Morphological and Geochemical Analysis of the Laguna Blanca/Zapaleri Obsidian Source in the Atacama Puna

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This paper describes a large obsidian deposit located along the southern banks of Laguna Blanca, on the eastern slope of the Jarellón volcanic caldera near the Chilean–Bolivian border. The obsidian at this site occurs in flows or sheets of deflated black or reddish to brown pebbles, redeposited on the shores of a lake. Blocks of obsidian are only found around the caldera rim. Here we analyze the shape of the obsidian pebbles and their geochemistry, comparing them with previously published data. The results indicate that the geochemical composition of the samples strongly matches previous analyses of obsidian procurement since at least the Formative Period in the Atacama Puna region. © 2010 Wiley Periodicals, Inc.

INTRODUCTION

This study was conducted in 2005 with the objective of detecting deposits of vitreous lithic resources in the Chilean region of the Atacama Puna. We were able to locate and analyze three sources of obsidian, one of which is described in detail here. At the onset of this project, previous systematic studies to locate possible sources of obsidian in this region had been unsuccessful. Although archaeological obsidian had been detected in sites in the area of Laguna Meniques (Pino, 1976), and in Puripica (Núñez, Grosjean, & Cartajena, 1999:135), to the south and north of the Atacama salt flat (Salar de Atacama), respectively, their geologic source has not been identified. Moreover, De Souza et al. (2002) describe finding numerous flakes and nodules of obsidian in archaeological sites bordering the ravine of Pelun (also

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known as Felon), to the north of the Atacama salt flat basin, without finding the source of origin.¹ Until now, there has been no effort to systematically identify and characterize the origins of this obsidian, or to find new sources.

In a 1999 project aimed at describing pre-Hispanic travel routes in the Chilean–Bolivian–Argentinian region, a team of archaeologists led by A. Nielsen described a large obsidian deposit south of the altiplanic province of Lípez, on the Chilean–Bolivian border. They named this deposit Laguna Blanca, referring to the name of the basin where the obsidian is located, some distance from its actual origin (Nielsen et al., 1999:117). The authors describe this obsidian as small to medium-sized rounded pebbles, translucent black to reddish chestnut-brown in color, originating from a secondary source and redeposited on the banks of the lake (Nielsen et al., 2000:124; Nielsen, 2004:863). They found concentrations of flaking debris and small semicircular stone parapets erected apparently by ancient knappers, and dispersed through the grassy plain from the Laguna Blanca extractive site and nearby associated settlements such as "Ojitos de Guayaques" and the "*jara*" Guayaques, or caravan resting places (cf. Nielsen, 2004).

The publication by Nielsen et al. (1999) is the first reference to the existence of obsidian in this area, to the presence of lithic workshops, and to the remains of an Inca roadside resting place (*tambo*), among other archaeological sites. Under the name of Laguna Blanca, Nielsen describes the obsidian deposit found on the plain south of the Guayaques River, called "Pampa de Torringo" on the Bolivian side and "Pampa de Guayaques" on the Chilean side. Later, Yaccobaccio et al. (2002, 2004) and Escola (2004) referred to the same obsidian, identified and characterized only from archaeological sites, as Zapaleri obsidian, since they believed its origin to be near or at the Zapaleri volcano, at the border point of Chile, Argentina, and Bolivia. However, the geologic source of this obsidian remained uncertain until our investigation.

GEOLOGICAL AND ARCHAEOLOGICAL CONTEXT OF THE SOURCE

The volcanic formation known as "Caldera Jarellón" was identified and named by geologist Nicolás Marinovic around 1975 (Marinovic, personal communication, 2006). It comprises a volcanic caldera 5 km in diameter, located next to the "Cerros de Jarellón" in the Atacama Puna (Antofagasta Region). Laguna Blanca is located on the eastern slope of the Jarellón volcanic caldera,² with the Chilean and Bolivian border passing through its center (Figure 1). This caldera developed during a pre-glacial, Pliocene eruption associated with Volcanic Group II (Gardeweg & Ramírez, 1985:59),

¹ The authors believed the obsidian from Pelun to be a secondary source, with its primary origin in one of the many volcanic flows of the lower puna area. We discovered in the Pelun area a widely dispersed subsurface punice stratum containing obsidian nodules that macroscopically look very similar to those described in the archaeological sites. Geochemical analysis performed later on the obsidian nodules from the punice stratum and obsidian flakes from archaeological sites at Pelun and the wider region indicated that this was indeed one of the sources used prehistorically in the Atacama region (Seelenfreund et al., 2009a, 2006).

 $^{^{\}rm 2}$ The caldera is located at UTM 19H 7469262 N and 660117 E (Provisional South American Datum of 1956), at an altitude of 4582 m asl.



