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Title

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Breakthrough in precision (0.3%) of neutron activation analyses applied to provenience studies of obsidian

Frank Asaro, Fred H. Stross Ernest Orlando Lawrence Berkeley National Laboratory (LBNL) and Richard L. Burger Yale University Peabody Museum

Abstract

A gamma ray spectrometer at LBNL (the Luis W. Alvarez Iridium Coincidence Spectrometer), that was specifically designed for high sensitivity measurements of iridium abundances, has been significantly modified in order to provide precisions of measurement in neutron activation analysis of obsidian significantly better than previously obtained (about 1%).

Repeated measurements on a single sample of obsidian from a deposit near Chivay, Arequipa, Peru, showed a precision (average coefficient of variation) of 0.19% for the 6 best-measured elements, the value anticipated from the known random errors of measurement. In measurement of samples made from 7 different obsidian nodules from two locations near Chivay, a group of 5 had a spread of 0.30% for the 6 elements measured with counting statistics of better than 0.3% (and 1.8% for the remaining 6 elements). The data suggest there are source inhomogeneity and/or sample preparation contamination errors totaling $0.24 \pm .05\%$ for the 6 best measured elements. A sixth obsidian sample could be distinguished from the main group because it differed by +0.8% for most elements, and the last sample could be easily distinguished because several elements differed by more than 1%.

The precision of measurements now being developed may provide a significantly more precise determination of the provenience of obsidian artifacts than has been heretofore possible. Also the techniques of measurement developed for obsidian will provide even better precisions with pottery, as many elements are more abundant in pottery than in obsidian.

Equipment and sample preparation

The Luis W. Alvarez Iridium Coincidence Spectrometer (LWAICS), shown in Fig. 1 before its right anti-Compton shield was installed and the electronics were connected, was constructed in 1986 and dedicated in 1995. It has two 5 cm diameter x 5 cm long intrinsic Ge gamma ray detectors, each capable of handling 150,000 counts per second (cps). The Ge detectors are completely surrounded by two mineral oil anti-Compton shields spiked with a scintillator. The faces of the two Ge detectors are only 20 mm apart and in between are two high voltage shields, two heat shields, two vacuum shields, a sample track and an Al encapsulated sample. The machine can count gamma ray singles or gamma ray coincidences with or without the anti-Compton shields. In the present work the anti-Compton shields were not used and the count rates were about 20,000 cps.

Powder samples of 100 mg were encapsulated in 0.2 mm thick high purity Al foil. A 100 mm stack of nearly 40 encapsulated samples was sealed in a quartz tube along with standards of Standard Pottery and DINO-1 at the top, middle and bottom of the tube. The stack along with other stacks was irradiated in the University of Missouri Research Reactor for 2 days at a flux of 2.5 x 10^{13} neutrons per second per cm². Obsidian samples were counted in the LWAICS for periods ranging from 90 minutes to 14 hours.

Previous work

The most precise measurements by the LBNL neutron activation group in its 24 year history between 1967 and 1991 were made in 1976 on a basalt standard prepared by the Atlantic Richfield at Hanford company. Up to 7 measurements each were made on duplicate samples of 3 splits of the basalt. An average coefficient of variation (see Table 1) of 0.4% was obtained. This was never repeated, probably because the U.C. Berkeley reactor (which was used for the experiments) had a variation in neutron capture

cross section of about 12% per cm, and sample capsules could not be rotated after the first few years (for reactor safety reasons). That and the spreading of the gamma ray peaks by count rates in excess of 2,500 cps led to minimum precisions of 1%. The most precise measurements of other INAA laboratories was also about 0.8-1%.

Reason for the present study

As part of a project to determine the provenience of a group of 21 Peruvian obsidian artifacts (called the Titicaca Basin chemical group), 7 samples of obsidian nodules from 2 sources west and east of Cerro Ancachita (near Chivay, Arequipa, Peru) were studied by INAA (Burger et al. 1996). These samples were optimum for the present study because obsidian can be very homogeneous. Also it has a water content of only a few percent which can be lost during irradiation. So it is possible to check weights after irradiation to determine if any powder has been lost. (All obsidian samples should lose weight during irradiation due to the loss of volatiles, but comparison of the changes for samples with the same origin can determine if any sample lost an unusual amount, i.e. obsidian powder.)

