Final Report on Qualification of Volcanism Isotope, Trace-Element, and Halogen Data Using Procedure YAP-SIII.1Q/Rev. 3/ICN 0.

Qualification Team:

John Savino // 3-18-99

John Savino Ph.D., Chairperson — Date
MTS/Golder Associates

Paul R. Dixon // 3-18-99

Paul R. Dixon, Ph.D. — Date
NEPO/Los Alamos National Laboratory

Pat Auer // 3-18-99

Pat Auer, B.S., M.B.A. — Date
OQA/MACTEC

Darrell Porter // 03/18/99

Darrell Porter, Ph.D. — Date
NEPO/SAIC

Approvals:

Gail S. Abend // 3/19/99

Gail Abend — Date
Technical Data Management Data Qualification Oversight Point of Contact

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Final Report on Qualification of Volcanism Isotope, Trace Element, and Halogen Data Using Procedure YAP-SIII.1Q/Rev. 3/ICN 0

Executive Summary:

This report describes the approach and results of an evaluation of the qualification status of isotope and trace-element data submitted by Los Alamos National Laboratory (LANL) to the Technical Data Management System (TDMS) and reported in the Level 3 Milestone Report 3781MR1, "Synthesis of Volcanism Studies for the Yucca Mountain Site Characterization Project," (VSR) , dated February 6, 1998, and in a report by F.V. Perry and K.T. Straub, "Geochemistry of the Lathrop Wells Volcanic Center," LA-13113-MS, March 1996. The analytical data services were procured by LANL from three nationally recognized laboratories: the University of Colorado at Boulder, Colorado; the Department of Earth and Planetary Sciences at Washington University in Saint Louis, Missouri; and the EES-1 Wet Chemistry Laboratory at LANL. The data developed from the analytical results supplied by these three laboratories are identified as qualified data in Table 1.1 of the VSR and in the TDMS. This qualification status was subsequently determined by the Office of Quality Assurance (OQA) to be incorrect, as outlined in the following.

An earlier version of the VSR and supporting data were the subject of a performance-based audit (YM-ARP-96-014) conducted in September 1996 by OQA. As a result of the audit, Deficiency Report (DR) YM-96-D-107 was issued documenting use of unqualified data. Based on a subsequent DR verification effort by OQA, it was determined that the LANL sample plan process developed for the acquisition of the geochemical analytical data had been used prior to the process being endorsed in the Quality Assurance Requirements and Description document (QARD) as an alternative to making a "Q" procurement. Therefore, services obtained from the University of Colorado and Washington University were considered outside of the QA program. The DR response required qualification via the YAP-SIII.1Q procedure and, as a result, the CRWMS M&O proceeded to appoint a data qualification team in accordance with procedural requirements. Additionally, the responsible project participant at LANL identified analytical services from the EES-1 Wet Chemistry Laboratory as being performed outside the QA program, thus producing non-Q data.

YAP-SIII.1Q, Attachment 3, provides for one or a combination of up to five methods that can be used to qualify data. The data qualification team selected the "Equivalent QA Program" method. The team reviewed, in whole or in part, all pertinent Scientific Notebooks and Attachments, and data sets in the TDMS and project reports, to determine the LANL sample plan method, the consistent application of the method, adequacy of documentation, and accuracy and traceability of data and documentation to the TDMS. Based on this evaluation, the data qualification team recommends that the geochemical data sets provided by the three laboratories and identified in Table 1.1 of the VSR and

Appendices B and C of Perry and Straub (1996) be accepted as qualified. This recommendation, if accepted, results in no change to the qualification status of the data in the TDMS.

Scope of Task:

The purpose of this task is to evaluate the qualification status of geochemical data sets submitted by LANL to the TDMS and included in the VSR and Perry and Straub, 1996. The evaluation is a three-phase process. First, the data qualification team examined relevant LANL documentation (e.g., scientific notebooks and reports) to determine if the LANL Principal Investigators (PIs), responsible for acquiring and using the data, developed and consistently used a vendor sample plan process that fulfills the requirements listed in Appendix C.2.3 of the QARD. In the second phase, the team reviewed documentation of the analytical results supplied by the vendors. The objective of this review was to determine whether the analytical data were received, documented, and consistently evaluated against acceptance/rejection criteria developed by the PIs. Finally, the team evaluated the traceability to the TDMS of the documentation pertaining to the sample plan process, the analytical data evaluation, and final data use and reporting. This included a check for accuracy of data transcription from the vendor reports, to LANL reports, and finally to the TDMS. This qualification evaluation addressed the review criteria described in the Data Qualification Plan included as Attachment A to this report.

Data Sets Evaluated:

The data sets evaluated for qualification were identified in an e-mail, dated 11-24-98, from Dick Spence (Assistant Manager Office of Project Execution) to Gail Abend (the Technical Data Management Data Qualification Oversight Point of Contact appointed in accordance with YAP-SIII.1Q). A copy of this e-mail will be included in the records package being assembled under AP-17.1Q. The data sets are: 1) whole-rock trace-element data obtained by instrumental neutron activation analysis (INAA) from Washington University, St. Louis, Missouri; 2) whole-rock isotopic analyses obtained by solid source mass spectrometry and trace-element chemistry obtained by isotope dilution at the University of Colorado at Boulder, CO; and 3) halogen concentrations determined from ion chromatography performed at the LANL EES-1 Wet Chemistry Laboratory. These data sets are cited in Chapter 4 (Tables 4.1, 4.2, 4.3, and Appendix 4.2) and Chapter 5 (Tables 5.4 and 5.5) of the VSR and in Appendices B and C of Perry and Straub (1996). All final data sets have been submitted to the TDMS.

Qualifications of the Team Members:

Chairperson: Dr. John Savino (MTS). Dr. Savino obtained a Ph.D. (Geophysics-Seismology) from Columbia University in 1971. Between 1971 and 1991, he worked on earthquake prediction, earthquake-explosion seismology, and plate tectonics. In December 1991 he joined the YMP as an advisor to DOE on various geophysical site investigations including the Probabilistic Volcanic Hazards Analysis. Dr. Savino was a member of the performance-based audit team that reviewed the LANL volcanism program in September 1996.