Figure 1. Map of the Jarellón Caldera on the Chilean–Bolivian border, and of archaeological sites mentioned in the text.

and is comprised mainly of dacitic and rhyolitic lavas, in addition to reddish brown spherulitic and striped vitrophyres. These volcanic formations have been defined by Lahsen and Munizaga (1979, 1983), Marinovic (1979), Marinovic and Lahsen (1984), and later by Gardeweg and Ramírez (1985), although the caldera has never been formally described as such (Marinovic, personal communication, 2006). A K-Ar date of 3.6 ± 0.1 Ma exists for the vitrophytic rhyolite from the subcircular Jarellón structure (Gardeweg and Ramírez, 1985:63).³

³ Yacobaccio et al. (2004:176–178) assign an age of 9.6 Ma to the obsidian they called Zapaleri. It is not clear from their article, however, if this age corresponds to obsidian from the environs of Laguna Blanca, or from the Vilama Caldera (Jujuy Province, Argentina), located to the northeast of Laguna Blanca, near the Argentinean–Bolivian border.

The Jarellón volcano is a vitrophyric stratovolcano consisting of obsidian, pyroxene andesites, biotite dacites, and hornblende. The caldera retains three-quarters of its wall. On its east-southeast and south sides, various obsidian flows have detached from the caldera, forming a continuous floor of obsidian pebbles. In the largest flow (Flow 1), the obsidian is found on the volcanic slope within a radius of at least 5 km, and with 112 m difference in elevation between the highest part of the caldera and the lowest point of dispersal.

In general, the obsidian in this zone appears to be associated with volcanism of andesitic–dacitic lavas and enormous ignimbritic deposits. These deposits are the product of plinian eruptions that are initially violent, emitting large eruptive columns and pyroclastic flows. The explosions are intense, producing extensive downfalls of ash and lapilli. This type of eruption can cause the collapse of volcanic structures and the subsequent formation of a caldera (Wright & Pierson, 1992).

In addition to being dispersed in flows, obsidian from the Jarellón Caldera was redistributed on the slopes by superficial processes over a wide area. Field observations revealed three discreet, long flows, with other smaller flows interspersed among them (see Figure 2). In Flow 1, the obsidian nodules have a density of 100 per m² in the lower altitude zones, while in the areas near the rim of the crater the density reaches between 500 to 1000 nodules per m² (Figures 3a, 3b, 3f). Material from this flow is distributed in a heterogeneous manner at variable densities, producing a uniform sheet without a soil matrix, apparently deflated by the wind, as is evident from the superficial patina and the existence of a soil under the pavement of pebbles.

The other two major flows are located on the hillside southeast and south of the caldera (Flows 2 and 3). Between them are flows of smaller dimensions but with a high density of nodules, where two semicircular wind-shelter parapets can be observed. Around these parapets a large number of nodules of various sizes (between 5 and 30 cm long) were collected for artifact manufacture (Figures 3c, 3d). Here we find quantities of much primary reduction, waste flakes, chips, and other remains of flaking activities, and occasionally some artifact preforms not associated directly with any of the stone structures or worksites.

All flows show the same type of rounded pebbles, although the density of these may vary between flows. The only place where larger angular blocks are to be found is near the rim of the caldera at Flow 1. These blocks can measure up to 60×70 cm. Some of these have flaking scars.

On the eastern slope in the direction of Laguna Blanca, where Flow 1 is found, six rather small archaeological sites were recorded, located at different altitudes and in more or less sheltered places. These sites are mainly simple stone parapets or wind shelters with associated lithic workshops. These workshops contain few preforms, but mainly consist of flaking debitage from the reduction of nodules. On Flow 3, there are no workshops or associated stone structures, and the obsidian nodules are not rounded, but angular shard pebbles of diverse sizes up to approximately 25 cm long. Also observed were sectors with some accumulation of nodules located around circular depressions approximately 2 m in diameter that would have been efficient worksites; today these depressions have been transformed into dust bath holes by wild camelids.

Bolivia Chile Jarellón Caldera 3 2

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Figure 2. Satellite image (Google Earth 2006) of the Jarellón Caldera. The white line shows the border between Chile and Bolivia; areas marked by dotted white lines correspond to the obsidian flows. Obsidian samples analyzed for this study come from Flows 1, 2, and 3.

