowlands and the Upper Maipo basin (Durán et al., 2004; Giesso et al., 2011). These results also indicated, unexpectedly, that obsidian from Las Cargas source dominates the archaeological record in the Maipo Valley, although this source is located more than 100 km to the south (Giesso et al., 2011).

The samples from six obsidian sources (Laguna del Maule, Las Cargas, Cerro Huenul, El Peceño, Laguna del Diamante and Arroyo Paramillos) (Fig. 1) were previously characterized by the X-Ray Fluorescence (XRF) analytical method on powder and by the non-

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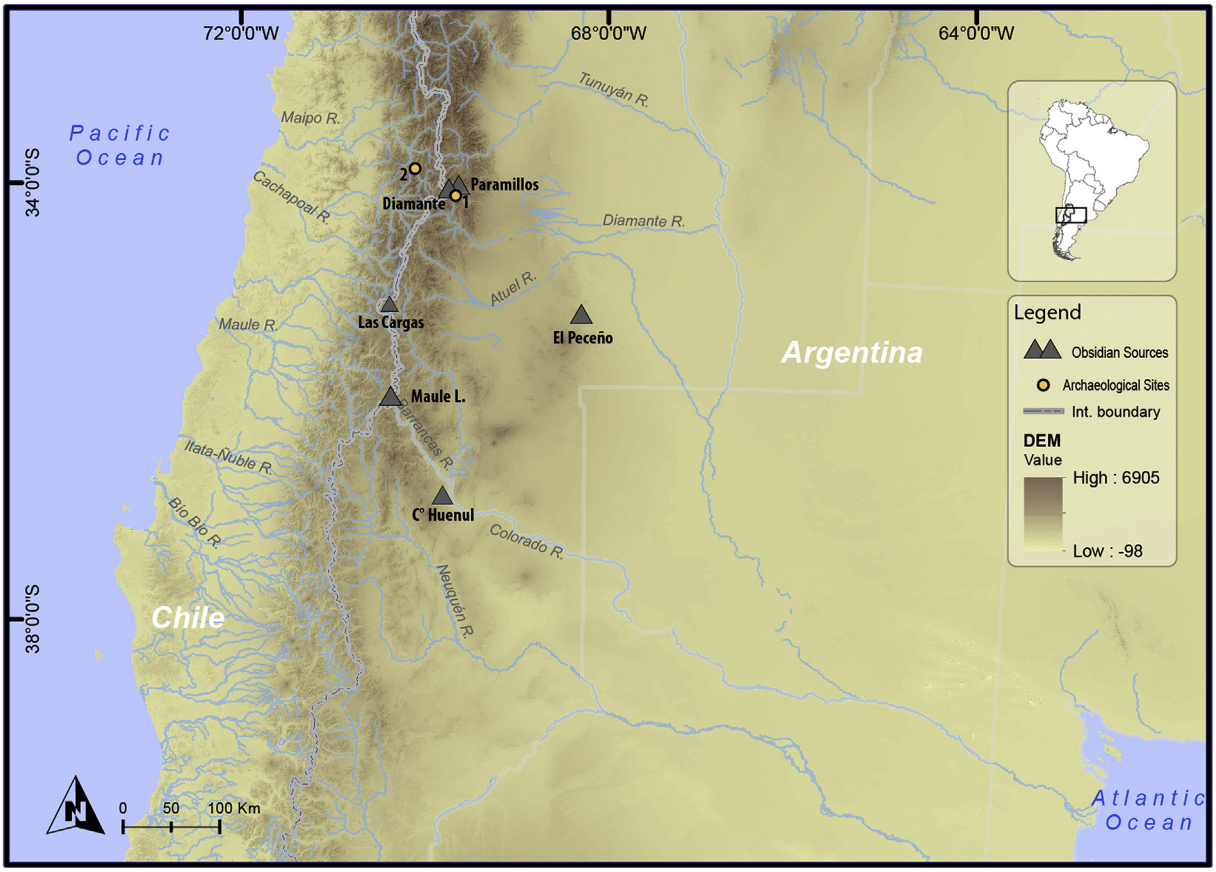


**Fig. 1.** Localization of the obsidian sources and of archaeological sites (after Fernández et al. (2017). Archaeological sites: 1-Laguna del Diamante - Argentina (LD-S4-E1 and LD-S2-E1); 2 - Los Queltehues - Chile.

destructive Wave Dispersion -XRF method proposed by Crisci et al. (1994) and De Francesco et al. (2008), the results of which are reported in De Francesco et al. (2006). In latter paper, the provenance of 34 obsidian archaeological fragments from two sites LD-S4 and LD-S2 of the Laguna del Diamante area was determined with the non-destructive XRF method. The same method was then used to trace the origin of 101 archaeological fragments (Durán et al., 2012) from several archaeological sites of central western Argentina and central Chile.

