IAOS

International Association for Obsidian Studies

Bulletin

Number 49 Summer 2013

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International Association for Obsidian Studies

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NEWS AND INFORMATION

Student Paper Award

We are again seeking nominations for the Student Paper Award. This award is open to any student who has presented a paper at an academic conference in 2013. Self-nominations are also accepted. Please send your nominations to Ellery Frahm at e.frahm@sheffield.ac.uk

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!

PUBLISH ANNOUNCEMENTS, NEWS, AND EVENTS IN THE *BULLETIN*

Do you have a new obsidian-related publication that you wish to announce? Or an upcoming conference that you would like to advertise? Want to notify our members of new lab services?

Please send news and announcements to IAOS.Editor@gmail.com for inclusion in the next issue of the *IAOS Bulletin*.

NOTES FROM THE PRESIDENT

Happy summer to those in the north, and happy winter to those in the south! For all members preparing for fieldwork, have a productive and safe season!

The results are in for the IAOS presidential election. It was a close race, and many members remarked that it was difficult decision due to the quality of both candidates. I am pleased to announce that Dr. Jeffrey Ferguson will be taking over the IAOS leadership at the Society for American Archaeology annual meeting in Austin, Texas next year. It will be a bit expensive, though, to ship the Obsidian Throne from South Yorkshire to Missouri.

IAOS had a strong presence at the SAA conference this year in Honolulu. Jeffrey Ferguson and Kyle Freund organised the IAOS-sponsored session "Obsidian Characterization in the Pacific Ring of Fire," which was quite well attended for a Sunday morning timeslot. Several IAOS members, including myself, presented in the "Improving XRF Methods for the Geochemical Characterization of Archaeological Materials" session. In other sessions, I noted at least twenty additional talks and posters involving obsidian sourcing, dating, technology, and production from around the world. Last SAA in Memphis was the year of the Americas for obsidian research, but studies presented this year represented much of the world, from Greece to Japan to Mesoamerica.

Next year is the 25th anniversary of the IAOS and the 50th anniversary of Cann and Renfrew's foundational "Obsidian in the Aegean" paper, so we are working on special plans for SAA in Austin. Rob Tykot is the lead organiser of what we hope will be a mega-session that covers all aspects of obsidian studies, from sourcing and dating to lithic technology and social organisation of production to symbolism and identity. Suggestions for speakers are welcome. Think big and outside-the-box! Let's try to get some of the biggest figures in archaeology and make it a "can't miss" session for Austin! Send your best or craziest suggestions to Rob Tykot.

One of the main topics of discussion at the IAOS business meeting was attracting and retaining more student members. Two proposals were discussed, and I would be happy to have additional input from the membership. The first suggestion is that student membership simply be free. At present, IAOS has so few student members that their annual membership fees are a trivial source of revenue. The society would be better off in the long run to attract more student members and retain some fraction of them as paying members later. The second suggestion was an overhaul of the IAOS student award, making it a modest cash award to pay for conference costs, giving it a name (say, the Roger C. Green Student Award), and having students apply for the award ahead of the SAA annual meeting. I am in favour these changes, but I think that, if we have a monetary award, IAOS should have an official "awards committee" to select the award winner(s). Again I welcome input from the membership regarding these proposals.

Another issue for attracting members is the value of membership. Two frequent suggestions are making the IAOS Bulletin – or at least some fraction of the issues – available to members only. Another idea has been restricting the PDF library to members only. If you have not visited the IAOS website recently, please do so -- Craig Skinner has continued to work on the PDF library. There one can find a variety of obsidian-focused articles, reports, manuscripts, theses, and more for download as PDFs. Personally, I prefer the suggestion of restricting the PDF library, rather than the IAOS Bulletin, to members; however, the IAOS board welcomes input and creative suggestions about adding motivation for and value to IAOS membership.

To further raise the visibility of the IAOS Bulletin, I would like to encourage that, if you have an Academia account, please add your bulletin articles and give them the relevant tags or keywords. Academia appears to be an increasingly common tool that students and scholars are using to find papers of interest, so adding your IAOS Bulletin articles raises the visibility of the newsletter, the society, and, of course, your own research.

While on the topic of the IAOS Bulletin, I wish to recognise and highlight the continuing efforts of our newsletter editor, Carolyn Dillian. She has served as the editor, typesetter, and all-around assembler of the newsletter since 2004. As of this issue, she has overseen the publication of 20 issues containing news, announcements, resources, and research reports. Under her editorship for the last nine years, the bulletin has become the most visible aspect of our organisation, and its reports are frequently cited in *Journal of Archaeological Science* and other top-tier archaeology journals. Likely no one else has ever contributed so much time and effort to the IAOS, and I wish to acknowledge her long-term support and contributions to the organisation.

I wish to remind everyone that IAOS is a sponsor of the Fifth Archaeoinvest Symposium, to be held in Romania, titled *Stories Written in Stone: International Symposium on Chert and Other Knappable Materials*. IAOS members will benefit from a 10% reduction on the attendance fee, which is €150 for professionals or €75 for students. This is an excellent opportunity for IAOS to raise its profile with the international community and lithic analysts. It would also be tempting, if one travels as far as Romania, to explore the Carpathian Basin obsidian sources. Iași, though, lies in the northeastern corner of Romania, near the border with Moldova, so it would take some travel to reach obsidian sources to the west in Slovakia, Hungary, and Ukraine.

Let me again say that it is a pleasure to serve as the IAOS President. Please feel free to contact me with any comments or ideas you have. In particular, your suggestions for promoting IAOS and giving our organisation great visibility would be most welcome.

Best regards,

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NEWS AND NOTES: Have announcements or research updates to share? Send news or notes to the *Bulletin* Editor at IAOS.Editor@gmail.com with the subject line “IAOS news.”

