



IAOS

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International Association for Obsidian Studies

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NEWS AND INFORMATION

NEWS AND NOTES

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

CONSIDER PUBLISHING IN THE IAOS BULLETIN

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

International Obsidian Conference 2021 Videos Available!

Video recordings of presentations from the 2021 International Obsidian Conference are now available via YouTube.

Day 1: <https://youtu.be/Wjv7wAP-Y3U>

Day 2: <https://youtu.be/JZ4PpTP9KvA>

Day 3: https://youtu.be/a4wIY0_qtw4

You'll find timestamp shortcuts to particular talks in the YouTube description field below each video. Please see the conference schedule beginning on page 5 of this issue of the *IAOS Bulletin* to assist in navigating the YouTube video library.

NOTES FROM THE PRESIDENT

Hello IAOS members. I hope everyone has stayed safe over the fall and winter. Now that the Covid-19 vaccine is available, I'm optimistic that field schools and thesis/dissertation field projects will resume this summer. Also, I know the pandemic has closed many university laboratories and research facilities, and so I hope you're able to get those radiocarbon dates and samples analyzed.

In May, the International Obsidian Conference (IOC) had their meeting. Although it was held online, the IOC Organizing Committee (Kyle Freund, Lucas Johnson, Lisa Maher, Tom Origer, and Nicholas Tripcevich) did an amazing job! Many IAOS members attended and contributed research papers and posters, and so thank you so much for attending and contributing! The Organizing Committee sent out a post-conference update and they mentioned the potential publication of the conference proceedings. I look forward to that publication because there were several interesting presentations.

Also, during the conference, the IAOS awarded the first Craig E. Skinner Best Poster Award. Congrats to Theodora Moutsiou and colleagues for their poster, *Obsidian Maritime Interconnections in Early Holocene Eastern Mediterranean*. This new award is named in honor of Craig Skinner in recognition for his outstanding contributions in the field of obsidian studies. Winners will receive \$200 (USD) and a one-year IAOS membership. We will continue to give out this poster award at future conferences.

We had our annual IAOS business meeting during the IOC. It was our second virtual meeting in a row due to the pandemic, but we still discussed several new items like the development of members certificates and having a table at the 2021 Great Basin Archaeological Conference later this year in Las Vegas, Nevada. Lucas Johnson also reported that there was an increase in

membership during this year. Thank you to all of the new members and to everyone who renewed! The meeting minutes are available on the IAOS website. We plan to have the next business meeting in Chicago, Illinois, during the 2022 Society for American Archaeology (SAA) meeting.

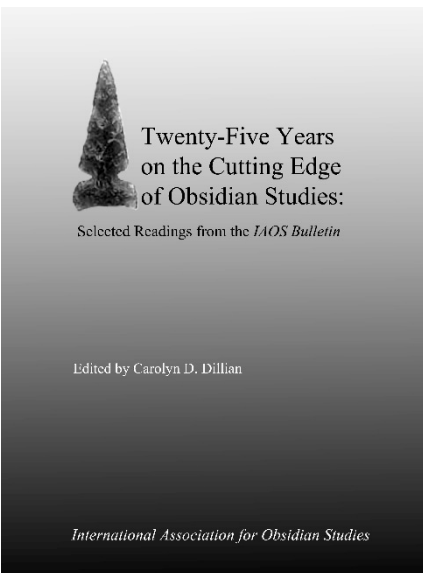
If you are interested in helping out the IAOS more, please consider running for IAOS office. We are looking to elect a new IAOS President. Please reach out if you are interested. Also, we are still looking for someone to take over as the IAOS Webmaster. If you are familiar with webpage development, HTML coding, and design, please email Craig at obsidianlab@gmail.com.

Finally, if you presented a research poster or talk at the SAA or IOC this year, please consider submitting an article, research update, news, or lab report projects to the *IAOS Bulletin*. You can submit your work to Carolyn Dillian at IAOS.Editor@gmail.com.

Sean Dolan, IAOS President
sgdolan@gmail.com

CALL FOR NOMINATIONS

Due to the pandemic, our cycle of nominations and elections has been delayed. However, now that things are returning to normal, it is time to resume our regular election procedures. That means that it's now time for nominations for our next IAOS President. Candidate statements will be printed in the Winter issue of the *IAOS Bulletin*, with elections soon to follow and the winner announced at the 2022 IAOS meeting at the SAAs. The winner will then serve as President-Elect for one year and begin the term of President in 2023. If you, or someone you know, would be interested in serving as IAOS President, please send a nomination and candidate statement to Sean Dolan, IAOS President, at sgdolan@gmail.com



Twenty-Five Years on the Cutting Edge of Obsidian Studies: Selected Readings from the IAOS Bulletin

Edited volume available for purchase online!

As part of our celebration of the 25th anniversary of the IAOS, we published an edited volume highlighting important contributions from the *IAOS Bulletin*. Articles were selected that trace the history of the IAOS, present new or innovative methods of analysis, and cover a range of geographic areas and topics. The volume is now available for sale on the IAOS website for \$10 (plus \$4 shipping to U.S. addresses).

http://www.deschutesmeridian.com/IAOS/iaos_publications.html

International addresses, please contact us directly at IAOS.Editor@gmail.com for shipping information.

A note from the organizers of the 2021 International Obsidian Conference:

First, we wish to thank you for your contributions and attention during this truly international conference! We hope you found the venue engaging and informative. We have several post-conference announcements:

1) The conference organizers intend to publish the conference proceedings in the University of California, Berkeley Archaeological Research Facility (ARF) Contribution Series. This publication series began in 1965 and has seen many seminal works on obsidian studies, and the conference proceedings will be an important addition to this legacy. Further details can be found at <https://arf.berkeley.edu/publications/contribution-series>

2) The final IOC Program with abstracts can be found here:
http://arf.berkeley.edu/files/attachments/pages/IOC2021_Program_0.pdf

3) Poster Awards:

a. The Society for Archaeological Sciences (SAS) R.E. Taylor Student Poster Award was awarded to Benjamin Smith for his poster titled: Imports and Outcrops: A Preliminary Characterization of the Baantu Obsidian Quarry, Wolyta, Ethiopia Using Portable X-Ray Fluorescence.

b. The International Association for Obsidian Studies (IAOS) Craig E. Skinner Poster Award went to Theodora Moutsiou and co-authors for their poster titled: Obsidian Maritime Interconnections in Early Holocene Eastern Mediterranean.