Laguna del Diamante and Arroyo Paramillos are the northernmost obsidian chemical types known for the macro-region of study. The primary source of the latter has not been found yet, although few isolated and small nodules of this obsidian were found near Arroyo Paramillos. It is compositionally similar to Las Cargas, producing an overlapping geochemical signal that complicates its discrimination and, hence, archaeological interpretations in Giesso et al. (2011). Cortegoso et al. (2014) compared the results obtained at the University of Calabria using the non-destructive XRF method (De Francesco et al., 2006) with those of Giesso et al. (2011), and they highlighted the separation between these two sources. Based on the presence of nodules in Arroyo Paramillos near Laguna del Diamante, and on the archaeological distribution concentrated in Upper Maipo basin documented in this paper, we infer that its primary position would be located in the western slope of the Andes (Cortegoso et al., 2016). Correct identification of this source is a necessary step to evaluate the home ranges of the people who exploited the highlands seasonally.

In order to solve these problems, we are conducting a regional program of chemical characterization of sources and artifacts. The main sources and 32 archaeological samples already analyzed by XRF methods (De Francesco et al., 2006; Duran et al., 2012; Cortegoso et al., 2014) have been re-analyzed by Laser Ablation (LA) with Inductively Coupled Plasma Mass Spectrometry (ICP-MS). In a previous study (Barca et al., 2007), the comparison of data obtained through non-destructive XRF method and LA-ICP-MS applied to geological and archaeological obsidians of the Mediterranean gave us good results. The LA-ICP-MS analytical method combines non-destructivity with the capacity for analyzing a large number of trace and REE elements with high sensitivity in a very short time. These features make the LA-ICP-MS method a widely recognized and very powerful tool for the characterization and determination of the provenance of archaeological obsidians. The greater number of trace and REE elements analyzed in this paper confirms the distinction between Las Cargas and Arroyo Paramillos sources. These results produce important archaeological implications linked to the exploitation of obsidian and to the mobility of human societies that occupied the highlands of central and southern Mendoza Province of Argentina during the Late Holocene.

## 2. Obsidian sources and environment in southwestern south America

The study area covers a large part of central Chile and Argentina (32°-37° S, 67°-72° W). This large territory extends from the coast of the Pacific Ocean on the west to the central western Argentinean plains. The region is divided by the Andean mountains, which have an average width of 150 km and heights reaching up to 6900 m a.s.l. The eastern plains include some prominent geological features,

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such as the southern volcanic fields located in the southern part of the region, and, reaching heights up to 3500 m a.s.l. Precipitation occurs through frontal systems associated with migratory cyclones that tend to migrate eastward along narrow latitudinal bands known as storm tracks (Garreaud et al., 2009). As a consequence of the rain shadow effect produced by the forced subsidence of the surface winds over the Andes, precipitations present a strong west-east decreasing gradient. The slopes to the east of the Andes are arid to semiarid. As one moves upward, rainfall increases and temperature decreases. Vegetation distribution follows this precipitation gradient. These differences are more striking on the Chilean side, where the altitude descends from 6000 to 500 m a.s.l. in less than 70 km.

Numerous volcanoes, some still active, are located in the central and southern portions of the region. Volcanic activity decreases north of 34°, but it continues to the south in Patagonia. Extra-Andean volcanism is abundant in southern Mendoza, an extension of several thousand $km^2$ of volcanoes that were active during the Holocene in the Payunia region; the distribution of volcanoes and silicic lavas determines the presence or absence of obsidian sources throughout the region (Durán and Mikkan, 2009).

### 2.1. Obsidian sources

Six obsidian sources have been located (Fig. 1). The first four are in the highlands: Laguna del Diamante, Arroyo Paramillos, Las Cargas, and Laguna del Maule. The other two sources are located in the eastern plains: Cerro Huenul and El Peceño. The large amount of obsidian knapping debris recorded in Laguna del Maule, El Peceño, Cerro Huenul and Las Cargas, suggests that they were utilized as quarries.

#### 2.1.1. Laguna del Diamante locality

This is a lagoon within a volcanic caldera of 300 $km^2$ located at 3200 m a.s.l. near the border between Argentina and Chile. The access to this source is seasonally restricted from both sides. The area includes ignimbrites and pyroclastic deposits. The size of obsidian nodules is more than 30 cm in diameter on the edge of the caldera, high ground above 3800 m a.s.l., progressively decreasing along the streams that drain into the lagoon. Nodules found on the beaches of the lagoon are 2–3 cm in diameter. Two chemical types can be geochemically distinguished in this volcanic complex: Laguna del Diamante and Arroyo Paramillos.

#### 2.1.2. Las Cargas

The source is located in the border between Argentina and Chile, at 2350 m a.s.l. in the volcanic complex Planchón-Peteroa. Access to the source is seasonally restricted from both sides. The surveyed area of the primary source is around 1 $km^2$, though the presence of obsidian nodules transported along the ravines reaches nearly 4 km downstream. The distribution of the obsidian in the area may be greater and even outcrops are likely to exist in Chile (Salgán et al., 2015). The obsidian appears to be associated with volcanic tuff with glass inclusions and blocks that can reach 0.5 $m^3$ in volume. It is a source of good-quality obsidian, and includes a great amount of knapping debris over large surfaces.