LIKELY SOURCE ATTRIBUTION FOR A PALEOINDIAN OBSIDIAN GRAVER FROM NORTHWEST LOUISIANA

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In 1984, archaeologist David Jeane reported that an obsidian graver (Figure 1) had been found at the Cross Lake site (16CD118) in Caddo Parish, Louisiana. The graver, along with four fluted points (Figure 2), Archaic dart points, and Caddoan-style pottery were observed in the collection of Claude McCrocklin (Jeane 1984). McCrocklin and other members of the Northwest Chapter of the Louisiana Archaeological Society collected material from the site and later recorded their finds with the state. Here, we report our recent attempt to determine the geological provenance (source) of the flake\graver from 16CD118 using previously published geochemical data. We make no attempt to evaluate the integrity of McCrocklin's claim of finding the artifact at this particular site, though we note that there is no apparent reason to question the reported find location.

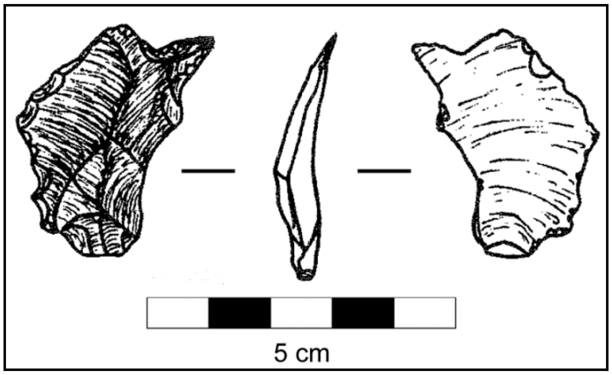

Figure 1. Obsidian flake\graver from Cross Lake (16CD118). After Jeane (1984).

Figure 2. Two fluted-point bases recovered from Cross Lake (16CD118) along with the obsidian graver discussed here. Image courtesy of David Jeane.

McCrocklin reported having found the graver while conducting surface surveys at 16CD118 with members of the Northwest Chapter of the Louisiana Archaeological Society. Jeane observed the graver while examining McCrocklin's collection, and suspected that it may be obsidian. Wanting to independently verify this assessment, Jeane sent the graver to the University of Texas–San Antonio (UT–SA) for examination. Archaeologists at UT–SA confirmed that the piece was obsidian. While there, the graver came to the attention of Thomas Hester who was, and still is, pursuing a long-term research project into the provenance of obsidian artifacts found in Texas and neighboring areas (e.g., Hester 2011; Hester et al. 1982; Hester et al. 1985). Hester sent the graver to be analyzed by X-ray fluorescence (XRF) at the Lawrence Berkeley Laboratory (LBL) by Frank Asaro and Helen Michel.

	Rb	**Sr**	**Zr**	**Ba**
LOUIS-13	189	42	127	150

Table 1. Chemical characterization of the obsidian graver (LOUIS-13) from Cross Lake (16CD118). Analysis of LOUIS-13 was conducted by XRF at Lawrence Berkeley Laboratory and published by Jeane (1984).

At the time of analysis, LBL did not have any specimens in their database that matched the composition of the flake\graver from 16CD118 (Table 1). Therefore, all that could be done at the time was report the composition of the piece, and describe it as coming from an as-yet unknown source. The situation remained unchanged until the autumn of 2012. At that time, Boulanger encountered paperwork concerning this specimen in the archives of the LBL archaeometry program. Based on paperwork in the LBL archives, the specimen from 16CD118 was received at LBL on January 17, 1983, and returned to Hester on September 20, 1983. The laboratory assigned the identifier LOUIS-13 to the specimen, and analyzed it in XRF run number 8132, position Q. No other information concerning this specimen—including the resulting compositional data—was located in the LBL archives. This is not unusual for the laboratory; results of analyses were not always included in the archives, and XRF data were frequently sent directly on to collaborating archaeologists (e.g., Boulanger et al. 2012).

Boulanger stumbled across Jeane's (1984) publication describing the graver and its analysis by coincidence while searching for additional information concerning other reported finds of obsidian in Louisiana Having previously taken an interest in the provenance of Eastern obsidian finds (e.g., Boulanger et al. 2007; Dillian et al. 2010), we were particularly interested in further evaluating the graver from 16CD118. Jeane included the composition of the specimen. As such, we are able to compare the concentrations reported for this specimen to databases of obsidian source samples at various archaeometry laboratories.

The elemental concentrations published by Jeane (1984) were compared against the MURR NAA and XRF source databases (Table 1). In both instances, the results were identical and the most-likely geological source of the 16CD118 graver was found to be the Pumice Hole Mine subsource of the Mineral Mountain Range obsidian source located in Beaver County, Utah (Nelson 1984; Nelson and Holmes 1979). Importantly, no specimens from any other obsidian source were identified as having the same ranges of the four elements listed by Jeane. As an independent check on these results, these data were sent to Skinner (Northwest Research Obsidian Studies Laboratory [NWROSL]) and Shackley (Geoarchaeological XRF Lab) for comparisons against their obsidian-source databases (both generated using XRF).

Skinner found that the 16CD118 data are most similar to the Wild Horse Canyon obsidian source, located less than 3.5 km (2.15 miles) southwest of the Pumice Hole Mine source area. The two obsidian sources are similar in chemistry, though Wild Horse Canyon specimens tend to be higher in Rb, and lower in Sr and Zr than those from Pumice Hole Mine. Similarly, Shackley found that the concentrations reported by Jeane are most similar to the Wild Horse Canyon source. He further suggests that the composition is similar to late Paleoindian artifacts recovered from southern Arizona and New Mexico. Shackley's observation is particularly significant, as neither he nor Skinner had been informed of the Paleoindian association of the 16CD118 graver. The consensus, then, is that the published XRF data for the Paleoindian graver from 16CD118 is that it is made on obsidian from one of two sources in Beaver County, Utah.

The purported discovery of an obsidian artifact in Louisiana—far from any geological source of obsidian—should raise skepticism. However, the distance between 16CD118 and Beaver Co., Utah, is not outside the documented range of other obsidian-artifact-sourcing projects (e.g., Hester et al. 1985). The graver is associated with other Paleoindian artifacts, and gravers are quite rare in later Archaic and Woodland times. We also see little to no reason to doubt the integrity of the reported find spot associated with this piece.