Procedures in present work

In the previous LBNL work errors could be reduced to the level of detection, i.e. about 1%. But there were many such errors and these were slowly reduced to hopefully lower levels over a period of 5 years between 1991 and 1996. The precision did not improve markedly until 1996 when the "last" error was reduced to a much lower level.

Encapsulated Al samples are wiped clean with ethyl alcohol on a cotton Q-tip before and after irradiation to remove any contaminating powder.

The neutron capture cross section is interpolated for each sample position in the quartz tube with standards. Four of the 7 obsidian samples studied in this work were in the same capsule as the standards. Fortuitously, the quartz tube containing the other three obsidian samples happened to have its samples in exactly the same positions that they would have had in the tube with standards. In the future each sealed quartz tube will have its own triplicate set of Standard Pottery standards.

The obsidian samples were weighed in triplicate before and after encapsulation in Al foil and after irradiation. Some significant loss of powder during irradiation (or sample handling during tube vacuum sealing or opening) was detected in two of the 7 samples (see Table 2).

The sample track between the Ge detectors allows the sample position to vary 1-2 mm. The counting rate of the 46 Sc 1121 keV gamma ray is counted in the two detectors and the ratio determines the exact relative position of all of the samples and standards. The uncertainty can be reduced to less than 0.1% in a gamma ray count of several hours. Such errors in geometry will cause all singles measurements to vary coherently, while coincidence measurements will be rather insensitive to the position of the sample along the axis of the two detectors.

The efficiency of the electronic system for detecting gamma rays depends strongly on the count rate. This efficiency is measured with pulsers feeding each of the two detector preamplifiers and the electronic system measuring the pulser output of the preamplifiers. The uncertainty from this pulser measurement can be reduced to about 0.1% with counts of several hours. Again the errors for each element measured by singles will vary coherently, but the errors in coincidence measurements will vary nearly coherently with those of the singles.

Counting errors in coincidence measurements will be much larger than those in singles because their count rate is much lower. For this reason only singles results were included in the study of the 6 most precisely measured elements in this work. The particular gamma ray singles or coincidences used for the measurement of each element are shown in Table 3.

The LWAICS has low levels of contamination from earlier INAA studies, and these were measured and corrections were made in the abundances for each sample. The Al encapsulating foil is warranted 99.9999% pure, but contains impurities or laboratory contaminations of many elements. The Sc impurity is very high, 0.2 ppm, (see Table 3) but is very homogeneous and can be quantitatively subtracted out. We measure the weight of Al in each capsule and the weights are sufficiently similar that the variation in weight has a minimal effect on the subtracted Sc component. Nevertheless for the obsidian measurements, the Sc impurity for each sample was calculated from the measured Al weight. Sb may be homogeneous in the Al foil but it is also a contaminant that can be introduced in our laboratory. Zn is very high in the Al and not homogeneous. This results in a much larger precision in the Zn determinations (about 0.6%) than would be expected from the sample counting statistics. Impurity levels in the Al encapsulating foils are calculated for all elements studied in this work and are subtracted from each sample.

Results

Three measurements were made on the same sample on three consecutive days to determine the precision attainable exclusive of any source variation or laboratory contamination (see Table 4). The coefficient of variation for the 6 best measured elements was 0.19%, the value expected from the counting, precision and geometry errors. If ratios are taken to one of the elements, then the geometry and precision errors (each of which behaves coherently for all of the 6 elements) should disappear. This is exactly what happened.

Five of the obsidian samples taken from two areas about 2 km apart had very nearly the same abundances (see Table 5). We call this the main Chivay group. The average coefficient of variation was 0.26%, larger than the 0.19% expected from the known errors (see Table 6a). This left $0.18 \pm .06\%$ from other causes. When ratios were taken to one of the element abundances, the coefficient of variation did not drop, but was 0.25% (see Table 6b). This suggests that there is an inhomogeneity in the source samples studied or contamination in the sample preparation procedures of $0.25 \pm .05\%$.

