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1972-04-01

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ON THE UNIFORMITY OF COMPOSITION IN OBSIDIANS AND EVIDENCE FOR MAGMATIC MIXING *

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April 1972

ABSTRACT

Neutron activation measurements on several Northern California obsidian sources show chemical compositions that range from extremely homogeneous to extremely variable. The uniformity of a source in Napa County, California was as good as the precision of the measurements even when measuring errors were less than 1%.

In contrast, the flow at Borax Lake (Lake County, California) revealed variable composition of the obsidian. However, the elements showed a dramatic linear coherence which also extended through the compositions of an underlying dacite layer. The faithful relationship of the many elements suggests that magmatic mixing occurred prior to eruption.

INTRODUCTION

The original intent of this work was to make detailed elemental analysis of obsidians from three sites in Northern California, with emphasis on trace elements, to determine the degree of uniformity within each flow (or source) and to test the distinctiveness of each with respect to the others. Aside from geological implications, the establishment of a chemical "fingerprint" is of importance to the archaeologist as it serves to locate the source material employed in fashioning ancient obsidian artifacts (Cann and Renfrew, 1964).

Although the initial study was largely exploratory and aimed at archaeological applications, it was hoped that it would lay a foundation for using accurate trace element data in the study of geochemical processes pertaining to volcanism. The preliminary measurements on obsidians have since been supplemented with the analysis of other volcanic rock types from one of the areas where the obsidian was found to be quite variable in composition.

The method employed for the present study was neutron activation analysis which now has the capacity of determining many trace elements with high accuracy and without the tedium of chemical separations. Tests were made for some forty elements but the accuracies attainable vary considerably and for some of these elements the results are of little use. For a number of elements, however, the precision of measurement was 1% or less. The value of obtaining highly precise analytical information rests in those cases in which the geochemical processes result in extremely uniform materials or where variations occur in which the elements behave with a high degree of coherence. It will be seen that obsidian from a flow in Napa County showed a dispersion in composition for 19 samples of only about 1% for those elements which could

be measured with that precision. Another source (Borax Lake in Lake County) put the method to a quite different test, since the elemental compositions varied considerably. They were found, however, to be linearly related to each other, again within the precision of measurement. Furthermore, the linear relationships extended smoothly into a series of rocks classed as dacites.

The results of this work are presented in two parts. The first deals with two sites, one of which proved to have obsidian of extreme uniformity and the other which showed slight variation in composition. The second part pertains to the third site in which the obsidian showed considerable variation.

SOURCES OF MATERIALS

The three obsidian sources sampled were all from a region northeast of San Francisco Bay. The majority of the samples were taken from highway-cuts or exposed banks and were usually found associated with what appeared to be tuff. Usually 4 or 5 specimens were taken from a single locus of about 10 meters radius, and then similar samplings were made at greater distances. Large blocks of obsidian were broken open and smaller center chips were taken as samples.

1. Napa obsidian: Nineteen samples were examined from 4 loci referred to locally as Glass Mt., near St. Helena in Napa County, California. Osmont (1904) attributed this flow to the Pliocene period. Jack and Carmichael (1969) describe this material as obsidian pebbles in an ash cone and suggest that this is the eruptive center in Napa County.

2. Mt. Konocti obsidian: Thirty-nine samples were examined from 8 loci south of Mt. Konocti in Lake County along Bottle Rock Rd., Lower Lake Road and Highway 175. Obsidian from Mt. Konocti is quite extensive and could be sampled readily for several miles. Anderson (1936) estimated that these rhyolitic obsidian flows covered an area of 12 sq. miles with no central vent indicated, and suggested that these lavas were erupted either from fissures or from scattered vents.

3. Borax Lake samples: Thirty-three obsidian and 10 dacite samples were taken from this source, which consists of a small flow (less than 1 sq. mile) located south of Borax Lake and just off the south east corner of Clear Lake. The Borax Lake and Mt. Konocti obsidian have been dated as Pleistocene and in part recent (Anderson, 1936).

These obsidian sources are undoubtedly of great interest to archaeologists because there is abundant evidence that artifacts were made in the area and it

is always possible that obsidian itself was an article of commerce. At Borax Lake, a habitation site was found which has unusual importance because it provides evidence that man existed there some 10,000 years ago (Meighan, 1970).

METHOD OF ANALYSIS

The system of analysis, with a detailed explanation of the accuracies attainable, has been described by Perlman and Asaro (1969). In brief, the elemental compositions were determined by comparing the intensities of gamma-ray peaks observed in the samples with those of a calibrated composite standard irradiated along with them. The precision of measurement for each element depends upon the intensity of the γ -ray peak used and the background intensity under the peak, and varies considerably from element to element. The absolute accuracy involves other factors including the accuracy to which the individual elements in the standard are known. With sufficient incentive a better composite standard could be formulated so the accuracies cited in this paper are not necessarily the best that can be obtained by this method. The composite standard used in these measurements was a fired pottery clay referred to hereafter as "standard pottery". A detailed description of the preparation and calibration of standard pottery has been given (Perlman and Asaro, 1969).

RESULTS (Part I)

Napa and Mt. Konocti

Before considering the results obtained, attention is called to Table Ia for an explanation of the format used in listing dispersions and measuring errors.

In the first four data columns, the analyses are grouped according to sampling locus. Each entry is the mean value and the standard deviation from the mean for that locus. Column [5] shows, for each element, the mean value and standard deviation for the combined 19 samples from the four loci. To the extent that the sampling was adequate, this column expresses the uniformity of the respective elements in this obsidian flow as discerned by our system of analysis. A cursory view of the data reveals that some elements, at least, must be extremely uniform. For example, the spread for the element thorium in the 19 samples is 0.13 ppm which is only 0.72% of the mean value. It will be recognized that this spread includes both the actual variation in thorium content and the precision of the method for this element. We shall first examine the precision of measurement.