#### 2.1.3. Laguna del Maule

This is a vast volcanic complex located in the high Cordillera, between Argentina and Chile, at altitudes around 2400 m a.s.l. It is the largest obsidian source in the study region, covering an area of approximately 900 $km^2$. The source has several outcrops in Laguna Negra (Argentina) including blocks that can reach 1 $m^3$ in volume, dispersed in a 20- $km^2$ area. In other sectors, like Arroyo Pehuenche, the nodules are smaller, between 2 and 5 cm in diameter, but they have high quality. Fernández et al. (2017) distinguished within the Maule area two sources, named Maule I and Maule II.

#### 2.1.4. El Peceño

El Peceño is located at around 1450 m a.s.l., on the northwestern flank of El Nevado Volcano, in eastern Mendoza (Durán et al., 2004). Raw materials are dispersed over a radius of ~1000 m around the cone. The nodules vary between 30 and 2 cm of diameter. The raw material availability is good, its quality is variable, and there is not a massive outcrop like the other sources. The source is available year round.

#### 2.1.5. Cerro Huenul

This source is located between 900–1800 m a.s.l. in association with ignimbrite deposits associated to the Tilhué Formation (Barberena et al., 2011; Durán et al., 2004; Seelenfreund et al., 1996). Access is easy and year round, and the obsidian is of high quality. The source includes a lot of ravines that have scattered obsidian fragments over several square kilometers. The nodules are of medium to small size, usually not larger than 10 cm in diameter. Raw material suitable for knapping is quite abundant (Durán et al., 2004).

Two obsidian types dominate the macro-regional archaeological record: Las Cargas and Laguna del Maule (Seelenfreund et al., 1996; Durán et al., 2004; Giesso et al., 2011). One pattern previously recorded indicates the significant presence of obsidian from the highlands in the eastern lowlands (Cortegoso et al., 2012). However, recent geoarchaeological work has confirmed that obsidian from Laguna del Maule is transported to the lowlands (ca. 900 m a.s.l.) by the fluvial processes along the Barrancas and Colorado rivers (Fernández et al., 2017).

Laguna del Diamante and Cerro Huenul sources show less intensive human use, being underrepresented even in nearby areas. Accordingly, they have been considered as minor sources at a macro-regional scale (Barberena et al., 2011; Durán et al., 2012; Cortegoso et al., 2016). In the case of Laguna del Diamante, its seasonal availability, relative circumscription of the source to the volcanic caldera, and the restricted dispersion and size of the nodules may explain this pattern. In addition, the exploitation of these rich summer environments could have attenuated the pronounced effects of the dry summer season in lower areas of the western slope. Considering the asymmetric archaeological representation of the obsidian types in the two sides of the Andes, the provenance of the ceramic recovered from the sites, and the results of strontium isotopes analysis in human remains, we proposed a predominant use of the highlands by people located in western Andean slope, expressed as a dominant geographic vector of access to the highlands (Durán et al., 2017).

## 3. Materials analyzed

The 26 geological obsidian source samples were previously analyzed by both XRF analytical methods on powder and by non-destructive WD-XRF method by De Francesco et al. (2006) and Durán et al. (2012). In the present work nine selected representative geological obsidian samples were reanalyzed by LA-ICP-MS. They consist of two obsidian samples from Laguna del Maule, two from Laguna Negra, one from Las Cargas, one from Cerro Huenul, two from Laguna del Diamante and one from Arroyo Paramillos.

The archaeological fragments represent 23 artifacts, mainly knapping debris, selected among the 40 artifacts already analyzed (De Francesco et al., 2006; Durán et al., 2012), using the non-destructive XRF method from two Argentine archaeological sites: LD-S4 and LD-S2 in the Laguna del Diamante area and nine obsidian artifacts from one archaeological site in Chile: Los Queltehues (selected among samples already analyzed in Durán et al., 2012) (Table S1). LD-S2 and LD-S4 are open sites located in the west side of Diamante lagoon and both have a same subcircular structures with stone walls of 50 cm height with a sequence of occupation extended to the last 2000 years. Los Queltehues is a rock-shelter, located on the eastern margin of the Maipo River at 1589 m a.s.l. with a sequence of human occupation beginning at 7000 years BP up to 500 years BP (Fig. 1).

## 4. Analytical methods

In the present work, the analyses were carried out using a combination of Laser Ablation (LA) with Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The equipment was an Elan DRCe (Perkin Elmer/SCIEX) connected to a New Wave UP213 solid-state Nd-YAG laser probe (213 μm). Samples were ablated by laser beam in a cell, and the vaporised material was then flushed (Gunther and Heinrich, 1999) to the ICP, where it was quantified. The constant laser repetition rate was 10 Hz and fluence about 20 J/$cm^2$. Each ablation crater was generally 50 μm in diameter and nearly invisible to the naked eye. The above instrumentation can rapidly analyse solid samples and determine trace and REE concentrations to parts-per-million and parts-per-billion levels, with very low detection limits and without any sample manipulation.

For geological specimens, a small piece of about 5 × 5 mm was sampled from each nodule, fragments were then fixed on slides, with the fresh side facing upward. For archaeological samples, in order to remove any trace of soil, each find was cleaned by ultrasound in Millipore water.