We stress that comparisons such as the ones described here (i.e., comparisons of previously published laboratory data to data generated at other laboratories) are necessarily qualitative. Differences in instrumentation and calibrations among laboratories result in slight differences in the elemental abundances determined for specific pieces. Increases in precision and accuracy of instrumentation may result in finer chemical distinctions than were previously possible. The four laboratories represented here have historically exchanged and compared data, typically finding good to excellent agreement for obsidian specimens from the same sources—particularly for the elements published for the 16CD118 specimen (e.g., Shackley 1998: 267). Therefore, while we remain fairly confident in our determination of provenance for this piece, we conservatively refer to it as a "most-likely" determination.

After our comparisons, Boulanger contacted Dennis Jones, editor for *Louisiana Archaeology,* with the intent to submit a short article for publication there. Jones took an immediate interest in the story of this graver. Over the course of several weeks, Jones took it upon himself to locate the graver and arrange for it to be obtained for reanalysis. We are incredibly grateful for his work in this regard, and we are currently undertaking a complete reanalysis of the specimen by XRF and obsidian hydration. We plan to publish the results of all these studies in a future issue of *Louisiana Archaeology*. Initial results of XRF at MURR suggest that the graver is indeed from the Mineral Mountain Range, though we are unable to assign it to a specific subsource.

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DOES AN OBSIDIAN HYDRATION RIM CARE WHEN A TEMPERATURE FLUCTUATION OCCURS?

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Abstract

Obsidian hydration is usually described by an equation relating the hydration rim thickness t^n, where $n \approx 0.5$. The proportionality constant between the two—the hydration rate—is temperature-dependent. Because hydration rim growth proceeds more rapidly early in the depositional history of an artifact than later, a consequence of the "square-root-of-time" relationship, it seems intuitive that early temperature variations should have the greatest effect on ultimate rim thickness. This should not be the case, however, according to the first principles of diffusion physics, which show that the rim thickness depends on the time average of the hydration rate, regardless of when a fluctuation occurs. A laboratory experiment using induced hydration confirms this, with rim thickness being determined by the time-average of the hydration rate, irrespective of when variations occur.

It is well known that obsidian hydration is a temperature-dependent process, and corrections for temperature must be made when using obsidian hydration dating for chronometric purposes. Corrections for artifact burial depth are a prime example of this. It is also well known that a collection of artifacts of nominally the same date may exhibit a spread of hydration rim values. This is primarily a result of temperature-altering changes in context that occur in an artifact's depositional history.

Because obsidian hydration is argued to be at least approximately a square-root-of-time relationship, the speed at which the hydration rim proceeds into the glass falls off with age. Since the rate is temperature-dependent, it seems intuitive that temperature fluctuations early in the depositional history of an artifact would have a greater effect on ultimate rim value than the same fluctuations later in its history, simply because the hydration front is progressing more rapidly early on. The mathematical theory of temperature-dependent hydration, however, indicates that the effect of a temperature fluctuation is the same, regardless of when in the artifact's history it occurs. This presents a quandary.

In this paper we provide a definitive answer to this question. First, we review the mathematical theory, showing that the effect of a temperature change should be the same regardless of whether it is early or late. We then report the results of an experiment using hydration induced in the laboratory, which confirms the theoretical model and demonstrates that the effect of a temperature fluctuation is the same, regardless of when in the artifact's depositional history it occurs.

Obsidian Hydration

Obsidian hydration, in its most basic aspect, simply describes the process by which water is absorbed by obsidian, and involves both physical and chemical changes in the glass (Doremus 2002; Anovitz et al. 2008). Five steps may be distinguished in the process:

1. When a fresh surface of obsidian is exposed to air, water molecules adsorb on the surface. Since any unannealed obsidian surface exhibits cracks at the nano-scale, the amount

of surface area available for adsorption is much greater than the macro-level surface area would suggest, creating a large surface concentration.

2. Some of the adsorbed water molecules, plus others impinging directly from the atmosphere, are absorbed into the glass and diffuse into the interstices in the glass matrix. The diffusion process seems to be driven by two properties of the water molecules: a concentration gradient (Doremus 2002) and intra-matrix capillary action (Vesely 2001, 2008). Although it has been suggested that chemical reactions play a role (Doremus 2002:108ff.), it is unlikely that they are a major factor below the glass transition temperature (Anovitz et al. 2008), and thus the "diffusion-reaction" nomenclature of Doremus is likely inappropriate for archaeological temperatures. The glass transition temperature is the temperature at which the glass starts to exhibit fluid-like properties (Ochs and Lange 1999).

3. The molecules entering the glass by diffusion and capillary action stretch the glass matrix, causing an increase in volume and openness of the hydrated region. Since the hydrated region is expanded and the non-hydrated region is not, a stress region exists between the two.

4. As time passes, the region of increased water concentration progresses into the glass, its rate being a function of the initial openness of the glass, temperature, and the dynamics of the process itself.

5. When the hydrated layer becomes thick enough, typically greater than 20 microns, the accumulated stresses cause the layer to spall off as perlite.

Three general classes of methods have been proposed for measuring obsidian hydration: measurement of water mass uptake or loss vs. time (Ebert et al. 1991; Stevenson and Novak 2011); direct measurement of water profiles vs. depth (Anovitz et al. 1999, 2004, 2008; Riciputi et al. 2002; Stevenson et al. 2004); and observation of the leading edge of the stress zone by optical microscopy (many papers, e.g. Friedman and Smith 1960; Friedman and Long 1979).

Measurement of the mass of water absorbed or lost by an obsidian sample, per unit obsidian mass, is the most physically fundamental method of measuring hydration, and has a long history. Methods employed for such measurements have been mass loss on heating (e.g. Ebert et al. 1991), IR transmission spectrometry (e.g. Newman et al. 1986), and IR photo-acoustic spectrometry (e.g. Stevenson and Novak 2011). It has been shown that mass gain or loss proceeds proportional to t^n where t is time and n is an exponent between approximately 0.5 and 0.6 (Stevenson and Novak 2011).

Water profile measurement is generally performed by Secondary Ion Mass Spectrometry (SIMS) or the electron microprobe. The principle is to measure the concentration of H^+ ions, as a proxy for water, as a function of depth. The depth of the half-amplitude point is found to be proportional to t^n, where t is time and n is an exponent lying between approximately 0.6 and 0.7 (Anovitz et al. 1999, 2004; Delaney and Karsten 1981; Karsten and Delaney 1981; Stevenson et al. 2004; Stevenson and Novak 2011).