Team Member: Pat Auer (OQA). Mr. Auer has a B.S. in Metallurgical Engineering from the University of Arizona and MBA from the University of Nevada, Las Vegas. He has 11 years experience in QA issues relating to auditing, procurement, QC, program and procedure development and vendor auditing. Mr. Auer participated in the initial development of guidelines for QC sample plan purchases intended to invoke QARD Appendix C. He also developed the recommended outlines for the QC sample plan in conjunction with NEPO, the USGS and LANL.

Team Member: Dr. Paul R. Dixon (M&O NEPO). Dr. Dixon has a Ph.D. in Geochemistry from Yale University and 15 years professional experience in collecting and evaluating related geochemical and isotopic information where statistical approaches to data analysis were used as a normal practice for data QA/QC. He has expertise in the content of the subject matter being reviewed and he is also the M&O Geochemistry Technical Lead for the Natural Environment Program Office (NEPO) which managed the collection of the volcanism data.

Team Member: Dr. Darrell Porter. Dr. Porter has a Ph.D. in Mineral Engineering from the University of Minnesota in 1972 and over 30 years experience in the earth sciences. He has been associated with the development and implementation of the YMP QA program since 1985 and is intimately familiar with the use of Scientific Notebooks, traceability of scientific results, requirements for the procurement of quality services, and the use of the sample plan approach for accepting analytical services from a non-Q supplier as permitted in the QARD.

Method of Qualification:

The method selected for evaluation of the qualification status of the volcanism geochemical data sets is the "Equivalent QA Program" described in Attachment 3 of YAP-SIII.1Q. Under this method, the data qualification team assessed whether the LANL sample plans used to acquire the geochemical data sets are consistent with the sample plan requirements in Appendix C.2.3 of the QARD. The applicable guidelines listed in Attachments 3 and 4 of YAP-SIII.1Q were compared to the sample plans developed and used by the LANL PI(s).

Evaluation of Sample Plans and Analytical Data:

In the following subsections of this report, the first two phases of the evaluation process described in the Scope of Task are addressed sequentially for each of the three data sets. The third phase of the evaluation process, dealing with traceability of documentation and accuracy of data reporting, will be addressed for the three data sets in a later section.

1. Isotope and Trace-Element Chemistry Data

Vendor Qualifications and Procurement of Services

The qualifications of the vendor selected for the analytical services are described in Purchase Request LA-PR X1809. As explained by the PI, the isotope data are required for modeling the mechanisms of basalt generation in the Yucca Mountain region (YMR). However, LANL did not have facilities for routinely analyzing basalts samples for the isotopes of interest. As a result, the PI decided to procure commercial-grade Sr, Nd, and Pb isotope analyses and Sm, Nd, Sr, Rb, and Pb concentrations from the Cooperative Institute for Research in Environmental Sciences at the University of Colorado at Boulder, Colorado (UCB). This laboratory has a history of supplying isotope analyses on a commercial basis, and the analytical techniques used at UCB have been thoroughly documented in the refereed geologic literature (e.g., Farmer, G.L., Broxton, D.E., Warren, R.G., and Pickthorn, W., "Nd, Sr, and O Isotopic Variations in Metaluminous Ash Flow Tuffs and Related Volcanic Rocks at the Timber Mountain/Oasis Valley Caldera Complex, SW Nevada: Implications for the Origin and Evolution of Large Volume Silicic Magma Bodies," Contrbutions to Mineralogy and Petrology, **109**, p. 53-68, 1991). The PI sent a copy of this article to the data qualification team for review.

Qualifications of the Data Analyst (LANL PI)

The LANL PI for this data set is Frank Perry. Frank Perry received his PH.D. in Geology (emphasis on isotope geochemistry) at the University of California, Los Angeles, in 1988. He has 18 years experience in the fields of igneous petrology, isotope geochemistry, volcanic geology, and the geochronology of volcanic rocks. He has published numerous professional papers in the areas of petrology, geochemistry, volcanology, and geochronology.

Sample Plan Process

Between May 1991 and July 1994, the LANL PI submitted four sets of basalt samples to UCB for analyses. The sample sets are described in Scientific Notebooks TWS-EES-13-LV-12-89-05 (SN-05) and TWS-EES-13-07-93-044 (SN-044). The PI notes on page 33 of SN-05 that, while accuracy of measurements is required, precision is perhaps more important for his magmatic modeling purposes (e.g., discriminating between a polygenetic and a monogenetic volcanic system at Lathrop Wells). As seen in the following, this requirement dictates the quality control (QC) sample plan strategy of standards and replicates. Accuracy of the analytical measurements is determined at UCB

based on analyses of accepted isotopic standards. UCB routinely submitted results of their analyses of standards in reports stored in Print-out Binder I (TWS-EES- 13-LV-10-89-04) and Attachment 1 to SN-044.

For replicate analysis, the PI chose a particular basalt sample from Lathrop Wells to make splits and include as blind duplicates in each sample set submitted to UCB. This sample is designated LW41FVP-P2. Note that the PI used an alphanumeric identification system for all samples submitted for analyses. This identification system proved to be successful for tracking sample data from the UCB reports to project reports and, finally, to the TDMS. A summary of the basalt sample sets submitted to UCB, number of samples and duplicates, standards used at UCB, and documentation of the analytical results from UCB is given in the following.

Set 1: SN-05, page 34, May 15, 1991; 12 basalt samples from Lathrop Wells sent to UCB. Set included blind duplicates LW41FVP-P2 and LW13FVP-P2. Isotope standards used at UCB included the La Jolla standard for isotopic Nd, NBS-987 for Sr, and NBS-981 for Pb. Accuracy of Pb concentrations were determined using a USGS ^{208}Pb spike (JW-1). Analytical measurements of standards and 12 samples are contained in Print-out Binder I TWS-EES-13-LV-10-89-04 in UCB reports dated 12/12/91, 01/10/92, and 05/21/92.