On the higher slope of Flow 3, close to the rim of the caldera, we found a few obsidian flakes that clearly belong to obsidian from a different source. The presence of these flakes might possibly correspond to an "offering," similar to present day *ch'allas*,⁴ culturally significant locations (cf. Nielsen et al., 1999; Pimentel, 2003). Among these artifacts, we found two untanged projectile points, one made of reddish brown silica and the other in black obsidian (Figure 3e), in addition to flakes of possibly opaque gray aphanitic obsidian that macroscopically looks very different from the obsidian from the Jarellón Caldera and thus is unlikely to have originated from the Laguna Blanca/Zapaleri source. Only the black obsidian point appears to have been made with local material.⁵

In the present work, we present a morphological analysis of the obsidian pebbles in order to understand or infer the mechanism(s) of transport deposition, beginning

⁴ *Ch'alla* is an offering performed on various occasions by Quechua and Aymara people, involving the sprinkling of a small amount of alcohol on a floor to honor the *pachamama* goddess, on objects or animals to be used in a ritual, or as a type of blessing. *Ch'alla* is also performed in the field at times of sowing or any time during the period of growth of the plants, when new tools are used for the first time, or when setting the foundations of a new house, or during a trip when passing the mountain top (van den Berg, 1985:49).

 $^{^{\}scriptscriptstyle 5}$ All archaeological artifacts were left $in\ situ$ and not analyzed for this study.



Figure 3. Photographs of obsidian materials associated with Flow 1 (images a–e) and Flow 2 (image f). Sampling plot (a); size and density of pebbles on the rim of the crater of the Caldera (b); parapet and area of workshop and detail with accumulations of nodules and flaking debris (c and d); example of red obsidian nodule (e); view of a large deflated obsidian pebble pavement (f).

with the pebble forms that created this large, quasi-pavement surface of obsidian. In addition, we present the chemical composition of the Jarellón Caldera obsidian, comparing it with previously published data from archaeological samples assigned to the source called Laguna Blanca and/or Zapaleri (Nielsen et al., 1999, 2000; Yacobaccio et al., 2002, 2004; Seelenfreund et al., 2009a). Herein we refer to this location as the Laguna Blanca/Zapaleri obsidian source.

METHODS

Sampling and Morphological Analyses

We collected obsidian samples (1) to obtain a representative sample of the geochemistry of the source flow, and (2) to understand the natural formation of the rounded nodules, something not commonly found at this proximity to this type of volcanic flow. The analysis of the lithic workshops and the reduction sequence was not addressed in the present project, but should be considered in the future for the fuller understanding of this source and its use.

To collect samples in Flow 1, a transect with a NNW orientation, composed of 30 stations, was established with the extreme ends located at coordinates UTM 19H 665800 N and 7466500 E (Datum PSAD 1956), at an altitude of 4531 m asl, and at coordinates 658500 N and 7465900 E, at an altitude of 4643 m asl (stations 6 and 30, respectively). Samples were collected in stations 6, 8, 10, 11, 23, 27, 29, and 30. Between stations 6 and 30, there was an altitudinal difference of 92 m and a horizontal distance of approximately 7 km. In each station we collected all pebbles within a 1-m² quadrant. The number of pebbles collected in each station varied between 95 and 1070.

In the laboratory, each pebble was numbered and measured with a digital caliper. The form and size of the pebbles between adjacent quadrants was analyzed using variance. The data had to be normalized by means of the log expression (x + 1) because the distribution was not normal. When the variances between groups were not homogeneous, the nonparametric Kruskal-Wallis test was used. Statistical analyses were carried out using the Statgraphics 5.2 computer program.

Geochemical Analyses

For the geochemical analysis, we selected seven pebbles from quadrants 8, 10, 11, 23, 27, and 30 in Flow 1. Samples were randomly chosen, one from each quadrant, except from quadrant 30 at the crater rim, where we selected two samples based on color variations. Each sample was divided into three parts. One part was sent to the University of Missouri Research Reactor (MURR) for analysis by instrumental neutron activation analysis (INAA). The other parts of each sample were analyzed in the Laboratory of Experimental Physics at the University of Chile, by energy dispersive X-ray fluorescence (EDXRF) and proton induced X-ray emission (PIXE), as described below, and in the analytical laboratory of the National Geology and Mining Service, Chile (SERNAGEOMIN), by inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma-optical emission spectrometry (ICP-OES). Here we report only results for the INAA and PIXE/EDXRF analyses; the comparative results from the other analyses will be presented in another paper. In the particular case of this source, it was of primary importance to conduct the geochemical analysis by INAA in the laboratory in Missouri, in order to compare our results with obsidian samples from the same source sent to the same laboratory by other researchers in the region. This helps ensure that we are, in fact, dealing with the same obsidian reported initially under the name of Laguna Blanca by Nielsen et al. (1999), and later called Zapaleri in various publications (e.g., Escola, 2004; Yacobaccio et al., 2002, 2004).