4) The conference recording is available via YouTube. See page 5 of this *IAOS Bulletin* for the schedule of presentations to assist in navigating the YouTube recordings.

Day 1: <https://youtu.be/Wjv7wAP-Y3U>

Day 2: <https://youtu.be/JZ4PpTP9KvA>

Day 3: https://youtu.be/a4wly0_qtw4

5) A few of us (Nico, Matt Boulanger, Lucas) have been using Slack to communicate regarding archaeological geochemistry. It has mostly been concerned with obsidian calibrations on Bruker XRF instruments, but other threads are available on the channel as well. We welcome others from this group in the Geochemistry Slack channel and you can join here https://join.slack.com/t/geochemistryhq/shared_invite/zt-ndnwtd1x-eiW4zsDdM2UM4znjHYgPWg

We look forward to seeing you again for the IOC 2023 in Japan!

Sincerely,
Lucas, Kyle, and Nico

Day 1: April 30, 2021
(9am-5pm Pacific Daylight Time)

9:00 **Welcome and Introductions.**

9:30 **Keynote**, *Dr. Steven Shackley*, Professor Emeritus, UC Berkeley

Obsidian Sourcing in Archaeology: South America (10:30-11:50am)

10:30 The Charaña Obsidian Source and Its Role in the Prehispanic Exchange Networks of the Titicaca Basin. *Richard L. Burger, Martin Giesso, Vanessa Jimenez Balderrama, Paul Goldstein, Michael D. Glascock*

10:50 Obsidian Exchange among Hunter-Gatherers in Northwestern Patagonia. *Fernando Franchetti, Clara Otaola, Laura Salgán, Miguel Giardina*

11:10 (pre-recorded) Prehistoric Use of an Obsidian-Rich Ignimbrite Deposit, Northwestern Patagonia. *Raven Garvey, Ramiro Barberena, Agustina Rughini, M. Victoria Fernández, Guadalupe Romero Villanueva, Brandi MacDonald*

11:30 A 12,000-Year Sequence of Human Use of the Alca Obsidian Source, Peru. *Kurt Rademaker, David Reid, Michael Glascock, Bruce Kaiser*

11:50 **Lunch Break**

Obsidian Sourcing in Archaeology: Mesoamerica (1:00-2:50pm)

1:00 pXRF Obsidian Analysis of Two sites in the Southern Basin of Mexico: From Early to Late Postclassic. *Guillermo Acosta-Ochoa, Berenice Jiménez-González*

1:20 Marketplaces and Market Exchange of Obsidian During the 8th – 10th Centuries at El Zotz, Guatemala. *Joshua Kwoka, Anna Bishop, Thomas Garrison, Hector Neff, Stephen Houston, Elizabeth Marroquín*

1:40 **Coffee break**

1:50 Obsidian Exchange Spheres in Late Postclassic Mesoamerica: New Perspectives from Tlaxcallan, Mexico, Utilizing an Olympus Vanta Portable X-Ray Fluorescence Spectrometer. *Marc Marino, Lane F. Fargher, Wesley D. Stoner*

2:10 Networks of Procurement and Provisioning: Geochemical Evidence from Late-Classic Cotzumalhuapa, Guatemala. *David McCormick*

2:30 New XRF Provenance Research on The Obsidian Jewelry from The Great Temple of Tenochtitlan, Mexico. *Emiliano Melgar-Tisco, Guillermo Acosta-Ochoa, Victor García-Gómez, Reyna Solís-Ciriaco, Luis Coba-Morales, Eder Borja-Laguna*

Obsidian Sourcing in Archaeology: North America (2:50-3:50pm)

2:50 (pre-recorded) Mesoamerican Obsidian in the American Southwest: What It Means for Southwest-Mesoamerican Connections and Coronado's Mexican Allies. *Sean Dolan*

3:10 Prehistoric Obsidian Procurement and Exchange in West-Central Arizona. *Michael Kellett*

3:30 Finding Obsidian Sources in Yellowstone National Park: Further Work. *Andrea Vianello, Robert H. Tykot*

Poster Session 1 (4:00-5:00pm)

1 What Determines the Chromatic Features of the Obsidian? The Example of Sierra de las Navajas (State of Hidalgo, Mexico). *Paola Donato, Luis Barba, Maria Caterina Crocco, Mariano Davoli, Rosanna De Rosa, Sandro Donato, Raffaele Filosa, Giancarlo Niceforo, Alejandro Pastrana, Gino Mirocle Crisci*

2 The Character and Use of Ferguson Wash Obsidian in Eastern Great Basin Prehistory. *Kyle P. Freund, Lucas R. Martindale Johnson, Daron Duke*

3 Morphology and Texture of Microlites in the Baekdusan and Kyushu Obsidian with Implication for the Different Cooling Condition of Rhyolitic Magmas. *Yong-Joo Jwa, Seonbok Yi*

Day 2: May 1, 2021

(9am-5pm Pacific Daylight Time)

Obsidian Sourcing in Archaeology: Asia and Europe (9:00-11:40am)

- 9:00 Exploitation of Obsidian at Psytuaje Rockshelter, North-Central Caucasus, Russia. *Ekaterina Doronicheva, Liubov Golovanova, Vladimir Doronichev, Galina Poplevko, Andrey Nedomolkin, Steven M. Shackley*
- 9:20 Obsidian Exploitation in Upper Paleolithic Layer 1A-2 at Mezmaiskaya Cave, North-Western Caucasus, Russia. *Ekaterina Doronicheva, Steven M. Shackley, Liubov Golovanova, Vladimir Doronichev, Galina Poplevko*
- 9:40 The “Kozushima Obsidian Shuttle” across the Pacific and the Migration of *Homo sapiens* to the Japanese Archipelago. *Nobuyuki Ikeya*
- 10:00 Archaeological Research of Khrami Valley: Transportation of Obsidian in Neolithic-Chalcolithic Times (Preliminary Results of a New Archaeological Survey). *Saba Jokhadze*
- 10:20 **Coffee break**
- 10:40 Traditions of Obsidian Use at Körtik Tepe from the Late Epi-Palaeolithic to the Pre-Pottery Neolithic in the Upper Tigris Basin. *Rose Moir, Tristan Carter, Sarah Grant, Metin Kartal, Abu Bakar Siddiq, Vecihi Özkaya*
- 11:00 Obsidian Artefacts from Tell Hódmezővásárhely-Gorzsa (SE Hungary): Preliminary Results of a Provenance Study using pXRF. *Elisabetta Starnini, Ferenc Horváth, Barbara Voytek, Clive Bonsall*
- 11:20 A Timeline for the Utilization of the Carpathian Obsidian Sources. *Katalin T. Biró*
- 11:40 Geochemical and Technological Characterization of Obsidian Artefacts from the Neolithic Site of Opatów in Southeast Poland. *Dagmara H. Werra, Richard E. Hughes, Marcin Szeliga*

