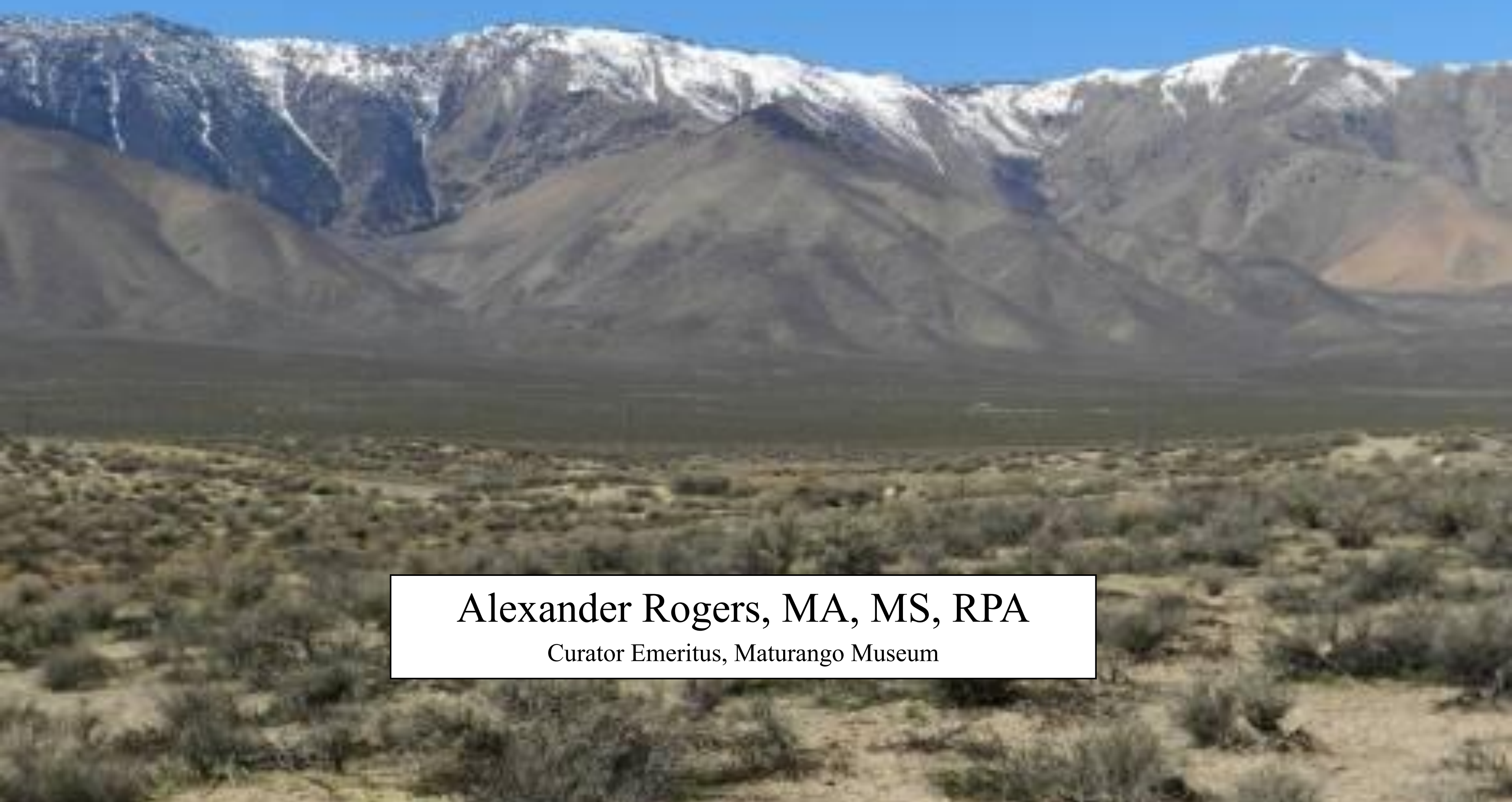
Archaeological Chronometrics by Obsidian Hydration Dating

PSU First Thursday Lecture, Feb. 3, 2022

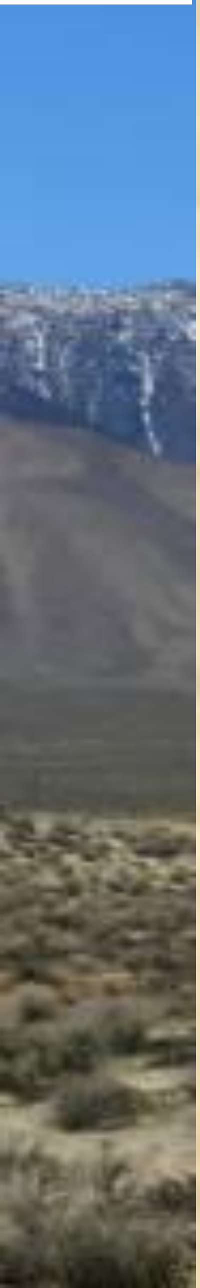


Alexander Rogers, MA, MS, RPA

Curator Emeritus, Maturango Museum

What does Obsidian Hydration Dating (OHD) offer to Chronometrics?

- Obsidian frequently found in western sites lacking other dating materials
  - Better accuracy than projectile point typology
  - Will work on debitage as well as diagnostic artifacts
  - Potential for directly dating obsidian artifacts
- Obsidian often studied to determine trade and exchange patterns; OHD can provide dates
- Relatively cheap
  - $50 - $60 per specimen vs. $350-500 for radiocarbon



Introduction – History of the Method

- First proposed in 1960 by Friedman and Smith, amplified in 1979 by Friedman and Long
- Checkered career since then
  - Wild enthusiasm/abject disappointment
- Kept alive at elementary level by CRM firms
- Major advances since 2007
  - Application of principles of physics, physical chemistry, glass science, and geochemistry
- OHD works if you employ these advances

Introduction –
Scope of Lecture

- Describe the science behind OHD
- Summarize key points in the method
- Provide two examples of OHD application

Introduction – Basic Science

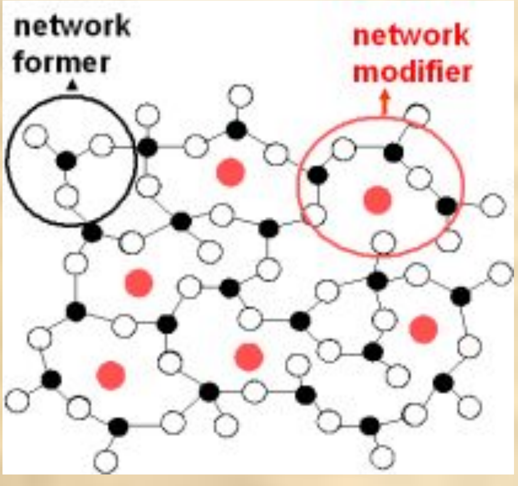
- Any glass absorbs water through a fresh surface
- Age can be estimated if amount of water absorbed and rate of absorption are known
- Amount of water absorbed can be measured
- Rate of absorption is primarily determined by two factors
  - Compositional: intrinsic water content
  - Environmental: temperature history

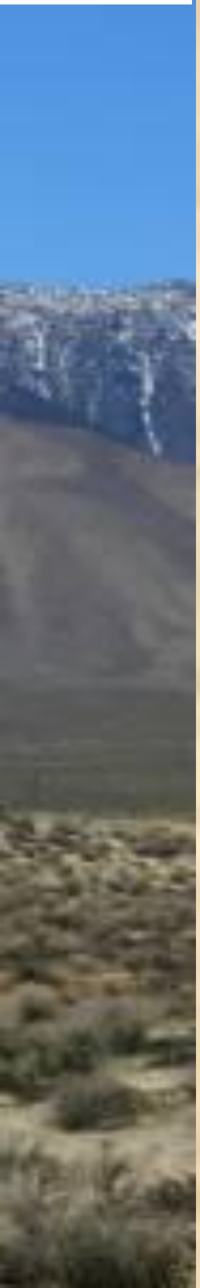
Introduction –
What are the Steps in the Method?

