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

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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 2.5×10^{13} neutrons per second per cm^2 . 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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Table 1. Previous best precision measurements by INAA.

Facility	Reference	Type of material	Material name	Number of samples	Number of elements	C. of V. (%)
LBL	F. Asaro, 1976	Columbia River Basalt	ARHCO-1	6	7	0.4
MURR	Cobean et al. 1991	Obsidian from Otumba, Mex.	From Yale Collection	7	6	0.8
NHM	Williams and Wall, 1991	3 pottery standards	Podmore Red, E4 and BMSP	4 of each	6	0.9
HUJ	J. Yellin, 1995	Obsidian from Nenezi Dag, Anatolia	NNZD-C	8	6	0.9

LBL = Ernest Orlando Lawrence Berkeley National Laboratory

MURR = University of Missouri Research Reactor

HUJ = The Hebrew University of Jerusalem

NHM = Natural History Museum, London, England

Table 2. Mean weights and root-mean-square deviations (in mg from triplicate measurements) for Chivay obsidian source samples and their Al capsules.

Sample number	Al capsules			Sealed Al capsules + obsidian		
	Empty	With obsidian powder	Before initial swabbing & irradiation	After irradiation & final swabbing	Total Δ (mg)	Obsidian weights used
Samples from west of Cerro Ancachita, 6 km east of Chivay (Burger et al. 1996)						
Weight measurements before irradiation were made on May 9, 1995						
S16-104	255.65 \pm .01	357.10 \pm .01	357.07 \pm .03	356.86 \pm .08	-0.24	101.21
S16-105	253.84 \pm .01	353.61 \pm .02	353.59 \pm .01	353.38 \pm .06	-0.23	99.54
S16-106	256.97 \pm .03	358.30 \pm .02	358.30 \pm .01	Tare	-0.00	101.33
Samples from east of Cerro Ancachita, 8 km east of Chivay (Burger et al. 1996).						
Weight measurements before irradiation were made on August 15, 1995						
S16-266	258.22 \pm .03	363.93 \pm .01	363.82 \pm .03	363.80 \pm .06	-0.13	105.64
S16-267	262.26 \pm .01	361.99 \pm .04	361.42 \pm .03	359.01 \pm .10	-2.34	97.26
S16-268	261.43 \pm .02	367.46 \pm .08	367.43 \pm .03	Tare	-0.03	106.03
S16-269	251.78 \pm .03	355.22 \pm .03	354.85 \pm .00	353.63 \pm .00	-1.22	102.16

Table 3. Effective background abundances from contamination in the LWAICS and the 99.9999%-pure Al^a

Isotope and/or element	Energy of gamma rays (keV) ^m	LWAICS ^L - background	Means and RMSD for 5 empty Al capsules (with assumed weight) ^b	Means and RMSD for 5 empty Al capsules (with true Al weight) ^b
⁴⁶ Sc	889.25	0.0017 ± .0000	0.2079 ± .0020	0.0812 ± .0003
²³³ Pa (Th)	312.01	0.0011 ± .0001	0.0061 ± .0028	0.0024 ± .0011
¹³⁴ Cs	795.87	0.0044 ± .0001	0.0017 ± .0022	0.0007 ± .0009
⁵⁹ Fe (%)	1099.25	0.0005 ± .0000	0.0012 ± .0003	0.00045 ± .00010
¹⁸² Ta	67.75	0.0002 ± .0000	0.0001 ± .0003	0.0000 ± .0001
¹⁴¹ Ce ^e	145.44	0.0040 ± .0006	0.011 ± .010	0.004 ± .004
¹⁸¹ Hf	132.9-482.0	0.0003 ± .0000	0.0026 ± .0006	0.0010 ± .00025
¹⁵² Eu	344.3-778.9	0.004 ± .000	0.0004 ± .0004	0.00015 ± .00014
⁸⁶ Rb	1076.69	0.007 ± .009	0.10 ± .14	0.038 ± .055
⁶⁰ Co	1173.2-1332.5	0.0362 ± .0005	0.014 ± .006	0.0056 ± .0023
⁶⁵ Zn	1115.52	0.067 ± .002	3.5 ± .6	1.38 ± .23
¹²⁴ Sb	1690.98	0.0003 ± .0002	0.043 ± .005	0.0167 ± .0018
⁷⁵ Se (ppb)	136.0-264.7	1.75 ± .08	6.1 ± 2.2	2.4 ± 1.6
True weight of Al (mg)			255.7 ± 2.2	

