The annual IAOS meeting will be held during the 2008 Society for American Archaeology meetings in Vancouver, British Columbia, Canada. Please join us on Friday, March 28, 2008 from 3-5pm. Check the final program for location information. All are welcome to attend!

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, or lab report for publication in the IAOS Bulletin! Articles and inquiries can be sent to cdillian@princeton.edu Thank you for your help and support!

SPONSORED EVENTS AT THE SAAs IN VANCOUVER

We are pleased to announce two IAOS sponsored events at the 2008 Society for American Archaeology meetings in Vancouver, BC. Please see the program for room locations:

IAOS Workshop on Sourcing and Dating of Obsidian: Updates on X-ray Fluorescence and Surface Analysis Methods, organized by Chris Stevenson and Mike Glascock. Saturday, March 29, 1-6pm.

AND

Current Studies on Obsidian Sourcing, Trade, Use, and Dating, organized by Rob Tykot. Saturday, March 29, 8am-12 noon.
NOTES FROM THE PRESIDENT

IAOS is pleased to sponsor a variety of events coming up in the next few months. The first is an international conference February 21-24, 2008 in Delphi, Greece, entitled The Dating and Provenance of Obsidian and Ancient Manufactured Glasses and organized by Ioannis Liritzis and Chris Stevenson. In April, IAOS is sponsoring two events at the SAA Annual Meetings: a workshop and an organized paper session. The IAOS Workshop on Sourcing and Dating of Obsidian: Updates on X-ray Fluorescence and Surface Analysis Methods is organized by Chris Stevenson and Mike Glascock. The IAOS-sponsored paper session, Current Studies on Obsidian Sourcing, Trade, Use, and Dating, is organized by Rob Tykot and includes a dozen papers representing hydration analysis and geochemical characterization studies from regions across the globe. See the announcements elsewhere in this Bulletin for additional information about each of these events.

IAOS is also pleased to announce the 2007 student award for an obsidian-related paper presented during conferences or meetings, granted to Emmanuel Ndiema, Rutgers University, for his paper entitled “Mid-Holocene Pastoralists Adaptations in East Africa: Evidence from Geochemical Analysis of Obsidian Sources and Artifacts from Koobi Fora, Kenya” presented in the symposium, Xenophile: The Allure of the Exotic, at the 72nd Annual Meeting of Society for American Archaeology in Austin, Texas. If you see outstanding papers or posters presented at conferences or meetings, please send nominations to me for consideration for future awards.

As IAOS seeks to enhance the multi-disciplinary cross-fertilization among archaeology and other disciplines involved in obsidian studies, I encourage you to send news items, recent publications, conference announcements, and abstracts of obsidian-related research in such fields as geology, volcanology, geochemistry, petrology, materials studies, glass science, and other studies of contemporary and ancient glasses.

Finally, a few business items:

- As announced by IAOS Secretary/Treasurer in this Bulletin, and noted in the prior Bulletin (Summer 2007, No. 37), IAOS will be changing its membership year to coincide with the calendar year. Renew your memberships now for 2008 as you celebrate the New Year.

- At the 2007 IAOS Annual Meeting we discussed appropriate uses of the IAOS membership email list. The current (informal) policy is to only use the email list for IAOS-related announcements (e.g., calls-for-papers for IAOS sponsored conferences). However, we are interested in hearing your thoughts on judiciously expanding the use of the email list to announce other conferences, meetings, and events of interest to the membership. All requests for use of the list would be evaluated by the President for applicability and interest to the IAOS membership, and actual distribution of emails would be conducted only by the IAOS President or the IAOS Secretary/Treasurer. IAOS is not proposing to ever share the email list with any outside party. Please weigh in with your thoughts directly to me; your comments and opinions will help IAOS develop an email policy that serves the membership well without overburdening your inbox with unwanted emails.

- The 2008 IAOS Annual Meeting will be held on Friday afternoon, March 28, at the SAA Annual Meetings. Check the SAA final program for the time and location. Please join us at the meeting to discuss current business and to bring your new ideas to the table.

I look forward to seeing you all in April in Vancouver!

Ana Steffen
asteffen@unm.edu
asteffen@vallescaldera.gov
AN IMPORTANT MEMBERSHIP NOTE FROM IAOS SECRETARY-TREASURER:

Dear IAOS Members,

At the 2007 IAOS Annual Meeting held earlier this year at the Austin SAA annual meetings, the members in attendance voted to make a change in the way that individual IAOS memberships are structured. Instead of asking members to renew their memberships on the anniversary of the date they joined, all memberships will now be due for renewal at the beginning of the calendar year (January 1, 2008). This will help streamline our administrative duties and hopefully make it easier for members to remember to renew their annual membership (with helpful reminders from us, of course). Those members who recently joined in the last half of 2007 will be grandfathered-in to the 2008 membership.

Our goal is to have all memberships renewed in time for the 2008 IAOS Annual Meeting being held on March 28 in conjunction with the SAA annual meetings in Vancouver, BC. So please plan on renewing your membership in the New Year. We appreciate your continued support, and if you have any questions or concerns about your IAOS membership, please contact me directly.

Regards,
S. Colby Phillips
IAOS Secretary-Treasurer
colbyp@u.washington.edu

CALL FOR NOMINATIONS

It’s time for elections for IAOS Secretary-Treasurer. Our current Secretary-Treasurer, Colby Phillips, is willing to continue in the position, though we are also seeking nominations for additional candidates. The term is for two years.

