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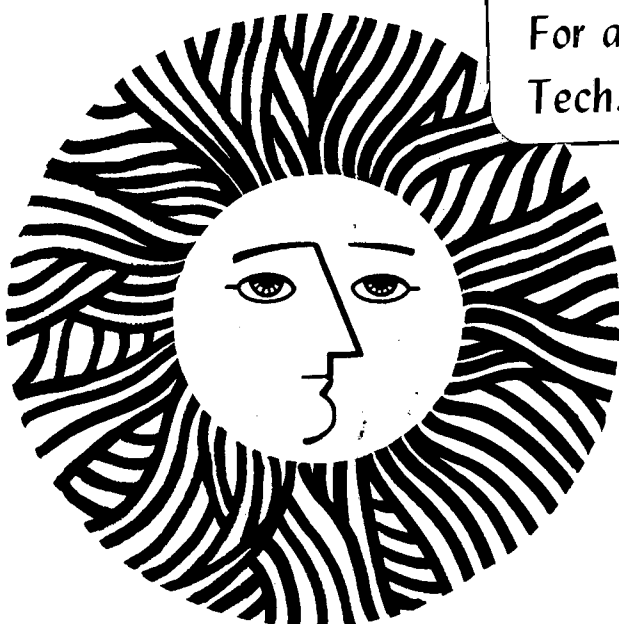## UNIVERSITY OF CALIFORNIA

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CHEMICAL SOURCE GROUPS IN ECUADORIAN OBSIDIAN

by

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Chemical Source Groups in Ecuadorian Obsidian

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ABSTRACT

Studies of 40 samples of Ecuadorian archaeological obsidian and primary and secondary obsidian sources were made by high-precision neutron activation analyses and by x-ray fluorescence measurements. The samples fall into 6 different chemical groups, and these groups can be distinguished by neutron activation analyses or relatively inexpensive measurements of Sr and Zr or Sr and Fe by x-ray fluorescence. One very prominent chemical group in the archaeological obsidian matches in composition obsidian from the Rodeo Corrales secondary source, and one artifact matches in composition the Mullumica source. The four other chemical groups have unknown proveniences. One sample was unusally low in both Sr and Ba, a composition pattern dif-

ferent from all the other samples and Peruvian obsidian. It

is possible the Mullumica obsidian source may be variable in

composition and may encompass some of the five other chemi-

cal groups.

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I. INTRODUCTION

The present study was undertaken in collaboration with personnel
from   the Museo del Banco Central del Ecuador to determine the chemical
composition patterns and origin of archaeological obsidian in Ecuador.
Archaeological obsidian from a given source is often chemically very
homogeneous. Since obsidian flows in different geographical areas have
distinctly different chemical abundance patterns, chemical measurements
can be very effective in determining the provenience of obsidian
artifacts.   These data are useful in the determination of trading pat-
terns.

Rarely obsidian deposits are very unhomogeneous e.g., obsidian from
the locality near Borax Lake in Central California in the United
States.[1,2] In that deposit chemical abundances of obsidian and dacite
(another type of volcanic rock) are all linearly related to each other.

Such geochemical relationships have been interpreted as due to differentiation of magmas or to mixing of two magmas prior to eruption. Because of the high degree of linearity over a large abundance range in the Borax Lake patterns, e.g., the cobalt abundance decreased by 70 while the iron increased by a factor of 7, the latter interpretation was favored.[1]

Neutron activation analysis (NAA) under carefully controlled conditions can measure elemental abundances with very high precision and accuracy.[3-6] Such studies can accurately define chemical groups of obsidian, determine if they are homogeneous and suggest the best elements for distinguishing between chemical groups. Then less expensive (although often less reliable) techniques may be used to determine the provenience of artifacts.

X-ray fluorescence (XRF) analysis is generally a complementary measurement technique to NAA in that different groups of elements are best measured by one or the other method. There are some elements measured in common, with similar precision, which may be used to check or cross-calibrate the two systems of measurement. XRF analyses can be made with precision and accuracy[7] but the process involves destruction of part of the sample. XRF measurements can also be made relatively inexpensively, without destroying the sample, but with poor precision and accuracy. A combination of the latter technique with high precision NAA has been used to obtain reasonably definitive assignments for large numbers of artifacts at a moderate cost.[8]

In this procedure, obsidian chemical groups are defined by NAA of samples from likely sources or artifacts. Alternatively artifacts may

be analyzed by XRF, divided into chemical groups and then representative members of each group can then be analyzed by NAA. From these studies, the different chemical groups are defined and the homogeneity of each chemical group (or source) is determined as are the best elements for distinguishing between these groups. Those distinguishing elements which can be measured by inexpensive XRF analysis (usually Ba, Rb, Sr, or Zr) are then used to determine the provenience of large arrays of artifacts. Generally there will be uncertainities for about 15% of the artifacts. These are then measured by an abbreviated NAA sequence, i.e., one neutron irradiation instead of two, one gamma-ray analysis of the neutron-irradiated sample instead of five, and five elements measured instead of 20 or 30. Normally about 15% of the artifiacts measured in this way (about 2% of the total) have further uncertainties, and the NAA sequence is completed for those samples. These latter measurements usually define new chemical groups or sources.

The above methods were used in a study of over 840 Andean obsidian artifacts from Peru.[8] Ninety-eight percent of the artifacts fell into eight chemical groups. The principal group was directly correlated with a specific source, Quispisisa, while the others were correlated with general areas.

In a previous study [9] of 43 obsidian artifacts from the archaeological sites of Guangala, El Inga and Chobchi Cave in Ecuador by similar techniques, two major chemical groups were identified which contained 40 artifacts. The two chemical groups, which will be later correlated with the present work, could not be assigned a provenience.