Set 2: SN-05, page 35, October 15, 1991; 10 samples from YMR sent to UCB. Set included two replicates of LW41FVP-P2 sent as blinds (DP3FVP-P2 and DP4FVP-P2). Isotope standards used at UCB included the La Jolla standard for isotopic Nd, USGS AGV-1 for Rb and Sr concentrations, and the ^{208}Pb spike (JW-1) for Pb concentrations. Analytical measurements of standards and 10 samples are contained in Print-out Binder I TWS-EES-13-LV-10-89-04 in a UCB report dated 01/26/93.

Set 3: SN-044, page 3, August 20, 1993; 10 samples from YMR sent to UCB. Set included two replicates of LW41FVP-P2 sent as blinds (DP5FVPFVP-P1 and DP8FVPFVP-P1; note the redundant FVP is in SN-044). Isotope standards used at UCB included the La Jolla Nd standard, NIST (SRM-987) for Sr, NIST (SRM-981) for Pb, and USGS AGV-1 for Rb and Sr concentrations. Analytical measurements of standards and 10 samples are contained in Attachment 1 to SN-044 in a UCB report dated 08/17/94.

Set 4: SN-044, page 23, July 27, 1994; 10 samples from YMR sent to UCB. Set included one replicate of LW41FVP-P2 sent as a blind (BD5FVP-P1). Isotope standards used at UCB included La Jolla Nd, NIST (SRM-987) Sr, and NIST (SRM-981) Pb. Analytical measurements of standards and 10 samples contained in Attachment 1 to SN-044 in a UCB report dated 03/20/95. There are two issues raised with this sample set. The first has to do with only one blind replicate being submitted and how this will allow for evaluation of results in terms of precision of measurements. The second issue is based on low Nd concentrations for all 10 samples as pointed out in the UCB report. How these issues were addressed by the PI in terms of his sample plan process is discussed in more detail in later sections of this report.

Disposition of Sample Remnants

There were no remnants of sample splits submitted to UCB for isotopic analyses. Remaining samples at LANL were subsequently submitted to the Sample Management Facility as reported in Document #SPC325EM4, "Volcanism Samples Submitted to the SMF," dated August 12, 1997.

Acceptance/Rejection Criteria

On page 33 of SN-05, the PI defined the acceptance/rejection criteria to be applied to the analytical data received from UCB. The criteria are stated in terms of upper bounds on % precision (% relative standard deviation) for five isotopic ratios and five element concentrations. The % precision is defined as 100(standard deviation/mean), where the standard deviation and the mean are computed from the analytical measurements for the duplicates submitted in each sample set. These criteria were applied to all four sets of analytical measurements received from UCB.

Evaluation of Analytical Data

The application of the acceptance/rejection criteria are discussed in the following sections of the LANL scientific notebooks:

Set 1: SN-05, page 35, January 20, 1992; page 37, April 13, 1992; and page 39, May 29, 1992.

Set 2: SN-05, page 41, March 2, 1993.

Set 3: SN-044, page 24, August 22, 1994; and page 25, August 26, 1994.

Set 4: SN-044, page 37, May 3, 1995.

A spot check of the % precision calculations was performed by the data qualification team. The results are given in Table 1. The isotopes analyzed and the corresponding acceptance criteria are listed in the first two columns. Values of % precision computed by the PI and 20 values computed by the data qualification team (numbers in parentheses) are listed in the remaining four columns.

One of the issues noted in the previous Sample Plan section of this report had to do with the fact that the PI only submitted one blind replicate in sample set 4 to UCB. As explained on page 37 of SN-044, in order to compute the standard deviation required in the % precision relation, the PI compared the analytical data for the blind replicate included in set 4 to the mean values of the isotope and element data for the six blind replicates previously submitted to UCB in sets 1-3. The team checked five of the 10 mean values and found exact agreement with the PI to the reported number of significant

TABLE 1. % Precision Verification

ISOTOPES/ TRACE ELEMENTS	ACCEPTANCE CRITERIA %	%PRECISION			
		[1]SET 1	[1]SET 2	SET 3	SET 4
$^{87}Sr/^{86}Sr$	<0.01	0.0044	0.0023 (0.0016)	0.0006	0.0011
$^{143}Nd/^{144}Nd$	<0.005	0 (0)	0.0031 (0.0022)	0.0007 (0.0007)	0.0017 (0.0017)
$^{208}Pb/^{204}Pb$	<0.5	0.0235	0.1228	0.0425	0.0757
$^{207}Pb/^{204}Pb$	<0.5	0.0322	0.0902	0.0319	0.0820 (0.0638)
$^{206}Pb/^{204}Pb$	<0.5	0.0546	0.0436	0.0077	0.0924
Sr	<1	1.087 (0.7644)	0.3554 (0.2508)	0.454 (0.454)	0.0591 (0.0591)
Rb	<1	4.785 (3.305)	0 (0)	0	0.1399
Nd	<1	0.287	0 (0)	0.245	7.8367 (7.8367)
Sm	<1	0.333 (0.235)	0.5004 (0.3547)	0.587 (0.587)	1.1099 (1.1099)
Pb	<1	0 (0)	0.9346 (0.6578)	3.804 (3.804)	6.4369 (6.4369)

[1] As part of the review of the data, a check of calculations was made to verify correctness of the numbers. The numbers in parentheses were calculated by the data qualification team. It was discovered that an incorrect equation to calculate standard deviation was used for sample sets 1 and 2. The "large sample" version of the equation had been used where "N" is used in the denominator instead of "N-1" as required for small samples. In this case, the number of samples available for the calculation of standard deviation is two.

figures. We conclude that the PI's substitution of one of the replicates in set 4 by the mean values based on previously submitted replicates was an acceptable alternative. This approach allowed the PI to apply the sample plan acceptance/rejection criteria to the isotope and trace-element analytical data received from UCB for sample set 4.