Deadline for nominations is February 1, 2008. Nominations may be sent via email to IAOS President, Anastasia Steffen at asteffen@unm.edu.

IAOS WORKSHOP

Sourcing and Dating of Obsidian: Updates on X-ray Fluorescence and Surface Analysis Methods

Saturday, March 29, 2008 from 1-6pm

The IAOS will be sponsoring a workshop on the characterization and dating of obsidian at the next Society for American Archaeology annual meeting in Vancouver (March 26-30, 2008). Mike Glascock, Chris Stevenson and other invited speakers will present an overview of the latest methods in the discipline. This will include obsidian hydration by infrared spectroscopy and secondary ion mass spectrometry. A demonstration of a portable X-ray florescence system is planned so bring a sample or two. This workshop should be very rewarding for those involved in obsidian studies everywhere. Check final SAA Program for location at the meetings.

**Archaeological Obsidian Studies in Hokkaido, Japan: Retrospect and Prospects**  
Masami Izuho\(^1\) and Hiroyuki Sato\(^2\)  
\(^1\)Sapporo Buried Cultural Property Center, izuhom@serenade.plala.or.jp  
\(^2\)University of Tokyo hsato@u-tokyo.ac.jp

Recent research has identified an extended exchange network in the Japan Sea Rim area extending over 3,000 km and including the mainland. This paper reviews current knowledge about obsidian studies in Hokkaido, a part of this region, and makes proposals for future research. The geology of Hokkaido and its 21 known obsidian sources are reviewed and results of chemical analyses of some sources described. Archaeological studies of exchange networks, exploitation patterns and site variation are described. Proposals for the direction of future studies include additional research on the location, geological history and characterization of obsidian sources and the use of new models concerning procurement range, mobility patterns, and behavioural strategies.

**Late Pleistocene and Early Holocene Uses of Basaltic Glass in Primorye, Far East, Russia: A New Perspective based on Sites Near the Sources**  
Nikolay A. Kluyev and Igor Y. Sleptsov  
Russian Academy of Sciences lab39@front.ru

Basaltic glass artefacts are common at many sites dating from the Late Pleistocene-Early Holocene in the Primorye region of Far East Russia. Sourcing by various geochemical techniques indicates that the vast majority are derived from outcrops in the nearby Shkotovo Plateau. This raises the problem of where and how the large quantities of basaltic glass were acquired: e.g. through trade, embedded procurement, or direct access to outcrops. A recent survey has located 10 new sites (Tigrovy 1-10) on river terraces near these basaltic glass sources. Study of the material can provide information about which form of procurement was used in the past. Some of the sites are proposed as primary ‘quarries,’ whereas others are hypothesized as temporary camps or longer term base camps. Our preliminary conclusion is that the sites located near the sources are linked to distant settlement sites, possibly as part of seasonal movements between the forest and the river valleys.

**PIXE Provenancing of Obsidian Artefacts from Paleolithic sites in Korea**  
J.C. Kim\(^1\), D.K. Kim\(^1\), M. Youn\(^2\), C.C. Yun\(^2\), G. Park\(^2\), H.J. Woo\(^3\), Mi-Young Hong\(^3\), and G.K. Lee\(^5\)  
\(^1\)School of Physics, Seoul National University, jckim@phya.snu.ac.kr, kyun4@snu.ac.kr  
\(^2\)AMS Laboratory, Seoul National University, myoun@myounpc.snu.ac.kr, ccyun@snu.ac.kr, danielp@snu.ac.kr  
\(^3\)Korean Institute of Geology and Mineral Resources, hjwoo@rock25t.kigam.re.kr  
\(^4\)Kijon Institute of Cultural Heritage, hongmy@chollian.net  
\(^5\)Museum of Chosun University, kklee@chosun.ac.kr

The trace element composition (based on Fe, Rb, Sr, Zr) of 50 obsidian artefacts from the Hopyung, Samri and Shinbuk Paleolithic sites were measured by the external beam PIXE method using the 3 MV Tandetron Accelerator Facility at the Seoul National University AMS Laboratory. About 85% of these obsidians originated from the Paektusan volcano (Korea); obsidian of Japanese origin was found only at Shinbuk. INAA analyses on 6 obsidian samples from the Hahwageri and Janghungni sites are in good agreement with our PIXE results and those of the previous report by Popov et al. (2005).
Philippine Obsidian and its Archaeological Applications
Leee Anthony M. Neri
University of the Philippines
leee_anthony.neri@up.edu.ph

Obsidian sourcing has been used in Philippine archaeology for the first time. This paper discusses the potential of this new approach for studying mobility patterns and exchange networks of early Filipinos. Currently, two obsidian sources have been identified in the Philippines. The Nagcarlan and Pagudpod sources are both located on the island of Luzon. X-ray fluorescence spectroscopy (XRF) was used to obtain a chemical signature of these sources and to link obsidian artefacts recovered at three archaeological sites to their geological source. The results provide evidence for long distance movement of obsidian in the past. A review of all known obsidian artefacts recovered from archaeological sites in the different islands and provinces of the Philippines provides essential background for further studies of obsidian movement and exchange.