II. SAMPLE LOCATIONS

In the present work 40 samples were obtained from the six locations in Ecuador shown in Table I. Mullumica is a primary source of obsidian in the high Andes.[10] Rodeo Corrales is a secondary source of obsidian not to distant from Mullumica (∿10 km in a direct line), but it is in a different drainage system. The other four areas sampled are archaeological sites. Five samples were obtained from three different archaeological levels in Cotocollao, and five samples each from Mullumica, Quito, La Chimba, Rodeo Corrales and La Tolita island. The samples from La Tolita (from the northwest frontier) were all from one block of obsidian which had been quarried at an unknown source.

III. SAMPLE PREPARATION

Parts of each obsidian sample are broken off of the main. rock and then ground with an agate mortar and pestle. The agate (in contrast to porcelain) does not.contribute impurities which are detectable by the measurements used in this work. One hundred mg of powder is mixed with 50 mg of cellulose and compressed into a pill 1.00 cm in diameter at a pressure of 25,000 pounds per square inch in a tool-steel die. The pills are each heat-sealed in .0025 cm polyethylene film. The thickness of each encapsulated pill is measured and is usually about .11 cm. These pills are then used in the XRF measurements and can also be used subsequently for NAA measurements.

IV. MEASUREMENTS

A. X-ray fluorescence

In the XRF procedures used in this work, a beam of x-rays or gamma rays is directed upon the encapsulated pill. The various elements in the sample, whose atomic electrons are bound with energies below the energy of the excitation beam, will fluoresce with x-rays characteristic of each of those elements. For a number of these elements a fraction of the fluorescence is measured with a silicon solid state detector. Also measured are Compton gamma-rays scattered from the sample, and their intensity is roughly proportional to the mass of the sample. The output of the silicon detector consists of small electronic pulses proportional to the energies of the emitted fluorescence. These pulses are amplified and fed into a pulse-height analyzer which can distinguish and separate the x-rays of different elements. The output of the latter instrument is stored on a magnetic tape which is later processed by computer.

The counts in each fluorescence peak of interest are summed, a background is subtracted, interferences are removed and the net counts are divided by the sum of the Compton-scattered radiation. Comparison of this ratio for a given element with the ratio for the same element in a standard of known composition, leads to the abundance of that element in the artifact.

Two XRF analyses were made on each of the 40 samples. The samples were placed in a 48-position automatic sample changer and analyzed first with 60 kev gamma-rays from ^{241}Am (for Ba) and then with Ag x-rays from ^{109}Cd (for Rb, Sr, Zr, and Fe). One position in the sample changer was

used for the standard, STANDARD POTTERY, and one position was used for a background for the Compton radiation. The abundances in the standard for Ba, Fe, Rb and Sr have been published,[4] and the abundances used for Zr (252 ppm) was subsequently measured by XRF.[11]

The abundances of Rb, Sr, Zr, Fe, and Ba are shown in Table 2. The samples have been divided into six groups determined by similarity in chemical composition. The names of the groups are arbitrary, except for the Mullumica source. The typical experimental precision is shown for the Ecuador B chemical group. The root-mean-square deviation (RMSD) for Rb is considerably smaller than the precision partly by statistical coincidence and partly because most of the latter uncertainty is due to the uncertainty in the measurement of the Standard, which has only 70 ppb Rb.

One sample from Quito, Ecua-27, was similar to the Ecuador B group in composition but deviated somewhat in Sr, Zr and Fe. It was therefore not assigned by XRF but was later assigned by NAA. One sample from La Chimba, Ecua-16, was of a completely different composition from any of the other samples and was not assigned.

B. Neutron Activation Analyses

The systems of high precision neutron activation analyses initially used at the Lawrence Berkeley Laboratory have been previously described.[3] Typically about 50 elements are searched for, 40 are usually detected in materials similar in composition to the earth's crust, ∿30 are detected with good precision (somewhat less with obsidian) and ∿20 are useful for provenience determination. The present system is

described in the Appendix.

In the present work, two representative samples were selected for NAA measurement from the Ecuador A, Ecuador B, La Chimba and Mullumica groups and one such sample from the Cotocollao A and Cotocollao B groups. In addition the two samples which could not be assigned were selected for further measurement as was the Quito sample assigned to the Mullumica source. The deviation of the Quito sample from the Mullumica average was somewhat greater than that of the Mullumica samples so a confirmation was desirable. The pills previously prepared for XRF measurements were irradiated for 18 minutes at a flux of 3×10^{11} neutrons per cm^2-sec, along with two standards of ARHCO-1, a tertiary standard calibrated at the Lawrence Berkeley Laboratory, against the secondary standard, STANDARD POTTERY. One gamma-ray count of 6.0 minutes was made on each sample and standard starting about one hour after irradiation. The resulting data for Mn, Na, Dy, K and Ba for the fourteen samples are shown in Table 3. Dual measurements of representative samples agreed very closely with each other relative to the errors of measurement. As a result of these measurements the Quito sample Ecua-27 was definitely assigned to the group Ecuador B, and the assignment of the Quito sample Ecua-30 to Mullumica was confirmed. Nearly all six chemical groups can be distinguished by this abbreviated NAA sequence, but Cotocollao A and Cotocollao B are very similar except for a small difference in the Mn abundance. The La Chimba sample, Ecua-16, was much different in composition from all of the other samples just as in the XRF measurements.

One sample from each of the six groups was selected for completion of the NAA sequence plus an additional sample from both Ecuador A and

Ecuador B, as well as Ecua-16, the unassigned sample. Some of these samples had been counted for 1 minute soon after the short irradiation, and that analysis provided the aluminum value. All nine samples were rewrapped in .0025 cm Al foil and irradiated for 8 hours at the full flux of the reactor, 2.7 x 10^{13} neutron/sec-cm^2. The samples were counted ∿8 days and ∿30 days after irradiation with a high resolution intrinsic (1cc) Ge gamma-ray detector and at ∿25 days with the same lower resolution (but more efficient) 7cc intrinsic Ge detector used after the short irradiation. These abundance data are shown in Table 4. The data for the two samples of Ecuador A deviate on the average by 3.0% and the two samples of Ecuador B deviate by 3.6% if the element with poorest statistics, Co, is excluded. The difference of 10% for the Fe abundances in Ecuador B is rather large considering the precision of the Fe measurement, and possible reasons are discussed subsequently.