12:00 **Lunch Break**

Analytical Methods (1:00-4:00pm)

- 1:00 (pre-recorded) Cl/Na₂O As A Geochemical Index of Obsidian Aging. *Franco Foresta Martin, Enrico Massaro*

1:20 Confidence in Sourcing Small Obsidian Objects: Applying the Mahalanobis Distance Statistic in Ternary Diagrams with R. *Lucas R. Martindale Johnson, Kyle P. Freund, Kathy Davis, Daron Duke*

1:40 Portable X-ray Fluorescence for Non-Destructive Provenance Studies on Sardinian Obsidian. *Valentina Mameli, Carlo Lugliè, Carla Cannas*

2:00 Obsidian Hydration Dating by Infrared Transmission Spectroscopy. *Christopher Stevenson, Thegn N. Ladefoged, Alex Jorgansen, Alexander K. Rogers*

2:20 **Coffee break**

2:40 Archaeological Significances and Geochemical Characterizations of Obsidian Sources in the Central Highlands, Central Japan, by Wavelength-Dispersive XRF and LA-ICP-MS. *Yoshimitsu Suda*

3:00 Inter-Instrumental Calibration and Data Comparison for XRF Analysis of Obsidian. *Robert H. Tykot*

3:20 An SEM-based Micro-XRF and Portable XRF Spectrometry Study of Mesoamerican Obsidian Tablets. *Edward Vicenzi, Meredith Sharps Noyes, Maria Martinez, Michael Brandl, Thomas Lam*

Poster Session 2 (4:00-5:00pm)

4 The Carpathian Obsidian – Differences between C1, C2, and C3 Types. *Milan Kohút, Adrián Biroň, František Hroudá, Tomáš Mikuš, Stanislava. Milovská, Juraj Šurka*

5 Lithic Raw Materials Procurement Networks in Corsica in the 2nd and 1st Millennia: The I Casteddi Case. *Arthur Leck, Cheyenne Bernier, Bernard Gratuze, H el ene Paolini-Saez, Fran ois-Xavier Le Bourdonnec*

6 Obsidian Maritime Interconnections in Early Holocene Eastern Mediterranean. *Theodora Moutsiou, Phaedon Kyriakidis, Andreas Nikolaidis, Georgios Leventis, Alexandros Constantinides, Evangelos Akylas, Constantine Michailides, Carole McCartney, Stella Demesticha, Vasiliki Kassianidou, Zomenia Zomeni, Daniella Bar-Yosef Mayer*

7 Annadel and Glass Mountain Obsidian Sources in Sonoma County, California. *Robert H. Tykot, Michelle Hughes Markovics*

Day 3: May 2, 2021

(9am-4pm Pacific Daylight Time)

Lithic and Technological Concerns (9:00-9:40am)

- 9:00 The Obsidian Jewelry from West Mexico: Technology Characteristics and Precedence. *Rodrigo Esparaza*
- 9:20 Getting to the Point: Wari Obsidian Distribution, Reduction, and Use on the Southern Frontier. *Donna Nash*

Theoretical and Cultural Concerns: Part 1 (9:40-11:20am)

- 9:40 Digitization and Preservation of Legacy Datasets: Continued Adventures in Salvage Archaeometry. *Matthew Boulanger, Nicholas Tripcevich, Richard Burger*
- 10:00 Building on a Repository of Obsidian Geochemistry for South America. *Nicholas Tripcevich, Michael D. Glascock, Eric Kansa*
- 10:20 **Coffee break**
- 10:40 Obsidian in the Near East: New Challenges and Future Directions. *Elizabeth Healey, Stuart Campbell, Osama Maeda*
- 11:00 (pre-recorded) Assembling Obsidian in the South of Calchaquíes Summits (Tucumán Province, Argentina) between 300 BC - 1450 AD. *Juan Montegu*
- 11:20 **Lunch Break**

Theoretical and Cultural Concerns: Part 2 (1:00-1:40pm)

- 1:00 Depositional Pattern of Obsidian Artefacts: Understanding the Diverse Value Concepts in the Neolithic Carpathian Basin. *Kata Szilágyi*
- 1:20 Obsidian Sourcing and the Study of Island Colonization. *Tristan Carter*

Poster Session 3 (2:00-3:30pm)

- 8 Obsidian and Salt in the Khoy Plain: Uncovering the Early Bronze Age Obsidian Procurement System of the Salt Mine of Tappeh Doozdaghi, North-Western Iran. *Marie Orange, Akbar Abedi, François-Xavier Le Bourdonnec, Afrasiab Garavand, Fatemeh Malekpour, Catherine Marro*

- 9 Provenance Study of Silicic Stone Tools from Hajdúság (E Hungary) by Using PIXE and PIGE Techniques. *Peter Rozsa, Árpád Csámer, Sándor Tóth, Zita Szikszai, Zsófia Kertész, Ákos Csepregi, Sándor Gönczy, Béla Rácz*
- 10 Measurement of Magnetic Susceptibility of Obsidian from Shirataki, Hokkaido, Japan, to Identify the Source of Obsidian Tools. *Kyohei Sano*
- 11 Imports and Outcrops: A Preliminary Characterization of the Baantu Obsidian Quarry, Wolyta, Ethiopia, Using Portable X-Ray Fluorescence. *Benjamin Smith*

Closing announcements and updates on the next IOC meeting by Dr. Akira Ono (3:30-4:30pm)