Next consider the % precision values entered for $^{207}Pb/^{204}Pb$, set 4. The PI computed a value of 0.0820 while the team computed 0.0638. The difference in the values is most likely explained by the fact that the PI used an individual isotope value for the sixth replicate (i.e., DP8FVP) instead of the mean value of the six replicates; probably caused by a simple misread of the tabulated values. When the team used the incorrect value for the mean, we reproduced the PI's value of 0.0820 to three significant figures. Other than the Pb isotope ratio in set 4, a check of eight other values in sets 3 and 4 showed exact agreement between the PI's and the team's calculations.

For sets 1 and 2, however, the check yielded totally different results. As indicated in Table 1, there is a systematic difference between the PI's % precision values and the team's. The difference is approximately the square root of two, with the PI's calculations larger than the team's. We attribute the difference to the use of a large sample (population) relation for standard deviation (N in the denominator) by the PI for values in sets 1 and 2; switching over to the small sample relation (N-1 in the denominator) for sets 3 and 4. The use of the large sample version of standard deviation actually resulted in more conservative acceptance criteria, and, thus, did not negatively impact the QC sample plan. The zeroes in Table 1 simply mean that the isotope measurements were identical for the corresponding set of replicates.

The second issue raised in the Sample Plan section had to do with the low Nd concentration measurements reported by UCB for sample set 4. As seen in Table 1, the % precision for Nd is about 7.8, considerably higher than the <1 % threshold for acceptance. On pages 38 and 39 of SN-044, the PI described the way he resolved this issue. As noted in the SN, he determined a correction factor and applied it to the Nd data for all samples in set 4. The "corrected" concentrations are reported in Perry and Straub (1996), the VSR, and the TDMS.

Sm (set 4) and Pb (sets 3 and 4) are discussed on pages 38 and 39 of SN-044. The PI noted that the % precision (1.1099) for Sm only exceeds the threshold by about 0.1 % and deemed this inconsequential for his modeling purposes. The % precision values for Pb were noted to be too variable and the data were not used in modeling.

2. Trace-Element Analysis INAA

The technical requirements for the INAA process are addressed in Purchase Requests LA-PR Z9664 and PR#8727 U. As explained in LA-PRZ9664, INAA data are required to

characterize the trace-element compositions of basaltic rocks in the YMR. The trace-element data are used in modeling the mechanisms of basalt generation and eruption.

PR#8727 applies to basalt and silicic tuff samples from two natural analog study sites: Paiute Ridge located in the northeastern part of the Nevada test Site and Grants Ridge in west-central New Mexico. In this study the INAA data are used to evaluate the effect of contact metamorphism on the rare earth-element compositions of vitric and zeolitized tuffs.

Between July 1990 and April 1996, the LANL PI submitted six sets of basalt samples from volcanic units in the YMR and one set of basaltic and silicic rock samples from the analog study sites for INAA. The sample sets are described in scientific notebooks SN-05, SN-044, and LA-EES-1-NBK-95-006 (SN-006).

Vendor Qualifications and Procurement of Services

As pointed out in the Purchase Requests, LANL did not have facilities to perform INAA for basaltic rocks at the level of precision and accuracy required for geochemical modeling, and no laboratory had met the requirements of the LANL YMP QA program. As a result, the PI decided to procure commercial-grade INAA for trace elements Sc, Cr, Co, Ni, Cs, Ba, La, Ce, Nd, Sm, Bu, Tb, Yb, Lu, Hf, Ta, Th, U, and Sr from the Department of Earth and Planetary Sciences at Washington University (WU) in Saint Louis, Missouri, and accept the analytical results in accordance with the LANL QC sample plan. The WU laboratory was chosen because it has an established international reputation of excellence and the laboratory has supplied INAA to the international community on a commercial basis for many years. The analytical techniques used by this laboratory have been well documented in the refereed geologic literature (e.g., Kortev, R.L., National Bureau of Standards Coal Flyash (SRM 1633a) as a Multielement Standard for Instrumental Neutron Activation Analysis, Journal of Radioanalytical and Nuclear Chemistry, **110**, p. 159-177, 1987). The PI sent a copy of this article to the data qualification team for review.

Qualifications of the Data Analyst (LANL PI)

The analyst and LANL PI for this data set is Frank Perry. His qualifications were discussed in an earlier section. Giday Woldegabriel, a geochemist at LANL, assisted Dr. Perry with the preparation, submission, and documentation of the samples from the analog study sites sent for INAA.

Sample Plan

The QC sample plan process adopted by the LANL PI for the seven sets of samples submitted to WU for INAA consisted of the following:

Set 1: SN-05, pages 29 and 30, July 23, 1990; 48 basalt samples from Lathrop Wells sent to WU. Set included the standard BHVO-1 and three replicates of a basalt sample from

Lathrop Wells (LW27FVP-P1). Standard and replicates included as blinds. The accuracy and precision of the INAA results are estimated using the standard and replicate measurements, respectively. INAA results from WU are contained in Print-out Binder I TWS-EES-13-LV-10-89-04 in a report dated October 9, 1990.

Sets 2-6: Four replicates of LW27FVP-P1included as blinds in each of the four sample sets to test for precision and long-term reproducibility of INAA results. For set 2, 39 samples submitted (SN-05, page 37, May 13, 1992) and INAA results in Print-out Binder I TWS-EES-13-LV-10-89-04 in a report from WU dated August 20, 1992. Set 3, 61 samples submitted (SN-044, page 4, August 20, 1993) and INAA results in Attachment 1 to SN-044 in reports from WU dated October 11, and 25, 1993. Set 4, 19 samples submitted (SN-044, pages 33 and 34, November 15, 1994) and INAA results for 12 of the 19 samples in Attachment 1 to SN-044 in a report from WU dated January 9, 1995 (see below). Set 5, 50 samples submitted (SN-044, page 45, June 13, 1995) and INAA results in Attachment 1 to SN-044 in a report from WU dated August 21, 1995. Set 6, 20 samples submitted (SN-044, page 57, April 1, 1996) and INAA results in Attachment 1 to SN-044 in a report from WU dated July 1, 1996.