- Data preparation
  - Obtain data set, make sure it is complete
  - Get specimens sourced and read by lab(s)
  - Obtain hydration rate for the obsidian source(s)
- Computations
  - Perform adjustments to control for temperature
  - Compute ages and age standard deviations
- Analyze and present results

Basic Concepts and Models – Obsidian Mineralogy

- Alumino-silicate (rhyolitic) glass
- Volcanic origin
  - Formed by cooling of rhyolitic magma
  - Primary flows and lag deposits, some pyroclastic deposits
- Water diffuses into surface and creates a hydrated layer ("hydration rim" or "hydration rind")
- Hydrated layer eventually spalls off as perlite





Basic Concepts and Models – Typical Obsidian Composition

- Matrix
  - SiO_2 74%
  - Al_2O_3 14%
  - Na_2O 5%
  - K_2O 4%
  - Fe_2O_3 2%
  - MnO <1%
  - MgO <1%
  - CaO <1%
  - TiO_2 <1%

Network Formers (SiO_2, Al_2O_3)

Network modifiers (Na_2O through TiO_2)

- Trace elements (all <<1%)
  - Yt
  - Sr
  - Rb
  - Ba
  - Zr
  - Nb

Source-unique, used for geochemical sourcing. Labs provide the service.

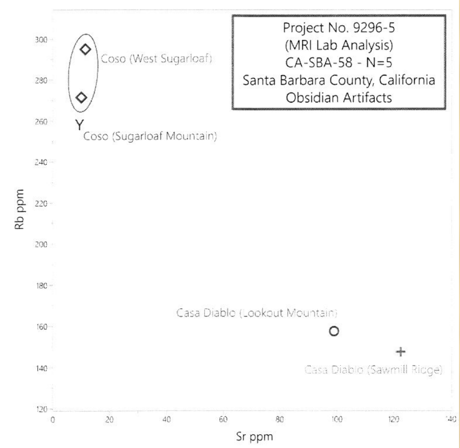
SiO_2 and Al_2O_3 percentages very consistent across obsidian sources

Basic Concepts and Models – Sourcing Lab Report

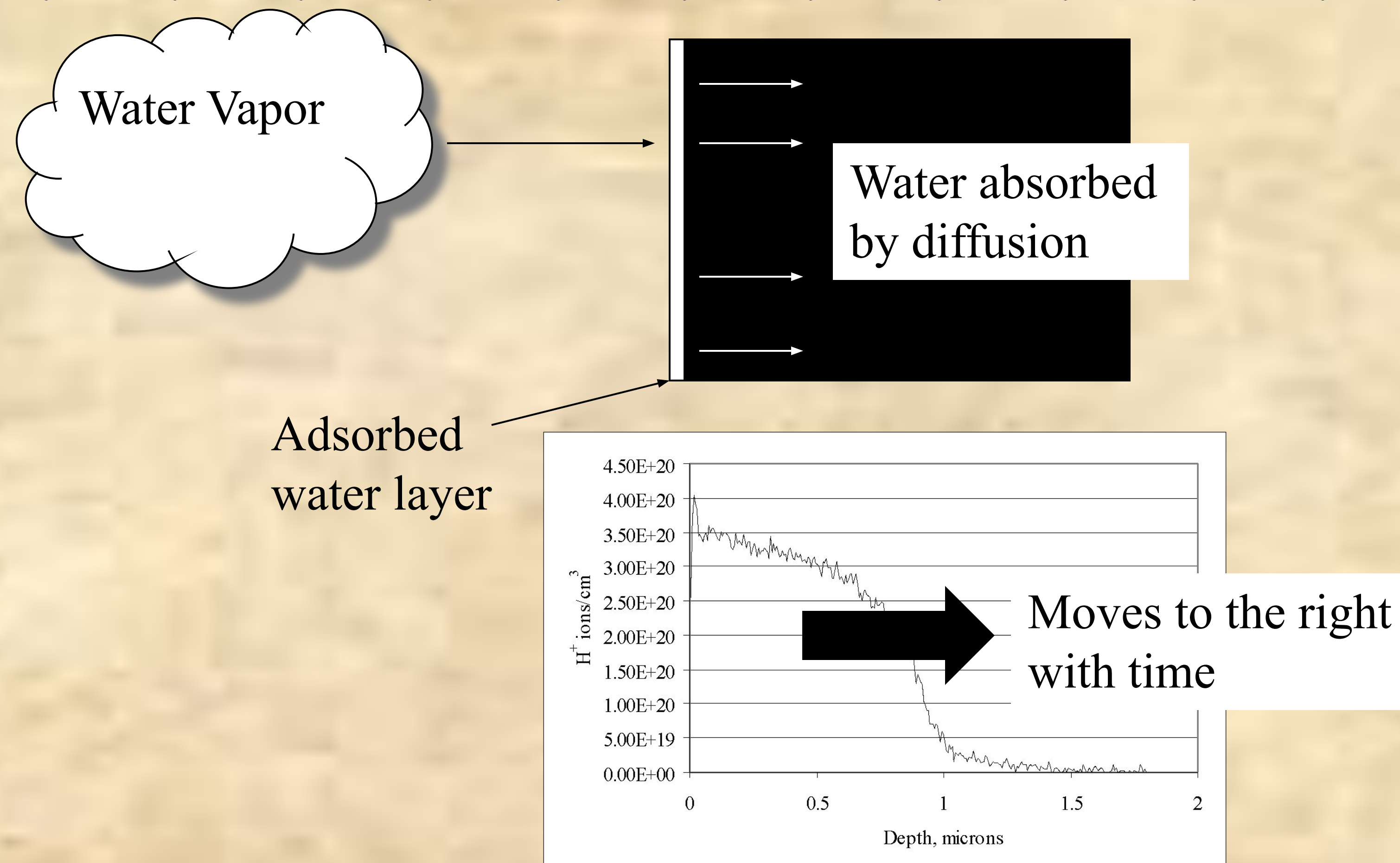
Northwest Research Obsidian Studies Laboratory

Table A-1. Results of XRF Studies: CA-SBA-58, Santa Barbara County, California

Site	Specimen No.	Catalog No.		Trace Element Concentrations									Ratios		Geochemical Source
				Rb	Sr	Y	Zr	Nb	Ti	Mn	Ba	Fe^2O^{3T}	Fe:Mn	Fe:Ti	
CA-SBA-58	1	10.L.A.1.13		148	122	19	188	12	NM	NM	670	NM	NM	NM	Casa Diablo (Sawmill Ridge) *
			±	3	3	2	3	2	NM	NM	34	NM			
CA-SBA-58	2	15.L.A.1.5		158	99	21	190	15	NM	NM	753	NM	NM	NM	Casa Diablo (Lookout Mountain)
			±	3	3	2	3	2	NM	NM	30	NM			
CA-SBA-58	3	15.L.A.1.11		295	11	57	144	54	NM	NM	0	NM	NM	NM	Coso (West Sugarloaf) *
			±	4	2	2	3	3	NM	NM	30	NM			
CA-SBA-58	4	18.L.A.1.5		272	10	51	136	46	NM	NM	0	NM	NM	NM	Coso (West Sugarloaf)
			±	4	2	2	3	2	NM	NM	24	NM			
CA-SBA-58	5	1.L.A.1.b		258	9	51	113	48	NM	NM	0	NM	NM	NM	Coso (Sugarloaf Mountain)
			±	4	2	2	2	2	NM	NM	26	NM			
NA	RGM-1	RGM-1		147	106	27	225	10	NM	NM	711	NM	NM	NM	RGM-1 Reference Standard
			±	3	3	2	3	2	NM	NM	23	NM			



Basic Concepts and Models – Hydration = Water Absorption



Secondary Ion Mass Spectrometer (SIMS) profile

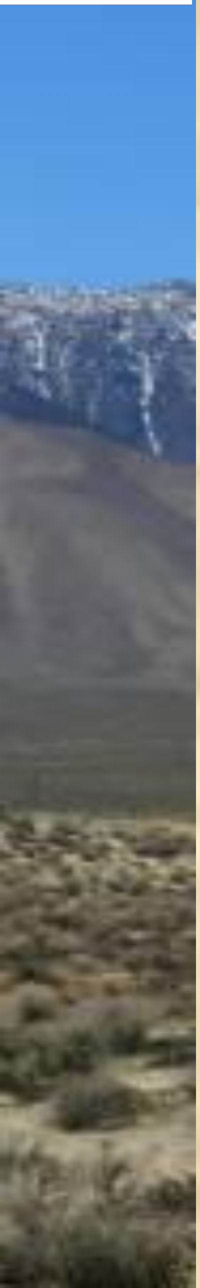
Basic Concepts and Models – What is a Diffusion Process?

- Transport of mass driven by concentration gradient
- By definition, diffusion depth is proportional to the square root of time
  - $r \propto t^{0.5}$ or $t \propto r^2$
  - Laboratory hydration data support this model
- Square root of time dependence leads to the archaeological age equation

  $t = r^2/k$

  k = hydration rate in μ^2/year (or per 1000 years)

Refs: Crank. *Mathematics of Diffusion*. Oxford University Press, 1975;
Zhang. *Geochemical Kinetics*. Princeton University Press, 2008.