METHODS AND ALGORITHMS FOR USE OF SIMS IN OBSIDIAN HYDRATION ANALYSIS

Alexander K. Rogers^a and Christopher M. Stevenson^b

^a Maturango Museum, Ridgecrest, California, USA

^b Virginia Commonwealth University, Richmond, Virginia, USA

Abstract

We describe an analytical exploration of four issues involved in use of secondary ion mass spectrometry (SIMS) in obsidian hydration dating (OHD): determining the location of the surface and the surface concentration; computation of intrinsic water content based on SIMS; determination of water mass gained by hydration; and computation of measures of depth of water penetration. The data set used as an example is from specimen number DHR-1235, from Orito quarry on Easter Island; the hydration occurred naturally, over a period of approximately 600 years. We discuss methods for smoothing SIMS data and computing slope, and conclude that the best method for defining the surface is based on the SIMS profile for silicon (Kuroda et al. 2018). We also conclude that intrinsic water concentration can be computed very simply from SIMS data, as can the total mass of water gained. The inflection point of the SIMS curve is a good approximation for the location of the optical hydration front. On the other hand, the full-width half-maximum (FWHM) point, despite its frequent use, is not a good measure of depth of water penetration.

Introduction

This paper describes an analytical exploration of the issues involved in use of secondary ion mass spectrometry (SIMS) in obsidian hydration dating (OHD). Virtually all OHD analyses performed by practicing archaeologists today employ optical microscopy to measure the depth of the visible hydration rim, which is due to stress birefringence caused by water absorption. Some researchers have applied SIMS to obsidian hydration analysis (e.g., Anovitz et al. 1999; Kuroda et al. 2018; Liritzis and Laskaris 2012; Riciputi et al. 2002; Stevenson et al. 2004; Stevenson and Novak 2011), which has the advantage of showing the hydration process at a molecular level. However, matching SIMS data with optical microscopy or with theoretical models can be difficult. The issues addressed here include: determining the location of the surface and the surface concentration; computation of intrinsic water content based on SIMS;

determination of water mass gained by hydration; and computation of measures of depth of water penetration.

The data set (provided by C. M. Stevenson) examined here is from specimen number DHR-1235, from the Orito quarry on Rapa Nui (Easter Island); the hydration occurred naturally, over a period of approximately 600 years. In SIMS studies, hydrogen ion (H⁺) concentration is typically used as a proxy for total water, H₂O_t. This data set includes SIMS measurements of silicon, aluminum, and hydrogen vs. depth. The data set for each element extends from the physical surface to a depth of approximately 5μ, in increments of 0.0172μ, and contains approximately 290 data points. The profile for this specimen (Figure 1) is typical; other specimens may exhibit a different morphology, but the same features are generally present.

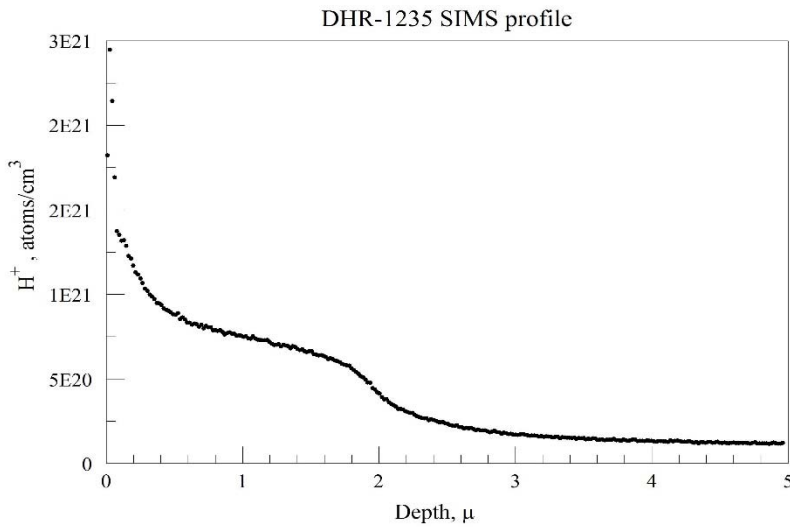


Figure 1. Hydrogen ion concentration vs. depth for DHR-1235, showing a typical SIMS profile. Hydrogen ion (H^+) is a proxy for water content.

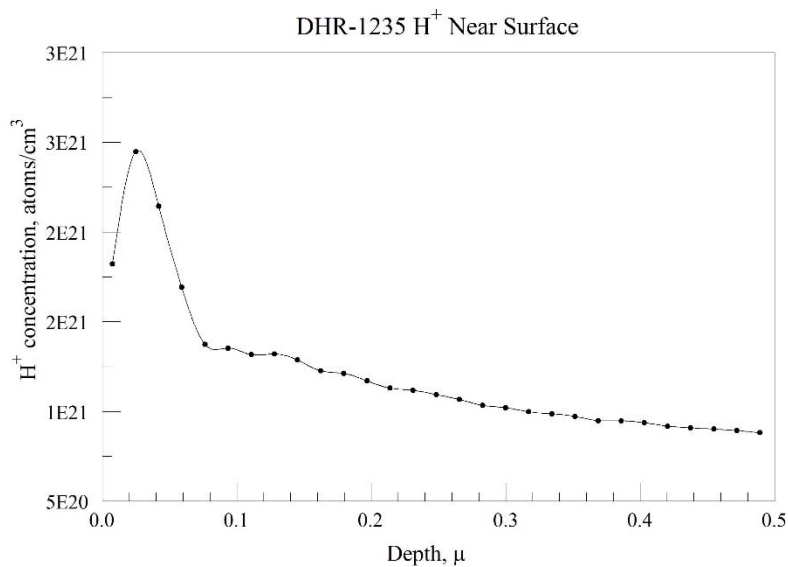


Figure 2. Near-surface region, showing effects of adsorbed water.