V. DISCUSSION AND CONCLUSIONS

Of thirty samples from archaeological sites, ten had a distinct chemical composition which is (arbitrarily) called Ecuador A, twelve had a distinct composition which is called Ecuador B, one matched the Mullumica source, four had a distinct composition which is called Cotocollao A, three had a distinct composition called Cotocollao B, and one sample had a different composition from all of the others. None of these six groups or the unassigned sample match any of the Peruvian obsidian groups.[8] Ecuador A contains the Rodeo Corrales secondary source, but whether the other samples in this group originate from Rodeo Corrales or the unknown primary source is not yet known. The two main groups, Ecuador A and B, agree in composition with the two main groups

found in an earlier study of Ecuadorian obsidian from El Inga, Chobchi Cave and Guangala.[9]

All of the six groups can be distinguished by XRF. Sr and Zr or Sr and Fe appear to be the most useful elements in this regard. The abbreviated sequence of NAA distinguishes most of the six groups, but does not appear to be as effective as the XRF measurements used in this work. The complete sequence of NAA is very effective and definitive in distinguishing these groups. The agreement for some elements, however, is sufficiently poor, e.g., Fe in Ecuador B, as to suggest that one or more sources may not be homogeneous. To test this hypothesis the XRF data on Rb, Sr and Zr were plotted vs. Fe for all samples except those from La Chimba (Fig.1). As the precision of the XRF analyses for Fe was much better than the estimated accuracy (∿10%), the XRF data were cross-calibrated with the NAA data shown in Table 4. Increasing the XRF values by 7% made them consistent with the NAA values within ∿2%. All XRF Fe values shown in Fig. 1 have been increased by that amount, and a 2% uncertainity is indicated in the Fig. It is seen that the Cotocollao A group, the Cotocollao B group, Mullumica obsidian and a Quito artifact lie on families of straight lines. If this trend for all elements is valid it suggests that these groups are geochemically related. The Ecuador B group may also be part of the same geochemical relationship, although the Ecuador A group does not appear to be on the same curve for Rb. This effect for Ecuador A is more pronounced for the element Cs as seen in Table 4. Further study by high precision neutron activation analysis with many more elements could determine if the various groups are geochemically related.

VI. ACKNOWLEDGMENTS

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(11) R.D. Giauque, Lawrence Berkeley Laboratory, unpublished data.

TABLE 1

SAMPLE AND SITE CONCORDANCE

SITE OR SOURCE	ARCHAEOLOGICAL IDENTIFIER	SAMPLE NAME	XRF NAME	NAA NAMES	
				SHORT IRRADIATION	LONG IRRADIATION
Cotocollao –	PHD	Ecua-1	8077-D		
Archaeological	"	-2	-E		
site near Quito	"	-3	-F		
	"	-4	-G	1033-R	
	"	-5	-H	-J	1061-U
	B1	-6	-I	-F	
	"	-7	-J		
	"	-8	-K	-S	1061-O
	"	-9	-L		
	"	-10	-M		
	B6	-11	-N	-Q	1061-N
	"	-12	-O		
	"	-13	-P	-H	1065-Y
	"	-14	-Q		
	"	-15	-R		
La Chimba		-16	-S	-T	1061-P
(Late Formative		-17	-T	-K	1061-K
archaeological		-18	-U		
site on the west		-19	-V		
side of Mt. Cayambe		-20	-W	-M	
above Ibarra)					
Mullumica		-21	-X		
(Primary source)		-22	-Y	-P	
		-23	-Z		
		-24	-1		
		-25	-2	-N	1061-M
Quito	48B2	-26	-3		
(Integration	"	-27	-4	-G	1065-U
archaeological	"	-28	-5		
site)	"	-29	-6		
	"	-30	-7	-O	

TABLE 1 (continued)

SAMPLE AND SITE CONCORDANCE

SITE OR SOURCE	ARCHAEOLOGICAL IDENTIFIER	SAMPLE NAME	XRF NAME	NAA NAMES	
				SHORT IRRADIATION	LONG IRRADIATION
La Tolita Island		Ecua-31	8077-8	1033-E	1065-X
(Archaeological		-32	-9		
coastal site.		-33	-+		
All samples are		-34	--		
from one block of		-35	-*		
quarried obsidian					
of unknown origin)					
Rodeo Corrales		-36	-/		
(Secondary source)		-37	-(		
		-38	-$		
		-39	-●		
		-40	-[		

TABLE 2

X-RAY FLUORESCENCE MEASUREMENTS ON ECUADORIAN OBSIDIAN

(ACCURACY ~ 10%)