The classical field of OHD is based on measuring the position of the stress zone caused by the diffusion process. The stress arises because the volume behind the optical hydration front has enlarged due to penetration of the glass matrix by water molecules, while the matrix of the unhydrated glass has not (Vesely 2001). The stress zone is visible under a polarized microscope due to stress birefringence (Born and Wolf 1980:703-705). Laboratory data (Stevenson and Scheetz

1989; Stevenson et al. 1998a,b; Rogers and Duke 2011) indicate that the position of this stress zone, or hydration front, progresses into the obsidian proportional to t^n, where n is approximately 0.5 within limits of experimental error. The agreement with classical diffusion theory, in particular Fick's formulations and the Boltzmann transformation (Crank 1975:105ff.; Rogers 2007, 2012), may be a coincidence or may be due to an as-yet-undiscovered property of the hydration process itself.

The square-root-of-time relationship was proposed by Friedman and Smith (1960) at the inception of OHD (also see Friedman and Evans 1968; Friedman and Long 1976; Hull 2001; Michels and Tsong 1980; Rogers 2007), and continues to be widely accepted in archaeological analyses. It has been questioned by some (e.g., Anovitz et al. 1999, 2004, 2008; Bettinger 1989; Ericson 1978; Kimberlin 1976; Meighan et al. 1968a,b; Meighan 1983; Riciputi et al. 2002), on at least two different bases. Earlier criticisms (e.g. Bettinger 1989, and Meighan 1983) arose from attempts to make the archaeological record fit the model without taking into account the physics and chemistry of the process; it is likely that the blame for lack of fit rests on uncorrected temperature factors combined with other sources of error, such as geochemistry and radiocarbon associations. Later criticisms (e.g. Anovitz et al. 1999, 2004; Riciputi et al. 2002; Stevenson et al. 2004; Stevenson and Novak 2011) are based on measurements of water mass uptake or SIMS measurements of concentration profiles, and have not been demonstrated to apply to the classical case.

Although the classical approach to OHD is the furthest removed from the basic physics of hydration, it is the basis of most practical work in OHD in archaeology today, owing to its apparent simplicity and low cost. The results reported here are based on this classical approach.

Classical Theory of Hydration

The hydration process is described by the equation:

$$r = D \sqrt{(t)} \qquad (1)$$

where r is the hydration rim in μ, t is age in years, and D is a rate in $\mu/\mathrm{yr}^{1/2}$.

When glass is exposed to air, water molecules diffuse into the glass, probably by a combined effect of concentration gradient and intra-matrix capillary action (see above). The process is described by the equation

$$\partial W/\partial t = \partial(D\partial W/\partial x)/\partial x \qquad (2)$$

where W is concentration of the diffusing water species (H_2O; OH^- is bound to the matrix and does not diffuse [Behrens and Nowak 1997; Silver at al. 1990; Zhang et al. 1991; Zhang and Behrens 2000]), and D is the effective diffusion coefficient, which is generally a function of concentration (Anovitz et al. 1999; Doremus 2002). For a diffusion process dominated by the concentration gradient, it can be shown that concentration at any point in the glass is dependent on a single variable z, given by

$$z = x/[2\sqrt{(Dt)}] \qquad (3)$$

where x is depth into the material and t is time (Crank 1975). Even if intra-matrix capillary action is of comparable magnitude, equation 3 is still approximately valid, which is the basis of classical hydration theory.

The coefficient D in equation 2 is also a function of temperature,

$$D = D_0 \exp(-E/[RT]) \qquad (4)$$

where E is the activation energy, R is the universal gas constant, T is the absolute temperature, and D_0 is a pre-exponential constant. Equation 4 has been shown to be valid by laboratory studies (Ebert et al. 1991;

Friedman et al. 1994; Karsten et al. 1982; Mazer et al. 1991; Doremus 2002:114-118; Stevenson et al. 1989, 1989, 2004; Zhang et al. 1991; Zhang and Behrens 2000).

In the archaeological case, temperature varies diurnally and annually and also reflects long-term climatic trends (e.g. Rogers 2010; West et al. 2007); thus, D is a function of time D(t). It can be shown that, if the constant value of D in equation 2 is replaced by the average value of D(t) over the time period of interest, the diffusion problem can be solved as though D were time-invariant (Crank 1975:104). The time average of D over the interval t_1 to t_2 is

$$D_{av} = (\int D dt)/(t_2 - t_1), \qquad (5)$$

where the integral is taken between t_1 and t_2 (Rogers 2007, 2012).

Examination of equation 5 shows that the value of D_{av} is unaffected by whether the variation in D occurs early or late in the time period; thus, theory shows that there should be no difference in ultimate rim value between the effects of early or late temperature variations.

Qualitative Insight

The question posed here is whether, for an obsidian artifact, temperature fluctuations immediately after manufacture influence ultimate rim thickness more than similar fluctuations later on. Intuitively it would seem that they should. If we define "hydration speed" v as the increase in rim thickness per unit time, which is given by the time derivative of equation 1, we have

$$v = D/[2\sqrt{(t)}] \qquad (6)$$

As an example, for the obsidian considered here, $D \approx 0.08\mu/yr^{1/2}$ at a temperature of 16°C. Figure 3 shows the curve for v as a function of t, which clearly shows that the hydration speed is highest when the artifact is young, i.e. shortly after it was manufactured. Thus it would seem that any change in k would have a greater effect at that time, contradicting equation 5.

