

International Association for Obsidian Studies

Bulletin

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CONTENTS

News and Information	1
Notes from the President	2
Structural Water Variability in Obsidian	8
Sub-Sources around Volcán Tequila, Mexico	14
A 2000Kyr Paleo-Temperature Curve	36
Instructions for Authors	38
About the IAOS	39

International Association for Obsidian Studies

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Web Site: http://www.deschutesmeridian.com/IAOS/

NEWS AND INFORMATION

NEWS AND NOTES

Have news or announcements to share? Send them to <u>IAOS.Editor@gmail.com</u> for inclusion in 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!

CALL FOR NOMINATIONS: SECRETARY/TREASURER AND WEBMASTER

We thank Lucas R. M. Johnson and Craig Skinner for their service as IAOS Secretary/ Treasurer and IAOS Webmaster. Craig has served as Webmaster since the beginning, and created our incredibly helpful IAOS web site. Thank you both for your service! We are now seeking nominations for both positions. If you are interested in either of these roles, please reach out to IAOS President, Dora Moutsiou moutsiou.theodora@ucy.ac.cy

Winter 2024

NOTES FROM THE PRESIDENT

Hello IAOS members and welcome to 2025! I hope everyone had a happy, relaxing and safe holiday and may the new year bring many joyful moments and exciting obsidian experiences! I can hardly believe how fast 2024 went by, not least because of having to juggle motherhood and academia. Once again, several scientific events took place last year and plenty is also scheduled for this year, giving us the opportunity to meet and discuss all things obsidian!

2024 saw the publication of the IOC 2021 proceedings in a volume that highlights a diverse range of research themes. Reflections on Volcanic Glass: Proceedings of the 2021 International Obsidian Conference (Contributions of the Archaeological Research Facility at University of California Berkeley, Number 70) contains contributions by M. Steven Shackley, Lucas Johnson et al., Kata Furholt, Clive Bonsall et al., Dagmara Werra et al., Ben Smith et al., Emiliano Melgar Tísoc, et al., Donna Nash, Franco Foresta Martin et al., and Nico Tripcevich et al. featuring studies from across the globe, organised broadly by region, including Europe, Africa, Central America, America, South and methodological and developments. The volume, which is edited by Lucas R.M., Johnson, Kyle P. Freund and Nicholas Tripcevich, can be downloaded for free from this permalink:

https://escholarship.org/uc/item/75c689n2 (also available at the IAOS website). The volume and its contributors is a testament to the fact that although small, our obsidian community is very active and engaging.

Upcoming events to look forward to in 2025 include the 90th Annual Meeting of the Society for American Archaeology (SAA) in Denver, Colorado, 23-27 April, as well as Great Basin Anthropological Association (GBAC) Conference between October 15-18 in Reno, Nevada and the Society for Cultural Anthropology Biennal, May 8-11, in Stony Point, New York. We are also aiming to strengthen our reach to the other side of the pond with engaging the European archaeological community in the forthcoming Computer Applications and Quantitative Methods in Archaeology (CAA) International Conference taking place in Athens, Greece, 5-9 May 2025, and at the 31st Annual Meeting of the European Association of Archaeologists (EAA) in Belgrade,

Serbia, 3-6 September 2025. There is an exciting obsidian session planned for the latter event (see the flyer in this issue of the *Bulletin*).

An important international effort organised by the Global p-XRF Network (GopXRF.net) and endorsed by the European Academy of Sciences and Arts, has scheduled a series of online Colloquia on the hot topic of portable XRF for cultural heritage, art and archaeology, geoarchaeology issues. I am sure many of you will find it very useful and interesting or may even want to actively participate. The Colloquia are video recorded, and reviews or case study presentations can be submitted for publication in PEASA free of charge (www.peasa.eu). If you are interested in participating in this colloquium, know someone who might be, or would like to propose a topic for the series, please feel free to reach out to Michaela at michaela.schauer@univie.ac.at and/or Ioannis at ioannis.liritzis@euro-acad.eu; or ioannis.liritzis@almamater.si.

We hope that the move of the IAOS website to its new permanent Internet address will be completed in 2025. We have purchased the **obsidianstudies.org** domain name but some web hosting issues have resulted in some little delays in our move. We will, of course, let you know when we go live.

We are looking for a webmaster if anyone is interested in signing up for the role, many thanks to Alex Nyers for his invaluable help thus far! Lucas R.M. Johnson is also stepping down as the IAOS secretary and treasurer so anyone interested in this position, do get in touch. Thank you for all your hard work, Lucas!

Lastly, please consider submitting an article, research update, or lab report to the IAOS Bulletin. You can submit your work to Carolyn Dillian at IAOS.Editor@gmail.com. And, please, do not forget to renew your IAOS membership dues as they help support student research, awards, and travel stipends.

Dora Moutsiou <u>moutsiou.theodora@ucy.ac.cy</u> Special Scientist Archaeological Research Unit University of Cyprus





COLLOQUIA ON PORTABLE X-RAY FLUORESCENCE

The Global p-XRF Network (GopXRF.net)

Endorsed by the

European Academy of Sciences & Arts/ STEMAC Expert Group

Organises a series of online Colloquia

The fast, accurate, cost effective, non-destructive techniques applied in archaeology & cultural heritage to Archaeo- & Geoarchaeo-materials have always been a focus of archaeological sciences; The last centuries also saw the development of a series of portable instruments with X-Ray Fluorescence analysis being one of the first methods introduced.

Since its introduction to the commercial market in the 1950s, portable X-Ray Fluorescence (pXRF) equipment has seen significant improvements. Fortunately, the once large, heavy, and radioactive box has been replaced by a handheld, somewhat light instrument that produces results that are on par with those obtained in a lab. These days, a wide range of industries, including archaeological sciences, use these instruments extensively.

One of the greatest challenges for pXRF studies remaining until today is the definition of precision, accuracy and in general standards and guidelines for archaeological and cultural heritage applications.

Along this aim we, as the initiators and core team, undertook the task to initiate an international p-XRF network that serves as a scientific home, as a hub for the exchange of knowledge, skills and support of the archaeology and heritage p-XRF community. The goal is to establish a self-sustaining egalitarian network of practitioners. The development of the network will be determined by the community's needs and interests.

Along our aims and objectives several topics shall be touched on a Series of online Colloquia presented by experts in the field. Two experts one from natural sciences and one from humanities (archaeology, anthropology, art, history), shall present a half an hour talk each and then 30mins discussion:

Colloquia schedule:

30 min – Presentation Archaeological Specialist
30 min – Presentation Natural Science Specialist
30 min – Discussion

Topics include but not limited to:

- Provision and promotion of resources and guidance to XRF community
- Focused opportunities for the exchange of ideas and knowledge
- Case study problems
- Exemplary Applications

The Colloquia are video recorded, and reviews or case study presentations can be submitted for publication in PEASA free of charge (<u>www.peasa.eu</u>). If you are interested in participating in this colloquium, know someone who might be, or would like to propose a topic for the series, please feel free to reach out to Michaela at <u>michaela.schauer@univie.ac.at</u> and/or loannis at <u>ioannis.liritzis@euro-acad.eu; ioannis.liritzis@almamater.si</u>.

On behalf of the Global p-XRF Network Core Team Michaela Schauer (<u>VIAS</u>, Uni. Vienna,) & Ioannis Liritzis (EASA & AMEU, https://adahn.almamater.si/)



Call for Contributions for Session: #128 Submission Deadline: 6th February 2025

The Production and Diffusion of Obsidian Artefacts: Exploring Socio-Economic and Symbolic Behaviours from a Techno-Functional Perspective

The archaeological records of material culture are fundamental for understanding past societies, where lithic industries often play a key role. Obsidian has been frequently selected as a raw material for tool making, particularly in regions with volcanic rocks. Studies on obsidian have significantly expanded over years, ranging from the analysis of its geological provenance to its technological, typological and functional characterisation. These approaches allow us to trace the mobility of communities providing a deeper understanding of the economic, social and symbolic dynamics of the societies that relied on this specific lithic resource.

This session aims to bring together researchers specialising in different methods and approaches to study lithics, with a focus on techno-typological and functional analyses of obsidian. Obsidian is particularly suitable for analyzing technological processes, typological variations, and use-wear patterns. We welcome contributions that illustrate the diversity of technological solutions used for its extraction, exploitation, circulation and diffusion of this material through case studies from various regions worldwide, aiming to highlight similarities and differences that enhance our understanding of its role in past societies.

Key themes of the session will include:

- Comparative studies of core reduction techniques and technological strategies
- Typological analyses of tool assemblages
- Experimental archaeology for understanding the techniques of knapping and use
- Use-wear studies that shed light on tool function and activity areas
- Data sharing for standardisation of methodologies related to technology and function
- Procurement, diffusion and circulation of obsidian

By welcoming contributions from different regions and periods, we encourage discussion and collaboration among specialists to advance our understanding of obsidian as a lively material in lithic studies. This session seeks to generate new perspectives and interdisciplinary approaches to broaden our knowledge in lithic studies and strengthen academic exchange.

Keywords: Obsidian, Techno-Typology, Use-wear Analysis, Comparative Lithic Studies, Diffussion

Organisers

Zeynep Beyza Agirsoy (Turkey)- Ankara University, Faculty of Letters, Department of Archaeology-Prehistory **Idaira Brito-Abrante (Spain)**- Tarha Research Group, Departamento de Ciencias Históricas, Universidad de Las Palmas de Gran Canaria

Bogdana Milić (Spain)- National Spanish Research Council, Milá y Fontanals Institute (IMF-CSIC) – ASD research group **Fiona Pichon (Spain)**- National Spanish Research Council, Milá y Fontanals Institute (IMF-CSIC) – ASD research group **Ivana Jovanović (United Kingdom)**- The British Museum, Department of Britain, Europe and Prehistory

Call for Session Participants: 27th meeting of SAfA at the University of Algarve in Faro, hosted by the Interdisciplinary Centre for Archaeology and Evolution of Human Behaviour (ICArEHB)

Session title: African Perspectives on Obsidian Studies in Archaeology

Session organizers:

- Benjamin D. Smith (Cultures et Environnements, Préhistoire, Antiquité, Moyen Age (CEPAM) CNRS - UMR 7264 -Université Côte d'Azur), <u>bdsmith1991@gmail.com</u>
- Lamya Khalidi (Cultures et Environnements, Préhistoire, Antiquité, Moyen Age (CEPAM) CNRS -UMR 7264 -Université Côte d'Azur)
- Yonatan Sahle (Department of Archaeology, University of Cape Town, Rondebosch 7701, South Africa)

Description:

Obsidian has played a central role in archaeological studies of past technology in Africa for decades. Much of this research has centered on compositional studies aimed at sourcing tools made from volcanic glasses to their geographic origins. The past two decades in particular have seen an increase in obsidian sourcing studies due the introduction of portable X-ray fluorescence spectroscopy to the discipline, prompting a re-examination of analytical techniques and legacy datasets. Nonetheless, Africa's potential for advancing the field of obsidian research continues to be underestimated despite its unique geology, exceptional paleontological and archaeological record, and numerous obsidian hotspots.

More than just an easy-to-source raw material, obsidian has also held an enduring place in the imaginations of natural scientists and Africanists since early historical periods. In fact, the term derives from *Obsidius*, a Roman general said to have collected the material in Ethiopia. In archaeological contexts Obsidian constitutes a unique and enduring component of many lithic toolkits dating to all periods across the continent. Ethiopia alone contains both the oldest examples of obsidian tool manufacture, and examples of contemporary uses by hide-workers whose economic and ontological worlds center around this material.