For the INAA analysis, we added an archaeological sample (PAT094) to the samples from the Laguna Blanca/Zapaleri source. This sample is an obsidian artifact of the Late Formative Period component of the site 02Tu02 (Turi Aldea) (Sinclaire, 2004), located

in the upper basin of the Salado River, in the Upper Loa River region (ca. 100 B.C.–A.D. 400). Results from other archaeological obsidian samples collected from Formative contexts at several sites in the region (1400 B.C.–A.D. 900) were analyzed by EDXRF and PIXE methods and are discussed elsewhere (Seelenfreund et al., 2009a).

Prior to sample preparation, the source samples were washed in water to remove dirt and other loose materials from the surface. Samples for INAA were prepared by placing the source specimens between two steel plates and crushing them with a press to obtain a number of fresh interior fragments of approximately 25–50 mg. The fragments were examined with a magnifier to eliminate those with metallic streaks or crush fractures that could possibly contain contamination. Several grams of clean fragments were obtained from each sample and stored temporarily in plastic bags. Two subsamples were prepared from each sample for short and long irradiation.

The first sample used for short irradiations was made by placing 100 mg of fragments into clean high-density polyethylene vials. A second sample used for long irradiation and weighing about 250 mg was placed in clean, high-purity quartz vials. Individual sample weights were recorded to the nearest 0.01 mg using an analytical balance. Both irradiation vials were sealed prior to irradiation. Standards derived from the National Institute of Standards and Technology (NIST) certified standard reference materials SRM-1633a (coal fly ash), SRM-278 (obsidian rock), and SRM-688 (basalt rock) were similarly prepared.

The INAA method applied to the archaeological samples was subjected to two irradiations and took three measurements of emitted gamma rays. The short irradiation was carried out through a system of automatic irradiation. All short irradiations were conducted through the pneumatic-tube irradiation system at MURR. Samples and standards in polyethylene vials were sequentially irradiated, two at a time, for five seconds by a thermal neutron flux of 8×10^{13} n cm⁻² s⁻¹. Following irradiation, the samples were allowed to decay for 25 minutes so that radioactivity from the dominant short-lived radioisotope ²⁸Al (half-life = 2.24 min) could decline to a level compatible with the other elements. Sample vials were mounted in holders at a distance of 10 cm from the face of separate high-purity germanium (HPGe) detectors. The sample holders rotated continuously during a 12-min counting period in order to compensate for slight differences in shape between individual samples. The short-lived elements measured in obsidian are: Al, Ba, Cl, Dy, K, Mn, and Na. However, Cl is poorly measured by INAA, with an error of 25% or more, and is therefore usually not used for discriminating between sources.

The long irradiation samples and standards in high-purity quartz vials were wrapped in bundles of approximately 32 unknowns and 6 standards each. Two sample bundles were placed inside an aluminum can and irradiated for a total of 50 hours by a thermal neutron flux of 5×10^{13} n cm⁻² s⁻¹. Following irradiation, the sample bundles were unwrapped and the quartz vials were washed in *aqua regia* to remove possible surface contamination. Two gamma measurements were performed on the individual samples from each bundle, using a pair of HPGe detectors coupled to automatic sample changers with rotating sample holders. The first count, for 2000 seconds each (i.e., the "middle count"), was made about eight days after the

end of irradiation to allow ²⁴Na (half-life = 15 hr) to decay to a reasonable handling level. The middle count yields data for the determination of several medium half-life elements, including Ba, La, Lu, Nd, Sm, U, and Yb. After an additional three or four weeks of decay, a final measurement of approximately 3 hours on each sample (i.e., the "long count") was carried out. The latter measurement yields the data for several long-lived elements, including Ce, Co, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Sr, Ta, Tb, Th, Zn, and Zr. Additional details about gamma-ray spectroscopy, neutron activation analysis, and standardization can be found in Glascock (1992).

Additionally, at a later stage of this research, samples from Flows 1, 2, and 3 were analyzed by PIXE and EDXRF. From Flow 1, we analyzed some of the same pebbles as for INAA (samples ZZ020–ZZ025, ZZ039A). The samples from Flows 2 (n = 5) and 3 (n = 4) were chosen randomly, in order to check for possible geochemical intrasource variability. Special care was taken when sampling these, to include samples of the red and brownish obsidian, which was more abundant in these flows. These analyses were performed at the Nuclear Physics Laboratory of the University of Chile. Sample preparations and protocols are described in Morales et al. (2007). Proton beams for PIXE 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-lm-thick Mylar film. The detector encompasses a solid angle $\Delta\Omega/4\pi$ equal to (2.8 ± 0.3) 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 ²⁴¹Am source. For the present work, 2.2 MeV proton beams were used with typical beam currents in the range of 0.1-0.5nA up to a total charge of $0.1 \,\mu$ C. The spectra were fitted with functions generated with the GUPIXWIN code (version 1.2) (Campbell et al., 2000), obtaining the net number of counts in each peak for the determination of elemental concentrations.