Samples found in	Sample Name	Abundances (Fe in %, others in ppm)				
		Rb	Sr	Zr	Fe(%)	Ba
Ecuador A chemical group (source unknown) 9 members						
Cotocollao PHD	Ecua-5**	170	84	72	.37	--
B-6	-13**	193	85	74	.39	--
"	-14	200	91	80	.36	899
Quito 48B2	-29	203	87	79	.39	894
Rodeo Corrales	-36	189	82	77	.36	914
	-37	187	86	73	.38	863
	-38	190	86	79	.35	864
	-40	187	88	76	.36	901
	-39	196	85	78	.37	924
	Mean	191	86.0	76.4	.37	894
	RMSD	10	2.6	2.9	.014	23
Ecuador B chemical group (source unknown) 12 members						
Cotocollao PHD	Ecua-1	157	143	110	.53	1036
"	-3	155	127	98	.50	1061
B1	-6**	155	138	98	.50	--
"	-7	165	140	104	.52	1081
"	-9	159	124	99	.50	1074
B6	-12	157	138	107	.50	1101
La Tolita	-31**	156	136	100	.50	--
	-32	166	136	101	.50	1065
	-33	156	134	96	.50	1089
	-34	150	129	98	.49	1087
	-35	167	136	97	.51	1068
Quito 48B2	-28	164	133	99	.50	1090
	Mean	158.9	134.5	100.6	.504	1075
	RMSD	5.3	5.5	4.3	.011	19
	Typical precision	12	4.3	3.0	.011	43
La Chimba chemical group (source unknown) 4 members						
La Chimba	Ecua-17**	158	159	95	.49	--
	-18	161	160	92	.48	1090
	-19	165	170	100	.47	1063
	-20**	176	178	94	.49	--
	Mean	165	167	95.2	.483	1076
	RMSD	8	9	3.4	.010	19
Mullumica source 6 members						
Mullumica	Ecua-21	146	252	185	.84	1123
	-22**	152	259	195	.83	--
	-23	146	249	184	.84	1141
	-24	139	237	171	.78	1090
	-25**	147	244	179	.73	--
Quito 48B2	-30**	142	278	197	.92	--
	Mean	145	253	183	.82	1118
	RMSD	6	14	10	.06	26
Cotocollao chemical group A (source unknown) 4 members						
Cotocollao PHD	Ecua-4**	167	174	121	.58	--
B6	-11	150	180	132	.61	--
"	-15	155	180	125	.58	1058
Quito	-26	154	162	123	.60	1106
	Mean	156	174	125	.59	
	RMSD	7	8	5	.015	
Cotocollao chemical group B (source unknown) 3 members						
Cotocollao PHD	Ecua-2	154	210	152	.70	--
B-1	-8**	149	200	147	.71	--
B-1	-10	150	220	154	.70	1052
	Mean	151	210	151	.70	
	RMSD	5	10	3.6	.011	
Other samples with no (Ecua-16) or poor (Ecua-27) chemical correlations by XRF measurements						
La Chimba	Ecua-16**	228	12	76	.60	170
Quito	-27**	159	111	90	.46	--

(Neutron activation analysis showed Ecua-27 was a member of the Ecuador B chemical group)

**Abbreviated neutron activation analyses were also made on these samples.

TABLE 3

ECUADORIAN OBSIDIAN OBTAINED IN MID 1978

ABBREVIATED NEUTRON ACTIVATION ANALYSIS ON REPRESENTATIVE

MEMBERS OF ECUADORIAN OBSIDIAN CHEMICAL GROUPS DETERMINED BY XRF**

| Samples found in	Pill Name	Mn	Na%	Dy	K%	Ba
Ecuador B chemical group (source unknown)						
La Tolita	Ecua-31	349+3	3.06+.03	1.53+.08	3.26+.26	1012+24
Cotocollao	-6	349+3	3.03+.03	1.60+.08	3.37+.26	1031+25
Quito	-27	344+3	2.97+.03	1.59+.08	3.70+.26	1031+26
	Mean	347	3.02	1.57	3.44	1025
	RMSD	3	.05	.08	.26	25
Ecuador A chemical group (source unknown)						
Cotocollao	Ecua-13	333+3	2.88±.03	1.27+.09	4.05+.27	853+26
	-5	335+3	2.73+.03	1.32+.09	4.06+.27	882+27
	Mean	334	2.80	1.30	4.06	868
	RMSD	3	.11	.09	.27	27
La Chimba chemical group (source unknown)						
	Ecua-17	327+3	3.03+.03	1.20+.09	3.59+.26	994+29
	-20	320+3	2.93+.03	1.22+.09	3.28+.25	1007+31
	Mean	324	2.98	1.21	3.44	1000
	RMSD	5	.07	.09	.26	30
Mullumica source						
Mullumica	Ecua-25	403+4	3.42+.03	1.67+.11	3.46+.26	1081+35
Quito	-30	432+4	3.50+.03	1.62+.11	3.03+.25	1114+37
Mullumica	-22	418+4	3.42+.03	1.57+.12	3.24+.25	1067+38
	Mean	418	3.45	1.62	3.24	1087
	RMSD	15	.05	.11	.25	37
Cotocollao chemical group A (source unknown)						
Cotocollao	Ecua-11	384+4	3.28+.03	1.59+.06	3.35+.16	1105+27
	-4	375+4	3.25+.03	1.56+.07	3.41+.17	1101+30
	Mean	380	3.26	1.58	3.38	1103
	RMSD	6	.03	.06	.16	28
Cotocollao chemical group B (source unknown)						
	Ecua-8	397+4	3.24+.03	1.54+.15	3.43+.25	1081+58
Uncorrelated sample						
La Chimba	Ecua-16	505+5	3.11+.03	3.73+.16	3.90+.26	93+58*

*The best Ba abundance is measured by XRF, 170+23ppm.

**Abundances are expressed in parts-per-million except for those of Na and K which are in percent. The indicated errors are estimated standard deviations. Mean is the average abundance of an element in a given chemical group or source, and RMSD is the larger of the average error or the root-mean-square deviation of the group.