In our system of analysis, each element has its counterpart in the standard pottery which is irradiated with the samples, and the respective gamma-ray intensities are compared. There is a dispersion introduced in such measurements due to the statistics of counting radioactivity, and this "counting error" includes the error in counting the standard as well as the sample. Thus, each element in each sample has an error, due to gamma-ray counting only, which limits the precision of the measurement. The magnitudes of these errors, expressed as average values for the samples in this group, are shown in Column [6].

A comparison of Column [6] with the standard deviations in Column [5] reveals the fact that for a few elements (e.g. Rb) the spread in values

is actually smaller than the counting error of a single measurement. This can arise where (1) the material is more uniform than the counting error, and (2) the counting error for a particular element in the standard is large compared with the counting error for that element in the samples. Those samples irradiated together with a single set of standards obviously will agree with each other according to their intrinsic uniformity and counting errors, no matter what the counting errors of the standards might be. When the counting errors due to the standard are removed from the Rb data in Column [6] the counting error due to the sample alone is rather small as shown in parentheses.

The elements are listed in Table Ia in descending order of precision of measurement: Th, Sm and U are measured to better than 1%; elements above La are better than 2%; and those above Yb are better than 5%. In viewing such data as an index of what can be done in analyzing other geological materials it is necessary to be aware of a singular feature of neutron activation analysis. It turns out that for many elements the absolute gamma-ray counting error is largely independent of the level at which it appears. For example, in these obsidians Cr is present at 7 ppm and the counting error is about 0.7 ppm, which gives a fairly large percent error ($\sim 10\%$). In another material, Cr might be present at 100 ppm level, and it might be found that the counting error has only gone up to 1.0 ppm (1%).

As well as one can tell from the samples taken, the Napa County Glass Mountain obsidian flow is extremely uniform. Indeed, the spread in composition in the 19 specimens is virtually indistinguishable from the precision of measurement given by the gamma-ray counting statistics.

It is important to point out that although the standard deviations listed in Column [5] of Table Ia reveal the uniformity of the respective elements, the absolute errors for the listed values of the respective elements can be greater.

The largest of these uncertainties has to do with subtraction of the background under each peak and is termed the "background error". The rock specimens have similar background profiles so the uncertainties in the absolute backgrounds appear to cancel, although for Ce and Yb there appears to be a residual effect. However, in calibrating the standard pottery, pure chemical compounds were employed and the backgrounds for the latter are usually negligible. This means that there is an absolute error for each element in the standard pottery introduced by the absolute uncertainty in estimating the background.

We have estimated these background errors for the various elements, combined them with other errors and listed them as "absolute errors" in Column [7], Table Ia. In order to make clear the usage of the various entries in Table Ia, a single example will be given: The uniformity of the thorium in the Napa County flow is expressed by 17.93 ± 0.13 ppm. The precision of a single measurement is 0.09 ppm, but the absolute error of a thorium value is estimated as 0.52 ppm. Since these absolute errors have proved to be larger than the dispersions encountered in this particular flow, it is necessary to use them in comparing the present results with those of other authors who have analyzed obsidian from these sources. Such comparisons are shown in Table Ib and Table Iib (Jack and Carmichael, 1969, Griffin et al., 1969, Stevenson et al., 1971, and Becker, 1888).

The Mt. Konocti flow, as shown in Table II, is also quite uniform but there appears to be a small systematic variation. (Stevenson et al., 1971, reported that this obsidian flow is uniform within their errors of measurement.) This flow was sampled in eight loci: 5 on Bottle Rock Road, 2 on Lower Lake Road and 1 on Highway 175. The 17 specimens from loci 1-4 (Bottle Rock Road) were quite homogeneous. Those from locus 5 (Bottle Rock Road, 5 specimens) were slightly

different, and the 15 specimens from the other 3 loci made up a group which was significantly different in certain elements. Comparing respectively the group of 17 with the group of 15 the spreads in composition are: for Fe, 0.97 ± 0.02 vs. $1.07 \pm 0.03\%$; for Mn, 184 ± 5 vs. 208 ± 5 ppm; for Co, 1.49 ± 0.11 vs. 1.81 ± 0.06 ppm; and for Cs, 15.3 ± 0.2 vs. 14.6 ± 0.2 ppm. For other elements, the effect is even smaller or undiscernable. For the 2 groups given above, counting errors in the standards could contribute only a small part to the differences.

DISCUSSION (Part I)

Napa and Mt. Konocti

A number of reports have referred to the uniformity in composition of an obsidian flow. The term "uniformity" must be assessed, of course, in terms of the precision of measurement and it is always possible that small undetected differences carry useful information. In the present study it is seen that in the Napa County flow the uniformity of each of the various elements follows closely the respective precision of measurement even when measuring error is very small. Three elements could be measured to <1% precision and these elements showed similarly small standard deviations for the 19 samples. These elements have nothing in common other than the sensitivity by which they can be measured so it's a reasonable supposition that the chemical homogeneity of this flow lies within a dispersion of about 1%.

As already stated, the Mt. Konocti obsidian divides into two closely-similar chemical groups, and these are related to the positions in the flow from which they came. The iron values are 10% higher in one group than the other, and Mn and Co differ in the same direction. For Co, the difference is about 20%. For the element Cs the difference is about 5%, and Cs is lower in the samples in which Fe, Mn, and Co are higher. A difference of only 5% is significant because the dispersion of Cs in each of these groups is only 1.3%.

The possible geological significance of such variations is examined in Part II of this report which is concerned with obsidian and dacite from Borax Lake where this effect was much enhanced.

The preceding discussion has been confined to the issue of chemical uniformity of the two flows, but potentially, the values themselves for the various elements should be of use in interpreting the geology. Unfortunately, there are not yet available comparable bodies of information on other materials

to test ideas on the distribution of these elements. Quite obviously, two rhyolitic obsidians will be similar in their major components and, in this example, even in many of the trace elements. Differences do appear, however, and perhaps point the way to more detailed views of geochemical processes. A few of our observations will be pointed out.