EDXRF analysis utilized a Canberra Si(Li) detector, an Ortec preamplifier and Ortec amplifier, and a multi-channel analyzer (MCA). Samples were irradiated with a ²⁴¹Am (30 mCi, 01/1985) and a ¹⁰⁹Cd (50 mCi, 04/2004) annular source. A piece of Laguna del Maule obsidian was used to control against NIST standards (coal fly ash and obsidian). Spectra were analyzed using the AXIL software (Van Espen, Janssens, & Swenters, 1991).

RESULTS

Dimensional analysis included the variables long axis (L), intermediate axis (I), short axis (S), S/L, and (L-I)/(L-S) (Folk, 1980) and was conducted on 3270 samples. The maximum length of the pebbles varied between 8 and 228 mm, and the minimum length between 1 and 127 mm. Pebbles tended to be leaf-shaped, with variable oblateness; those from stations 23 and 27 tended to be more oblate (Figure 4). Results



Figure 4. Sphericity-form diagram including the mean shape of pebbles for each quadrant (simplified diagram after Sneed & Folk, 1958).

indicate that there is a clear grouping of samples by size, but it is also possible to differentiate between equidimensional and oblate pebbles.

In most of the cases there are significant differences between adjacent quadrants, using L, I, and S variables (Table I). No differences are observed between stations 8 and 10. The long axis increases from station 6 (L = 19 mm) to station 23 (L = 44 mm, maximum value), decreases slightly to L = 35 mm at station 27, and then increases again at station 29 (L = 39 mm), to fall again at station 30 (L = 33 mm).

A few very large, equidimensional pebbles (11.8%), which stood out from the majority, corresponded to large cores, while those that were very oblate and small generally corresponded to flakes or chipped material, highly eroded by wind and water over time. Thus, approximately 12% of the total has possibly been modified by cultural activities. This agrees with field observations in that these workshops are discrete and located at deliberate loci along Flow 1.

The INAA results (Table II) indicate that the seven samples from Flow 1 analyzed with this technique are chemically similar to each other. Their composition corresponds to rhyolite with high silica content, and the ranges of concentrations of the elements analyzed fall within the expected average.

We compared the chemical composition of our samples with the statistical average of the 58 samples previously assigned to Zapaleri by Yacobaccio et al. (2002, 2004), measuring concentrations of the incompatible elements (Ba, Cs, Hf, Rb, Sr, and Zr), which are generally associated with alkaline or calco-alkaline obsidian (Shackley, 2005). In this lava, Ba and Sr in general show high concentrations compared to Rb and Zr. Figures 5 and 6 show that the chemical composition of our samples and those

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Table I. Result of the comparison of the
variance (Kruskal-Wallis analysis) between
adjacent quadrants. The asterisks indicate
a significant difference at the 95% confi-
dence level.

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Quadrants	L	Ι	S
6 vs. 8	*	*	*
8 vs. 10			
10 vs. 11	*	*	
11 vs. 23	*	*	
23 vs. 27	*	*	
27 vs. 29	*	*	*
29 vs. 30	*	*	*

Table II. Concentrations of elements from the Laguna Blanca/Zapaleri source samples analyzed by INAA (all values are expressed in ppm, except Na, K, Al, and Fe, which are given in percentages). All source samples are from Flow 1. The archaeological sample (PAT94) from the Turi Aldea site (site 02Tu02) was subject only to short irradiation, which identifies seven elements (Al, Ba, Cl, Dy, K, Mn, and Na)