TABLE 4

ELEMENT ABUNDANCES MEASURED BY NEUTRON ACTIVATION ANALYSES

OF REPRESENTATIVE MEMBERS OF ECUADORIAN OBSIDIAN CHEMICAL GROUPS

CHEMICAL GROUP:	Ecuador A		Ecuador B		La Chimba	Cotocollao A	Cotocollao B	Mullumica source	Uncorrelated sample
SITE:	COTOCOLLAO	COTOCOLLAO	LA TOLITO	QUITO	LA CHIMBA	COTOCOLLAO	COTOCOLLAO	MULLUMICA	LA CHIMBA
SAMPLE NAME:	ECUA-13	ECUA-5	ECUA-31	ECUA-27	ECUA-17	ECUA-11	ECUA-8	ECUA-25	ECUA-16
ELEMENTS									
% Al	6.67±.13	---	6.65±.11	6.35±.21	---	---	---	---	---
Ba	866±16	934±20	1056±19	1033±19	1101±22	1024±21	1088±22	1103±22	185±12
Ce	32.7±.5	32.2±.6	49.1±.6	47.2±.6	47.3±.7	52.0±.7	52.9±.7	54.7±.7	35.3±.6
Co	.18±.05	.17±.05	.36±.05	.31±.05	.43±.06	.54±.06	.73±.06	.70±.06	.07±.06
Cs	10.87±.14	10.84±.15	7.67±.11	8.01±.12	8.55±.13	6.78±.11	6.41±.11	5.99±.10	11.35±.17
Dy	1.27±.09	1.32±.09	1.48±.06	1.51±.06	1.20±.09	1.59±.06	1.54±.15	1.67±.11	3.73±.16
Eu	.284±.007	.302±.008	.413±.008	.400±.007	.426±.008	.482±.009	.511±.009	.548±.009	.097±.006
% Fe	.392±.007	.375±.007	.536±.008	.485±.008	.511±.08	.656±.009	.738±.010	.782±.010	.625±.009
Hf	2.53±.05	2.50±.05	2.97±.05	2.87±.05	2.83±.05	3.67±.06	3.93±.06	4.32±.07	3.52±.06
% K	4.05±.27	4.06±.27	3.50±.17	3.37±.16	3.59±.26	3.35±.16	3.43±.25	3.46±.26	3.90±.26
La	16.2±.7	17.3±.5	28.1±.9	26.0±.8	27.3±.5	28.8±.5	29.6±.5	30.8±.6	15.4±.4
Mn	333±3	335±3	349±3	344±3	327±3	384±4	397±4	403±4	505±5
% Na	2.88±.03	2.72±.03	3.08±.03	2.98±.03	3.03±.03	3.28±.03	3.24±.03	3.42±.03	3.11±.03
Rb	185±7	175±6	156±6	158±8	146±5	135±5	135±5	132±5	203±7
Sb	1.79±.12	1.78±.13	1.58±.11	1.41±.11	1.58±.11	1.07±.09	1.00±.09	.79±.07	2.53±.16
Sc	1.365±.014	1.393±.014	1.530±.015	1.534±.015	1.499±.015	1.534±.015	1.571±.016	1.537±.015	2.494±.025
Sm	1.697±.018	1.753±.018	2.424±.024	2.382±.024	2.326±.023	2.456±.025	2.514±.025	2.548±.025	3.338±.033
Ta	1.134±.011	1.159±.012	.966±.010	.975±.010	.960±.010	.949±.009	.947±.009	.922±.009	1.321±.013
Th	20.71±.21	20.74±.21	20.00±.20	20.03±.20	20.23±.23	18.60±.19	18.21±.18	18.07±.18	18.08±.18
U	9.50±.10	9.73±.10	7.87±.09	8.05±.09	8.30±.08	7.09±.07	6.86±.05	6.70±.07	9.13±.09
Yb	.881±.020	.896±.022	.881±.020	.894±.020	.814±.020	.944±.021	.984±.022	1.003±.022	2.161±.030

Abundances are in parts-per-million except for Al, Fe, K and Na which are in percent.
Errors are the estimated (one sigma values) precisions of measurement.

Figure 1 - Chemical relationships between groups of Ecuadorian
obsidian defined by XRF measurements
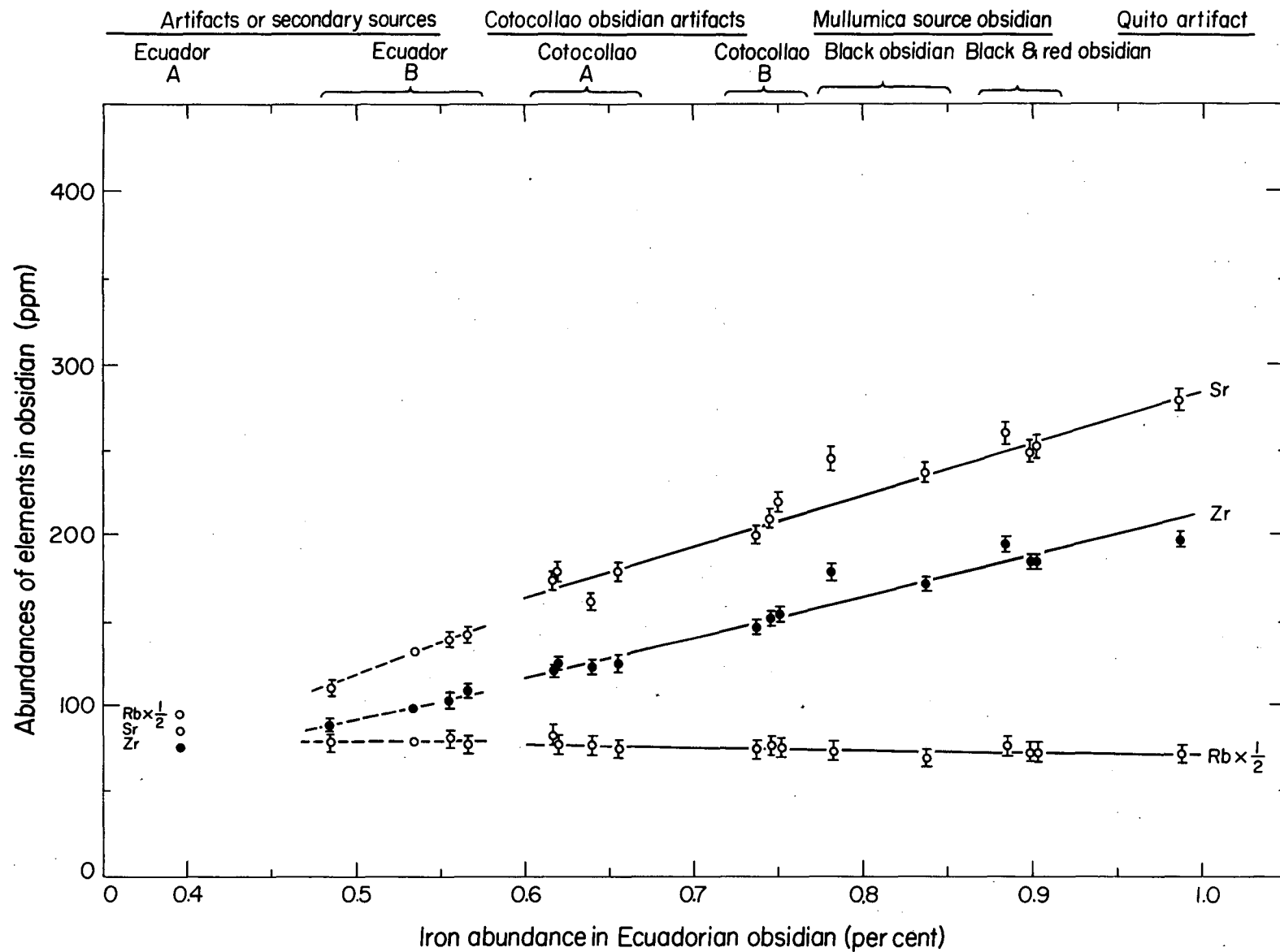
Fig. 1