Hydration Measurement

- Methods
  - Optical microscopy
  - Secondary Ion Mass Spectrometry (SIMS)
  - Infrared transmission spectroscopy
  - Infrared photo-acoustic spectroscopy
  - Mass loss on heating

Hydration Measurement– Optical Microscopy

- Thin slice of obsidian cut from specimen with diamond saw
- Slice mounted on microscope slide and polished until transparent
- Hydrated region visible under polarizing microscope (~400X)
- Gypsum quarter-wave plate may be used to improve contrast

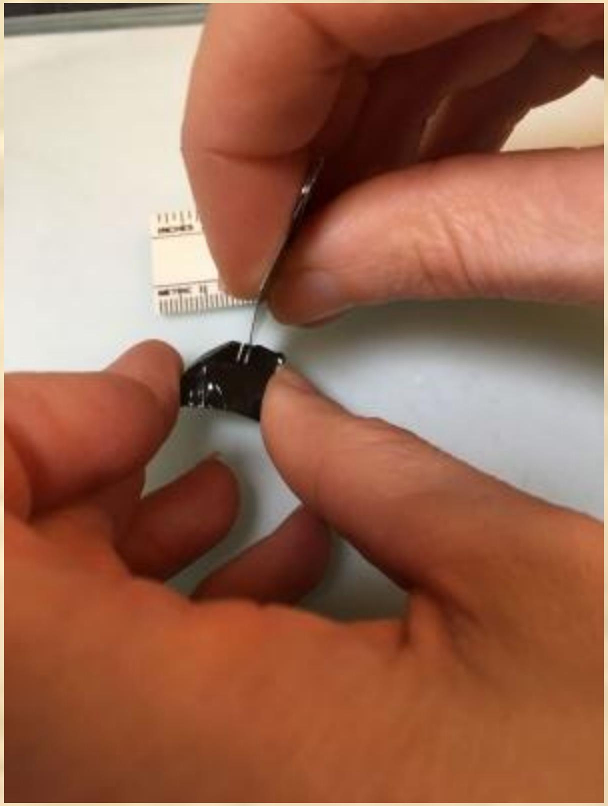
Hydration Measurement – Saw and Blades

Images courtesy of J. Thatcher, Willamette Analytics

Hydration Measurement – Cutting the Notch

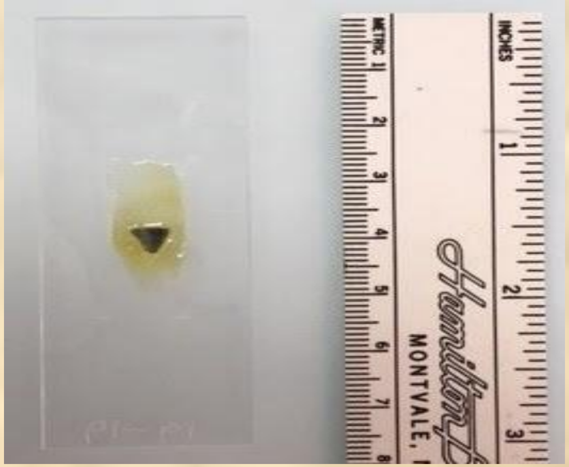
Images courtesy of J. Thatcher, Willamette Analytics

Hydration Measurement – Specimen to Mount on Slide and Polish



Images courtesy of J. Thatcher, Willamette Analytics

Hydration Measurement – Specimens Mounted on Slide



Before polishing

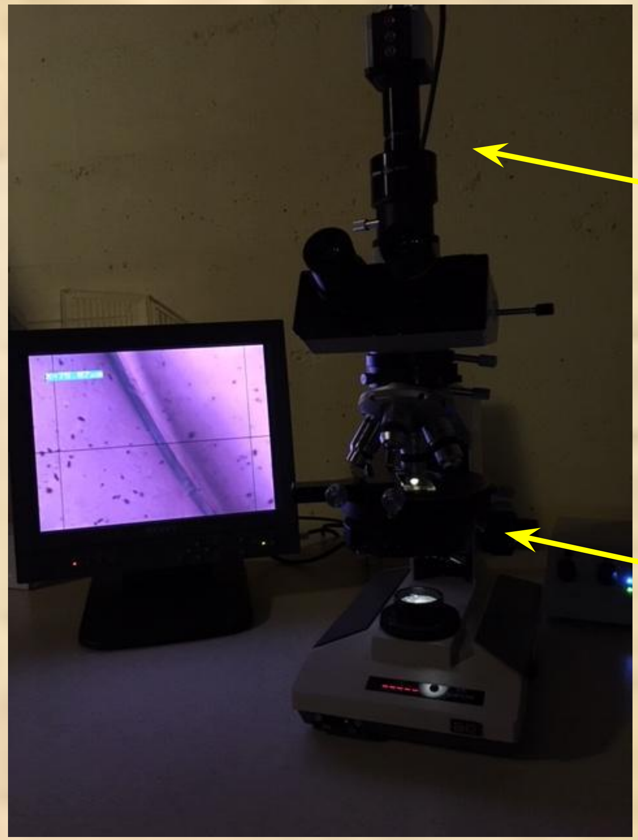
After polishing

Images courtesy of J. Thatcher, Willamette Analytics

Hydration Measurement – Petrographic Microscope System

Digital camera

Monitor



Microscope

Images courtesy of J. Thatcher, Willamette Analytics

Hydration Measurement – Typical Microscope Image

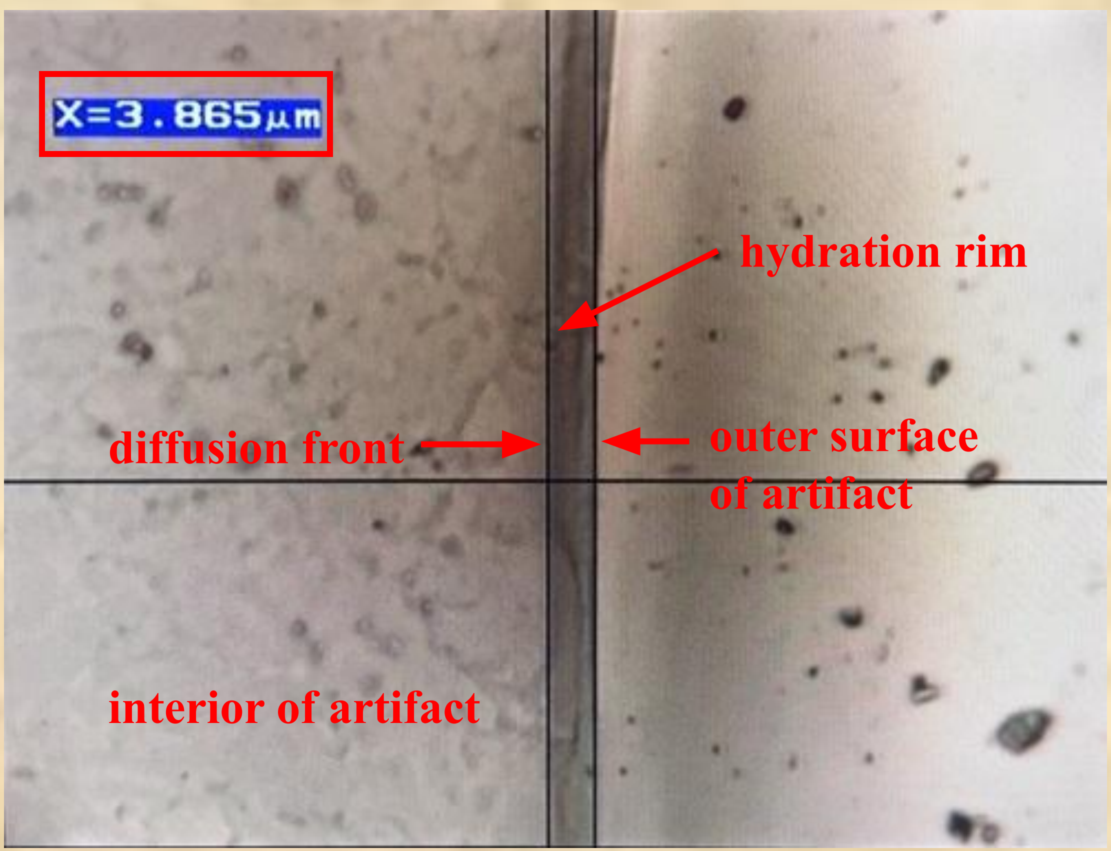


Image courtesy of J. Thatcher, Willamette Analytics

Hydration Measurement – Typical OH Lab Report

Willamette Analytics, LLC

Table A-1. Obsidian Hydration Results and Sample Provenience: Artifacts from CA-INY-7833, Inyo County, California

