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Nevada System of Higher Education

TECHNICAL REPORT

Bomb-Pulse Chlorine-36 at the Proposed Yucca Mountain Repository Horizon: An Investigation of Previous Conflicting Results and Collection of New Data

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EXECUTIVE SUMMARY

Previous studies by scientists at Los Alamos National Laboratory (LANL) found elevated ratios of chlorine-36 to total chloride (^{36}Cl/Cl) in samples of rock collected from the Exploratory Studies Facility (ESF) and the Enhanced Characterization of the Repository Block (ECRB) at Yucca Mountain as the tunnels were excavated. The data were interpreted as an indication that fluids containing "bomb-pulse" ^{36}Cl reached the repository horizon in the ~50 years since the peak period of above-ground nuclear testing. Moreover, the data support the concept that so-called fast pathways for infiltration not only exist but are active, possibly through a combination of porous media, faults and/or other geologic features.

Due to the significance of ^{36}Cl data to conceptual models of unsaturated zone flow and transport, the United States Geological Survey (USGS) was requested by the Department of Energy (DOE) to design and implement a study to validate the LANL findings. The USGS chose to drill new boreholes at select locations across zones where bomb-pulse ratios had previously been identified. The drill cores were analyzed at Lawrence Livermore National Laboratory (LLNL) for ^{36}Cl/Cl using both active and passive leaches, with the USGS/LLNL concluding that the active leach extracted too much rock-Cl and the passive leach did not show bomb-pulse ratios. Because consensus was not reached between the USGS/LLNL and LANL on several fundamental points, including the conceptual strategy for sampling, interpretation and use of tritium (^{3}H) data, and the importance and interpretation of blanks, in addition to the presence or absence of bomb-pulse ^{36}Cl, an evaluation by an independent entity, the University of Nevada, Las Vegas (UNLV), using new samples was initiated. This report is the result of that study.

The overall objectives of the UNLV study were to investigate the source or sources of the conflicting results from the previous validation study, and to obtain additional data to determine whether or not there are bomb-pulse isotopes at the repository horizon. To that end, we have engaged in discussions with previous investigators, reviewed reports, and analyzed archived samples. We have also collected new samples of rock from the ESF, soil profiles from the surface of Yucca Mountain, and opportunistic samples of seep water from inside the south ramp of the ESF.

Our sampling strategy in the ESF was to collect new rock samples in a manner that would optimize our chances of finding a ^{36}Cl bomb-pulse signature, if one was present. Therefore the sampling and analytical methodology that yielded prior bomb-pulse ratios was replicated (to the extent possible). Specific geologic features (e.g., faults, cooling joints) and strategic locations (including the Ghost Dance, Sundance, Bow Ridge and Drill Hole Wash faults) were targeted. Moreover, extreme precautions were taken to collect samples, excavating a meter into the tunnel wall in some cases. Experiments were performed measuring trace elements and anions in leachates as a function of time to help guide our leaching conditions. Samples were analyzed for ^{36}Cl/Cl ratios, as well as ^{99}Tc and ^{129}I, two other radionuclides that can be associated with the bomb-pulse, in select samples. Finally, a column experiment was conducted mimicking the passage of bomb-pulse ^{36}Cl through Yucca Mountain tuff (Topopah Spring Tuff middle nonlithophysal unit (Tptpmn)).

The work faced several obstacles including an extended shutdown of the tunnel. In addition, some of the data collected early in the study were suspect because of unreasonably high ^{36}Cl/Cl ratios. Attempts to pinpoint the cause of the seemingly random and spurious results were unsuccessful. After moving to a different laboratory in a separate building and employing new supplies, control was gained over the background and blank results were consistent and acceptably small. Because of the setbacks only half (seven) of the ESF samples, but all of the soil and column-study samples, were analyzed in the favorable laboratory setting before the project ended. Overall, the experience highlights the challenging nature of the work and the high sensitivity of accelerator mass spectrometry (AMS) for ^{36}Cl.

Among the samples that produced reasonable results accompanied by low blanks, only one yielded a background corrected ^{36}Cl/Cl ratio that was higher than the accepted bomb-pulse threshold (1250 x 10^{-15}). Specimen 01034214 obtained from the Drill Hole Wash fault (19+33) had a ratio of 1590 ± 80 (1σ) x10^{-15}, whereas the other separate sample from this fault zone yielded 1160 ± 50 (1σ) x 10^{-15}. Three samples collected from Alcove 6 averaged 490 ± 100 (1σ) x10^{-15}; a sample from Sundance Fault resulted in a ratio of 920 ± 60 (1σ) x10^{-15}, and a sample from the Bow Ridge Fault produced 530 ± 20 (1σ) x10^{-15}. The above results are significant because: 1) they tend to be lower than LANL data for comparable samples, albeit in agreement with the range of data produced in the area, and 2) they show that a bomb-pulse ^{36}Cl/Cl ratio was measured in rock collected at the repository horizon level by a second and independent group of investigators (UNLV). The generally lower values compared with LANL data may be interpreted as supporting the contention that at least some of the LANL data may have been artificially high. On the other hand, detection of a bomb-pulse ^{36}Cl/Cl ratio in the UNLV study supports the LANL assessment that water traveled from the surface to specific locations at repository horizon depths within the last 50 years. However, it should be emphasized that because of time we were not able to replicate the results, and these few data points are insufficient to conclude whether either interpretation is legitimate.

Leachates of soil samples collected from the surface above the north and south ramps of the ESF and analyzed using the same preparation protocol as the welded tuff samples yielded several ratios indicative of bomb-pulse ^{36}Cl, particularly for samples encompassing the wetting front, and demonstrated that our analytical technique was appropriate for detecting a bomb pulse ^{36}Cl signal when present. Soil samples collected above the south ramp, where there was limited soil coverage due to a large amount of rock outcrop, had relatively large ratios ranging from 2170 ± 110 (1σ) x10^{-15} to 5670 ± 350 (1σ) x10^{-15}. In contrast, soil samples from profiles from above the north ramp ranged from 820 ± 70 (1σ) x10^{-15} to 2390 ± 160 (1σ) x10^{-15}, which compare favorably with previous measurements near the site by Norris et al. (1987).

Water seepage into the ESF south ramp in response to elevated levels of precipitation during the winter of 2005 and ^{36}Cl standards made from NIST reference material were prepared separately from the samples that produced the spurious results early in the project. Also, the seepage and standards contained relatively high chloride concentrations and contamination apparently had little impact on their ratios. The standards were produced to have nominal ^{36}Cl/Cl ratios (10^{-15}) of 500, 2,500 and 10,000 and the results showed good agreement with the calculated ratios: means (n=3) of 580 ± 40 (1σ) x10^{-15}, 2,580 ± 150 (1σ) x10^{-15}, and 10,030 ± 500 (1σ) x10^{-15}, respectively. This exercise showed that we could generate accurate ^{36}Cl/Cl ratios for known solutions and served as an independent calibration check for PRIME data. Furthermore, for each standard the precipitate was divided into three unequal amounts (~2, 6, and 25 mg) to test for variability associated with the amount of sample submitted for analysis. There were no significant differences between the results for the differing masses, although the samples with the lowest mass tended to have higher errors associated with the measurement. Data for the seepage samples ranged between 680 ± 40 (1σ) x10^{-15} to 1110 ± 40 (1σ) x10^{-15}, consistent with that found for modern meteoric water, with a small bomb-pulse component (Phillips et al., 1988). Bomb-pulse ^{36}Cl may not have been incorporated in this fast-path water because the surface above the infiltration zone consists mostly of outcrop with sporadic areas of shallow soil. Thus the flow pathways have probably mostly been leached.

^{99}Tc was measured in five of nine leaches of ESF rock but poor analytical recoveries and lack of data overlap with ^{36}Cl limit interpretations of these data. The detection capability of the inductively coupled plasma mass spectrometer (ICP-MS) was insufficient for measuring ^{129}I without preconcentration, and detection by AMS may be preferable.

In the column experiment, 200 mL (~3 rock volumes) of a spike solution containing a bomb-pulse ratio (~2500 x 10^{-15}) was slowly passed through columns of ESF tuff (Tptpmn). This was followed by two separate washes of distilled water of the same volume. ^{36}Cl/Cl ratios determined in the second wash were similar to the original spike solution, suggesting that a bomb-pulse in tuff media may require multiple meteoric flow events before the ratio is diminished.

Exploratory experiments were conducted using bromide instead of chloride as a carrier, which is advantageous because it essentially eliminates the need for blank subtraction, a potential source of error in the analysis. ESF samples prepared using bromide had ^{36}Cl/Cl ratios ($\times 10^{-15}$) with acceptable levels of uncertainty (1σ): 720 ± 30 and 1250 ± 90 for SPC01034210 (Bow Ridge Fault) and SPC01034215 (Drill Hole Wash Fault), respectively. The result for Drill Hole Wash fault is noteworthy because it constitutes a second detection of a ^{36}Cl/Cl bomb-pulse ratio at the site, albeit from an unqualified measurement. In summary, the bromide procedure should be considered for use in future ^{36}Cl work.

The source(s) of the conflicting results between USGS/LLNL and LANL could not be definitively determined. Most of the samples from the validation and prior studies were exhausted and therefore we could not produce an additional set of data for direct comparison. The facility at LANL that performed much of the work is no longer accessible and a trailer containing relevant samples was infested by rodents and sprayed with Cl-bleach rendering the samples useless. There was no evidence that the different AMS facilities (PRIME and CAMS) were a source of the discrepancy between the results. On the contrary, samples split and analyzed by CAMS and PRIME were in good agreement.

Much of the information regarding the USGS-led ^{36}Cl validation study comes from a draft report authored by that agency and dated July 2003. We were informed that a revised version of the report that addresses, but does not resolve, the most contentious issues is due out later this year.

Finally, it is noted that the UNLV study experienced several setbacks including sampling delays, a limited number of sample sites that could be excavated, and early anomalous results. In the end, several data sets in which we are confident were obtained, but there was no time to replicate the analyses, despite having gained valuable experience with various sample preparation techniques. Because of our experience and the fact that quality unleached sample material is retained, including six samples that have yet to be analyzed in the low-background laboratory, we recommend a follow-up study to deliver additional information on these samples. Resolution of the bomb-pulse ^{36}Cl issue at Yucca Mountain is within reach.

1.0 TABLE OF CONTENTS

ABBREVIATIONS, ACRONYMS, AND SYMBOLS

AMS:	Accelerator Mass Spectrometry
CAMS:	Center for Accelerator Mass Spectrometry
DOE:	United States Department of Energy
ECRB:	Enhanced Characterization of the Repository Block
EDS:	Energy Dispersive X-ray Spectroscopy
ESF:	Exploratory Studies Facility
HRC:	Harry Reid Center for Environmental Studies
IC:	Ion Chromatography
ICP-MS:	Inductively Coupled Plasma Mass Spectrometry
IPLV:	Implementing Procedure Las Vegas
LANL:	Los Alamos National Laboratory
LDPE:	Low Density Polyethylene
LLNL:	Lawrence Livermore National Laboratory
NA:	Not Available or Not Applicable
NIST:	National Institute of Standards and Technology
NSHE:	Nevada System of Higher Education
NTS:	Nevada Test Site
OCRWM:	Office of Civilian Radioactive Waste Management
PTn:	Paintbrush Tuff non-welded
PRIME:	Purdue Rare Isotope Measurement Laboratory
QA:	Quality Assurance
REEs:	Rare Earth Elements
RSD:	Relative Standard Deviation
SEM:	Scanning Electron Microscope
SMF:	Sample Management Facility
SN:	Scientific Notebook
SNL:	Sandia National Laboratory
TBM:	Tunnel Boring Machine
TCw:	Tiva Canyon Tuff welded
Tptpmn:	Topopah Spring Tuff middle nonlithophysal unit
Tptpll:	Topopah Spring Tuff lower lithophysal unit
Tptpul:	Topopah Spring Tuff upper lithophysal unit
TSw:	Tonapah Spring Tuff welded
UCCSN:	University and Community College System of Nevada
UNLV:	University of Nevada, Las Vegas
USGS:	United States Geological Survey
UQ:	Unqualified Data
UZ:	Unsaturated Zone
^{3}H:	Tritium
^{36}Cl/Cl:	Ratio of ^{36}Cl to total Cl, usually expressed with a 10^{-15} factor

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LIST OF TABLES

LIST OF FIGURES

2.0 PURPOSE

The overall objective of the UNLV study was to determine the cause of conflicting results for $^{36}Cl/Cl$ that were previously determined by USGS/LLNL and LANL, and to obtain additional data that can be used to evaluate whether or not young water containing bomb-pulse isotopes has infiltrated to the level of the repository horizon. The scope of the work included discussions with previous investigators, review of prior relevant reports, analysis of archived samples (where available), and collection and analysis of new samples, including rock from the ESF, surface soils above the north and south ramp of the ESF, and seepage water collected near the entrance to the south ramp. This technical report is intended to document the study's purpose, methods, results, conclusions, and recommendations.

2.1 Organization of the Report

The report begins with an executive summary (p. 2-4), which highlights the study's purpose, methods, and main findings. Section 1 lists abbreviations, acknowledgments, the study team, and tables and figures. Section 2 discusses the purpose of the study. Section 3 provides specific quality assurance information. Section 4 includes a brief introduction to the subject, the study objectives and scope, a comment on quality assurance, and an overview of the organization of the report. A brief time-line and outline of the study is presented in Table 1. Section 4.1 provides additional background information and a timeline of project showing select milestones. Section 3 focuses on the sampling strategy and related information and issues. Section 5 discusses the analytical methodology employed. Section 6 discusses assumptions used in the study. Section 7 consists of the results and discussion beginning with results obtained for ^{36}Cl in more or less chronological order. Subsection 7.1 presents data from our first runs that produced some spurious results. Section 7.2 contains ^{36}Cl data from samples prepared in a new laboratory with a low ^{36}Cl background. Section 7.3 presents results for ^{99}Tc and ^{129}I. The remaining subsections discuss other relevant data and information collected during the study. Section 7.9 presents the study's conclusions and recommendations. Section 8 lists inputs (source data) and references cited in this report. Appendix 1 contains anion data collected during the study. Appendix 2 discusses background subtraction for ^{36}Cl. Appendix 3 shows some photographs of the sampling areas.

3.0 QUALITY ASSURANCE

The work described here was subject to the University and Community College System of Nevada (UCCSN) Quality Assurance (QA) Program requirements. This section provides an overview of the QA program used in the UNLV study, specific QA procedures and other program information can be found at the following website: http://hrc.nevada.edu/QA/. In addition, qualified data are also documented in the scientific notebooks and at relevant locations within this technical report. No conclusions of this report are based on unqualified data. It should be noted that previous work by the USGS, LANL, and LLNL followed OCRWM-approved QA procedures.