Element	ZZ020	ZZ021	ZZ022	ZZ023	ZZ024	ZZ025	ZZ039	PAT094
Na	2.20	2.42	2.54	2.89	2.85	2.89	2.93	2.95
Al	7.34	7.34	7.33	7.44	7.56	7.11	7.55	7.38
Cl	485	429	486	513	436	448	467	453
K	5.12	4.13	4.46	3.75	3.48	3.70	3.63	3.62
Sc	4.21	4.26	4.21	4.18	4.17	4.30	4.27	_
Mn	571	569	571	568	555	555	559	544
Fe	1.13	1.13	1.07	1.09	1.05	1.24	1.08	_
Со	0.20	0.21	0.18	0.20	0.19	0.25	0.21	_
Zn	68	69	69	66	66	74	67	_
Rb	213	215	228	212	211	215	215	_
Sr	127	151	174	158	174	181	144	_
Zr	298	301	253	229	251	327	277	_
Sb	0.39	0.45	0.41	0.41	0.40	0.43	0.41	_
Cs	10.8	11.4	10.9	10.7	10.7	10.8	10.9	_
Ba	657	662	656	626	659	653	664	679
La	45.7	46.0	46.1	45.4	45.3	46.1	46.5	_
Ce	95.5	95.9	96.3	95.4	94.8	96.4	97.7	_
Nc	39.3	40.4	42.7	41.9	41.6	39.2	42.3	_
Sm	8.30	8.34	8.46	8.31	8.24	8.47	8.47	_
Eu	1.21	1.24	1.21	1.22	1.23	1.24	1.25	_
Tb	1.08	1.05	1.08	1.06	1.06	1.06	1.07	_
Dy	6.73	6.35	6.28	5.72	6.84	6.45	6.86	6.54
Yb	3.05	3.04	3.01	2.93	2.89	3.13	3.01	_
Lu	0.55	0.55	0.51	0.51	0.52	0.56	0.52	_
Hf	7.59	7.38	6.18	6.02	6.22	8.09	6.50	_
Та	1.95	1.94	1.94	1.93	1.92	1.95	1.95	_
Th	21.5	21.7	21.6	21.4	21.5	21.6	21.9	_
U	7.65	7.51	7.04	7.11	7.47	7.33	7.08	—



Figure 5. Rare earth elements (REEs) diagram from Nakamura (1974), showing the relationship and congruence between the abundance of selected standardized elements, compared to chondrite values from the samples from Jarellón (triangles), and the average of 58 samples previously analyzed and published by Yacobaccio et al. (2002) (squares).



Figure 6. Diagram showing similarity in relative abundance of the trace elements Rb, Zr, and Ba in the seven samples from Flow 1 analyzed by INAA (triangles) and the statistical average of the 58 samples published by Yacobaccio et al. (2004) (squares).

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	Samples in Table I	Yacobaccio et al., 2002:181
Element	(n = 7)	(n = 58)
Na	2.67 ± 0.29	2.86 ± 0.10
Al	7.38 ± 0.15	7.34 ± 0.25
Cl	466 ± 30	615 ± 75
K	4.04 ± 0.58	3.76 ± 0.20
Sc	4.23 ± 0.05	4.22 ± 0.08
Mn	564 ± 7	556 ± 9
Fe	1.11 ± 0.06	1.09 ± 0.04
Co	0.21 ± 0.02	0.28 ± 0.17
Zn	68 ± 3	72 ± 9
Rb	216 ± 6	212 ± 4
Sr	158 ± 19	180 ± 28
Zr	276 ± 34	266 ± 26
Sb	0.42 ± 0.02	0.41 ± 0.05
Cs	10.9 ± 0.2	10.8 ± 0.2
Ba	654 ± 13	664 ± 27
La	45.9 ± 0.4	46.3 ± 1.0
Ce	96.0 ± 0.9	95.9 ± 2.2
Nc	41.1 ± 1.4	41.4 ± 4.8
Sm	8.37 ± 0.10	8.50 ± 0.29
Eu	1.23 ± 0.01	1.23 ± 0.03
Tb	1.06 ± 0.01	1.06 ± 0.05
Dy	6.5 ± 0.4	6.4 ± 0.5
Yb	3.01 ± 0.08	3.10 ± 0.18
Lu	0.53 ± 0.02	0.53 ± 0.03
Hf	6.85 ± 0.82	6.63 ± 0.52
Та	1.94 ± 0.01	1.94 ± 0.04
Th	21.6 ± 0.2	21.6 ± 0.4
U	7.31 ± 0.24	7.48 ± 1.17

Table III. Mean and standard deviation values for elements analyzed by INAA in the samples in Table II
compared with published data by Yacobaccio et al. (2002:181) (all values are expressed in ppm, except
for Na, Al, K, and Fe, which are given in percentage).

of Yacobaccio et al. (2002, 2004) are in strong agreement (see also Table III). Moreover, the elemental concentrations of the archaeological sample from the Turi Aldea (PAT094) site also show strong similarities with the six samples we collected from the Laguna Blanca/Zapaleri source and analyzed by INAA (Figure 7). Although the number of samples analyzed was small, these were chosen randomly and they agree with the geochemistry of the archaeological artifacts analyzed previously and assigned to the Laguna Blanca/Zapaleri source.