RECENT OBSIDIAN PUBLICATIONS

The New Mexico Geological Society has just released a new publication relevant for obsidian researchers interested in obsidian sources in the Jemez Mountains in northern New Mexico. Geology of the Jemez Region II (2007) is edited by B. S. Kues, S. A. Kelly, and V. W. Lueth, and contains several papers with new information on artifact-quality obsidian geological deposits. This volume is an excellent addition to the 1996 volume, “Jemez Mountains Region”, edited by F. Goff, B. S. Kues, M. A. Rogers, L. D. McFadden, and J. G. Gardner. The publication is available for order in hardcover and softcover at the NMGS website at: http://nmgs.nmt.edu/publications/home.cfm

Fractography of Ceramics and Glasses (2007) edited by G. D. Quinn, has been released as a Special Publication of the Materials Science and Engineering Laboratory, National Institute of Standards and Technology. As noted in the preface, “fractography is an underutilized tool for the analysis of fractures in glasses.” and is an engineering and materials science approach with great promise for researchers in lithic technology and obsidian studies. The volume has excellent illustrations and will serve as an introduction to the literature of this specialization for those who find that their interest is piqued. The publication is available for order at the www.nist.gov website or as a free pdf file at: http://www.nist.gov/public_affairs/practiceguides/SP960-161.pdf

Free Non-Destructive Obsidian Sourcing for Anatolia Near East Artifacts

The University of Minnesota's Electron Microprobe Laboratory has now allotted instrument time for obsidian sourcing using the MinOAN reference collection. This service is free of charge thanks to the lab, although a few conditions do exist. The obsidian artifacts must, of course, have originated in Turkey, Syria, Lebanon, Iraq, or elsewhere in the Near East for the MinOAN collection to be useful. Interested researchers should submit a proposal that includes the area, the approximate number of artifacts, research goals, etc. Other policies of the Electron Microprobe Laboratory will apply. Researchers at any level, from graduate students to faculty, and in any country are eligible and welcome to participate. Any researchers interested in participating or in further details are encouraged to contact Ellery Frahm at frah001@umn.edu. Further information is available on-line at: http://probelab.geo.umn.edu
X-ray Fluorescence and Neutron Activation Analysis of Obsidian from the Red Sea Coast of Eritrea

Michael D. Glascock, University of Missouri
Amanuel Beyin, SUNY-Stony Brook
Magen E. Coleman, University of Missouri

Introduction

The strategic location of Eritrea along the Red Sea coast and the Horn of Africa makes it an important place to study human prehistory over a long span of time. However, recurrent political instability and the environmental adversity in the region have hindered comprehensive archaeological investigation. Paleolithic research in Eritrea began after the country obtained independence from Ethiopia in 1991. Geological survey in the Abdur area, along the Gulf of Zula coast (Figure 1), identified Paleolithic artifacts embedded in reef limestone dating to ~ 125 Ka BP (Walter et al., 2000). Based on this evidence, human coastal adaptation during the Late Pleistocene has been proposed.

To explore the archaeological potential of the region, surveys and excavations were recently initiated along the Gulf of Zula and Buri Peninsula portions of the Red Sea coast. The survey documented a series of prehistoric sites from coastal and inland contexts featuring Acheulian, Middle Stone Age (MSA) and Later Stone Age (LSA) artifacts (Beyin and Shea, 2007). The Acheulian and MSA Lithic assemblages include highly deflated surface scatters of handaxes, prepared core products and retouched points made on locally available materials such as basalt, shale, and rhyolite. These assemblages however, lack secured stratigraphic contexts and obtaining radiometric dating is problematical.

Excavations at three sites, Asfet, Misse East and Gelalo NW (Figure 1) in 2006 produced archaeological deposits of LSA affinity with mollusk shell association. A large quantity of debitage, blades, bladelets, backed tools and microliths characterize the lithic artifacts. A few of the artifacts are shown in Figure 2. The LSA bearing archaeological strata have been dated to the Early Holocene by 14C (AMS).

Raw Material Exploitation

Obsidian is the dominant lithic material at a majority of the LSA sites along the Red Sea coast, but few sources comparable to its availability in the assemblages are known. This could be due to the limited time invested in searching for source areas and the lack of detailed geological maps to guide surveyors. It is also possible that the source areas could have collapsed or may have been buried. Obsidian generally occurs in the form of cobbles and pebbles along streams and in gravel piles as well as in lava flows eroding out of tuffaceous bedrock. Those found in the eroding surfaces are usually smaller in size and unconsolidated.

For this study, source samples were collected from a single rich obsidian source area called Kusrale Basin. Kusrale is a wide multi-tributary river basin along the southeastern margin of the Gulf of Zula. During rainy times, sediments and obsidian cobbles and pebbles are transported into the basin from a steep mountain on the eastern side. The approximate distances from the Kusrale Basin to Asfet, Misse and Gelalo NW are 20 km, 15 km and 30 km, respectively. A collection of 93 obsidian artifacts from the three sites and three raw material samples from the Kusrale Basin were submitted to the Archaeometry Lab at the University of Missouri (MURR) for chemical analysis.