This session welcomes all recent studies of archaeological obsidian from across the continent. These may include studies of volcanic glass geochemistry, obsidian geology and geochronological studies, techno-typological and/or functional aspects of obsidian artifacts as well as recent research into obsidian sources, quarries, lithic economies, ethnoarchaeology, human dispersal, population mobility, history, and materiality theory. To celebrate the often-overlooked importance and potential of the continent's obsidian resources and their use from deep prehistory until today, the session organizers will guest edit a special issue in a journal (TBD) to feature the results of recent and ongoing obsidian research across the continent.

Instructions for paper submission:

Participants can submit their abstracts during the call for individual submissions, which will be open from December 5, 2024 – January 31, 2025. Session participants <u>must select the session title</u> ("African Perspectives on Obsidian Studies in Archaeology ") when they submit their abstract otherwise it will not be associated with this session. All relevant information for individual submissions will be posted on <u>https://safa2025.icarehb.com.</u> A preliminary program will be posted on the <u>SAfA</u> website in January 2025.



International Obsidian Conference 2026 (Armenia, Yerevan)



The Institute of Geological Sciences and Institute of Archaeology and Ethnography of the Armenian National Academy of Sciences announce the International Obsidian Conference to be held in Yerevan, 2026.





The Gutansar obsidian carrier



Products of explosive eruptions of rhyolite pumice and perlite pyroclastics(left). Obsidian cliff from Pokr Arteni volcano (right).

1st Circular will be distributed in May 2025

Local Organization Committee,

Obsidian exhibition at the Geological Museum

The Gutansar volcanic complex represents a bi-modal volcanic system: rhyolithic dome c u t b y b a s a l t i c - a n d e s i t e c i n d e c o n e. It is o n e o f m o s t archaeological important obsidian sources in the South Caucasus.

Conference excursion: We are going to visit Arteni obsidian volcano (1.5 Ma), Gutansar obsidian carrier, Barozh middle Paleolithic open air site.





Chairs: Dr. Sci. Kh. Meliksetian (km@geology.am) Dr. A. Bobokhyan (arsenbobokhyan@yahoo.com) Dr. Sci. R. Badalyan (r.badalyan@yahoo.com)

Artifacts from the test trench at Middle Paleolithic site Barozh 12



Further information will be available on the website of the institute of Geological sciences https://geology.am/en/

Fellowship in Honor of Ana Steffen

Dear IAOS Members,

In keeping with Ana Steffen's wishes, donations in honor of her memory and accomplishments may be made to the Earthwatch Institute's Girls in Science program. The Girls in Science fellowship empowers teens to expand their interest in science and technology and to build confidence through hands-on environmental research. Since launching the program in 2016, Earthwatch has awarded 70 high school girls the fully funded opportunity to perform scientific research alongside female experts in the field. Ana was one of those experts.

You can read more about Earthwatch and their fellowship programs here: https://earthwatch.org/education/education-fellowships/student-fellowships/girls-in-science.

Donations may be made at <u>https://earthwatch.org/support-us/donate</u>. On the website, please indicate a donation to the **Dr. Ana Steffen Fund** in the *Designate Your Gift* "Honor/Memorial" dropdown menu.

All donations are 100% tax-deductible and you will receive a gift acknowledgement for your tax records. Should you have additional questions or need assistance with a donation you may reach out to Heather Wilcox, Earthwatch's Director of Giving, at https://www.hwilcox@earthwatch.org

Please forward this to others in Ana's community of friends and colleagues. Thank you for your generosity as we celebrate Dr. Ana Steffen's remarkable life and achievements by creating opportunities for future women in science!

Ann Ramenofsky, Shawn Penman, Rachel Loehman, Nancy Karraker, and Eliza Frank.



P.S. A link to one of several lovely articles published at the time of Ana's passing <u>https://losalamosreporter.com/2024/02/17/valles-</u> <u>caldera-mourns-for-dr-ana-steffen-who-passed-away-</u> <u>feb-16/</u>

Photo screenshot from the Valles Caldera Instagram page: <u>https://www.instagram.com/vallescaldera/ree</u> <u>l/C3bVbKrLi-s/</u>

STRUCTURAL WATER VARIABILITY IN OBSIDIAN: RECOMMENDED VALUES FOR CHRONOMETRIC ANALYSIS BASED ON SOURCES IN EASTERN CALIFORNIA

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Abstract

The water content of obsidian is one of the two major determinants of hydration rate. Standard practice in obsidian hydration dating (OHD) is to segregate specimens by geochemical source and assign a hydration rate to the source, which amounts to a rough proxy for mean water content; the intra-source water variability then becomes a major component of the statistical error (uncertainty) in the computed age. In this paper we describe and quantify the variability of structural water based on 304 specimens from thirteen geochemical sources in eastern California and western Nevada, to provide a basis for estimating OHD age uncertainty. We find the coefficient of variation (CV =standard deviation/mean) of the structural water content to be in the 5–40% range for these sources, with 30% as a recommended value in OHD analyses.

Introduction

The water content of obsidian is of great interest archaeologically, as it is one of the two major determinants of hydration rate (the other is temperature history, not addressed here; see Rogers and Stevenson 2023a). Standard practice in obsidian hydration dating (OHD) is to segregate specimens by geochemical source and assign a hydration rate to the source, which amounts to a rough proxy for mean water content. Measuring the water content for a specimen and computing a hydration rate for each specimen yields a significant improvement in accuracy (Rogers and Stevenson 2022a); however, it is not customary in archaeological analyses since measurement of water content requires specialized laboratory methods and is frequently destructive to the specimen.

Ascribing a rate to the source corrects for the mean value of structural water for that source, and the intra-source water variability contributes to statistical error in the computed age; it is, in fact, a major component of the uncertainty. In this paper, we describe and quantify the variability of structural water based on 112 specimens from the Bodie Hills geochemical source in eastern California. We further illustrate the variability in structural water across sources by extending the analysis to 191 specimens from twelve other obsidian sources in eastern California and western Nevada, to provide a basis for estimating age uncertainty in OHD calculations.

Analytical Framework

Water occurs in obsidian as two species, molecular water (H₂O_m) and hydroxyl (OH); the total water, H_2O_t , is the sum of the two. Zhang and colleagues (Zhang et al. 1991; Zhang and Behrens 2000; summarized and discussed in Zhang 2008) developed an equation relating water content, pressure, and temperature to hydration rate; however, their data set is for conditions of interest in vulcanology (900 \leq T \leq 1100K and P \approx 500 mPa) and their equation does not yield valid rates at archaeological conditions. Rogers and Stevenson (2022b) subsequently derived an equation for the hydration rate of obsidian for archaeological conditions ($200 \le T \le 300K$ and P = 0.1 mPa):

$$k = \exp[36.29 - (10005 - 354^{*}H_{2}O_{t})/T] \quad (1)$$

where k is hydration rate in $\mu^2/1000$ years, H₂O_t is total water content in wt.%, and T is temperature in Kelvins. The equation is based on a data set of 29 data points, drawn from seven geochemical sources, with temperatures ranging from 20°C to 180°C (293.15K to 453.15K). The form of equation (1), which is similar to the equation of Zhang et al. (1991) but with different numerical constants, is based on glass science and the Arrhenius equation. The numerical constants for the least-squares best fit were computed by the Levenberg – Marquardt method using PSIPlot (Rogers and Stevenson 2022b). The accuracy of this equation at typical archaeological conditions is affected by two factors: the accuracy with which H₂O_t can be measured. and the rms residuals between the data set and equation (1). Analysis showed that the error contribution by the measurement accuracy of water content was negligible, and the overall accuracy is dominated by the rms residuals; the resulting standard deviation of the computed rate is $\sigma_k \approx 0.3427 \text{ u}^2/1000 \text{ years}$ (Rogers and Stevenson 2022b).

Water content can be measured by infrared (IR) spectroscopic methods (Newman et al. 1986), since both water species absorb infrared. The IR absorbance of each species can be measured by transmission IR spectroscopy, and water content computed from the Beer-Lambert law (Newman et al. 1986). For a specimen of thickness t (cm) and density d (gm/L), the content of either species is

$$w = 100*M*A/(d*t*\varepsilon)$$
(2)

where w is in wt.%, M is effective molecular weight of water in gm/mole (=18.02 per Newman et al. 1986), A is IR absorbance in absorbance units, and ε is the molecular absorption coefficient (or extinction coefficient) for the water species being measured.

Use of equation (2) requires measurement of density, which can be determined by gravimetry (Archimedes' Principle). The glass specimen is weighed in air and again when immersed in a heavy liquid (typically Unigrav 1.6), and the density computed by

$$d_0 = m_0 * d_1 / (m_0 - m_1)$$
 (3)

where d_0 is the density of the obsidian, m_l is the weight of the specimen when immersed, m_o is weight of the specimen in air, and d_l is the density of the immersion liquid. To obtain valid results, the method requires careful control of accuracy, including calibration of the density of the immersion liquid for temperature; details of the method are described in Stevenson et al. (2019). Stevenson et al. (2019:234, Table 3) report a standard deviation of the density measurement in the range of 0.0009 – 0.0016 gm/ml.

Finally, the coefficient of variation of the hydration rate due to intra-source variability in water content, CV_{ke} , can be obtained by taking the partial derivative of equation (1) with respect to H_2O_t :

$$CV_{ke} = 354*\sigma_{H2Ot}/T$$
⁽⁴⁾

where T is effective hydration temperature in Kelvins and σ_{H2Ot} is the standard deviation of H₂O_t in wt.%.

Structural Water in Obsidian

Obsidian is a natural glass formed by cooling of a very hot magmatic melt under high pressure to typical archaeological temperatures and atmospheric pressure. The melt is a liquid, composed primarily of silica (SiO₂) and alumina (Al₂O₃), with no internal order at the molecular level; as the temperature is lowered the degree of order increases as a glass network starts to form (Shelby (2005:145ff). Typical temperatures for the magma are in the range of 900–1100K, with pressures around 500 mPa, while archaeological specimens are typically found at temperatures of about 293K and 0.1 mPa pressure (atmospheric pressure). As the melt cools and solidifies it passes through a temperature region known as the glass transition temperature, T_g , in which the properties of the melt change from viscous and rubbery to glass-like. Nominal values of T_g are 400–800K, with T_g decreasing as water content increases (Ochs and Lange 1999).

Both density and structural water content of archaeological obsidian are the result of the cooling history of the magma, which involves changes in both pressure and temperature. However, the processes which result in the final values differ, and the process resulting in the density is simpler than that which results in water content. The temperature coefficient of expansion of glasses is positive, which means density increases as the melt cools. Above T_g the increase in density as the melt cools is rapid because the molecules are relatively mobile and are able to pack closer together as the glass matrix forms; below Tg the matrix is essentially "frozen in" and the molecules cannot rearrange themselves, so any increase in density is due to thermal shrinkage of the matrix itself. Also, if the cooling pauses at some plateau the density change also pauses, so the pause has a effect negligible on final density. Furthermore, variations in pressure have very little effect on the density.

For structural water content, the critical parameters are the water loss rate and the length of time available to lose water; the observed water content in a specimen is then the integrated result of water loss rate over the cooling time. Water loss is more rapid at temperatures above T_g because water is lost both by bubble formation and by outward (Fickian) diffusion. Below T_g bubble formation cannot occur and the loss is due only to diffusion. In either case, the loss rate is

a strong function of temperature by the Arrhenius equation. Furthermore, even if the temperature decrease pauses, the water loss continues unabated, and the higher the temperature at which the pause occurs, the higher the water loss rate. Decreases in pressure tend to increase the water loss rate, while increases in pressure will retard it. Thus, even with identical initial and final conditions, two specimens with different cooling and pressure histories are unlikely to have the same water content, although the densities may be similar.

Data and Discussion

In the real world the cooling history is complex and involves changes in both temperature and pressure over time. There are probably significant variations in the cooling history experienced by natural obsidian specimens, even within a given flow, so variations in water content with the same chemistry and essentially the same density can be expected, and, in fact, experimental data show that the water content of natural obsidians can exhibit considerable variability (Ambrose and Stevenson 2004; Stevenson et al. 2019).