APPENDIX

NEUTRON ACTIVATION ANALYSIS METHODS

A. Neutron Activation Analysis Quality Control

In the neutron activation analysis regime typically used at LBL, ~50 elements are searched for, ~40 are usually detected in materials similar in composition to the Earth's crust and about 30 are measured with precision. The precision of measurement (see Section C) is usually fairly-well represented by the statistics in counting the gamma rays of neutron irradiated samples. Other random errors have been held to relatively low values (probably less than 1 percent of the abundance of a given element) by intensive investigations of the cause of measurement error. Systematic errors have also been subjected to intensive investigations and most are now hopefully smaller than the counting errors (when the latter are 1 percent or larger). The major source of the remaining systematic uncertainty is in the abundances of Standard Pottery, the calibration standard. These uncertainties are given in Perlman and Asaro.[4] Standard Pottery is one of the very few standards in which the uncertainties are known for nearly all of the elements we measure.

B. Detailed Procedures

1. Sample Preparation

100 mgm of rock material from a cleaned fresh area is powdered and then mixed with 50 mgm of cellulose binder and compressed into a pill 1.00 cm in diameter and ~1.2 mm thick. Pill thickness is measured.

2. Short Irradiation--11 kW, 18 min, 3×10^{11} nsec/cm^2,

Berkeley Triga Reactor

a. Five unknowns per capsule (high density polyethylene capsule) and

2-100 mgm "Standard Pottery" standards (Mn, Na, Dy, Eu, Ba, Sr, As, Ga, K);

1-100 mgm CaCO$_3$ standard (Ca);

1-30 mgm KCl standard (Cl);

1-20 mgm Al foil standard (used to calibrate Mg originating from Al).

Samples placed in radial array in capsule which is rotated in reactor, insuring same flux-time irradiation of all samples.

2 capsules irradiated in morning (42 min apart) and 2 in afternoon (42 min apart).

b. (1) 1 min Υ-ray analysis on each unknown pill, starting ~8 min after end of irradiation. Then 2 min on Standard Pottery, 2 min on Al foil, 8 min on $CaCO_3$ and 2 min on KCl. 7 cc Ge detector, 2-3 keV under operating conditions (2048 channels).

Al and Ca are well determined, and Mg, V Cl, Br, and Ti are also measured in these runs. Ti can be better determined after the second neutron irradiation. V will be detected, but the precision is poor.

(2) 6 min Υ-ray analysis on each unknown pill from pair of irradiations starting ~60 min after the end of irradiation, followed by 25 min analysis of each of the two Standard Pottery pills. 7 cc Ge detector 1.5-2.5 keV under operating conditions (2048 channels).

Na (2 peaks, double determination), Mn, Dy well-determined and best determined in this analysis. K, Sr, Ga, and In will be poorly determined. As, Eu, Ba are measured in this analysis but are determined better in a later analysis.

3. **Long Irradiation--1 MW 8 hours, 2.7 x 10^{13} nsec/cm^2, Berkeley Triga Reactor**

   a. Twenty unknowns per capsule (high purity Al capsule) are arranged in radial array in two tiers of ten, each tier containing two "Standard Pottery" standards diametrically opposite. One $CaCO_3$ standard (for calibration of Ca contribution to ^{47}Sc peak used for Ti measurement) is in each capsule. Four capsules are in a train per irradiation (80 unknowns, plus 20 standards total); the capsule train is lowered into the reactor and rotated a number of times during the irradiation, insuring all samples in a given tier see the same neutron flux. Each tier in each capsule is separately calibrated for all elements except for the Ca contribution to the Ti measurements, which is calibrated for each capsule in the train. Because of special handling problems at the reactor, we are charged 9 hours for each 8-hour irradiation.

   b. (1) A 20 min γ-ray analysis is made on each sample (plus a blank for background check), starting 6 days after the end of irradiation. 1 cc Ge detector, 600 eV operating resolution at 103 keV. (8092 channels). U, Ba, As, Sm (2 peaks, double determination), Lu, La (2 peaks, double determination) are well-determined. Nd, Ho, W, Mo are also determined. Mo has a U fission contribution which must be removed, Au is bugged by contamination in the "high purity" Al foil used to wrap samples. Sb, Eu, Th, Yb are not determined as well as on a later NAA measurement. Br can be bugged by the irradiation or lost in heatings. Cd will be looked for and probably not usually detected.

(2) 60 min γ-ray analysis is made on each sample (plus a blank for background check) starting 3 weeks after end of long irradiation. 7 cc Ge detector, operating resolution = 1.9 keV (8096 channels) at 1.12 MeV. Co, Sc (doubly determined), Fe (doubly determined), Th, Cr, and Cs (doubly determined) are well determined--Sb, Rb, Tb, Sn, Ni are also determined as is Ir. Sn, Se, Hg, Ag, will be looked for and probably not usually detected. Ta, Ba, Ce, Hf are determined but are measured better on the next analysis.