Effective Surface

Obsidian is always characterized by a surface layer of water, due to adsorption and the presence of nano-cracks which admit water and increase the effective surface area. In addition, water reacts with network modifier atoms, notably Na and K (Morgenstein et al. 1998), and also breaks down the $SiO_2 - Al_2O_3$ matrix of the glass

itself (Kuroda et al. 2018). All of these phenomena lead to a saturated surface (SS) layer and ambiguity as to the location of the surface. A rigorous and repeatable definition of the surface is critical for determining the penetration depth in diffusion studies, since both the full-width half-maximum (FWHM) and inflection point (IP) must be measured relative to a surface; further, the surface layer

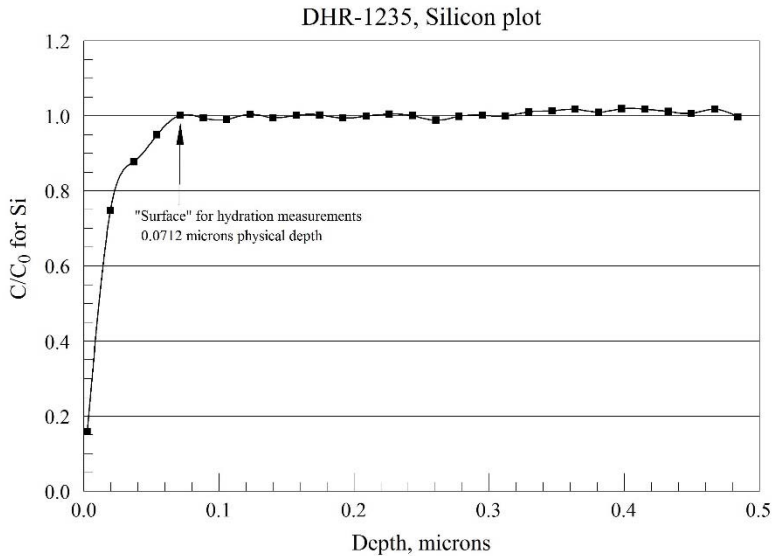


Figure 3. Silicon concentration vs. depth. For this case the depth of the effective surface d_s is 0.0712μ . Silicon concentration is normalized to its value at 1μ depth.

must be excluded from computations of total water gained in hydration.

The mathematical and physical model used in analyzing the diffusion of water into the glass has two components: a surface layer of infinitesimal thickness which provides a concentration of water C_0 to drive the diffusion, and a homogeneous material into which the diffusion occurs (Crank 1975:20). However, when confronted with a typical SIMS profile of H^+ concentration vs. depth in the near-surface region (Figure 2), the first question is “where in the world is the surface”?

Kuroda et al. (2018) resolved the quandary by using the SIMS profile for Si concentration to find the undegraded surface. Figure 3 shows the near-surface portion of the Si profile for this specimen; for convenience the count of Si ions is normalized to the count at 1 micron depth. The Si concentration is degraded near the surface ($<0.07\mu$) by water dissolution, and the SIMS profile for Al for this specimen (not shown here) shows the same effect. This is also the same region where the spike in water content occurs in Figure 2, and corresponds to

the SS layer. Thus, for diffusion analyses, Kuroda et al. (2018) suggest the “effective” surface is the point where the Si profile flattens; from this depth onward the glass matrix is uniform and has not been degraded by reactions with surface water, so diffusion laws should apply.

Thus, the recommended procedure is as follows, using a SIMS profile for Si vs. depth and also a profile for H^+ vs. depth:

1. Examine the Si profile. The effective surface for OHD analyses is at the depth (d_s) where the curve flattens.
2. Going to the H^+ data, subtract d_s from each depth measurement. This is now the depth from the effective surface. Points to the left of d_s represent the saturated surface layer and are ignored.
3. The H^+ concentration corresponding to d_s is the effective surface concentration C_0 for diffusion analysis. Dividing each concentration value by C_0 gives the relative concentration C/C_0 , which lies between zero and one, and is a convenient basis for analysis.

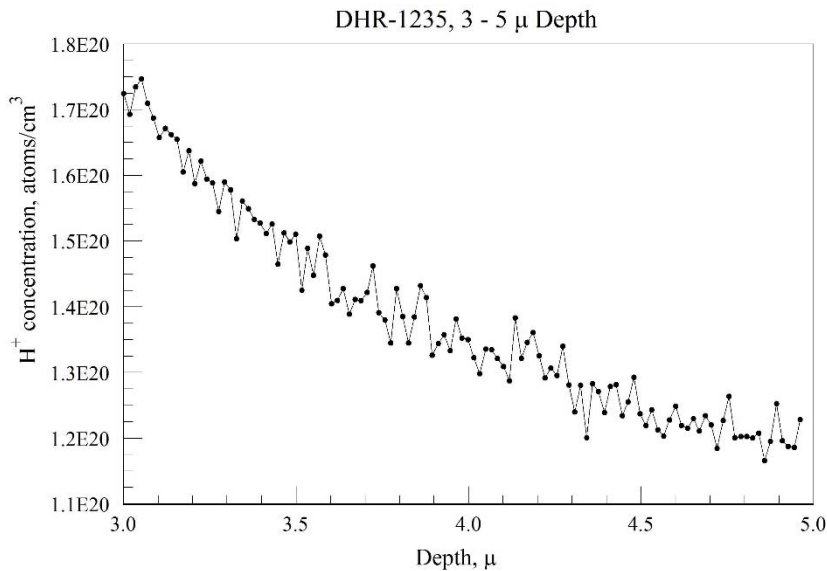


Figure 4. Hydrogen ion concentration between 3 and 5 μ depth. Note that the overall trend is still downward, indicating that the profile has not yet reached the intrinsic water concentration level.

Intrinsic Water

Intrinsic water concentration can be computed from the SIMS data set. Figure 1 showed the H^+ profile for this specimen, with the concentration expressed in terms of atoms/cm³. Note that the concentration never goes to zero, which is due to the intrinsic water content. Thus, the asymptote of the H^+ curve, shown by a dotted line, represents the intrinsic water.

The hydrogen ion concentration, H^+ , is a proxy for water, and the concentration C is calibrated in terms of H^+ atoms/cm³. The concentration of water in gm/cm³ is then

$$W = C \cdot 18.02 / N_a$$

where N_a is Avogadro's number, 6.02×10^{23} atoms/mole. The weight fraction of H_2O_t in the obsidian is the ratio W/ρ , where ρ is the density of the obsidian in gm/cm³. Working out the numbers,

$$\text{wt\% } H_2O_t = 100 \cdot C \cdot 18.02 / (\rho \cdot 6.02 \times 10^{23}). \quad (1)$$

Figure 4 is a detailed plot of the profile in the 3 – 5 μ range. It is clear that the H^+ concentration has not yet reached the asymptote, but is still descending; if the profile were continued another 2 – 3 μ it would probably reach the intrinsic water concentration. This problem can be resolved by making a decreasing exponential fit to the data in the 4 – 5 μ range, using the form

$$\text{wt\% } H_2O_t = A \cdot \exp(-B \cdot d) + C \quad (2)$$

where d is depth in microns and C is the asymptote of interest. A least-squares best fit to this equation yields $C = (0.96 \pm 0.01) \times 10^{20}$ atoms/cm³ as an estimate of the asymptote. The density of Orito obsidian is 2.4383 gm/cm³ (Stevenson et al. 2019), so equation (1) gives

$$\text{wt\% } H_2O_t = [(0.96 \times 10^{20}) \cdot 18.02 / (2.4383 \cdot 6.02 \times 10^{23})] \quad (3)$$

or 0.11 ± 0.01 wt% for this specimen. The value reported based on FTIR and the Beer-

Lambert law is 0.10 wt% (Stevenson et al. 2019), which is reasonable agreement.