Analytical Procedures

The artifacts and source materials were analyzed by X-ray fluorescence (XRF) and neutron activation analysis (NAA) using well established procedures which we will describe here very briefly. All of the samples were initially analyzed by an ElvaX desktop energy-dispersive-XRF spectrometer. The instrument consists of an X-ray generator, X-ray detector, and a multi-channel analyzer (MCA). The detector is a solid-state Si-pin-diode with an area of 30 mm2 and a resolution of 180 eV at 5.9 keV (at a count rate of 1000 counts per second). The X-ray tube is an air-cooled, tungsten anode with a 140 micron beryllium end-window.
Fig. 1. Map showing the location of the excavated LSA sites and source area, Kusrale.
The XRF analyses were conducted at 35 kV using a tube current of 45 microamps and an operating time of 400 seconds. Concentrations were calculated in parts per million by the ElvaX Regression program based on use of a quadratic regression model for a series of obsidian reference samples previously characterized by both XRF and NAA. The XRF analysis permits quantification of the following elements in obsidian: K, Ti, Mn, Fe, Zn, Ga, Rb, Sr, Y, Zr, and Nb. After completing the analysis by XRF, a subset of the artifacts and the three Kusrale Basin samples were analyzed by NAA to obtain higher resolution data. Due to the destructive nature of sample preparation by NAA, only twenty artifacts were available for analysis. The procedures employed were described in Glascock et al (1999).

Two irradiations and three measurements were used to determine the maximum number of elements possible by NAA. The elements measured were (1) six short-lived elements: Al, Cl, Dy, K, Mn, and Na; (2) seven medium-lived elements: Ba, La, Lu, Nd, Sm, U, and Yb; and (3) 15 long-lived elements: Ce, Co, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Sr, Ta, Tb, Th, Zn, and Zr.

Results

The XRF results obtained for the entire collection of artifacts and raw material samples in this study are illustrated in Figure 3 using the elements Fe and Rb. Although the artifacts cover a broad range of concentrations for Fe from 1.5 to 3.4%, the Kusrale Basin source samples are tightly grouped around an Fe concentration of about 2.0%. The figure suggests that subgroups might exist within the data. To search for possible differences in source exploitation, the artifacts were plotted with different symbols according to their archaeological site. Careful examination of the plot suggests a possible difference for the artifacts from Gelalo NW versus those from Asfet, but the Misse E artifacts cover the entire range of Fe. Although the data are sparse, it appears that the Kusrale Basin samples are associated with Gelalo or Misse E, but not with Asfet.

The higher resolution NAA data were also examined to search for the possibility of chemical subgroups as suggested by the XRF results. A plot of Fe versus Th indicates that a majority of the artifacts can be assigned to one of three groups, with a significant number of outliers (25%) not

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Fig. 3. Bivariate plot of Fe and Rb showing the XRF data obtained for three Kusrale Basin source samples and 93 obsidian artifacts from three sites along the Red Sea Coast of Eritrea. Note that Fe can be converted from ppm to percent by dividing by 10,000
belonging to any of the groups as shown in Figure 4. Group 1 has the highest Fe concentration of 2.7% and it has Ba concentrations below detection by NAA (less than 50 ppm). It consists of nine artifacts with no particular association to a specific archaeological site. Group 2 is made up of five samples (two artifacts and the three Kusrale Basin samples) with an intermediate concentration for Fe of about 2.2% and it also has Ba concentrations below detection. Group 3 consists of four artifacts with an average Fe concentration of 1.9% and a relatively high average Ba concentration of about 900 ppm. Although the outlier samples are unclear, it is quite possible that other chemical groups may be present. Until we are able to analyze more artifacts and obtain a representative collection of source samples, we are left with the results obtained to date.

Conclusions
In reviewing the results of site survey and excavations on the Red Sea Coast, there is a clear contrast in raw material use between the Acheulian and MSA assemblages on one hand and the LSA and Neolithic assemblages on the other. The LSA sites are dominated by obsidian and (to a lesser extent) quartz, whereas the Acheulian and the MSA assemblages display higher diversity of raw materials with more emphasis on locally available rocks, such as shale, basalt and rhyolite. The LSA humans had different mode of adaptation and they selectively utilized obsidian over other local lithic raw materials. One possible explanation for this is due to the variation in the nature of resources exploited by the two groups and the duration of settlement. It suggests that the LSA groups had a better information network to

Fig. 4. Bivariate plot of Fe and Th showing the NAA data obtained for three Kusrale Basin source samples and 20 obsidian artifacts from three sites along the Red Sea Coast of Eritrea. Ellipses around the subgroups are plotted at the 95% confidence level. The Kusrale Basin samples are members of Group 2.
explore for high-quality raw material sources, such as obsidian. Obsidian seems to have been transported more than 15 km to the LSA sites. Whether this implies higher mobility associated with resource scarcity or “provisioning place” model of technological organization (Kuhn, 1995) awaits further scrutiny from the overall dataset that one of the authors (Beyin) hopes to generate in the near future as part of his dissertation.

The results reported here show that obsidian was widely used along the Red Sea coast of Eritrea and indicate that the obsidian can be grouped into at least three chemical fingerprints (i.e., different sources). Unfortunately, at this time we have no information concerning the primary deposits of obsidian in the region. And, we do not know to what extent the obsidian from primary deposits may have been eroded to create secondary deposits in the Kusrale Basin. It is clear that much more can be learned after chemical analysis by XRF and NAA of a more systematic collection of raw material from potential source areas is performed.

References

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Glascock, M.D., R. Kunselman, and D. Wolfman

Kuhn, S. L.

Walter, R. C., et al.