Set 7: SN-006, pages 54 and 55, August 25, 1995; 20 samples sent to WU. This sample set included four replicates; two splits of standard NBS-278 and two splits of standard NBS-688, all submitted as blinds. The remaining 16 samples consisted of eight samples, replicates of each, from the analog study sites. INAA results contained in SN-066, pages 57-59, in a report from WU dated October 16, 1995. Recommended trace-element concentrations reported for standards NBS-688 and NBS-278 in K. Govindaraju (1989) are reproduced on page 45 of David Vaniman's Scientific Notebook TWS-EES-1-12-90-4. In addition, David Vaniman showed that there is excellent long-term agreement between WU's measurements of the standards and the accepted values. The analysis is given in pages 119-123 of Scientific Notebook TWS-EES-1-5-92-3.

Disposition of Samples

As noted in purchase requests to WU (e.g., PR#145AW and PR#8727 U), the PI specified that excess sample remnants from the INAA be returned to LANL. Document #SPC325EM4, "Volcanism Samples Submitted to the SMF," dated August 12, 1997, indicates that remnants of all included in the INAA were shipped by LANL to the Sample Management Facility.

Acceptance/Rejection Criteria

The acceptance/rejection criteria (tests) that were applied to the six sets of basalt samples from volcanic units in the Yucca Mountain region are defined on page 29 of SN-05. The criteria are stated in terms of % accuracy and % precision. The % accuracy is based on WU measurements of the standard BHVO-1. Recommended values for BHVO-1 are listed on page 1 of Appendix I in the report by K. Govindaraju (1989). % accuracy is defined as 100x (WU measurement – standard value) /standard value.

The definition of % precision, or % relative standard deviation, is the same as used for evaluating the isotope data; 100 (standard deviation/mean). As noted under the Sample Plan for these data, the PI only included the standard BHVO-1 with the first sample set. He used the four replicates sent with set 1 to compare with the standard results to establish a baseline and tested for any systematic shifts in the trace-element concentrations with subsequent submissions of four replicates of the same original sample (LW27FVP) in sample sets 2-6. The % accuracy test was applied to set 1, the % precision test to all six sample sets.

The acceptance/rejection criteria applied to the sample set from the analog study sites are described on page 56 of SN-006. In this case, the PI used the INAA results from standards NBS-278 and NBS-688 and two replicates from each of the analog samples to evaluate the accuracy and precision of the measurements. No specific criteria, such as upper bounds on % accuracy or % precision, are identified. However, the PI did subsequently consider the accuracy of the INAA measurements for the standards in the evaluation and acceptance of the INAA results for the analog site samples.

Evaluation of Analytical Data

The acceptance/rejection criteria referred to in the previous section of this report were consistently applied to the INAA data for the seven sample sets received from WU. The criteria are discussed in terms of acceptance or rejection of the trace-element concentrations in the following sections of the scientific notebooks.

Set 1: SN-05, page 31, October 25, 1990. PI rejects INAA data for Cr, Ni, and U on the basis of % precision analysis. Accepts data for 16 other trace elements. % accuracy results for Nd (i.e., 12.7%) exceed acceptable threshold (< 10%), but deemed acceptable by the PI for studying rare earth element patterns. The data qualification team checked % accuracy values for nine of the 19 elements reported in SN-05, page 31. The calculations were based on concentrations recommended for the standard BHVO-1 in Govindaraju (1989) and WU analytical results for the standard listed in Print-out Binder I TWS-EES-13-LV-10-89-04. The team's calculations agreed exactly with the PI's.

Set 2: SN-05, page 40, September 8, 1992. All data are acceptable in terms of the QC sample plan criteria.

Set 3: SN-044, pages 21 and 22, January 20, 1994. All data are acceptable. However, PI notes that relatively large % precision values for Rb, Cs, and U mean that data are probably not reliable for discerning small differences in compositions among basalts.

Set 4: SN-044, pages 36 and 37, January 18, 1995. All data acceptable in accordance with the QC sample plan criteria.

Set 5: SN-044, pages 46 and 47, August 29, 1995. PI rejects U data on basis of % precision. Accepts all other element concentrations.

Set 6: SN-044, page 61, July 10, 1996. U data rejected on % precision. All other elements accepted. PI notes that relatively low precision of Cr, Rb, Cs, Nd, and Lu may render them unsuitable for certain types of geochemical interpretations.

Set 7: SN-006, pages 60 and 61, August 22, 1996. Detailed comparison of WU and recommended values for standards NBS-278 and NBS-688. Precision of data is excellent with exception of Ba.

Table 2 gives the results of a check of % precision values reported by the PI in SN-05 and SN-044 for the six basalt sample sets submitted to WU for INAA. For this check, the data qualification team calculated % precision estimates for approximately 32% of the total number of values reported (i.e., 6 elements out of 19 for 6 sets versus 19 elements for 6 sets; 36/114). Each % precision value in Table 2 is based on element concentrations reported by WU for the four replicates included in each of the six sample sets. The second column in Table 2 lists the acceptance threshold % precisions for the six elements. Note that there are only four cases (Nd sets 2 & 3, Sr sets 1& 2) where the PI's values (upper) differ from the team's (lower in parentheses). In three of the four cases the differences are insignificant. In the case of Sr in set 1, the values differ significantly, although both indicate acceptance compared to the threshold value of <5%. For the remaining 32 values in Table 2, there was exact agreement between the PI's and the team's % precision calculations.

Table 2 % Precision Check

Element	Acceptance Criteria (%)	% Precision					
		Set 1	Set 2	Set 3	Set 4	Set 5	Set 6
Sc	< 3	0.4	0.21	0.74	0.83	0.78	0.26
Nd	< 10	5.1	0.64 (0.65)	2.93 (2.94)	1.56	3.79	1.28
Sm	< 4	1.2	0.71	1.16	1.78	0.69	0.62
Yb	< 5	2.4	1.46	0.82	2.05	1.08	1.06
Th	< 5	1.2	0.55	1.81	0.67	0.73	0.44
Sr	< 5	0.7 (2.3)	0.40 (0.38)	2.52	2.74	0.72	1.29

3. Halogen Data

The technical requirements for the Halogen data are described on page 49 of SN-006. Basaltic and silicic rocks, collected for the Paiute Ridge and Grants Ridge natural analog study, were selected for analysis of their concentrations of B, Br, Cl, F, Li, P_2O_5, and S. These elements, together with water, form the bulk of the volatile content escaping from a volcanic center.

