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International Association for Obsidian Studies

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NEWS AND INFORMATION

NEWS AND NOTES

Have news or announcements to share? Send them to <u>IAOS.Editor@gmail.com</u> for the next issue of the *IAOS Bulletin*.

CONSIDER PUBLISHING IN THE IAOS BULLETIN

The *Bulletin* is a twice-yearly publication that reaches a wide audience in the obsidian community. Please review your research notes and consider submitting an article, research update, news, or lab report for publication in the *IAOS Bulletin*. Articles and inquiries can be sent to <u>IAOS.Editor@gmail.com</u> Thank you for your help and support!

CONFERENCES

Look inside for announcements of two upcoming conferences of interest to IAOS members. From November 7-12, 2017, the 11th International Conference on Knappable Materials will be held in Argentina; and an early announcement for the International Obsidian Conference to be held May 27-29, 2019 in Hungary. See details in this issue of the *IAOS Bulletin*.

Summer 2017

NOTES FROM THE PRESIDENT-ELECT*

Greetings from sunny Florida! I'll begin by expressing my gratitude to all of those who voted in the IAOS election. Although there was a limited field, your support is much appreciated and I look forward to serving in the upcoming years. It was really great to see many of you this past April in Vancouver for the SAA Annual Meeting. Having lived in Canada for several years, this was a welcome return to the land of maple syrup and loonies and toonies. At the IAOS meeting we discussed the success of the International Obsidian Conference held last year in Lipari, Italy and our excitement for the next one being held in Hungary in 2019. Being part Hungarian myself, I'm looking forward to a new cultural experience - and of course visiting the Carpathian obsidian sources.

Summer is always a hectic time when many of us are in the field or feverishly trying to catch up on backlogged projects. For me, this summer has been no different. I recently finished putting together a manuscript on the long-term exploitation of Lipari obsidian, a paper that builds upon my dissertation and extensive work on prehistoric obsidian consumption in ancient Sicily. I also found time to get to Sardinia, where I was able to export a selection of metal slags for SEM analysis. The adoption of metalworking in this region appears to have been a driving force in the reconfiguration of long-standing obsidian exchange networks, and this work is part of a larger project exploring the Neolithic-Chalcolithic transition and the intersections between obsidian and early metal technology.

Separate from my work in the Mediterranean, I also just returned from a conference on cemetery resource protection. You heard right! Last year I begin working in collaboration with Florida Public the Archaeology Network (FPAN) on the Florida Cemetery Recording Historic Project (FLHCRP). This is now a formal class at IRSC in which students are systematically recording gravemarkers in historic cemeteries as a means of studying the diverse ways in which various cultural groups have commemorated those who have passed. This type of research and fieldwork is certainly a new challenge for me, but I have found it particularly rewarding. I even had the opportunity to discuss our work as part of a National Public Radio (NPR) segment.

Have a great summer!

Kyle Freund, IAOS President-Elect Department of Anthropology Indian River State College <u>kfreund@irsc.edu</u>



*Editor's Note: Though this is typically a space for comments from our IAOS President, we are pleased to introduce our IAOS President-Elect with this issue of the *IAOS Bulletin*. Dr. Freund will step into the role of President beginning in the spring of 2018. Congratulations!



Organiser of the Conference

• Hungarian National Museum (HNM)

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First Announcement International Obsidian Conference 2019

27–29 May 2019, Budapest and Sárospatak (Hungary) IOC 2019

Partner institutions

 HNM Rákóczi Museum (HNM-RM), Sárospatak, Hungary

Hungarian Geological

and Geophysical Institute (MFGI)

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Academy of Sciences (MTA EK), Budapest,

Dear colleagues, We invite you to participate in the next International Obsidian Conference, in May 2019 in Hungary, Budapest and Sárospatak

The conference is intended as consecutive to the Lipari Obsidian Conference held in 2016 (http://rtykot.myweb.usf.edu/Obsidian%202016/).

The meeting's programme will include issues related to different fields of obsidian studies – archaeology, geology, anthropology, and archaeometry. The meeting's venue in Budapest is the Hungarian National Museum and in Sárospatak the Rákóczi Museum of the HNM.

The registration fee is 100 € (125 US \$) for professionals, and 50 € (65 US \$) for students. Early bird registration fee is 80 € (100 US \$) and 40 € (50 US \$), respectively. Transport and accommodation facilities will be communicated on our website (http://ioc-2019.ace.hu/). You can already use our Pre-registration form to be kept personally informed (http://ioc-2019.ace.hu/node/15). Formal registration will start in May 2018.

The planned sessions of the Conference are the following: • Formation and geology of obsidian • Sources and their characterisation • Analytical / methodological aspects of obsidian studies • Archaeological obsidian by chronological periods • Lithic technology and use wear • Theoretical and cultural anthropological issues

Your ideas concerning other sessions are welcome!

Contact organisers at: tbk@ace.hu (Katalin T. Biró) markoa@hnm.hu (András Markó)





11th INTERNATIONAL SYMPOSIUM ON KNAPPABLE MATERIALS

"From toolstone to stone tools"

Buenos Aires and Necochea (Argentina), November 7-12th, 2017

Second Announcement – Call for Abstracts

Dear friends and colleagues

We have been working on the sessions proposals received and we are happy to announce that there are 11 sessions which cover a wide range of topics. We believe the symposium will lead to some very interesting and fruitful discussions. Hence, we invite you to send your abstracts. Please find the list of sessions at the end of this announcement.

Abstracts should not exceed 200 words in length each, should be 1.5 spaced with 2.5 cm margins on all sides, and use Verdana font, 12 point. The title should be centred and in bold letters. The full name(s), institutional affiliation(s) and email address(es) of the author(s) should be included as footnotes, left aligned.

When you send your abstract, please choose the session you will be presenting your paper at and indicate if the presentation will be given online (a distance presentation) or in person (attending the symposium). Abstracts must be sent to the organizers of the session and also to the official email address of the symposium (11iskm2017@gmail.com).

The deadline for submitting abstracts is **May 15th**, **2017**. The abstracts received will be evaluated by the Organizing Committee and sessions organizers and, if there are any changes to make, we will let you know by June 1st. The final list of presentations will be made afterwards in a future announcement.

We would like to remind you that English is the official language of the symposium.

WE LOOK FORWARD TO SEEING YOU AT THE SYMPOSIUM!

Contact us at:

⊠11iskm2017@gmail.com

Look for us at:



http://www.imhicihu-conicet.gov.ar/iskm2017/

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STEADY-STATE HYDRATION AND PROTOCOLS FOR INDUCED HYDRATION OF OBSIDIAN

Alexander K. Rogers Maturango Museum

Abstract

Induced hydration is a frequently-used method of determining hydration rates of obsidian, in which hydration is measured at elevated temperatures and mathematically related to archaeological temperatures. It has the advantage that it is not subject to the error sources which plague hydration rates based on association with radiocarbon or temporally-sensitive artifacts. However, on occasion the induced hydration method yields incorrect hydration rates, particularly when abbreviated hot-soak times are used. Obsidian seems to undergo a transient state when hydration begins, and a finite time interval is required to reach steady state hydration; measurements made before this will yield incorrect results. This paper proposes a simple equation for estimating the hot-soak times required in an induced hydration protocol.

Introduction

Induced hydration is based on the principle that the temperature dependence of hydration rate is known. Obsidian can be hydrated at elevated temperatures, at which measurable hydration rims form rapidly; analysis of these measurements then allows computation of hydration rate at archaeological temperatures. Induced hydration has the advantage that the hydration rate is determined entirely by laboratory methods. Other methods require associating obsidian with other temporal data such as radiocarbon or temporally-sensitive artifacts, and hence are subject to association errors.

However, on occasion the induced hydration method yields incorrect hydration rates (Rogers and Duke 2014), particularly when abbreviated hot-soak times are used. There is a strong motivation to use hot-soak times which are as short as possible, to avoid tying up laboratory equipment any longer than necessary, so the standard protocol employs relatively short hydration times which are just sufficient to develop measurable hydration rims. The incorrect results seem to be the result of a transient phase at the initiation of the hotsoak process, and do not arise if longer hotsoak times are used (Rogers and Duke 2011).

This paper proposes a simple model of the transient phase as a guide for designing induced hydration profiles.

Obsidian Hydration

"Obsidian hydration", in its most basic aspect, describes the process by which water is absorbed by obsidian, and involves both physical and chemical changes in the glass (Doremus 2002; Anovitz et al. 2008). When a fresh surface of obsidian is exposed to air, water molecules adsorb on the surface. Since any unannealed obsidian surface exhibits cracks at the nano-scale, the amount of surface area available for adsorption is much greater than the macro-level surface area would suggest, creating a large surface concentration. Some of the adsorbed water molecules, plus others impinging directly from the atmosphere, are absorbed into the glass and diffuse into the inter-atomic spaces in the glass matrix. The diffusion process is driven primarily by the water concentration gradient, and resisted by the viscosity of the glass. The diffusing molecules stretch the glass matrix, causing an increase in volume in the hydrated region; they also cause an increase in the openness of the itself, facilitating further glass matrix absorption of water. Since the hydrated region

is expanded and the non-hydrated region is not, a stress region exists between the two. As time passes, the region of increased water concentration progresses into the glass, its rate being a function of the initial openness of the glass, temperature, and the dynamics of the process itself. When the hydrated layer becomes thick enough, typically greater than 20 microns, the accumulated stresses cause the layer to spall off as perlite.