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DELPHI, GREECE, OBSIDIAN CONFERENCE

The Dating and Provenance of Natural and Manufactured Glasses

Ioannis Liritzis, Laboratory of Archaeometry, Dept. of Mediterranean Studies, University of the Aegean, Rhodes, Greece, (liritzis@rhodes.aegean.gr)

Christopher M. Stevenson, Virginia Department of Historic Resources, Richmond, Virginia, USA, (chris.stevenson@dhr.virginia.gov)

The intensive investigation of archaeological problems and technological advancements in instrumentation requires the frequent updating of an interdisciplinary science such as archaeology. It is the goal of the workshop organizers to bring together examples of recent investigations in obsidian provenance and dating that reflect successful applications of well developed technologies to cultural problems as well as new developments in the field. The scope of the workshop also includes ancient glasses since many of the problems and applications in the obsidian studies field are directly related to research on natural glasses. The first readings of the contributions will be conducted at the European Cultural Center of Delphi, Greece on January 11-14, 2008. Please see the workshop web page for a listing of the topics and presenters (http://www.rhodes.aegean.gr/tms/delphiobsidian2008/index.htm). The workshop has been generously supported by a contribution from the IAOS.
Obsidian Hydration Dating and Relative Humidity: An Issue and a Suggested Protocol

Alexander K. Rogers, Maturango Museum, Ridgecrest, CA

Abstract
Theory and data are difficult to reconcile on the question of whether relative humidity affects the results of obsidian hydration dating when the rim thickness is measured by optical microscopy. This paper briefly reviews the experimental data and the relevant theory of hydration, based on the diffusion-reaction model of Doremus. It concludes that the apparent divergence may be due to an unexamined assumption in the hydration model, as regards the mathematical definition of the “hydration front”. A protocol for resolving the question is suggested.

Introduction
Does relative humidity affect the results of obsidian hydration dating when the rim thickness is measured by optical microscopy? Initially Friedman and Smith (1960) argued that it did not; recently published data suggest it does, but the effect is difficult to reconcile with theory. This paper briefly reviews the experimental data and the relevant theory of hydration, based on the diffusion-reaction model of Doremus (2000). I conclude the apparent divergence may be due to an unexamined assumption in the models, particularly regarding the definition of the “hydration front”, and I suggest a protocol for resolving the question.

In the discussion below I use “solute” and “diffusing species” interchangeably, both indicating the molecular water which diffuses into the glass.

Reported Measurements
Ebert et al. (1991) reported that the hydration rate is affected by relative humidity. Their measurement technique involved exposing powdered glass (obsidian, and a nuclear water glass) to water vapor and measuring mass gain. Their work explicitly corrected for adsorption and for pore filling in the process of hydration; they found a steady-state mass gain of 3.75 µg/hr \( \frac{1}{2} \) at 84% relative humidity, and 2.2 µg/hr \( \frac{1}{2} \) at 58% relative humidity.

Friedman et al. (1994) used a similar mass gain protocol. They again reported a humidity dependence, reporting that the hydration rate at 81% relative humidity was roughly twice the rate at 31%.

Mazer et al. (1991) employed a different protocol using optical microscopy. They placed obsidian discs in water vapor for specified lengths of time, and then measured the resulting hydration rims. They reported that the hydration rate was relatively unaffected by humidity, as long as humidity was under about 80%. Above that level, the hydration rate was strongly dependent upon humidity, reporting that the hydration rate increased by a factor of approximately 1.2 between 90% and 100% relative humidity.

Theory
The experimental results described above involve two different techniques of measuring the hydration process, mass transfer and optical position of the front. This requires two different theoretical formulations, starting from the diffusion process itself. Diffusion-reaction theory of hydration suggests the concentration of diffusing molecules with depth in the solid is given by

\[
C = C_0 f(z) \tag{1}
\]

where \( C_0 \) is the concentration at the surface, \( z = x/(4Dt)^{\frac{1}{2}} \), and \( 0 \leq f(z) \leq 1 \). Furthermore, \( f(z) \) obeys the boundary conditions

\[
\begin{align*}
f(z) &\rightarrow 1 \text{ as } z \rightarrow 0 \\
z(z) &\rightarrow 0 \text{ as } z \rightarrow \infty .
\end{align*}
\]

In some cases a specific form for \( f(z) \) can be defined. If the diffusion coefficient \( D \) is independent of concentration \( C \), then \( f(z) \) is given by the complementary error function \( \text{erfc} \ (z) \) (Crank 1975). If \( D \) depends linearly on \( C \), Wagner (1950) and Crank (1975) show the solution to be as plotted in Crank 1975, page 122, Fig. 7.5; this solution has the additional property that \( f(z) = 0 \) for finite values of \( z \). Anovitz et al. (1999) have developed a solution for a higher-order dependence of \( D \) on \( C \). All share as a minimum
the boundary conditions above. Rogers (2007) showed that the form of equation 1 is valid no matter what the functional dependence of $D$ on $C$, as long as the dependence on $x$ and $t$ can be expressed as a function of the composite variable $z$ (the so-called Lorentz transformation).

For a mass transfer model, the value of $C_0$ can be determined from the Ostwald solubility,

$$S = C_s/C_g$$

where $C_g$ is the concentration of solute (the diffusion species) in the gaseous state and $C_s$ the steady-state concentration of solute in the solid. At temperatures of interest archaeologically (i.e. $<100^\circ$C) the Ostwald solubility is a function only of the partial pressure of the solute in the gaseous state (Doremus [1994:123ff.; 2002:78]).