Site	Specimen No.	Catalog No.	Unit	Depth (cm)	Artifact Type [A]	Artifact Source [B]	Hydration Rims: Rim 1	Hydration Rims: Rim 2	Comments [C]
CA-INY-7833	17	42.2	STU9	20-30	DEB	Coso (Sugarloaf Mountain)	5.3 ± 0.1	NM ± NM	--
CA-INY-7833	18	73.1	STU18	0-10	DEB	Coso (Sugarloaf Mountain)	NA ± NA	NM ± NM	HV, UNR, WEA
CA-INY-7833	19	73.2	STU18	0-10	DEB	Coso (West Sugarloaf)	5.9 ± 0.1	NM ± NM	--
CA-INY-7833	20	73.3	STU18	0-10	DEB	Coso (West Sugarloaf)	3.0 ± 0.1	NM ± NM	REC
CA-INY-7833	21	73.4	STU18	0-10	DEB	Coso (Sugarloaf Mountain)	5.8 ± 0.1	NM ± NM	--
CA-INY-7833	22	76.1	STU18	10-20	DEB	Coso (Sugarloaf Mountain)	9.9 ± 0.1	NM ± NM	REC; BEV, DFV
CA-INY-7833	23	76.2	STU18	10-20	DEB	Coso (West Sugarloaf)	3.2 ± 0.0	7.0 ± 0.1	Smaller rim on BRE
CA-INY-7833	24	76.3	STU18	10-20	DEB	Coso (Sugarloaf Mountain)	10.0 ± 0.1	NM ± NM	DFV
CA-INY-7833	25	82.1	STU19	10-20	DEB	Coso (Sugarloaf Mountain)	8.7 ± 1.1	NM ± NM	DFV
CA-INY-7833	26	82.2	STU19	10-20	DEB	Coso (Sugarloaf Mountain)	5.4 ± 0.1	NM ± NM	IRR
CA-INY-7833	27	82.3	STU19	10-20	DEB	Coso (Sugarloaf Mountain)	5.6 ± 0.1	NM ± NM	NVH on BRE
CA-INY-7833	28	92.1	TU2	0-10	DEB	Coso (Sugarloaf Mountain)	5.9 ± 0.1	NM ± NM	--
CA-INY-7833	29	92.2	TU2	0-10	DEB	Coso (West Sugarloaf)	5.4 ± 0.1	NM ± NM	DFV
CA-INY-7833	30	92.3	TU2	0-10	DEB	Coso (West Sugarloaf)	6.0 ± 0.1	NM ± NM	REC
CA-INY-7833	31	92.4	TU2	0-10	DEB	Coso (Sugarloaf Mountain)	9.5 ± 0.1	NM ± NM	DFV, IRR (fissures)
CA-INY-7833	32	96.1	TU2	10-20	DEB	Coso (Sugarloaf Mountain)	6.0 ± 0.1	NM ± NM	DFV

[A] DEB = Debitage
[B] Obsidian Source Data: Geoarchaeological XRF Laboratory
[C] See text for explanation of comment abbreviations
NA = Not Available; NM = Not Measured; * = Small XRF sample

A - 2

Hydration Measurement – Caveats and Cautions

- Some glasses eroded by chemical reaction with soil salts
- Mechanical erosion (sand blasting) can occur in deserts
- Results can be affected by fire
- OH reading damages the specimen

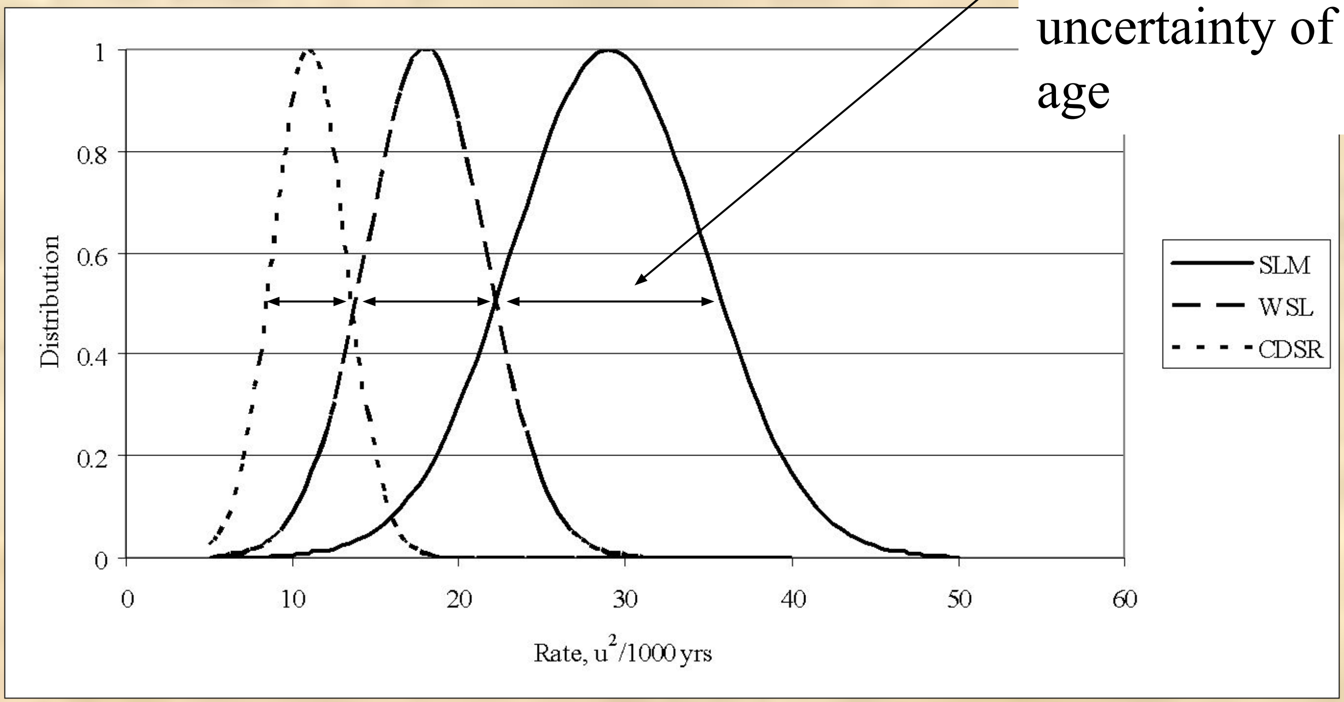
First Elephant in the Room
Intrinsic Water in Obsidian

- All rhyolitic magmas (melts) contain water
- Obsidian forms from cooling of rhyolitic melt
- Water molecules are bigger than inter-atomic spacing of the glass matrix
- The glass forms around the water molecules, causing voids in the glass and enhancing diffusion
- Hydration rate is therefore a strong function of intrinsic water content of the obsidian
- Water content typically < 3 % by weight

Intrinsic Water Effects – Controlling for Intrinsic Water

Sourcing controls for central tendency

Intra-source variation contributes to statistical uncertainty of computed age



Hydration rate distributions due to intrinsic water variation for three obsidian sources in eastern California

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Intrinsic Water Effects – Conclusions

- Hydration rates are assigned to sources
  - Casa Diablo Sawmill Ridge, Bodie Hills...
- Controlling for source is a proxy for controlling for intrinsic water content
  - Intra-source variation included in calculation of age standard deviation
- Must use correct rate for your specimens
- Must not mix specimens from different sources
- Specimens should be sourced by XRF or INAA

Second Elephant in the Room
Temperature History

- Hydration rate is a strong function of temperature
- A 10°C increase in temperature doubles the hydration rate
- Arrhenius equation

  $k = k_0 * \exp(-E/RT)$

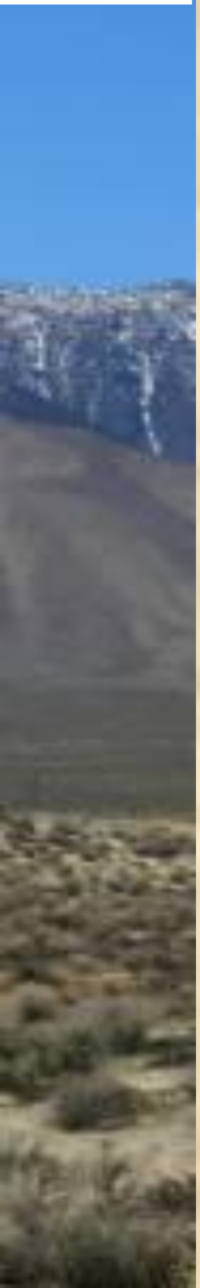
  Obsidian parameters

  k_0 = pre-exponential factor, in μ^2/unit time

  E = activation energy in J/mol

  R = universal gas constant (8.314 J/mol°K)