LLNL and PRIME were subcontracted for ^{36}Cl analyses; however, only PRIME was qualified as a supplier. For Accelerator Mass Spectrometry (AMS) measurements background levels were determined by analysis of "machine blanks" and "reagent or process blanks". The former are samples that are known to have negligible radionuclide content, whereas the latter are samples prepared to assess contamination from reagents and sample preparation steps. Process blanks were run as unknowns and the machine blank was subtracted from the result.

For techniques other than AMS, determination of precision and accuracy of the analytical measurements were described in each corresponding implementing procedure. Generally, precision was addressed through the use of field and/or laboratory replicates, and accuracy was evaluated using initial and continuing calibration verifications and analysis of check standards (where applicable). Calibration standards were purchased directly from NIST or qualified vendors. No software or models were developed in the UNLV study. Balances and pipettes were calibrated annually by a qualified supplier or in-house using appropriate implementing procedures.

Scientific notebooks used in the UNLV study:

1. UCCSN-UNLV-059 Vol. 1
2. UCCSN-UNLV-065 Vols. 1-4
3. UCCSN-UNLV-068 Vol. 1

Implementing Procedures (IPLVs) used in the UNLV study:

1. IPLV-003, "Analytical and Top Loading Balance Use", Rev. 2 and 3.
2. IPLV-008, "Measurements of Anions in Water Samples by the Ion Chromatography System", Rev. 4 and 5.
3. IPLV-009, "Measurement of Trace Elements in Water Samples by the Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)", Rev. 2, 3, 4.
4. IPLV-015, "Electron Microprobe Analysis on the JEOL 8900-R", Rev. 2.
5. IPLV-017, "Pipettor Use and Calibration Check", Rev. 2.
6. IPLV-019, "Carbon Coating Thin Sections for Electron Microprobe Analysis", Rev. 1.
7. IPLV-062, "Scanning Electron Microscope Analysis on the JSM-5600, Rev. 0."
8. IPLV-076, "Polished Thick Section Preparation for use in the Electron Probe Microanalyzer, Rev. 0"

Other pertinent procedures used with slight modifications as documented in the appropriate scientific notebook:

1. LANL-CST-DP-92, R2 “Sample Leaching to Extract Soluble Chloride and Bromide”.
2. LANL-INC-DP-95, R1 “Preparation of Samples for Chlorine-36 Analysis”
3. LANL-INC-DP-97, R0 “Preparation of Carrier Solution for Chlorine-36 Analysis”.

4.0 INTRODUCTION

The chloride anion is one of the least reactive and most commonly used hydrological tracers (e.g., Fabryka-Martin and Davis, 1987; Elmore et al., 1987). It is also widely distributed in nature and is found in all natural waters and rock formations. One particular isotope of chlorine, ^{36}Cl, is radioactive with a half-life of 301,000 years (Browne and Firestone, 1986) and can be used to date groundwater with ages approaching one million years (Bentley et al., 1986). ^{36}Cl is produced naturally both in the atmosphere and in the sub-surface (in-situ production) (Lehmann et al., 1993). ^{36}Cl is also artificially produced by the thermal neutral irradiation of Cl, and the amount of ^{36}Cl in the atmosphere increased significantly during thermonuclear weapons tests conducted in proximity of sea-water in the 1950's (Elmore et al., 1982). This pulse of ^{36}Cl can be used to trace and date young groundwater (Phillips et al., 1988).

Yucca Mountain, the site for a proposed high-level nuclear waste repository, is comprised of volcanic rock that contains fractures that vary in size and extent. These fracture patterns have been considered in the conceptual model as providing fast pathways that could transmit recharge water from the surface into the repository horizon. The motivation for the previous studies was to use bomb-pulse ^{36}Cl to test for the presence of fast pathways. Ratios of ^{36}Cl/Cl greater than 1250x10^{-15} in tuffaceous rock, particularly near fractures, (e.g., salts left behind from fracture flow) were interpreted to indicate the passage of bomb-pulse water into the repository horizon within the past 40 to 50 years (Fabryka-Martin et al., 1997).

Previous studies by scientists at Los Alamos National Laboratory (LANL), Lawrence Livermore National Laboratory (LLNL), and the United States Geological Survey (USGS) quantified ^{36}Cl/Cl to test for the presence of fast pathways at the proposed Yucca Mountain high-level nuclear waste repository. The goal of these studies was to determine whether or not fluids containing bomb-pulse ^{36}Cl traveled along fast pathways and reached the proposed waste emplacement horizon; however, the groups followed somewhat different procedures and sometimes produced conflicting results. For example, the ^{36}Cl/Cl ratios of Niche #1 core crushed and leached as part of the USGS study ranged between 226x10^{-15} and 717x10^{-15} and can be interpreted as containing no bomb-pulse ^{36}Cl. On the other hand, ^{36}Cl/Cl ratios for core from the same boreholes crushed and leached at LANL ranged between 1016x10^{-15} and 8558x10^{-15}, which supports the presence of bomb-pulse ^{36}Cl. These inconsistent results may be due to differences in the procedures used by the two groups, but initial attempts to determine the causes of the discrepancies were unsuccessful (Paces et al., 2003).

Chloride may be introduced into the leachate solution from sample surface coatings and pores, and by dissolution from the rock matrix. The possibility also exists that it can be introduced into sample leaches via contamination during sample preparation, especially as chloride is ubiquitous in most laboratory environments. The impact of chloride contamination on the ^{36}Cl/Cl ratio depends on the isotopic nature of the contaminating chloride and of the sample. Chloride that has been exposed to a neutron source may enhance the ^{36}Cl/Cl ratio, whereas chloride with natural abundance would diminish the ^{36}Cl/Cl ratio. Thus, "environmental factors" such as proximity of samples and/or the laboratory to neutron sources have been suggested as possible reasons for conflicting USGS/LLNL and LANL results. Road salt was ruled out as an explanation for the USGS/LLNL results (J. Paces, personal comm., 2003).

4.1 Background

Yucca Mountain, located in Nye County, Nevada, has been proposed by the United States as a repository for the nation's spent nuclear fuel and high-level nuclear waste. The Department of Energy has been tasked with evaluating the suitability of the site for long-term geologic storage of the waste and has conducted and funded numerous studies to that end. The Exploratory Research Facility (ESF) is an approximately 8 km long tunnel dug into Yucca Mountain to provide scientists access to collect samples and conduct in-situ studies that would have been otherwise impossible. A tunnel boring machine (TBM) dug the ESF between September 1994 and April 1997.

Studies to quantify ^{36}Cl and other isotopes in tuffaceous rock collected in the tunnel commenced as the TBM progressed through the mountain. There were a number of goals for these investigations including, but not limited to, testing of conceptual and numerical models of unsaturated zone (UZ) flow. ^{36}Cl data in particular were of interest to test whether certain geologic units above the repository horizon, namely (in the sequence observed in the field) the densely-welded base of the Tiva Canyon Tuff (TCw), the non-welded Paintbrush Tuff (PTn), and crystal-rich Topopah Spring Tuff (TSw) were effective barriers to vertical flow and whether fault systems within the mountain might provide fast pathways for transport of water to the repository horizon (Paces et al., 2003).

Several reviews describe the application and interpretation of ^{36}Cl data for hydrology and infiltration studies (e.g., Elmore et al., 1987; Phillips, 1994). Multiple sources for ^{36}Cl are present in the subsurface environment, however, the primary sources are meteoric and in-situ production (Lehmann et al., 1993). The former stems from interactions of cosmic radiation in the upper atmosphere with stable Cl and Ar resulting in production of ^{36}Cl that reaches the surface of the earth through wet and dry precipitation. Whereas production and deposition rates can vary with the geomagnetic field strength and climatic conditions, in the vicinity of Yucca Mountain the meteoric signal for ^{36}Cl/Cl had ratios of about 500×10^{-15} throughout the Holocene (CRWMS M&O 2000a). This ratio was interrupted when high concentrations of ^{36}Cl were produced as a result of activation of chloride during testing of thermonuclear weapons in the Pacific during the 1950's. Much of this bomb-pulse ^{36}Cl can be attributed to a few tests that were detonated within or near the ocean. Alternatively, the subsurface production ratio for ^{36}Cl/Cl from natural neutron fluxes within the host tuffs is smaller and is thought to produce ^{36}Cl/Cl values of about 40×10^{-15} (Fabryka-Martin et al., 1997).

Taking into account all potential sources of ^{36}Cl, Fabryka-Martin et al. (1997) used statistical methods to establish a cutoff ^{36}Cl/Cl value of $1{,}250 \times 10^{-15}$ as an upper limit of the normal distribution of background samples. Samples with ^{36}Cl/Cl ratios above this cutoff were interpreted to unambiguously reflect at least some component of bomb-pulse ^{36}Cl percolation. This threshold value was employed in our study to be consistent with previous studies and because there was no compelling reason to modify it; however, it is worth noting that Murphy

(1998) provided statistical evidence that samples with ^{36}Cl/Cl ratios greater than 950 x 10^{-15} to 1000 x 10^{-15} are likely to have a bomb-pulse component.

The USGS and LANL co-authored validation study report, due out latter this year, provides a history and reference list of studies of ^{36}Cl and fracture minerals in the ESF, as does a summary report currently available (Paces et al., 2003). LANL coauthored the final version of the validation study report due out later this year. It also includes a compilation of LANL data and presents a summary of a conceptual model explaining the distribution of ^{36}Cl in the Yucca Mountain UZ. Regarding the conceptual model, the report states that the dominant factor in controlling the location of bomb-pulse ^{36}Cl is the presence of faults cutting the PTn and providing a pathway to bypass matrix flow through the highly porous, nonwelded tuffs (Fabryka-Martin et al., 1997, Flint et al., 2001; Campbell et al., 2003). The report goes on to explain that surface infiltration rates are another important factor for subsurface movement of the bomb-pulse and that various simulations have been conducted using numerical flow and transport models that permit rapid percolation of bomb-pulse aged solutes to the proposed repository horizon depth using modified fault zone PTn properties (Fabryka-Martin et al., 1997; Wolfsberg et al., 2000). Predating the validation study report is a review and assessment of previous ^{36}Cl work at Yucca Mountain by Gascoyne (2001).

The validation study implemented by the USGS included a suite of samples crushed at the DOE Sample Management Facility in Area 25 of the Nevada Test Site, leached at USGS labs in Denver, with separate splits sent to both LLNL and LANL for target preparation and analysis at different AMS laboratories. ^{36}Cl/Cl ratios for these particular samples agreed within analytical error. However, there were large differences between USGS/LLNL and LANL results for Niche #1 core which was split between the groups and consensus was not reached on several fundamental points, including the cause of the different results (presence/absence of bomb-pulse ^{36}Cl), the conceptual strategy for sampling (systematic vs. feature-based), interpretation and use of tritium data (detection limit considerations), and the importance and interpretation of some blank values.

Much has been written regarding past studies of ^{36}Cl at Yucca Mountain, including a peer review report on ^{36}Cl studies at Yucca Mountain (YMP 1998) and a summary of ^{36}Cl validation studies at Yucca Mountain (Paces et al. 2003). A draft validation study report (dated July 2003) was provided to us by its USGS authors; however, it was subsequently revised, in part because scientists from LANL thought it presented a set of interpretations and overall tone that was biased toward the USGS conclusions. The final version of the validation study report was not completed and was unavailable to us at the conclusion of our study. We thus refer to both the published reports and the final validation study report (due out latter this year) in this document.

Table 1. Brief Timeline and Overview of Project

Approximate Date	Select Items
26-Aug-03	Funding awarded through cooperative agreement #DE-FC28-98NV12081, task 39
16-Sep-03	Project staff attended the NWTRB meeting to hear the discussion regarding the results of the previous Cl-36 studies
19-Nov-03	A meeting was conducted at the HRC that included interested parties from the USGS, LANL, DOE, members of the NWTRB and the UNLV Co-PIs. Various aspects of the project were discussed including issues related to sample collection and analytical procedures
20-Nov-03	Field trip to the ESF to discuss sampling issues/locations; attended by USGS, LANL and other
20-Nov-03	Scientific Investigation Plan (SIP) was approved
Dec-04	Sampling team completes necessary training and permits for underground work
2004, All	Sampling delayed >1 full year while upgrades and maintenance of the Mine Power Centers in the ESF were performed
Jan-04	PRIME was audited and added to the qualified supplier list for Cl-36 analyses by AMS
Mar-04	Completed a scientific audit on Cl-36 task by UCCSN Quality Assurance Program personnel
1-Oct-04	Quality assurance surveillance found no deficiencies
Oct-04	A series of blanks were prepared for Cl-36 measurements
Jan-05	A project extension was requested due to delayed access to the ESF
19-Feb-05	First set of blanks were analyzed for Cl-36 by PRIME and found to meet acceptance criteria
24-Feb-05	Personnel change as Cizdziel becomes Principal Investigator
Mar-05	The project was granted a 1 year extension (through 3-31-06)
2-Mar-05	Excavation and sampling of Sundance Fault was completed
21-Mar-05	Hand samples were collected from Bow Ridge Fault and Alcove 6
31-Mar-05	Task audited by NSHE QA group, no deficiencies found.
Apr-05	Samples were seived to separate the rock into different size fractions
May-05	Leach experiments were conducted to study the evolution of dissolved species over time
19-May-05	Cizdziel presents status of the Cl-36 project at the Devil's Hole Conference
Jun-05	Thirty-nine samples, standards and blanks were prepared and submitted for Cl-36 analysis
19-Jul-05	Excavation and sampling of Alcove 6 was completed
Aug-05	First set of samples were analyzed by PRIME and show possible Cl-36 contamination problem
21-Sep-05	Surface soil samples were collected above the north and south ramps of the ESF
Sep-05	Attempts to reduce background were made (e.g., lab cleaning, new water source)
Oct-05	A new series of blanks were prepared and submitted for analysis
Nov-05	October blanks were analyzed by AMS and although improved they were still relatively high on a mass basis; consensus was to abandon the current lab and supplies and try elsewhere.
Dec-05	New blanks were prepared in a different building at UNLV. Samples were submitted to CAMS to expedite analysis and results were found to be much better. The decision was made to analyze rock samples for PRIME's next run.
Jan-Feb-06	Samples were prepared for Cl-36 analyses
Feb 06	PRIME added to QSL for I-129 analyses
30-Mar-06	Last set of samples were analyzed for Cl-36 by PRIME
31-Mar-06	Project end date

5.0 METHODS AND MATERIALS

5.1 Sample Information

Collection of samples for bomb-pulse ^{36}Cl analysis was recognized as a key component in project and therefore considerable thought and discussion was undertaken to identify the most appropriate sampling strategy. The following sampling strategy was employed:

- Focus on sites where LANL obtained high ^{36}Cl/Cl anomalies
- To the extent possible collect material that "geologically" similar to LANL sample material
- Collect material free from contamination caused by tunnel activities
- Collect sufficient samples to permit replicate analyses
- Collect multiple samples per site that are defined as being "geologically" distinct, (i.e. more versus less broken, brecciated versus non brecciated, different location with respect to fault)
- Collect some sample material with known or expected anomalous ^{36}Cl/Cl to demonstrate that our laboratory techniques provide acceptable results (e.g. soil samples)

The best way to implement the strategy was to utilize a small DOE bobcat (excavator) to assist in excavating approximately one meter into the tunnel wall. This technique provided the best opportunity to avoid collecting potentially contaminated material lining the tunnel walls. Several sampling sites were selected and discussed with DOE personnel. DOE was willing to excavate three sites. The following three excavation sites were selected based on either multiple or strongly anomalous ^{36}Cl/Cl values obtained by LANL and also to test both fault zones and cooling joints for the presence of bomb-pulse ^{36}Cl: Sundance Fault Zone (ESF 35+93), Drill Hole Wash Fault Zone (ESF 19+33), and the cooling joint location in Alcove 6 at 1+68. In addition to the excavation sites, several sites were sampled that had previously-detected bomb pulse ^{36}Cl, and sites with no previously-detected bomb-pulse ^{36}Cl, were also chosen for hand-sampling. Sites in Alcove 6 were selected because the alcove walls had been washed down by workers less extensively than the main ESF tunnel, possibly reducing the potential for contamination of the tunnel walls. Hand sample sites include: 0+93 (west of the Sundance Fault), 1+52 (Ghost Dance Fault), and 1+60 (cooling joints).