Only two point analyses were carried out on portions of archaeological finds without roughness or alterations, and were sufficient to assign provenance. Each analytical sequence was executed on two or three obsidian at a time, in association with the standard material used to calibrate the equipment (Barca et al., 2007, 2008). Data were transmitted to a PC and processed by the GLITTER program (van Achterberg et al., 2001); calibration was performed on glass reference material produced by the National Institute of Standards and Technology (NIST) SRM 612 at nominal concentrations of trace elements of 50 ppm in conjunction with internal standardisation, applying $SiO_2$ concentrations (Fryer et al., 1995; Longerich et al., 1996) to each archaeological find determined independently by SEM-EDS analyses. In order to evaluate possible errors within each analytical sequence, determinations were also made on glass reference material NIST SRM 610, with nominal concentrations of trace elements of 500 ppm, as unknown sample, and element concentrations were compared with reference values. Since the NIST certifies only eight elements in this glass, the mean values of measurements carried out in the various analytical sequences in this study were compared with published data (Pearce et al., 1997; Dulski, 2001; Gao et al., 2002). Accuracies, expressed as the relative difference from reference values, was always better than 10%, and for the most of elements in the range ± 5%.

To check the presence and size of microliths, representative geological fragments for each obsidian source have been suitably cut and polished. Their surfaces were then coated with a graphite layer and analyzed by Electron Probe Micro Analyzer (EPMA) – JEOL- JXA 8230, equipped with five wavelength-dispersive spectrometers (WDS). The EPMA was used under the following operating conditions for the image acquisition:15 kV, Probe current at 1 nA and Solid State detector (SSD), Everhart Thornley detector (SE).

## 5. Results and discussion

Nine samples of geological obsidian were analyzed, as well as 32 archeological artifacts from central western Argentina and central Chile, the provenance of which had already been determined by non-destructive XRF (De Francesco et al., 2006; Duran et al., 2012; Cortegoso et al., 2014).

The analysis of 20 trace elements, including REE, obtained by LA-ICP-MS instrument from representative obsidian fragments of the geological sources are listed in Table 1

Table S2 lists the results on 23 artifacts from Argentina and nine from Chile.

The concentration ratios of only a few chemical elements were used to compare the LA-ICP-MS data with the XRF oldest ones. The new results confirm that the Sr, Rb, Nb, and Zr are able to separate the obsidian sources (De Francesco et al., 2006; Durán et al., 2012). In addition, Ba content measured by LA-ICP-MS allows a good discrimination among the geological obsidians; indeed, the Arroyo Paramillos source show always Ba contents more than 600 ppm and Las Cargas source a Ba values less than 550 ppm. On the contrary, the REE concentrations are scarcely able to separate the sources; in general, the geological obsidians show enrichment in LREE (Light REE) compared to HREE (Heavy REE) (Table 1).

The diagram Sr/Rb vs. Nb/Zr (Fig. 2) shows the comparison between the data acquired on the obsidian sources by LA-ICP-MS and by XRF powder (De Francesco et al., 2006). The data obtained by these two analytical methods fit quite well, and all the obsidian sources are distinguishable, but it should be noted that the LA-ICP-MS data show compositional variability within the same sample (Fig. 2).

On the contrary, the data obtained by XRF show a remarkable homogeneity, even on different samples from the same source, as for Laguna del Diamante and Laguna Negra (Maule I - Fernández et al., 2017) and minor compositional variations on Cerro Huenul and Laguna del Maule (Maule II - Fernández et al., 2017) sources (Fig. 2). Using XRF data, Arroyo Paramillos source is represented by a single obsidian sample, while Las Cargas source is represented by the mean value of 11 specimens displaying unambiguously well-defined chemical composition.

The compositional homogeneity or heterogeneity can be explained by taking into account not only some important methodological considerations, but also the processes of obsidian formation. When the obsidians are not perfectly glassy, they are better described as rocks of rhyolitic composition with obsidian-like appearance, and these rocks can contain numerous microliths.

The XRF analysis is carried out on obsidian powder pellet that is representative of whole rock and so the surface irradiated by X-rays corresponds to a few square centimeters. Using the LA-ICP-MS, as described in the analytical methods, the ablation crater area is only 50 μm in diameter and quite similar in depth, therefore it is a very small volume which may represent the whole composition only in those vitreous and perfectly homogeneous obsidians.

As highlighted by the Sr/Rb and Nb/Zr ratio variation (Fig. 2), all the sources show considerable heterogeneity, which is especially evident for Arroyo Paramillos, Laguna del Diamante, and Las Cargas.