Vendor Qualifications and Procurement of Services

Unlike the previous data sets, facilities for the measurement of the required element and P_2O_5 concentrations existed at LANL. As a result, the PI prepared a list of analytical services required in a format similar to a Purchase Request. The list is reproduced on page 49 of SN-006 and includes specification of concentrations in parts per million (ppm), expected date of receipt of results, and instructions to the laboratory to return excess samples to the PI for storage.

The PI prepared the samples and hand delivered them to the EES-1 Wet Chemistry laboratory at LANL. The samples were analyzed using Ion Chromatography. A complete description of the sample preparation techniques and the instrumentation employed at the EES-1 Wet Chemistry Laboratory is given on pages 188 and 189 in Attachment 1 to SN-006.

Qualifications of the Data Analyst (LANL PI)

The analyst and LANL PI for this data set is Dr. Frank Perry. His qualifications were discussed in the section on isotopic data. Giday Woldegabriel, a geochemist at LANL, assisted Dr. Perry with the preparation, submission, and documentation of the samples sent for halogen analysis.

Sample Plan

On page 49 of SN-006, the PI describes his sample plan process. The PI selected two standards that are lithologically similar to the unknown rock samples to determine the accuracy of the analytical results from the EES-1 Wet Chemistry Laboratory at LANL. The standards are JA-1 (andesite)and JR-1 (rhyolite) from the Geological Survey of Japan. Recommended trace-element concentrations for these two standards are listed on page 16 of Appendix I in Govindaraju (1989). The two standards were split and included in the sample set as duplicates. Then eight rock samples, and replicates of each of the

eight, were prepared for analysis. The resultant set of 20 samples was then submitted to the EES-1 laboratory, with the standards and replicates sent as blinds.

The ten samples are described (alphanumeric identifiers) on page 49 of SN-006, August 21, 1996. The analytical results from EES-1 are contained in Attachment 1 to SN-006, pages 185-187.

Disposition of Samples

Excess sample from the Wet Chemistry Laboratory and original samples in the PI's possession were submitted to the Sample Management Facility according to Document # SPC325EM4, "Volcanism Samples Submitted to the SMF," dated August 12, 1997.

Acceptance/Rejection Criteria

The PI defined the acceptance/rejection criteria to be applied to the analytical data on page 50 of SN-006. Data will be evaluated on an element-by-element basis and considered acceptable if within 25% of the standard analysis. If the data vary by >25%, the data will be rejected.

Evaluation of Analytical Data

Evaluation of the analytical data from the EES-1 Laboratory is documented on pages 51-53 of SN-006. The PI compared two sets of duplicate analyses of the standards JA-1 and JR-1 to recommended concentrations for these standards taken from Govindaraju (1989). On the basis of the acceptance/rejection criteria, all the data, except that for Br, are determined to be acceptable.

Traceability and Accuracy of Documentation:

Table 3 provides traceability to the Technical Data Management System (TDMS), the Records Processing Center (RPC), and the Technical Information Center (TIC) of the documentation used, in whole or in part, by the data qualification team in this qualification process.

Table 3: Traceability of Data and Supporting Documentation

1. LANL Scientific Notebooks

TWS-EES-13-LV-12-89-05	NNA.19940607.0177
TWS-EES-13-07-93-044	MOL.19980217.0262

TWS-EES-13-07-93-044, Attachment 1	MOL.19980217.0264
TWS-EES-13-LV-10-89-04 Print-out Binder I	(TBD) During the course of this review, it was determined that the Print-out Binder I was not in the TDMS. The LANL PI supplied the data qualification team with all the analytical results from UCB and WU that were needed for the team's evaluation. LANL is in the process of submitting the complete binder to the TDMS.
LA-EES-1-NBK-95-006	MOL.19980217.0061
LA-EES-1-NBK-95-006 Attachment 1	MOL.19980217.0258
TWS-EES-1-5-92-3	MOL.19980212.0503
TWS-EES-1-12-90-4	NNA.921009.0018

2. LANL Isotope, INAA, and Halogen Data

Table 4.1 from VSR: Isotopic compositions of basalts from the YMR	Data Tracking Number (DTN) LAFP831811AQ97.001 MOL.19971110.0113
Table 4.2 from VSR:INAA of tephra and silt from Lathrop Wells	DTN: LAFP831811AQ97.001
Table 4.3 from VSR: INAA of basaltic ash from fault trenches near Yucca Mountain	DTN: LAFP831811AQ97.001
Appendix 4.2 from VSR: INAA of basalts from the YMR	DTN: LAFP831811AQ97.001
Table 5.4 from VSR: INAA and Halogen data from Paiute Ridge, NTS, Nevada	DTN: LAGV831812AQ97.001 MOL.19971110.0117 (Note, table incorrectly referred to as Table 5.3 in the DTN – all values are correct except for number of significant figures reported)
Table 5.5 form VSR: Halogen data from Grants Ridge	DTN: LAGV831812AQ97.001 (Note, table incorrectly referred to as Table 5.4 in the DTN – all values are correct except for the number of significant figures reported)
Appendix B, B:1 from Perry and Straub, 1996: Trace-element composition of	MOL.19951026.0324

Lathrop Wells basalts determined by INAA

Appendix B, B:2 from Perry and Straub, 1996: Replicate INAA analysis of LW27FVP	MOL.19951026.0324
Appendix C, C:1 from Perry & Straub, 1996: Isotopic and trace-element compositions of Lathrop Wells basalts determined by solid-source mass spectrometry	MOL.19951026.0324
Appendix C, C:2 from Perry and Straub, 1996: Replicate solid-source mass spectrometry analyses of LW41FVP	MOL.19951026.0324