Confirmation of laboratory techniques required sampling from locations known to have contained bomb-pulse levels of ^{36}Cl. Based on measurements from previous studies, the Bow Ridge Fault Zone (ESF 1+99.8) was the best candidate location for tuff containing elevated levels of ^{36}Cl and therefore rock from this zone was selected for hand-sampling. Surface soil sites above the north and south portal were also chosen for sampling to test our laboratory techniques. These sites were chosen based on previous ^{36}Cl/Cl results in LANL studies.

5.1.1 Subsurface Samples

Sampling techniques differed at the three excavation sites. Because of this, each excavation is described separately in the following paragraphs. All samples were numbered using SMF barcodes. All site descriptions are located on the SMF Sample Collection forms. At each sampling site the silicon blank was opened and placed a few meters from the sampling location. Table 2 lists information on the rock samples collected, and also the LANL samples and results that we attempted to replicate. Appendix 3 contains photos of some of the sample sites.

The first excavation took place on March 2, 2005 at the Sundance Fault (ESF 35+93). Prior to use, the bobcat was cleaned with distilled water by Yucca Mountain employees. The bobcat excavated ~0.5 m into the tunnel wall and two samples were collected from the footwall of the fault using hammers and chisels cleaned with distilled water from the Harry Reid Center at UNLV. Plastic sheeting was placed underneath the desired rock and the plastic sample bag was held flush against the rock. Much of the sample just fell into the sample bag after lightly hitting the rock. The bobcat then excavated another 0.3 m into the tunnel and reached the fault plane and two additional samples of material from the footwall of the fault were obtained. The final excavation removed remaining material from the footwall and allowed a sample from the hanging wall of the fault to be collected using the same methods. Each sample was labeled and taped closed and then placed and sealed in a labeled cloth bag. The blank was also sealed in a plastic bag and labeled. Sample collection forms were completed and sent to the SMF.

The second excavation took place on March 31, 2005 at the Drill Hole Wash Fault (ESF 19+33). Prior to use the bobcat was cleaned with distilled water. Because of the hardness of the rock at this location the bobcat was used to loosen the material for our sample. After the bobcat excavated approximately 0.5 m into the tunnel wall the exposure was examined and the sample area identified. Plastic sheeting was laid underneath this area and the bobcat excavated rock between 0.5 and 0.8 m into the wall. Latex gloves were used to move the excavated rock from the plastic sheeting into the plastic sample bag. Another sample was collected in a similar fashion from 1.08 to 1.28 m into the wall. During each sampling event the silicon blank was opened and placed a few meters away from the collection site. Each sample was then sealed, labeled and placed in a cloth bag that was then labeled and sealed. Sample collection forms were completed and sent to the SMF.

The third excavation took place on July 19, 2005 at the Cooling Joint location in Alcove 6 (1+68). Prior to use the bobcat was cleaned with distilled water. Again the bobcat was allowed to loosen the sample owing to the hardness of the rock. After the bobcat excavated approximately 1 meter of rock the exposure was examined and a suitable sample site in the face was chosen. Plastic sheeting was laid over the excavated material and the bobcat then removed the chosen sample material from the wall. The sample was placed into the plastic sample bag using the plastic sheeting to guide the rock into the bag. The silicon blank, placed adjacent to the sampling site, was left open during sampling, but not during excavation. Each sample bag was sealed, labeled and placed in a cloth bag that was then labeled and sealed. Sample collection forms were completed and sent to the SMF.

Several locations were also hand-sampled on March 21, 2005 in an effort to obtain a larger sample set than the limited number of excavations allowed by DOE due to limited resources. These sites include ESF 1+99.8 (Bow Ridge Fault Zone) and the following locations in Alcove 6: 0+93 (west of the Sundance Fault), 1+52 (Ghost Dance Fault), and 1+60 (cooling joints). Prior to sampling at each site a clean plastic sheet was placed at the foot of the sample site, hammers were cleaned using >18 MΩ/cm water from the HRC and wiped with clean rags, and the silicon blank was opened and placed 0.5 meter from the sample location. The rock was chipped out onto the plastic sheeting and then guided into the plastic sample bag using the plastic sheeting. Care was taken not to touch the sample. Each sample was sealed, labeled and placed in a cloth bag that was then labeled and sealed. Sample collection forms were completed and sent to the SMF. Two silicon blanks were used, one for the ESF site and the second for the Alcove 6 sites.

Table 2. Sample information for rocks and field blanks collected by UNLV (this study) and LANL from the Exploratory Study Facility.

UNLV					LANL		
SMF ID	Location	Date	Matrix	Description	SMF ID	Location	^{36}Cl/Cl (10^{-15})
SPC01034200	ESF 35+93	3/2/2005	Rock	1 bag: Tptpmn, excavated fractured wall rock, footwall of Sundance Fault	SPC00512511	ESF 35+93	2840 ± 231
SPC01034201	ESF 35+93	3/2/2005	Rock	1 bag: Tptpmn, excavated fractured wall rock, footwall of Sundance Fault	SPC00512511	ESF 35+93	2840 ± 231
SPC01034202	ESF 35+93	3/2/2005	Rock	1 bag: Tptpmn, excavated fractured wall rock, footwall adjacent to Sundance Fault plane	SPC00512511	ESF 35+93	2840 ± 231
SPC01034203	ESF 35+93	3/2/2005	Rock	1 bag: Tptpmn, excavated fractured wall rock, footwall adjacent to Sundance Fault plane	SPC00512511	ESF 35+93	2840 ± 231
SPC01034204	ESF 35+93	3/2/2005	Rock	1 bag: Tptpmn, excavated fractured wall rock, within Sundance Fault zone	SPC00512511	ESF 35+93	2840 ± 231
SPC01034205	Alcove 6 1+60	3/21/2005	Rock	1 bag: Tptpmn, hand sampled, fractured rock within cooling joint	SPC00525142	Alcove 6 1+60	1699 ± 70
SPC01034206	Alcove 6 1+60	3/21/2005	Rock	1 bag: Tptpmn, hand sampled, brecciated rock adjacent to cooling joints	SPC00525142	Alcove 6 1+60	1699 ± 70
SPC01034207	Alcove 6 0+93	3/21/2005	Rock	1 bag: Tptpmn, hand sampled, fractured rock/fault gouge, several meters west of Sundance Fault	SPC00525131	Alcove 6 0+93	1511 ± 48
SPC01034208	Alcove 6 1+52	3/21/2005	Rock	1 bag: Tptpmn, hand sampled, fractured wall rock adjacent to Ghost Dance Fault	SPC00525141	Alcove 6 1+52	3357 ± 132
SPC01034209	Alcove 6 1+52	3/21/2005	Rock	1 bag: Tptpmn, hand sampled, fault gouge adjacent to Ghost Dance Fault	SPC00525141	Alcove 6 1+52	3357 ± 132
SPC01034210	ESF 1+99.8	3/21/2005	Rock	1 bag: Tmbt1, hand sampled, fault gouge within Bow Ridge Fault zone	SPC00509016 SPC00509017 SPC00509018 SPC00509019 SPC00509020 SPC00509751	ESF 1+99.8	2138 ± 137, 2444 ± 169, 720 ± 49, 2378 ± 153, 2398 ± 154, 381 ± 16
SPC01034211	ESF 35+93	3/2/2005	Blank	Silicon, lump 98.5% (Aldrich)	NA	NA	NA
SPC01034212	Alcove 6	3/21/2005	Blank	Silicon, lump 98.5% (Aldrich)	NA	NA	NA
SPC01034213	ESF 1+99.8	3/21/2005	Blank	Silicon, lump 98.5% (Aldrich)	NA	NA	NA
SPC01034214	ESF 19+33	3/31/2005	Rock	2 bags: Tptpul, excavated wall rock, Drill Hole Wash Fault, 0.5 to 0.8 m into tunnel wall	SPC00503920	ESF 19+31	3023 ± 94 1838 ± 65
SPC01034215	ESF 19+33	3/31/2005	Rock	2 bags: Tptpul, excavated wall rock, Drill Hole Wash Fault, 1.08 to 1.28 m into tunnel wall	SPC00503920	ESF 19+31	3023 ± 94 1838 ± 65
SPC01034216	ESF 19+33	3/31/2005	Blank	Silicon, lump 98.5% (Aldrich)	NA	NA	NA
SPC01034228	Alc. 6 1+68	7/19/2005	Blank	Silicon, lump 98.5% (Aldrich)	NA	NA	NA
SPC01034229	Alc. 6 1+69	7/20/2005	Rock	2 bags: Tptpmn, excavated wall rock, fractured rock surrounded by cooling joints	SPC00525143	Alc. 6 1+68	1792 ± 77 499 ± 20

* UNLV samples were collected by Robyn Howley (Scientific Notebook #UCCSN-UNLV-059 Vol. 1). LANL DTN: LAJF831222AQ98.004

5.1.1.1 Geologic description of individual samples

The following sample descriptions were based on field notes and detailed examination at the Harry Reid Center at UNLV. The samples were handled in a manner that wouldn't disturb or contaminate the material. Latex gloves were used to handle a minimal amount of the sample.

SPC01034200: ESF 35+93; Right Rib; Tptpmn; Sundance Fault; Footwall

Sample is a densely welded tuff and breccia that consists of elongate rock fragments and very angular pieces of breccia. The largest fragment is 16 cm long by 10 cm wide but most fragments are < 5 cm. Sample color is purple-brown but some fragment surfaces are coated with white vapor-phase minerals including feldspars. Other surfaces are coated with an unknown purple mineral. Some slickensides are present on surfaces. Fine sand and silt coat all rock pieces (from sampling and transport).

SPC01034201: ESF 35+93; Right Rib; Tptpmn; Sundance Fault; Footwall

Sample is a densely welded tuff and consists of mostly elongate angular rock fragments. The largest fragment is 18 cm long by 10 cm wide but most pieces are under ~ 8 cm. Sample color is predominately purple-brown but some pieces are brown-orange. White vapor-phase feldspars coat some fracture surfaces and other samples have an unknown purple mineral coating fracture surfaces. Fracture surfaces are fairly smooth. Fine sand and silt coat all rock fragments (produced during sampling and transport).

SPC01034202: ESF 35+93; Right Rib; Tptpmn; Sundance Fault; Footwall-Fault Surface

Sample is a densely welded tuff and consists of predominately angular elongate rock fragments with rare pieces of breccia. The largest fragment is 20 cm long by 10 cm wide but most fragments are < 10 cm. Sample color is purple-brown but some fragment surfaces are coated with white vapor-phase feldspars. Some samples have slickensides and others are composed of cemented breccia. Fine sand and silt coat all rock pieces (from sampling and transport).

SPC01034203: ESF 35+93; Right Rib; Tptpmn; Sundance Fault; Footwall-Fault Surface

Sample is a densely welded tuff and breccia and consists of angular elongate rock fragments. The largest fragment is 16 cm long by 8 cm wide but most fragments are < 6 cm. Sample color is predominantly purple-brown with rare light brown-orange mixed with the purple-brown. Some fragment surfaces are coated with white vapor-phase feldspars and other surfaces are coated with an unknown purple mineral. Fine sand and silt coat all rock pieces (from sampling and transport).

SPC01034204: ESF 35+93; Right Rib; Tptpmn; Sundance Fault; Hanging Wall

Sample is a densely welded tuff and consists of angular elongate rock fragments and very angular pieces of breccia. The largest fragment is 20 cm long by 12 cm wide but most fragments are < 5 cm. Sample color is purple-brown with some light brown-orange areas. White vapor-phase feldspars with black specs coats some fracture surfaces while an unknown purple mineral coats other fracture surfaces. Fine sand and silt coat all rock pieces (from sampling and transport).

SPC01034205: Alcove 6 1+60; Left Rib; Tptpmn; NE Striking Fractures/Cooling Joints

Sample is a welded tuff and consists of angular elongate to equant rock fragments. The largest fragment is 13 cm long by 11 cm wide but most fragments are < 10 cm and > 2 cm. Sample color is light brown-orange with rare dark purple-brown spots. Fracture surfaces are rarely coated with vapor-phase feldspars, whereas other fracture surfaces are coated with an unknown black and purple coating. Fracture/joint surfaces are smooth and dark in color (almost polished). Minor amounts of white calcite and hematite are present. Fine sand and silt coat all rock pieces (from sampling and transport).

SPC01034206: Alcove 6 1+60; Left Rib; Tptpmn; Breccia near NE Striking Fractures/Cooling Joints

Sample is a welded tuff and consists of angular elongate rock fragments with rare breccia. The largest fragment is 10 cm long by 5 cm wide but most fragments are < 4 cm. Sample color is light brown-orange with dark purple-brown spots. Vapor-phase feldspar coating with black specs was only rarely identified. Slickensides are present on some samples. Fine sand and silt coat all rock pieces (from sampling and transport).

SPC01034207: Alcove 6 0+93; Left Rib; Tptpmn; West of Sundance Fault

Sample is a welded tuff and consists of angular rock fragments with rare breccia. The largest fragment is 7 cm long by 5 cm wide but most fragments are < 4 cm and > 1 cm. Sample color is light brown-orange with dark purple-brown spots. Vapor-phase feldspars were only rarely identified coating surfaces and in vapor phase partings. Slickensides are rare. Fine sand and silt coat all rock pieces (from sampling and transport).

SPC01034208: Alcove 6 1+52; Left Rib; Ghost Dance Fault; Tptpmn; Wall Rock Adjacent to Fault Gouge

Sample is a welded tuff and consists of angular rock fragments. The largest fragment is 9 cm long by 6 cm wide but most fragments are < 4 cm. Sample color is light brown-orange with dark purple-brown spots. White calcite is coating some surfaces of the purple-brown colored samples. Fracture surfaces are smooth with a black (shiny) coating. Fine sand and silt coat all rock pieces (from sampling and transport).