The results from analysis of 17 samples by PIXE and EDXRF, including the seven samples analyzed also by INAA, are shown in Table IV. The PIXE and EDXRF facilities at the University of Chile were designed for nondestructive analysis. Therefore, surface geometries of the samples analyzed, particularly by EDXRF for the lower Z



Figure 7. Diagram showing similarity in the relative abundance of the trace elements Dy, Ba, and Mn in the seven source samples from Flow 1 and the sample from the Turi Aldea site, all analyzed by INAA.

elements from Fe and below, can have a significant effect on the concentration data. This is noted by the greater spread in values for Al, K, Ca, and Fe in contrast to the values for the higher Z elements. For the elements above Fe, our results show a strong coherence with the INAA data. And, more importantly for the present purpose, this agreement indicates that the different flows are chemically uniform. Therefore, we can argue that the source appears homogeneous based both on the total number of analyses currently available by INAA (both from the source in Chile and from the archaeological sites in Argentina, as reported by Yacobaccio et al., 2002, 2004, and Escola 2004), and on the analyses performed with PIXE and EDXRF.

DISCUSSION

The oblate leaf shape of the pebbles suggests that they acquired their shape due to transport and deposition on the shores of a lake, thus recording formerly higher levels of present-day Laguna Blanca. Beach activity formed obsidian pebble bars, but given the antiquity of the eruption (pre-glacial), these pebbles have been redistributed by rain, snowmelt, and the force of gravity. Ongoing wind deflation has removed finer sediments, leaving a pavement of obsidian pebbles.

The shape analysis easily permits differentiation between pebbles of natural origin from others that show cultural or transport type modifications. Although the shapes described (Dobkins & Folk, 1970) are typical of lake beaches, it is possible that the fluidity of the original obsidian flows strongly determined the homogeneity of the shapes of the pebbles.

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Table IV. Con age, minimum	centration of maj	jor, trace, and alues and sta	rare eart ndard de	h element: viation (al	s from the l values a	e Laguna re expre	Blanca/Z ssed in pr	apaleri se pm, excej	ource san pt, Al, Si,]	ıples mea K, Ca, and	sured by I I Fe, whic	PIXE and F h are giver	DXRF, wi as perce	ith aver- ntages).
					PIXE						EDXRF			
			Ы	Si	К	Ca	Fe	Rb	\mathbf{Sr}	Υ	Zr	La	Ce	Nd
Provenance	Color	Sample	%	%	%	%	%	mqq	bpm	mqq	bpm	bpm	bpm	mqq
Flow 1	Black	ZZ020	5.28	37.55	5.33	0.76	1.27	244	181	158	248	56	104	52
Flow 1	Black	ZZ021	5.75	37.42	4.75	0.79	1.24	216	164	182	228	69	172	87
Flow 1	Black	ZZ022	5.93	32.08	4.28	0.68	1.17	226	170	202	246	55	130	67
Flow 1	Black	ZZ023	5.39	35.12	3.82	0.70	1.37	190	140	103	216	50	121	59
Flow 1	Black	ZZ024	5.85	37.41	4.28	0.85	1.37	204	155	110	222	74	158	72
Flow 1	Black	ZZ025	5.69	37.75	4.02	0.77	1.25	225	170	194	247	73	169	85
Flow 1	Black	ZZ039A	2.41	16.35	1.83	0.40	0.88	193	157	202	205	19	34	14
Flow 2	Black	ZZ052	4.38	27.89	5.49	1.19	1.75	296	230	109	306	53	74	23
Flow 2	Reddish	ZZ053	6.36	35.58	2.93	0.52	0.75	366	276	112	367	42	55	18
	brown													
Flow 2	Red with	ZZ054	4.12	35.54	4.62	0.97	1.52	225	155	106	238	20	97	32
	some black													
Flow 2	Black + red	ZZ055	4.01	31.35	5.17	1.10	2.37	309	229	72	283	32	44	18
Flow 3	Black	ZZ056	3.41	33.01	4.81	1.03	2.12	322	214	93	333	74	96	42
Flow 3	Red	ZZ057	5.46	32.82	3.68	0.76	1.16	266	164	88	276	10	13	5
Flow 2	Black	ZZ058	5.22	34.8	2.68	0.71	1.66	254	176	92	274	11	14	9
Flow 3	Black	ZZ059	4.45	28.69	3.08	0.63	0.98	265	191	107	274	25	34	13
Flow 3	Red	ZZ060	5.75	33.21	3.45	0.59	0.87	269	211	96	282	54	78	31
Lake shore	Black	ZZ061	6.11	33.04	3.37	0.76	1.22	279	191	66	292	64	83	34
		Mean	5.03	32.92	3.98	0.78	1.35	256	187	125	267	48.78	86.77	38.70
		$^{\mathrm{SD}}$	1.07	5.18	1.01	0.20	0.43	48	35	44	43	22.18	51.41	27.02
		Max	6.36	37.75	5.49	1.19	2.37	366	276	202	367	74	172	87
		Min	2.41	16.35	1.83	0.40	0.75	190	140	72	205	10	13	5