Fig. 3 shows the Back Scattered Electron (BSE) images of a representative sample of all studied obsidian geological sources. It shows that the obsidians are not completely glassy, and they contain numerous ten micron-sized microliths of plagioclase, biotite, amphibole and oxides. When using the LA-ICP-MS the spot involves the plagioclase microlite, the effect is primarily on Ba and Sr values, while if the analysis affects partly biotite microliths, higher Zr values are obtained. Indeed, the diagram of Fig. 2 shows the high variability of Sr/Rb ratio of the Arroyo Paramillos, Las

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**Table 1**
List of the analyzed archaeological obsidians.

| Chilean archaeological sites | sample | Argentine archaeological sites | sample | Argentine archaeological sites | sample |
|---|---|---|---|---|---|
| Los Queltehues | Ch13-01 | LD_S4 | Arg2-01 | LD_S2 | Arg32-01 |
| Los Queltehues | Ch13-02 | LD_S4 | Arg2-02 | LD_S2 | Arg32-02 |
| Los Queltehues | Ch13-03 | LD_S4 | Arg10-1 | LD_S2 | Arg32-03 |
| Los Queltehues | Ch14-03 | LD_S4 | Arg10-2 | LD_S2 | Arg31-01 |
| Los Queltehues | Ch15-01 | LD_S4 | Arg11-1 | LD_S2 | Arg31-02 |
| Los Queltehues | Ch15-02 | LD_S4 | Arg11-2 | LD_S2 | Arg33-01 |
| Los Queltehues | Ch15-03 | LD_S4 | Arg11-3 | LD_S2 | Arg33-02 |
| Los Queltehues | Ch16-01 | LD_S4 | Arg12-1 | | |
| Los Queltehues | Ch16-02 | LD_S4 | Arg12-2 | | |
| Los Queltehues | Ch16-03 | LD_S4 | Arg15-1 | | |
| Los Queltehues | Ch20-01 | LD_S4 | Arg15-2 | | |
| Los Queltehues | Ch20-02 | LD_S4 | Arg18-1 | | |
| Los Queltehues | Ch20-03 | LD_S4 | Arg18-2 | | |
| Los Queltehues | Ch17-01 | LD_S4 | Arg20-1 | | |
| Los Queltehues | Ch17-02 | LD_S4 | Arg20-2 | | |
| Los Queltehues | Ch17-03 | LD_S4 | Arg21-1 | | |
| Los Queltehues | Ch18-01 | LD_S4 | Arg21-2 | | |
| Los Queltehues | Ch18-02 | LD_S4 | Arg27-01 | | |
| Los Queltehues | Ch18-03 | LD_S4 | Arg27-02 | | |
| Los Queltehues | Ch18-04 | LD_S4 | Arg28-01 | | |
| Los Queltehues | Ch19-01 | LD_S4 | Arg28-02 | | |
| Los Queltehues | Ch19-02 | LD_S4 | Arg29-01 | | |
| Los Queltehues | Ch19-03 | LD_S4 | Arg29-02 | | |
| Los Queltehues | Ch21-01 | LD_S4 | Arg30-01 | | |
| Los Queltehues | Ch21-02 | LD_S4 | Arg30-02 | | |
| Los Queltehues | Ch21-03 | LD_S4 | Arg35-01 | | |
| | | LD_S4 | Arg35-02 | | |
| | | LD_S4 | Arg35-03 | | |
| | | LD_S4 | Arg19-1 | | |
| | | LD_S4 | Arg19-2 | | |
| | | LD_S4 | Arg17-01 | | |
| | | LD_S4 | Arg17-01 | | |
| | | LD_S4 | Arg4-1 | | |
| | | LD_S4 | Arg4-2 | | |
| | | LD_S4 | Arg9-01 | | |
| | | LD_S4 | Arg9-02 | | |
| | | LD_S4 | Arg23-1 | | |
| | | LD_S4 | Arg23-2 | | |
| | | LD_S4 | Arg23-3 | | |
| | | LD_S4 | Arg23-4 | | |
| | | LD_S4 | Arg26-01 | | |
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| | | LD_S4 | Arg14-01 | | |

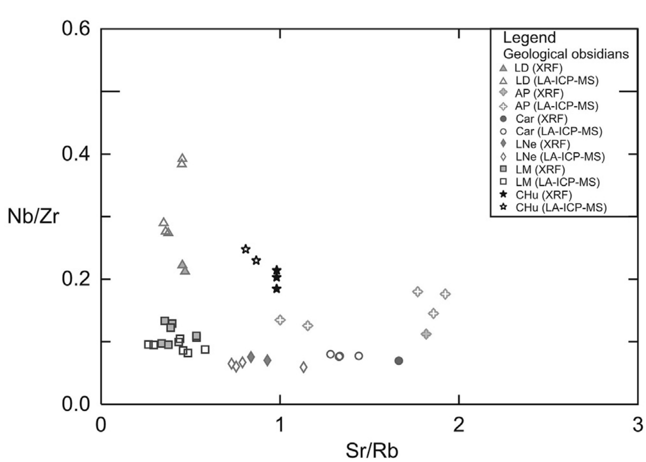


**Fig. 2.** Sr/Rb vs. Nb/Zr plot: comparison between the data obtained on the obsidian sources by LA-ICP-MS and by XRF on powder (after De Francesco et al., 2006; modified). LD - Laguna del Diamante; , AP -Arroyo Paramillos, ACar - Las Cargas; LM - Laguna del Maule; LNe – Laguna Negra; CHu- Cerro Huenul.

Cargas and Laguna Negra obsidian sources; at the same time, Nb/Zr ratio varies mainly in the Laguna del Diamante source.