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

	Date						Mean & RMSD ^b	C.V. ^c	M.E. ^d
	4-1-96	4-2-96	4-3-96						
Elements with sample counting errors of less than 0.3% (all are singles measurements)									
Sc	3.385 ± .002	3.378 ± .002	3.391 ± .003	3.385 ± .0065	0.19	0.06			
Th	25.220 ± .036	25.146 ± .036	25.244 ± .038	25.203 ± .051	0.20	0.10			
Cs	10.277 ± .023	10.299 ± .024	10.338 ± .025	10.305 ± .031	0.30	0.11			
Fe(%)	0.5104 ± .0013	0.5103 ± .0014	0.5108 ± .0016	0.5105 ± .0003	0.06	0.24			
Ta	1.690 ± .003	1.689 ± .003	1.695 ± .003	1.691 ± .0032	0.19	0.11			
Cee	43.815 ± .070	43.688 ± .077	43.814 ± .085	43.772 ± .073	0.17	0.16			

Averages (%)
 Average uncertainty in efficiency (%) 0.19
 Average uncertainty in geometry (%) 0.11
 Overall uncertainty (%) 0.08

Deduction: Average coefficient of variation is consistent with expected uncertainties. (Coefficients of variation for the 6 elements with larger counting errors are consistent with those errors.) If we take the ratio of all of the element abundances in the second and third runs to their respective Sc abundances and multiply by the Sc abundance in the first run, 3.385 ppm, we should eliminate the uncertainties due to efficiency and geometry, and, if 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

Sc	3.385 ± .002	3.385	3.385	3.385	0.05	0.10
Th	25.220 ± .036	25.198	25.199	25.206 ± .012	0.24	0.11
Cs	10.277 ± .023	10.320	10.320	10.306 ± .025	0.16	0.24
Fe(%)	0.5104 ± .0013	0.5114	0.5099	0.5106 ± .0008	0.07	0.11
Ta	1.690 ± .003	1.692	1.692	1.691 ± .0012	0.09	0.16
Cee	43.815 ± .070	43.779	43.736	43.777 ± .040	0.12	0.14

Averages (%)

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

Table 5. Element abundances in samples of the main group from the Chivay obsidian source (Burger et al. 1996)^a.

Element	Main Chivay obsidian source group					
	Collected from 6 km East of Chivay		Collected from 8 km East of Chivay			
	Chivay-1 S16-104	Chivay-2 S16-105	Chivay-4 S16-266	Chivay-5 S16-267	Chivay-7 S16-269	
Elements with sample counting errors of less than 0.3% (all are singles measurements)						
Sc	3.378 ± .003	3.373 ± .003	3.378 ± .007	3.368 ± .004	3.365 ± .007	
Th	25.12 ± .03	25.11 ± .03	25.21 ± .06	25.16 ± .05	25.10 ± .06	
Cs	10.26 ± .02	10.27 ± .02	10.26 ± .03	10.29 ± .03	10.21 ± .03	
Fe(%)	0.509 ± .001	0.507 ± .002	0.507 ± .002	0.506 ± .001	0.509 ± .002	
Ta	1.677 ± .003	1.681 ± .003	1.688 ± .005	1.678 ± .004	1.682 ± .005	
Ce ^e	43.76 ± .07	43.57 ± .05	43.59 ± .12	43.78 ± .09	43.34 ± .12	
Elements with sample counting errors greater than 0.3%						
Hf ^f	3.934 ± .017	3.873 ± .014	3.882 ± .027	3.878 ± .020	3.860 ± .027	
Eu ^f	0.294 ± .002	0.290 ± .002	0.297 ± .005	0.295 ± .003	0.286 ± .005	
Rb	249.3 ± 3.7	248.3 ± 3.5	250.6 ± 3.8	247.7 ± 3.9	247.4 ± 4.1	
Co ^f	0.333 ± .007	0.320 ± .006	0.329 ± .015	0.324 ± .010	0.336 ± .015	
Zn	32.4 ± .6	31.7 ± .6	31.9 ± .6	33.1 ± .6	32.2 ± .6	
Sb	0.896 ± .018	0.953 ± .016	0.899 ± .029	0.900 ± .022	0.920 ± .030	

Table 6a. Comparison of coefficients of variation of main Chivay source with theoretical expectations^a.