The visual appearance of this obsidian is bright black, slightly grayish and yellowish to translucent, and occasionally reddish brown, permitting easy identification by sight. The geochemical results indicate that the obsidian collected by Nielsen and collaborators in the grasslands at the edge of Laguna Blanca, and later mentioned as the Zapaleri source by Yacobaccio et al. (2002, 2004) and Escola (2004), originated from the volcano called Jarellón. Therefore, all the obsidian designated by Nielsen as Laguna Blanca and mentioned by Yacobaccio et al. (2002, 2004) and Escola (2004) and other researchers in the region as Zapaleri, stems from flows associated with the Jarellón Caldera.

In their obsidian source study in the southern Argentine puna, Yacobaccio et al. (2004:201) proposed the existence of two principal "distribution spheres" in the circum-puna area since the Formative period. The Laguna Blanca/Zapaleri source encompasses the first of these "spheres," including the northern part of northwestern Argentina and the tri-country border area of Argentina–Chile–Bolivia. It has a dispersion area as far as 350 km from the source, which supplied innumerable archaeological sites ranging from the puna and ravines of Jujuy to the subtropical forest of Salta. The second "sphere" involves the southern part of northwestern Argentina, with the Ona–Las Cuevas as its most important source, having a similar distribution range and supplying obsidian to sites located in the puna and ravines of the Catamarca and Salta provinces, and possibly ranging as far west as the Upper Loa Region in northern Chile, where artifacts from this source have been identified in archaeological sites (Seelenfreund et al., 2006).

We are currently conducting further geochemical analyses of obsidian samples from the Turi Aldea site. Based on the single sample (PAT094) analyzed and presented here, we can preliminarily suggest that this site, located in Chile approximately 200 km northwest of the source, is one further link in a long chain of interregional relationships and cultural exchanges with contemporary Formative settlements in northwestern Argentina (cf. Sinclaire, 2004). In particular, we propose that the Formative population of the Salado basin could be the same population that occupied temporary settlements in southwest Lípez Province in Bolivia, traveling seasonally in a circuit to access high puna lake area resources, including birds, eggs, and raw materials such as obsidian (Nielsen et al., 2000; Nielsen, 2004) and vitreous rhyodacitic lavas (Seelenfreund et al., 2004, 2009b).

As was proposed by Lazzari (2006), during the Formative Period one sees a complex landscape of connections that, in diverse ways, affected social strategies. This observation, in particular, supports the notion that the presence of obsidian denotes or demonstrates the existence of the "others," either in terms of far-away spaces, or else of far-away communities. It is possible that the Laguna Blanca/Zapaleri source and Lípez region were connected by one of the many pre-Hispanic trade routes, linking directly or indirectly at different times the northern part of northwestern Argentina with the Atacama salt flats and the Upper Loa river area, in the circum-puna area.

The Laguna Blanca/Zapaleri source constitutes one of various obsidian sources originating from or circulated in the Atacama puna. Its relevance for the prehistoric region, in terms of mobility and circulation of goods and raw materials, however, lies in its being the most important source during the Formative Period I (ca. 200 B.C.–A.D. 200)

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together with the Ona–Las Cuevas source. This period includes the occupation of the Turi Aldea site (source of sample PAT094), which was recently dated to ca. 200 B.C.– A.D. 400 (Sinclaire, 2006). In the Formative Period II (ca. A.D. 200–900) its use was considerably reduced, being restricted to the Jujuy Province. Its importance was then reestablished during the Late Intermediate Period (ca. A.D. 900–1450), achieving the same popularity as the Ona–Las Cuevas source (Yacobaccio et al., 2004:182–190). In the archaeological sites of the Jujuy and Salta Provinces in Argentina, especially at Jujuy, almost all obsidian comes from Laguna Blanca/Zapaleri, and its use increases toward the late period, comprising almost 53% of the total sample analyzed by Yacobaccio et al. (2004). The presence of Inca sites close to the obsidian source suggests to Nielsen et al. (2006:231) that the exploitation and eventually also the circulation of its raw materials could have come under the control of the Inca empire or its contemporaries at ca. A.D. 1450–1530.

Thus Laguna Blanca/Zapaleri obsidian appears to have been a key source in the region, used in the same intensity as the Ona–Las Cuevas source for the same period across the South Andean area. Our analyses help to better characterize this source, and we propose that the 350-km radius distribution sphere of Laguna Blanca/Zapaleri obsidian as proposed by Yacobaccio et al. (2006:201) extends at least another 250 km to the northwest, toward the Atacama region.

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