Using traditional XRF, the obsidians become homogeneous by powdering, and similarly analyzing the entire fragments by non-destructive XRF, the dimension of the radiated area is a circle of about 1 cm in diameter, and is, indeed, representative of composition bulk of the obsidian.

The results obtained on the obsidian fragments from the Argentine and Chilean archaeological sites are shown in the diagram Sr/Rb vs. Nb/Zr (Fig. 4), together with the geological obsidian sources, detected by LA-ICP-MS and XRF.

Using LA-ICP-MS, for each fragment multiple results (from two to four) were obtained. Moreover, the average of the analyses has not been used since the fragments, analogously to the sources, show chemical heterogeneity. The most significant changes affect particularly the chemical elements capable of discriminating the obsidian sources such as Sr, Rb, Nb, and Zr. The Fig. 4 shows that most of the obsidian artifacts from Argentina belong to three sources: Laguna del Diamante, Arroyo Paramillo and Las Cargas.

The artifacts from Chile, belong only to Laguna del Diamante and Arroyo Paramillos sources. The Arg 4 and Arg 14 artifacts are out of all the plotted source areas, while Arg 23 sample fits in the range of Sr/Rb ratios of Arroyo Paramillos (Table S2 and Fig. 4). Two artifacts Ch13 and Arg 26, with the highest Sr/Rb ratio, definitely belong to the same source.

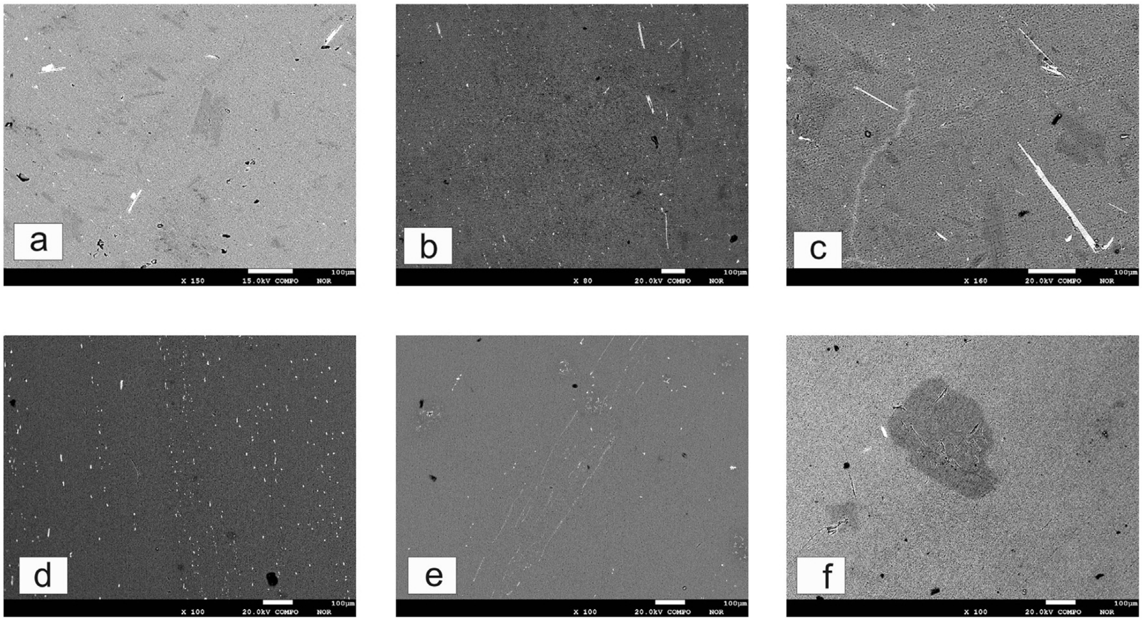


**Fig. 3.** Obsidian source by BSE images: a) C16 - Laguna Negra; b) CAR - Las Cargas; c) AP - Arroyo Paramillos sub source; d) C5Ma - Laguna Maule; e) E10 - Cerro Huenul; A6- Laguna del Diamante.

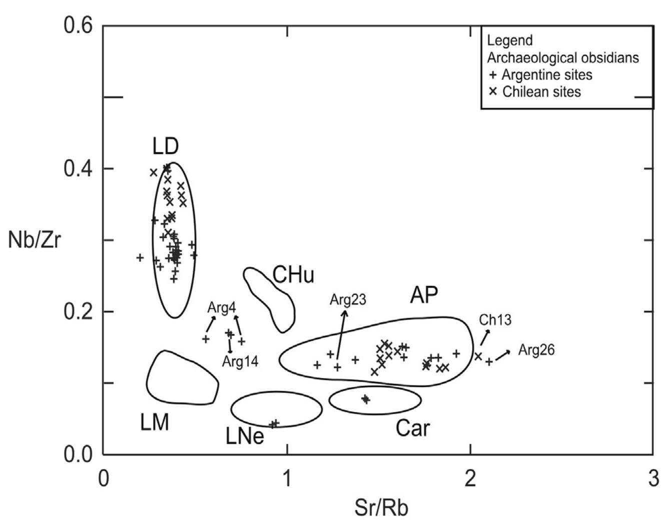


**Fig. 4.** Diagram Sr/Rb vs.Nb/Zr of the artifacts. Legend of the obsidian sources is on Fig. 3. For names of archaeological samples, see Table S1.