In Fig. 1 are displayed the relations between the rare earth elements from Napa County and Mt. Konocti expressed as ratios. The points represent the Konocti/Napa ratios obtained from the mean values of all samples taken from the respective sites. The "error limits" were computed from the standard deviations of the two groups. (It should be noted that the large standard deviations for some elements are attributable to the error of measurement and should not be interpreted as actual spreads in composition.) It is seen that there is systematic divergence of the rare earths with increasing atomic number from the virtually identical values for lanthanum. (The europium value is off the smooth curve, a phenomenon attributable to the fact that it can exist as a divalent ion unlike the other rare earth elements.) It is not profitable at present to speculate on the meaning of this trend other than to point out the obvious: The Napa County obsidian came from a magma whose earlier history caused it to be enriched somewhat in the heavier rare earths relative to that from Mt. Konocti. This diagram also compares the rare earth elements from 10 specimens of rhyolitic obsidian obtained from Borax Lake with those of Napa County. It seems difficult to explain such behavior by any single process of rare earth fractionations. More likely, the magma resulted from the admixture of two rocks, one of which was relatively depleted in the heavier rare earths and the other relatively enriched. Haskin and Frey (1966) show a curve for a metasomatized granitoid in which the heavy rare earths are much enriched.

Among the other trace elements, the high values for Cs are noteworthy. Both the Napa County and Mt. Konocti obsidians have 15 ppm as does that from Borax Lake mentioned above. Accurate values for Cs are rare in the existing literature but Gordon (1968) has found 3.5 ± 0.7 ppm in a rhyolitic obsidian from southeast Oregon, which shows that considerable variations exist. Two tetravalent ions, Th and Hf, are considerably different in their proportions between our two obsidians, and a number of other examples of distinct differences will be found.

The main point to be made in this brief discussion is that there is a vast diversity in chemical behavior represented in the trace elements and therefore, that their study might well have something to say about geochemical processes.

BORAX LAKE OBSIDIAN AND DACITE

As mentioned earlier, the Borax Lake flow lies just off the southeast border of Clear Lake in Lake County, California and is small in extent. It has been described by Anderson (1936) as a relatively thin layer of dacite (15-25 ft.) overlain by a thicker layer of obsidian (40-50 ft.). The dacite is exposed only at the southern extremity. There is much alluvial filling around the flow; as a result, most of the samples were obtained where cuts had been made for various reasons. The largest of these cuts is a gravel pit at the southern end of the flow. According to Anderson (1936), the two layers were apparently erupted from closely associated vents and the petrographic evidence indicated that a more basic differentiate may have been incorporated into both magmas prior to eruption.

The present results indicate that the dacite and rhyolitic obsidian were probably erupted from the same chamber and could be thought of as a single eruption of a lava of continuously variable chemical composition. In all, 33 samples of obsidian were analyzed and 10 of dacite. This study revealed a continuous gradation in composition in these materials, and there are borderline specimens for which the classification between obsidian and dacite is quite arbitrary. Some of the dacite samples had been collected by Anderson in his early study of this region and we wish to thank him for placing them at our disposal.

RESULTS AND DISCUSSION (Part II)
Borax Lake Obsidian and Dacite

The results of the analyses for the obsidians are shown in Table III where the 33 specimens have been divided into 10 groups, one of which has 10 members and several only 1 or 2. If one views all of the data it is apparent that some elements are virtually constant but most vary considerably. The division of the data into 10 groups was a device for grouping the samples according to iron content. The reason for this will be explained presently.

The data for the 10 dacite specimens are shown in Table IV and again they have been ordered according to iron content, in this case, in five groups. It will be noted that the composition of "dacite" of lowest Fe value virtually coincides with that of obsidian of highest Fe value, hence the earlier statement concerning an absence of a clear line of demarcation.

Figures 2-7 show graphs for 19 elements, each plotted against Fe content. The points represent all obsidian and dacite samples from the area. It is seen that all of the functional relations are linear, that the slopes vary considerably, and both positive and negative slopes are represented. The actual lines shown are least-squares fits to the data.

Visual examination of Figs. 2-7 reveals the close adherence of the data points of each element to the straight line obtained by least-squares fitting. In order to provide quantitative expression to the coherence of variations relative to iron, some numerical data are presented in Table V. The range of values encountered is listed for each element and the precision of a single measurement at each end of the range. In the last column, the scatter of all data points is expressed as the RMS deviation from the straight

line in ppm. Scandium is one of the elements measured with very high precision. and its relation to iron is shown in Fig. 2. The adherence to linearity is impressive and the RMS deviation from the straight line (0.11 ppm), seen in Table V, is comparable to what would be expected from the Fe and Sc counting errors.

In order to subject the data on scandium to a more rigorous test, it is possible to eliminate one of the sources of dispersion by examining a restricted part of the data. The 10 dacite samples were irradiated at one time with one set of standards; therefore any dispersion introduced by inhomogeneity of our standard material and by errors in measuring the standards, drop out. We are left simply with the statistics of gamma-ray counting in the dacite samples themselves, and a number of random errors which are difficult to assess. Tests on other materials in our laboratory have shown these random errors to be about 0.4% (Perlman and Asaro, 1969). If we now consider the Sc-Fe relation for the 10 dacites, and remove the small error due to counting statistics, we find an average deviation of the data points from the straight line is 0.6%. This tells us that the actual randomness of scandium relative to iron is less than 0.6%.

It is this fine adherence to linearity that must be taken into account in any model for the geological process which produced this sequence of compositions. The linear relationships suggest mixing in different proportions of two homogenous bodies and we propose to examine the nature of these phases.*

*The term phase is used for convenience to indicate uniform elemental composition in the body. It need not consist of a single phase in the thermodynamic sense.