Table 1 shows total water content for 13 geochemically-identified obsidian sources from eastern California and western Nevada. In each case the mean and standard deviation of the water content was measured by Fourier Transform IR (FTIR); the hydration rate was computed by equation (1), and the coefficient of variation of the hydration rate (CV_{ke}) by equation (4).

The values of CV_{H2Ot} range from 5.8% (Mt. Hicks) to 53.5% (West Cactus Peak), with two major caveats. First, the highest value, for Coso West Cactus Peak, should be treated with caution. The water content data for West Cactus Peak appear to be bimodal, which may suggest the presence of an unidentified geochemical source (Rogers 2010; Stevenson et al. 1993) and may be

Source	Mean H20t, wt.%	Std dev H ₂ O _t , wt.%	CV _{H2Ot} **	Hydration Rate, k *	CVke**	N	Ref.
Casa Diablo Lookout Mountain, CA	0.389	0.056	0.144	13.90	0.069	5	1
Casa Diablo Sawmill Ridge, CA	0.352	352 0.053 0.151 13.30				5	1
Bodie Hills, CA	0.136	0.054	0.396	10.22	0.065	112	2
Coso West Sugarloaf, CA	0.620	0.160	0.258	18.14	0.190	22	3
Coso Joshua Ridge, CA	0.810	0.300	0.370	22.27	0.360	63	3
Coso Sugarloaf Mountain, CA	1.020	0.180	0.176	29.87	0.216	21	3
Coso West Cactus Peak, CA	1.010	0.540	0.535	27.28	0.650	20	3
Saline Range V1, CA	0.129	0.025	0.191	10.14	0.030	3	4
Saline Range V2, CA	0.147	0.007	0.045	10.37	0.008	2	4
Saline Range V3 CA	0.144	0.019	0.133	10.33	0.023	4	4
Mt. Hicks, NV	0.103	0.006	0.058	9.82	0.007	5	4
Pine Grove Hills, NV	0.136	0.056	0.412	10.25	0.068	9	5
Truman-Queen, NV	0.139	0.041	0.294	10.37	0.057	5	6

* Rate in $\mu^2/1000$ yrs. at EHT = 20°C; ** CV = standard deviation/mean; Refs listed in References Cited, below.

Table 1. Structural water variability and hydration rate in obsidians.

causing an unusually large standard deviation. Second, the rate values for Mt. Hicks are still under evaluation and the low 5.8% value of CV_{H2Ot} may not be real. Excluding these two sources, the remaining CV_{H2Ot} values fall in the 5-40% range, and the values of CV_{ke} fall in the 6–36% range.

Recommended Procedure in Obsidian Hydration Dating

The uncertainty in an age computed by OHD, as measured by the coefficient of variation CV_t , is given by (Rogers and Stevenson 2023a)

$$CV_t^2 = (2\sigma_r/r)^2 + CV_k^2 + CV_{hum}^2 + (0.116*\sigma_{EHT})^2$$
 (5)

where σ_r is the uncertainty in hydration rim reading (typically $\approx 0.1\mu$), r is the hydration rim reading, CV_k is the CV of the hydration rate, CV_{hum} is the CV of the rate due to humidity fluctuations (typically $\approx 6\%$), and σ_{EHT} is the standard deviation of the effective hydration temperature (typically $\approx 1^{\circ}$ C). In turn, CV_k is comprised of two terms,

$$CV_k^2 = CV_{ks}^2 + CV_{ke}^2$$
(6)

where CV_{ks} is the CV of the rate ascribed to the geochemical source (typically $\approx 5\%$) and CV_{ke} is the CV of the rate due to intra-source water variability (Table 1 above). The CV of rate due to intra-source water variability is in equation (4) above, so finally

$$CV_k^2 = CV_{ks}^2 + (354*\sigma_{H2Ot}/T)^2$$
 (7)

The two dominant terms in equation (5) are CV_{ke} and σ_{EHT} .

If the water content for each specimen is measured, the hydration rate k can be computed from equation (1), and then equation (7) is replaced by

$$CV_k = 0.3427/k$$
 (8)

which significantly reduces the uncertainty in age. However, if the water content is not measured for each specimen, and instead a rate is ascribed to the source, then equation (7) applies and a value of CV_{ke} must be assumed based on a model or data. If the source is one of those in Table 1, the corresponding value of CV_{H2Ot} can be used. If not, a conservative value of CV_{H2Ot} of 30% is recommended based on the data above. The equation for

uncertainty in Rogers and Yohe 2021 (equation 15 in that paper) assumes 30%. **References cited**

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CHARACTERISING OBSIDIAN SUB-SOURCES AROUND VOLCÁN TEQUILA, MEXICO

Chris Lloyd, Consulting Geologist

Abstract

Analysis by ICP-AES of 48 samples on and around the Volcán Tequila successfully identified eight obsidian sub-sources related to Volcán Tequila, as well as distinguishing two outlying flows. This is the first study to include all of these different flows in one common set of analysis. Bivariate scatter plots and PCA plots both clearly separated all ten flows, with Ba and Mn being the two strongest elements for discriminating these flows. One of these flows, here named Guevara, was a new discovery, which still needs additional mapping to determine its full size. The method of ICP-AES produced quality data and agreed well with past NAA analysis done at the MURR laboratory. The homogeneity of the elements sampled was generally quite good, though when the actual value is very low and near the limit of detection, the data gets very noisy. Comparing this new data set with past data helped to clear up the previous confusion as to which flow was sampled in previous studies. Geologically, three of these flows (La Joya, Santa Teresa, and Los Saavedra) are all rhyolite flow dome complexes with associated coulee flows that were subsequently covered in part by younger lava flows. This recognition of rhyolite flow dome complexes helps explain why obsidian of similar geochemical characteristics can be found in geographically distinct locations many kilometers apart, and thus complicates the concept of a single obsidian source or sub-source.

Introduction

This study is focused on the early rhyolite Tequila Flow Dome Complex (TFDC), and more particularly on the rhyolite flows that have obsidian. These obsidian flows have been studied by various authors over the years from both the geologic and archeological points of view, but no single study has actually focused on characterizing all the obsidian flows geochemically and determined exactly where they are located and described their geologic source. This study will attempt to combine and confirm the results of previous studies, to resolve the outstanding conflicting information, and to add to the understanding of the obsidian related to Volcán Tequila.

The opportunity to characterize all the obsidian sub-sources around Volcán Tequila arose when a source for multi-element assaying became available to the author while consulting for an un-related mineral exploration project that required "blank" (unmineralized) rock material to insert into their sample assay stream as part of normal Quality Assurance / Quality Control (QA/QC) protocol. Mineral exploration companies use this protocol to confirm that the assay company is cleaning the crushing circuit properly between samples and thus not contaminating the next sample. The exploration project was quite large, and a considerable number of blank samples were needed. This provided a unique opportunity to fund the analysis of multiple samples from many different sites around the volcano. It was also possible to complete many repeat analyses of the same sample to provide data on the homogeneity of the obsidian.

The homogeneity of the geochemistry of obsidian is something that has been identified since the early days of geochemical characterization of obsidian (Cann and Renfrew 1964; Stross et al. 1976), but since the work of Bowman et al. (1972), has seldom been well presented with repeatable data from either one sample site, or multiple sites. In addition to being able to do multiple repeat testing, this project allows for the comparison of ICP-AES analyses to the more commonly used NAA and XRF analysis in obsidian characterization, as three of the sampled flows on Volcán Tequila have both types of previous results available. The objectives of this study are to attempt to combine and confirm the results of previous studies, to correlate all the previous data with the new ICP-AES data, to resolve any outstanding conflicting information, and to add to the understanding of the obsidian related to the TFDC.

Past Obsidian studies in the Tequila Area

The extent of previous studies of the obsidian occurrences around the Tequila area is quite varied; some flows have received extensive sampling and little mapping, while most have been only briefly visited to collect samples for characterization studies, usually accompanied by a brief paragraph with no mapping to describe the whole area. Figure 1 shows the known obsidian sites around the Tequila area as red triangles.

The first description of the obsidian associated with Volcán Tequila was in Breton (1902). Cobean et al. (1971) reported the first obsidian samples from Volcán Tequila, but gave no information on who collected them or who generated the results included in the article. Additional results from those same samples were published in Ericson and Kimberlin (1977), along with brief site details. Demant (1979) produced the first detailed geologic map of Volcán Tequila. Part of La Joya flow was mapped in detail by Weigand and Spence (1982), but their published map has no recognizable landmarks, so it is unknown as to where their mapping or sample collecting was physically located.

Harris (1986) made a more complete description of the rhyolite flows and collected many obsidian samples, but did not map (or at



Figure 1. Location of known obsidian sites around the Tequila area.



Figure 2. Location of Volcán Tequila in Mexico along with known obsidian locations.

least identify) the actual extent of the obsidian in those rhyolite flows. In some of the rhyolite flows identified as having obsidian, no samples were collected and the data in the Masters thesis was never published. Only La Lobera (Darling 1993) and La Mora / El Pedernal / Teuchitlán (Esparza-López 2008), have well documented site descriptions.

Lewis-Kenedi et al. (2005) describes a few samples of obsidian from this area and dated some of them, but the presence of obsidian in the mapped rhyolite flows was generally not mentioned. Most of the sites shown in Figure 1 are described briefly in Glascock et al. (2010).

Regional Geologic Setting

Volcán Tequila is located in the western end of the Trans Mexican Volcánic Belt (TMVB) and immediately south of the Miocene aged Sierra Madre Occidental

(SMO) rhyolite province, as illustrated in Figure 2. The TMVB is a 900 km long volcanic belt stretching from coast to coast through central Mexico that formed starting approximately 10 million years ago, and is still active today. It is likely the result of the subduction of the Cocos plate under the North American plate (Ferrari et al. 1999; Ferrari et al. 2012) while other researchers consider it to be a rift zone similar to the East African Rift (Ferrari et al. 1999; Verma 2009; Verma 2015). It has a decidedly bimodal character, hosting large mafic basalt fields and local, but widespread, siliceous rhyolite centers in the form of calderas or rhyolite flow dome complexes, as well as large stratovolcanoes that are typically interlayered basalt through andesite and often some dacite. As is common in rift zones (and some subduction zones) the TMVB is rich in obsidian deposits, hosting the



Figure 3. Location of Volcán Tequila along the north edge of the Jalisco Block. Abbreviations – CA - Acatlán Caldera, CP - Primavera Caldera, CSP - San Pedro Caldera, VC - Volcán Ceboruco, VJ - Volcán San Juan, VN - Volcán Las Navajas, VS - Volcán Sanganguey, VT - Volcán Tepetltic, VTQ – Volcán Tequila.

majority (72) of the 92 known deposits in Mexico.

Volcán Tequila is located along the northern boundary of the Jalisco Block, currently considered a tectonic micro-plate that is rifting away from the rest of Mexico (Ferrari et al. 1999). It is bounded by the Tepic-Zacoalco Graben on the north side and the Colima Graben on the east as illustrated in Figure 3. Volcán Tequila is located within the northwest trending Tepic-Zacoalco Rift (Frey et al. 2007). The largest nearby volcanic features are the rhyolitic Primavera Caldera some 30 km to the SE (Mahood 1980) and the basaltic to dacitic Volcán Ceboruco stratovolcano approximately 75 km to the NW (Sieron and Siebe 2008). The history of the Volcán Tequila began with early basalt flows a little over 1 Ma followed by dacite flows and

multiple rhyolite flow dome complexes between 900,000 to 400,000 ya (Lewis-Kenedi et al. 2005). After a relative quiet period, volcanic activity began again around va when the main andesite 200,000 stratovolcano began to form, which lasted approximately 100,000 years and covered the whole centre portion of the volcanic field. This study is focused on the early rhyolite Tequila Flow Dome Complex (TFDC), and more particularly on the rhyolite flows that have obsidian. (Note: the term obsidian is used here to indicate glassy rhyolite / or vitrophyre (glassy rhyolite matrix with phenocrysts), while rhyolite is used to indicate crystalline (non glassy) rhyolite).