## 6. Conclusions

The present study reports the results obtained by LA-ICP-MS on the obsidian sources and on the archaeological artifacts from Laguna del Diamante and the upper Maipo valley, which were already analyzed by XRF (De Francesco et al., 2006; Durán et al., 2012). The LA-ICP-MS analysis has many advantages, including the micro-destructiveness, and it is particularly important for archaeological obsidians. The best results are obtained when the obsidians are vitreous and homogeneous. In a previous study, the comparison of data obtained through non-destructive XRF method and LA-ICP-MS applied to geological and archaeological obsidians of the Mediterranean provided solid results.

The LA-ICP-MS results obtained on Argentinian and Chilean obsidian sources confirm the distinction between Las Cargas and Arroyos Paramillos sources.

The provenance of 32 obsidian artifacts from central western Argentina and central Chile, obtained by LA-ICP-MS method, is generally very consistent with the results generated by non-destructive XRF method (De Francesco et al., 2006; Durán et al., 2012).

The analyses data obtained by LA-ICP-MS highlighted the significant compositional heterogeneity of all the obsidian sources, due to the presence of abundant microliths in the partially glassy texture. The heterogeneity observed in the obsidian sources is noticeable in the artifacts because they evidenced a high compositional variability in the multiple spot analyses performed on the same fragment.

Archaeological implications of this enhanced geochemical resolution are of great value to assess past human acquisition and use of this obsidian sources and, hence, of the highlands Laguna del Diamante locality, where they are situated. While this area could certainly been accessed and occupied from diverse demographic nodes located in lower-altitude settings, the spatial analysis of artifacts made on these rocks, as well as other lines of evidence such as ceramic types and the ranges of paleomobility of individuals inferred from strontium isotopes analysis, show a distribution skewed towards the western Andean slope, indicating the existence of a dominant geographical vector of access to the highlands connecting with the western valleys and lowlands of Chile (Barberena et al., 2017; Cortegoso et al., 2016; Durán et al., 2017). This research is integrated into a wider regional project aimed to study the human use of the Andes by means of diverse archaeological proxies measuring the transport of artifacts and the movements of people in the past.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.quaint.2017.10.004.

## References

Barberena, R., Durán, V.A., Novellino, P., Winocur, D., Benítez, A., Tessone, A., Quiroga, M.N., Marsh, E.J., Gasco, A., Cortegoso, V., Lucero, G., Llano, C., Knudson, K.J., 2017. Scale of human mobility in the southern Andes (Argentina and Chile): a preliminary framework based on strontium and oxygen isotopes. Am. J. Phys. Anthropol. 164 (2).

Barberena, R., Hajduk, A., Gil, A., Neme, G., Durán, V., Glascock, M., Giesso, M., Borrazzo, C., Pompei, M., Salgán, L., Cortegoso, V., Villarosa, G., Rughini, A., 2011. Obsidian in the south-central Andes: geological, geochemical, and archaeological assessment of north Patagonian sources (Argentina). Quat. Intern 245, 25–36.

Barca, D., De Francesco, A.M., Crisci, G.M., 2007. Application of Laser Ablation ICP–MS for characterization of obsidian fragments from peri-Tyrrhenian area. J. Cult. Herit. 8, 141–150.

Barca, D., De Francesco, A.M., Crisci, G.M., Tozzi, C., 2008. Provenance of obsidian artifacts from site of Colle Cera, Italy, by LA-ICP-MS method. Period. Mineral. 77, 41–52.

Cortegoso, V., Neme, G., Giesso, M., Durán, V., Gil, A., 2012. El uso de la obsidiana en el sur de Mendoza. In: Neme, G., Gil, A. (Eds.), Paleoecología humana en el Sur de Mendoza. Sociedad Argentina de Antropología, Buenos Aires, pp. 181–211.

Cortegoso, V., Barberena, R., Durán, V., Lucero, G., 2016. Geographic vectors of human mobility in the Andes (34-36°S): comparative analysis of 'minor' obsidian sources. Quat. Int. 422, 81–92.

Cortegoso, V., Glascock, M., De Francesco, A.M., Durán, V., Neme, G., Gil, A., Giesso, M., Sanhueza, L., Cornejo, L., Barberena, R., Bocci, M., 2014. Chemical characterization of obsidian in central western Argentina and Central Chile: archaeological problems and perspectives. In: Kligmann, D.M., Morales, M.R. (Eds.), Physical, Chemical and Biological Markers in Argentine Archaeology: Theory, Methods and Applications. Archaeopress, Oxford, pp. 17–26. BAR International Series.

Crisci, G.M., Ricq-De Bouard, M., Lanzafame, U., De Francesco, A.M., 1994. Nouvelle méthode d'analyse et provenance de l'ensemble des obsidiennes néolithiques du midi de la France. Gall. Préhistoire 36, 299–327.

De Francesco, A.M., Duran, V., Bloise, A., Neme, G., 2006. Caracterización y procedencia de obsidianas de sitios arqueológicos del área natural protegida Laguna del Diamante (Mendoza, Argentina) con metodología no destructiva por fluorescencia de rayos (XRF). An. Arqueol. Etnol. 61, 53–67.