One of the bodies (Phase A) is obviously a rhyolite so it will be referred to as such. The second will only be termed "Phase B" for the present. Some of the lines with positive slope extrapolate to zero concentration of the elements while the iron value is still positive. We shall first examine one of these. As seen in Fig. 3 the line for Co becomes zero at a higher Fe value than those for the other elements with positive slope. The significance of this point of intersection is that it establishes one of the limits in the composition of the rhyolitic phase because the content of Co cannot be less than zero. The content of each of the other elements in this limiting composition is given by the intercept of each line with the iron content representing zero-Co. The other limit to the composition of the rhyolitic phase is given by that obsidian group with lowest Co value. Limit lines are not shown on the graphs because the respective points for the elements are already entered. It is seen that the limits of composition are so close to each other that the rhyolitic phase is quite sharply defined. In other words, those obsidian specimens of lowest Fe content represent this phase quite well.

In this type of reasoning it is seen that one limit of a phase composition is given precisely by an extrapolation to zero concentration of a single element and the other limit by an actual sample with the lowest concentration noted for that element. If these almost coincide, the possible range is small. Turning to Phase B, we shall see that it is not possible to obtain a narrow range because the lowest concentration of the reference element in available samples is not close to the zero concentration. The element selected for extrapolation is Cs which has a negative slope, and, as seen in Fig. 3 it extrapolates to zero concentration at an Fe content of 7.93%. The highest iron content in any of the dacites analyzed is 4.98%, so the range of permissible compositions for all elements correspond with the band between these limits. All that can be said at present is that the linear variation of elements can be explained by mixing of a rhyolitic phase with another, more basic, phase whose composition limits have just been mentioned.

The actual Phase B could very well be the dacite with the highest iron content found among our specimens. However, it is of interest to postulate a continuous series of compositions toward more basic rocks and to examine the composition near the limit.

Table VI gives two columns of figures headed by "Calculated Phase-A" and "Calculated Phase-B". The least-squares-fit lines of the data were used to calculate two compositions; one for which the iron content is 0.67% and the other, 7.7%. The lower iron content is that of a group of obsidians analyzed

and the calculated values for the other elements agree well with the experimental values as they must when the lines are so sharply defined. The hypothetical Phase B with iron content 7.7% gives a cesium value of 0.5 ppm which means that we are near the limit of the possible range for Phase B. The reason for stopping at this composition rather than going all the way to zero-cesium is of little consequence but values for Cs of about 0.5 ppm are about the lowest found in a number of basalts.

The calculated composition for the postulated Phase B has the general characteristics of basalts which have been analyzed. This is not surprising since we have extrapolated the data toward more basic rocks. Unfortunately, no basalt outcroppings from Borax Lake have come to our attention which would permit an experimental test of whether there exist more basic rocks as a member of this particular series. Several samples from the general area were analyzed but the analyses showed them to be unacceptable as the actual Phase B although one specimen was closely similar in most respects. The composition of this sample (BASA2) is also shown in Table V where it is seen that many elements agree remarkably well with the calculated values for Phase B. However, the values for sodium and for the rare earth elements are distinctly low and this means that BASA2 cannot represent the unaltered basaltic material which we have postulated for Phase B. According to Anderson (1936), the basalts of this general area belong to an earlier period than the obsidian-dacite flow. The failure to find basalts at Borax Lake which clearly belong to the sequence might mean that this extreme of the possible range was never involved, or that it did exist but never reached the surface.

We shall now comment briefly on the proposition that the observed pattern of compositions could result from differentiation. The genesis of rock suites was discussed many years ago by Bowen (1928), who concluded that they are the result of fractional crystallization. More recently, Thompson (1972) called attention to the general acceptance of this mechanism. Wright and Fiske (1971), on the other hand, have presented impressive evidence that certain magmas can mix.

It seems a priori probable that there will be different chemical and physical environments pertaining to the formation and emptying of different magma chambers and that one should not expect an identical sequence of steps for all. These steps could embrace a complex sequence of both differentiations and mixings. Where a single process is dominant, the observations should be most amenable to interpretation, and the Borax Lake flow appears to be a simple case. It seems most unlikely that such a linear continuum of compositions could result from a complex series of chemical changes as is implied in fractional crystallization.

ACKNOWLEDGMENTS

We gratefully acknowledge the continued help of Mr. Duane Mosier, Mrs. Helen V. Michel, Miss Susanne Halvorsen, Mr. Edward Minasian, Mr. Edward Arnold, and Mr. Wally Chin. The arduous job of changing samples in the after hours was done by the Safety Services Department, and the reactor irradiations were made in the Berkeley Research Triga Reactor.

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TABLE CAPTIONS

Table Ia. The chemical compositions of Napa (California) obsidian (in ppm or %):

Table Ib. The chemical composition of Napa obsidian compared to other measurements.

Table IIa. The chemical compositions of Mt. Konocti (California) obsidian (in ppm or %).

Table IIb. The chemical composition of Mt. Konocti obsidian compared to other measurements.

Table III. The chemical compositions of Borax Lake (California) obsidian (in ppm or %). *The indicated errors are the RMS group values except for col 1,4,9 where counting errors are used.

Table IV. The chemical composition of dacite from Borax Lake (California) (in ppm or %).

Table V. The range of elemental compositions encountered in Borax Lake obsidian and dacite and the precision of a single measurement for each extreme of the range. The scatter or the RMS deviation of the data points from a straight line are shown in the last column.

Table VI. The calculated compositions of Phase-A and Phase-B materials at Borax Lake compared to a Basalt from the general area (BASA-2).