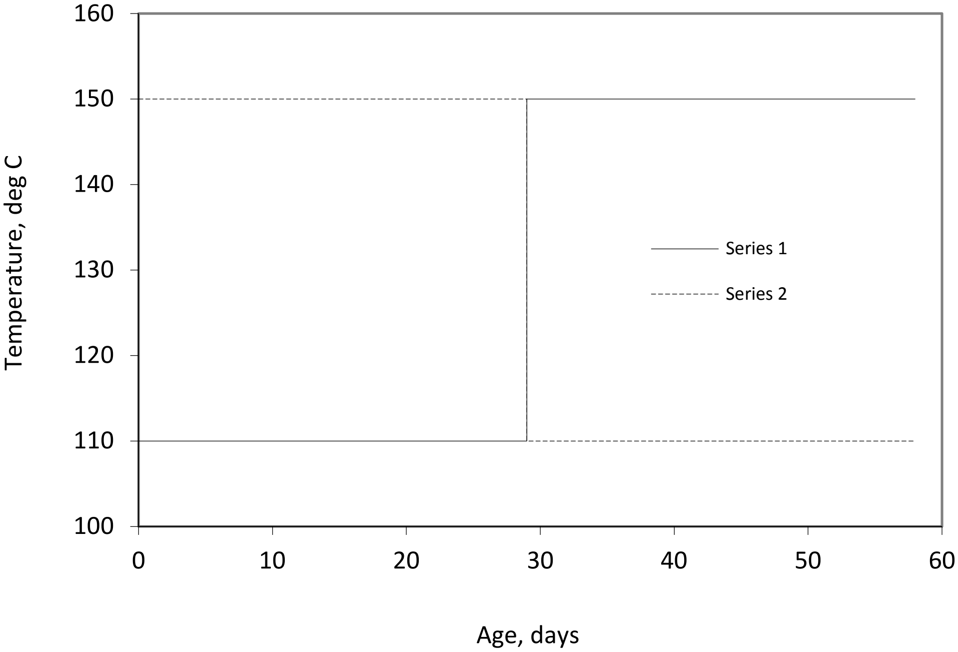

Figure 1. Temperature-time profiles used in the induced hydration experiment.

	Hydration rim data, microns			
	Series 1		Series 2	
Obsidian	Mean	SD	Mean	SD
Utah Opaque	5.92	0.10	5.95	0.05
Utah Opaque	6.03	0.05	6.02	0.10
Utah Red	5.98	0.08	5.93	0.05
Utah Red	6.02	0.08	5.92	0.04
Utah Translucent	6.00	0.09	6.03	0.08
Utah Translucent	6.03	0.05	5.97	0.05
Ensemble	6.00	0.04	5.97	0.05

Table 1. Hydration rim values at end of series.

Experimental Investigation

Since the theoretical conclusion is counterintuitive, an experiment was designed to test whether temperature variations early in the life of an artifact affected ultimate rim values more than fluctuations later in its life. The obsidian tested was from Topaz Mountain in Utah. The experiment consisted of inducing hydration in the laboratory at elevated temperatures using known temperature profiles, and measuring the resulting hydration rim values. Figure 1 shows the temperature-time profiles. If the intuitive understanding of hydration is valid, Series 2 should yield the larger rim, while if equation 7 is valid, the results from the two series should be the same.

The experiment was run according to the following protocol:

Series 1: Eight specimens were exposed to 110 degree temperatures for 29 days, after which the hydration rims were measured (Job R-69). The same specimens were then exposed to 150 degree temperatures for 29 days, and the hydration rims again measured (Job R-71).

Series 2: Eight specimens were exposed to 150 degree temperatures for 29 days and the hydration rims measured (Job R-70). The same specimens were then exposed to 110 degree temperatures for 29 days and the hydration rims again measured (Job R-72).

Hydration was induced in all cases by immersion of the specimens in 300 milliliter of deionized water containing three grams of silica gel. Parr thermo-regulated pressure reactors were used. The stainless steel reaction vessels were lined with glass containers, which contained the specimens, to reduce contact of the aqueous solution with metal. The hydration rim measurements were obtained with a filar micrometer eyepiece mounted on a Nikon Labophot-Pol petrographic microscope.

Table 1 presents the hydration rim data at the end of each series. The hydration rims are statistically indistinguishable at the 95% confidence level, showing that the rim is the same no matter whether the higher temperature occurred early or late in the process. Figure 2 shows the hydration rim values at the 29-day point as well as the 58-day point. The strong temperature dependence of the hydration process is clear, as is the fact that the two sequences yielded the same ultimate value for hydration rim.

Discussion

The question posed here was whether, for an obsidian artifact, temperature fluctuations early in its life have a greater influence on final rim value than fluctuations later. Both hydration theory (equation 5) and the experiment described above demonstrate that this is not true. How can this be understood?

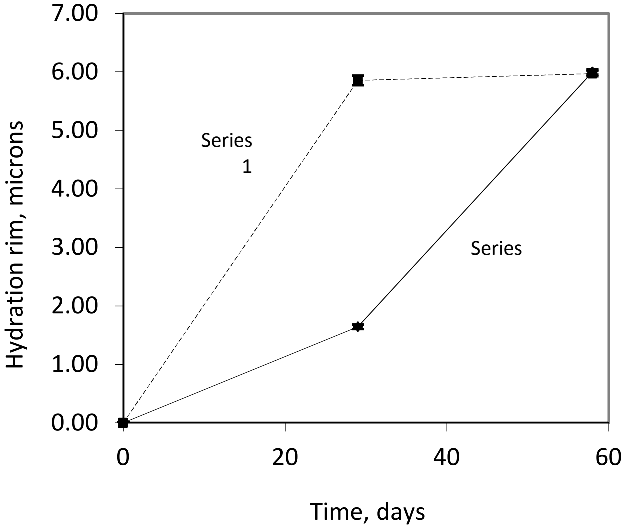

Figure 2. Hydration progress for the two series. Note strong temperature dependence of intermediate rim value.

Viewed from the standpoint of diffusion physics, the water concentration at any point in the obsidian depends on not only the immediate value of k but also on (1) its history and on (2) the surrounding values of water concentration. Early in the use-life of an artifact, a change in k is accompanied by a large value of hydration speed; however, at this point there is very little diffused water in the obsidian. Late in use-life the hydration speed is small but the amount of diffused water is much larger.