  T = temperature in °K (°K = °C + 273.15)
- For obsidian, E ≈ 83,140 J/mol
  - E/R ≈ 10,000°K

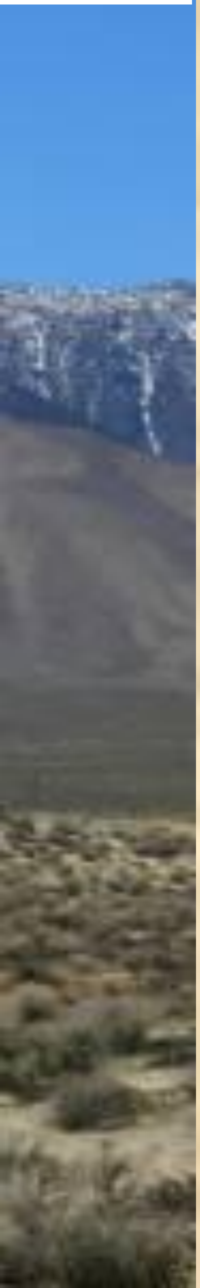


Capturing History in a Single Parameter

Effective Hydration Temperature (EHT)

- Archaeological temperatures fluctuate in complex manner
  - Diurnally, seasonally, annually, and longer term
  - Therefore hydration rate fluctuates as well
- Definition of EHT
  - *Constant temperature which would yield the same hydration rim as the actual temperature history over the same time*
- Higher than the average temperature

Ref: Rogers. Effective hydration temperature of obsidian: a diffusion theory analysis of time-dependent hydration rates. *JAS* 34 (2007) 656-665.



Temperature History – Model

- Computing EHT requires a temperature history model
- Temperature history characterized by three parameters
  - Annual average temperature (T_a)
  - Monthly mean temperature variation (seasons) (V_{a0})
  - Mean diurnal temperature variation (V_{d0})
- Temperature modeled mathematically as sum of a constant term and two sinusoids

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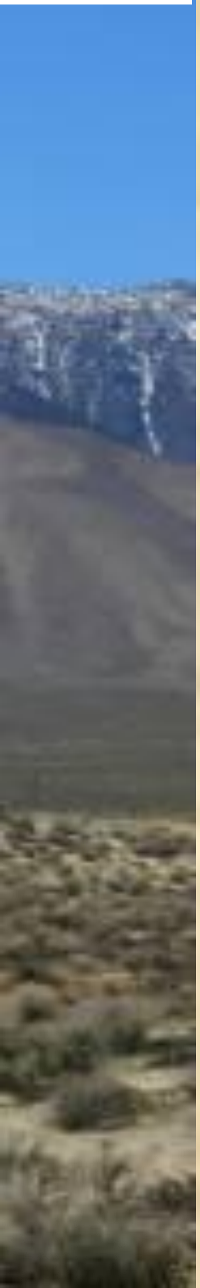
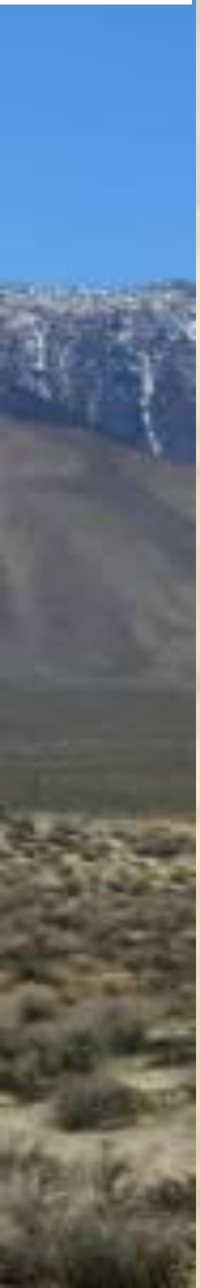


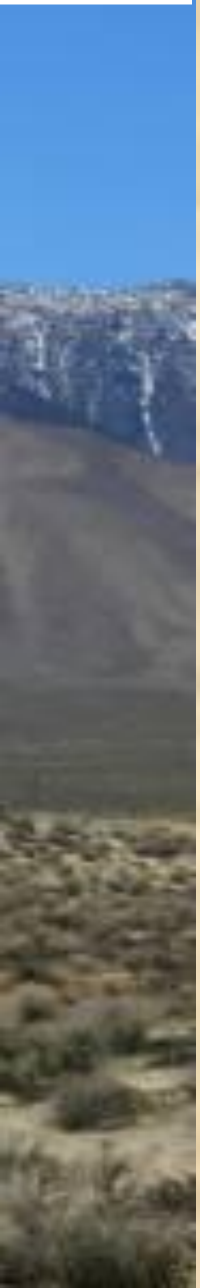
Temperature History – EHT Computation

- Need to assign numerical values to the annual average temperature and the amplitudes of annual and diurnal variations (T_a, V_{a0}, and V_{d0})
- Data sources
  - 30-year temperature records from weather station data
    - Available from Western Regional Climate Center (www.wrcc.dri.edu)
  - Temperature sensors at a site
- Also must correct for burial depth



Temperature History – How do we get EHT?

- Integration of the Arrhenius equation over the model temperature history
- The integral cannot be solved analytically – numerical methods must be used
- Practical computation requires software package such as *MatLab* or *Mathematica*



Temperature History – Archaeological Computation of EHT

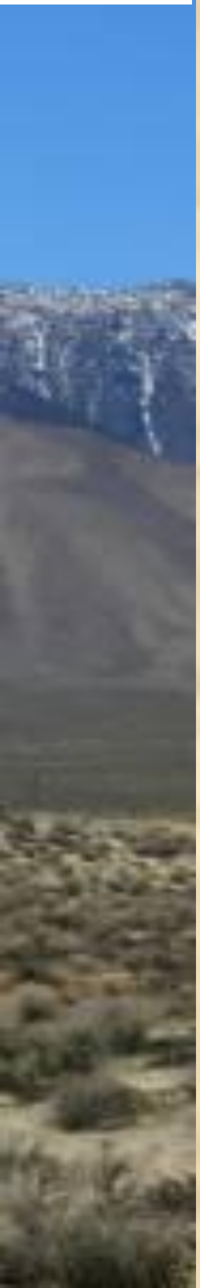
- Best fit model based on multiple computer runs

$$EHT = T_a + 0.0062 \times (V_a^2 + V_d^2)$$

- Simple form gives good results for typical archaeological conditions
  - $\sigma_{EHT} < 0.20°C$
- Use EHT to control for temperature
  - Adjust rim data to match rate EHT

Hydration Rates –
Hydration Rate Determination

- Methods
  - Find a published hydration rate that you can trust
  - Compute a rate by obsidian-radiocarbon association
  - Compute a rate based on time-sensitive artifacts
  - Compute a rate based on similarity
  - Measure the rate with lab methods
- Remember – the rate is unique to the obsidian geochemical source!

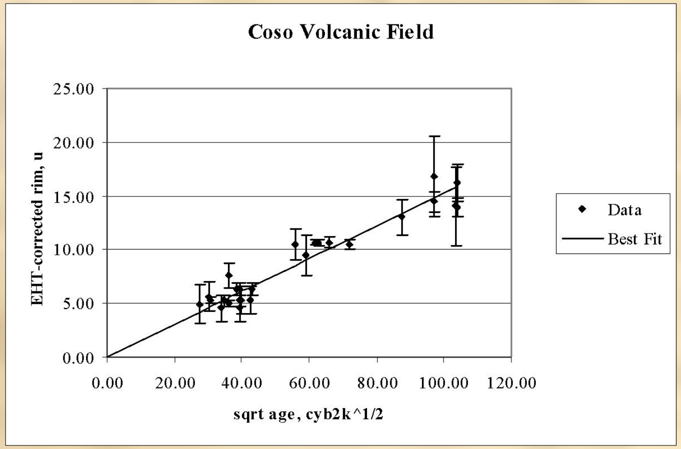


Hydration Rates – I - Caveats on Published Rates

- Be sure you understand how it was obtained
- Questions to ask yourself
  - Were obsidian data sorted by geochemical source?
  - Was source determined geochemically or by eyeball?
  - Did the analyst take EHT into account correctly?
  - Was burial depth included in EHT?
  - What is the EHT? What site is it based on?
  - Can you compute or infer a correct EHT from site data?
  - Did the analyst use calibrated years or RCYBP?
  - Did the rate yield archaeologically reasonable results?