Table Ia

Location	40	41	42	43	Average Composition 19	Error in a Single Measurement	Absolute Error
No. of Samples	5	5	5	4			
Element	Composition in ppm or %						
Th	17.99±.07	17.91±.10	17.95±.08	17.82±.23	17.93±.13	±.09	±.52
Sm	5.98±.02	5.93±.02	5.86±.03	5.95±.03	5.93±.05	±.02	±.13
U	6.89±.02	6.84±.06	6.80±.06	6.86±.09	6.85±.06	±.04	±.63
Na%	3.39±.05	3.37±.03	3.34±.06	3.38±.03	3.37±.04	±.04	±.07
Sc	2.89±.03	2.86±.01	2.87±.03	2.80±.03	2.86±.04	±.02	±.06
Mn	147±3	151±1	150±2	147±5	149±3	±3	±3.5
Cs	15.5±.2	15.4±.1	15.4±.1	14.9±.2	15.3±.3	±.3	±1.1
La	31.6±.5	31.6±.4	30.8±.7	31.5±.5	31.3±.6	±.6	±.7
Fe%	.92±.02	.93±.02	.93±.01	.90±.01	.92±.02	±.02	±.02
Al%	6.4±.2	6.3±.2	6.6±.2	6.3±.2	6.4±.2	±.1	±.2
Dy	7.54±.21	7.74±.04	7.79±.12	7.41±.25	7.63±.21	±.19	±.4
Hf	7.49±.27	7.48±.31	7.68±.17	7.61±.29	7.57±.25	±.23	±.5
Ba	447±15	426±3	423±11	433±7	432±14	±13	±24
Rb	201±6	197±3	204±5	207±9	202±6	±15(4)	±20
Ce	66.5±1.4	67.3±1.4	69.7±2.4	65.6±1.1	67.4±2.2	±.6	±3.9
Lu	.635±.014	.629±.009	.611±.009	.609±.011	.622±.015	±.018	±.06
Nd	28.4±1.7	28.5±1.4	28.7±.9	27.7±1.7	28.83±1.4	±1.9	±4.0
Yb	4.71±.09	4.84±.18	5.00±.27	4.55±.06	4.79±.23	±.09	±.6
Tb	.98±.06	.97±.08	.94±.05	.99±.02	.97±.05	±.03	±.10
Ta	.93±.05	.90±.06	.92±.05	.97±.07	.93±.06	±.05	±.07
Eu	.29±.02	.26±.02	.26±.03	.27±.03	.27±.03	±.03	±.03
K%	4.1±.3	4.9±.2	4.2±.2	3.8±.2	4.3±.5	±.5	±.5
Sb	1.3±.3	1.3±.1	1.2±.1	1.13±.05	1.23±.15	±.10	±.2
Zn	64±9	65±10	73±12	60±3	66±10	±3	±11
Cr	6.9±1.3	7.4±1.1	6.5±.4	5.9±.6	6.7±1.0	±.7	±1.1
Ti%					<.05		
Ca%					<2		
Ni					<40		
V					<30		
As					<60		
Cu					<100		
Ag					<2		
Au					<.02		
Ir					<.01		
Sr							
Co							

Table Ib

of Samples	Present Work 19	Jack (1969) 2	Griffin (1969) 3	Stevenson (1971) 6
Element	Composition in ppm or %			
Th	17.9±.5	(25)(15)		
Sm	5.9±.1		11	
Na%	3.37±.07		3.6±.4	
Sc	2.86±.06		3.4±.4	
Mn	149±4	(190)(200)	170±20	160
La	31.3±.7	(40)(40)	57±3	
Fe%	.92±.02		1.0±.2	.98
Ba	432±24	(420)(430)		440
Rb	202±20	(190)(200)	140±20	185
Ce	67±4	(80)(70)		
Nd	29±4	(30)(25)		
K%	4.3±.5	(3.76)		3.44
Zn	66±11	(55)(50)		
Ti%	<.05	(.052)(.054)		.053
Ca%	<2			.0985
Ni	<40	(5)(5)		
Cu	<100	(10)(5)		
Sr	<400			≤ 30