SPC01034209: Alcove 6 1+52; Left Rib; Ghost Dance Fault; Tptpmn; Fault Gouge

Sample is a welded tuff and fault gouge breccia, and consists of angular rock fragments and abundant breccia. The largest fragment is 7 cm long by 4 cm wide but most fragments are < 3 cm. Sample color is light brown-orange with dark purple-brown spots. Clay is present in the breccia. Fine sand and silt coat all rock pieces (from sampling and transport).

SPC01034210: ESF 1+99.8; Right Rib; Bow Ridge Fault; Tmbt1; Fault Gouge

Sample is a lithophysal welded tuff and fault gouge breccia and consists of angular rock fragments and abundant breccia. The largest fragment is 7 cm long by 6 cm wide but most fragments are < 3 cm with a large sand, silt, and clay size fraction. Sample color is whitish-purple; fines are white. Clay is present in the breccia. Fine sand and silt coat all rock pieces (from fault gouge, sampling, and transport).

SPC01034214: ESF 19+33; Right Rib; Drill Hole Wash Fault; Tptpul; Unfractured Wall Rock; 0.5 to 0.8 m from Fault Plane

Sample consists of angular rock fragments of lithophysal welded tuff with rare breccia. The largest fragment is 14 cm by 4 cm by 5 cm but most fragments are < 6 cm by 5 cm by 3 cm. Sample color is light purple-pink in some areas and dark brown in other areas. Lithophysal cavities are bleached white with a crystalline calcite and hematite lining. White pumice fragments are common. Fine sand and silt coat all rock pieces (from sampling and transport).

SPC01034215: ESF 19+33; Right Rib; Drill Hole Wash Fault; Tptpul; Unfractured Wall Rock; 1.08 to 1.28 m from Fault Plane

Sample is a lithophysal welded tuff and consists of angular elongate to equant rock fragments with rare breccia. The largest fragment is 17 cm by 10 cm by 5 cm but most fragments are < 7 cm by 5 cm by 3 cm. Sample color is light purple-pink in some areas and dark brown in other areas. Lithophysal cavities are white and lined with crystalline calcite. White pumice fragments are common. Fine sand and silt coat all rock pieces (from sampling and transport).

SPC01034229: Alcove 6 1+68; Left Rib; Cooling Joints; Tptpmn; Highly-Fractured Wall Rock; Near-Vertical NW-Trending Cooling Joints & Near-Horizontal Vapor-Phase Partings

Sample is a densely welded tuff and consists of angular elongate rock fragments with rare breccia. The largest fragment is 10 cm by 4 cm by 3 cm but most fragments are < 5 cm. Sample color is light reddish-brown but with irregular mottled light purple areas. Rare off-white fragments that may be vapor-phase mineralization are present. Vapor-phase feldspars are abundant. Fine clay coats all rock pieces (from sampling and transport).

5.1.2 Surface Samples

Samples of soil were collected from three general sites: two on Yucca Mountain above the north and south ESF portals (YM1-SR and YM2-NR) and one in the Las Vegas Valley (LV1). Soil profile samples were collected at undisturbed locations by first digging a shallow trench using a shovel and then collecting samples at measured depths. Several kilograms of soil were placed into plastic bags, labeled and stored for analysis. Locations and detailed sample information are provided in Table 3. The purpose of collecting these samples was, in part, to test whether our analytical methodology was able to detect elevated ratios of ^{36}Cl in samples expected to contain the bomb-pulse signal.

Soil from Las Vegas was collected because of the significant delay in obtaining the special clearances needed to collect the Yucca Mountain samples (surface sampling was scheduled relatively late in the study) and because the results from the soil analyses could prove useful early in the project. A soil profile was collected in the south part of Las Vegas Valley near the Interstate Highway (I-15) from an undisturbed vacant plot of land adjacent to the Southern Highlands community. The terrain was flat and, although the site was near a wash, it was outside the confines of the main channel. A trench was dug with the dimensions of ~ 1 m by 0.5 m with a depth of ~ 0.45 m. Samples were collected at ~15 cm intervals and placed into plastic bags. For the Las Vegas Valley samples, soil was passed through sieves with openings of 12.5 mm (to remove larger rocks and debris) and 2 mm (to obtain the gravel fraction).

Collection of soil over the south portal was problematic and more difficult than the north portal because the terrain had significant rock outcrop and soil coverage was sporadic and thin. Where soil was present a hard barrier (possibly caliche) was encountered at a relatively shallow depth. In contrast, the soil at the north ramp was more uniform (lack of outcrop, no caliche, thicker soil layer) and greater sampling depths were attained.

Table 3 Sample information for surface soils

SMF ID	UNLV ID	Depth (cm)	Location		
			N	W	Elevation (m)
SPC01034237	YM-SR1-1	0-15	36°49'42.7"	116°26'21.9"	1193
SPC01034238	YM-SR1-2	13-22			
SPC01034236	YM-SR1-3	20-30			
SPC01034239	YM-SR2-1	0-13	36°49'43.3"	116°26'24.5"	1202
SPC01034240	YM-SR2-2	10-25			
SPC01034231	YM-NR1-1	0-14	36°51'35.9"	116°26'48.8"	1245
SPC01034232	YM-NR1-2	14-30			
SPC01034230	YM-NR1-3	30-43			
SPC01034234	YM-NR2-1	0-11	36°51'35.9"	116°26'53.6"	1252
SPC01034235	YM-NR2-2	11-30			
SPC01034233	YM-NR2-3	30-40			
NA	LV1-1	0 – 15	35°59'48"	115°11'02"	2287
NA	LV1-2	15 - 30			
NA	LV1-3	30 – 45			

MOL.20060531.0195. Locations are UQ and provided for informational purposes only.

5.1.3 ESF South Portal Seepage Samples

During the course of the UNLV study, water began to drip (seep) from the tunnel walls near the entrance to the south ramp of the ESF. The cause of the seepage was presumed to be related to the relatively high levels of precipitation incurred during the winter of 2004/2005. About 300 mm (11.8 in) of rainfall was recorded at nearby precipitation monitoring station 412 during the period of 10/1/04 – 02/28/05 (DTN: MO0604UCC007AB.003), which is well above the prior 10 year average of ~92 mm (3.6 in) for the same period. The 10 year average for winter rainfall was calculated based on 1987-2004 data, excluding 1996 – 1999 due to lack of available data for that period (DTNs: GS950208312111.001, GS970308312111.003, GS000808312111.004, UN020SPA030AB.001, 030AB.003, 007AB.001, 007AB.002). Whereas the increased precipitation may have initiated the event, it is not clear whether the infiltration was inducing older water to exit or if there was some fast and direct transport of the recharge, or both. Because of keen interest in these seeps among scientists studying Yucca Mountain, select samples were obtained for ^{36}Cl analysis.

Seepage water was collected by Chuck Savard (USGS) and John Kelly (Sandia National Laboratory) on 8 March 2005 between 9:30 am and 3:00 pm. Sampling activity was documented in scientific notebook # SN-SNL-SCI-023-V4 and additional details are presented in Table 4. In short, drips were fed into plastic (LDPE) or amber glass bottles using a large plastic funnel. Conductivity and pH were measured (Ultrameter; SN 606098) when volume permitted analysis. Samples were stored in a refrigerator until shipping or delivered to the HRC laboratory. At the HRC, the samples were passed through 0.45 μm PVDF Whatman syringe filters and analyzed using the same procedure as the leachates (Section 5.4).

Table 4. Sample information for ESF south portal water seepage

SMF ID	ESF Coordinates	Drip Location	Field Measurements		
			Conductivity		pH
			(µs)	(PPM)	
SPC01034573	76+00	middle ceiling	NA	NA	NA
SPC01034574	76+00	ceiling near left rib	882	580	6.9
SPC01034575	75+97	ceiling near right rib	583	380	7.5
SPC01034576	75+94	ceiling near left rib	645	419	7.6
SPC01034578	75+75	middle ceiling	NA	NA	NA

Samples were collected by J. Kelly (SNL) and C. Savard (USGS). Data are from Sanchez (2005) and are considered unqualified. Data are provided here for information purposes only.

5.1.4 Archived samples

After multiple discussions with USGS and LANL personnel it became apparent that very little sample material from previous studies was available for further study. Most of the samples from prior studies had been consumed in the course of those investigations, whereas others were kept in conditions that made them questionable or unsuitable for analyses. Several core samples from USGS were, however, received via chain-of-custody. Table 5 shows data for the core section received with the highest TU. Several of these samples were of interest because they represent sections of core that were previously distilled for tritium analysis. Two of these samples had very low values (TU: <0.1 and 0.22 ± 0.34) and two were relatively high (10.3 ± 1.8 TU and 14.3 ± 2.0 TU). Whereas the entire core was available for the samples with low TU, portions of the other two cores were unavailable. For the core section, which resulted in 10.3 ± 1.8 TU (4.3-7.1m), 4.3-5.0 m and 6.4-7.1 m were obtained but 5.0-6.4 m was missing. For the core that yielded 14.3 ± 2.0 TU (4.5-6.9 m), 4.5-5.4 m and 6.5-6.9 m were obtained but 5.4-6.5 was unavailable.

Table 5. Archived drill core received with the highest TU (selected for Cl-36 analysis)

SMF ID	Borehole Name	Intervals (m) analyzed by USGS for tritium	TU	Intervals (m) available for UNLV study
SPC01004844 SPC01004848	ESF-SR-MOIST STDY#19	4.5-6.9	14.3 ± 1.0	4.5-5.4 6.5-6.9

DTNs: GS060308312272.001

5.2 Sieving of samples and size classifications

Select samples were sieved to separate the rock into different size fractions. Roback et al. (2003) illustrated that leaching of the finest particles, commonly termed "rock flour" and produced along faults, results in loss of meteoric ^{36}Cl signal (produced low ^{36}Cl/Cl ratios) due to dilution by stable Cl leached from the rock matrix. At the other extreme, leaching of large chunks of rock may not yield enough meteoric Cl because of reduced surface areas available for leaching (e.g, Roback et al., 2003). As a result, prior studies have commonly employed sieving to separate the size fractions for analysis. The USGS validation study samples were crushed and the 6-13 mm size fractions were leached and evaluated (Paces et al. 2003). LANL commonly leached unconsolidated material (such as fault gouge) in the same form as received (uncrushed). For most other samples, the rock was broken with a hammer to produce chips ~ 1 to 2 cm in size (Fabryka-Martin et al., 1996). In the UNLV study, both unaltered material and selected size fractions, particularly fines and gravel, were analyzed in an effort to increase the likelihood of obtaining a bomb-pulse signal if one was present in the rock.

A LLNL procedure for sieving soil and rock samples (TIP-CL-89) was followed with slight modifications. Details of our method are documented in scientific notebook number UCCSN-UNLV-065 Vol. 1. In short, a large portion (50% or greater) of the original sample was weighed for sieving. A.S.T.M. sieves were stacked in series from the largest mesh size to the smallest in the following order: 75 mm, 12.5 mm, 2.0 mm, and 0.125 mm. The sample was transferred into the top sieve until nearly full, the sieve was covered, and the stack was placed in a shaker. The entire column of sieves were shaken for a period of 10-15 minutes. The various size fractions were then transferred into pre-labeled plastic bags and the procedure was repeated until the entire sample was sieved. The following descriptions were selected for the size fractions: <0.125 mm = "rock flour", 0.125 – 2.0 mm = "fines", 2.0 – 12.5 mm = "gravel", 12.5 – 75 mm = "large pieces", >75 mm = "coarse rock".

5.3 UNLV leaching studies

A study measuring anions and rare earth elements in leachates of ESF rock as a function of time was conducted to guide our leaching conditions for ^{36}Cl. The time-series leach was conducted with two samples, one consisting of fractured rock (SPC01034203) with a relatively low 24 hr passive Cl^- leachate concentration (0.616 mg/kg rock) and the other consisting of fault gouge (SPC01034207) with a relatively high Cl^- leachate concentration (23.26 mg/kg rock). The 12.5 – 75 mm fraction was chosen because the gravel fraction (2 – 12.5 mm) had been used for ^{36}Cl measurements.

The samples were first blown down with a gentle stream of dry nitrogen gas to remove dust and other loosely bound particles. They were then weighed into stainless steel buckets and an equal mass of deionized water was added. The rock-water mixture was allowed to sit (passive leach). Thirty mL subsamples of water were drawn out of the bucket ~ 1 cm below the surface using a 50 mL syringe vial. A 0.45 µm PVDF Whatman syringe filter was fitted to the end of the vial and the subsample was pushed through the filter into two 50 mL centrifuge vials (~ 15 mL each) for IC (Cl^-, Br^-, SO_4) and ICP-MS (trace elements) analysis. Thirty mL of deionized water was returned to the buckets to maintain the same leach volume. The buckets were covered with parafilm between sampling. Samples were collected at 0.75, 1.5, 3, 6, 12, 24, and 48 hours after start of the leach (0 time). Three samples from different parts of the bucket were collected at the 48 hour period to assess sampling and analytical variability. The remaining leachates and rock samples were transferred to clean plastic containers and are stored in a locked laboratory.

5.4 Preparation of samples for ^{36}Cl analysis

Samples were leached following a batch extraction method for chorine isotope analyses prepared by Fabryka-Martin (LANL-CST-DP-92, R2), with slight modifications. Details of the procedure are documented in the scientific notebook (UCCSN-UNLV-065, Vol. 1). In short, rock or soil samples were combined with deionized water (>18.1 MΩ/cm) in an approximate proportion of 1:1 (on a mass basis) in stainless steel buckets. In later analyses, distilled water in plastic gallon containers was purchased from Walgreens Company and used for leaching. The distilled water was removed from the jugs and the plastic containers were cut to allow the addition of rock. Distilled water from an unopened container was added in equal weight to the rock. The mixture was allowed to sit passively for 24 hours before the water was decanted and vacuum-filtered through a 0.45 µm cellulose nitrate membrane.

An aliquot of the sample (~15 mL) was analyzed by IC to determine the chloride content. ^{35}Cl tracer obtained from Oak Ridge National Laboratory or chloride from an ammonium salt purchased from Aldrich was added to augment the recovered chloride to a total of 2.5 mg (before May 22, 2005) or 3.5 mg (after May 22, 2005). Samples containing sufficient chloride for processing were not spiked with the tracer or carrier solution. Addition of the tracer has the added benefit of allowing an independent measure of the chloride leachate concentration through the isotope dilution method.

Samples were neutralized to a pH of ~7 by addition of 1 or 2 drops of concentrated high purity ammonia prior to reducing the volume to ~500 mL by evaporation on a hotplate. These steps are necessary to prevent loss of chloride through volatilization of HCl and to facilitate precipitation of AgCl because it is difficult to recover good yields of chloride from highly dilute solutions. After concentrating the solution, the leachate was then processed to produce AgCl precipitate for ^{36}Cl analysis.