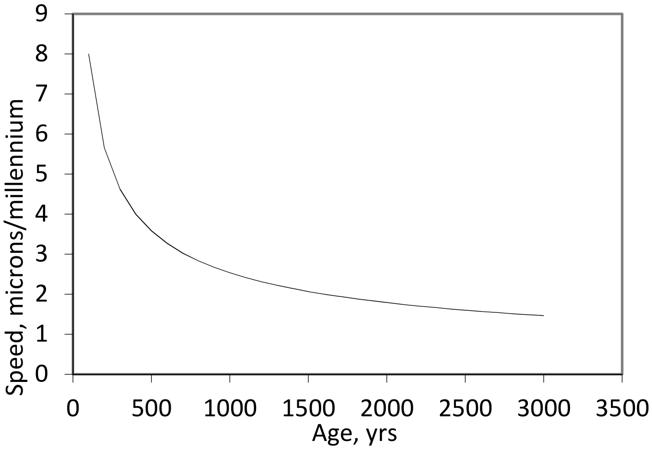

Figure 3. Hydration speed as a function of time for a typical Topaz Mountain obsidian (k = 0.08μ/yr ^{½}).

The complex inter-relationship between rate and water concentration is summarized in the differential equation describing diffusion, equation 2. The value of D in equation 1 is, by definition, the time-average computed by equation 5. This means that, at any point in the hydration process, whether one hour or a thousand years after manufacture, k is the integrated value of k up to that time. If D is time-varying, it must be averaged before being used in equation 1; trying to predict rim value by integrating the hydration speed (equation 6) is an inappropriate procedure and will yield an incorrect result.

Conclusions

In conclusion, it is demonstrated that the intuitive perception that early temperature variations should have a disproportionate effect on ultimate rim thickness is not valid. Our experiment indicates that a temperature perturbation of a given magnitude and duration has the same effect on ultimate hydration rim value, no matter whether it occurs early or late in an artifact's life. An analysis starting from the differential equations describing the hydration process shows that the ultimate rim thickness is determined by the time-average of the hydration rate, irrespective of whether variations occur early or late, and this result is borne out by the experimental data reported. This is useful clarification for archaeologists needing to compare hydration data from variable contexts, especially if early in time.

Acknowledgements

We thank Jaynie Hirschi, Hill Air Force Base, for partial funding of this effort, and Mr. Tom Origer for his careful conduct of the experiment. Kathleen Montgomery, Far Western Anthropological Group, Inc., generated the graphics files for us. Any errors of interpretation are, of course, ours.

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INTRINSIC WATER IN OBSIDIAN AND ITS EFFECT ON HYDRATION RATE: A CASE STUDY FROM THE COSO VOLCANIC FIELD, INYO COUNTY, CALIFORNIA.

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Abstract

Intrinsic water concentration in obsidian strongly influences hydration rate, but archaeological examples which show the effect are rare. An example is reported here based on a cache of Coso obsidian bifaces recovered during the Hay Ranch pipeline project in southern Inyo County, California. The age of the bifaces, established by morphological examination and obsidian hydration dating, is middle Newberry period, ca. 2500 BP. Since the bifaces were recovered as a cache and were deeply buried, they were probably manufactured over a short period and experienced essentially the same temperature history. Here I show that the spread of measured hydration rim values agrees with the known intrinsic water variability in the West Sugarloaf flow, providing an archaeological demonstration that the phenomenon is real and observable.

It is well established geologically that intrinsic water concentration in obsidian is a primary factor in determining hydration rate. However, archaeological examples which show the effect clearly are rare, since hydration rate is also influenced by other factors. A buried cache of 56 obsidian bifaces, recovered as part of the Hay Ranch pipeline project in southern Inyo County, California, presents an opportunity to see clearly the effects of intra-source intrinsic water variability on the hydration rate of obsidian.

The collection was found as a single cache, buried at a depth of 1.2 m. Fifty-four of the bifaces were geochemically sourced to West Sugarloaf, on which 53 valid hydration rim measurements were made. The site elevation is 4126 ft above mean sea level (amsl).

Obsidian Minerology

Obsidian is an alumino-silicate, or rhyolitic, glass, formed by rapid cooling of magma under the proper geologic conditions. Like any other glass, it is not a crystal, and thus it lacks the lattice structure typical of crystals at the atomic level. Glasses do, however, possess a matrix-like structure exhibiting some degree of spatial order (Doremus 1994:27, Fig. 2; 2002:59-73). Obsidian is typically about 75% SiO_2 and about 20% Al_2O_3 by weight, the remainder being trace elements, some of which are source-specific (Doremus 2002:109, Table 8.1; Hughes 1988; Stevenson et al. 1998; Zhang et al. 1997). The anhydrous composition of obsidian from a wide variety of sources has been shown to be remarkably consistent, within a few tenths of a weight percent (Zhang et al. 1997). The minute interstices within the glass matrix, on the order of 0.1 - 0.2 nanometer in diameter, are where water penetration takes place.

All obsidian also contains small amounts of natural water, known as intrinsic water or structural water, resulting from the magma formation process; the amount is generally <2% by weight (% wt) in natural obsidian, although cases of somewhat higher concentration are occasionally encountered. The water occurs as two different species, molecular water (H_2O), and hydroxyl ion (OH^-), and the so-called "total water" is the sum of the two in wt%. Hydroxyl ions are immobile, usually bound to silicon or aluminum sites in the glass matrix, while the molecular water is unbound and able to move. At total water concentrations below 2% wt, hydroxyl ion is the dominant species, while molecular water predominates at higher total water concentrations (Silver et al. 1990).

Obsidian anhydrous chemistry, or chemical composition independent of water, has traditionally been regarded as a major influence on hydration rate (see attempts to determine a chemical index to hydration, e.g. in Friedman and Long 1976 or Stevenson and Scheetz 1989). However, Stevenson et al. (1998, 2000) found no consistent influence of anhydrous chemistry on hydration rate. Zhang and Behrens (2000) and Behrens and Nowak (1997) found the effect of anhydrous chemistry to be negligibly small, although Karsten et al. (1982) reported that Ca^{2+} concentration may influence hydration rate to a very slight extent. It now appears that anhydrous chemistry has negligible effect on hydration rate. In archaeological analyses, anhydrous chemistry is controlled by grouping and analyzing the obsidian by geochemical source, based on trace element composition as determined by X-ray fluorescence (XRF), neutron activation analysis, or laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

Intrinsic water, on the other hand, has a profound effect on hydration rate, which is directly proportional to water content (Behrens and Nowak 1997; Delaney and Karsten 1981; Karsten et al. 1982; Lapham et al. 1984; Stevenson et al. 1998, 2000; Stevenson and Novak 2011; Zhang et al. 1991; Zhang and Behrens 2000). Four methods are currently used for measuring intrinsic water in obsidian: micro-densitometry (Ambrose and Stevenson 2004); mass loss when obsidian powder is baked (usually called manometry or "loss-on-ignition", LOI) (Newman et al. 1986; Steffen 2005); infrared (IR) transmission spectrometry (Newman et al. 1986); and IR photo-acoustic spectrometry (Stevenson and Novak 2011). Because all these techniques are costly and currently are destructive to the artifact, intrinsic water measurement is not conducted for most practical archaeological investigations in the United States today. The resulting uncontrolled intra-source rate variations increase the uncertainty (statistical error) in age analysis. Operationally, it is likely that controlling for source actually functions as a proxy for controlling for intrinsic water (Stevenson et al. 2000), albeit rather poorly (Stevenson et al. 1993; Rogers 2008, 2010).