Mass of Water Gained

The curve above the dotted line in Figure 1 represents water gained by hydration. The total water gained is the area under the curve, after subtracting off the intrinsic water. The algorithm here is:

1. Examine the SIMS data set and find where the H^+ concentration stops declining. This is the intrinsic water concentration. Determine the H^+ concentration at this point with the MIN function.
2. For each SIMS data point, subtract the intrinsic water (0.96×10^{20} atoms/cm³ in this case) from the measured concentration. This data set represents the water gained by hydration, C_h , as a function of depth.
3. Select the effective surface as described above, and ignore all data points at shallower depths.
4. Starting at the effective surface, add the C_h values, resulting in the area under the curve; this is the total number of H₂O atoms/cm³ gained in hydration. For this specimen it is 8.31×10^{22} H₂O molecules. Figure 5 shows the concentration gained vs. depth, overlaid on the SIME data.

Depth of Penetration

Three measures of depth of penetration are possible: the 50% point on the C/C_0 curve (the full-width half maximum, or FWHM); the inflection point on the C/C_0 curve (IP); and the point which corresponds to half the total mass of water gained by hydration (H_{50}). Each has advantages and drawbacks.

FWHM Point

The FWHM point has been frequently used as a measure of depth, but there are two problems with computing it. The first is the definition of the surface concentration C_0 , discussed above. The second is the noise on the SIMS profile (as shown in Figure 4),

which can obscure the 50% point. SIMS data, like many real-world data sets, consist of high-frequency noise superimposed on a slowly-varying signal, and the point of interest is the 50% point of the slowly-varying signal. The noise originates from two sources, the first and most obvious being instrument noise. This arises from statistical fluctuations in the arrival rate of the H^+ ions at the detector, and is exhibited as high-frequency “hash” on the profile. The second is lower-frequency and is probably due to nano-scale inhomogeneities in the composition of the obsidian. Neither source of noise is of interest in analysis, and performing SIMS analysis requires extracting the basic sigmoid shape.

Data smoothing is a set of general techniques for suppression of noise on experimental data. The underlying problem in data smoothing is to suppress unwanted noise on the signal, without unduly distorting the signal itself. Smoothing is distinguished from interpolation, which embraces methods for inferring data points between the existing points.

Smoothing algorithms fall into two general classes, global and local. Global methods make a mathematical fit to an entire set of data; the least-squares best fit to the logarithmic Arrhenius equation is an example of a global method. Global methods only work when a mathematical model of the entire process is available, as in the Arrhenius case. Local smoothing algorithms, on the other hand, smooth the data point by point based on data characteristics, with no *a priori* assumption about a model. In the SIMS case, no mathematical model of the sigmoid shape is available, so local methods must be used.

The method applied here is polynomial filtering. The principle is to create a least-squares best fit to a polynomial equation centered on a data point of interest and then substitute the computed point for the data point. The method assumes that the data points are equally spaced and that the higher-order

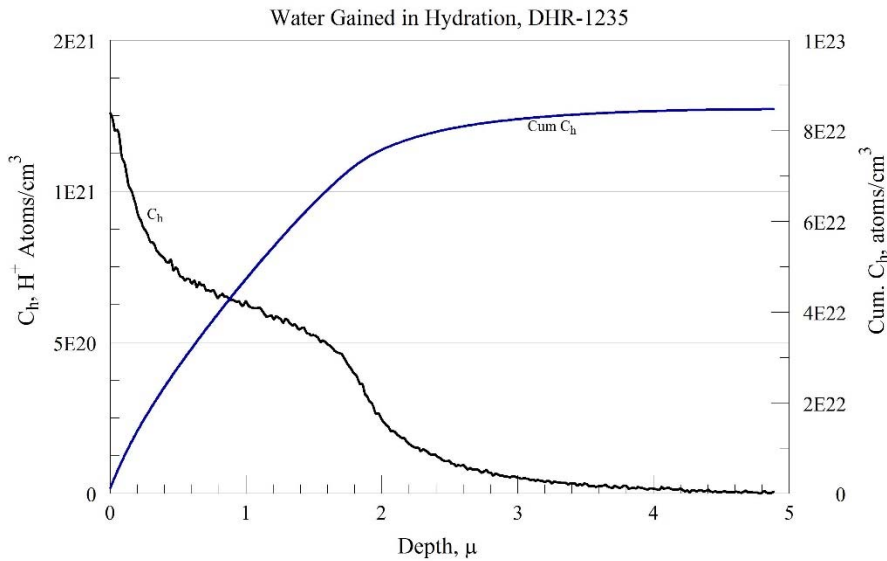


Figure 5. Water gained in hydration. Left axis is C_h , the SIMS H^+ concentration with intrinsic water subtracted. Right axis is the integral, or cumulative C_h from the effective surface, representing the area under the SIMS curve.

derivatives of the underlying curve do not change significantly over the smoothed region. An excellent tutorial on the method can be found in Lanczos (1956:317-321), who focuses specifically on the “method of fourth differences”. A formulation of the general case can be found in Guest 1961:349-355); the method is also called Savitzky-Golay smoothing (Savitzky and Golay 1964). The general form for the coefficients is in Appendix A to the present.

The filter applied here to smooth the C/C_0 curve is a 5-point quadratic fit. The specific form, implemented in MS Excel, is yields the smoothed value of C/C_0 at point n , \hat{y}_n , is

$$\hat{y}_n = \sum a_n * x_n, \quad (4)$$

with the sum running from $n = -2$ to $+2$. The values of the coefficients are as in Table 1. This reduces the noise on the SIMS profile. If there is still significant noise around the 50% point, a simple linear least-squares fit can be computed by MS Excel to interpolate the FWHM value; typically using about 20 points on each side of 50% is adequate.