The classical field of obsidian hydration dating (OHD) is based on measuring the position of the stress zone caused by the diffusion process. The interface between the hydrated and unhydrated volumes is a zone of optical contrast when observed under polarized light, due to the phenomenon of "stress birefringence" (Born and Wolf 1980, 703-705). The position of the stress region proceeds into the glass with the square root of time (Doremus 2002):

$$\mathbf{r}^2 = \mathbf{k}^* \mathbf{t} \tag{1}$$

where r is the hydration rim thickness, t is time, and k is the hydration rate. The hydration rate also varies with temperature as described by the Arrhenius equation

$$k = A^* \exp(-E/(R^*T))$$
(2)

where E is the activation energy, A is the preexponential, R is the universal gas constant (8.314 j/mol°K), and T is temperature in °K (Doremus 2002). Below the glass transition temperature the activation energy and preexponential are independent of temperature. This temperature dependence is the basis of induced hydration, and the validity of the method depends on the validity of equation (2).

Induced Hydration

To perform induced hydration, a set of specimens is first prepared. A number of flakes (in this case five) are removed from the same piece of obsidian; each flake is placed in a pressure vessel with distilled water, to which silica gel is added to create a saturated solution. The purpose of the silica gel is to prevent chemical erosion of the surface of the obsidian, which is otherwise attacked by the hot water bath. Alternatively, the specimens can be suspended in a vapor bath, above the water surface; in this case the silica gel is not needed.

The pressure vessel is then placed in a laboratory oven with a laboratory-grade temperature controller, and the temperature quickly raised to the hot-soak temperature specified. After the length of time prescribed by the experimental protocol for that temperature, the pressure vessel is removed from the oven, quickly cooled down, the specimen is removed and quenched, and the hydration rim measured. This measurement set (time, temperature, and hydration rim) constitutes one data point. The process is repeated with the other specimens at different temperatures and times. A detailed description is provided in Stevenson et al. 1998.

To analyze the data, equations (1) and (2) are combined to give

$$r^{2}/t = A^{*}exp(-E/(R^{*}T))$$
 (3)

Taking the natural logarithm of both sides gives the logarithmic Arrhenius equation

$$\ln(r^{2}/t) = \ln(A) - (E/R)^{*}(1/T)$$
(4)

If we define

$$Y = \ln(r^2/t) \tag{5}$$

and

$$X = 1/T \tag{6}$$

then equation (4) is a linear equation of the form

$$Y = I + S^*X \tag{7}$$

with I = ln(A) and S = -E/R. Equation (7) can then be solved for I and S by linear leastsquares methods (Cvetanovic et al. 1979).

Transient Phase Model

There are indications that, in some circumstances, the hydration rate is not constant with time at constant temperature (Stevenson and Novak 2011; Rogers and Duke 2014); equation (2) is thus not valid for these cases and the induced hydration method fails. The reason for this is not clear, but appears to be due to a period of transient behavior before hydration reaches a steady state.

The observable hydration rim is the result of stress between the hydrated and unhydrated volumes, as the glass in the hydrated region expends due to slight depolymerization caused by the absorbed water. The progress of the stress region is driven by the water concentration gradient, and resisted by the viscosity of the glass, which decreases with increasing water content and with increasing temperature (Doremus 1994). Experimental data suggest there is a period of transient behavior when hydration first starts, followed by a steady state hydration condition (Rogers and Duke 2014; Stevenson and Novak 2011; Stevenson and Rogers 2015). Induced hydration measurements made within this transient phase will not be representative of steady-state conditions and will yield incorrect rates.

Few data have been published, but it appears that, for Napa Glass Mountain obsidian at 90°C, steady state is achieved after approximately 90 – 110 days, while for Meadow Valley Mountains obsidian at 140°C it occurs at about 40 – 50 days (Rogers and Duke 2014:433 Fig. 2, and 434 Fig. 3). Both obsidians have intrinsic total water of approximately 0.1 wt%; an obsidian with higher intrinsic water content would have lower viscosity and would be expected to reach steady state more rapidly.

A simple model can be developed based on the physics of viscosity in glass (Doremus 1994). Viscosity is described by an Arrhenius equation of the form

$$v = K_1 * \exp(Q/T) \tag{8}$$

where v is viscosity, K_1 is a pre-exponential constant, Q is activation energy, and T is absolute temperature. Over temperature ranges of interest in archaeology (i.e., much less than the glass transition temperature), K_1 and Q are essentially independent of temperature (Doremus 1994).

As a first-order model, assume the time of onset of the steady state hydration process occurs more rapidly at lower viscosities, that is, t_s is proportional to viscosity. Then

$$t_s = K_2 * \exp(Q/T) \tag{9}$$

where K_2 is a proportionality constant. By transforming equation (9) into logarithmic form, the values of K_2 and Q can be estimated from the Napa Glass Mountain and Meadow Valley Mountains data cited above.

$$\ln(t_s) = \ln(K_2) + Q/T \tag{10}$$

Setting $t_s = 100$ days @ 90°C (363.15°K) and $t_s = 50$ days @ 140°C (413.15°K), solution of equation (10) yields $K_2 = 0.31$ days and Q = 2100 °K, so

$$t_s = 0.31^* \exp(2100/T) \tag{11}$$

Both the obsidian specimens cited have intrinsic water content of approximately $%H_2O_t = 0.1 wt\%$, so the pre-exponential is specific to one water concentration value.

Since viscosity decreases with increasing intrinsic water content (Friedman et al. 1963), the t_s values from equation (11) are conservative; use of them will yield steady state for specimens with higher water content, but may be unnecessarily long.

Since data for higher water content obsidians are lacking, a model is proposed based on the physics of the hydration process. A model of the hydration rate and its relationship to water content and temperature is

$k = \exp(37.76 - 2.289 * w - 10433/T + 1023 * w/T)$ (12)

where k is the hydration rate in $\mu^2/1000$ years, w is total intrinsic water in wt%, and T is temperature in °K (Rogers 2015). The form of the equation is well attested in geophysics (Zhang et al. 1991; Zhang and Behrens 2000), although the values of the numerical parameters vary based on pressure and temperature conditions. The hydration process is clearly related to the viscosity, since viscosity is the force resisting absorption of water. Therefore I am going out on a limb and suggesting a similar form of equation for viscosity and hence for t_s, although again the numerical parameters may vary. Then the factor Q in equation (9) corresponds to the last two terms in equation (12), and the principal variation with w is in the second term. As a rough approximation, I propose a form for K₂ of

$$K_2 = 0.38 \exp(-2*w)$$
 (13)

The prefactor of 0.38 causes K_2 to equal 0.31 when w = 0.1, agreeing with equation (11); the factor of 2 is a round-off of the factor of 2.289 in equation (12), since further precision is inappropriate without more experimental data. Thus the approximate form for the onset of steady state is

$$t_s = 0.38 \exp(-2*w + 2100/T)$$
(14)

with t_s in days, w in wt%, and T in °K.

Discussion

The model proposed in equation (14) can be used to compute minimum hot-soak times required for successful use of the induced hydration method. As an example, three cases are computed, for $H_2O_t = 0.1, 0.6, and 1.0 \text{ wt}\%$, corresponding to "dry", "intermediate", and 'wet" obsidians. Archaeologically these are represented by, for example, Napa Glass Mountain, Coso West Sugarloaf, and Coso Sugarloaf mountain, respectively. Temperatures between 110 and 150°C are chosen, since they are standard hot-soak temperatures. Table 1 shows results, rounded off to the nearest whole day.

The standard hot-soak protocol today is 30 days @ 110°C, 25 days @ 120°C, 20 days @ 130°C, 15 days @ 140°C, and 10 days @ 150°C. Figure 1 presents the data of Table 1, with the standard protocol shown for comparison.

Figure 1 shows that the hot-soak times for the standard protocol are too short for "dry" obsidians, those with $H_2O_t < 0.6$ wt%; steady-state conditions will not be reached and erroneous computations of hydration rate will result (as in Rogers and Duke 2014).

The longer hot-soak times in Rogers and Duke (2011) resulted in a rate which agreed with archaeology for a similarly "dry" obsidian.

| Temperature, °C | Hot-soak time in days, $H_2O_t = 0.1 \text{ wt\%}$ | Hot-soak time in days, H ₂ O _t = 0.6 wt% | Hot-soak time in days, H ₂ O _t = 1.0 wt% |
|-----------------|---|---|---|
| 110 | 101 | 37 | 17 |
| 120 | 75 | 27 | 12 |
| 130 | 65 | 24 | 11 |
| 140 | 57 | 21 | 9 |
| 150 | 50 | 18 | 8 |

Table 1. Minimum hot-soak times

Conclusions

This analysis proposes a simple model for the time required for obsidian hydration to reach steady state. The model is useful in designing induced hydration protocols so as to avoid transient conditions and the associated errors in hydration rate. A strong caveat is that the model should be regarded as preliminary, and subject to revision as more data become available, especially for higher water content.