Element	Mean & RMSD ^b for Chivay Main Group of 5	C. of V. (%) ^c	M. E. (%) ^d
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Elements with counting errors less than 0.3% (all are singles measurements)

Sc	3.372 ± .0059	0.18	0.06
Th	25.14 ± .045	0.18	0.10
Cs	10.26 ± .029	0.28	0.11
Fe(%)	0.508 ± .0013	0.26	0.23
Ta	1.681 ± .0043	0.26	0.12
Ce ^e	43.61 ± .18	0.41	0.14

Average (%)

Efficiency uncertainty(%)

Geometry uncertainty (%)

Overall expected uncertainty (%)

Source or laboratory problems (%)

0.26 ± .04

0.13

0.11

0.08

0.19

0.18 ± .06

Elements with counting errors greater than 0.3%

Hf ^f	3.885 ± .028	0.7	0.5
Eu ^f	0.292 ± .0044	1.5	1.1
Rb	248.7 ± 1.3	0.5	0.7
Co ^f	0.328 ± .0065	2.0	2.5
Zn	32.3 ± .54	1.7	1.8
Sb	0.914 ± .024	2.6	2.1

Average (%)

1.5 ± .2

1.5

Deduction: There is an average source inhomogeneity for the 6 best measured elements of $0.18 \pm 0.06\%$, or else there are unknown weight errors, efficiency or geometry measurement errors or laboratory contamination problems. Measurements of ratios should eliminate weight, efficiency and geometry concerns.

Table 6b. Coefficients of variation for the best measured elements of the main Chivay source after normalizing all abundances to the Chivay-1 Sc abundance of 3.378 ppm^a.

Element	Mean & RMSD ^b for Chivay Main Group	C. of V. (%) ^c	M. E. (%) ^d
Sc	3.378		
Th	25.182 ± .047	0.19	0.10
Cs	10.269 ± .036	0.30	0.11
Fe(%)	0.5085 ± .0014	0.28	0.23
Ta	1.684 ± .0046	0.27	0.12
Ce ^e	43.68 ± .16	0.37	0.14

Average (%)

0.28 ± .04

0.25 ± .05

Source inhomogeneity or lab contamination (%)

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.

Table 7. Deviation of element abundances of Chivay-6 and Chivay-3 from those of the main Chivay source group^a

Element	Main Group (5 samples) Mean & (RMSD ^b or M.E. ^d) ^h	Chivay-6 (3 counts) Mean & (RMSD ^b or M.E. ^d) ^h	(Chivay-6 - Main Group) / Main Group (%) ^j	Chivay-3 S16-106	(Chivay-3 - Main Group) / Main Group (%) ^j
Elements with sample counting errors of less than 0.5%					
Sc	3.361 ± .011	3.385 ± .007	0.71 ± .19	3.349 ± .003	-0.39 ± .11
Th	25.03 ± .03	25.20 ± .05	0.68 ± .13	25.14 ± .04	0.32 ± .17
Cs	10.21 ± .03	10.30 ± .03	0.88 ± .22	10.07 ± .03	-0.29 ± .31
Fe(%)	0.506 ± .002	0.510 ± .001	0.79 ± .21	0.528 ± .002	4.35 ± .44
Ta	1.675 ± .005	1.691 ± .003	0.96 ± .17	1.657 ± .004	-1.19 ± .26
Ce ^e	43.45 ± .15	43.77 ± .08	0.74 ± .19	43.54 ± .10	0.32 ± .26
Best value					
		0.78±	.07 %		

Elements with sample counting errors greater than 0.5%

Hf ^f	3.871 ± .031	3.881 ± .025	0.3 ± .5	4.025 ± .031	4.0 ± .9
Eu ^f	0.290 ± .003	0.295 ± .004	1.7 ± .9	0.300 ± .005	3.4 ± 1.9
Rb	247.1 ± 1.7	248.4 ± 2.1	0.5 ± .6	244.2 ± 3.9	-1.2 ± 1.7
Co ^f	0.329 ± .013	0.326 ± .005	-0.9 ± 2.0	0.382 ± .010	16.1 ± 3.5
Zn	32.3 ± .6	32.9 ± .5 ^j	1.9 ± 1.8 ^j	32.5 ± .6	0.6 ± 2.0
Sb	0.910 ± .029	0.860 ± .023	-5.5 ± 2.0	0.920 ± .033	1.1 ± 3.8
Best value			0.5		
			± .4 %		

Deductions:

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 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. 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.