A detailed procedure along with experimental notes describing how to process soluble chloride leached from rock or soil into purified AgCl precipitate for ^{36}Cl AMS analysis can be found in LANL-INC-DP-95, R1 (authored by Fabryka-Martin and Wightman) and scientific notebook UCCSN-UNLV-065, Vol. 1. Briefly, leachates are acidified with ~1mL/L of concentrated high purity nitric acid to increase the ionic strength of the aqueous sample. A solution of silver nitrate was added in stoichometric excess to form AgCl precipitate. The solution was allowed to settle overnight in the dark (AgCl is sensitive to light, and Cl may volatilize as Cl_2). To collect the precipitate, the solution was decanted and/or split into several centrifuge tubes, which were spun at ~3000 rpm for 5 minutes and the supernatant decanted. The AgCl precipitates were combined into a single tube and redissolved in a minimum of ammonium hydroxide; the supernatant was collected and any insoluble precipitate was discarded.

Sulfate was removed by adding 1 mL of saturated $Ba(NO_3)_2$ solution to the NH_4OH-AgCl solution and precipitating $BaSO_4$. The solution was centrifuged and the clear supernatant decanted into a clean centrifuge tube. The clear solution was acidified with drops of concentrated HNO_3 until no additional white AgCl precipitate formed. The centrifuge tube was spun (as before) and the supernatant discarded. The AgCl precipitate was washed in the centrifuge tube using deionized water, spun and the supernatant discarded. The water wash was repeated before drying the precipitate in a convection oven at ~85°C. The dry precipitate was weighed, wrapped, and shipped to PRIME for AMS measurements.

5.5 Preparation of ^{36}Cl standards

A ^{36}Cl standard (SRM 4943) obtained from the National Bureau of Standards (now the National Institute of Standards and Technology) was certified as containing 1.07×10^{4} β^{-} s^{-1} g^{-1}, which corresponds to 1.49×10^{17} atoms of ^{36}Cl g^{-1} of solution (Fabryka-Martin notebook, LA-CST-NBK-95-012, pages B8-B12). This standard was used to prepare three working standards with nominal ^{36}Cl/Cl ratios of 500×10^{-15}, $2{,}500 \times 10^{-15}$, and $10{,}000 \times 10^{-15}$. These standards were prepared as follows.

1. One mL of SRM 4943 solution (^{36}Cl solution I) was diluted to 1 liter in a volumetric flask (^{36}Cl Solution II). The resultant solution contains ^{36}Cl at a concentration of 1.49×10^{14} atoms/mL.

2. One mL of ^{36}Cl Solution II was diluted to 1 L to produce ^{36}Cl Solution III. This ^{36}Cl solution contains 1.49×10^{11} atoms ^{36}Cl/mL.

3. A solution of dead (^{36}Cl-free) chloride was prepared by dissolving 53.109 g of oven-dried NH_4Cl (Aldrich, 99.998%, Batch #15714EB) in 1 L of deionized water in a volumetric flask (^{36}Cl-free Solution). PRIME uses this material for its chloride blanks (typically around 1×10^{-15}) and our results show similarly low levels. Others have used Jurassic halite (NaCl) from the Weeks Island salt mine, but the actual ^{36}Cl/Cl ratios in solutions made from this material may be slightly higher than the calculated values due to trace impurities in the halite. The calculated chloride concentration in our solution is 35.2 g/L or mg/mL (5.98×10^{20} atoms of Cl/mL). A portion was submitted for IC analysis.

Three 250 mL portions of the ^{36}Cl-free solution were measured in volumetric flasks. To one portion was added 0.5 mL of ^{36}Cl Solution III, resulting in a ^{36}Cl/Cl standard with a calculated ratio of 498×10^{-15} (called the "500" standard); to another was added 2.5 mL of ^{36}Cl Solution III, resulting in a ^{36}Cl/Cl standard with a calculated ratio of 2492×10^{-15} (called the "2,500" standard); and to the third was added 10.0 mL of ^{36}Cl Solution III, resulting in a ^{36}Cl/Cl standard with a calculated ratio of 9970×10^{-15} (called the "10,000" standard). A 1 mL Eppendorf pipet (Bechtel ID 3310191), which typically has errors of <2%, was used for the ^{36}Cl additions.

5.6 Electron microscopy and imaging

After the rock samples were described a portion was split from the original for examination in the scanning electron microscope (SEM) and electron microprobe. These samples were selected to represent the entire sample, sealed in labeled plastic zip lock bags, and transferred to the UNLV Geoscience Department where they were stored in a locked cabinet. Several fragments were chosen from each sample for analysis in the SEM and electron microprobe. Latex gloves were used when handling the samples. Prior to use each fragment was given a geologic split number (e.g., -1, -2, etc...) to add to the original SPC barcode and each fragment was photographed.

Both rough and sawed samples were used for SEM analysis. Most of the samples were rough but some were cut at UNLV in TEC 121 using the Isomet Low Speed Saw with fresh Isocut fluid and clean blades following the procedure in IPLV-076, "Polished Thick Section Preparation for use in the Electron Probe Microanalyzer." After samples were cut they were each submersed in separate beakers of methanol (CH_3OH) for several hours until all of the Isocut fluid was removed. The use of methanol deviates from the procedure that calls for isopropanol but there is minimal difference between the two and neither will remove the soluble Cl ions (R. Fairhurst, personal comm. 2006). After drying, the samples were photographed and sealed in plastic containers.

Samples to be analyzed with the electron microprobe were sawed and prepared as described above. After drying, the samples were photographed and sealed in plastic containers. Samples were then shipped to Mark Mercer for polishing following IPLV-076. This procedure was written to make sure that the samples were not polished using any water or water-based products. Microprobe analyses were performed following the procedures in IPLV-015, "Electron Microprobe Analysis on the JEOL 8900-R, Rev. 2."

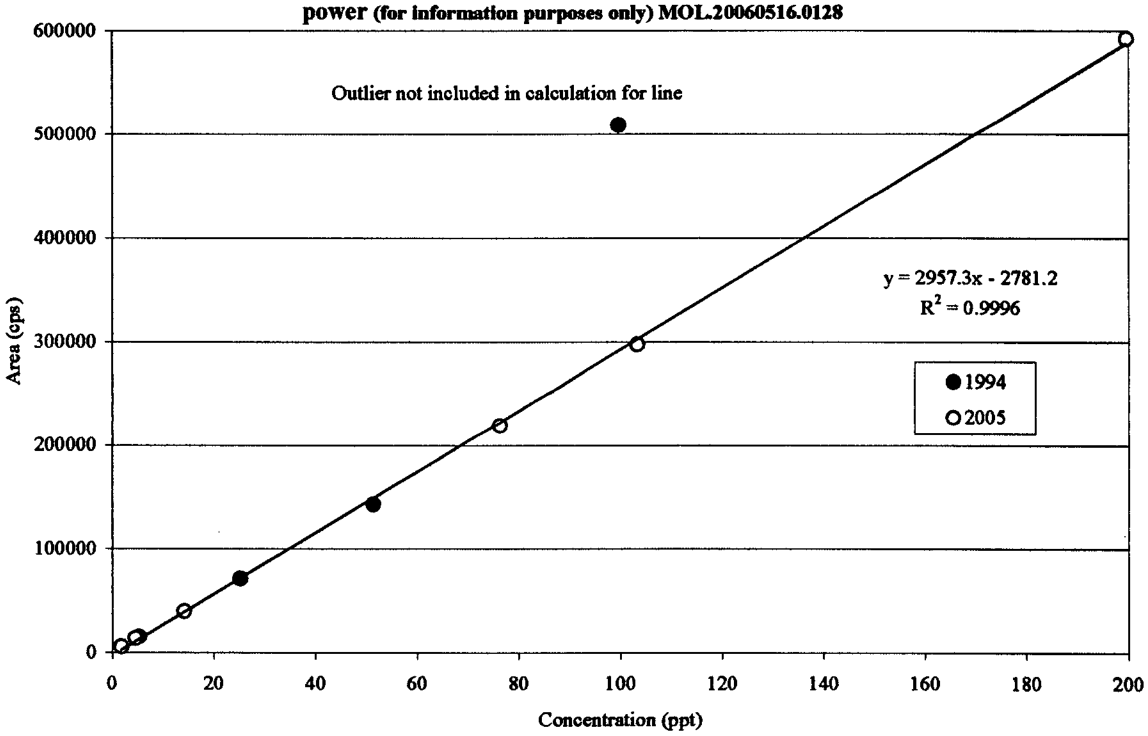
Prior to analysis, samples were carbon-coated according to IPLV-019, "Carbon Coating Thin Sections and Samples with Rough Surfaces for Electron Microprobe and Scanning Microscope Analyses." Carbon tape was placed on several samples, whereas other samples were mounted to holders using liquid carbon. When not in use, samples were stored in plastic containers within the desiccation cabinets. SEM analyses followed the procedures in IPLV-062, "Scanning Electron Microscope Analysis on the JSM-5600."

5.7 ^{99}Tc and ^{129}I analyses

Thirteen samples were selected and analyzed for ^{99}Tc. Samples were combined with deionized water in a 1:1 (weight) ratio and allowed to sit passively for 24 hours. Tc-99 was preconcentrated from the leachates using a Tc-specific resin (Teva Disc from Eichrom). The Tc was eluted in a minimum volume of nitric acid and the solution was introduced to an ICP-MS using a microflow nebulizer. The magnetic sector instrument was operated in low resolution mode. Typical instrument sensitivity is $\sim 1 \times 10^6$ cps for 1 ppb of In. Pt was used as an internal standard. The method detection limit was estimated at 26 ng L^{-1}. Measurement (internal) precision (RSD) of the analysis varied as a function of concentration: at ng L^{-1} concentrations it was about 3% or better and at pg L^{-1} concentrations it was below 10%.

A NIST standard (SRM 4288A) was used for ^{99}Tc calibration. Five solutions with concentrations ranging from 2 to 200 ng/kg (ppt) were prepared by diluting the reference material in 1% HNO_3. A second set of standards of similar concentrations prepared more than a decade earlier by a different person and from a different source were compared with the freshly prepared standards. Testament to the stability and solubility of the pertechnetate anion, 3 of the 4 older standards fell on the calibration line (Fig. 1). These results suggest that the calibration line was accurate and that the procedure used to prepare the standards did not result in any significant losses (through volatilization or adsorption) or additions (through contamination).

Fig. 1 ICP-MS calibration curve for Tc-99 for two sets of standards at ~4000 resolving power (for information purposes only) MOL.20060516.0128



For ^{129}I, difficulty was experienced in preparing samples for AMS measurements. Because of time constraints we instead attempted to measure the analyte by ICP-MS. Leachates were analyzed directly without preconcentration. The instrument was operated in high resolution mode (~10,000 resolving power) although no interfering peaks were observed. Other parameters were identical to those described for ^{99}Tc above.

^{99}Tc and ^{129}I were also measured on the surface of three samples of ESF rock before and after leaching with distilled water by laser ablation ICP-MS (for information purposes only). A 266 nm laser was used as a solid sample introduction device for a time-of-flight ICP-MS. Line scans were conducted across select surface features at full energy using a 200 micron spot size setting and the signal at mass 29 (Si), 99 (Tc), 129 (I), and 238 (U) were monitored. Additional details for all of the above measurements can be found in the scientific notebook (UCCSN-UNLV-065 and -068, V3 and V1, respectively).

5.8 ICP-MS and Ion Chromatography Procedures

Measurement of trace elements, including ^{99}Tc and ^{129}I, were conducted using an ICP-MS. Anions, including Cl$^-$, were determined using an ion chromatograph. Both procedures are detailed in implementing procedures, IPLV-009 R4 and IPLV-008 R5, respectively, and will not be discussed here. The procedures are available on the NSHE QA program's webpage at http://hrcweb.nevada.edu/qa/iplv.htm.

5.9 ^{36}Cl Column Experiment

A column experiment was conducted to mimic the passage of water containing bomb pulse levels of ^{36}Cl through/over repository rock. Five 200 mL columns containing a wire mesh/screen at its base to retain the tuff were cleaned with distilled water prior to addition of select samples. Column #1 (C1) was filled with 150.7 g of SPC01034200 (0.125-2mm); C2 with 168.4 g of SPC01034201 (2-12.5mm); C3 with 181.5 g of SPC01034205 (2-12.5mm); C4 with 158.4 g of SPC01034205 (12.5-75mm, ~25 pieces); C5 with 161.8 g of SPC00557088 (Eval#1, previously leached on 10/28/05); and C6 served as a blank.

Two hundred mL of distilled water (~ 3 pore volumes) was added to each column and the water was allowed to saturate the rock overnight before slowly draining into 250 mL polyethylene bottles labeled leach 1. Flow rates of ~1 mL per minute, about the mid point of the range of flow found for the south ramp seeps, were used (Sanchez, 2005). Approximately 200 mL of additional distilled water was added to each column to saturate and cover the rock, and ~15 mL was allowed to drain into the leach 1 bottle to capture the water trapped at the base of the column. The remaining water was slowly passed through the column and collected in a second bottle labeled leach 2. The columns were then placed in an oven at ~85°C overnight to dry.

A Cl-36 standard containing a nominal ^{36}Cl/Cl ratio of 2500 (SN UCCSN-UNLV-065, Vol. 1, p.49) was prepared with a Cl$^-$ concentration of 72.8 μg/g, similar to the average found for the ESF south ramp seep water (~73 ± 41μg/g, n=11). This new solution was named Cl-36 2500 standard V.

The columns were removed from the oven to cool. The extent of the drying depended on the rock fraction size. Column 5 and 6 were almost completely dry (as determined visually). Only the bottom 10% of the rock surfaces remained moist. In contrast, column #1 (containing the finest fraction) remained moist except for the top 20%. Moisture in the other columns was in between these extremes. Two hundred mL of Cl-36 2500 standard V was added to each column and the effluent was collected into labeled 200 mL polyethylene bottles (labeled spike) as before. The columns were once again dried - over the weekend at ~85°C.

The columns were removed from the oven to cool. Columns 2, 4, and 6 were completely dry, columns 3 and 5 were ~80% dry (bottom 20% moist), and column #1 was ~50% dry. Two hundred mL of distilled water (same size "event" as before) was passed through each column at a slow rate and captured into polyethylene bottles labeled as wash #1. The columns were placed in the oven to dry overnight at ~85°C. Columns 4, 5 and 6 were completely dry, columns 2 and 3 were ~70% dry (bottom 30% moist), and column #1 was ~20% dry. Again 200 mL of distilled water was passed through each column at a slow rate (~1 mL/min) and captured into polyethylene bottles labeled as wash #2. About 5-10 mL were passed through a 0.45 μm filter and submitted for chloride analysis by IC. The remaining portion was filtered and ten samples (due to limited time) were selected for ^{36}Cl analysis (prepared as described in Section 5.4). After the experiment was complete, rock volumes were determined by adding water to each column containing the dry rock until the rock was saturated and column was full. The volume of water added was subtracted from 200 mL (the volume of the empty column) to obtain the volume associated with the rock.