At steady-state conditions, $C_0$ is assumed to be equal to $C_s$, the concentration of the solute within the solid near the surface. Then equation 1 can be written as

$$C = kpf(z)$$

where $p$ is the partial pressure of gaseous solute, $f(z)$ is as defined in equation 1, and $k$ is a constant of proportionality. This is the diffusion equation for mass transfer.

In the next case, to define the position of the hydration front, equation 1 can be rewritten as

$$C/C_0 = f(z)$$

This states that the relative concentration of solute within the solid is determined solely by $z$. If the hydration front is defined by a specified value of $C/C_0$ (say, 0.5), then the corresponding value of $z$ (say, $z_f$) uniquely determines the relationship between depth ($x_f$) and age ($t_f$) of the front by rearranging the definition of $z$:

$$x_f^2 = 4z_f^2Dt_f.$$  (4)

Since $z_f$ and $D$ are both constants, this yields the familiar form of the hydration equation

$$x^2 = Kt,$$  (5)

which is the diffusion equation for optical measurement of the hydration front. To reiterate, the implicit assumption here is that the hydration front can be defined by a specified value of $C/C_0$, which is the same for all experimental conditions.

A further argument based on physics can be adduced as follows. It is well known that the concentration of hydrogen ($H$) in hydrated obsidian, as measured by a SIMS probe, exhibits a general shape as shown in Figure 1 (e.g. Anovitz et al. 1999; Stevenson et al. 2004). The region labeled A is the background or “floor”, reflecting the water and its reaction products inherent in the glass from the time of its formation. The region B is where diffusion is taking place, while region C is a diffusion-reaction zone, and region D is a zone of saturation. Region E is the surface-effects zone, and point F is the surface concentration corresponding to the Ostwald solubility of water in glass.

![Image of Figure 1: Typical variation of hydrogen concentration with depth in glass. Region A reflects the intrinsic hydrogen content. Region B is a diffusion zone, region C is a diffusion-reaction zone, and region D is a zone of saturation. Region E is the surface-effects zone, and point F is the surface concentration corresponding to the Ostwald solubility of water in glass.](image-url)
and alkali metals or earths increases the openness of the matrix, effectively increasing the ionic porosity \( Z \) of the matrix (Doremus 2002) and reducing the activation energy required for diffusion; second, the reaction removes \( \text{H}_2\text{O} \) from the glass interstices, thereby reducing back-pressure on the diffusion process and accelerating diffusion. In region D the combined effects of diffusion and reaction are approaching saturation. Finally, in region E, the curve is being influenced by surface effects, adsorption and pore/crack filling by \( \text{H}_2\text{O} \) molecules, which leads to an apparent concentration spike (on occasion, the surface may be a region depleted of water, e.g. Anovitz et al. 1999:742, Figs 3a-c). Ignoring surface effects, the nominal surface concentration \( C_0 \) lies at point F, reflecting the Ostwald solubility of water in obsidian (Doremus 1999; 2002).

It is also generally accepted that the hydration front, as observed by optical microscopy, represents a region of mechanical stress between the hydrated and unhydrated volumes of the glass (Anovitz et al. 1999). This phenomenon can be interpreted in terms of the ionic porosity \( Z \) and the effects of chemical reaction. Consider a uniform volume of obsidian, whose matrix dimensions can be characterized in terms of \( Z \), which is a measure of the open space in the matrix (Doremus 2002). If now a region of the obsidian has its characteristic dimension changed by increasing \( Z \), as by OH reacting with the glass matrix, a stress zone will exist between the hydrated and unhydrated regions, because the dimensions have changed but the glass matrix is still bonded together. The stress is related to the \textit{difference} in \( Z \) between the two zones, not the absolute value in either zone. Thus, the maximum stress will occur at the point of greatest slope in Figure 1. Examination of Figure 1 shows the slope increasing from right to left up to a maximum, then decreasing to the surface (we ignore the surface region E, since it does not affect reactions deep in the glass). The point of maximum slope is therefore the inflection point in the concentration curve, as shown by Anovitz et al. (1999:742, Fig. 3) tends to bear this out approximately.

If the hydration front coincides with the inflection point in the concentration curve, is the position of this point a function of absolute concentration \( C_0 \), or only of relative concentration \( C/C_0 \)? If it depends on relative concentration, then the position of the front should be only a function of time \( t \) and not of \( C_0 \); in this case, the rate of hydration should not be a function of partial pressure of water vapor (i.e. humidity). However, the data (Ebert et al. 1991; Friedman et al. 1994; Mazer et al. 1991) suggest the rate is, in fact, a function of humidity, which implies the functional form of equations 1 and 3 is inadequate.

**Discussion**

The quandary that arises is that equation 2 implies that hydration rate should depend on \( p \) and hence relative humidity, while equation 3 does not; the difference lies in the experimental protocol. Equation 2 applies if rate is being measured by mass transfer. Mass transfer is a proxy for the absolute number of dissolved molecules per unit volume, and it clearly depends on partial pressure of the solute, as Ebert et al. (1991) and Friedman et al. (1994) found. In fact the ratio of hydration rates Ebert et al. (1991) reported is very nearly equal to the ratio of partial pressure of water vapor in the two cases; the same is true of the results of Friedman et al. (1994). Thus, theory and measurements are in good agreement here.