Figure 1. Minimum hot-soak times for induced hydration protocols, as a function of specimen intrinsic water content (%H₂O_t in wt%).

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NEW ANALYSES OF LATE HOLOCENE OBSIDIANS FROM SOUTHERN PATAGONIA (SANTA CRUZ PROVINCE, ARGENTINA)

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Introduction

Patagonia is a region of ~1 million square km located south of the Colorado and Bio-Bio rivers in Argentina and Chile respectively. The Santa Cruz province, in Argentina's southernmost continental portion is a territory where obsidian was a valuable tool-making resource for hunter-gatherers who inhabited the region during the Holocene. With the use of different analytical methods, regional obsidian sourcing has been a topic of interest for many years. The methods have allowed identification of the origin of most archaeological volcanic glasses used in the region since the late 1990s (Belardi et al. 2006; Bellelli and Pereyra 2002; Espinosa and Goñi 1999; Fernandez et al. 2015; Stern 1999; Stern and Franco 2000; Stern et al. 2000, Vásquez et al. 2001). The aim of this current project was to build on these previous investigations. As such, we analyzed a number of archaeological samples collected along the North Central coast and SE Santa Cruz Province of the Argentine Republic (Fig. 1). Samples from sources located in the area were collected as well. The samples reported here provide an extension of the Pampa del Asador source, and evidence of two new sources from as of yet unknown locations.

Materials

Forty one obsidian samples from the North Central Coast (NCC) were recovered in a systematic survey performed between Puerto Deseado and Bahia Laura, Deseado



Figure 1. Map of Patagonia with the location of the sites mentioned in the text. PA: Pampa del Asador source, 1: North central coast, 2: Aristizabal Cave and Alero del Valle rockshelter.

Department. During this endeavor, sampling units 1 km long were used along the Atlantic shoreline. The survey was made following the maximum tide line where vegetation begins and 100 meters inward of the continent. This located archaeological shell middens, as well as secondary sources (*sensu* Luedke 1979) of diverse rocks. Concentrations of pebbles and cobbles were found on the beach and paleobeaches, but also on the eolian deposits along the strip of land bordering the coast. Remarkably, among these were pebbles of obsidian whose cortex indicates that they were rolled by the sea (Fig. 2). Radiocarbon dates obtained in the middens from the NCC of Santa Cruz indicate that the archaeological obsidian was used by Late Holocene huntergatherers.

The sample from southern Santa Cruz includes 14 specimens from Alero del Valle (AV), and two from Aristizabal Cave (AC). The former is a small rockshelter ~9 m wide by 1.5 m deep formed on a cliff on a terrace of the Chico River about 5 km north of the Markatch Aike ranch. The excavation revealed four natural strata. The artifacts analyzed were excavated from level III, corresponding to late Holocene huntergatherers dated between ~ 1.0 -3.0 kybp. Three carbon samples from these levels yielded uncalibrated radiocarbon dates of 1030 ± 60 (Beta-103247), 2520 ± 80 (Beta-103246), and 2870 70 ± (Beta-115678) years b.p. AC (51° 54.75'S, 69° 44.76'W) is ~10 km west of AV at the top of Felton Hill, one of the highest elevations in the area. It is 16 m long and 8 m wide at the mouth, making it one of the largest caves known in the Pali Aike region. Excavation revealed five natural stratigraphic layers. Archaeological remains in layer IV indicate that this cave was used by late Holocene hunter-gatherers.

Located in the northwest of Santa Cruz, the most important known obsidian source in the province is Pampa del Asador (PA, Stern 1999). Our results are consistent with the fact that Pampa del Asador is the only obsidian type present on the northern Santa Cruz coast as along as the southern Chubut coast. To compare with the sample reported in this paper, and using the same methodology, we analyzed some specimens from this source.



Figure 2. Examples of obsidian nodules found in the northeast coast of Santa Cruz province showing smooth and well-rounded surfaces eroded by the sea.

Methods, Analysis and Results

The studied sample (n = 81) comes from the following locations: NCC (n = 41); AV (n = 41); = 14), AC (n = 2), and PA (n = 24) (See Table 1). All obsidians were analyzed by X-ray fluorescence (XRF) and 32 by neutron activation analysis (NAA) at the University of Missouri Research Reactor (MURR). XRF was employed on the totality of the sample, while NAA was used for the specimens coming from PA and from sites in the north central coast. XRF was performed using a hand-held spectrometer made by Bruker Corporation (Tracer III-V, serial number K0557). The apparatus is equipped with an air-cooled, rhodium target anode and 140 micron Be window. X-rays were measured by a thermoelectrically-cooled Si-PIN diode detector. The detector has a nominal resolution of 180 eV when measuring the 6.4 keV peak from iron. For the analyses reported here, the X-ray tube was operated at 40 kV

| Table 1. XRI | F Results for Sa | nta Cruz | | | | | | | | | | | | | | |
|--------------|------------------------|----------|-------|-------|---------|-------|------|-------|------|-------|-------|-------|------|----------------|-------------------|--------------------|
| ANID | Compositional Group | К | Ti | Mn | Fe | Zn | Ga | Rb | Sr | Υ | Zr | Nb | Тћ | Sample Type | Site Name | Source Name |
| PAC001 | PDA-1 | 38925.5 | 672.3 | 503.9 | 10014.2 | 89.7 | 21.9 | 186.4 | 30.5 | 32.9 | 136.8 | 26.7 | 19.8 | source | Pampa del Asador | Pampa del Asador-1 |
| PAC002 | PDA-1 | 36714.9 | 776.9 | 274.9 | 10441.7 | 81.3 | 20.6 | 198.1 | 32.8 | 31.5 | 139.4 | 23.4 | 21.0 | source | Pampa del Asador | Pampa del Asador-1 |
| PAC003 | PDA-1 | 37663.6 | 688.7 | 490.7 | 10467.8 | 99.3 | 20.8 | 211.3 | 34.6 | 33.1 | 145.3 | 24.0 | 16.3 | source | Pampa del Asador | Pampa del Asador-1 |
| SCAV01 | SCAV-1 | 36139.4 | 517.6 | 329.1 | 19617.5 | 412.4 | 38.5 | 353.7 | 0.0 | 137.6 | 806.1 | 200.1 | 43.0 | artifact | Alero del Valle | Alero del Valle-1 |
| SCAV02 | SCAV-1 | 36660.2 | 522.2 | 278.4 | 14992.2 | 290.6 | 36.3 | 304.2 | 0.0 | 123.4 | 755.9 | 191.7 | 42.6 | artifact | Alero del Valle | Alero del Valle-1 |
| SCAV03 | SCAV-1 | 35003.4 | 599.4 | 377.8 | 16968.7 | 345.5 | 40.0 | 332.8 | 2.0 | 121.9 | 792.6 | 187.5 | 36.8 | artifact | Alero del Valle | Alero del Valle-1 |
| SCAV04 | SCAV-1 | 35257.4 | 698.6 | 383.6 | 25320.9 | 614.1 | 36.9 | 377.2 | 0.0 | 144.5 | 858.1 | 207.5 | 43.3 | artifact | Alero del Valle | Alero del Valle-1 |
| SCAV05 | SCAV-1 | 35697.8 | 720.6 | 534.9 | 24329.5 | 548.6 | 42.2 | 420.8 | 3.6 | 150.0 | 935.6 | 222.5 | 47.3 | artifact | Alero del Valle | Alero del Valle-1 |
| SCAV06-11 | SCAV-1 | 33832.6 | 696.5 | 383.0 | 23862.0 | 435.9 | 43.0 | 340.1 | 1.7 | 123.6 | 736.1 | 186.0 | 42.1 | artifact | Alero del Valle | Alero del Valle-1 |
| SCAV12 | SCAV-1 | 35246.8 | 678.1 | 342.8 | 18901.5 | 315.5 | 41.0 | 368.8 | 2.8 | 140.6 | 895.4 | 221.7 | 40.3 | artifact | Alero del Valle | Alero del Valle-1 |
| SCAV13 | SCAV-1 | 34997.6 | 730.0 | 430.1 | 19048.3 | 336.5 | 33.1 | 334.6 | 2.5 | 127.9 | 808.2 | 200.7 | 37.1 | artifact | Alero del Valle | Alero del Valle-1 |
| SCAV14-15 | SCAV-1 | 33821.6 | 537.4 | 274.9 | 18962.6 | 339.8 | 30.9 | 314.7 | 0.0 | 121.6 | 700.1 | 166.3 | 33.6 | artifact | Alero del Valle | Alero del Valle-1 |
| SCAV16 | SCAV-1 | 36926.7 | 579.2 | 281.9 | 17276.7 | 284.5 | 38.2 | 337.2 | 0.7 | 144.4 | 867.2 | 213.4 | 41.5 | artifact | Alero del Valle | Alero del Valle-1 |
| SCAV17 | SCAV-2 | 38366.4 | 541.3 | 227.3 | 8568.5 | 81.1 | 18.7 | 181.9 | 22.2 | 36.0 | 142.4 | 35.4 | 19.9 | artifact | Alero del Valle | Alero del Valle-2 |
| SCAV18 | SCAV-2 | 34083.0 | 484.9 | 210.2 | 10609.6 | 102.8 | 19.4 | 195.3 | 23.5 | 37.1 | 140.5 | 35.4 | 19.9 | artifact | Alero del Valle | Alero del Valle-2 |
| SCAV19 | SCAV-1 | 36271.8 | 361.8 | 412.4 | 19401.9 | 347.8 | 43.3 | 350.2 | 1.4 | 129.4 | 806.8 | 194.9 | 41.8 | artifact | Alero del Valle | Alero del Valle-1 |
| SCAV20 | SCAV-1 | 35752.6 | 485.3 | 476.4 | 21033.4 | 379.7 | 44.3 | 372.8 | 0.0 | 135.8 | 837.2 | 194.7 | 43.4 | artifact | Alero del Valle | Alero del Valle-1 |
| SCCA01 | SCCA-1 | 35856.8 | 486.2 | 461.3 | 13191.5 | 119.0 | 22.9 | 222.8 | 35.9 | 32.9 | 138.2 | 25.0 | 20.8 | artifact | Cueva Ariztizabal | Cueva Ariztizabal |
| SCCA02 | SCCA-1 | 36020.5 | 517.9 | 433.1 | 15138.7 | 134.8 | 24.2 | 246.5 | 41.6 | 42.3 | 155.7 | 24.2 | 25.3 | artifact | Cueva Ariztizabal | Cueva Ariztizabal |
| SCPA01 | PDA-1 | 36028.5 | 637.1 | 277.6 | 10048.0 | 60.3 | 23.0 | 189.3 | 29.1 | 33.8 | 150.5 | 26.0 | 23.7 | source | Pampa del Asador | Pampa del Asador-1 |
| SCPA02 | PDA-1 | 37971.9 | 511.9 | 392.5 | 10458.4 | 68.5 | 19.6 | 193.4 | 32.2 | 30.0 | 128.6 | 20.6 | 13.7 | source | Pampa del Asador | Pampa del Asador-1 |
| SCPA03 | PDA-2 | 35232.0 | 652.5 | 316.2 | 9474.4 | 81.8 | 19.7 | 225.3 | 0.4 | 49.2 | 138.0 | 26.5 | 20.5 | source | Pampa del Asador | Pampa del Asador-2 |
| SCPA04 | PDA-1 | 37249.7 | 695.9 | 338.4 | 11086.2 | 54.2 | 18.7 | 204.2 | 33.5 | 34.6 | 144.8 | 24.6 | 17.6 | source | Pampa del Asador | Pampa del Asador-1 |
| SCPA05 | PDA-3 | 35540.0 | 715.5 | 413.6 | 7158.6 | 45.5 | 15.7 | 145.3 | 35.5 | 12.4 | 141.0 | 26.2 | 19.2 | source | Pampa del Asador | OUTLIER |