The sample Chivay 6 used for determining variations associated with counting the same sample has a larger concentration of most elements measured than the main Chivay group, by about 0.8%. But the Sb abundance is significantly smaller. Chivay-6 then either represents a different composition profile than the main group or there are much larger weight or efficiency losses than expected (see Table 7).

Sample Chivay-3 has much different abundances (over 1%) for several elements and has a different composition than the main group or Chivay-6.

The element abundances in the main Chivay source group were compared with the Titicaca Basin chemical group of artifacts measured in 1977. The abundances for the 8 well measured elements in both studies agreed within 1.1%, which is excellent agreement. The provenience of the artifacts was assigned to Chivay in the Burger et al. 1996 publication. The coefficients of variation of the old work are about 5 times larger than in the present study. This could be due to either a larger natural variation in the artifacts because they come from a more extended source area or better measurement techniques than before.

Plans

We plan to remeasure all the artifacts in the 1977 Titicaca Basin chemical group with the LWAICS and the new INAA methodology (the powders are still available). This may determine if the 0.3% precision can be maintained and if the larger spread in the old artifact data was due to natural or instrumental causes.

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	N.	-	~	•					Obsidian	weights used		101.21	99.54	101.33			105.64	97.26	106.03	102.16
	C. of V. (%)	0.4	0.8	0.0	0.0				Total	A (mg)		-0.24	-0.23	-0.00			.13	-2.34	.03	.22
	Number of elements	7	9	9	9	and	ts)			∇ (0-	0-	0-			0-	-2	0-	-1
	Number of samples	9	7	4 of each	∞	HUJ = The Hebrew University of Jerusalem NHM = Natural History Museum, London, England	measurement	Sealed Al capsules + obsidian	After irradiation & final	swabbing		$356.86 \pm .08$	$353.38 \pm .06$				$363.80 \pm .06$	$359.01 \pm .10$		$353.63 \pm .00$
IA.			ion	BMSP		versity (Museum	olicate les.	l capsul	Afte			356.8	353.3	Tare			363.8	359.0	Tare	353.6
nts by INA	Material name	ARHCO-1	From Yale Collection	Podmore Red, E4 and BMSP	NNZD-C	Hebrew Uni ral History I	g from trip r Al capsu	Sealed A		$\Delta (mg)$		-0.03	-0.02	-0.00			-0.11	-0.57	-0.03	-0.37
easureme	Ma	A	From	Podmore I		HUJ = The NHM = Natu	ons (in m _g s and theii		swabbing ation			±.03	±.01	±.01			±.03	±.03	±.03	± .00
st precision m	of material	ver Basalt	tumba, Mex.	andards	Venenzi Dag, lia		square deviati source sample		Before initial swabbing & irradiation		al. 1996)	$357.07 \pm .03$	$353.59 \pm .01$	358.30 ± .01	(966)	.($363.82 \pm .03$	$361.42 \pm .03$	$367.43 \pm .03$	$354.85 \pm .00$
Table 1. Previous best precision measurements by INAA	Type of m	Columbia River Basalt	Obsidian from Otumba, Mex	3 pottery standards	Obsidian from Nenenzi Dag, Anatolia	onal Lal	ights and root-mean-square deviations (in mg from triplic for Chivay obsidian source samples and their Al capsules		With obsidian powder			$357.10 \pm .01$	$353.61 \pm .02$	$358.30 \pm .02$	/av (Burger et al 1	vugust 15, 1995	$363.93 \pm .01$	$361.99 \pm .04$	$367.46 \pm .08$	355.22 ± .03
Table				1		erkeley l arch Rea	eights a for Ch	sules	With 6		st of Chi ade on N	35	35	35	t of Chiv	ade on A	3(3(36	35
	Reference	F. Asaro, 1976	Cobean et al. 1991	Williams and Wall, 1991	J. Yellin, 1995	Ernest Orlando Lawrence Berkeley National Laboratory University of Missouri Research Reactor	Table 2. Mean weights and root-mean-square deviations (in mg from triplicate measurements) for Chivay obsidian source samples and their Al capsules.	Al capsules	Empty		Samples from west of Cerro Ancachita, 6 km east of Chivay (Burger et Weight measurements before irradiation were made on May 9, 1995	255.65 ± .01	$253.84 \pm .01$	$256.97 \pm .03$	Samples from east of Cerro Ancachita 8 km east of Chivav (Burger et	Weight measurements before irradiation were made on August 15, 1995	$258.22 \pm .03$	$262.26 \pm .01$	$261.43 \pm .02$	$251.78 \pm .03$
	Facility	LBL	MURR	MHM	HUJ	LBL = MURR =			Sample number		Samples from west Weight measuremen	S16-104	S16-105	S16-106	Samples from east of	Weight measureme	S16-266	S16-267	S16-268	S16-269