De Francesco, A.M., Crisci, G.M., Bocci, M., 2008. Non-destructive analytical method by XRF for determination of provenance of archaeological obsidians from the Mediterranean Area. A comparison with traditional XRF method. Archaeometry 50 (2), 337–350.

Dulski, P., 2001. Reference materials for geochemical studies: new analytical data by ICP-MS and critical discussion of reference values. Geostand. Newslett. J. Geostand. Geoanal. 25, 87–125.

Durán, V., Mikkan, R., 2009. Impacto del volcanismo holocénico sobre el poblamiento humano del sur de Mendoza (Argentina). Intersecc. Antropol. 10, 295–310.

Durán, V., De Francesco, A.M., Neme, G., Cortegoso, V., Cornejo, L., Bocci, M., 2012. Caracterización y procedencia de obsidianas de sitios arqueológicos del Centro Oeste de Argentina y Centro de Chile con metodología no destructiva por Fluorescencia de Rayos (XRF). Intersecc. Antropol. 13 (2), 423–437.

Durán, V., Giesso, M., Glascock, M., Neme, G., Gil, A., Sanhueza, L., 2004. Estudios de redes de aprovisionamiento y redes de distribución de obsidiana durante el Holoceno Tardío en el sur de Mendoza (Argentina). Estud. Atacameños 28, 25–43.

Durán, V., Cortegoso, V., Barberena, R., Frigolé, C., Novellino, P., Lucero, G., Yebra, L., Gasco, A., Winocur, D., Benítez, A., Knudson, K., 2017. 'To and fro' the southern Andean highlands (Argentina and Chile): archaeometric insights on geographic vectors of mobility. J. Archaeol. Sc., Rep. https://doi.org/10.1016/j.jasrep.2017.05.047 (in press).

Fernández, M.V., Barberena, R., Rughinic, A., Giesso, M., Cortegoso, V., Durán, V., Romero Villanueva, G., Borrazzo, K., Lucero, G., Garvey, R., MacDonald, B.L., Glascock, M.D., 2017. Obsidian geochemistry, geoarchaeology, and lithic technology in northwestern Patagonia (Argentina). J. Archaeol. Sc. Rep. 13, 372–381.

Fryer, B.J., Jackson, S.E., Longerich, H.P., 1995. The design, operation and role of the laser-ablation microprobe coupled with an inductively coupled plasma-mass spectrometer (LAM-ICP-MS) in the Earth sciences. Can. Mineral. 33, 303–312.

Gao, S., Liu, X., Yuan, H., Hattendorf, B., Gunther, D., Chen, L., Hu, S., 2002. Determination of forty-two major and trace elements in USGS and NIST SRM glasses by laser ablation-inductively coupled plasma mass spectrometry. Geostand. Newslett. J. Geostand. Geoanal. 26, 181–196.

Garreaud, R.D., Vuille, M., Compagnucci, R., Marengo, J., 2009. Present-day south America climate. Palaeogeogr. Palaeoclimatol. Palaeoecol. 281, 180–195.

Giesso, M., Durán, V., Neme, G., Glascock, M., Cortegoso, V., Gil, A., Sanhueza, L., 2011. Obsidian source usage in the central Andes of Argentina and Chile. Archaeometry 53, 11–21.

Gunther, D., Heinrich, C.A., 1999. Enhanced sensitivity in laser ablation-ICP mass spectrometry using helium-argon mixtures as aerosol carrier. J. Anal. At. Spectrom. 14, 1363–1368.

Longerich, H.P., Jackson, A.W., Gunther, D., 1996. Laser ablation inductively coupled plasma mass spectrometric transient signal data acquisition and analyte concentration calculation. J. Anal. At. Spectrom. 11, 899–904.

Pearce, N.J.G., Perkins, W.T., Westgate, J.A., Gorton, M.P., Jackson, S.E., Neal, C.R., Chenery, S.P., 1997. A compilation of new and published major and trace element data for NIST SRM 610 and NIST SRM 612 glass reference materials. Geostand. Newslett. J. Geostand. Geoanal. 21 (1), 115–144.

Salgán, L., Garvey, R., Neme, G., Gil, A., Giesso, M., Glascock, M.D., Durán, V., 2015. LasCargas: characterization and prehistoric use of a southern Andean obsidian source. Geoarchaeology 30, 139–150.

Seelenfreund, A., Rees, C., Bird, R., Bailey, G., Bárcena, R., Durán, V., 1996. Trace element analysis of obsidian sources and artifacts of central Chile (Maule River basin) and western Argentina (Colorado river). Lat. Am. Antiq. 7 (1), 7–20.

van Achterberg, E., Ryan, C.G., Jackson, S.E., Griffin, W.L., 2001. Data reduction software for LA-ICPMS: appendix. In: Sylvester, P.J. (Ed.), Laser Ablation-ICP-mass Spectrometry in the Earth Sciences: Principles and Applications, pp. 239–243. Mineralogical Association of Canada (MAC) Short Course Series, Ottawa, Ontario, Canada 29.

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