Sample Collection

This study collected 48 different samples from eight different rhyolite flows around Volcán Tequila, plus two nearby outlying flows (Huaxtla and La Quemada), that had not previously been mapped for their obsidian content as shown in Figure 4 below. The samples were collected mainly from outcrops, though a few were collected from fields where nearly all the rock material visible was obsidian nodules and these tended to extend for various square kilometres. Approximately 20 kg of rock was collected at each site from an area of 10 to 20 square meters. Each sample was then broken down into pieces about 1 cm in size and then split into multiple smaller samples of 0.5 to 1 kg. The smaller samples were sent to the accredited ALS Chemex laboratory in Zacatecas where they were dried, weighed and crushed and a 250-gram split pulverized to at least 85% passing 75 microns.

A 0.25 g sub-sample was split and sent to the ALS Chemex Vancouver assay laboratory for analysis using a four-acid digestion (nitric, perchloric, and hydrofluoric acid with a final dissolution stage using hydrochloric acid). This four-acid digestion breaks down most silicate and oxide minerals allowing for the "near-total" analyses of most minerals and analytes with an Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) finish. As part of the quality assurance and quality control procedures (QA/QC), each batch samples included certified of commercial reference standards for Au, Ag, Pb and Zn. The laboratory also inserted their own internal standards. Part of the QAQC procedure also inserts blanks that were supplied from the 48 different samples collected from the obsidian flows. The analysis package included 33 different chemical elements. Four of these elements



Figure 4. Location of the obsidian samples of C. J. Lloyd 2022-23 and rhyolite flows identified by Harris, 1986. IAOS Bulletin No. 73, Winter 2024 Pg. 18

(Fe, Mn, Sr and Zn) correspond with the elements covered in the Peabody-Yale Reference Obsidians (PYRO) reference set developed by (Frahm 2019) and one of the samples in the PYRO set is from this study area (La Joya). Each sample site ended up with at least two (the majority n > 20 as seen in Table 1) different assay results, which were then analysed and graphed to evaluate their homogeneity for various elements and then graphed to show the geochemistry variation between samples and different flows.

Geochemical Results

The package of analysis (ICP-AES) used in this study covered 33 different elements including: Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Sr, Th, Ti, U, V, W and Zn. The elements: Al, Ca, Fe, K, Mg, Na, S, and Ti were all measured in percentages (%), while the rest returned results measured in parts per million (ppm). The following elements returned values that were consistently below the level of detection for this particular method of analysis: Ag (<0.5 ppm), Bi (<2 ppm), Cd (<0.5 ppm), Co (<1 ppm), Ni (<1 ppm), S <0.01 %), Sb (<5 ppm), Th (<20 ppm), U (<10 ppm), and W (<10 ppm) and are thus not discussed any further. Other elements such as Cu, Mg and Mo had values that were very low, near the lower level of detection and thus not included in further analysis. The remaining elements were then tabulated, and the mathematical mean values and the Standard Deviation calculated, including: Al, Ba, Be, Ca, Cr, Fe, Ga, K, La, Mn, Na, P, Pb, Sc, Sr, Ti, V, and Zn. After a review of the results on bivariate scatter plots, and a review of the Standard Deviations, the following eight elements were selected as the best set of element to characterize the various obsidian flows around Volcán Tequila and are presented in Table 1.

Homogeneity of Different Elements

Studies of other obsidian sites have presented similar data, but rarely discuss the homogeneity of the individual elements. Since standard deviation is a direct function of the absolute size of the numerical average value, it is not very useful in determining the homogeneity of the particular element nor in comparing the level of homogeneity between elements. Thus, it was decided to try and compare variability within each sample site and between sample sites by dividing the standard deviation value by the average value to give a % type number such as was done in Yellin (1996). In this manner a very low percentage value indicated that there was little variation in the value between one assay and the other assays of the same element. Since the value is presented as a percentage (%), it also then can be used to compare variability (homogeneity) between different elements. The calculated results of this analysis are presented in the following four graphs, which are also ordered and marked to show the different obsidian flows as seen in Figures 5 through 8.

As illustrated, there are only four elements that have very low percentage values indicating low variability (i.e., good homogeneity) across all the samples. These elements are: Al, Be, K and Na (all below 3% variability), with Fe (2% to 5%), Zn (3% and 9%) and Ti (0% to 6%). The next most homogeneous elements are Ba and Mn, but in both cases have much higher variability (less homogeneity) in one of the obsidian flows compared to the other flows. That is, they both generally have variability in the 3% to 4% range in most flows but jump up to almost 40% for Ba and 7% for Mn in one particular flow - the La Joya flow for Ba and the Choloaca flow for the Mn. The high variability for Ba in that particular flow is probably a function of the fact that the average Ba values are extremely low (< 13 ppm) and

Table 1. Selected geochemical results (mathematical mean values in ppm except Fe which is in %).