Obsidian from the Coso volcanic field occurs as four geochemically distinct flows: West Sugarloaf, Sugarloaf Mountain, West Cactus Peak, and Joshua Ridge (Hughes 1988). Stevenson et al. (1993) measured the water content of obsidians from these four flows, and found significant variability both between flows and within flows. These data were further analyzed (Rogers 2008) and flow-specific hydration rates for Coso were computed (Rogers 2011), which significantly improve the quality of age estimation. However, flow-specific hydration rates do not address the issue of intrinsic water variability within a geochemical flow.

In an obsidian hydration analysis, age is typically computed from the equation

$$t = r^2/k \qquad (1)$$

where r is the hydration rim and k is the hydration rate. Both rim value (r) and rate (k) must be corrected to the same effective hydration temperature (EHT) (Rogers 2007, 2012).

Errors, or uncertainties, are introduced into any obsidian hydration age computation by errors in the input parameters, k and r; errors in r include measurement errors and errors arising from the process of correcting the rim value to the same effective hydration temperature (EHT) as the rate. The effects of these errors have been examined in detail, with the analysis documented in Rogers (2010), and results are summarized here.

If a set of specimens ($N > 1$) is grouped and analyzed as a single sample, the coefficient of variation (CV) of the hydration rims (CV_s) is

$$CV_s^2=(2s_r/r)^2+(0.06s_{EHT})^2+(CV_k/2)^2+(CV_{mfg}/2^{)2} \quad (2)$$

Here s_r is the standard deviation of the hydration rim measurement as reported by the laboratory, and is ~0.1m; r is the mean hydration rim for the sample; s_{EHT} is the uncertainty in EHT post-correction, and is ~1.0°C; CV_k is the CV of the hydration rate; and CV_{mfg} is the CV of the time span over which the specimens were manufactured. The CV of the hydration rate can be further broken down into two terms, a CV of the rate ascribed to the obsidian source assuming no intra-source variations (CV_{ks}), and a CV due to intra-source variations in rate (CV_{ke}). Typically CV_{ks} arises from laboratory errors in determining the rate, while CV_{ke} is caused by intrinsic water variations.

This equation is simplified if the specimens are all from the same geochemical source and if only the *spread* of ages is considered, irrespective of absolute accuracy; for this case $CV_{ks} = 0$. If, in addition, the specimens are from a cache, they will have experienced essentially the same temperature history, so $s_{EHT} = 0$. Finally, the items within a cache were probably manufactured over a short time span, so $CV_{mfg} \approx 0$. This leads to

$$CV_s^2 = CV_r^2 + (CV_{ke}/2)^2 \quad (3)$$

where $CV_r = s_r/r$. In this case $CV_r << CV_{ke}$, so $CV_s \approx CV_{ke}/2$. Finally, since the hydration rate is directly proportional to intrinsic water content, we have

$$CV_{iw} = CV_{ke} \approx 2CV_s \quad (4)$$

where CV_{iw} is the CV of the intrinsic water within the obsidian source. Thus, for a cache of obsidian specimens, all from the same geochemical source, the spread in the measured hydration rims should be approximately twice the spread of the intra-flow intrinsic water variations.

The Hay Ranch Biface Cache

The Hay Ranch biface cache provides a useful case study on the intrinsic water chemistry of the West Sugarloaf obsidian flow. The hydration rims for the West Sugarloaf artifacts in this cache ($N = 53$) cluster around a mean of 5.925μ, with a standard deviation of 0.589μ and a coefficient of variation of 0.10. The hypothesis here is that the observed CV_s for the Hay Ranch biface cache is due to variations in intrinsic water content within the West Sugarloaf obsidian flow.

Figure 1 presents the hydration rim data, as measured, in histogram form as a cumulative distribution, using bins of 0.1μ. In addition, a simple simulation in MS Excel was used to create $N = 53$ random hydration rims with the same mean and standard deviation as the data; these points are plotted in Figure 2 labeled "Sim". Finally, an analytic model based on the Gaussian (normal) distribution was used to compute $N = 53$ data points with the same mean and standard deviation; this line is labeled "Analytic" in Figure 1.

The three distributions can be compared using the Kolmogorov (or Kolmogorov-Smirnov) test. The Kolmogorov test is used to compare either data or simulation to the analytic model, and the Kolmogorov-Smirnov test to compare data and simulation; threshold values differ. Table 1 shows the pair-wise maximum differences (D_{max}) between the distribution curves, and the threshold value for distinguishability at the 95% confidence level with $N = 53$; if $D_{max} >$ threshold the distributions are distinguishable. The table shows that the hydration rim data distribution is indistinguishable from the simulation and