Table IIa

LOCATION	S1	S2	S3	S4	S5	S6	S7a	S7b	Average Composition 37	Error in a Single Measurement	Absolute Error
No. of Samples	4	5	4	4	5	5	5	5			
Element	Composition in ppm or %										
Th	23.34±.06	23.29±.09	23.15±.12	23.02±.24	22.97±.25	22.39±.19	22.60±.46	22.86±.30	22.95±.42	± 0.11	± 0.77
Sm	5.33±.03	5.36±.07	5.28±.05	5.28±.05	5.28±.05	5.37±.03	5.31±.02	5.28±.02	5.31±.05	± 0.016	± 0.12
U	7.52±.05	7.6±.15	7.44±.08	7.46±.05	7.45±.08	7.39±.04	7.36±.04	7.23±.08	7.43±.13	± 0.05	± 0.68
Na%	2.68±.03	2.66±.08	2.69±.04	2.67±.03	2.65±.03	2.71±.01	2.72±.02	2.79±.02	2.70±.06	± 0.03	± 0.07
Sc	5.07±.03	5.07±.05	5.06±.06	5.03±.06	5.12±.09	5.27±.12	5.20±.07	5.23±.08	5.14±.11	± 0.03	± 0.14
Mn	186±7	181±1	184±7	184±7	191±8	206±4	205±5	211±5	195±13	± 3	± 13
Cs	15.4±.1	15.3±.2	15.4±.2	15.2±.4	15.4±.2	14.6±.1	14.6±.2	14.5±.3	15.0±.4	± 0.3	± 1.1
La	31.6±.7	32.5±.6	31.8±.6	31.8±.8	31.6±.7	31.8±.6	31.6±.7	31.6±.4	31.8±.6	± 0.6	± 0.7
Fe%	.97±.04	.97±.01	.97±.02	.97±.02	1.01±.04	1.07±.03	1.05±.02	1.08±.03	1.02±.05	± 0.02	± 0.05
Al%	6.9±.4	7.0±.2	6.8±.3	6.8±.3	6.7±.3	6.7±.1	6.7±.1	6.9±.2	6.8±.2	± 0.1	± 0.2
Dy	5.9±.3	5.7±.4	6.2±.5	6.1±.2	5.9±.2	6.0±.1	5.9±.2	5.8±.1	5.9±.3	± 0.2	± 0.4
Hf	6.14±.16	6.23±.16	6.09±.33	6.03±.39	6.19±.21	6.19±.13	5.90±.17	5.81±.18	6.07±.25	± 0.21	± 0.4
Ba	627±21	644±31	618±10	612±18	619±7	653±18	648±16	657±7	636±24	± 16	± 37
Rb	233±32	233±27	209±25	218±36	217±24	229±4	214±5	216±9	221±22	± 17	± 30
Ce	68.0±.6	66.7±.3	67.7±.9	67.1±1.0	66.9±.6	66.4±.9	64.9±.2	65.0±.5	66.5±1.2	± 0.6	± 3.5
Lu	.47±.01	.50±.04	.49±.02	.47±.03	.47±.02	.46±.02	.46±.01	.44±.02	.47±.03	± 0.02	± .05
Nd	29.3±1.9	32.0±1.5	28.6±1.0	27.6±1.3	27.9±1.0	27.7±2.0	28.5±1.0	27.9±1.9	28.7±2.0	± 2.3	± 4.0
Yb	3.52±.07	3.56±.16	3.47±.01	3.46±.06	3.53±.05	3.44±.04	3.51±.05	3.48±.07	3.50±.08	± 0.07	± 0.46
Tb	.83±.04	.82±.05	.83±.01	.84±.02	.80±.05	.79±.06	.85±.04	.81±.01	0.82±.04	± 0.03	± 0.08
Ta	1.22±.15	1.14±.08	1.19±.09	1.21±.10	1.20±.06	1.20±.12	.99±.07	1.02±.04	1.14±.12	± 0.06	± 0.12
Bu	.40±.03	.38±.05	.40±.03	.40±.04	.40±.04	.41±.03	.42±.02	.43±.03	.41±.03	± 0.03	± 0.03
K%	4.7±.3	4.2±.3	4.1±.4	4.6±.4	5.0±.4	4.3±.3	4.3±.1	4.4±.3	4.4±.4	± 0.4	± 0.4
Sb	1.33±.05	1.30±.07	1.35±.13	1.32±.05	1.32±.16	1.22±.05	1.26±.11	1.20±.07	1.28±.10	± 0.10	± 0.11
Zn	35±2	35±2	35±3	33±3	35±2	35±4	34±2	36±2	35±3	± 3	± 9
Cr	10.3±3.2	9.3±1.0	9.5±.9	9.4±.6	9.4±.7	7.7±.7	8.3±1.0	8.4±.8	9.0±1.4	± 0.8	± 1.4
Ti%	.128±.008	.117±.014	.122±.023	.124±.016	.121±.008	.159±.019	.159±.012	.139±.017	.134±.021	± .014	± .022
Co	1.46±.08	1.52±.08	1.51±.12	1.49±.12	1.68±.19	1.81±.07	1.78±.05	1.83±.06	1.64±.18	± .07	± .18
Ca%									<2		
Ni									<40		
V									<30		
As									<50		
Cu									<100		
Ag									<2		
Au									<.1		
Ir									<.01		
Sr									<500		
Ga									<100		
In									<3		

Table IIb

No. of Samples	Present Work 37	Jack <u>et al.</u> (1969) 2	Becker (1888) 1	Stevenson (1971) 8
Element	Composition in ppm or %			
Th	23.0±.8	(25)(30)		
Na%	2.70±.07		3.96	
Mn	195±13	(230)(230)		205
La	31.8±.7	(40)(40)		
Fe%	1.02±.05		1.10	1.11
Al%	6.8±.2		6.86	
Ba	636±37	(610)(650)		625
Rb	221±30	(215)(215)		195
Ce	66±4	(80)(70)		
Nd	29±4	(30)(30)		
K%	4.4±.4	4.0	3.9	3.77
Zn	35±9	(25)(20)		
Ti%	.13±.02	(.152)(.154)	.15	.158
Co	1.6±.2	(15)(15)		
Ca%	<2		.71	.28
Ni	<40	(5)(5)		
Cu	<100	(5)(5)		
Sr	<500	(65)(65)		95
Ga	<100	(10)(15)		