Hydration Rates –
II - Obsidian-Radiocarbon Association

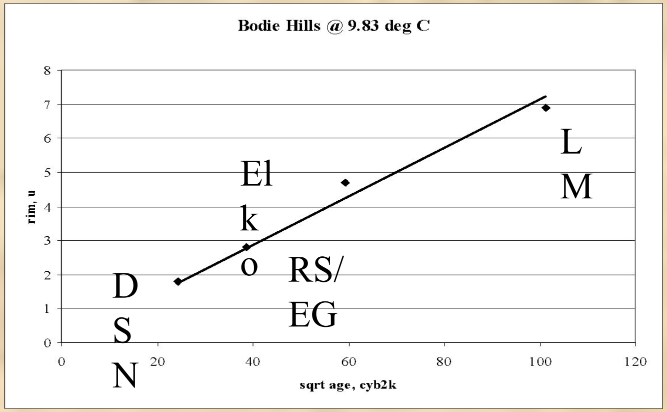
- Ages from radiocarbon associated with hydration rims from obsidian artifacts
- Convert ages to calibrated years before 2000
- Correct rim values for burial depth and site EHT
- Compute linear least-squares best fit between r and √t
- Rate = $(\text{slope})^2$



Accuracy ~ 5% possible

Hydration Rates –
III- Time-Sensitive Artifacts

- Use time-sensitive artifacts as the time markers instead of radiocarbon
- Again make best fit between EHT-corrected hydration rims and square root of age
- Less accurate than radiocarbon, but sometimes the best you can do

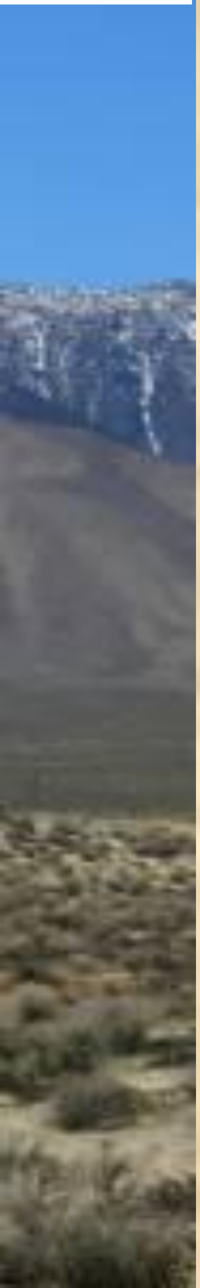


Ref: Rogers and Duke. Estimating Obsidian Hydration Rates from Temporally-Sensitive Artifacts: Method and Archaeological Examples. *IAOS Bulletin* no. 51, summer 2014, pp. 31-38.

Hydration Rates –
IV – Similarity Method

- Principle: compute unknown rate based on co-occurrence of similar artifacts with known rate
- Rates proportional to square of rim readings
- If rate for one source is known, the rate for the other source can be computed
    - On the assumption that the artifacts are the same age

Ref: Hydration Rates for Casa Diablo and Fish Springs Obsidians, Eastern California. *IAOS Bulletin* No. 56, winter 2017, pp. 5-10



Hydration Rates – V - Laboratory Methods (Induced Hydration)

- Based on temperature-dependence of hydration rate
  - Hydrate samples in lab at elevated temperatures for known time interval (hot soak)
  - Measure hydration rims
  - Use log-Arrhenius equation to compute obsidian parameters
  - Compute rate for archaeological temperature of interest

*Ref: Rogers and Stevenson. Protocols for laboratory hydration of obsidian, and their effect on hydration rate accuracy: A Monte Carlo simulation study. *JAS:Reports* 16 (2017) 117-126

Hydration Rates – Summary of Rate Determination

- Methods reviewed
  - Find a published hydration rate that you can trust
  - Compute a rate by obsidian-radiocarbon association
  - Estimate a rate based on time-sensitive artifacts
  - Compute a rate based on similarity
  - Measure the rate with lab methods
- Now that you have a rate, what do you do with it?

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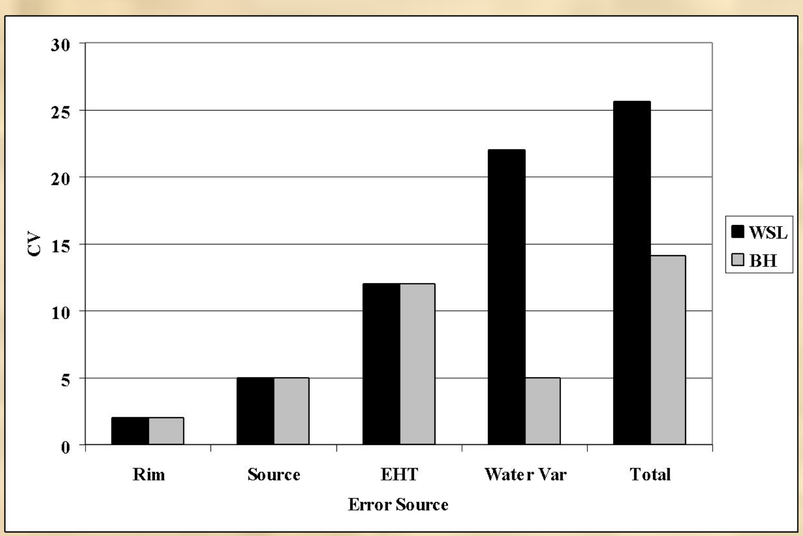
Age Computation

- Adjustment to control for temperature
  - Determine temperature parameters
  - Make depth corrections
  - Adjust all hydration rim data to a common EHT (usually same as EHT for rate, EHT_r)
- Compute ages using adjusted rim data
- Perform archaeological analyses

Rogers and Stevenson (2020) Archaeological Age Computation using Obsidian Hydration – A Summary and Current State of the Art. *Bulletin of the International Association for Obsidian Studies* Special Issue 63, pp. 2-44.

Age Computation – Typical Error Magnitudes

Error Source	CV
Hydration Rim	1 - 2%
Source Rate	5%
EHT	12%
Intra-source water variation	15 - 30%



$$CV_{age} = \mathrm{sqrt}(\sum \text{ of error source } CV^2)$$
$$\sigma_{age} = age * CV_{age}$$

Rogers and Stevenson (2020) Archaeological Age Computation using Obsidian Hydration – A Summary and Current State of the Art. *Bulletin of the International Association for Obsidian Studies* Special Issue 63, pp. 2-44.

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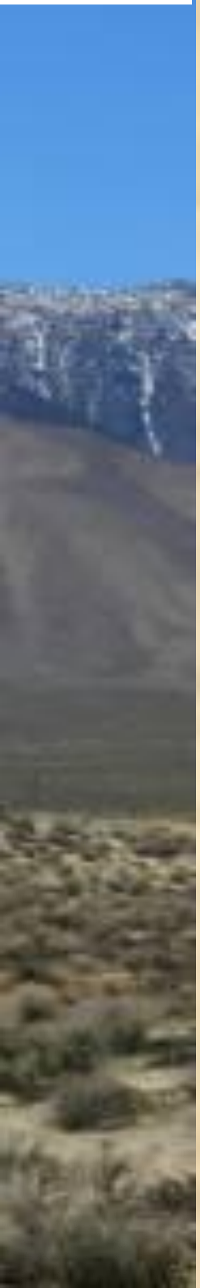
As an Archaeologist, How do you Compute Age Accuracy?