| Source Name | Pampa del Asador-3 | Pampa del Asador-2 | Pampa del Asador-3 | Pampa del Asador-1 | Pampa del Asador-2 | Pampa del Asador-1 | Pampa del Asador-3 | Pampa del Asador-2 | Pampa del Asador-1 | Pampa del Asador-1 | Pampa del Asador-3 | Pampa del Asador-1 | Pampa del Asador-2 | Pampa del Asador-2 | Pampa del Asador-2 | Pamap del Asador-3 | Pampa del Asador-2 | Pampa del Asador-1 | Pampa del Asador-2 | Pampa del Asador-1 |
|------------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| Site Name | Pampa del Asador | Punta Medanosa |
| Sample Type | source |
| Тћ | 19.2 | 16.8 | 16.0 | 21.3 | 17.4 | 18.4 | 21.7 | 17.7 | 16.5 | 18.8 | 21.0 | 15.7 | 17.4 | 17.7 | 21.4 | 20.2 | 22.7 | 17.3 | 19.6 | 20.0 | 18.5 | 15.0 | 20.7 | 18.4 | 18.4 |
| qN | 30.3 | 29.2 | 33.3 | 22.3 | 30.0 | 24.4 | 31.7 | 35.2 | 28.7 | 25.9 | 29.6 | 20.1 | 30.8 | 26.3 | 31.4 | 33.5 | 31.0 | 26.5 | 28.7 | 24.5 | 22.8 | 28.2 | 24.8 | 22.7 | 24.7 |
| Zr | 284.4 | 131.0 | 283.4 | 120.3 | 152.4 | 147.4 | 250.7 | 159.3 | 144.2 | 143.4 | 293.8 | 117.7 | 158.2 | 148.1 | 162.2 | 309.5 | 149.6 | 128.6 | 137.0 | 146.8 | 139.2 | 142.1 | 139.4 | 131.9 | 140.5 |
| Y | 32.0 | 37.2 | 30.8 | 23.5 | 41.4 | 37.9 | 32.6 | 54.5 | 25.6 | 36.2 | 30.2 | 25.4 | 43.1 | 39.3 | 42.3 | 31.3 | 46.6 | 26.3 | 41.1 | 32.1 | 30.3 | 28.5 | 32.3 | 30.5 | 28.7 |
| Sr | 63.2 | 0.0 | 58.3 | 29.9 | 2.7 | 34.3 | 44.0 | 0.4 | 35.7 | 36.3 | 64.5 | 27.6 | 3.7 | 0.7 | 1.8 | 63.7 | 2.9 | 27.7 | 0.5 | 31.5 | 32.2 | 31.9 | 28.4 | 28.5 | 30.5 |
| Rb | 181.0 | 206.1 | 186.4 | 193.5 | 242.2 | 201.2 | 191.4 | 258.5 | 197.1 | 197.5 | 180.9 | 173.5 | 244.3 | 226.5 | 265.2 | 191.5 | 230.1 | 186.6 | 220.9 | 202.5 | 204.8 | 200.1 | 210.3 | 193.3 | 199.3 |
| Ga | 19.2 | 15.0 | 17.6 | 17.6 | 24.7 | 23.3 | 20.2 | 21.7 | 17.8 | 17.5 | 21.1 | 19.0 | 19.4 | 23.7 | 22.0 | 22.4 | 22.5 | 20.3 | 18.6 | 20.3 | 17.4 | 20.0 | 21.7 | 23.9 | 20.9 |
| Zn | 85.0 | 67.1 | 51.8 | 87.6 | 101.9 | 79.1 | 87.9 | 115.4 | 78.5 | 99.3 | 88.8 | 111.2 | 77.8 | 94.5 | 100.5 | 83.1 | 105.8 | 78.8 | 92.4 | 81.2 | 59.0 | 73.8 | 76.5 | 85.2 | 64.7 |
| Fe | 13989.7 | 8181.9 | 14313.5 | 10263.9 | 10146.9 | 10860.0 | 12680.6 | 10137.7 | 10259.0 | 10839.3 | 14038.3 | 10129.8 | 10765.4 | 10928.9 | 11646.5 | 14799.5 | 9965.5 | 8927.9 | 8115.2 | 10376.3 | 10614.2 | 10538.3 | 10949.5 | 10426.0 | 10421.4 |
| Mn | 536.6 | 368.2 | 400.0 | 268.6 | 312.8 | 387.8 | 504.6 | 280.6 | 370.1 | 358.4 | 427.4 | 176.6 | 233.8 | 266.8 | 289.2 | 346.2 | 416.5 | 298.1 | 338.1 | 407.6 | 372.3 | 228.3 | 283.6 | 424.8 | 377.1 |
| Ti | 682.9 | 714.9 | 623.6 | 626.1 | 841.8 | 642.4 | 995.4 | 787.9 | 767.1 | 782.2 | 866.7 | 627.1 | 578.1 | 519.8 | 463.3 | 686.9 | 789.8 | 888.7 | 692.3 | 770.3 | 763.0 | 600.4 | 654.5 | 845.3 | 642.7 |
| К | 36371.2 | 35024.8 | 35363.0 | 35361.4 | 36350.4 | 37444.2 | 35260.5 | 36264.9 | 36579.5 | 36793.3 | 36148.3 | 35382.5 | 37258.6 | 35906.5 | 36228.4 | 34956.4 | 38855.3 | 37360.4 | 37783.0 | 38530.0 | 37770.4 | 36108.6 | 37300.4 | 36117.4 | 36971.6 |
| Compositional Group | PDA-2 | PDA-3 | PDA-1 | PDA-2 | PDA-1 | PDA-3 | PDA-2 | PDA-1 | PDA-1 | PDA-3 | PDA-1 | PDA-2 | PDA-2 | PDA-2 | PDA-3 | PDA-2 | PDA-1 | PDA-2 | PDA-1 |
| ANID | SCPA06 | SCPA07 | SCPA08 | SCPA09 | SCPA10 | SCPA11 | SCPA12 | SCPA13 | SCPA14 | SCPA15 | SCPA16 | SCPA17 | SCPA18 | SCPA19 | SCPA20 | SCPA21 | SCPM01 | SCPM02 | SCPM03 | SCPM05 | SCPM06 | SCPM08 | SCPM09 | SCPM10 | SCPM11 |