(3) 80 min γ-ray analysis is made on each sample (plus a blank for background check) started right after previous run. 1 cc Ge detector, operating resolution 600 eV at 145 keV. Eu, Hf, Ta, Yb, and Ce are well-determined. Th, and Cr, are measured but are better determined on other runs. Nd is moderately determined, and Gd and Tm are determined very poorly.

(4) Five minute to 8000 minute runs are made on selected samples with a 128 cc Li-Ge gamma-ray detector system. Operating resolution is about 1.5 KeV at 468 KeV. These measurements are primarily to determine Ir. Gold and Pt are also determined in special cases. Better precision and sensitivity are obtained for Rb, Ni, Sr, Cs, Hf and Sb than on the other analyses.

C. Precision of Measurement

The precision of measurement in NAA can be determined by repeated measurements of the same material, and many errors can cancel out. Uncertainties due to interferences will be the same in different batches of material, if it is homogeneous, and those errors cancel. Errors concerned with the standards cancel, both those errors actually made during the measurement and those associated with the known composition of the standard. Some of the corrections concerned with counting rates of samples also cancel. In Table I of this Appendix are shown 7 elements whose counting errors were less than 0.5 percent in the neutron activation measurements on replicate samples from 3 splits of a Columbia River basalt. Sm, Sc and Fe have two radiations which were precisely measured. The average root-mean-square deviation (RMSD) for the 6 samples and 10 entries is 0.41 percent. Part of this is due to the counting statistics in the gamma-ray analysis and part is due to procedural uncertainties. The latter would include inhomogeneity in the parent material and residual errors of measurement. The counting errors are known and are shown in column 3. These can be removed from the RMSD by subtraction of the squares and then taking the square root. These values are shown in column 4 and average 0.27 percent.[5] This value includes the sample inhomogeneity and residual errors of measurement, and it can be considered as a precision limit for current techniques at LBL for certain purposes. An example of these is the chemical fingerprinting of materials for which reference samples have been measured in the same way. Systematic errors dependent on the LBL measurement

Table I. Random errors in LBL NAA regime.[6]

	RMSD (percent)	Standard Deviation of Counting Error (percent)	Procedural Uncertainty (percent)
Sm	0.23	0.14	0.18
	0.27	0.09	0.26
Sc	0.30	0.20	0.22
	0.26	0.20	0.17
Mn	0.33	0.29	0.16
Ce	0.51	0.33	0.39
Fe	0.58	0.43	0.39
	0.57	0.37	0.43
Eu	0.49	0.43	0.23
Ta	0.56	0.49	0.27
Average	0.41		0.27

technique are normally included in the precision to facilitate comparison with other laboratories and techniques.

D. Neutron Activation Systematic Errors

The listed errors at LBL reflect usually 1σ standard deviations of the counting error but do not contain a component (calibration uncertainty) due to the uncertainties in Standard Pottery. The measurements of major elements would have a smaller calibration uncertainty as they have been indirectly calibrated vs the standard rock BCR-1. We have not generally used standard rocks for indirect calibration of trace elements as their abundances may not be known as accurately as those of Standard Pottery.

When a gamma ray of one isotope has an interference from a gamma ray of another isotope there can be additional errors due to the uncertainty in the subtraction process. For example, there is a sizeable component of ^{239}Np radiation (from U) and a smaller component of ^{233}Pa radiation (from Th) which must be subtracted from one of the Sm gamma rays.

Before making these subtractions, a ^{187}W interference at 106.54 keV must be subtracted (for large W abundance) from the ^{239}Np radiation at 106.13 keV, and the double escape peak of the 1332.47 keV gamma ray of ^{60}Co at 310.47 keV must be subtracted from the ^{233}Pa radiation at 311.89 keV.

Another example is the element Cr which is measured with the 320.08 keV gamma ray of ^{51}Cr. ^{51}Cr can be made in neutron irradiations by the n,α reaction on Fe as well as by the usual n,γ reaction on Cr. In addition a 319.4 keV gamma ray of ^{147}Nd interferes with the measurement. A more subtle interference due to ^{182}Ta radiations also occurs. ^{182}Ta has gamma rays of 100.10 keV and 222.10 keV. These gamma rays can strike the Ge detector at nearly the same time and cause a peak equal to the sum of their energies, 322.20 keV, although there is no detectable ^{182}Ta gamma ray of that energy. A similar interference is caused by 6.71 day ^{177}Lu which has a 321.4 KeV gamma ray and a sum peak of the same energy.

The fission of ^{235}U (an isotope of ordinary uranium) during the reactor irradiation produces interferences in the measurement of ^{140}La, ^{99}Tc(Mo) ^{141}Ce and ^{147}Nd. ^{139}Ba radiation and one of the gamma rays used to measure ^{131}Ba also have interferences from fission.

About one-half of all of the elements measured have one or more interfering radiations. The extent of each of these interferences have been carefully calibrated and the uncertainties in the calibration have been checked in many (but not all) cases. Uncertainties of 10 percent are assumed as a calibration error for any interference subtraction until proven otherwise on samples of diverse composition. Such proof involves measurement of two different gamma rays relating to the same element or the same gamma ray on detector systems with different energy resolution (see Table III). Error investigations have proceeded until, for most elements, the square root of the sum of the squares of all of the known errors (excluding the uncertainties in the standard) is less than the larger of 1 percent or the usual counting error.