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Isotope and/or element	Energy of gamma rays (keV) ^m	LWAICSL background	Means and R capsules (wit	Means and RMSD for 5 empty Al capsules (with assumed 100 mg Al weight) b	Means and RN capsules w	Means and RMSD for 5 empty Al capsules (with true Al weight) ^b
46	880.75	0.0017 + 0000	0,2070		0.0812	+ 0003
40Sc	C7.600	0.000 ± /100.0	0.2017	10700. I	0.0012	C000. H
233Pa (Th)	312.01	$0.0011 \pm .0001$	0.0061	± .0028	0.0024	± .0011
134 _{Cs}	795.87	$0.0044 \pm .0001$	0.0017	± .0022	0.0007	± .0009
59Fe (%)	1099.25	$0.0005 \pm .0000$	0.0012	± .0003	0.00045	± .00010
182 _{Ta}	67.75	$0.0002 \pm .0000$	0.0001	± .0003	0.0000	± .0001
141 _{Ce} e	145.44	$0.0040 \pm .0006$	0.011	± .010	0.004	± .004
181 _{Hf}	132.9-482.0	$0.0003 \pm .0000$	0.0026	± .0006	0.0010	± .00025
152 _{Eu}	344.3-778.9	$0.004 \pm .000$	0.0004	± .0004	0.00015	± .00014
⁸⁶ Rb	1076.69	$0.007 \pm .009$	0.10	± .14	0.038	± .055
60 _{C0}	1173.2-1332.5	$0.0362 \pm .0005$	0.014	± .006	0.0056	± .0023
65Zn	1115.52	$0.067 \pm .002$	3.5	÷.	1.38	± .23
124_{Sb}	1690.98	$0.0003 \pm .0002$	0.043	± .005	0.0167	± .0018
75Se (ppb)	136.0-264.7	$1.75 \pm .08$	6.1	± 2.2	2.4	± 1.6
f						255.7 ± 2.2
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	M.E.d	0.06 0.10 0.11 0.11 0.24 0.11 0.16	0.13 0.11 0.08 unting d, if	$\begin{array}{c} 0.10\\ 0.11\\ 0.24\end{array}$	0.11 0.16 0.14
	C.V.c	0.19 0.20 0.30 0.19 0.17	0.19 0.19 1 larger cou /e Sc 2metry, an	$\begin{array}{c} 0.05 \\ 0.24 \\ 0.16 \end{array}$	0.07 0.09 0.12
Date	Mean & RMSD ^b	 ± .0065 ± .051 ± .031 ± .0003 ± .0032 ± .073 	Averages (%)0.190.1Average uncertainty in efficiency (%)0.190.0Average uncertainty in geometry (%)0.190.0Average uncertainty in geometry (%)0.190.0Core fire in the table of an origination of all of the element abundances in the second and third runs to their respective Sc0.19abundances and multiply by the Sc abundance in the first run, 3.385 ppm, we should eliminate the uncertainties due to efficiency and geometry, and, if0.19Element abundances normalized to a 3.385 ppm Sc abundance0.116 average sample counting error.0.19	± .012 ± .025 ± .0008	± .0012 ± .040 Averages (%)
	Mean &	3.385 25.203 10.305 0.5105 1.691 43.772	Average in efficiency (%) in geometry (%) Overall uncertainty (%) ents of variation for the 6 second and third runs to t second and third runs to t inting error.	3.385 25.206 10.306 0.5106	1.691 43.777 Ave
	4-3-96 trements)	+ .003 + .038 + .025 + .0016 + .003	Deduction: Average coefficient of variation is consistent with expected uncertainties. (Coefficients of variation for errors are consistent with those errors.) If we take the ratio of all of the element abundances in the second and third abundances and multiply by the Sc abundance in the first run, 3.385 ppm, we should eliminate the uncertainties due our interpretation is correct, reduce the average coefficient of variation to the average sample counting error. Element abundances normalized to a 3.385 ppm Sc abundance		-
	4-1-96 4-2-96 4-3-96 Elements with sample counting errors of less than 0.3% (all are singles measurements)	3.391 25.244 10.338 0.5108 1.695 43.814	Average un Average un ted uncertainties. e element abunda pm, we should el n to the average s	3.385 25.199 10.320 0.5099	1.692 43.736
Date	4-2-96 aan 0.3% (all are s	+ .002 + .036 + .036 + .0014 + .003	stent with expect ratio of all of the irst run, 3.385 pl cient of variatior sc abundance		5
	4- fors of less than	3.378 25.146 10.299 0.5103 1.689 43.688	Deduction : Average coefficient of variation is consistent with expeerrors are consistent with those errors.) If we take the ratio of all of t abundances and multiply by the Sc abundance in the first run, 3.385 our interpretation is correct, reduce the average coefficient of variati Element abundances normalized to a 3.385 ppm Sc abundance	3.385 25.198 10.320 0.5114	03 1.692 70 43.779 22 5 5 7 5
	4-1-96 mple counting err	+ .002 + .036 + .0013 + .0013	e coefficient of v with those errors iply by the Sc ab correct, reduce th sorrect, reduce th	 ± .002 ± .036 ± .023 ± .0013 	± .003 ± .070
3	4- A-	$\begin{array}{c} 3.385\\ 25.220\\ 10.277\\ 0.5104\\ 1.690\\ 43.815\end{array}$	uction: Average s are consistent dances and mult nterpretation is c	3.385 25.220 10.277 0.5104	e 1.690 43.815
	Elen	Sc Th CS Fe(%) Ta Ce ^e	Ded error abun our ii Elerr	Sc Th Cs Fe(%)	Ta Ce ^e