| Name | Asador-1 | Asador-1 | Asador-2 | Asador-1 | Asador-3 | Asador-1 | Asador-3 | Asador-1 | Asador-2 | Asador-2 | Asador-1 | Asador-1 | Asador-1 | Asador-2 | Asador-2 | Asador-1 | Asador-2 | Asador-2 | Asador-1 | Asador-1 | Asador-1 | Asador-2 | Asador-1 | Asador-1 | Asador-1 |
|------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Source | Pampa del |
| Site Name | Punta Medanosa |
| Sample Type | source |
| Тћ | 23.0 | 15.7 | 18.0 | 21.6 | 20.5 | 14.8 | 19.4 | 23.5 | 16.4 | 22.7 | 21.1 | 18.5 | 21.5 | 14.7 | 19.3 | 21.3 | 21.7 | 19.4 | 23.9 | 19.2 | 19.5 | 21.6 | 19.9 | 18.5 | 20.2 |
| qN | 23.0 | 21.7 | 30.8 | 25.5 | 32.1 | 22.6 | 30.1 | 25.5 | 29.0 | 29.2 | 24.3 | 24.9 | 25.2 | 25.2 | 28.3 | 24.5 | 28.5 | 25.7 | 26.1 | 25.1 | 26.6 | 34.5 | 27.9 | 21.4 | 25.6 |
| Zr | 145.6 | 126.7 | 161.4 | 145.1 | 269.2 | 144.5 | 268.1 | 144.8 | 143.6 | 148.1 | 151.0 | 138.6 | 158.5 | 145.5 | 150.9 | 145.7 | 154.4 | 148.2 | 145.9 | 148.6 | 145.9 | 144.8 | 143.5 | 125.5 | 158.5 |
| Y | 31.1 | 32.8 | 45.1 | 34.0 | 23.0 | 33.9 | 30.0 | 32.9 | 39.9 | 48.0 | 39.8 | 28.1 | 32.2 | 40.8 | 42.4 | 32.7 | 43.8 | 41.7 | 32.1 | 31.0 | 31.8 | 42.8 | 36.5 | 30.7 | 40.0 |
| Sr | 32.0 | 30.1 | 3.0 | 33.6 | 67.3 | 32.9 | 61.3 | 30.6 | 3.4 | 3.6 | 34.1 | 35.9 | 30.3 | 3.7 | 2.0 | 34.7 | 2.6 | 2.6 | 32.9 | 34.0 | 34.3 | 0.6 | 35.2 | 27.3 | 33.6 |
| Rb | 207.6 | 188.9 | 235.5 | 200.1 | 181.0 | 196.2 | 175.6 | 220.7 | 213.5 | 236.3 | 213.4 | 201.3 | 209.9 | 215.3 | 215.6 | 195.1 | 239.6 | 227.3 | 203.3 | 208.9 | 200.7 | 238.3 | 205.9 | 176.0 | 201.5 |
| Ga | 19.0 | 22.0 | 15.7 | 16.9 | 21.8 | 20.5 | 16.6 | 20.3 | 18.1 | 23.4 | 20.6 | 19.1 | 18.8 | 22.7 | 21.1 | 21.3 | 18.9 | 19.6 | 26.9 | 22.2 | 16.2 | 26.8 | 20.6 | 21.3 | 23.3 |
| Zn | 87.8 | 67.3 | 84.4 | 72.5 | 44.7 | 56.9 | 70.3 | 89.0 | 78.1 | 73.4 | 101.8 | 70.3 | 58.8 | 86.1 | 77.2 | 71.3 | 90.5 | 72.2 | 68.5 | 62.9 | 80.3 | 60.4 | 84.5 | 101.5 | 63.1 |
| Fe | 10745.5 | 9806.9 | 10083.0 | 10709.1 | 13845.1 | 10669.5 | 14311.1 | 10914.1 | 9310.4 | 10013.3 | 11396.5 | 9904.8 | 11850.3 | 8803.1 | 9975.3 | 10719.6 | 10215.0 | 9568.2 | 10430.7 | 10896.4 | 10800.0 | 8645.1 | 11013.5 | 10200.2 | 10818.5 |
| Mn | 322.0 | 363.4 | 306.6 | 291.7 | 497.5 | 413.8 | 479.9 | 294.9 | 335.9 | 435.5 | 422.1 | 412.6 | 458.5 | 260.5 | 321.2 | 361.3 | 389.2 | 474.4 | 309.3 | 336.4 | 406.8 | 229.7 | 391.7 | 414.4 | 355.8 |
| Ti | 583.6 | 680.2 | 586.2 | 556.2 | 705.5 | 518.2 | 768.0 | 683.3 | 734.1 | 653.6 | 795.9 | 556.1 | 752.1 | 638.3 | 685.8 | 772.6 | 604.9 | 627.4 | 724.3 | 678.0 | 679.7 | 751.8 | 926.6 | 671.1 | 679.0 |
| K | 36782.4 | 36346.5 | 36397.9 | 38622.4 | 36362.8 | 37678.0 | 36616.7 | 36300.3 | 37165.4 | 37299.0 | 36582.6 | 37441.5 | 36671.9 | 37063.2 | 37512.6 | 37064.4 | 37146.0 | 36788.4 | 37337.2 | 37489.2 | 36452.7 | 36616.6 | 35921.3 | 37892.2 | 36934.2 |
| Compositional Group | PDA-1 | PDA-1 | PDA-2 | PDA-1 | PDA-3 | PDA-1 | PDA-3 | PDA-1 | PDA-2 | PDA-2 | PDA-1 | PDA-1 | PDA-1 | PDA-2 | PDA-2 | PDA-1 | PDA-2 | PDA-2 | PDA-1 | PDA-1 | PDA-1 | PDA-2 | PDA-1 | PDA-1 | PDA-1 |
| ANID | SCPM12 | SCPM13 | SCPM14 | SCPM15 | SCPM16 | SCPM17 | SCPM18 | SCPM19 | SCPM20 | SCPM21 | SCPM22 | SCPM23 | SCPM24 | SCPM25 | SCPM26 | SCPM27 | SCPM28 | SCPM29 | SCPM30 | SCPM31 | SCPM32 | SCPM33 | SCPM34 | SCPM35 | SCPM36 |

| ANID | Compositional Group | К | Ti | Mn | Fe | Zn | Ga | Rb | Sr | Y | Zr | qN | Тћ | Sample Type | Site Name | Source Name |
|--------|------------------------|---------|-------|-------|---------|-------|------|-------|------|------|-------|------|------|----------------|----------------|--------------------|
| SCPM37 | PDA-2 | 36362.9 | 622.6 | 366.8 | 9376.3 | 60.3 | 27.1 | 241.9 | 0.0 | 47.8 | 148.7 | 32.3 | 22.1 | source | Punta Medanosa | Pampa del Asador-2 |
| SCPM38 | PDA-1 | 36412.6 | 774.9 | 483.3 | 9971.1 | 59.5 | 19.8 | 203.9 | 30.0 | 29.4 | 139.5 | 28.5 | 22.1 | source | Punta Medanosa | Pampa del Asador-1 |
| SCPM39 | PDA-1 | 36335.3 | 869.7 | 436.0 | 10205.0 | 7.9.7 | 21.0 | 193.1 | 34.4 | 31.4 | 149.8 | 24.1 | 20.0 | source | Punta Medanosa | Pampa del Asador-1 |
| SCPM40 | PDA-1 | 36986.7 | 693.6 | 467.1 | 10298.8 | 62.9 | 20.5 | 211.4 | 33.8 | 32.3 | 150.2 | 28.8 | 24.8 | source | Punta Medanosa | Pampa del Asador-1 |
| SCPM41 | PDA-2 | 36741.4 | 519.3 | 325.7 | 9357.1 | 107.8 | 24.4 | 227.9 | 2.1 | 41.9 | 155.0 | 31.5 | 19.3 | source | Punta Medanosa | Pampa del Asador-2 |
| SCPM42 | PDA-1 | 36711.4 | 621.4 | 362.0 | 10810.7 | 81.8 | 17.2 | 201.7 | 34.4 | 34.0 | 144.4 | 27.4 | 18.5 | source | Punta Medanosa | Pampa del Asador-1 |
| SCPM43 | PDA-1 | 36446.5 | 652.4 | 311.1 | 10959.7 | 62.1 | 11.0 | 209.1 | 35.8 | 29.1 | 134.0 | 22.1 | 18.1 | source | Punta Medanosa | Pampa del Asador-1 |