- For each specimen you have
  - Geochemical source
  - Rate k for that source
  - Hydration rim r for each specimen
- For typical archaeological conditions, a best fit for CV of age is
  - $CV_t = \text{sqrt}[(.16/r)^2 + 0.007*k - 0.0581]$
  - $\sigma_t = t * CV_t$

Age Computation – Methods of Calculation

- Options
  - Calculator
  - MS Excel
    - Use/modify the OHD workbook
  - Design a production system in *Matlab** or *Mathematica*

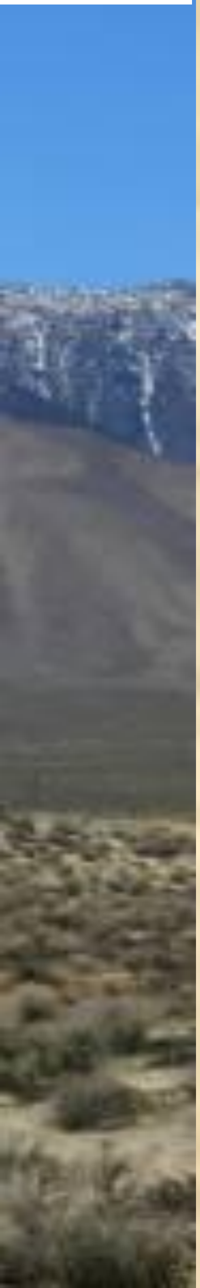
Analysis Example I – Bonneville Estates Rockshelter*

- On the Nevada-Utah border
- Ancient shoreline of Pleistocene Lake Bonneville
- Excavations since 2000 by BLM (Bryan Hockett) and University of Nevada (Kelly Graf, Ted Goebel, and team)
- Major Paleoindian site

* With Daron Duke of FWARG

Bonneville Estates Rockshelter
BLM # CrNV-11-4893

Photo courtesy of Daron Duke, FWARG



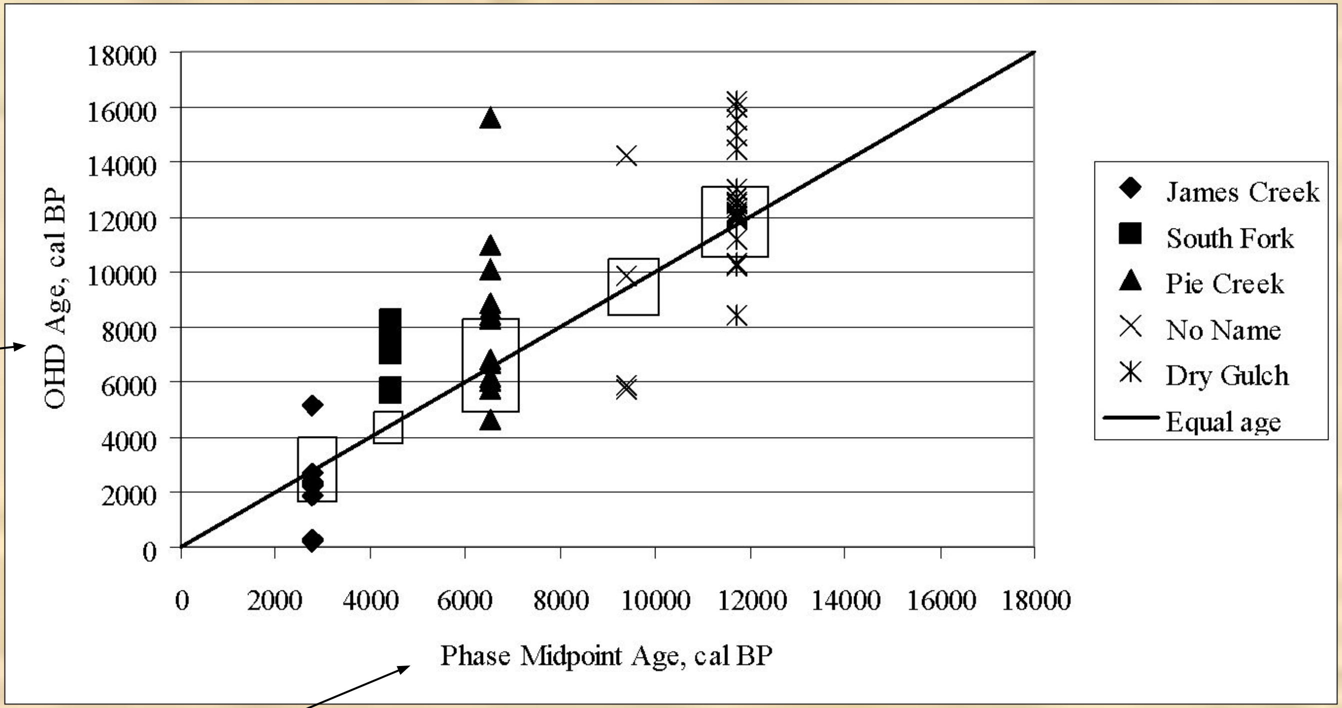
Bonneville Estates Rockshelter

- OHD analysis for the BER site
  - Obsidian specimens sourced to Brown's Bench (N = 50) and Topaz Mountain (N = 13)
  - Obsidian parameters for Topaz Mountain known*
  - Determined Brown's Bench parameters by radiocarbon association
  - Ages of BER specimens in good agreement with radiocarbon

* Rogers and Duke 2011. An Archaeologically Validated Protocol for Computing Obsidian Hydration Rates from Laboratory Data. *Journal of Archaeological Science* 38, 1340-1345.

BER Obsidian Dates vs. Radiocarbon-Derived Dates

Age computed by OHD



Calibrated age computed from radiocarbon

BER Caveat

- First attempted to get Brown’s Bench rate by similarity method
  - Artifacts of both sources from same provenience
- Similarity method did not work
  - Got results that did not make sense archaeologically
- Concluded that the two sources were exploited at different times, which invalidates the method

Analysis Example II-
Rose Spring (CA-INY-372)*

- Southern Inyo County, CA
  - Type site for the Rose Spring PPT
- Excavated 1951 – 61 by Fritz Riddell and UC; 1987 - 90 by Robert Yohe and UCR
- Site establishes date of introduction of the bow and arrow in the southwestern Great Basin

* With Robert Yohe of CSUB

Ref: Yohe: The Introduction of the Bow and Arrow and Lithic Resource Use at Rose Spring (CA-INY-372). *JCGBA* 20(1):26-52. (1998).

Rogers and Yohe. Obsidian Re-Use at the Rose Spring Site (CA-INY-372), Eastern California: Evidence from Obsidian Hydration Studies. JCGBA 34(2): 267-280 (2014)