6.0 ASSUMPTIONS

Fabryka-Martin et al. (1997) established a cutoff $^{36}Cl/Cl$ value of 1250×10^{-15} with ratios above this threshold interpreted to signify at least some component of bomb-pulse ^{36}Cl percolation. This cutoff value was assumed to be correct and was employed in our study to be consistent with previous studies.

7.0 DISCUSSION/CONCLUSIONS

7.1 Results of initial ^{36}Cl analyses

7.1.1 Elevated blanks: an unwanted surprise

Results for a series of blanks in the fall of 2004 were promising. Each of the four blanks had ^{36}Cl/Cl ratios below 5 (x10^{-15}) (Table 6) and were deemed acceptable, based on criteria established by LANL (MOL.20030205.0114, p. 16). The blanks were prepared with a chloride carrier solution (~1 mg/g) using an ammonium salt from Sigma Aldrich. The data were interpreted to signify that our laboratory reagents and environment were free of ^{36}Cl contamination. Three reagent/process blanks yielded ratios (x10^{-15} ± 1σ) of 1.3 ± 1.3, 1.2 ± 1.5, 0.5 ± 1.4, and the one silicon chip blank (purchased from Aldrich and used as field blanks) had a ratio of 3 ± 1.6 (x10^{-15} ± 1σ). For each of these blanks the corresponding amount of ^{36}Cl was <10 mg (x10^{-15}), which was similar to the blanks measured at USGS and LANL. At this point we were ready to analyze rock samples, but sampling was delayed until the spring of 2005 due to an extended shutdown of the tunnel (see Table 1).

In March and April 2005, soon after the tunnel was reopened to scientists, samples were collected and immediately leached and processed for ^{36}Cl measurements. Because of the infrequent occurrence of ^{36}Cl analytical runs by PRIME (typically only once every few months) a large number of samples were processed while awaiting the next opportunity for AMS analysis. PRIME was the only facility considered a qualified supplier by our QA program. The run was expected to yield the bulk of the project's data and guide follow-up work. Unfortunately, PRIME experienced some unexpected delays and held our samples for about three months before analyzing them on August 19th, 2005.

The first set of results were surprising in that several samples had extremely high measured ^{36}Cl/Cl ratios, with a few in excess of 50,000 (x10^{-15}) (Table 7). Among those samples was SPC00557088 (Eval#1) which had a ratio of 300,000 ± 110,000 (1σ) x10^{-15}. This sample was previously measured by USGS/LLNL and LANL and found to have ^{36}Cl/Cl ratios of 454 and 361, respectively. Moreover, the reagent/process blank (880 ± 20 (x10^{-15})) was much higher than earlier values. A sieving blank, 3200 ± 200 (x10^{-15}), and several field blanks, 850 ± 30, 470 ± 20, 410 ± 20, 740 ± 20, each (x10^{-15}), also had relatively high ratios. These blanks were processed the same way as those in the fall of 2004 except that ^{35}Cl tracer from Oak Ridge was used instead of the Aldrich salt. More important than the actual ratios was that the absolute amount of ^{36}Cl in the blanks had increased substantially. The field blanks (n=5) had an average of about 1000 mg (x10^{-15}) of ^{36}Cl and curiously the reagent blank had even more. These values are well above those found by the LLNL and LANL. The mean mass of ^{36}Cl (mg x 10^{-15}) in the two groups validation study blanks were 3.1 and 15.7, respectively (DTNs LL030605223121.030, LA0305RR831222.001).

Among the samples with unexpectedly high ratios were two core sections obtained from the USGS that were leached together. SPC20114361 and SPC2014365 produced a measured ratio of 33,600 ± 600 (x10^{-15}) (Table 7). Although the three other core sections produced reasonable ratios ($<1400 \times 10^{-15}$) and may not have been contaminated, the high blank values prevent interpreting these data with confidence.

Results for a series of ^{36}Cl standards and seepage samples submitted for analysis along with the rock samples appeared to be unaffected, possibly because they were prepared separately from the rock samples and may not have been contaminated. Another possibility is that the relatively high concentration of chloride in the standards and seepage may have swamped out any contamination problem.

These unreasonably high ratios and ^{36}Cl blank concentrations were disturbing and pointed to a possible contamination issue. Fortunately there was enough sample material and time to investigate the problem. The following sections document our approach to identifying and solving the problem (7.1.2), discussing those data that had reasonable ^{36}Cl/Cl ratios (7.1.3 and 7.1.4), and presenting results for rock and soil obtained after solving the blank crisis (7.2).

Note: in general, ^{36}Cl/Cl ratios presented in tables contain exact numbers for traceability, whereas in the text numbers may have been rounded.

Table 6. Cl-36 Accelerator Mass Spectrometry (PRIME) Results for Yucca Mountain Samples (initial blank analyses, Q data)

Aliquot ID for AMS	PRIME ID	SMF ID	Start Date of Leach or Preparation	Sample Information	Mass of Cl added (mg)	36Cl/(35Cl+37Cl) (E-15)						35Cl/37Cl			Target (mg)
						Measured Ratio	± SD	RSD (%)	Blank Corr Ratio	± SD	RSD (%)	Measured Ratio	± SD	RSD (%)	
2/19/2005 AMS Run															
B1-102504	200401038	NA	10/25/2004	Blank	5.00	1.2	1.3	108.3	NA	NA	NA	NA	NA	NA	1.8
B2-102504	200401039	NA	10/25/2004	Blank	5.00	1.3	1.5	115.4	NA	NA	NA	NA	NA	NA	11.9
B3-102504	200401040	NA	10/25/2004	Blank	5.00	0.5	1.4	280.0	NA	NA	NA	NA	NA	NA	10.5
B4-102604	200401041	NA	10/25/2004	Blank	5.00	3	1.6	53.3	NA	NA	NA	NA	NA	NA	13.5

DTN: 004JC.006; NA = Not Applicable

Table 7. Cl-36 Accelerator Mass Spectrometry (PRIME) Results for Yucca Mountain Samples (initial analyses, rejected data)

Aliquot ID for AMS	PRIME ID	SMF ID	Start Date of Leach or Preparation	Mass of Cl added (mg)	36Cl/(35Cl+37Cl) (E-15)						35Cl/37Cl			Target (mg)
					Measured Ratio	± SD	RSD (%)	Corrected Ratio*	± SD	RSD (%)	Measured Ratio	± SD	RSD (%)	
8/19/05 AMS Run														
1034200	200501262	SPC01034200	5/23/2005	1.68	420000	60000	14.3	1300000	200000	15.4	11.414	0.017	0.1	1.0
1034201-1	200501263	SPC01034201	5/23/2005	3.10	960	160	16.7	1600	1400	87.5	38.86	0.07	0.2	1.6
1034201-2	200501264	SPC01034201	5/23/2005	2.91	1220	40	3.3	2900	300	10.3	23.76	0.05	0.2	7.1
1034202	200501265	SPC01034202	4/21/2005	2.15	2400	130	5.4	11700	1000	8.5	21.42	0.27	1.3	1.7
1034203	200501266	SPC01034203	4/25/2005	1.66	350000	30000	8.6	1040000	94000	9.0	10.698	0.011	0.1	5.1
1034204	200501267	SPC01034204	4/25/2005	2.12	182000	4000	2.2	1200000	43000	3.6	20.06	0.04	0.2	1.0
1034205	200501268	SPC01034205	5/23/2005	2.61	748	29	3.9	360	150	41.7	16	0.15	0.9	6.5
1034206	200501269	SPC01034206	4/21/2005	1.98	49200	2200	4.5	230000	13000	5.7	16.45	0.1	0.6	3.4
1034207-1	200501270	SPC01034207	4/21/2005	0.00	630	40	6.3	630	40	6.3	3.148	0.004	0.1	25.6
1034207-2	200501271	SPC01034207	4/21/2005	0.00	610	40	6.6	610	40	6.6	3.141	0.002	0.1	18.6
1034208	200501272	SPC01034208	4/21/2005	0.00	99100	2400	2.4	99000	3700	3.7	3.143	0.001	0.03	14.3
1034209	200501273	SPC01034209	4/21/2005	0.00	7010	140	2.0	7010	240	3.4	3.232	0.024	0.7	30.4
1034210	200501274	SPC01034210	4/21/2005	0.00	16900	500	3.0	16900	700	4.1	3.152	0.007	0.2	11.7
1034211	200501275	SPC01034211	5/23/2005	3.27	848	29	3.4	380	640	168.4	64.1	1.5	2.3	2.4
1034212	200501276	SPC01034212	5/23/2005	2.94	473	18	3.8	830	170	20.5	67.37	0.22	0.3	6.0
1034213	200501277	SPC01034213	5/23/2005	3.05	405	18	4.4	**	**	NA	80.7	0.6	0.7	5.8
1034215-1	200501279	SPC01034215	4/21/2005	1.62	95000	3000	3.2	270000	11000	4.1	9.336	0.006	0.1	4.7
1034215-2	200501280	SPC01034215	4/21/2005	1.86	56400	700	1.2	220000	6800	3.1	13.06	0.007	0.1	3.2
1034216	200501281	SPC01034216	5/23/2005	3.05	743	23	3.1	3030	260	8.6	113.8	0.15	0.1	5.9
557088	200501282	SPC00557088	4/25/2005	0.00	300000	110000	36.7	300000	110000	36.7	3.164	0.004	0.1	6.5
2014361, 2014365	200501283	SPC02014361 SPC02014365	5/24/2005	3.05	33600	600	1.8	255000	8700	3.4	30.29	0.06	0.2	7.8
2014661	200501284	SPC02014661	5/24/2005	3.02	1080	60	5.6	2332	500	21.4	27.823	0.027	0.1	5.6
1004844	200501285	SPC01004844	5/24/2005	2.99	980	60	6.1	1560	460	29.5	31.79	0.06	0.2	7.6
2016028	200501286	SPC02016028	5/24/2005	3.22	1390	40	2.9	7200	700	9.7	182.6	0.7	0.4	5.7
RB-5-23-05	200501293	NA	5/23/2005	3.33	881	21	2.4	NA	NA	NA	395.2	0.7	0.2	6.9
LV1-1	200501294	NA	5/23/2005	2.76	3000	400	13.3	10900	1900	17.4	29.75	0.07	0.2	1.9
LV1-2	200501295	NA	5/23/2005	3.33	1360	30	2.2	10700	1020	9.5	180.2	0.6	0.3	6.3
LV1-3	200501296	NA	5/23/2005	3.11	2670	80	3.0	16900	950	5.6	112.66	0.05	0.04	6.1
Sieving Blank	200501297	NA	5/23/2005	2.39	3210	220	6.9	54000	5400	10.0	62	4	6.5	1.7

MOL.20060627.0069, MOL.20060505.0130. Data are provided for informational purposes only. Although some samples appear to have reasonable ratios, the data were rejected because they were processed along with others that had unreasonable ratios. NA = Not Applicable; *Ratio corrected for carrier and reagent blank; **Not displayed because the number was negative.

7.1.2 Solving the blank problem

A teleconference was held on September 29, 2005 to discuss the results. Representatives from the USGS, LANL, DOE and UNLV participated. UNLV opened the meeting by providing a summary of the results and followed by answering questions that were primarily intended to determine an origin of some seemingly high and unexpected results. The teleconference concluded with suggestions on how to proceed. Most thought that attention should be given to the blank issues and establishing a reservoir of reagents with acceptable low levels of ^{36}Cl.

Given the low blank levels measured during the fall of 2004, we retraced our steps and examined our procedures to identify the source of the problem, but we are unable to pinpoint an exact cause for the high ratios. There did not appear to be any systematic relationship to explain the high ^{36}Cl results (e.g., sieved vs. non-sieved, sieving order, analysis dates, sample sizes, etc). However, during the same period as the samples were being prepared for ^{36}Cl analysis, a series of ^{36}Cl standards containing relatively high numbers of ^{36}Cl atoms were also prepared. Although this work was done in a separate laboratory on a different floor it is possible that some pipettes or equipment may have inadvertently been transferred between the locations.

Whereas it is quite unlikely that the samples or reagents were exposed to a strong neutron source while in the laboratory, it is not impossible that the lab hoods or labware was contaminated at some time in the past by containing materials that had undergone neutron activation. It is difficult to be sure of the exact history of the laboratories employed. The blanks obtained in fall 2004 were relatively low, so the lab equipment would have to be exposed to this neutron source in the months following fall 2004 or different (contaminated) labware may been inadvertently used. In any case, it should be noted that we are confident that the raw bulk samples were not contaminated because they were stored in their original bags in a separate locked cabinet.

The only major difference between our first set of blanks (prepared fall 2004) and the second was that the former was prepared with an ammonium chloride salt from Sigma Aldrich, whereas the second used a ^{35}Cl tracer from Oak Ridge. The possibility that the ^{35}Cl tracer may have been contaminated was considered, however, some of the samples that had high ratios (e.g., SPC01034208) were prepared without addition of any chloride. Nevertheless, two new blanks were prepared quickly using "carrier" (Cl from Sigma Aldrich) and "tracer" (^{35}Cl from Oak Ridge) prior to the end of the ^{36}Cl AMS run. Results ($\times10^{-15}$) for these were 47 ± 10 and 235 ± 10, respectively. These data were obtained without the proper Q-procurement documents so they are considered unqualified and can be used for informational purposes only. Whereas the ratios improved, the background was still too high and it was decided to prepare fresh carrier and use a new source of water (distilled) with lower chloride concentrations (<0.11 ppm).

Subsequently, the entire laboratory was thoroughly cleaned, including all glassware and equipment that came in contact with the previous samples, and a new series of blanks was prepared using distilled water, which had lower chloride content than that previously used. Splits of the precipitate from select samples that had high ratios were sent to CAMS. The precipitates were split prior to submitting to PRIME and confirmation of the results would eliminate PRIME as a possible source of contamination. Indeed, results from CAMS were also high, which indicated that the problem occurred at UNLV.

The new series of blanks were analyzed by PRIME on November 20, 2005. Results were greatly improved with measured ratios averaging 90 ± 20 (1σ) $\times 10^{-15}$ and smaller, however they were still relatively high on an absolute mass basis, about the same as might be found in a typical sample. Because the project end date was quickly approaching, the drastic measure of abandoning the laboratory and supplies to the extent possible and moving elsewhere was undertaken. The remainder of our samples was prepared at the U.S. Environmental Protection Laboratory located on the UNLV campus. The approach was successful and our blanks decreased to acceptable levels. This suggests that the problem was contamination of labware or lab furniture with minute amounts of very high ^{36}Cl/Cl chloride. The results of the work conducted at the EPA lab with low ^{36}Cl in the blanks are presented separately in Section 7.2.