| Table 2. N | VAA Results for Santa | Cruz | | | | | | | | | | | | | | | |
|------------|------------------------------|---------|--------|---------|--------|--------|--------|---------|--------|---------|--------|---------|--------|--------|---------------|---------|---------------|
| ANID | Source Name | La | Lu | Nd | Sm | U | Yb | Ce | Co | Cs | Eu | Fe | Ηf | Rb | \mathbf{Sb} | Sc | \mathbf{Sr} |
| SCPA01 | Pampa del Asador-1 | 38.9754 | 0.5242 | 30.8480 | 6.7846 | 5.5674 | 3.3452 | 76.1854 | 0.2425 | 10.4550 | 0.2736 | 9867.7 | 5.4611 | 199.71 | 0.3283 | 7.2558 | 0.00 |
| SCPA02 | Pampa del Asador-1 | 39.3888 | 0.6315 | 30.2806 | 6.7731 | 6.1380 | 3.4283 | 77.0908 | 0.2823 | 10.5093 | 0.2784 | 10258.8 | 5.6319 | 201.81 | 0.3193 | 7.4161 | 0.00 |
| SCPA03 | Pampa del Asador-1 | 23.0629 | 0.8135 | 26.9336 | 7.9959 | 7.0285 | 4.6693 | 54.7534 | 0.2424 | 13.0272 | 0.0915 | 9209.0 | 6.2888 | 238.98 | 0.2939 | 9.5950 | 0.00 |
| SCPA04 | Pampa del Asador-1 | 38.6139 | 0.5143 | 30.1792 | 6.7728 | 6.4424 | 3.3825 | 75.7471 | 0.2491 | 10.3520 | 0.2734 | 9867.3 | 5.4197 | 200.15 | 0.3493 | 7.2470 | 43.61 |
| SCPA06 | Pampa del Asador-2 | 43.7467 | 0.5949 | 30.2429 | 6.2225 | 6.8291 | 3.1644 | 81.3558 | 0.6845 | 5.8331 | 0.7161 | 13356.9 | 7.7483 | 174.45 | 0.2628 | 4.9055 | 73.70 |
| SCPA08 | Pampa del Asador-2 | 44.1712 | 0.6012 | 32.0856 | 6.2023 | 6.5653 | 3.1305 | 81.7512 | 0.4824 | 5.8117 | 0.7143 | 12945.7 | 7.6354 | 174.98 | 0.2738 | 4.8828 | 65.26 |
| SCPA10 | Pampa del Asador-2 | 27.9944 | 0.6441 | 29.0919 | 7.7700 | 6.1335 | 4.2580 | 63.8701 | 0.0577 | 11.7089 | 0.1162 | 9066.2 | 6.1340 | 223.51 | 0.2613 | 9.6737 | 0.00 |
| SCPA11 | Pampa del Asador-1 | 38.1530 | 0.5120 | 28.4666 | 6.7195 | 6.2345 | 3.4202 | 74.4935 | 0.2256 | 10.2239 | 0.2575 | 9622.3 | 5.5245 | 201.36 | 0.3318 | 7.1208 | 41.67 |
| SCPA12 | Pampa del Asador-1 | 42.6818 | 0.5155 | 29.7491 | 5.9652 | 7.5047 | 3.0821 | 81.1185 | 0.3643 | 5.9886 | 0.6165 | 11818.1 | 7.1916 | 181.83 | 0.2435 | 4.7537 | 24.96 |
| SCPA13 | Pampa del Asador-2 | 22.8396 | 0.7349 | 27.5919 | 8.0069 | 7.7811 | 4.7351 | 53.9253 | 0.0623 | 12.8514 | 0.0918 | 8655.3 | 6.1477 | 241.61 | 0.3144 | 9.3380 | 0.00 |
| SCPA14 | Pampa del Asador-1 | 38.2955 | 0.5351 | 28.4103 | 6.6809 | 5.9100 | 3.3038 | 75.0155 | 0.2501 | 10.3159 | 0.2775 | 9775.9 | 5.4964 | 199.05 | 0.3128 | 7.1875 | 27.60 |
| SCPA15 | Pampa del Asador-1 | 38.3433 | 0.5149 | 29.9071 | 6.7337 | 5.9465 | 3.2687 | 76.0945 | 0.2286 | 10.3346 | 0.2700 | 9829.2 | 5.3859 | 199.76 | 0.3183 | 7.2410 | 31.74 |
| SCPA16 | Pampa del Asador-3 | 44.1448 | 0.5283 | 30.9620 | 6.2563 | 6.7424 | 3.1127 | 82.7756 | 0.4732 | 5.7793 | 0.7351 | 12918.8 | 7.6713 | 176.64 | 0.2394 | 4.8973 | 68.52 |
| SCPM01 | Pampa del Asador-2 | 29.2736 | 0.6958 | 39.9981 | 9.6151 | 7.5972 | 4.7527 | 66.7715 | 0.0579 | 12.2987 | 0.1126 | 9569.6 | 6.4065 | 229.90 | 0.2541 | 10.2147 | 0.00 |
| SCPM02 | Pampa del Asador-1 | 39.0725 | 0.5551 | 24.4990 | 8.2231 | 7.0056 | 3.5555 | 77.8402 | 0.2554 | 10.7076 | 0.2802 | 10152.8 | 5.4871 | 204.00 | 0.3093 | 7.5107 | 22.25 |
| SCPM03 | Pampa del Asador-2 | 23.3143 | 0.7740 | 25.8154 | 9.3109 | 7.6164 | 4.6181 | 56.2280 | 0.0411 | 13.3752 | 0.0844 | 8968.3 | 6.4564 | 244.42 | 0.2912 | 9.7078 | 0.00 |
| SCPM05 | Pampa del Asador-1 | 38.5702 | 0.5484 | 28.1851 | 8.0421 | 6.5393 | 3.3618 | 75.9376 | 0.2343 | 10.5024 | 0.2732 | 9922.4 | 5.3552 | 201.97 | 0.3099 | 7.2763 | 20.03 |
| SCPM06 | Pampa del Asador-1 | 38.9133 | 0.5654 | 26.3231 | 8.0676 | 7.6246 | 3.5487 | 76.8445 | 0.2400 | 10.5400 | 0.2805 | 10014.0 | 6.0786 | 202.38 | 0.3124 | 7.3802 | 35.40 |
| SCPM08 | Pampa del Asador-1 | 37.7025 | 0.5422 | 32.6496 | 7.7941 | 6.8570 | 3.1116 | 73.8475 | 0.2301 | 10.2631 | 0.2673 | 9637.8 | 5.4517 | 196.26 | 0.3166 | 7.1156 | 17.88 |
| SCPM09 | Pampa del Asador-1 | 38.0867 | 0.5643 | 27.2093 | 7.8876 | 6.8772 | 3.1832 | 74.9386 | 0.2279 | 10.3677 | 0.2715 | 9736.8 | 5.6127 | 200.41 | 0.3174 | 7.1915 | 25.24 |
| SCPM10 | Pampa del Asador-1 | 38.3841 | 0.6077 | 30.0916 | 7.9773 | 7.1017 | 3.2325 | 75.9857 | 0.2311 | 10.5762 | 0.2753 | 9924.7 | 5.4932 | 202.14 | 0.3147 | 7.3179 | 17.17 |
| SCPM11 | Pampa del Asador-1 | 38.1229 | 0.5655 | 30.4194 | 7.9891 | 7.0050 | 3.2135 | 76.3776 | 0.2302 | 10.5634 | 0.2694 | 9910.1 | 5.5573 | 203.03 | 0.3109 | 7.3053 | 26.19 |
| SCPM12 | Pampa del Asador-1 | 38.5882 | 0.5706 | 27.1248 | 7.9320 | 7.0408 | 3.2341 | 76.0036 | 0.2391 | 10.5217 | 0.2720 | 9890.8 | 5.5689 | 201.70 | 0.3406 | 7.3308 | 26.73 |
| SCPM13 | Pampa del Asador-1 | 39.3433 | 0.5812 | 31.3790 | 8.0646 | 7.2648 | 3.3901 | 77.6597 | 0.2511 | 10.6992 | 0.2784 | 10031.3 | 5.7348 | 200.96 | 0.3201 | 7.4385 | 37.25 |
| SCPM14 | Pampa del Asador-2 | 28.9675 | 0.6890 | 28.7009 | 9.3567 | 7.5991 | 4.0843 | 64.9954 | 0.0624 | 12.0281 | 0.1239 | 9309.3 | 6.2754 | 226.02 | 0.2311 | 9.9832 | 0.00 |
| SCPM15 | Pampa del Asador-1 | 38.7632 | 0.5700 | 27.0169 | 7.9603 | 7.5029 | 3.7408 | 76.9318 | 0.2755 | 10.4821 | 0.2738 | 10081.6 | 5.5001 | 201.51 | 0.3084 | 7.3819 | 26.73 |
| SCPM16 | Pampa del Asador-3 | 44.1749 | 0.5305 | 33.0233 | 7.2894 | 7.5838 | 3.0324 | 81.7702 | 0.4914 | 5.7740 | 0.7188 | 13112.2 | 7.7059 | 174.12 | 0.2523 | 4.8968 | 58.12 |
| SCPM17 | Pampa del Asador-1 | 38.7260 | 0.5662 | 30.8041 | 7.9992 | 7.0230 | 3.2491 | 76.3119 | 0.2391 | 10.5366 | 0.2781 | 9918.6 | 5.6197 | 200.44 | 0.3123 | 7.3424 | 12.93 |
| SCPM18 | Pampa del Asador-3 | 42.5377 | 0.5669 | 29.9240 | 7.1088 | 7.0461 | 2.8950 | 80.2286 | 0.4582 | 5.7392 | 0.6929 | 12589.1 | 7.5117 | 172.93 | 0.2160 | 4.7979 | 68.54 |
| SCPM19 | Pampa del Asador-1 | 39.3295 | 0.5834 | 30.8912 | 8.0824 | 7.1813 | 3.3111 | 76.8732 | 0.2313 | 10.4668 | 0.2757 | 9972.9 | 5.4319 | 199.48 | 0.3098 | 7.3728 | 28.14 |
| SCPM20 | Pampa del Asador-2 | 28.5391 | 0.7429 | 32.0780 | 9.3620 | 7.5244 | 4.5918 | 64.4797 | 0.0647 | 11.9871 | 0.1135 | 9184.8 | 6.2119 | 224.48 | 0.2329 | 9.8552 | 0.00 |
| SCPM21 | Pampa del Asador-2 | 28.5213 | 0.7173 | 27.4356 | 9.3127 | 7.3164 | 4.0897 | 64.3036 | 0.0549 | 11.9290 | 0.1191 | 9152.7 | 6.1603 | 222.92 | 0.2390 | 9.7739 | 0.00 |