3. Supporting Documentation

Volcanism Synthesis Report	MOL.19980722.0048
Purchase Request LA-PR X1809: University of Colorado Radiogenic Isotope Analysis of Volcanism Samples	MOL.19960207.0271
Purchase Request LA-PR Z9664: Washington University INAA analysis of Volcanism Samples	MOL.19960207.0269
Purchase Request PR#8727U: INAA Analysis of Basalt and Silica samples from natural analog sites (page 55 of SN-006)	MOL.19980217.0061
Document # :SPC325EM4: Draft Version Date: August 12, 1997 Volcanism Samples submitted to the SMF	MOL.19981006.0275
LANL Audit # YM-ARP-96-14	MOL.19961220.0058
1989 Compilation of Working Values and Sample Description for 272 Geostandards, K. Govindaraju, Geostandards Newsletter, 13, Special Issue (July 1989), p. 1-113.	MOL.19951002.0246

Geochemistry of the Lathrop Wells Volcanic Center, F.V. Perry and K.T. Straub, 1996 **(Technical Information Center TIC Catalog # 223932)**

Check on Transcription of Data

The data qualification team checked a subset of all the final data sets considered in this report for possible transcription errors in going from the original source documents (vendor reports) to project reports (VSR and Perry and Straub, 1996) and finally to the TDMS. The subset of data checked is as follows: 66 values in Table 4.1 (VSR); 152 values in Table 5.4 (VSR); 56 values in Table 5.5 (VSR); 210 values in Appendix B, B:2 (Perry and Straub, 1996); 81 values in Appendix C, C:2 (Perry and Straub, 1996). The results are summarized as follows:

1. There were only two instances of disagreement for all the numerical values checked. One instance was for halogen data reported on Table 5.4 in the VSR. The Cl mean concentration for sample PR95-11 reported in Table 5.4 is cited as 38.00, whereas, we computed a value of 33 based on analytical results from the LANL EES-1 laboratory reported on page 185 of Attachment 1 to SN-006. The second instance occurred in Appendix C, C:2 of Perry and Straub (1996). In this table the PI calculated a % precision value of 1.828 for Rb based on analysis of six replicates. We calculate a value of 1.824. In both cases, the differences are relatively insignificant.

2. While the numerical values of the measurements appear to be properly transcribed, there is a tendency to report too many significant figures (trailing zeroes), particularly in Tables 5.4 and 5.5 of the VSR, and to a lesser extent in Appendix C, C:2 in Perry and Straub (1996). The halogen concentrations in Table 5.5 are routinely listed to two decimal places. This degree of precision, however, is not warranted according to the EES-1 laboratory source data. For example, concentrations of Li for sample GR95-11 are listed in Table 5.5 as 55.00 and 57.00 ppm, while the EES-1 measurements reported on page 185 of Attachment 1 to SN-066 are 55 and 57 ppm. Of the 56 values in Table 5.5, 48 are in the Li category; the precision of the remaining eight values are overstated by only one significant figure.

3. The EES-1 analytical measurements of the halogen concentrations are reproduced exactly (except for the mean Cl value cited in 1. above) in the Site and Engineering Properties (SEP) database in the TDMS. The halogen source data are in reports S98263_026 and S98236_063 through S98236_068. Spot checks of other data referred to in 1. above (Isotope and INAA) indicate that the SEP contains the exact source data as reported by UCB and UW.

In summary, the documentation reviewed by the team is extensive and traceable to the TDMS. While there are minor problems with the transcription of some of the data from the sources (UCB, UW, and the EES-1 laboratory) to the TDMS, these problems do not affect the technical use of the data.

Recommendation Criteria for Qualification Status:

Evaluation of the LANL documentation of the sample plan process and resultant data is summarized in the following.

- The qualifications of the laboratories chosen for analytical services were documented and outside vendor services procured under Purchase Requests. In the case of the Wet Chemistry Laboratory at LANL, a list of services required was hand delivered with the samples to be analyzed.

- The LANL PI(s) developed quality control sample plans that provided for tracking of all samples, including standards and duplicates, from LANL to the analytical service vendor to the SMF. Standards and duplicates were submitted for analyses as blinds.

- Acceptance/rejection criteria as documented in the QC sample plan were established and consistently applied to the source data. Interpretations of the data in accordance with these QC sample plans were appropriate and successfully complemented this phase of the sample plan process.

- Measures of data accuracy and precision were defined and consistently applied.

- All necessary LANL documentation pertaining to the sample plans and data sets have been submitted to the TDMS as QA records.

Recommendation for Qualification Status of Data:

The data qualification team recommends that all of the isotope, INAA, and halogen data included in Chapters 4 (Tables 4.1, 4.2, 4.3, and Appendix 4.2) and 5 (Tables 5.4 and 5.5) of the VSR and Appendices B and C of Perry and Straub (1996) be accepted as qualified data.

Attachment A

Qualification of the Volcanism Geochemical Data Using Procedure YAP-SIII.1Q/Rev. 3/ICN 0

Data Qualification Plan

1. Data Sets to be Evaluated

The volcanism data sets to be evaluated for qualification were identified in an e-mail, dated 11-24-98, from Dick Spence (AMOPE) to Gail Abend (POC). The data sets are: whole-rock trace-element data obtained by instrumental neutron activation analysis (INAA) from Washington University, St. Louis, Missouri; whole-rock isotopic analyses obtained by solid source mass spectrometry performed at the University of Colorado, Boulder, Colorado; and halogen concentrations using ion chromatography performed at the EES-1/Los Alamos National Laboratory (LANL). These geochemical and isotopic data sets are cited in Chapter 4 (Tables 4.1, 4.2, 4.3 and Appendix 4.2) and Chapter 5 (Tables 5.4 and 5.5) of the Level 3 Deliverable 3781MR1, dated February 6, 1998, "Synthesis of Volcanism Studies for the Yucca Mountain Site Characterization Project," and in Appendices B and C of LANL Report LA-13113-MS, "Geochemistry of the Lathrop Wells Volcanic Center," by Frank V. Perry and Kelly T. Straub, issued March 1996.