Table 4. Comparison of abundances on three long runs on the same sample of obsidian, Chivay-6 (S16-268)^a.

Deduction: The average coefficient of variation is consistent with the expected errors due only to the statistics in counting gamma rays.

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					.007	.06	.03	.002	.005	.12		.027	.005	4.1	.015	9.	
		Chivay-7	S16-269		+1	+1	+1	+I	+I	+1		+I	+I	+I	+I	+1	
	ay	C	S		3.365	25.10	10.21	0.509	1.682	43.34		3.860	0.286	247.4	0.336	32.2	
	km East of Chiv	Chivay-5	S16-267		.004	: .05	: .03	.001	± .004	.09		± .020	± .003	± 3.9	± .010	+ 9.	
d	Collected from 8 km East of Chivay	Chiv	S16						1.678 ±			3.878	0.295	247.7	0.324	33.1	
dian source grou)	Chivay-4	S16-266		± .007	± .06	± .03	± .002	± .005	± .12		± .027			± .015		
Main Chivay obsidian source group		Chiv	S16	neasurements)	.003 3.378	25.21	10.26	0.507	1.688	43.59		3.882	0.297	250.6	0.329	31.9	
	ay	Chivay-2	S16-105	(all are singles r	± .003	± .03	± .02	± .002	± .003	± .05	0	± .014	± .002	± 3.5	± .006	9. +	. 017
	km East of Chiva	Chi	S16	of less than 0.3%	3.373	25.11	10.27	0.507	1.681	43.57	greater than 0.3%	3.873	0.290	248.3	0.320	31.7	
	Collected from 6 km East of Chivay	Chivay-1	S16-104	Elements with sample counting errors of less than 0.3% (all are	± .003	± .03	± .02	± .001	± .003	±.07	Elements with sample counting errors greater than 0.3%	± .017	± .002	± 3.7	± .007	9: +	. 010
)	Chiv	S16	ints with sample	3.378	25.12	10.26	0.509	1.677	43.76	ants with sample	3.934	0.294	249.3	0.333	32.4	
		Ele-	ment	Eleme	Sc	Th	Cs	Fe(%)	Ta	Cee	Eleme	Hff	Euf	Rb	Cof	Zn	5