In summary, our experience has once again shown that measuring miniscule amounts of ^{36}Cl is a difficult task, especially when chloride is so abundant and ubiquitous. The high sensitivity of AMS makes it ideally suited for ^{36}Cl measurements. On the other hand, mere thousands of atoms can influence the result. Sample preparation is tedious, requires careful thought, and involves a learning curve. We have great respect for previous investigators who over the years managed to obtain high quality data.

7.1.3 ^{36}Cl standards

As noted earlier the results for a series of ^{36}Cl standards appear to be unaltered by the background. These standards were prepared from NIST SRM 4943 at ^{36}Cl/Cl nominal ratios ($\times 10^{-15}$) of 500, 2,500 and 10,000 (see Section 5.5). Silver chloride was precipitated from ~1 mL aliquots of these solutions. To test for variability associated with the mass of the sample submitted for AMS analysis, each standard was submitted to PRIME in ~1 mg (L), ~5 mg (M), and ~20 mg (H) amounts. Results were generally in good agreement with expected (calculated) ratios and did not systematically vary by sample size, although the samples with the lowest mass tended to have higher errors associated with the measurement (Table 8). Mean (n=3) ^{36}Cl/Cl ratios for the standards were 580 ± 40, 2580 ± 150, and 10,030 ± 500, each (1σ) $\times 10^{-15}$ (DTN 004JC.006). Duplicate AMS runs agreed within 7% of one another. This exercise was necessary to show that we were capable of generating accurate ^{36}Cl/Cl ratios for known samples. It also served as an independent calibration check for PRIME's ^{36}Cl run.

7.1.4 ESF seepage samples

Samples of seepage collected from the south ramp of Yucca Mountain during the spring of 2005 also had high chloride concentrations and were prepared separately from the rock that experienced erratic results. The following seepage specimens (SPC#) were analyzed directly, without addition of deionized or distilled water: 01034573, 01034574, 01034575, 01034576, 01034578. The ^{36}Cl/Cl results ($\times 10^{-15}$ ±1σ) ranged from 680 ± 40 to 1110 ± 40 with a mean of 800 ± 80 (Table 8), which is consistent with ratios found for Pleistocene water, with a small bomb-pulse component. Except for SPC01034578 at 1110 ± 40 ($\times 10^{-15}$ ±1σ), the lack of a significant bomb-pulse in the seepage, which clearly represents infiltrating fast-path water, is of interest and should be addressed.

Although we measured clear bomb-pulse signals in the soil above the south ramp (Table 8), the area is dominated by outcrop and minimal soil coverage so infiltration chiefly occurs through bare rock or very shallow soil. Porosity in the slightly fractured tuff bedrock is low and fast flow paths have probably mostly been leached. In contrast, areas with thicker soil retain the precipitation from all but the heaviest events, and leaching is much slower with a significant part of the bomb-pulse being retained. Finding relatively low ^{36}Cl/Cl ratios from seeps originating from bare outcrop and much higher ^{36}Cl/Cl ratios within nearby soils (not directly supplying the seeps) is expected. Whereas this was the first time seepage had been observed in the ESF to this degree, it is possible, if not likely, that leaching of the seepage pathways by other precipitation events occurred between the early 1960's bomb-pulse years and the construction of the ESF in the mid to late 1990's.

In summary, capturing a clear bomb-pulse ^{36}Cl signal is a matter of timing. Areas overlain by mostly bare fractured bedrock would have been leached in just a few years and the ^{36}Cl pulse may be hundreds of meters down. Areas containing somewhat thicker soil cover may have only recently been leached and the bomb-pulse might be only a few tens of meters down. Finally, if the alluvium is substantial enough, it might take hundreds of years to leach to the bedrock, or the pulse may be permanently retained (F. Phillips, personal comm. 2006). The fact that we don't find clear bomb pulse at a particular tunnel location now could mean that the pulse hasn't made it there yet, but, perhaps more likely in this case, given the observed seepage flow and exposed surface rock, it could also mean that it has already passed through. Regardless, the use of bomb-pulse ^{36}Cl as an indicator of fast-path percolation in the Yucca Mountain environment should be viewed with these potential constraints in mind.

Table 8. Cl-36 Accelerator Mass Spectrometry (PRIME) Results for Yucca Mountain Samples (initial analyses)

Aliquot ID for AMS	PRIME ID	SMF ID	Start Date of Leach or Preparation	36Cl/(35Cl+37Cl) (E-15) Measured Ratio	± SD	RSD (%)	Corrected Ratio*	± SD	RSD (%)
8/19/05 AMS Run									
1034573	200501287	SPC01034573	6/3/2005				744	34	NA
1034574-1	200501288	SPC01034574	6/3/2005				564	23	4.1
1034574-2	200501289	SPC01034574	6/3/2005				796	34	4.3
1034575-A	200501290	SPC01034575	6/3/2005				823	36	4.4
1034576-A	200501291	SPC01034576	6/3/2005				646	26	4.0
1034578	200501292	SPC01034578	6/3/2005				1110	44	4.0
STD-500-L	200501314	NA	5/4/2005	574	23	4.0	574	30	5.2
STD-500-M	200501315	NA	5/4/2005	585	18	3.1	585	20	3.4
STD-500-H	200501316A	NA	5/4/2005	608	19	3.1	608	30	4.9
STD-500-H	200501316B	NA	5/4/2005	570	20	3.5	570	30	5.3
STD-2500-L	200501317	NA	5/4/2005	2640	80	3.0	2640	110	4.2
STD-2500-M	200501318	NA	5/4/2005	2550	70	2.7	2550	100	3.9
STD-2500-H	200501319A	NA	5/4/2005	2590	70	2.7	2590	100	3.9
STD-2500-H	200501319B	NA	5/4/2005	2500	80	3.2	2500	110	4.4
STD-10000-L	200501320	NA	5/4/2005	10240	290	2.8	10240	410	4.0
STD-10000-M	200501321	NA	5/4/2005	9950	250	2.5	9950	380	3.8
STD-10000-H	200501322A	NA	5/4/2005	9890	220	2.2	9890	360	3.6
STD-10000-H	200501322B	NA	5/4/2005	9900	290	2.9	9900	400	4.0

DTNs: 004JC.006, 004JC.007; NA=Not Applicable; *Ratio corrected for carrier and reagent blank. %RSD = (SD/Ratio)x100

7.2 ^{36}Cl results with low blanks

This section contains results and discussion for samples analyzed after having moved to an alternate laboratory and confirming that the ^{36}Cl background was favorable for measurements. Table 9 presents results for a series of blanks prepared at the US Environmental Protection Agency laboratory in Las Vegas (i.e., on the UNLV campus). The ^{36}Cl/Cl blank ratios and absolute mass of ^{36}Cl were generally lower than those found by USGS/LLNL and LANL. The mean mass of ^{36}Cl (mg x 10^{-15}) in the two group's validation study blanks were 3.1 and 15.7 for LLNL and LANL, respectively (DTNs LL030605223121.030, LA0305RR831222.001). The UNLV blanks determined by CAMS on 22-Dec-05 were deemed acceptable and we proceeded to analyze samples of ESF Rock, Yucca Mountain soils, and a column experiment mimicking the passage of a bomb-pulse solution through tuff. The blanks associated with rock, soil and column samples were also low giving us confidence in these data sets. Ratios presented in this section are corrected to blanks prepared on the same day as the samples. The chloride ion chromatography detection limit (3σ) based on data for the eight blanks in Table 9 is 0.011 ppm.

Table 9. Chlorine isotope ratios in blanks prepared at U.S. EPA Lab.

Sample ID	AMS Facility	AMS ID	^{36}Cl/Cl measured ratio (E-15)	Chloride concentration (ppm)
RB1(12-27-05)	PRIME	R06-0658,5A	3.1 ± 0.8	0.0349
RB2(12-27-05)	PRIME	R06-0659,5A	1.2 ± 0.9	0.0367
RB1-1-31-06	PRIME	R06-0660,5A	1.4 ± 1.3	0.0305
RB2-1-31-06	PRIME	R06-0661,5A	8 ± 1.7	0.0404

DTNs: 004JC.006, 004JC.008.

7.2.1 ESF Rock

With the improved background, seven samples collected from the ESF, along with SPC00557088 (EVAL-1) previously used for inter-laboratory comparisons of ^{36}Cl/Cl leachates by USGS/LLNL and LANL, were selected for ^{36}Cl analysis. The other seven ESF samples, some of which had little material left after earlier analyses, could not be analyzed due to time constraints. An inventory of the remaining (unleached) samples is presented in Section 7.8. Results for ESF samples are given in Table 10, which includes comparable data from LANL and USGS/LLNL, and in Table 11, which provides additional information. Only one sample yielded a clear bomb-pulse ratio (SPC01034214, Drill Hole Wash 19+33, 1590 ± 80 (1σ) x10^{-15}). The other sample from the Drill Hole Wash fault plane yielded a ratio of 1160 ± 50 (1σ) x10^{-15}, which is close to the 1250 x10^{-15} cutoff. The three samples collected from Alcove 6 averaged 500 ± 100 (1σ) x10^{-15}; the Sundance Fault sample resulted in a ratio of 920 ± 50 (1σ) x10^{-15}, and Bow Ridge Fault produced 520 ± 20 (1σ) x10^{-15}. Rock Cl (mg Cl/kg rock) ranged from 0.2 to 17 with a median of ~0.6. The data are significant because a bomb-pulse ^{36}Cl/Cl ratio has been measured at depths similar to the proposed waste emplacement horizon by a second and independent group of investigators.

Although the UNLV $^{36}Cl/Cl$ ratios were generally lower than those found by LANL, previous studies have shown large differences in samples collected in proximity to one another (R. Roback, personal comm., 2006). Thus, it is more appropriate to make comparisons to the range of data produced in a given area. In this case the UNLV data are in agreement with the range of data produced by LANL for samples from similar locations.

For LANL, loose or poorly consolidated material was leached without further size reduction but other samples were generally crushed prior to leaching; passive leaching times for the LANL samples were 48 hours (Fabryka-Martin et al., 1997, p. 4-1). Because UNLV samples were leached passively for 24 hours, over-leaching relative to LANL is unlikely. It would be of interest to analyze the same samples after screening out the fines to see if the generally lower ratios found by UNLV are due to leaching greater surface area. Samples with more surface area would increase efficiency for leaching of chloride associated with the rock matrix and fluid inclusion salts, which in turn may reduce the ratios (e.g., Roback et al. 2002).

Although efforts were made to reduce overleaching of the samples, namely passive leaching and limiting the time to 24 hours or less, several samples produced relatively high chloride concentrations. Analyses performed at LANL have shown that samples with leachable chloride concentrations greater than ~1 mg/L rarely show bomb-pulse ratio, which apparently is masked by sizeable amounts of Holocene meteoric chloride (e.g., Roback et al. 2002). Indeed, two of the three samples from Alcove 6, as well as the sample from Bow Ridge Fault, had leach chloride concentrations in excess of 2 mg/L and each of these had $^{36}Cl/Cl$ ratios near 500 (Table 10). The relatively high chloride leach concentration, particularly for SPC01034207 and SPC01034209, suggests the possibility that these samples were collected in a "dry-out" zone where Holocene porewater has migrated toward the tunnel and dried (Roback, personal comm. 2006).

The result for EVAL-1 (180 ± 10 (1σ) $\times10^{-15}$) was lower than values determined by both USGS/LLNL and LANL. In the UNLV study two separate leaches of the EVAL-1 produced 1.43 and 1.49 mg Cl/kg rock, which was significantly more than 0.11 mg Cl/kg rock to 0.25 mg Cl/kg rock found by LANL (DTN: LA0305RR831222.001). EVAL-1 was shipped to UNLV by the USGS in a plastic bag and was analyzed directly without any treatment (e.g., nitrogen blow-down, sieving, etc). Chloride concentrations in the associated blanks were low and could not be responsible for the relatively high values (Table 9). Over five years have passed since the EVAL-1 sample was collected and held in storage by the USGS so it is plausible that chloride was somehow introduced into the sample in the interim. A more plausible explanation may be that we over-leached the sample compared to the USGS/LLNL and LANL. The two groups performed a scant 1 hour leach (J. Paces, personal comm., 2006), whereas we kept with our 24 hour leach protocol. The longer leach may have yielded more rock-Cl and resulted in the lower $^{36}Cl/Cl$ ratio.

Other data for rock leachates comes from the column experiment (Section 7.2.3) and a scoping study using bromide as an alternative carrier (Section 7.2.4). In the column study, a sample from Alcove 6 (SPC0103205, 12.5 - 75 mm) yielded a ratio of 1060 ± 110 (1σ) $\times10^{-15}$. Although the flow through experiment extracted only 0.15 mg of Cl, much less than the 24 hour passive leaches of the other rock samples, the ratio appears to be reasonable. Rock data for the samples using bromide is considered unqualified and is presented in Section 7.2.4 for informational purposes only. ^{36}Cl/Cl ratios for SPC01034210 and SPC01034215 using bromide were 720 ± 30 (x10^{-15}) and 1250 ± 90 (x10^{-15}), respectively, compared with 520 ± 20 (x10^{-15}) and 1160 ± 50 (x10^{-15}) for the same samples prepared with chloride carrier. The result for SPC01034215 is of interest because it constitutes a second ^{36}Cl bomb-pulse ratio measured in ESF rock, albeit from a scoping experiment. Moreover, the sample was obtained adjacent to the other sample showing a ^{36}Cl bomb pulse ratio (SPC01034214) from the same Drill Hole Wash fault.