2. Method of Qualification

The method selected for evaluation of the qualification status of the volcanism geochemical data sets is the "Equivalent QA Program" listed in Attachment 3 of procedure YAP-SIII.1Q/Rev.3/ICN 0. The data qualification team organized for this effort and introduced in the following section will assess whether the LANL sampling plan used to acquire the geochemical data is consistent with the sampling plan requirements in Appendix C.2.3 of the Quality Assurance Requirements and Description (QARD) document and implemented in accordance with QAP-7-3. The data qualification team will examine documentation that describes the quality control sample plan instituted by LANL and assess the traceability of the documentation to the Technical Data Management System (TDMS). The applicable guidelines listed in Attachments 3 and 4 of YAP-SIII.1Q will be compared to the sample plan developed and used by LANL.

3. Qualifications and Personnel Make up of the Review Team

Chairperson: Dr. John Savino (MTS). Dr. Savino obtained a Ph.D. (Geophysics-Seismology) from Columbia University in 1971. Between 1971 and 1991, he worked on earthquake prediction, earthquake-explosion seismology, and plate tectonics. In December 1991 he joined the YMP as an advisor to DOE on various geophysical site investigations involving the two most significant projects: the Probabilistic Volcanic Hazards Analysis and the Probabilistic Seismic Hazard Analysis. Dr. Savino was also a member of the performance based audit team that reviewed the LANL volcanism program.

Team Member: Pat Auer (OQA). Mr. Auer has a B.S. in Metallurgical Engineering from the University of Arizona and MBA from the University of Nevada, Las Vegas. He has 11 years experience in QA issues relating to auditing, procurement, QC, program and procedure development and vendor auditing. Mr. Auer participated in the initial development of guidelines for QC sample plan purchases intended to invoke QARD Appendix C. He also developed the recommended outlines for the QC sample plan in conjunction with NEPO, the USGS and LANL.

Team Member: Dr. Paul R. Dixon (M&O NEPO). Dr. Dixon has a Ph.D. in Geochemistry from Yale University and 15 years professional experience in collecting and evaluating related geochemical and isotopic information where statistical approaches to data analysis were used as a normal practice for data QA/QC. He has expertise in the content of the subject matter being reviewed and he is also the M&O Geochemistry Technical Lead for the Natural Environment Program Office (NEPO) which managed the collection of the volcanism data.

Team Member: Dr. Darrell Porter. Dr. Porter has a Ph.D. in Mineral Engineering from the University of Minnesota in 1972 and over 30 years experience in the earth sciences. He has been associated with the development and implementation of the YMP QA program since 1985 and is intimately familiar with the use of Scientific Notebooks, traceability of scientific results, requirements for the procurement of quality services and the use of the sample plan approach for accepting analytical services from a non-Q supplier as permitted in the QARD.

4. Sampling Plan and Data Evaluation Criteria

The volcanism data qualification evaluation will be a three-phase process. First, the data qualification team will examine relevant LANL documentation (e.g., scientific notebooks and reports) to determine whether the LANL Principal Investigators (PIs), responsible for acquiring and using the data, developed and consistently used a vendor sample plan process that fulfills the requirements listed in Appendix C.2.3 of the QARD. In the second phase, the team will review documentation of the vendor supplied analytical results. The objective of the review is to determine whether the analytical data were received, documented, and consistently evaluated against acceptance/rejection criteria developed by the PIs. Finally, the data qualification team will evaluate the traceability to

the TDMS of the documentation dealing with the sample plan process, analytical data evaluation, and final data use and reporting.

Evaluation criteria to be considered by the data qualification team are the following:

A. SAMPLE PLAN EVALUATION CRITERIA

- Rationale of the sample plan compared with the context or premise of the QARD authority for use of a sample plan in lieu of ensuring analytic data quality through vendor controls.

- Adequacy of the sample plan process described in the LANL scientific notebooks.
- Evaluation of the applicable procurement documents for specification of data reporting requirements and documentation expected from the vendor.
- Capabilities of the laboratories (vendors) performing the analytical data analyses.
- The number of control samples/standards among the sample set submitted for analysis and approach used for submitting them (e.g., blind, replicate, etc.).
- The preparation and analysis of control samples/standards, or identification of the source (e.g., nationally recognized standards).
- Development of acceptance/rejection criteria
- Disposition of sample remnants.

B EVALUATION CRITERIA FOR ANALYTICAL RESULTS

- Qualification of the data analyst
- Extent and completeness of documentation of the receipt of the analytical results, including traceability of control samples/standards submitted by LANL to the laboratories (vendors) for analyses and analytical results received from vendors
- Evaluation of analytical data against acceptance/rejection criteria.
- Approach used to establish accuracy/precision of the data.
- Was professional judgement a part of the geochemist's determination of the appropriateness of the data?

C. TRACEABILITY OF DOCUMENTATION

- Ensure that LANL documentation pertaining to the sample plans, analytical data results, and reports describing the use of the data sets is traceable and has been entered as QA records in the TDMS.
- Documentation will include Scientific Notebooks including Attachments, Interim Reports and Final Reports that use the developed data sets.
- Review will include a check for accuracy of data transcription from the original source (i.e., vendor reports to the LANL PIs) to LANL Reports and finally to the TDMS.

5. Recommendation Criteria for Qualification Status.

- Review results of evaluation conducted according to 4. above.
- Equivalence of sample plan processes, analytical data results documentation, and traceability of data compared to the requirements of the QARD Appendix C.2.3.
- Adequacy of the data accuracy/precision compared to technical use of the data.

6. Final Recommendation on Qualification Status of Data

This will consist of a concise statement for or against changing the qualification status of the volcanism geochemical and isotopic data sets.

7. Schedule for Completing Work

02-26-99 Finalize qualification plan with team and submit to POC.

03-05-99 Finalize input to draft qualification report for the volcanism geochemical data sets.

03-11-99 Submit draft qualification report to the POC.