Coefficient	Value
a_{n-2}	-0.0857
a_{n-1}	0.3429
a_n	0.4857
a_{n+1}	0.3429
a_{n+2}	-0.0857

Table 1. Coefficients for C/C_0 Smoothing

The FWHM point should be computed based on water gained by hydration, excluding intrinsic water. Figure 6 shows the FWHM point for DHR-1235 and the importance of excluding intrinsic water.

Inflection Point

The inflection point is defined mathematically as the point where the second derivative of a curve changes sign; it is also the point of maximum slope of the C/C_0 curve (although, since the C/C_0 curve is decreasing as depth increases, the slopes are all negative, so the inflection point is where the slope exhibits its most negative value). Since stress in the glass is created by gradients in water concentration, the inflection point also corresponds physically with the region of

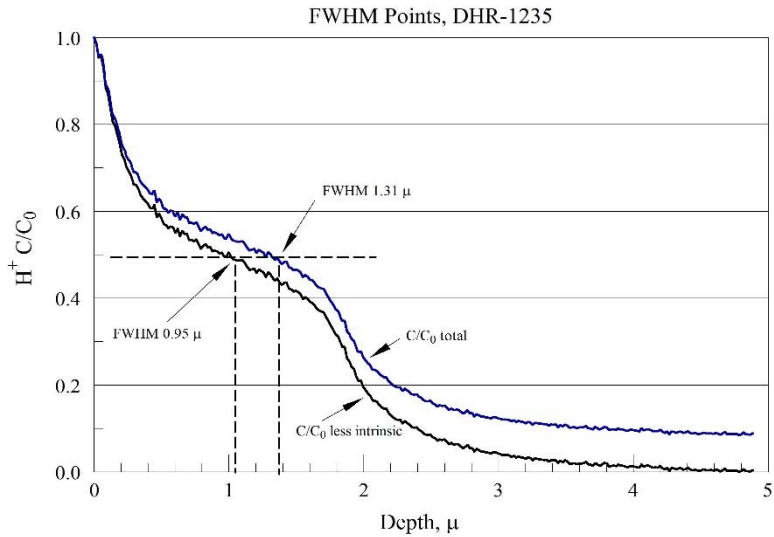


Figure 6. Position of the full-width half-maximum point. Note that including intrinsic water in the FWHM computation introduces an error of 0.36 μ, or over 30%.

greatest stress, and hence approximates the location of the optical hydration rim (Rogers 2008).

It is necessary to compute the slope of the C/C_0 curve to find the inflection point. The slope of any curve $y(x)$ is defined by

$$\dot{y} = \lim \Delta y / \Delta x \text{ as } \Delta x \rightarrow 0.$$

For experimental data, Δx is typically fixed and the slope is approximated by the finite difference

$$\dot{y} = \Delta y / \Delta x \quad (5)$$

However, if noise is present on the data, as with SIMS, the process of computing the finite difference by equation (5) amplifies the noise, which makes estimation of slope difficult.

Lanczos (1956:321-331) and Savitzky and Golay (1964) showed that slope can be computed by a least-squares best fit, similar to smoothing described above. This method of computing slope suppresses much of the noise that affects the simple difference method of equation (5).

Coefficient	Value
a_{n-3}	0.0873
a_{n-2}	-0.2659
a_{n-1}	-0.2302
a_n	0.0000
a_{n+1}	0.2302
a_{n+2}	0.2659
a_{n+3}	-0.0873

Table 2. Coefficients for Slope Smoothing

Two decisions must be made prior to performing the analysis. The first decision is between a second order fit (quadratic) and a third-order fit (cubic). The quadratic fit suppresses noise better but is based on the assumption that the second derivative of the underlying curve is not changing significantly. However, the point of maximum slope is near the inflection point, where the second derivative does change significantly. Thus, a cubic 7-point fit was chosen here; the specific form, implemented in MS Excel, yields the smoothed value of slope at point n , \dot{y}_n , by the expression

$$\dot{y}_n = \sum a_n * x_n, \quad (6)$$

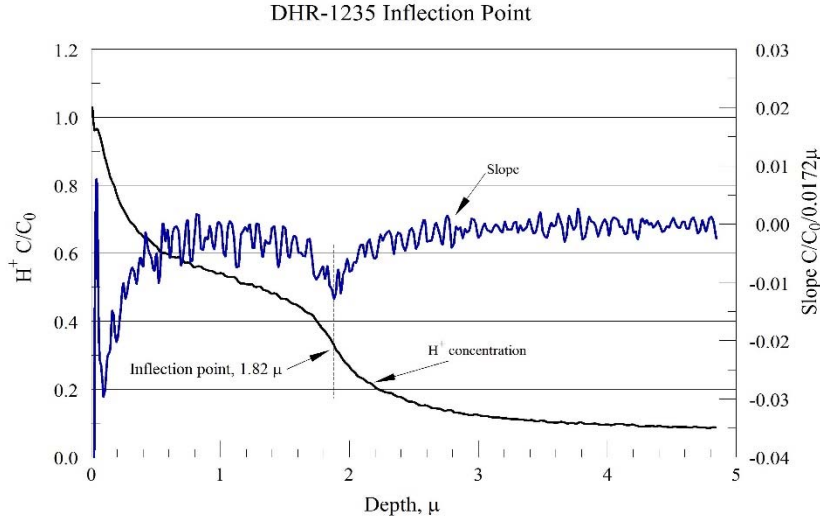


Figure 7. The inflection point is the point of minimum slope outside the surface layer. It is also the point of most rapid change in C/C_0 , and hence the point of maximum mechanical stress.

with the sum running from $n = -3$ to $+3$; the a_n coefficients are in Table 2. Again, the general form for the coefficients is in Appendix A.

Equation (6) yields smoother estimates of the slope than equation (5), but there is still considerable variation. Figure 7 shows the method applied to DHR-1235. The inflection point for total water is the same as for water gained by hydration, since intrinsic water shifts the curve without changing its shape.