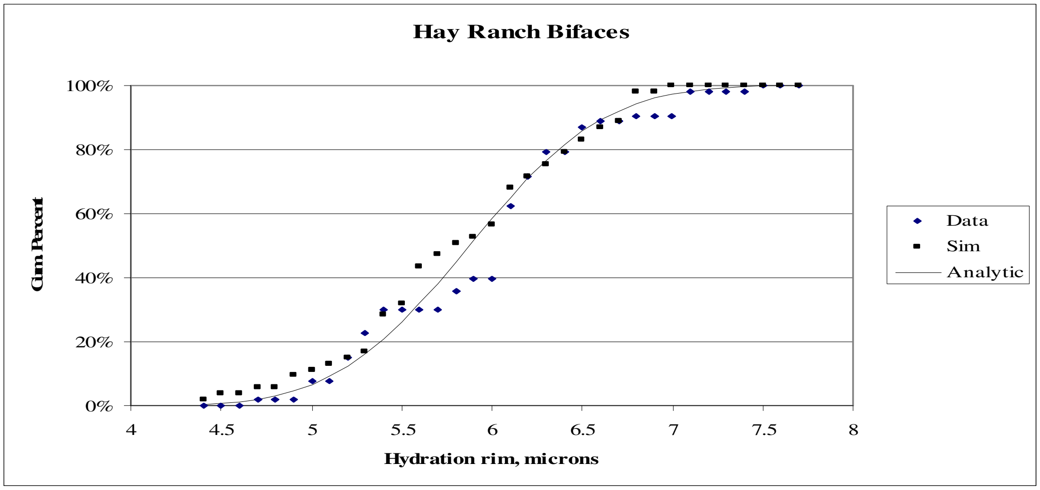

Figure 1. Cumulative distribution of West Sugarloaf hydration rim values for Hay Ranch bifaces (N = 53), comparing measured data (diamonds), simulation data (square), and analytic model (solid line).

from the analytic model of a normal distribution at this confidence level.

Curves Compared	Test	D_{max}	Threshold	Statistically Distinguishable?
Data-simulation	K-S	0.17	0.26	No
Data-analytic	K	0.19	0.19	No
Simulation-analytic	K	0.12	0.19	No

Table 1. Kolmogorov-Smirnov test for Hay Ranch hydration rims from the West Sugarloaf obsidian flow.

The distribution of measured West Sugarloaf hydration rim values from Hay Ranch shows a coefficient of variation CV_s = 0.10, which implies a CV_{ke} of 0.20 for the hydration rate (Taylor 1982). Analysis of the data of Stevenson et al. (1993), showed that the total intrinsic water content for West Sugarloaf had a $CV_{iw} \approx 0.26$ (N = 22) for intra-source variations (Rogers 2008).

However, more recent work suggests the CV_{iw} for West Sugarloaf intrinsic water may be too large (Stevenson and Novak 2011). The water content data in Stevenson et al. (1993) had been obtained by measuring IR absorbance via Fourier transform transmission spectrometry, and computing water content from the IR absorbance by an algorithm developed by Newman et al. (1986). The algorithm had been previously calibrated against water content measured by loss-on-ignition (Newman et al. 1986). Subsequently, however, Zhang et al. (1997) developed an improved algorithm for computing water content from IR absorbance, and compared it with the algorithm of Newman et al. (1986). They conducted a detailed analysis of the two algorithms, and found that the improved algorithm yields similar mean values for total water, but standard deviations which are reduced by >15% (Zhang et al. 1997:3096-3097). This suggests the CV_{iw} of 0.26 reported for West Sugarloaf obsidian by Rogers (2008) is probably also larger than it should be by >15 %. A reduction of 15 – 20% yields a $CV_{iw} = CV_{ke} = 0.21 - 0.22$ for West Sugarloaf, which can be compared to the CV_{ke} = 0.20 inferred from the spread of hydration rims.

Conclusions

The hydration rims for the 53 West Sugarloaf artifacts from the Hay Ranch biface cache exhibit a tight grouping with a coefficient of variation of 0.10, implying a $CV_{ke} = 0.20$. This coefficient of variation is in good agreement with the distribution of hydration rates expected from intra-source intrinsic water variations in West Sugarloaf obsidian as measured by IR spectrometry ($CV_{ke} \approx 0.21 - 0.22$). The distribution of the rim values is Gaussian (normal) at the 95% confidence level. Cautious inferences which can be drawn are that (1) the spread of rim values for the Hay Ranch biface cache is fully explained by the known Coso intrinsic water variability, (2) the variation of hydration rate with intrinsic water content is real and archaeologically observable, and (3) few other error sources are contributing to the spread of rim values in this case.

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Regular Members are individuals or institutions who are interested in obsidian studies, and who wish to support the goals of the IAOS. Regular members will receive any general mailings; announcements of meetings, conferences, and symposia; the *Bulletin*; and papers distributed by the IAOS during the year. Regular members are entitled to vote for officers.

*Membership fees may be reduced and/or waived in cases of financial hardship or difficulty in paying in foreign currency. Please complete the form and return it to the Secretary-Treasurer with a short explanation regarding lack of payment.

NOTE: Because membership fees are very low, the IAOS asks that all payments be made in U.S. Dollars, in international money orders, or checks payable on a bank with a U.S. branch. Otherwise, please use PayPal on our website to pay with a credit card. http://members.peak.org/~obsidian/

For more information about the IAOS, contact our Secretary-Treasurer:

Kyle Freund
IAOS
c/o McMaster University
Department of Anthropology
Chester New Hall Rm. 524
1280 Main Street West
Hamilton, Ontario, Canada
L8S 4L9
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Membership inquiries, address changes, or payment questions can also be emailed to freundkp@mcmaster.ca

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.

MEMBERSHIP RENEWAL FORM

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

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

___ Yes, I'd like to renew my membership. A check or money order for the annual membership fee is enclosed (see below).

___ Yes, I'd like to become a new member of the IAOS. A check or money order for the annual membership fee is enclosed (see below). Please send my first issue of the IAOS *Bulletin*.

___ Yes, I'd like to become a student member of the IAOS. I have enclosed either an obsidian-related article for publication in the IAOS *Bulletin* or an abstract of such an article published elsewhere. I have also enclosed a copy of my current student ID. Please send my first issue of the IAOS *Bulletin.*

NAME: ____

TITLE: ______________________ AFFILIATION:___________________________________

STREET ADDRESS: ____

CITY, STATE, ZIP: ____

COUNTRY: ____

WORK PHONE: ___________________________ FAX: ______________________________

HOME PHONE (OPTIONAL): ____

EMAIL ADDRESS: ____

My check or money order is enclosed for the following amount (please check one):
___ $20 Regular
___ $10 Student (include copy of student ID)
___ FREE Student (include copy of article for *Bulletin* and student ID)
___ $200 Lifetime

Please return this form with payment to: (or pay online with PayPal)
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