Table III

No. of Samples *	1	2	2	1	4	3	3	6	1	10	Jack et al. (1969)	Anderson (1936)	Stevenson et al. (1971)
Element	Composition in ppm or %												
SiO ₂ %	71.7±.1									75.7±.4		76.53	
Th	15.1±.1	15.7±.1	15.7±.3	16.6±.1	16.7±.2	16.7±.2	17.0±.1	17.0±.4	17.4±.1	17.6±.1	10		
Sm	5.71±.02	5.72±.13	5.70±.13	5.77±.02	5.75±.08	5.71±.11	5.75±.11	5.81±.09	5.64±.02	5.87±.10			
U	5.77±.05	5.99±.18	5.96±.14	6.30±.04	6.27±.11	6.24±.14	6.36±.04	6.46±.11	6.41±.04	6.75±.12			
Na%	2.77±.04	2.75±.03	2.72±.05	2.68±.03	2.75±.03	2.75±.04	2.73±.02	2.76±.01	2.75±.03	2.75±.03		2.70	
Sc	10.48±.04	9.12±.07	8.73±.06	7.41±.03	7.02±.06	6.68±.02	6.19±.09	5.84±.11	5.20±.02	4.71±.04			
Mn	337±7	295±8	283±2	230±4	223±3	206±3	187±5	178±8	150±3	134±7	240	160	240
Cs	13.6±.3	14.0±.4	14.1±.2	14.9±.3	15.2±.4	15.0±.3	15.2±.5	15.5±.4	15.1±.3	15.9±.3			
La	22.0±.8	21.6±1.5	21.6±.5	21.9±.5	22.3±.9	22.1±1.1	22.2±.3	22.1±.3	22.2±.6	22.6±.7	40		
Fe%	1.88±.03	1.58±.02	1.51±.02	1.25±.02	1.15±.02	1.09±.01	.97±.02	.89±.02	.77±.01	.67±.01		.86	1.23
Al%	6.9±.1	6.8±.4	6.7±.2	6.4±.1	6.8±.2	6.8±.1	6.6±.2	6.5±.2	6.4±.1	6.6±.2		6.79	
Dy	7.9±.5	8.3±.2	8.4±.2	7.0±.2	7.2±.5	7.6±.5	7.5±.3	7.7±.3	7.4±.2	8.0±.2			
Hf	3.9±.1	3.7±.1	3.8±.1	3.8±.1	3.8±.3	3.7±.3	3.7±.1	3.7±.2	3.7±.1	3.8±.1			
Ba	100±40	40±11	90±10	80±12	90±75	110±76	80±30	75±47	140±10	90±40	80		<125
Rb	230±20	210±20	200±10	210±10	260±30	250±20	250±20	220±30	250±20	240±20	215		233
Ce	50±1	50±1	49±1	53±1	52±2	51±1	52±2	51±2	52±1	53±1	60		
Lu	.52±.04	.51±.03	.51±.03	.54±.02	.50±.01	.51±.03	.50±.03	.52±.02	.51±.02	.52±.03			
Nd	26±5	25±4	24±3	25±2	25±5	27±3	27±3	27±3	27±2	26±4	25		
Yb	3.7±.1	3.9±.1	3.8±.1	4.2±.1	3.9±.1	3.9±.3	4.0±.2	4.1±.2	4.2±.1	3.9±.3			
Tb	1.00±.03	1.01±.02	1.02±.02	1.02±.03	1.05±.02	1.06±.03	1.08±.02	1.00±.07	1.06±.03	1.05±.02			
Ta	1.2±.1	1.1±.1	1.1±.1	1.2±.1	1.14±.01	1.1±.1	1.10±.03	1.13±.05	1.09±.04	1.18±.02			
Eu	.35±.04	.29±.02	.30±.02	.24±.03	.19±.05	.20±.01	.15±.02	.16±.03	.11±.02	.10±.02			
K%	3.5±.4	4.2±.3	4.6±.4	4.4±.4	4.1±.3	4.5±.2	4.5±.3	4.2±.4	4.4±.4	4.8±.3		3.9	3.8
Sb	1.0±.1	1.5±.2	.95±.10	1.0±.1	1.0±.1	1.0±.1	.93±.10	1.1±.1	1.0±.1	1.2±.2			
Zn	54±5	50±4	49±3	50±3	47±3	43±3	45±4	55±14	44±3	44±4	45		
Cr	40±1	35±1	31±1	26±1	20±1	18±1	15±1	16±2	9±1	10±2			
Ti%	.20±.02	.15±.01	.14±.01	.10±.01	.09±.01	.08±.01	.07±.01	.06±.02	.03±.02	.03±.02	.083	.07	.118
Co	7.0±.2	5.8±.1	5.1±.1	3.4±.1	3.0±.1	2.8±.1	2.0±.2	1.7±.2	.91±.04	.36±.07	10		
Ca%	1.8±.5	2.3±.5	2.0±.4	1.4±.5	1.6±.5	1.6±.6	1.1±.2	1.2±.4	1.1±.4	.8±.7		.56	.317
V	50±20	60±10	45±26	40±20	30±15	30±10	5±30	15±15	25±15	13±14			
As	<70												
Cu	<100										<5		
Ag	<2												
Au	<.1												
Ir	<.01												
Sr	<600										15		<40
Ga	<100										20		
In	<40												
Ni	<50										10		