Rose Spring Site
View North-East

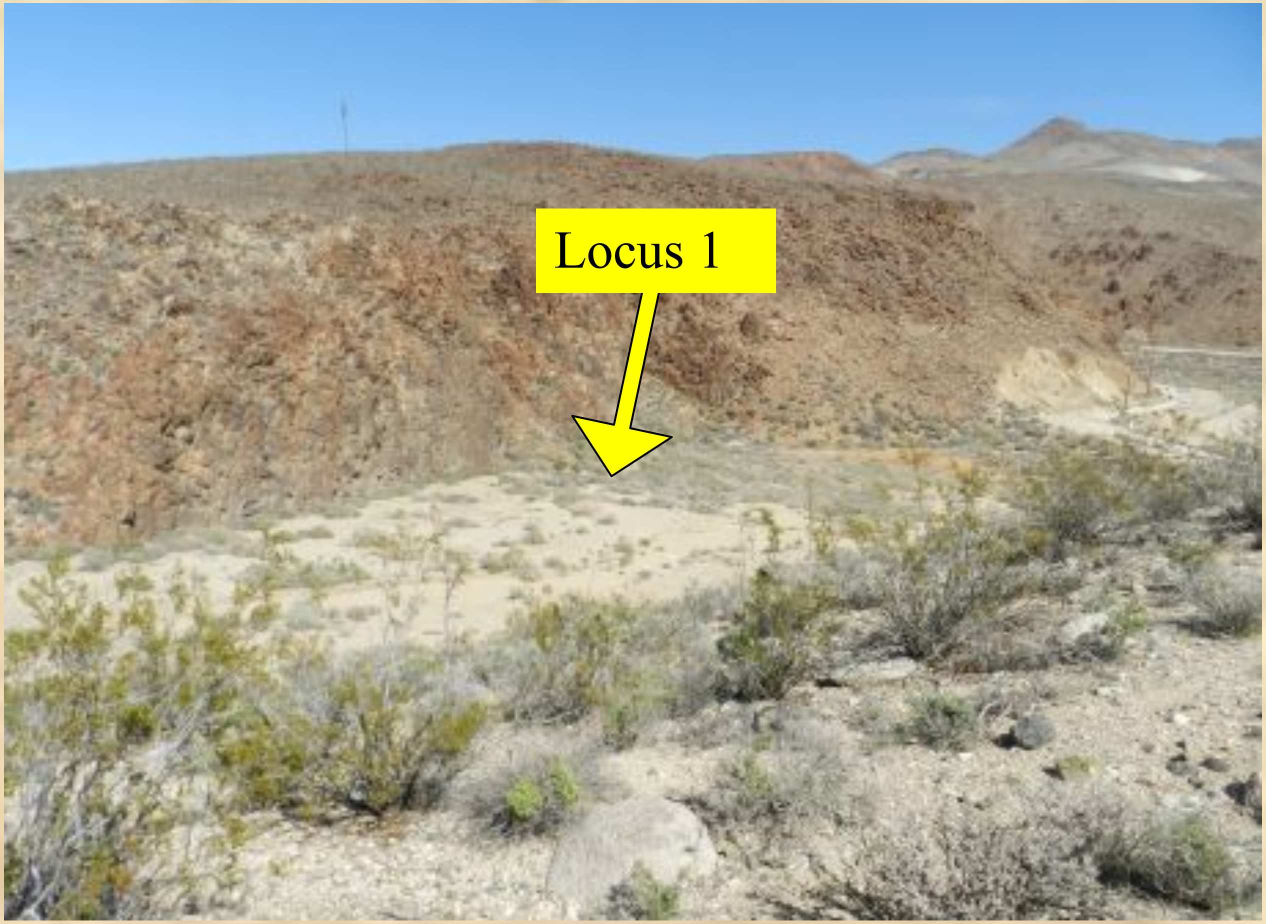


Photo by the author

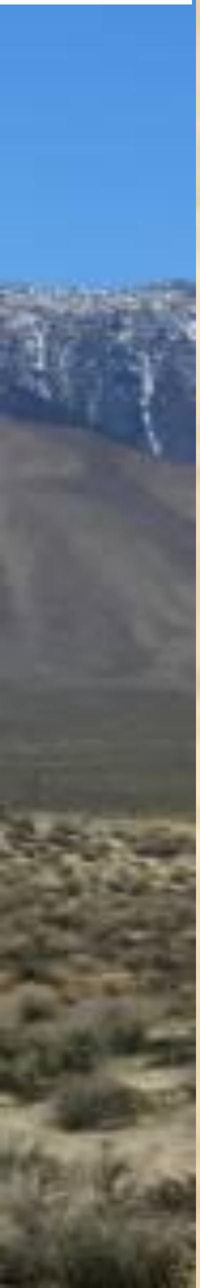
Rose Spring OHD Sample

- 36 Rose Spring PPTs cut for reading
  - 4 appeared to be modified Elko and were cut a second time
- 28 major pieces of debitage cut
- Coso West Sugarloaf obsidian
- Temperature data from the Western Regional Climate Center
- OHD analysis by the techniques described here

Rose Spring Results*

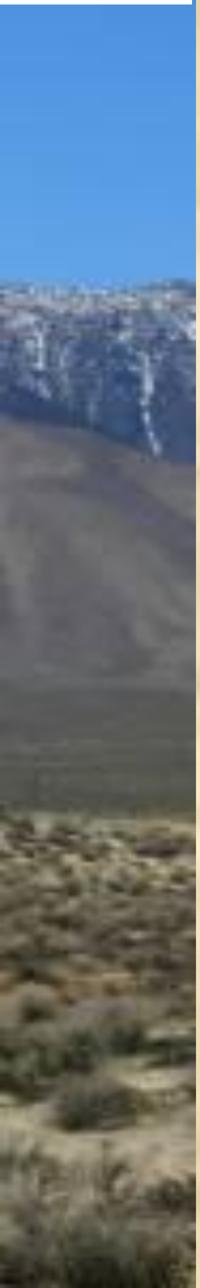
- Ages of Rose Springs points agreed with expectations
- Statistically significant difference in age
  - Between old and new surfaces of reworked points
  - Between points and debitage
- Indicates obsidian was being scavenged on site to avoid a trek to the quarry

*Rogers and Yohe. Obsidian Re-Use at the Rose Spring Site (CA-INY-372), Eastern California: Evidence from Obsidian Hydration Studies. JCGBA 34(2): 267-280 (2014)



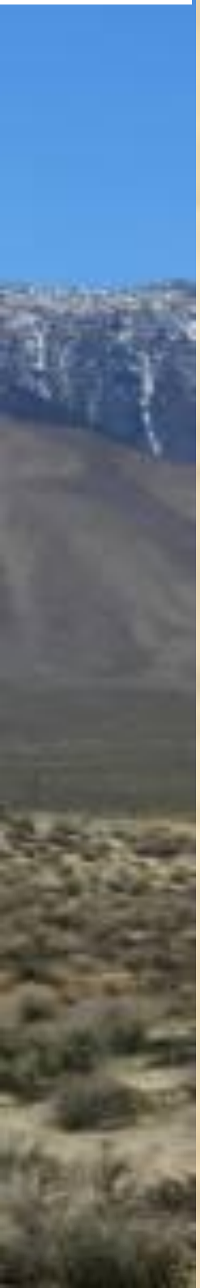
Conclusions on OHD Practice

- Significant progress in the last decade
- Can assign artifacts to archaeological periods with high confidence
- Relatively inexpensive method
- Can answer interesting anthropological questions
- Major uncertainties arise from
  - Intrinsic water content
  - Temperature history



Obsidian Science at Present

- Basic models and key parameters understood
  - Models and techniques fully published
  - Refinements on-going
- Major caveat: current models are "open loop"
  - Temperature history applies to site
  - Hydration rates apply to source (no water content data)
  - Neither is specific to the individual specimen
- Further major improvements in accuracy unlikely with open loop models



What is the Future?
Obsidian Science

- Research on-going on three key issues in the underlying science
  - Dynamics of the hydration process at molecular level
  - Non-destructive intrinsic water measurement
  - Temperature compensation by intrinsic methods
- And we really need a low-cost, “non-consumptive” method of reading hydration rims!

MATURANGO MUSEUM

Basic Reference – “OHD Method Summary Paper Rev”

ARCHAEOLOGICAL AGE COMPUTATION BASED ON OBSIDIAN HYDRATION: A SUMMARY AND CURRENT STATE OF THE ART

Alexander K. Rogers[a] and Christopher M. Stevenson[b]

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[b] Virginia Commonwealth University, Richmond, Virginia, USA

Abstract

Obsidian hydration dating (OHD) is a method of computing archaeological ages based on measuring water absorption by obsidian artifacts, and is widely used in the desert west. The field has seen significant advances over the past decade, many papers having been published describing advances in the field, but to date they have not been pulled together to provide a coherent picture. This paper aims to do just that, providing a single resource for the OHD analyst. The paper describes obsidian mineralogy as it affects OHD; the effects of intrinsic water content on hydration; the mathematical form of the hydration law; the mathematics of diffusion theory; the mathematical techniques for controlling for temperature, humidity, and water content; methods for computing hydration rates, with mathematical details; and a recommended method for conducting on OHD analysis. A table of hydration rates for the south-eastern California and southern Nevada region is included. Appendices include computer codes in MatLab for OHD analysis, plus a useful workbook in MS Excel. The paper addresses OHD as currently practiced in the western United States, based on optical microscopy, and does not describe newer, experimental methods such as Secondary Ion Mass Spectrometry or infrared spectroscopy.

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Questions?

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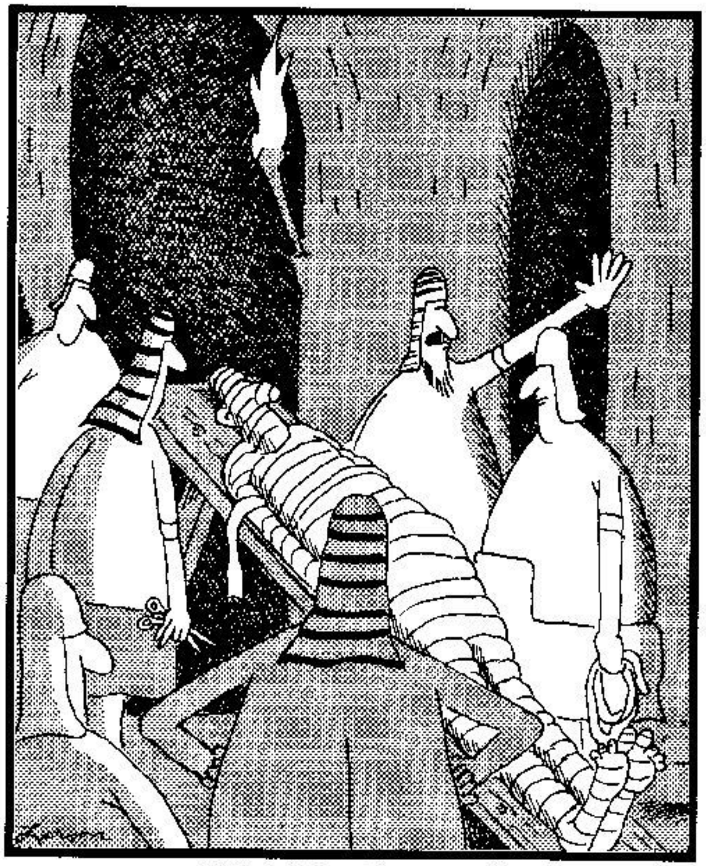
OK, Folks! ... It’s a Wrap!



“OK, folks! … It’s a wrap!”

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