H₅₀ Point

The H_{50} point is computed by the same method as Mass of Water Gained, above. It is again computed by a numerical integration process, but applied to C/C_0 rather than directly to the SIMS data. In this case the integral (area under the curve) represents the cumulative fraction of water gained by hydration, measured from the effective surface. The H_{50} point represents the depth at which 50% of the water gained is accounted for. Figure 8 shows the method graphically.

Summary of Measures

Table 3 summarizes the three measures of depth of penetration, with numerical examples from DHR-1235.

Measure	Definition	Remarks	DHR-1235 Example
FWHM based on total water	50% point on curve of C/C_0 vs. depth		1.31 μ
FWHM, based on water gained in hydration	50% point of C/C_0 (less intrinsic water) vs. depth		0.95 μ
Inflection point	Point of minimum slope of C/C_0 curve	Maximum stress, approximates optical hydration front	1.82 μ
H_{50} , based on water gained in hydration	Depth where 50% of water gained is accounted for		0.86 μ

Table 3. Measures of Depth of Penetration by Water

Discussion

The foregoing analysis shows that the determination of the effective surface is critical, since it defines both the starting point for depth and the initial concentration C_0 . The method proposed by Kuroda et al (2018),

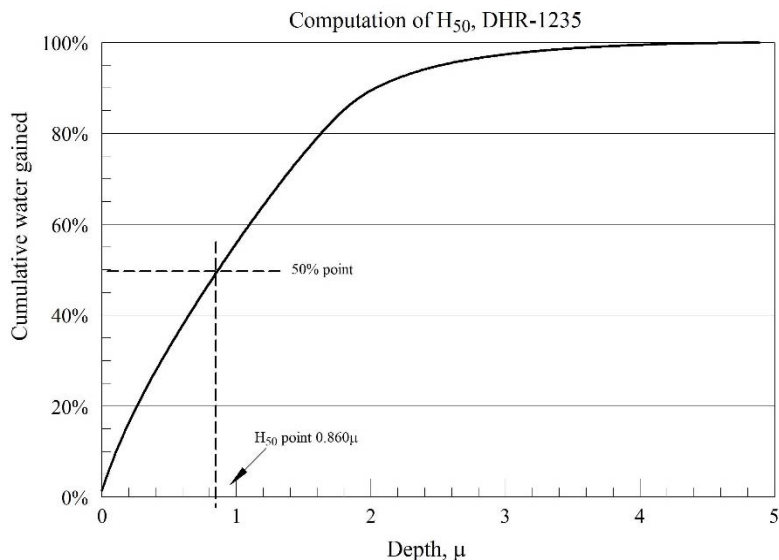


Figure 8. Determination of H_{50} depth.

which defines the effective surface based on the silicon profile is probably the best method, since it defines the beginning of the region where the glass has not been degraded by surface water. It is also repeatable. Use of this method requires a SIMS profile of silicon as well as hydrogen.

We also show that intrinsic water content in weight fraction or weight percent can be computed from the asymptote of the SIMS H^+ data by equation (3). In fact, since the intrinsic water component must be subtracted before computing the FWHM point or mass gained by hydration, the intrinsic water content is essentially a by-product of the analyses. As a caveat, the accuracy of such intrinsic water determinations relative to FTIR is currently unknown.

Third, the mass of water gained in hydration is easily calculated from SIMS data. The gain in atoms/cm³ is computed by numerical integration, and converted to weight percent by equation (1). The integration process has the effect of smoothing errors and suppressing noise on the data; thus, it is inherently more accurate than measures such as FWHM (computed based on concentration data) or inflection point

(computed by differentiation). It has the further advantage that it is directly comparable with diffusion theory, which predicts that mass gain should grow with the square root of time (Crank 1975:32ff.).

However, despite its frequent use, the FWHM point not a good measure of water penetration depth. In the first place, it is highly sensitive to the concentration value chosen as C_0 , and the noise on the SIMS data creates ambiguities in the FWHM point. In addition, it does not correspond with any particular point on the theoretical diffusion curve unless the exact form of concentration dependence is known. Finally, the SIMS data must be corrected for inherent water before computing the FWHM point, or significant error is introduced.

The H_{50} depth, which corresponds to the depth which includes 50% of the total water gained, is not useful in terms of matching a physical model. As shown above, computing H_{50} requires first computing the total water gained, which is a preferable measure of hydration.

The inflection point in the SIMS curve is the most difficult to compute, since it requires determining the slope of a noisy curve. This

requires taking the derivative of the SIMS profile. Since the noise on the curve is greatly amplified by the numerical differentiation process, noise-suppressing filtering is necessary (a 7-point cubic was used in the analysis here). On the other hand, the inflection point corresponds to the point of maximum mechanical stress due to hydration, and thus is the best match to the hydration rim observed by optical microscopy.

Finally, all these calculations can be performed with MS Excel; no fancy software is required. In fact, specialized packages such as SIMSVIEW can obscure the basic physics of the process.

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Appendix A

Coefficients for polynomial filters (Savitzky and Golay, 1964). C_0 is the set of coefficients for smoothing the profile; C_1 is the coefficient set for computing the slope; m is the order of the polynomial, so $m = 2$ is quadratic and $m = 3$ is cubic; i is the number of each data point.

General form:

Coefficients for smoothing:

$$C_0 = [(3*m^2 - 7 - 20*i)/4]/[m*(m^2-4)/3]$$

Coefficients for numerical differentiation (i.e. computing slope):

$$C_1 = \text{NUM}/\text{DEN}$$

$$\text{NUM} = 5*(3*m^4 - 18*m^2 + 31)*i - 28*(3*m^2 - 7)*i^3$$

$$\text{DEN} = m*(m^2 - 1)*(3*m^4 - 39*m^2 + 108)/15$$

Coefficients for this analysis are shown in tabular form below. In each case the coefficients used in the present analysis are in bold face.

5-point quadratic for smoothing
($m = 2$; $-2 \leq i \leq 2$)

i	C₀	C₁
-2	-0.0857	2.3539
-1	0.3429	0.4686
0	0.4857	0.0000
1	0.3429	-0.4686
2	-0.0857	-2.3539

7-point cubic for slope ($m = 3$; $-3 \leq i \leq 3$)

i	C₀	C₁
-3	-0.0952	0.0873
-2	0.1429	-0.2659
-1	0.2857	-0.2302
0	0.3333	0.0000
1	0.2857	0.2302
2	0.1429	0.2659
3	-0.0952	-0.0873

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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