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| | NAME TO AND AND THE | | | () | | | | | | | | | | |
|--------|---------------------|--------|------------------------|---------|-------|--------|-------|---------|--------|-------|---------|---------|--------|---------|
| ANID | Source Name | Та | $\mathbf{T}\mathbf{b}$ | Тh | Zn | Zr | Br | AI | Ba | CI | Dy | К | Mn | Na |
| SCPA01 | Pampa del Asador-1 | 2.0856 | 0.9916 | 18.4604 | 67.32 | 153.71 | 2.091 | 68883.2 | 246.00 | 506.5 | 6.3808 | 39774.2 | 275.38 | 28790.0 |
| SCPA02 | Pampa del Asador-1 | 2.1132 | 0.9827 | 18.6455 | 71.10 | 170.12 | 2.222 | 74041.8 | 279.40 | 510.9 | 6.4023 | 40842.2 | 287.36 | 29297.2 |
| SCPA03 | Pampa del Asador-1 | 2.5597 | 1.4396 | 19.2048 | 89.23 | 149.03 | 1.954 | 67803.6 | 22.80 | 444.6 | 10.1688 | 40374.4 | 237.34 | 29460.7 |
| SCPA04 | Pampa del Asador-1 | 2.0374 | 0.9793 | 18.3670 | 68.58 | 159.40 | 1.959 | 71335.9 | 262.00 | 502.2 | 6.4200 | 41758.9 | 283.07 | 29108.5 |
| SCPA06 | Pampa del Asador-2 | 2.3797 | 0.8101 | 20.7581 | 62.22 | 317.23 | 2.847 | 72842.2 | 559.80 | 612.3 | 5.2645 | 39097.2 | 390.78 | 33778.0 |
| SCPA08 | Pampa del Asador-2 | 2.3970 | 0.8130 | 20.7375 | 65.28 | 308.95 | 3.078 | 73626.4 | 568.80 | 593.3 | 5.1069 | 41470.3 | 390.85 | 33476.4 |
| SCPA10 | Pampa del Asador-2 | 2.3322 | 1.2455 | 18.4157 | 82.49 | 186.75 | 1.614 | 69978.0 | 0.00 | 446.1 | 9.3777 | 41190.0 | 241.34 | 29658.0 |
| SCPA11 | Pampa del Asador-1 | 2.0222 | 0.9635 | 18.0948 | 67.78 | 155.76 | 2.490 | 70129.5 | 262.60 | 407.9 | 6.4807 | 42974.7 | 287.20 | 29870.7 |
| SCPA12 | Pampa del Asador-1 | 2.4702 | 0.8394 | 21.3119 | 60.81 | 270.22 | 3.445 | 72251.3 | 529.30 | 544.2 | 5.2732 | 41068.4 | 378.60 | 34134.6 |
| SCPA13 | Pampa del Asador-2 | 2.5651 | 1.4042 | 18.9593 | 88.51 | 141.49 | 1.573 | 70867.1 | 0.00 | 515.0 | 9.8362 | 41727.6 | 219.34 | 29552.0 |
| SCPA14 | Pampa del Asador-1 | 2.0535 | 1.0895 | 18.1563 | 67.44 | 163.50 | 2.440 | 67603.8 | 251.10 | 515.2 | 6.3018 | 42257.5 | 278.88 | 29002.7 |
| SCPA15 | Pampa del Asador-1 | 2.0462 | 1.0070 | 18.2547 | 67.31 | 176.34 | 2.687 | 71773.2 | 256.90 | 464.6 | 6.0564 | 42797.5 | 282.89 | 29708.2 |
| SCPA16 | Pampa del Asador-3 | 2.3533 | 0.8367 | 20.7488 | 62.92 | 302.28 | 2.297 | 70500.9 | 564.40 | 517.7 | 5.4186 | 39304.2 | 390.15 | 33898.5 |
| SCPM01 | Pampa del Asador-2 | 2.4250 | 1.3603 | 19.2156 | 88.05 | 177.30 | 1.776 | 68225.6 | 0.00 | 451.4 | 8.3408 | 39471.3 | 237.77 | 29098.1 |
| SCPM02 | Pampa del Asador-1 | 2.1178 | 1.0805 | 18.8095 | 70.05 | 174.00 | 2.197 | 69098.1 | 274.70 | 148.5 | 6.8236 | 40784.3 | 283.45 | 29479.1 |
| SCPM03 | Pampa del Asador-2 | 2.6210 | 1.4381 | 19.5977 | 82.42 | 170.40 | 1.964 | 70112.5 | 0.00 | 480.0 | 9.1220 | 40674.1 | 216.16 | 29414.1 |
| SCPM05 | Pampa del Asador-1 | 2.0812 | 0.9794 | 18.4161 | 72.41 | 163.96 | 1.787 | 69768.1 | 292.70 | 503.2 | 6.7207 | 40890.2 | 281.75 | 29144.2 |
| SCPM06 | Pampa del Asador-1 | 2.0786 | 0.9915 | 18.7064 | 68.77 | 186.64 | 2.446 | 70106.6 | 249.10 | 533.0 | 6.6276 | 40099.5 | 282.34 | 29400.5 |
| SCPM08 | Pampa del Asador-1 | 2.0179 | 1.0580 | 18.0099 | 70.61 | 165.34 | 2.466 | 71665.7 | 266.80 | 482.6 | 6.0616 | 43674.1 | 283.81 | 29509.8 |
| SCPM09 | Pampa del Asador-1 | 2.0617 | 0.9721 | 18.1818 | 71.55 | 166.92 | 2.024 | 67160.4 | 294.20 | 486.3 | 6.7210 | 42741.0 | 281.89 | 29945.9 |
| SCPM10 | Pampa del Asador-1 | 2.0872 | 1.0068 | 18.5985 | 72.82 | 165.00 | 1.963 | 73898.9 | 283.40 | 513.9 | 5.8181 | 43129.5 | 282.32 | 29615.0 |
| SCPM11 | Pampa del Asador-1 | 2.0874 | 1.0142 | 18.5903 | 72.10 | 169.19 | 2.160 | 67686.1 | 232.80 | 532.2 | 6.9185 | 39630.9 | 280.38 | 29444.2 |
| SCPM12 | Pampa del Asador-1 | 2.0580 | 1.0420 | 18.3837 | 72.36 | 172.38 | 2.268 | 66641.2 | 245.20 | 539.0 | 7.1851 | 41294.3 | 282.07 | 29311.3 |
| SCPM13 | Pampa del Asador-1 | 2.0736 | 1.0352 | 18.6703 | 73.57 | 176.04 | 2.610 | 68016.1 | 245.30 | 506.0 | 6.2929 | 37106.3 | 277.93 | 29295.3 |
| SCPM14 | Pampa del Asador-2 | 2.3823 | 1.4270 | 18.6764 | 96.92 | 178.64 | 1.816 | 70304.1 | 0.00 | 472.3 | 8.9260 | 43273.0 | 241.34 | 29799.2 |
| SCPM15 | Pampa del Asador-1 | 2.0804 | 0.9766 | 18.5326 | 78.91 | 166.00 | 2.351 | 66991.0 | 274.60 | 516.4 | 6.4098 | 42044.7 | 279.76 | 27303.1 |
| SCPM16 | Pampa del Asador-3 | 2.3572 | 0.8407 | 20.5954 | 66.47 | 303.49 | 3.368 | 75297.3 | 611.80 | 570.2 | 5.2568 | 39264.7 | 392.43 | 33379.2 |
| SCPM17 | Pampa del Asador-1 | 2.0595 | 1.0674 | 18.4998 | 73.13 | 169.10 | 2.548 | 69376.1 | 279.20 | 452.7 | 6.5235 | 42390.0 | 279.54 | 29343.4 |
| SCPM18 | Pampa del Asador-3 | 2.3542 | 0.8151 | 20.3848 | 64.26 | 301.85 | 3.610 | 65464.8 | 591.20 | 549.9 | 5.9566 | 40688.5 | 384.20 | 33381.6 |
| SCPM19 | Pampa del Asador-1 | 2.0707 | 1.0388 | 18.4687 | 76.11 | 169.63 | 2.245 | 71991.3 | 284.80 | 493.0 | 6.1041 | 44493.9 | 282.99 | 29599.6 |
| SCPM20 | Pampa del Asador-2 | 2.3493 | 1.3690 | 18.6227 | 92.14 | 173.80 | 2.088 | 65470.4 | 62.50 | 285.7 | 9.4515 | 41467.3 | 239.84 | 29587.0 |
| SCPM21 | Pampa del Asador-2 | 2.3490 | 1.3056 | 18.6630 | 86.04 | 156.19 | 1.513 | 67415.2 | 0.00 | 437.7 | 9.3731 | 40799.3 | 239.73 | 29485.1 |