Site Flow Name μ Ba Be Fe Mn P Sc S7 Za TQ03 La Joya 20 10 5.88 2.2 618 17.5 1 1.5 162 TQ18 La Joya 20 9 5.84 2.1 614 21.0 1.0 1.4 143 TQ21 La Joya 20 9 5.84 2.1 614 21.0 1.0 1.4 143 TQ21 La Joya 25 11 5.80 2.1 615 20.8 1.0 1.2 144 TY02 La Joya 35 11 5.8 2.1 603 1.3 1.4 19.1 1.4 19.1 TY09 La Joya 10 1.5 5.8 2.1 631 18.5 1 1.9 160 TY04 La Joya 10 1.5 5.8 2.1 631 18.1 1.0 0.5 1.9	Sample										
TQ03 La Joya 20 10 5.88 2.2 618 17.5 1 1.5 162 TQ18 La Joya 45 10 5.81 2.2 615 20.0 1.0 1.7 145 TQ19 La Joya 40 10 5.79 2.1 610 18.8 1.0 1.2 141 TQ31 La Joya 22 12 5.83 2.2 630 21.3 1.0 1.4 148 JY07 La Joya 10 12 5.86 2.1 605 23.5 1 3.4 143 JY09 La Joya 10 12 5.86 2.1 605 1.5 1 1.9 1.4 151 JY08 La Joya 10 13 5.86 2.1 631 18.5 1 1.9 1.60 JY10 La Joya 16 13 5.66 1.5 340 15.0 0.5 1.60	Site	Flow Name	n=	Ba	Be	Fe	Mn	Р	Sc	Sr	Zn
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	TQ03	La Joya	20	10	5.88	2.2	618	17.5	1	1.5	162
TQ19 La Joya 20 9 5.84 2.1 614 21.0 1.0 1.4 143 TQ21 La Joya 25 11 5.80 2.1 615 20.8 1.0 1.2 141 TQ31 La Joya 22 12 5.83 2.2 630 21.3 1.0 1.2 144 TQ21 La Joya 17 10 5.69 2.1 605 23.5 1 3.4 143 JY07 La Joya 10 1.2 5.86 2.2 623 22.0 1 1.4 151 JY08 La Joya 20 13 5.86 2.1 631 18.5 1 1.9 146 JY10 La Joya 20 13 5.86 2.2 620 1.5 0.5 0.7 159 TQ24 Teuchitlán 2 10 6.05 1.1 172 160 TQ33 La Quemada 18 7.60 1.3 280 15.0 0.5 1.1 172	TQ18	La Joya	45	10	5.81	2.2	615	20.0	1.0	1.7	145
TQ21 La Joya 25 11 5.80 2.1 610 18.8 1.0 1.2 144 TQ31 La Joya 22 11 5.80 2.1 615 20.8 1.0 1.4 148 TQ22 La Joya 17 10 5.69 2.1 600 20.3 1 3.4 143 JY07 La Joya 10 12 5.86 2.2 630 21.2 1 1.4 151 JY08 La Joya 10 12 5.86 2.2 623 22.0 1 1.4 151 JY08 La Joya 16 13 5.86 2.2 621 21.9 1 1.7 150 TQ24 Teuchitifan 31 13 6.09 1.6 331 17.1 0.5 1.9 160 TQ24 Teuchitifan 21 18 7.0 1.3 280 15.0 0.5 1.6 1.6 1.1 17.7 TQ16 La Quemada 27 9 7.74 2.1	TQ19	La Joya	20	9	5.84	2.1	614	21.0	1.0	1.4	143
TQ31 La Joya 25 11 5.80 2.1 615 20.8 1.0 1.2 144 TQ32 La Joya 17 10 5.69 2.1 605 23.5 1 3.4 143 JY07 La Joya 35 11 5.8 2.1 605 23.5 1 3.4 143 JY07 La Joya 25 12 5.8 2.1 622 22.0 1 1.4 151 JY08 La Joya 20 13 5.86 2.1 621 21.9 1 1.7 150 TQ23 Teuchitlán 48 7 6.06 1.5 326 15.6 0.5 0.7 159 TQ24 Teuchitlán 21 0 6.05 1.1 172 160 0.5 0.5 1.6 131 17.1 0.5 0.5 160 TQ33 Teuchitlán 20 11 8.70 1.3 280 15.0 0.5 1.1 172 TQ16 La Quemada 18	TQ21	La Joya	40	10	5.79	2.1	610	18.8	1.0	1.2	141
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	JY10	La Joya	16	13	5.86	2.2	621	21.9	1	1.7	150
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$\begin{array}{c c c c c c c c c c c c c c c c c c c $	TQ24	Teuchitlán	31	13	6.09	1.6	331	17.1	0.5	1.9	160
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	TQ33	Teuchitlán	2	10	6.05	1.5	341	15.0	0.5	0.5	160
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	TQ20	Amatitán	20	11	8.70	1.3	280	15.0	0.5	1.1	172
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	TQ16	La Quemada	18	8	7.60	2.1	384	18.9	0.8	1.2	178
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	TQ30	La Quemada	27	9	7.74	2.1	379	17.0	0.8	1.2	188
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	JY01	Santa Teresa	22	62	4.93	1.2	450	38.2	2	7.4	74
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	JY04	Santa Teresa	32	62	4.96	1.2	458	38.8	2	6.1	75
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	ST04	Santa Teresa	25	78	4.79	1.2	444	45.6	2	7.2	74
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	TQ06	Santa Teresa	19	82	4.89	1.2	450	45.8	2	8.1	75
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	MG01	Santa Teresa	12	83	4.83	1.2	469	41.7	2	7.2	71
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	TQ15	Santa Teresa	48	60	5.01	1.2	454	39.8	2.0	7.2	75
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	TQ17	Santa Teresa	30	60	4.98	1.2	467	40.0	2.0	6.4	73
TQ27Santa Teresa22644.921.246342.02.07.275TQ25Santa Teresa11654.961.245641.82.07.475TQ13Santa Teresa48844.961.346048.62.49.072HX01Huaxtla9226.281.952832.215.4150HX02Huaxtla22106.631.956220.92.51.3152ST05Guevara242434.441.346061.73.313.363TQ26Guevara242434.441.346672.23.014.064TQ01Los Saavedra223844.201.346672.23.522.270ST02Los Saavedra233444.201.344678.5321.070ST01Los Saavedra363704.021.344883.1320.963ST08Los Saavedra394224.041.346895.4325.664TQ05Los Saavedra314243.981.346895.4325.664TQ05Los Saavedra314243.981.346896.7325.965TQ10Los Saavedra344264.051.34699	TQ22	Santa Teresa	40	81	4.93	1.3	460	49.2	2.4	8.1	73
TQ25Santa Teresa11654.961.245641.82.07.475TQ13Santa Teresa48844.961.346048.62.49.072HX01Huaxtla9226.281.952832.215.4150HX02Huaxtla22106.631.956220.92.51.3152ST05Guevara132504.421.244259.2312.363TQ26Guevara242434.441.346061.73.313.363TQ28Los Saavedra22354.501.245465.03.014.064TQ01Los Saavedra223844.201.346672.23.522.270ST02Los Saavedra363704.021.346678.5321.070ST01Los Saavedra363704.021.346895.4323.268ST07Los Saavedra394224.041.346895.4325.664TQ05Los Saavedra314243.981.347294.5326.067TQ04Sandovales247912.791.3336208.93112.039TQ04Sandovales217932.81.3331206.0	TQ27	Santa Teresa	22	64	4.92	1.2	463	42.0	2.0	7.2	75
TQ13Santa Teresa48844.961.346048.62.49.072HX01Huaxtla9226.281.952832.215.4150HX02Huaxtla22106.631.956220.92.51.3152ST05Guevara132504.421.244259.2312.363TQ26Guevara242434.441.346061.73.313.363TQ28Los Saavedra22354.501.245465.03.014.064TQ01Los Saavedra223844.201.346672.23.522.270ST02Los Saavedra363704.021.346785.5321.070ST01Los Saavedra363704.021.344883.1320.963ST07Los Saavedra183974.11.346291.1323.268ST07Los Saavedra394224.041.346895.4325.664TQ05Los Saavedra314243.981.347294.5326.067TQ10Los Saavedra344264.051.346996.7325.965TQ04Sandovales247912.791.3336208.9	TQ25	Santa Teresa	11	65	4.96	1.2	456	41.8	2.0	7.4	75
HX01Huaxtla9226.281.952832.215.4150HX02Huaxtla22106.631.956220.92.51.3152ST05Guevara132504.421.244259.2312.363TQ26Guevara242434.441.346061.73.313.363TQ28Los Saavedra22354.501.245465.03.014.064TQ01Los Saavedra223844.201.346672.23.522.270ST02Los Saavedra363704.021.346785.5321.070ST01Los Saavedra363704.021.344883.1320.963ST08Los Saavedra183974.11.346291.1323.268ST07Los Saavedra394224.041.346893.5324.565TQ10Los Saavedra314243.981.347294.5326.067TQ05Los Saavedra344264.051.346996.7325.965TQ09Los Saavedra564324.011.347497.5426.464TQ04Sandovales247912.791.3336208.9	TQ13	Santa Teresa	48	84	4.96	1.3	460	48.6	2.4	9.0	72
HX02Huaxtla22106.631.956220.92.51.3152ST05Guevara132504.421.244259.2312.363TQ26Guevara242434.441.346061.73.313.363TQ28Los Saavedra22354.501.245465.03.014.064TQ01Los Saavedra223844.201.346672.23.522.270ST02Los Saavedra43504.21.346785.5321.070ST01Los Saavedra363704.021.344883.1320.963ST08Los Saavedra183974.11.346291.1323.268ST07Los Saavedra394224.041.346895.4325.664TQ05Los Saavedra234223.981.347294.5326.067TQ11Los Saavedra344264.051.346996.7325.965TQ09Los Saavedra564324.011.347497.5426.464TQ04Sandovales217932.81.3331206.03111.037TQ02Choloaca3910202.931.235885	HX01	Huaxtla	9	22	6.28	1.9	528	32.2	1	5.4	150
ST05Guevara132504.421.244259.2312.363TQ26Guevara242434.441.346061.73.313.363TQ28Los Saavedra22354.501.245465.03.014.064TQ01Los Saavedra223844.201.346672.23.522.270ST02Los Saavedra43504.21.346785.5321.070ST01Los Saavedra363704.021.344883.1320.963ST08Los Saavedra183974.11.346291.1323.268ST07Los Saavedra394224.041.346895.4325.664TQ05Los Saavedra234223.981.346893.5324.565TQ10Los Saavedra314243.981.347294.5326.067TQ11Los Saavedra344264.051.346996.7325.965TQ09Los Saavedra564324.011.3336208.93112.039TQ04Sandovales217932.81.3331206.03111.037TQ02Choloaca3910202.931.2358	HX02	Huaxtla	22	10	6.63	1.9	562	20.9	2.5	1.3	152
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	ST05	Guevara	13	250	4.42	1.2	442	59.2	3	12.3	63
TQ28Los Saavedra22354.501.245465.03.014.064TQ01Los Saavedra223844.201.346672.23.522.270ST02Los Saavedra43504.21.346785.5321.070ST01Los Saavedra363704.021.344883.1320.963ST08Los Saavedra183974.11.346291.1323.268ST07Los Saavedra394224.041.346895.4325.664TQ05Los Saavedra234223.981.346893.5324.565TQ10Los Saavedra314243.981.347294.5326.067TQ11Los Saavedra344264.051.346996.7325.965TQ09Los Saavedra564324.011.347497.5426.464TQ04Sandovales217932.81.3331206.03111.037TQ02Choloaca3910202.931.235885.2448.850TQ07Choloaca3410202.861.237285.9449.249TQ08Choloaca5810292.941.2370	TQ26	Guevara	24	243	4.44	1.3	460	61.7	3.3	13.3	63
TQ01Los Saavedra223844.201.346672.23.522.270ST02Los Saavedra43504.21.346785.5321.070ST01Los Saavedra363704.021.344883.1320.963ST08Los Saavedra183974.11.346291.1323.268ST07Los Saavedra394224.041.346895.4325.664TQ05Los Saavedra234223.981.346893.5324.565TQ10Los Saavedra314243.981.347294.5326.067TQ11Los Saavedra344264.051.346996.7325.965TQ09Los Saavedra564324.011.347497.5426.464TQ04Sandovales217932.81.3331206.03111.037TQ02Choloaca3910202.931.235885.2448.850TQ07Choloaca3410202.861.237082.8448.949TQ08Choloaca5810292.941.237082.8448.949	TQ28	Los Saavedra	2	235	4.50	1.2	454	65.0	3.0	14.0	64
ST02Los Saavedra43504.21.346785.5321.070ST01Los Saavedra363704.021.344883.1320.963ST08Los Saavedra183974.11.346291.1323.268ST07Los Saavedra394224.041.346895.4325.664TQ05Los Saavedra234223.981.346893.5324.565TQ10Los Saavedra314243.981.347294.5325.965TQ01Los Saavedra344264.051.346996.7325.965TQ09Los Saavedra564324.011.347497.5426.464TQ04Sandovales247912.791.3336208.93112.039TQ05Sandovales217932.81.3331206.03111.037TQ02Choloaca3910202.931.235885.2448.850TQ07Choloaca3410202.861.237285.9449.249TQ08Choloaca5810292.941.237082.8448.949	TQ01	Los Saavedra	22	384	4.20	1.3	466	72.2	3.5	22.2	70
ST01Los Saavedra363704.021.344883.1320.963ST08Los Saavedra183974.11.346291.1323.268ST07Los Saavedra394224.041.346895.4325.664TQ05Los Saavedra234223.981.346893.5324.565TQ10Los Saavedra314243.981.347294.5326.067TQ11Los Saavedra344264.051.346996.7325.965TQ09Los Saavedra564324.011.347497.5426.464TQ04Sandovales247912.791.3336208.93112.039TQ02Choloaca3910202.931.235885.2448.850TQ07Choloaca3410202.861.237285.9449.249TQ08Choloaca5810292.941.237082.8448.949	ST02	Los Saavedra	4	350	4.2	1.3	467	85.5	3	21.0	70
ST08Los Saavedra183974.11.346291.1323.268ST07Los Saavedra394224.041.346895.4325.664TQ05Los Saavedra234223.981.346893.5324.565TQ10Los Saavedra314243.981.347294.5326.067TQ11Los Saavedra344264.051.346996.7325.965TQ09Los Saavedra564324.011.347497.5426.464TQ04Sandovales247912.791.3336208.93111.037TQ02Choloaca3910202.931.235885.2448.850TQ07Choloaca3410202.861.237285.9449.249TQ08Choloaca5810292.941.237082.8448.949	ST01	Los Saavedra	36	370	4.02	1.3	448	83.1	3	20.9	63
ST07Los Saavedra394224.041.346895.4325.664TQ05Los Saavedra234223.981.346893.5324.565TQ10Los Saavedra314243.981.347294.5326.067TQ11Los Saavedra344264.051.346996.7325.965TQ09Los Saavedra564324.011.347497.5426.464TQ04Sandovales247912.791.3336208.93112.039TQ06sSandovales217932.81.3331206.03111.037TQ02Choloaca3910202.931.235885.2448.850TQ07Choloaca3410202.861.237285.9449.249TQ08Choloaca5810292.941.237082.8448.949	ST08	Los Saavedra	18	397	4.1	1.3	462	91.1	3	23.2	68
TQ05Los Saavedra234223.981.346893.5324.565TQ10Los Saavedra314243.981.347294.5326.067TQ11Los Saavedra344264.051.346996.7325.965TQ09Los Saavedra564324.011.347497.5426.464TQ04Sandovales247912.791.3336208.93112.039TQ06sSandovales217932.81.3331206.03111.037TQ02Choloaca3910202.931.235885.2448.850TQ07Choloaca3410202.861.237285.9449.249TQ08Choloaca5810292.941.237082.8448.949	ST07	Los Saavedra	39	422	4.04	1.3	468	95.4	3	25.6	64
TQ10Los Saavedra314243.981.347294.5326.067TQ11Los Saavedra344264.051.346996.7325.965TQ09Los Saavedra564324.011.347497.5426.464TQ04Sandovales247912.791.3336208.93112.039TQ06sSandovales217932.81.3331206.03111.037TQ02Choloaca3910202.931.235885.2448.850TQ07Choloaca3410202.861.237285.9449.249TQ08Choloaca5810292.941.237082.8448.949	TQ05	Los Saavedra	23	422	3.98	1.3	468	93.5	3	24.5	65
TQ11Los Saavedra344264.051.346996.7325.965TQ09Los Saavedra564324.011.347497.5426.464TQ04Sandovales247912.791.3336208.93112.039TQ06sSandovales217932.81.3331206.03111.037TQ02Choloaca3910202.931.235885.2448.850TQ07Choloaca3410202.861.237285.9449.249TQ08Choloaca5810292.941.237082.8448.949	TQ10	Los Saavedra	31	424	3.98	1.3	472	94.5	3	26.0	67
TQ09Los Saavedra564324.011.347497.5426.464TQ04Sandovales247912.791.3336208.93112.039TQ06sSandovales217932.81.3331206.03111.037TQ02Choloaca3910202.931.235885.2448.850TQ07Choloaca3410202.861.237285.9449.249TQ08Choloaca5810292.941.237082.8448.949	TQ11	Los Saavedra	34	426	4.05	1.3	469	96.7	3	25.9	65
TQ04Sandovales247912.791.3336208.93112.039TQ06sSandovales217932.81.3331206.03111.037TQ02Choloaca3910202.931.235885.2448.850TQ07Choloaca3410202.861.237285.9449.249TQ08Choloaca5810292.941.237082.8448.949	TQ09	Los Saavedra	56	432	4.01	1.3	474	97.5	4	26.4	64
TQ06sSandovales217932.81.3331206.03111.037TQ02Choloaca3910202.931.235885.2448.850TQ07Choloaca3410202.861.237285.9449.249TQ08Choloaca5810292.941.237082.8448.949	TQ04	Sandovales	24	791	2.79	1.3	336	208.9	3	112.0	39
TQ02Choloaca3910202.931.235885.2448.850TQ07Choloaca3410202.861.237285.9449.249TQ08Choloaca5810292.941.237082.8448.949	TQ06s	Sandovales	21	<u>7</u> 93	2.8	1.3	331	206.0	3	111.0	37
TQ07Choloaca3410202.861.237285.9449.249TQ08Choloaca5810292.941.237082.8448.949	TQ02	Choloaca	39	1020	2.93	1.2	358	85.2	4	48.8	50
TQ08 Choloaca 58 1029 2.94 1.2 370 82.8 4 48.9 49	TQ07	Choloaca	34	1020	2.86	1.2	372	85.9	4	49.2	49
	TQ08	Choloaca	58	1029	2.94	1.2	370	82.8	4	48.9	49



Figure 5. Variability in elements Al, Ba, Be, Ca and Cr.