However, when it comes to measuring the position of a “hydration front”, equation 3 suggests there should be no dependence on humidity at all. Since the measurement defined by equation 3 is of \textit{relative} concentration, the surface concentration should not matter. However, Mazer et al. (1991) did show a dependence of hydration rate on relative humidity, as measured by optical microscopy. This brings us back to the assumption underlying equation 4, that the hydration front can be defined by a specified value of \( C/C_0 \) which is the same under all experimental conditions. The discussion of the physics of stress generation above suggests that the inflection point is the more important point in terms of defining the hydration front. The usual assumption, inherent in most hydration calculations that the location of the front depends solely on \( C/C_0 \) may be an approximation which applies only over a limited range of absolute concentrations.
Proposed Protocol
One way to investigate this would be by Secondary Ion Mass Spectrometry (SIMS). A set of glass samples could be subjected to a hydration protocol similar to that employed by Mazer et al. (1991), and then the hydrogen ion concentration (a proxy for dissolved water) could be measured as a function of depth by SIMS. At the same time, the samples could be “read” optically. If the theoretical discussion above is correct, the absolute concentration of hydrogen ions at a given depth should be approximately proportional to partial pressure of the water vapor (i.e. relative humidity), while the location of the 50% point should be independent of it. Similarly, overlaying the location of the optically-determined hydration front on the SIMS traces should show whether it coincides with the inflection point.

Consequences
If it is true that the implicit assumption that the optical hydration front as defined by a given value of C/C₀ under all conditions is breaking down, this could hold implications beyond the question of humidity. In the first place, it would imply that our use of equation 4 would need to be restricted to a range of water concentration values in a way which has not been considered before. Put another way, if the location of the hydration front can be affected by C rather than C/C₀ alone, this would require controlling for another variable when we do hydration dating. Secondly, and for the same reason, it could affect the validity of induced hydration protocols when used with optical microscopy. On the other hand, the issue would not affect induced hydration measurements by SIMS (as by Stevenson et al. 2004), because SIMS gives an explicit profile of concentration rather than inferring the location of the hydration front.

I would very much like to hear the views of other researchers on this issue matmus1@maturango.org

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In recent years, several studies on obsidian procurement and distribution were undertaken in western and southern Argentina, with the location of numerous sources and the mapping of areas of distribution of different types of obsidian (Duran et al. 2004, Laguens et al. 2007, Stern 1999, Yacobaccio et al. 2002, among others). Hunter-gatherer populations of central and southern Argentina have procured obsidian from Andean regions and its vicinity since at least 9000 BP and into the Colonial period (Duran et al. 2004, Laguens et al. 2007, Stern 1999). Sixteen obsidian samples from two Late Holocene sites in the La Pampa province (Figure 1) were analyzed by INAA at the Missouri University Research Reactor, and their results were compared to the MURR database from central and southern Argentina and Chile. Two open air sites of Tapera Moreira and El Chenque I are located in the Lihue Calel Provincial Park, La Pampa, Central Argentina. Both sites contain transparent and grey-black obsidian and other non-local elements, tentatively coming from regions to the East (orthoquartzite from Pampa, ornaments made on malacological fauna from the Atlantic coast) and to the West (obsidian, and Valdivia ceramics from southern Chile) (Berón 1997, 2004). The closest obsidian quarry is located 300km to the northwest.

The site of Tapera Moreira has 3 components, the earliest date is 3900 ± 60 BP. No projectile points were recovered from the earliest occupation. The most common lithic raw materials are silica and basalt. Silicified wood and quartzite were used in less quantity. The inhabitants of Tapera Moreira based their subsistence on the hunting of guanaco. The intermediate occupation was dated to between 2110 ± and 1800 ± 80 BP. The most recent occupation contains the earliest evidence of pottery manufacture in the area and are dated to between 1190 ± 60BP to 480 ± 60 BP (Berón 1994:152-53). Medium and thicker stemless projectile points coexist with thin and small points, abundant bifaces and performs, small scrapers of short-wide modulus, characteristic of the Pampean Region contexts (Berón 1994:152). Two engraved plates on fragments of gray slate have incised geometrical designs on both sides. Similar ones were found in the Intihuasi Cave, San Luis (Berón 1994, 153). Chilean Valdivia pottery and some metal ornaments suggest that there was contact with groups living on the western side of the Andes (Berón 2007a).

Fig. 1. Map of project area.

The 10 obsidian samples analyzed from Tapera Moreira correspond to 3 different time periods:

1) samples LPTM01, 02, 06-08 are from the most recent occupation (500 BP),
2) samples LPTM04, 05 and 09 are from the Initial Ceramic Stage (1200 BP)
3) samples LPTM03 and 10 are from the earliest occupation, without ceramics (3000 BP).
The site of Chenque I is a hunter-gatherer cemetery. It is the largest assemblage of human burials in the La Pampa province, with an MNI of 216. Chenque I is located 70 km northeast of Tapera Moreira. The earliest dates correspond to 1050 BP and the most recent ones to 320 BP, which is contemporaneous with the most recent component of Tapera Moreira. No European elements were found. All 6 obsidian samples (LPEC01 to 06) date to 500 BP or earlier. Females and males of all ages were buried, with offerings of bone and stone, metal ornaments, shells and stone tools. One of the largest burials, # 29, has an MNI of 15 individuals, with multiple signs of violence including 36 projectile points inserted or associated with human bones, in many cases they were the cause of death of the individual (Berón 2007). Corresponding lithic artifacts include several types of instruments, cores, and debitage, with a predominance of the latter. Among the tools, unstemmed projectile points, end- and side-scrapers, notches, bifaces and some pecked and polished tools such as mortars, manos and bolas (Berón 2003). Most of the raw materials are local (gray rhyolite and chert), with some from outside of the region (chert, orthoquartztite).