Table 2. NAA Results for Santa Cruz (continued)

with a tube current of 17µA. The beam dimensions are about 2 x 3 mm. Measurement times were 180 seconds. The counting rate was approximately 1,200 counts per second for samples larger than the minimum recommended size. Smaller samples produced count rates as low as 300 counts per second. Peak deconvolution was accomplished using the Bruker spectral analysis package which enabled measurement of thirteen elements in most samples, including K, Ti, Mn, Fe, Zn, Ga, Rb, Sr, Y, Zr, Nb, Pb, and Th. The instrument was calibrated using compositional data from a series of well-characterized source samples in the MURR obsidian reference collection, including eleven Mesoamerican sources (El Chayal, Ixtepeque, San Martin Jilotepeque, Guadalupe Victoria, Pico de Orizaba, Otumba, Paredon, Sierra de Pachuca, Ucareo, Zaragoza, and Zacualtipan) and three sources Peruvian (Alca, Chivay, and Quispisisa). Consensus values for the obsidian calibration sources were previously determined at MURR (using both NAA and XRF) and other laboratories (XRF only). Concentration ranges for the reference samples span the range of probable concentrations for obsidian from different sources around the world.

NAA is a technique that analyzes a larger number of chemical elements (up to 32), it is more expensive and takes several weeks to collected the data. It is also destructive. NAA of obsidian at MURR consists of two neutron irradiations by neutrons followed by three

of the emitted measurements gamma radiation. The first irradiation for five seconds was applied to samples weighing about 100 mg encapsulated in a polyethylene vial using a thermal neutron flux of 8×10^{13} n cm⁻² s⁻¹. This short irradiation was followed a 25minute decay and 12-minute count which allowed measurement of seven short-lived elements (i.e., Al, Ba, Cl, Dy, K, Mn, and Na). The second irradiation was applied to a bundle of obsidian samples and standards weighing between 50 and 250 mg which were encapsulated in high-purity quartz vials and subjected to a long irradiation of 70 hours using a thermal neutron flux of 5×10^{13} n cm⁻² s⁻¹. The long irradiation was followed by two gamma-ray counts. The first count was performed between seven and eight days after the end of irradiation, using a sample changer to count each sample for 30 minutes, to detect seven medium-lived elements (i.e., Ba, La, Lu, Nd, Sm, U, and Yb). The second count was performed about four weeks after the end of irradiation, using the sample changer for three hours per sample, to detect fifteen longlived elements (i.e., Ce, Co, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Sr, Ta, Tb, Th, Zn, and Zr). When the long irradiation is performed, the barium concentration from measurement of the medium-lived isotope (i.e., ¹³³Ba) is normally superior and it is used in lieu of the value for Ba measured following the short-lived The irradiation. data from all three converted measurements were to concentrations by comparing the unknown

| Locality/Site | Samples (n) | Provenance | Observations |
|---------------|-------------|------------------|------------------------------|
| NCC | 28 | PA 1 | Analyzed by XRF and NAA |
| NCC | 11 | PA 2 | Analyzed by XRF and NAA |
| NCC | 2 | PA 3 | Analyzed by XRF and NAA. |
| | | | Characterized by very low Sr |
| AV | 12 | Unknown Source a | Characterized by high Zr |
| AV | 2 | Unknown Source b | |
| AC | 2 | Unknown Source c | |

Table 3. Provenance and techniques applied.

samples to the count rates for standards counted with the samples. All concentration data were compiled into a spreadsheet.

The detailed results by elements and provenience are respectively depicted in Tables 1 and 2.

Of the 14 artifacts from Alero del Valle, 12 belong to one source and two to another (AV17 and 18). The two samples from Aristizábal Cave belong to a third unknown source. At the moment we cannot attribute these three unknown sources with the other Patagonian sources in the MURR database, but we can presume that Unknown Source b could potentially match Cordillera Baguales.

Of the known sources, there is a green striped type of obsidian named Cordillera Baguales, which is found in Lago Argentino, and in the Fell and Pali Aike caves, where it represents one-third to one-fifth of the total obsidian (Stern and Franco 2000). In other words, it was procured by peoples living to the east and south of the source, particularly along the Atlantic coast (Fig. 4). It is characterized by very small amounts of Sr in ppm, as Unknown Sources a and b.

Discussion and Conclusion

New data obtained for obsidian artifacts from diverse locales in Santa Cruz province, Argentina have been found to contain trace elements indicating diverse origins. Detailed XRF and NAA analyses show that the provenance of samples from NCC is the wellknown source of PA, the obsidian source most often used in southern Argentine Patagonia. These artifacts have the fingerprints of the three sub sources differentiated by Stern (1999). Tools made using this natural glass are found at sites in the provinces of Chubut and Santa Cruz, in the cordillera, in the central sector and along the Atlantic coast (Belardi et al. 2006, Fernandez et al. 2015, Stern 1999, Castro Esnal et al. 2011). However, it is worth mentioning that obsidian pebbles collected at secondary sources in the North Central Coast of Santa Cruz also originated from the same were primary source, and displaced downstream from the Andes, under what are called the "Rodados Tehuelches" or "Patagónicos" and "Gravas Tehuelches" (i.e., Auer 1956, Fidalgo and Riggi 1965, Martínez and Kutschker 2011, Franco et al. 2017) which



Figure 3. Rb-Sr Bivariate plot showing separation of three obsidian types.



Figure 4. Cordillera Baguales and southernmost Patagonia sites.

are ubiquitous outcrops of pebbles and boulders with a diversity of rocks and varied lithology available depending on the area. Hence, due to the existence of obsidian nodules in the eolian deposits of the northeast coast of Santa Cruz, we suggest the possibility that obsidian nodules from PA were transported by some of the geological episodes deposited "rodados that the patagónicos" in the region (Martínez and Kutschker 2011). Similar PA obsidian was found in a secondary source 170km southeast of the main Pampa del Asador source (Franco et al 2017). Therefore, the secondary sources existing in the northeastern coast of Santa Cruz might contain some isolated PA obsidian nodules useful for stone tool manufacture, a fact that needs further investigation. In southeast Santa Cruz. obsidian was transported along the Chico River valley. Hence, some considerations may be made on the obsidian from unknown sources from AV and AC. Chaitén obsidian was found in archaeological sites of southern Santa Cruz. Cordillera Baguales, a green obsidian, is the most common obsidian in inland southern

Patagonia. Among coastal sites, the also green Seno Otway obsidian is predominant. The only relationship we could establish is that Alero del Valle 1 has some resemblance to Cordillera Baguales, based on Mn, Rb, Sr, and particularly a very high Zr. Inhabitants from the Pali Aike region utilized obsidian from the main southern sources: Pampa del Asador, Cordillera Baguales and Seno Otway.

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The International Association for Obsidian Studies (IAOS) was formed in 1989 to provide a forum for obsidian researchers throughout the world. Major interest areas include: obsidian hydration dating, obsidian and materials characterization ("sourcing"), geoarchaeological obsidian studies, obsidian and lithic technology, and the prehistoric procurement and utilization of obsidian. In addition to disseminating information about advances in obsidian research to archaeologists and other interested parties, the IAOS was also established to:

- 1. Develop standards for analytic procedures and ensure inter-laboratory comparability.
- 2. Develop standards for recording and reporting obsidian hydration and characterization results
- 3. Provide technical support in the form of training and workshops for those wanting to develop their expertise in the field.
- 4. Provide a central source of information regarding the advances in obsidian studies and the analytic capabilities of various laboratories and institutions

MEMBERSHIP RENEWAL FORM

We hope you will continue your membership. Please complete the renewal form below.

NOTE: You can now renew your IAOS membership online! Please go to the IAOS website at <u>http://members.peak.org/~obsidian/</u> and check it out! Please note that due to changes in the membership calendar, your renewal will be for the next calendar year. Unless you specify, the *Bulletin* will be sent to you as a link to a .pdf available on the IAOS website.

- Yes, I'd like to renew my membership. A check or money order for the annual membership fee is enclosed (see below).
- Yes, I'd like to become a new member of the IAOS. A check or money order for the annual membership fee is enclosed (see below). Please send my first issue of the IAOS *Bulletin*.
- Yes, I'd like to become a student member of the IAOS. I have enclosed either an obsidian-related article for publication in the IAOS *Bulletin* or an abstract of such an article published elsewhere. I have also enclosed a copy of my current student ID. Please send my first issue of the IAOS *Bulletin*.

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