Because of uncertainties at the 1 percent level, minimum precision errors of 1 percent are normally used for very precisely measured elements (even though the counting errors are smaller). The preparation of sample pills with a tool-steel die, at ~25,000 lbs/in.^{2}, adds small impurities of Fe, Mn, Cr, W and Co. Although these are negligible for most samples, the die introduces an added uncertainty in the measurement of Mn gamma rays from the standard, which has only 40.9 ppm Mn. A 2 percent minimum error is used for Mn. Count rate corrections for some of the samples in spectra where Na is measured, are significant and have uncertainties associated with them. A minimum error of 2 percent is also used for Na. When a calibrated flux monitor (a gamma ray of another element besides that being considered) is used as a standard, minimum errors of 10-20 percent are assumed for the precision when such data are compared with anything other than results from the same irradiation.

E. Quality Assurance

The NAA regime is monitored continually for calibration shifts. These are held to a minimum by using a standard for nearly every element measured in every neutron irradiation. The conditions of irradiation of standards and unknown are as identical as we can make them as are the conditions for counting gamma rays. All samples are identical in diameter. The thickness

of each pill is measured and calibrated corrections (usually less than 1 percent) are made in the abundances. The pulse height analyzer operates on live time, but corrections due to sample counting rates are necessary and have been calibrated and incorporated into the computer calculations. As a check on any calibration shifts, archaeological obsidian (which tends to be rather homogeneous for many given sources) is measured periodically. Table II of this Appendix shows data from a sample (1070 Q) measured in 1979 and a reference group measured 5 years earlier. The shift in the 16 most precisely measured elements was less than 1.7 percent on the average. Between these times all gamma-ray detectors had been replaced.

The NAA regime is monitored continuously for short-term errors. In each of 5 separate gamma-ray counts made on each sample, two gamma rays or radiations which give abundances for the same element are compared in each count. Examples of such comparisons are shown in Table III of this Appendix. In addition, the different gamma-ray counts are cross-compared to be sure there are no systematic errors (such as a sample improperly positioned by the automatic sample changer). The cross-comparisons are also shown in Table III.

Cross-comparisons with other laboratories and techniques are frequently made as another way of assuring the quality of measurement.[5] Comparison of high precision trace element measurements with another NAA facility (6) indicate our 1 percent minimum error is reasonably conserviative.

Table II. Evaluation of long term NAA technique variations. Monitor:
Obsidian from Ixtepeque volcano in Guatemala.

Sample	1070 Q	Reference Group
Year of Analysis	1979	1974
Al percent	7.21 ± 0.16	7.26 ± 0.17
Ba	1051 ± 26	1013 ± 31
Ce	44.2 ± 0.6	42.8 ± 0.5
Co	1.12 ± 0.07	1.01 ± 0.07
Cs	2.61 ± 0.07	2.78 ± 0.08
Dy	2.55 ± 0.09	2.32 ± 0.07
Eu	0.557 ± 0.010	0.551 ± 0.005
Fe percent	0.920 ± 0.012	0.942 ± 0.021
Hf	4.51 ± 0.07	4.502 ± 0.055
K percent	3.53 ± 0.24	3.63 ± 0.17
La	23.1 ± 0.5	23.3 ± 0.6
Lu	0.262 ± 0.016	0.288 ± 0.010
Mn	440 ± 3	446 ± 4
Na percent	3.054 ± 0.015	3.013 ± 0.026
Nd	17.1 ± 0.6	15.7 ± 1.2
Rb	101 ± 4	110 ± 6
Sb	0.219 ± 0.043	0.209 ± 0.036
Sc	2.074 ± 0.013	2.116 ± 0.027
Sm	2.633 ± 0.010	2.669 ± 0.019
Ta	0.759 ± 0.005	0.755 ± 0.015
Th	7.18 ± 0.05	7.19 ± 0.07
U	2.240 ± 0.030	2.286 ± 0.029
Yb	1.794 ± 0.026	1.816 ± 0.024

Table III. Evaluation of sediment sample 9a for short-term NAA problems.

Code Name for Specific γ-Ray Counting Arrangement	γ Ray or X Ray Measured	Element Symbol	Abundance (ppm or %)
Ideck-8	103 keV	Sm	1.261 ± 0.008
8	Eu Kα$_{1,2}$		1.254 ± 0.005
12	1120	Sc	6.742 ± 0.035
12	889		6.758 ± 0.033
12	1292	Fe	1.591 ± 0.027
12	1099		1.625 ± 0.025
12	796	Cs	0.48 ± 0.11
12	605		0.52 ± 0.13
5	1369	Na	0.736 ± 0.007
5	1732		0.733 ± 0.009
4	1369		0.692 ± 0.029
4	1732		0.704 ± 0.032
5	167	Ba(^{139}Ba)	172 ± 17
8	124	(^{131}Ba)	184 ± 10
8	312	Th(^{233}Pa)	1.64 ± 0.23
12	312		1.360 ± 0.033
9	312		1.59 ± 0.13
9	U Kα$_2$		1.38 ± 0.05
12	145	Ce	9.75 ± 0.15
9	145		9.67 ± 0.43

Notes to Table III.

The errors are 1 sigma values of the counting errors from both sample 9a and the calibration standard, STANDARD POTTERY.

Code names for ray counts and descriptions:

Ideck 4 - 7 cc intrinsic Ge detector, 1.00 minute γ-ray count started 0.011 days after an 18 min. irradiation in the central thimble of the Berkeley Triga Research Reactor operating at 11 kilowatts of power.

Ideck 5 - This is a 6.00 min. run started 0.064 days after the 18 minute irradiation. The other conditions are the same as for Ideck 4.

Ideck 8 - 1 cc intrinsic Ge detector, 20.00 minute γ-ray count started 6.94 days after an 8 hr irradiation in the central thimble of the Berkeley Triga Research Reactor operating at 1 megawatt of power.

Notes to Table III (Continued).

Ideck 12 - 7 cc intrinsic Ge detector, 60.00 minute γ-ray count started 21.32 days after the 8 hr irradiation. The other irradiation conditions are the same as for Ideck 8.

Ideck 9 - 1 cc intrinsic Ge detector, 80.00 minute γ-ray count started 28.24 days after the 8 hr irradiation. The other conditions are the same as for Ideck 8.