**Instrumental Neutron Activation Analysis**

Neutron activation analysis of obsidian at MURR consists of two irradiations with a total of three measurements. The first irradiation for five seconds is applied to samples weighing about 100 mg encapsulated in a polyethylene vial using a thermal neutron flux of $8 \times 10^{13}$ n cm$^{-2}$ s$^{-1}$. The short irradiation is followed a 25–minute decay and 12–minute count which allows measurement of seven short-lived elements (i.e., Al, Ba, Cl, Dy, K, Mn, and Na). The second irradiation is applied to samples weighing about 250 mg encapsulated in high-purity quartz vials and subjected to one long irradiation of 70 hours using a thermal neutron flux of $5 \times 10^{13}$ n cm$^{-2}$ s$^{-1}$. The long irradiation is followed by two measurements. The first count occurs about seven or eight days after the end of irradiation, using a sample changer to measure each sample for 30 minutes, in order to determine seven medium-lived elements (i.e., Ba, La, Lu, Nd, Sm, U, and Yb). The second count occurs about four weeks after the end of irradiation, again using the sample changer for about 3 hours per sample, in order to measure fifteen long-lived elements (i.e., Ce, Co, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Sr, Ta, Tb, Th, Zn, and Zr). When the long irradiation is performed, the barium concentration from measurement of the medium-lived isotope (i.e., $^{133}$Ba) is normally superior and it is used in lieu of the value measured following the short-lived irradiation. The data from all three measurements are compiled into a spreadsheet (see also Glascock 1998).

**OBSIDIAN SOURCES:**

**Laguna del Maule-Paso Pehuenche sources:** A large number of outcrops are located around Maule Lake, in central Chile (Seelenfreund et al. 1996), and in the vicinity of the border between Argentina and Chile (Duran et al. 2004:30). Laguna del Maule-3 type is present in Tapera Moreira and El Chenque I. Laguna del Maule-3 obsidian is present in the middle and late
occupations of Tapera Moreira and in El Chenque I, indicating its use from 1200 to 500 BP.

**Cerro Huenul:** Cerro Huenul is an obsidian quarry located along the river Colorado in northern Neuquén, close to the modern town of Buta Ranquil (Duran et al. 2004:31). Obsidian from Cerro Huenul is present in northern San Luis (Intihuasi cave) (Laguens et al. 2007). Cerro Huenul obsidian is present in the earliest and middle occupations of Tapera Moreira. This indicates that the source was utilized from 3000 to 1200 BP. Cerro Huenul obsidian was not present in El Chenque I.

**La Bandera:** Located in the province of Neuquén, some 100km to the south of Cerro Huenul (Gil and Neme, pers. comm.). Tapera Moreira and El Chenque I are the only sites in the north Patagonia – Pampa region where obsidian from La Bandera was found, suggesting that there could have been a North-South border between Cerro Huenul and La Bandera (see Duran et al. 2004). La Bandera obsidian is present in the middle and late occupations of Tapera Moreira and in El Chenque I, indicating its use from 1200 to 500 BP.

**Unknown sources:** Four unknown sources were identified (unknown 1 to 4). One artifact from unknown-1 and one from unknown-4 were found in El Chenque I, two artifacts from unknown-2 and one from unknown-3 were found in Tapera Moreira. Unknown-2 obsidian is present in the earliest and late occupations of Tapera Moreira, indicating that it was in use around 3000BP and then again around 500 BP. Unknown-3 obsidian is present in the latest occupation of Tapera Moreira. Thus unknown-1, -3 and -4 were only found in the 500 BP occupations, while unknown-2 seems to have been used earlier in the sequence, then abandoned and reutilized by the most recent inhabitants. As these 4 unknown sources don’t match any of the other unknown sources, we can assume that they are located between Cerro Huenul and La Bandera, or south in the northern or central part of the Neuquen Province.

No obsidian from the Payún Matrú or El Peceño sources (Duran et al. 2004:28-30, Gil 2006), the 2 closest to the La Pampa sites, was found in Tapera Moreira or in El Chenque I. The lack of evidence could be related to small sample
size, as in the Late Holocene these sources were exploited by local groups (Duran et al. 2004).

Conclusions

Late Holocene inhabitants in the southern Dry Pampa obtained obsidian from several sources located between 36 and 38 degrees south, and from the high Andes and extra-Andean volcanoes. The 16 samples analyzed correspond to 7 different sources. This variety suggests that the inhabitants of the southern Dry Pampa had connections with a wide network of hunter-gathering groups living along the foot of the Andes, as they had with others of the Sierras Centrales 450km to the north, and the Eastern Humid Pampas. These connections in some cases lasted from one occupation to the next, suggesting a long term continuity over several hundred years.

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