Figure 7. Variability in elements Na, P, Pb, Sc, and Sr.

near the detection limit of 10 ppm for Ba using the ICP-AES analysis technique. This means that even with a very low standard deviation it has a large impact on the % variability used for this comparison method. So, it is reasonable to include Ba in with the first group of homogeneous elements. While the average values of Mn for the Choloaca flow (367 ppm) are not near the detection limit for Mn (5 ppm) they are the lowest Mn values of all the various flows, and thus any variability has a bigger impact on the final variability number. Thus, it is reasonable to include the Mn variability in the same group as the Zn, which is still fairly homogeneous.

Next there is a group of elements (Ca, Sc, Ga and La), that are generally quite homogeneous, but in certain flows have a



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Ga

Obsidian

Sample

La

Deviation Value

0.0

Figure 6. Variability in elements Fe, Ga, K, La, and Mn.



Figure 8. Variability in elements Ti, V, Zn, and Sc.

much higher variability value. The Ca values are generally in the 3% to 4% range, but in the La Joya flow the values are very noisy and spike up to 13%. This is another case of this sample site having much lower ppm values than the other sample sites, so even though the standard deviation values are very low (in the 0.1% to 0.2 % range) any bump in values has a bigger impact on the variability % method used in this study. So Ca can be grouped in with Zn and Mn as still fairly homogeneous. In the case of Sc, the values in all the flows are very low and near the level of detection (1 ppm), and three of the five flows had zero variability between repeat assays - thus perfectly homogeneous. But the other two flows had much nosier data, due to standard deviations in the 1 ppm range related to IAOS Bulletin No. 73, Winter 2024

Volcán Tequila - Homogenity of Elements

average values of 3 or 4 ppm. So that small absolute value had a big impact on the variability value this method is using. Thus, Sc could be grouped in with the most homogeneous group of Al, Be K and Na, recognizing that in discriminant plots there may be some spread in Sc values for certain flows (Los Saavedra and Santa Teresa).

The case of Ga is somewhat similar such that in three of the five flows it has zero variability, but was quite noisy in the other two flows. Again the values in all samples are quite low and near the limit of detection, so small variations have a bigger impact on the variable % used in this study. An additional problem appears to be that this ICP-AES method does not have very good precision for this particular element as evidenced by the values jumping in units of 10 ppm, rather than in 1 ppm increments as it does for most other elements. Considering the zero variability in three of the flows and the low variability (9% to 17 %) in the other two flows it is reasonable to include Ga in the strongly homogeneous group of Al etc. with the same caveat as Sc, that there will be some noise in some flows on a discriminant plot. The situation for La is very similar to Ga in that many samples had zero variability while others spiked higher on minor changes in a few assays based on low overall values and an analysis method that is not very sensitive to this element. Overall, it is fairly homogeneous, but the variations it experiences at these low levels make it less than ideal for discriminant plots.

Next there are three elements (P, Pb and Sr) that have quite high variability (poor apparent homogeneity) as illustrated in Figure 7. P has variability values that range from 1.68% to a high of 27.6%. As seen in previous elements, levels of variability are dependent on the different flows, and how high the actual value is in each sample. In the Sandovales flow P is very homogeneous with only a 2.6% to 3.19% variability and the highest average values (206 to 209 ppm), while in the La Joya

flow it ranges from 8.2% to 27.6% variability and has the lowest average values (between 17.5 and 22.4 ppm). Average Pb values do not change much over all five flows (ranging from only 19 to 29 ppm), but the % variability range from 5.1% to 16.2%. The same pattern is seen in the Sr variability values, with the samples with the lowest average values (the La Joya flow with a range from only 1.5 to 3.4 ppm) having the highest variability percentages (54% to 85%), and the Sandovales flow with the highest average value of 111 ppm Sr having a variability of only 2%. Clearly, this method of comparison has some limitations when the average value of an element is very low and especially when near the limits of detection using this ICP-AES analysis. If the samples that have very low average values are taken out of consideration, these three elements show reasonably good homogeneity (<10% variability).

Finally, there are two elements (Cr and V) that show very erratic values across all the flows, as illustrated in Figures 5 and 8, with variability values generally ranging between 20% and 60%. For both elements, the actual average values are quite low, which strongly impacts how the standard deviation affects the homogeneity. appearance of This is particularly evident in the Sandovales flow which happens to have the highest V values (11 ppm compared to the others below 3 ppm) and a variability percent of only 3% to 5% compared to the rest that are between 30% to 60%. Once again, the very low average values make comparisons between samples and flows difficult. Note there are gaps in the V data results due to the laboratory dropping that element from that assay package later in this study.

Geochemical Characterization of Individual Obsidian Flows

By plotting the geochemical results of the samples collected in this study on bivariate scatter plots, it is possible to distinguish the different obsidian flows around Volcán Tequila. Figures 9 through 12 show the combination of results for Ba, Be, Mn, P, and Sr and clearly distinguish ten different flows, nine of which have been identified by previous work.

Sample ST05 and TQ26 are two samples that do not fit into one of the groups identified in Figures 9 through 12 and occur in a geographical location within one previously identified flow (Santa Teresa). It is proposed that this new geochemical grouping be referred to as the Guevara Flow. Sample TQ28 is also a sample that plots on the edge of the Los Saavedra grouping in some plots and by itself in other plots, so additional analysis is needed to help clarify that sample site.



Figure 9. Bivariate Scatter Plot of P vs. Mn.



Figure 11. Bivariate Scatter Plot of Ba vs. Mn.

Principal component analysis (PCA, Figure 13) of the elements presented in Table 1 was completed to present another method to distinguish all ten flows and help clarify the situation of sample TQ28 in particular and is displayed in Figure 13 below. Most of the variance in the PCA plot is accounted for by Mn (71.0%) and Ba (12.9%) in this particular sample group. The plot clearly separates all ten flows around Volcán Tequila and clarifies the situation of sample TQ28, including it in the newly identified Guevara flow.

Obsidian Flow Descriptions / Comparisons

One of the problems of distinguishing the various individual obsidian flows around Volcán Tequila has been the use of different names for the same flows by different authors



Figure 10. Bivariate Scatter Plot of Sr vs. Be.



Figure 12. Bivariate Scatter Plot of Sr vs. Mn.

IAOS Bulletin No. 73, Winter 2024 Pg. 23



Figure 13. Principal Component Analysis plot of the obsidian flows identified in this study showing their geochemical groupings.

and the lack of appropriate site descriptions sample identify each that with its corresponding location. The work of Harris (1986) was the earliest and best mapping of the location of rhyolite flows (though did not separate out the obsidian), so the same numbering / naming of flows used in this study is as was presented in her thesis, at least where there is no naming over-lap. After compiling the results from eight different authors, listed in Table 2, an attempt is made to confirm the location of the samples from 13 different flows. The following discussion will review the various names given to sampled flows and how well the sample data coordinates between authors.

The first area described in Table 2 is the **Chapulimita / La Providencia** area. Based on the names given and sample location maps it was presumed that these were from the same flow, however, the geochemistry is clearly different. These flows were not sampled in this current program due to landowner access issues, but from the topography appear to be

rhyolite flow domes with some amount of obsidian.

The sample location for Loma La Isla is well located in Harris (1986), and identified in Figure 14 below, but this author failed to find any obsidian in that location, so it is likely a very localized obsidian occurrence. The sample site San Juanito Escobedo described in Glascock et al. (2010) is reported in the text to be from near the village of the same name and is interpreted to be the same site as the recently described Isla de Atitlán from Blanco-Moreles et al. (2023). The Isla de Atitlán is a rhyolite flow dome with flow banded crystalline rhyolite interlayered with thin obsidian layers outcropping on the higher parts of the dome and flanked by pumice rich lapilli tuff that also has occasional obsidian lapilli. Blanco-Morales et al. (2023) reported collecting eroded obsidian pieces on the upper part of the dome and their geochemical results match reasonably well with past results reported in Glascock et al. (2010) for San Juanito Escobedo.

> IAOS Bulletin No. 73, Winter 2024 Pg. 24

Table 2. Comparison of selected mean value results between the various studies on Volcán Tequila obsidian. Flow numbers correspond to: 1 = Chapulimita / La Providencia,2 = Loma La Isla, 2b = San Juanito Escobedo / Isla de Atitlán, 3 = Los Ocotillos, 5 = Amatitán, 6 = Teuchitlán / La Mora / El Pederal, 7 = La Joya, 8 = Santa Teresa, 9 =Los Saavedra, 10 = Choloaca, 11 = Los Sandovales, 12 = Tecuanapa, 13 = Atizcoa, 14 = Huaxtla, 15 = La Quemada. Values in ppm except where noted as %.

Flow	Sample	<i>n</i> =	Analysis Type	Ba	Fe (%)	K (%)	La	Mn	Na (%)	Sc	Sr	Ti	Zn	Source
1	63		XRF	1617			33				56		69	Harris (1986)
1	PRJ	11	XRF		0.9	3.8		201			67	1144	42	Glascock et al. (2010)
1	PRJ	39	NAA-MURR	480	1.0	4.1	32	293	3.1	2.4	65			Glascock et al. (2010)
2	145		XRF	634			53				31		85	Harris (1986)
2b	?	14	pXRF		2.7			929			194			Blanco-Morales et al. (2023)
2b	JEJ	5	XRF		2.7	3.7		802			229	3875	158	Glascock et al. (2010)
2b	JEJ	6	NAA-MURR	8	2.5	3.7	36	803	3.9	7.8	186			Glascock et al. (2010)
3	257		XRF	1046			35				208		46	Harris (1986)
5	260	2	XRF	nd	1.1		40				nd		180	Harris (1986)
5	TQ20	20	ICP-AES	11	1.3	3.9	37	280	3.4	0.5	1	500	172	Lloyd, this study
6	Teuc	1	INAA	2282	1.4									Ericson & Kimberlin (1977)
6	TJ	16	XRF		1.3	3.6		211			<2	581	143	Glascock et al. (2010)
6	147	3	XRF	nd	1.4		46				nd		162	Harris (1986)
6	1075-147	1	DCP	dl	1.4	3.2		310	3.0	0.5	2	600		Trumbold et al. (1993)
6	TJ	52	NAA-MURR	30	1.3	3.7	48	298	3.5	0.1	<15			Glascock et al. (2010)
6	E9	4	NAA-MURR		1.0		44			0.3				Esparza et al. (2017)
6	TJ	3	NAA-MURR	nd	1.3	3.3	47	287	3.5	0.1			139	Cobean et al. (1991)
6	TQ23,24,33	81	ICP-AES	10	1.5	3.7	41	333	3.6	0.5	1	600	159	Lloyd, this study
7	Magdal	1	INAA	2330	2.0									Ericson & Kimberlin (1977)
7	JJ	23	XRF		1.9	3.5		333			5	1070	153	Glascock et al. (2010)
7	Teq35	1	ICP-MS	53	1.2	3.3		460	2.7			660		Lewis-Kenedi et al. (2005)
7	MJ	1	NAA-MURR	50	1.0	4.3	49	430	3.3	2.3			66	Cobean et al. (1991)
7	E7	5	NAA-MURR		1.5		69			0.8				Esparza et al. (2017)
7	JJ	152	NAA-MURR	4	1.9	3.4	67	572	3.5	0.7	<15			Glascock et al. (2010)
7	55	6	XRF	nd	2.0		64	581			nd	939	146	Harris (1986)
7	?	20	pXRF		2.0			648			1			Blanco-Morales et al. (2023)
7	1075-142	1	DCP	dl	2.1	3.1		620	3.0	1.1	10	840		Trumbold et al. (1993)
7	12 samples	295	ICP-AES	11	2.1	3.7	61	617	3.6	1.0	2	900	148	Lloyd, this study
8	STJ	195	XRF		1.0	3.8		184			4	793	67	Glascock et al. (2010)
8	Teq18	1	ICP-MS	55	1.2	3.3		390	2.6			660		Lewis-Kenedi et al. (2005)
8	Teq45b	1	ICP-MS	81	1.1	3.4		460	2.8			720		Lewis-Kenedi et al. (2005)
8	75	16	XRF	61	1.1		53				8		64	Harris (1986)