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	Table 5. Eleme

Deduction: Taking ratios did not improve the agreement. So there is an average variation in abundance of $0.25 \pm .05\%$ which is due either to inhomogeneity of the source for the elements studied or contamination in the sample preparation procedures.

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tent Main Group Main Group Chivay-6 Chivay-6 (5 samples) Mean & (RMSD ^b or M.E. d)h (3 counts) Mean & (3 counts) Mean	(Chivay-6 - Main Group) Main Group (%) ⁱ Main Group (%) ⁱ 0.71 $\pm .19$ 0.68 $\pm .13$ 0.88 $\pm .22$ 0.79 $\pm .21$ 0.74 $\pm .17$ 0.74 $\pm .19$	-6 - hup) / lp (%) ^j .19 .13 .22 .21 .17 .17 .19	Chiv S16 3.349 25.14 10.07 0.528 1.657	Chivay-3 S16-106 ± .003 ± .003 ± .003 ± .002 + .002	Main Gro Gro -0.39	(Chivay-3 - Main Group) / Main Group (%) ¹	
W + + + + + + +	Main Gro 0.71 ± 0.68 ± 0.88 ± 0.79 ± 0.79 ± 0.74 ±	-(%) qL 	510- 3.349 25.14 10.07 0.528 1.657			ıp (%)'	
+1 +1 +1 +1 +1 +1			3.349 25.14 10.07 0.528 1.657		-0.39		
.011 3.385 \pm .03 25.20 \pm .03 10.30 \pm .002 0.510 \pm .005 1.691 \pm .15 43.77 \pm			3.349 25.14 10.07 0.528 1.657		-0.39		
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.002 0.510 \pm .005 1.691 \pm .15 43.77 \pm			0.528 1.657		-0.29	± .31	
.005 1.691 ± .15 43.77 ±			1.657		4.35		
.15 43.77 ±					-1.19	± .26	
Best valu			43.54	± .10	0.32	± .26	
	ue						
	$0.78 \pm$.07 %					
Elements with sample counting errors greater than 0.5%							
$\pm .031$ 3.881 $\pm .025$	0.3 ±	5.	4.025	± .031	4.0	+ 6.	
0.295 ±	1.7 ±	6.	0.300	± .005	3.4	± 1.9	
± 1.7 248.4 ± 2.1	0.5 ±	.6	244.2	± 3.9	-1.2	± 1.7	
$\pm .013$ 0.326 $\pm .005$	± 0.0-	2.0	0.382	± .010	16.1	± 3.5	
32.9 ±	1.9 ±	1.8 j	32.5	+ 9. +	0.6	± 2.0	
$\pm .029$ 0.860 $\pm .023$	-5.5 ±		0.920	± .033	1.1	± 3.8	

Deductions:

are consistent with this value (as well as no enhancement) except for the abundance of Sb, which appears to be lower than that of the main Chivay group. The best measured elements in Chivay-6 are enhanced in abundance by 0.8% relative to the main Chivay group. Abundances of all of the other elements Either Chivay-6 represents a distinctly different composition or else there is an unexpected weight or efficiency error. The latter explanations necessitate a three sigma error in the measurement of the ratio of Sb in Chivay-6 to the main Chivay group or else Sb contamination of all of the samples in the latter.

Chivay-3 has a different composition pattern than any of the other 6 Chivay samples.