Table IV

No. of Samples	(3)	(2)	(1)	(2)	(2)	Anderson's results (1936)
Elements						
Th	8.24 ± 0.10	10.33 ± 0.10	11.09 ± 0.10	12.8 ± 0.14	15.47 ± 0.10	
Sm	5.05 ± 0.15	5.25 ± 0.02	5.29 ± 0.02	5.52 ± 0.03	5.64 ± 0.04	
U	3.00 ± 0.07	3.87 ± 0.06	4.15 ± 0.04	4.76 ± 0.06	5.64 ± 0.06	
Na%	2.51 ± 0.10	2.67 ± 0.04	2.62 ± 0.04	2.68 ± 0.04	2.72 ± 0.07	2.60
Sc	24.77 ± 0.24	20.37 ± 0.09	18.78 ± 0.06	15.54 ± 0.02	10.57 ± 0.04	
Mn	902 ± 20	720 ± 13	641 ± 12	537 ± 11	347 ± 10	700
Cs	6.5 ± 0.3	8.6 ± 0.3	9.5 ± 0.3	10.7 ± 0.3	13.0 ± 0.3	
La	16.1 ± 0.8	17.4 ± 0.7	18.3 ± 0.7	20.2 ± 0.7	22.7 ± 0.7	
Fe%	4.98 ± 0.06	4.04 ± 0.06	3.61 ± 0.05	3.01 ± 0.02	1.93 ± 0.03	3.62
Al%	7.6 ± 0.2	7.5 ± 0.2	7.1 ± 0.1	7.2 ± 0.2	6.8 ± 0.2	7.53
Dy	7.2 ± 0.3	7.6 ± 0.4	7.6 ± 0.3	7.4 ± 0.3	7.9 ± 0.3	
Hf	3.3 ± 0.1	3.6 ± 0.1	3.6 ± 0.1	3.5 ± 0.1	3.6 ± 0.1	
Ba	130 ± 20	107 ± 13	115 ± 12	107 ± 12	86 ± 12	
Rb	114 ± 20	131 ± 15	141 ± 14	172 ± 15	200 ± 16	
Ce	36.3 ± 0.8	41.5 ± 1.3	43.2 ± 0.7	45.0 ± 0.6	49.1 ± 0.7	
Lu	0.47 ± 0.02	0.45 ± 0.02	0.49 ± 0.02	0.48 ± 0.02	0.51 ± 0.02	
Nd	20.3 ± 1.6	22.4 ± 1.7	20.1 ± 1.6	23 ± 1.6	25.6 ± 1.7	
Yb	3.2 ± 0.1	3.4 ± 0.1	3.7 ± 0.1	3.6 ± 0.1	3.8 ± 0.1	
Tb	0.90 ± 0.04	0.95 ± 0.04	0.95 ± 0.4	0.98 ± 0.04	0.97 ± 0.04	
Ta	0.79 ± 0.08	0.88 ± 0.08	0.78 ± 0.08	0.91 ± 0.07	1.09 ± 0.06	
Eu	1.01 ± 0.06	0.81 ± 0.05	0.69 ± 0.05	0.59 ± 0.04	0.39 ± 0.03	
K%	2.4 ± 0.5	2.3 ± 0.4	3.2 ± 0.5	3.0 ± 0.5	3.5 ± 0.5	2.47
Sb	0.6 ± 0.1	0.6 ± 0.1	0.7 ± 0.1	0.8 ± 0.1	0.95 ± 0.10	
Zn	91 ± 9	72 ± 7	74 ± 6	72 ± 5	56 ± 4	
Cr	113 ± 3	90 ± 2	80 ± 2	66 ± 2	37 ± 1	
Ti%	0.56 ± 0.03	0.43 ± 0.03	0.40 ± 0.03	0.34 ± 0.03	0.17 ± 0.03	0.46
Co	24.4 ± 0.5	19.1 ± 0.4	17.4 ± 0.3	13.5 ± 0.2	7.4 ± 0.2	
Ca	4.8 ± 0.7	4.5 ± 0.7	3.8 ± 0.6	2.6 ± 0.6	2.6 ± 0.7	3.39
V	194 ± 35	160 ± 34	99 ± 23	100 ± 28	47 ± 25	

Table V.

Element	Range of Values (ppm)	Precision of Measurement (ppm)	RMS dev. (ppm)
Sc	4.71 - 24.77	.02 - 0.07	.11
Co	0.37 - 24.4	.04 - 0.35	.20
Cr	10 - 113	0.6 - 2.1	2
Mn	134 - 902	3 - 16	8
U	6.75 - 3.00	0.06 - 0.04	.11
Th	17.62 - 8.24	.07 - .10	.22
Cs	15.9 - 6.5	.3 - .3	.3

Table VI.

Elements	Compositions in % or ppm		
	Calculated Phase-A	Calculated Phase-B	Measured BASA-2
Th	17.6	2.5	2.2 ± 0.1
U	6.7	0.72	0.81 ± 0.02
Sc	4.76	37.5	39.2 ± 0.1
Mn	134	1369	1304 ± 19
Cs	15.9	0.5	0.8 ± 0.3
Fe%	<u>0.67</u>	<u>7.7</u>	7.74 ± 0.10
Al%	6.5	8.4	8.2 ± 0.2
Hf	3.8	3.2	3.0 ± 0.1
Rb	245	27	40 ± 15
Ta	1.18	0.52	0.45 ± 0.09
K%	4.6	0.8	0.92 ± 0.45
Sb	1.1	0.3	0.4 ± 0.1
Zn	45	114	99 ± 10
Cr	9.4	178	194 ± 3
Ti%	0.03	0.90	0.93 ± 0.02
Co	0.40	39.6	40.7 ± 0.5
Ca%	1.04	7.5	7.5 ± 0.6
V	9	300	280 ± 40
Na%	2.76	2.43	2.00 ± 0.03
La	22.7	12.5	8.3 ± 0.5
Ce	52.8	27.6	20.0 ± 1
Nd	25.6	18	11 ± 2
Sm	5.85	4.6	3.72 ± 0.01
Eu	0.10	1.6	1.3 ± 0.1
Tb	1.05	0.81	0.81 ± 0.04
Dy	7.8	7.1	5.7 ± 0.2
Yb	4.0	2.7	2.4 ± 0.2
Lu	0.52	0.43	0.34 ± 0.02

FIGURE CAPTIONS

- Fig. 1. The rare earth pattern for Mt. Konocti obsidian (upper points) and Borax Lake, obsidian of lowest iron content (lower points). All values are normalized to Napa obsidian rare-earth abundances.
- Fig. 2. The chemical variation of Scandium plotted against total iron for 43 obsidian and dacite samples from Borax Lake, California.
- Fig. 3. The chemical variation of cobalt and cesium plotted against total iron content for Borax Lake obsidian and dacite.
- Fig. 4. The chemical variation of Mn, U, Th, and Cr plotted against total iron content for Borax Lake obsidian and dacite.
- Fig. 5. The chemical variation of Sm, Na, La, Eu, and Lu plotted against total iron content for Borax Lake obsidian and dacite.
- Fig. 6. The chemical variation of Al, K, and Ti plotted against total iron content for Borax Lake obsidian and dacite.
- Fig. 7. The chemical variation of Hf, Rb, Ta, and Ca plotted against total iron content for Borax Lake obsidian and dacite.

XBL725-2880

Fig. 1

XBL727-3448

Fig. 2

XBL727 - 3551

Fig. 3

Fig. 4

XBL726-3384

Fig. 5

XBL727-3449

Fig. 6

XBL 727-3450

Fig. 7

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