Flow	Sample	<i>n</i> =	Analysis Type	Ba	Fe (%)	K (%)	La	Mn	Na (%)	Sc	Sr	Ti	Zn	Source
8	STJ	195	NAA-MURR	85	1.0	4.2	50	439	3.3	2.3	<15			Glascock et al. (2010)
8	E5	3	NAA-MURR		0.8		50			2.2				Esparza et al. (2017)
9	11 samples	309	ICP-AES	71	1.2	4.1	45	457	3.3	2.1	7	800	74	Lloyd, this study
9	1075-27	1	DCP	265	1.1	3.5		460	2.7	3.4	13	960		Trumbold et al. (1993)
9	1075-201	1	DCP	236	1.1	3.6		460	2.8	3.4	12	960		Trumbold et al. (1993)
9	1075-71	1	DCP	438	1.2	3.5		460	2.9	3.8	27	1020		Trumbold et al. (1993)
9	201	10	XRF	321	1.1		45	426			19	0	51	Harris (1986)
9	E1	3	NAA-MURR		0.8		34			4.0				Esparza et al. (2017)
9	Teq21a	1	ICP-MS	342	1.3	3.4		460	2.8			900		Lewis-Kenedi et al. (2005)
9	10 samples	265	ICP-AES	386	1.3	4.1	40	465	3.4	3.3	23	1100	66	Lloyd, this study
10	Tequil	1	INAA	1251	1.3									Ericson & Kimberlin (1977
10	Teq22	1	ICP-MS	940	1.1	3.3		310	2.7			900		Lewis-Kenedi et al. (2005)
10	1075-46	1	DCP	1081	1.1	3.4		390	2.8	3.8	44	1020		Trumbold et al. (1993)
10	1075-117	1	DCP	1092	1.1	3.4		390	2.8	4.2	46	1020		Trumbold et al. (1993)
10	QJ	12	XRF		1.1	3.8		201			23	1003	68	Glascock et al. (2010)
10	106		XRF	931			29				118		28	Harris (1986)
10	46	5	XRF	1006	1.1		35	329			51	738	35	Harris (1986)
10	QJ	3	NAA-MURR	932	1.0	3.8	34	332	3.2	3.9			45	Cobean et al. (1991)
10	QJ	77	NAA-MURR	354	1.1	4.1	44	452	3.4	3.5	23			Glascock et al. (2010)
11	3 samples	131	ICP-AES	1023	1.2	4.0	30	367	3.3	4.0	49	1000	49	Lloyd, this study
11	194		XRF	770			32	308				1009	40	Harris (1986)
11	1075-193	1	DCP	810	1.2	3.3		310	2.5	3.0	97	1500		Trumbold et al. (1993)
11	1075-194	1	DCP	827	1.2	3.3		310	2.5	3.2	98	1500		Trumbold et al. (1993)
11	193	3	XRF	788	1.2		28				114		23	Harris (1986)
11	TQ02, 06s	53	ICP-AES	792	1.3	3.9	30	336	3.0	3.0	200	1500	38	Lloyd, this study
12	182		XRF	375			44	311			55		42	Harris (1986)
13	1075-75	1	DCP	75	1.1	3.5		460	2.7	2.5	9	720		Trumbold et al. (1993)
14	HXJ	5	XRF		1.9	3.4		272			12	1276	168	Glascock et al. (2010)
14	HXJ	16	NAA-MURR	44	1.8	4.0	99	538	3.4	1.3	<15			Glascock et al. (2010)
	HX01,													
14	HX02	31	ICP-AES	16	1.9	3.8	82	545	3.4	1.8	3.41	1000	151	Lloyd, this study
15	LQJ	10	XRF		0.8	3.7		146			<2	543	43	Glascock et al. (2010)
15	LQJ	21	NAA-MURR	3	0.9	3.9	40	371	3.2	2.1	<15			Glascock et al. (2010)
15	TQ16, 30	45	ICP-AES	11	1.5	3.7	40	336	3.6	0.8	1	700	183	Lloyd, this study



Figure 14. Location map of the obsidian flows identified in this study along with their geochemical grouping.

The Amatitán rhyolite flow dome is located immediately south of the town of Amatitán and only Harris (1986) collected any samples there (two samples), which showed strong difference between each other. Attempts to re-locate sample 261 on the west side of the dome were un-successful in this current program, while a small area of mahogany colored obsidian was found in the area of sample 260. It appears that obsidian makes up a very small part of this large rhyolite flow dome. The mahogany obsidian occurs as small nodules, 1 to 10 cm in size (but generally less than 5 cm) over an area of only about one hectare. It appears to have eroded out of thin obsidian layers in the flow banded rhyolite flow as is exposed in a recent roadcut that was made for the autopista. Due to the small size of the nodules, it is unlikely to have been worked much in the past.

Six different authors (Ericson and Kimberlin (1977); Harris (1986); Cobean et al. (1991), Trombold et al. 1993; Glascock et al. (2010), Esparza et al. 2017) report on the Teuchitlán obsidian flow (also called El Pedernal or La Mora), but there is only a complete set of results for Rb and Fe. The Rb results are all in good agreement, while the Fe results show some variations, but are within range, so this flow seems well characterized and is only one of two flows to have previous detailed mapping as reported in Esparza et al. (2008). This obsidian flow is a typical coulee flow that is some 2 km long and 200 m to 500 m wide as illustrated in Figure 14. Obsidian occurs as broken fragments, 1 cm to 60 cm in size, and make up almost 100% of the rock fragments exposed on surface. The main color visible on the flow is back, but Esparza et al. reported abundant grey-greenish (2008)obsidian and much lesser red, brown and black IAOS Bulletin No. 73, Winter 2024

plus combinations of mixed red, brown or black. Little actual outcrop occurs. Much of the flow has now been plowed and been planted with blue agave obliterating the old shallow mines and workshops documented by Esparza et al. (2008).

The La Joya flow has geochemical data from eight authors (Cobean et al. (1971); Ericson & Kimberlin (1977), Harris (1986), Trombold et al. (1993), Lewis-Kendi et al. (2005), Glascock et al. (2010), Esparza et al. (2017); Blanco-Morales et al. (2023)). It is one of the most misunderstood flows as it was often referred to as the Magdalena flow, due to its proximity to the town of Magdalena. The village of La Joya is actually on top of outcropping obsidian, and is the more logical and commonly used name. The "La Joya" mapping flow detailed also saw (archeological) by Weigand and Spence (1982), but their published map has no reference points so it is not known where the mapping and sample collecting was actually done. However, this author suspects mapping and sample collection to have been in the western surface coulee flow area.

The geochemical results here are quite mixed. Fe analysis is the only complete set of analysis among the seven authors, followed by Mn. But even using the in-complete data sets, it is clear at least two flows are represented in the data, which is also what this author found in recent sampling. Mapping during this program noted a large continuous area with obsidian covering the whole surface on the western portion (west of the current highway between Magdalena and the village of La Joya) of this area which would likely be from a singular, or more likely, multiple coulee flows, flowing west and NW and separately S and SSE. This area is hereby referred to as the La Joya flow source and is approximately 6.2 km long NNW-SSE by 3.2 km wide. The obsidian currently visible in this flow is black, but in the past this area was renowned for its green, golden brown and occasional rainbow

colors. Those colors appear to have been mined out now. It appears that the PYRO Calibration sample 18 described in Frahm (2019) come from this obsidian source area, though curiously the sample from Table 2 that best fits the recommended values in Frahm (2019) actually comes from a flow located 9.3 km to the east, which has been referred to in the past as the Huitzizilapan (or Huitzilapa) flow. That sample was collected by Harris in 1986, and returned similar results as sample TO21 from the current study. Another separate flow sampled 2.2 km farther to the SE also returned values that places it within the La Joya group of results. These satellite flows show that the rhyolite flow domes producing the obsidian at that point in time were part of a large rhyolite flow dome complex with multiple eruption centers. It is likely that there are additional flow domes from that period of eruptions but they have been covered by other post volcanic flows.

Three additional rhyolite flow domes were also located in the La Joya area (samples JY01, JY02 and TQ17) that have obsidian and appear to predate the large western coulee La Joya flow (per K-Ar dating by Harris (1986) and Lewis-Kenedi et al. (2005)). These have recent mining of obsidian in them, and may be the source of the fabled La Joya green obsidian. These three outcrops belong geochemically with the larger Santa Teresa flow, located some kilometers to the NE.

The **Santa Teresa** "flow" has data from four authors (Harris (1986), Lewis-Kenedi et al. (2005), Glascock et al. (2010), Esparza et al. (2017)). The main part of this collection of samples is located around the town of Santa Teresa and continues 6.6 km to the SW, and 1 km to the NE, with eroded pieces of obsidian present in the agave fields for various kilometers farther to the NE. Once again though, there are samples (such as sample 75 from Harris (1986) and TQ21 and TQ25 from this study) that are located 5.5 to 7 km S and SE of the main flow. These outlaying samples make this the most widespread geochemical group. As was noted for the samples near La Joya, the samples in the main "flow" area are actually individual rhyolite flow domes that are part of a rhyolite flow dome complex, with obsidian making up only part of the individual domes. Exceptions are the areas immediately north of the town of Santa Teresa that appears to be a coulee flow about 1 km in length, sample TQ22 in the Huitzizilapan coulee flow and likely sample TQ25. All the obsidian seen in these sample sites is black in color, though the recent open pit mine at sample site TQ17 is possibly the source of the fabled La Joya green and rainbow obsidian.

For the Los Saavedra area there is reasonably good agreement between the four previous authors (Harris (1986), Trombold et al. (1993), Lewis-Kenedi et al. (2005), Esparza et al. (2017)) in Na, K, Ca, Zr, Mn and Sc though there is not a complete set for all samples. Other elements such as Fe, Rb, Ti, Ba and Sr have clear differences. Recent

sampling in this study over a wider area from nine samples had good consistency with elements; Al, Be, Ca, Fe, Ga, K, La, Mn, Na, Pb, Sc, Sr, Ti and Zn, so it is not clear why there are consistency differences in the older data. It is very likely one of the previous samples is mis-located. This area has another rhyolite flow dome complex dated at 547 ka (Lewis-Kenedi et al. (2005), portions of which have an obsidian component. The three northern ST series of samples are smaller individual domes, while the TQ samples (plus ST08) are part of a large coulee flow (or flows) that may have originated in the tall Los Saavedra dome marked on topographic maps just west of the indicated flow area. All the obsidian seen in this area is black and of large size and quality, but no evidence of past workings was noted. Much of this area is currently being plowed to plant blue agave or being built on. This geochemical group has one outlier located 1.9 km to the south, which is partially cut by the autopista access road.



Figure 15. Photo cross section of the TQ01 sample site. Actual TQ01 sample site is in the basal breccia just off the right side of the photo, right next to the road.

This roadcut exposes a classic cross section through a zoned rhyolite - obsidian coulee flow as seen in Figure 15.

Harris (1986) identified a separate flow area located to the SW of the Los Saavedra flow, and grouped this with the Magdalena (La Joya) flow. This is located in the area of Huitzizilapan and from recent mapping and sampling appears to have an upper coulee flow that is approximately 1300 m long that corresponds to the Santa Teresa geochemical signature and a lower 600 m long coulee flow that corresponds to the La Joya suite (samples 55 from Harris (1986) and TQ21 this study). The obsidian in both these areas is black and of good quality, but no evidence of past work was seen during the current mapping. The lower flow is now mainly plowed under and planted with blue agave, while the upper flow is the site of a rural subdivision.

The Choloaca flow is located immediately to the east and south of the town of Tequila and has past data from six authors (Ericson & Kimberlin [1977], Harris [1986], Cobean et al. [1991], Trombold et al. [1993], Lewis-Kenedi et al. [2005], Esparza et al. [2016]). This coulee flow is about 4.5 km long and up to 3 km wide and has mainly a continuous surface of broken obsidian fragments up 1 m across that are from a coulee flow originating near the autopista in the south-most portion. While the values for Fe are fairly consistent across seven samples, all the other elements show strong differences suggesting plotting errors and/or multiple Much more detailed sampling, flows. accurately located, would be needed to confirm the extent of this flow, though this will be complicated by recent fencing and planting of blue agave. This is likely the same flow referred to as Tequila by (Cobean 1991) and that had no reported past obsidian mining. The obsidian here is of good quality and good sized so was likely worked in the past, but much of the area has now been plowed and blue agave planted.

Los Sandovales is a smaller coulee flow located 2.5 km SE of the Choloaca flow and is about 1.7 km long and up to 1 km wide. It is composed of large broken fragments of black obsidian covering 100% of the surface, and most of it has now been plowed to plant blue agave, which would destroy any evidence of past obsidian mining. The size of the fragments and good quality of the material suggest that it was a likely source of past mining. Here there is only past data from two authors (Harris [1986] and Trombold et al. [1993]). The past data agrees closely with current results with the Ba and Mn results best distinguishing this flow from others in the region.

Harris (1986) identified a couple of other rhyolite flows to the SW of Huitzizilapan – with her samples 75 and 182. The area **Tecuanapa** around sample 182 was reviewed in this program of mapping and no rock could be found outcropping, so confirmation of that sample was not made. The area of her sample 75 could not be reached due to new fences and landowner restrictions, so is also not confirmed.

The zone referred to as **Huaxtla** is outside the actual volcanic field of Volcán Tequila to the SE, but lies along the same NW trend that controlled the eruption of the various pulses of magma that created Volcán Tequila. Huaxtla is a low, wide rhyolite flow dome with substantial obsidian exposed around the outer edges. Much of it has been cleared for cattle grazing and more recently for industrial buildings. Here there is only past data from Glascock et al. (2010), which shows that their two samples are quite different from each other (likely one is a misidentified sample), but one of them agrees with current results in the values for Fe, K, La, Mn and Na.

La Quemada is another obsidian site outside of the Volcán Tequila complex, along the NW trend, 10 km NW of the town of Magdalena. It is a very small site, that is composed of two narrow bands of black obsidian hosted within a crystalline rhyolite flow dome. The lower flow band has seen recent trenching to try and expose more of the obsidian, without success. Nodules from both bands have been eroding over the years and are spread out downslope for some hundreds of meters. Here again, there is only past data from Glascock et al. (2010), which has two samples that have very different values, so likely include another misidentified sample. Their other sample agrees reasonably well with the low Ba of current results, plus similar K, La, Mn, and Na values.

This study has also identified a new flow, named the Guevara flow, for which there is no past data. Samples ST05, TQ26, and TQ28 were found to have a unique combination of elements that distinguish them from the other known flows. Sample ST05 has flow banded obsidian, locally with abundant spherulites, that is part of a rhyolite flow dome. The horizon with the obsidian is only a few meters thick and is overlain in places by talus blocks where its own dome collapsed as it grew and in other parts by pumice rich lapilli tuffs which mark the start of the next rhyolite dome to grow over the earlier one. This outcrop is exposed in a quarry used for road fill for the construction of the autopista, so it is unlikely that obsidian from this particular site could have been used in the past. The other two samples located 1,000 m NE and NW are part of a surface coulee flow with large blocks of black obsidian covering the ground surface with good quality obsidian. The material from this area certainly could have been used in the past, though evidence of past use was not noted during this study and current expansion of the blue agave fields in this area will likely obliterate any existing evidence. The outer boundaries of this sub-source area are still not well defined. Topographically, it appears that the Guevara Flow is post the Santa Teresa flow and locally covering part of the Santa Teresa flow.

Discussion

The collection of 48 obsidian samples on and around Volcán Tequila has helped to clarify the size and geologic nature of 10 different obsidian sources. Two of these sources (La Joya and Teuchitlán) were sites of abundant past mining efforts by ancient cultures, while the other sources are lacking in studies to confirm whether they were mined or not. The ICP-AES assay technique used this study produced usable data for eight elements (Ba, Be, Fe, Mn, P, Sc, Sr, and Zn) that when plotted in bivariate scatter plots and PCA plots clearly separated ten different geochemical sub-sources. Among all elements, Ba and Mn were the two most useful elements in distinguishing between these sources. A review of the homogeneity of the individual elements confirmed that many elements are indeed very homogeneous amongst samples in the same flow, except when the values are very low and near the level of detection for that element. When those low levels are encountered variations in the data can be over 50%. The actual values produced by the ICP-AES method were generally in good agreement with the values obtained by the NAA done at the MURR laboratory. The reason these values are in better agreement with the NAA results than the XRF values is likely due to the complete destruction of the sample material and the four acid digestion method making sure all the material was actually available for analysis. The analysis of all these samples was successful in identifying a previously unknown geochemical source – named in this study as the Guevara Flow.

Geologically, the mapping from this study was able to confirm the existence of a series of rhyolite flow dome complexes that were then partially covered by later volcanic eruptions. While past geologic age dating is far from extensive, it does indicate that four different flows (La Joya, Santa Teresa, Amatitán and Teuchitlán) were active approximately 600,000 to 700,000 years ago

(Lewis-Kenedi et al. 2005). The Teuchitlán and Amatitán flows were the earliest around 670,000 ya, followed by the Santa Teresa flow around 640,000 ya and then the La Joya flow. The Teuchitlán flow was a single coulee flow and Amatitán a particularly large rhyolite flow dome, while the other two were flow dome complexes with associated coulee flows, spread out over tens of square kilometers. This aspect of flow dome complexes and later covering flows has led to the situation of geochemically similar obsidian being located in geographically distinct locations many kilometers apart. The Los Saavedra group is another rhyolite flow dome complex and associated coulee flows occurring some 80,000 years after the La Joya flow, and which has been partially covered by much younger lavas from the main Volcán Teguila stratovolcano. The Choloaca coulee flow is the youngest flow for which there is data and was emplaced about 410,000 ya. The two distal flows included in this study cannot be linked to the Volcán Tequila magma chamber, but are likely controlled by the same deepseated fault system that facilitated the eruption of the various Tequila Rhyolite Flow Dome Complexes and later stratovolcano eruptions. The rhyolite flow dome at Isla Atitlán is probably part of the Volcán Tequila volcanic complex, but no samples were collected from that complex for this study.

The recognition of rhyolite flow dome complexes as obsidian sources is likely to have an impact on future analysis of obsidian source evaluations, since it means that the same geochemical signature can be found many kilometers apart in geographically separate locations. This complicates the idea of the "Provence Postulate" as laid out in Weigand, (1977) and which Frahm, (2024) discusses in more detail. More detailed sampling of accurately located samples will be needed to confirm the real extent of individual sources, and perhaps additional studies such as magnetic susceptibility will be then needed to try to distinguish between the different geographic parts of a single sub-source.

Conclusions

Analysis by ICP-AES of 48 samples on and around the Volcán Tequila volcanic complex successfully identified eight subsources related to Volcán Tequila, as well as distinguishing two outlaying flows. Bivariate scatter plots and PCA plots both clearly separated all ten flows, with Ba and Mn being the two strongest elements for discriminating these flows. One of these flows, here named Guevara, was a new discovery, which still needs additional mapping to determine its full surface exposure. The method of ICP-AES produced quality data and agreed well with past NAA analysis done at the MURR laboratory. The homogeneity of the elements sampled was generally quite good, though when the actual value is very low and near the limit of detection, the data gets very noisy. Geologically, three of these flows (La Joya, Santa Teresa and Los Saavedra) are all rhyolite flow dome complexes with associated coulee flows that were subsequently covered in part by younger lava flows. This recognition of rhyolite flow dome complexes helps explain why obsidian of similar geochemical characteristics can be found in geographically distinct locations manv kilometers apart, thus complicating the concept of what is an obsidian source.

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IAOS Bulletin No. 73, Winter 2024 Pg. 33

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A METHOD FOR CONSTRUCTING A 200KYR PALEO-TEMPERATURE CURVE FOR OBSIDIAN HYDRATION DATING IN EQUATORIAL REGIONS

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Introduction

Obsidian hydration dating (OHD) is a method for estimating age of an obsidian artifact based on time-dependent absorption of water. The process is temperature-sensitive, and its application to archaeological dating currently requires making assumptions about the temperature regime to which an artifact has been exposed. The usual assumption is that the parameters which characterize the current temperature regime, whether by of determined use sensors or meteorological records, are a reasonable approximation to ancient temperatures. The assumption is generally valid for ages in the Holocene.

However, data have been published which show significant shifts in ancient temperatures relative to the present (e.g., West et al. 2007), especially for ages before 12-13Kyrs. For these ages the prevailing temperatures were significantly cooler than today, and ages computed assuming current conditions will be too young. A previous analysis (Rogers 2015) proposed a method for computing a paleo-temperature correction based on a temperature proxy curve for northtemperate latitudes (West et al. 2007:17, Fig. 2.2); however, the proxy curve over-corrects for equatorial latitudes. This paper develops a proxy curve for equatorial regions, based on published data.

Method

Global temperature data used were those of Bintanja et al. (2005), and equatorial data were from Bonnefille et al. (1990: 348, Fig. 2). In each case the temperature is expressed as a δT (in °C) with respect to the present. The equatorial curve was reconstructed from data in Figure 2 in Bonnefille et al. (1990: 348), which extend back to 46.6 Kyrs. Data were smoothed and interpolated by Stineman interpolation (implemented in PSI Plot^(C) per Stineman 1980) at 100-year intervals. A north temperate curve zone was reconstructed back to 150 Kyrs from Figure 2.2 of West et al. (2007:17), by the same method.

Global temperature data back to 200 Kyrs at 100-year intervals were downloaded directly from NOAA archives. Proxy data for equatorial temperatures are lacking beyond about 46.6 Kyrs. The method used to extrapolate a curve back to 200 Kyrs is:

- 1. The morphology of the global curve and the equatorial curve agree back to 46.6 Kyrs, with a temperature offset. At 46.6 Kyrs, the maximum age for the equatorial data by Bonnefille et al. (2005), the offset is 9.7317°C.
- The north temperate and the global curves are similarly offset, but coincide at the Eemian Interglacial maximum (δT = +2.1878°C), about 126 Kyrs. Since both the global average and the north temperate curves coincide, it is likely that the equatorial curve did as well.
- The final algorithm was: For age ≤ 46.6 Kyrs, equatorial temperature is per Bonnefille et al. (1990). For age > 46.6 Kyrs, equatorial temperature = global temperature per Bintanja et al. (2005) + 9.7317°C. A scaling technique was used to ensure the reconstructed equatorial temperature delta never exceeded the Eemian maximum (2.1878°C).



Figure 1. Paleo-temperature relative to the present.

The resulting equatorial curve (Figure 1) is consistent in morphology with global curves (e.g., Bintanja et al. (2005). A table of δT values at 100-year intervals back to 200 Kyrs, to assist in obsidian hydration dating studies, is posted on the IAOS website. The δT values should be regarded as provisional, until verified by further proxy data from the field.

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ABOUT THE IAOS

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