Table 10. Comparison of Cl-36/Cl ratios in leachates of ESF rock for samples collected from similar locations by UNLV, LANL, and USGS

	UNLV Study			LANL			USGS/LLNL**		
General Location	SMF ID	Specific Location / Description	36Cl/(35Cl+37Cl) (E-15)*	SMF ID	Specific Location / Description	36Cl/(35Cl+37Cl) (E-15)	SMF ID	Specific Location / Description	36Cl/(35Cl+37Cl) (E-15)
Sundance Fault	SPC01034204	ESF 35+93	919 +/- 64	SPC00512511	ESF 35+93 fault: breccia >~0.5cm breccia <~0.5cm	2840 +/- 231 1674 +/- 141	SPC01015120	ESF 35+90 ESF-SD-CIV#10 (2.0-3.9)	552 +/- 386
Alcove 6	SPC01034206	Alcove 6/1+60; Breccia near NE striking fractures / cooling joints	518 +/- 24	SPC00525142	Alcove 6/1+60 cooling joints, representative bulk material	1699 +/- 70			
Alcove 6	SPC01034207	Alcove 6/0+93; mostly welded tuff	463 +/- 16	SPC00525131	Alcove 6/1+93 breccia zone, bulk material	1511 +/- 48			
Alcove 6, Ghost Dance Fault	SPC01034209	Alcove 6/1+52; welded tuff + fault gouge breccia	497 +/- 25	SPC00530000 SPC00525141	Alcove 6/1+52 fault - breccia fault - wall rock	1250 +/- 65 3357 +/- 132			
Bow Ridge Fault	SPC01034210	ESF 01+99.8; lithophysal welded tuff + fault gouge breccia	529 +/- 23	SPC00509016 SPC00509017 SPC00509018 SPC00509019 SPC00509020 SPC00509751	ESF 01+99.8 Breccia Breccia Rubble Rubble Breccia Breccia	2138 +/- 137 2444 +/- 169 720 +/- 49 2378 +/- 153 2398 +/- 154 381 +/- 16			
Drill Hole Wash Fault	SPC01034214	ESF 19+33; mostly lithophysal welded tuff; 0.5-0.8 m from fault plane	1588 +/- 79	SPC00503920	ESF 19+31 Fault Zone; Breccia >~0.5 cm	3023 +/- 94			
Drill Hole Wash Fault	SPC01034215	ESF 19+33; mostly lithophysal welded tuff; 1.08-1.28 m from fault plane	1162 +/- 48	SPC00503920	ESF 19+31 Fault Zone; Breccia <~0.5 cm	1838 +/- 65			
YM Muck (Eval #1)	SPC00557088	Niche #5 in ECRB	177 +/- 9	SPC00536902	Niche #5 in ECRB	361 +/- 42	SPC00536901	Niche #5 in ECRB	454 +/- 109

DTNs: 004JC.007 (for UNLV data); LAJF831222AQ98.004 (for LANL data); LL031200223121.036 (for USGS data). SMF = Sample Management Facility. Ratios were corrected for Cl-36 and chloride background values measured in process blanks included in the same AMS runs. UNLV errors are 1SD cumulative and include Cl-36 measurement uncertainty and a conservative 2% factor for uncertainty associated with sample preparation (e.g., weighing and pipetting). **USGS focused their efforts primarily on drill core. Core from Drill Hole Wash fault was only analyzed for leachable anions by ion chromatography. The USGS ran out of time and resources before Cl-36 analyses completed. The USGS never collected samples from Alcove 6, but did expend significant efforts trying to reproduce LANL results from Niche#1 core. This was the best attempt at a direct comparison of analyses of the same material in the same boreholes from which LANL obtained bomb-pulse Cl-36 (J. Paces, personal comm.).

Table 11. Cl-36 Accelerator Mass Spectrometry Results for Yucca Mountain Samples (with low blanks)

UNLV Sample ID for Cl-36 Analysis	UNLV Sample ID for Leachate Cl Analysis	PRIME ID	SMF ID (SPC #)	Sample Information	Start Date of Leach or Preparation	Leachate Cl concentration (ppm)*	36Cl/(35Cl+37Cl) (E-15)						Target (mg)
							Measured Ratio	± SD	RSD (%)	Corrected Ratio**	± SD	RSD (%)	
3/31/2006 AMS Run													
01034237(1-31-06)	01034237(1-31-06)	R06-0646,5A	01034237	South Ramp Soil #1 (0-15 cm)	1/31/2006	0.327	231	10	4.3	2172	114	5.3	3.9
01034238(1-31-06)	01034238(1-31-06)	R06-0647,5A	01034238	South Ramp Soil #1 (13-22 cm)	1/31/2006	0.203	161	6	3.7	2368	114	4.8	4.5
01034236(1-31-06)	01034236(1-31-06)	R06-0648,5A	01034236	South Ramp Soil #1 (20-30 cm)	1/31/2006	0.206	221	10	4.5	3998	218	5.5	3.5
01034239(1-31-06)	01034239(1-31-06)	R06-0649,5A	01034239	South Ramp Soil #2 (0-10 cm)	1/31/2006	0.190	333	18	5.4	5669	351	6.2	4.0
01034240(1-31-06)	01034240(1-31-06)	R06-0650,5A	01034240	South Ramp Soil #2 (10-25 cm)	1/31/2006	0.541	840	30	3.6	4476	205	4.6	5.1
01034231(1-31-06)	01034231(1-31-06)	R06-0651,5A	01034231	North Ramp Soil #1 (0-14 cm)	1/31/2006	0.130	35.3	2.4	6.8	821	74	9.0	6.6
01034232 (1-31-06)	01034232 (1-31-06)	R06-0652,5A	01034232	North Ramp Soil #1 (14-30 cm)	1/31/2006	0.423	280	11	3.9	2066	101	4.9	4.0
01034230(1-31-06)	01034230(1-31-06)	R06-0653,5A	01034230	North Ramp Soil #1 (30-43 cm)	1/31/2006	0.125	73	4	5.5	2386	160	6.7	5.3
01034234(1-31-06)	01034234(1-31-06)	R06-0654,5A	01034234	North Ramp Soil #1 (0-11 cm)	1/31/2006	0.0831	23.7	1.8	7.6	1093	125	11.4	4.5
01034235(1-31-06)	01034235(1-31-06)	R06-0655,5A	01034235	North Ramp Soil #1 (11-30 cm)	1/31/2006	0.340	132	6	4.5	1219	68	5.6	4.3
01034233(1-31-06)	01034233(1-31-06)	R06-0656,5A	01034233	North Ramp Soil #1 (30-40 cm)	1/31/2006	0.117	40	3	7.5	1194	113	9.5	5.5
01034233D(1-31-06)	01034233D(1-31-06)	R06-0657,5A	01034233	North Ramp Soil #1 (30-40 cm)	1/31/2006	0.106	33.5	2.1	6.3	1074	93	8.7	5.7
RB1-1-31-06	RB1-1-31-06	R06-0658,5A	NA	Process Blank	1/31/2006	0.0305	1.4	1.3	92.9	NA	NA	NA	4.8
RB2-1-31-06	RB2-1-31-06	R06-0659,5A	NA	Process Blank	1/31/2006	0.0404	8	1.7	21.3	NA	NA	NA	5.6
RB1(12-27-05)	RB1(12-27-05)	R06-0660,5A	NA	Process Blank	12/27/2005	0.0349	3.1	0.8	25.8	NA	NA	NA	6.2
RB2(12-27-05)	RB2(12-27-05)	R06-0661,5A	NA	Process Blank	12/27/2005	0.0367	1.2	0.9	75.0	NA	NA	NA	4.4
01034204(12-27-05)	01034204(12-27-05)	R06-0662,5A	01034204	Sundance Fault	12/27/2005	0.166	47.5	2.8	5.9	919	64	6.9	6.5
01034206(12-27-05)	01034206(12-27-05)	R06-0663,5A	01034206	Alcove 6	12/27/2005	0.513	83	3	3.6	518	24	4.7	5.2
01034207(12-27-05)	01034207(12-27-05)	R06-0664,5A	01034207	Alcove 6	12/27/2005	14.3	462	10	2.2	463	16	3.6	8.2
01034209(12-27-05)	01034209(12-27-05)	R06-0665,5A	01034209	Alcove 6, Ghost Dance Fault	12/27/2005	7.43	495	21	4.2	497	25	5.1	9.9
01034210(12-27-05)	01034210(12-27-05)	R06-0666,5A	01034210	Bow Ridge Fault	12/27/2005	2.37	411	14	3.4	529	23	4.4	5.6
01034214(12-27-05)	01034214(12-27-05)	R06-0667,5A	01034214	Drill Hole Wash Fault	12/27/2005	0.472	245	10	4.1	1588	79	5.0	3.0
01034215(12-27-05)	01034215(12-27-05)	R06-0668,5A	01034215	Drill Hole Wash Fault	12/27/2005	0.264	99.5	2.9	2.9	1162	48	4.2	4.8
00557088(12-27-05)	00557088(12-27-05)	R06-0669,5A	00557088	Muck (Eval #1)	12/27/2005	1.11	75	3	4.0	177	9	5.0	6.3
RB-1-25-06(C6-W2)	C6 (1-30-06)	R06-0641,5A	NA	Column Exp. Wash 2 Process Blank	1/25/2006	0.0244	19.4	1.5	7.7	NA	NA	NA	7.7
01034200(C1-W2)	C1 (1-30-06)	R06-0636,5A	01034200	Column Exp. Wash 2 (0.125-2 mm)	1/25/2006	0.756	103	6	5.8	2772	222	8.0	5.3
01034201(C2-W2)	C2 (1-30-06)	R06-0637,5A	01034201	Column Exp. Wash 2 (2-12.5 mm)	1/25/2006	0.980	163	5	3.1	2882	135	4.7	6.4
01034205(C3-W2)	C3 (1-30-06)	R06-0638,5A	01034205	Column Exp. Wash 2 (2-12.5 mm)	1/25/2006	0.412	94	4	4.3	3987	261	6.5	5.5
01034205(C4-W2)	C4 (1-30-06)	R06-0639,5A	01034205	Column Exp. Wash 2 (12.5-75 mm)	1/25/2006	0.763	115	5	4.3	2680	168	6.3	5.6
00557088(C5-W2)	C5 (1-30-06)	R06-0640,5A	00557088	Column Exp. Wash 2 (0.25-0.5 in)	1/25/2006	0.661	97	4	4.1	2369	150	6.3	5.1
01034205(C4-L1)	C4-L1	R06-0642,5A	01034205	Column Exp. Leach 1 (12.5-75 mm)	1/25/2006	1.23	63	4	6.3	1057	108	10.2	5.5
01034200(C4-L2)	C4-L2	R06-0643,5A	01034200	Column Exp. Leach 2 (12.5-75 mm)	1/25/2006	0.884	7.3	1.3	17.8	292	80	NA	8.1
01034200(C4-S1)	C4-S1	R06-0644,5A	01034200	Column Exp. Spike 1 (12.5-75 mm)	1/25/2006	65.7	2450	70	2.9	2451	99	4.0	8.1
01034200(C4-W1)	C4-W1	R06-0645,5A	01034200	Column Exp. Wash 1 (12.5-75 mm)	1/25/2006	0.978	136	9	6.6	2343	195	8.3	5.5

DTNs: 004JC.006, 004JC.007, *004JC.008; NA = Not Available/Applicable; RB = Reagent Blank; Exp = Experiment; **Ratio corrected for carrier and reagent blank.

7.2.2 Yucca Mountain Soils

Leachates of soils from the surface of Yucca Mountain above the ESF north and south ramps yielded ^{36}Cl/Cl ratios (x10^{-15}) ranging between 820 ± 70 to 5670 ± 350 (Tables 11 and 12). Samples collected above the south ramp, where there was significant outcrop and limited soil coverage, had relatively large ratios (x10^{-15}) ranging between 2170 ± 110 to 5670 ± 350. In contrast the soil samples collected from above the north ramp ranged from 820 ± 70 (1σ) x10^{-15} to 2390 ± 160 (1σ) x10^{-15}. The ^{36}Cl/Cl ratios for the upper layer of soil from both north sites were 820 ± 70 (1σ) x10^{-15} and 1090 ± 110 (1σ) x10^{-15}, both of which are relatively low values generally consistent with soils partially leached with recent meteoric water. Duplicate runs for sample SPC010342333 showed good reproducibility: 1190 ± 110 (x10^{-15}) and 1070 ± 90 (x10^{-15}). For most of the soil samples, about half as much Cl was leached (mean ~0.3 mg) compared with the rock samples collected in the ESF.

The deeper layers of soil from the two north sites differed. Results from sample NR1 collected from the hill side-slope showed ^{36}Cl/Cl bomb-pulse ratios (2070 ± 100 x10^{-15} and 2390 ± 160 x10^{-15}) at the 14-30 cm and 30-43 cm depth intervals, respectively, whereas results from sample NR2 collected in a flat area at the base of the hill showed lower (borderline bomb-pulse) and uniform ratios throughout the soil column (Table 12). A clear bomb pulse signal at the latter site presumably lies at greater depth due to more water infiltration. The maximum ratio measured at NR2 was 1220 ± 70 (x10^{-15}).

Our results are consistent with soil bomb-pulse ^{36}Cl profiles measured on the Nevada Test site and worldwide (Phillips, 2000). Previous measurements of soil at Yucca Mountain by Norris et al. (1987) showed a similar range of ratios and infiltration peak depths that varied by site. The researchers found a maximum ^{36}Cl/Cl ratio at a depth of 0.5 m at one location and a more complex profile at another.

A number of factors affect the depth of the bomb-pulse, including infiltration amounts, vegetation, and slope (e.g., Tyler and Walker, 1994; Phillips et al., 1994). Areas with greater soil and alluvial coverage may retard infiltration of the bomb-pulse, whereas areas with minimal surficial deposits and shallow bedrock with faults may allow deeper penetration of the bomb pulse signal. However, if no fractures or faults are present it is conceivable that the bomb-pulse may be trapped at the soil/bedrock interface. Discussion of the movement of Cl in a soil column with respect to wetting fronts, root zones, drought, etc is beyond the scope of this work. The reader is instead referred to the literature (e.g., Phillips, 2000). With regard to the objectives of the UNLV study, the data are significant because they show that we were unambiguously able to measure a bomb-pulse ^{36}Cl signal from a relevant environmental sample where the bomb pulse is known to be present.

Table 12. Cl-36/Cl ratios in soil profiles above the ESF (Yucca Mountain)

SMF ID	Aliquot ID for AMS	General Location	Observations	Depth (cm)	36Cl/(35Cl+37Cl) (E-15) ± SD
SPC01034231	01034231 (1-31-06)	slope of hill above the north ramp	Wet	0-14	821 +/- 74
SPC01034232	01034232 (1-31-06)		Dry/Wet	14-30	2066 +/- 101
SPC01034230	01034230 (1-31-06)		Dry	30-43	2386 +/- 160
SPC01034234	01034234 (1-31-06)	wash surface down from slope	Wet	0-11	1093 +/- 125
SPC01034235	01034235 (1-31-06)		Wet/Dry	11-30	1219 +/- 68
SPC01034233	01034233 (1-31-06)		Dry	30-40	1194 +/- 113 1074 +/- 93
SPC01034237	01034237 (1-31-06)	Lower depression above south portal	Wet	0-15	2172 +/- 114
SPC01034238	01034238 (1-31-06)		Wet	13-22	2368 +/- 115
SPC01034236	01034236 (1-31-06)		Dry/Wet; has laminar carbonate horizon	20-30	3998 +/- 218
SPC01034239	01034239 (1-31-06)	Upper slope above south portal	Wet	0-10	5669 +/- 351
SPC01034240	01034240 (1-31-06)		Wet	10-25	4476 +/- 205
NA	RB1-1-31-06 RB2-1-31-06	Reagent/Process Blanks	NA	NA	1.4 +/- 1.3 8 +/- 1.7

DTNs: 004JC.006 (reagent blanks), 004JC.007 (ratio data), 004JC.009 (depth data). Cl-36 AMS results from PRIME; samples collected on Sept. 21, 2005.

7.2.3 Column experiment

Examination of bomb-pulse ^{36}Cl as an indicator of fast-path percolation in the Yucca Mountain environment is beyond the scope of this project. Nevertheless, in light of the discussion in Section 7.1.4 about possible restrictions to measuring bomb-pulse ^{36}Cl in infiltrating water pulsed through the unsaturated zone, a simple column experiment was conducted mimicking the passage of bomb-pulse ^{36}Cl through Yucca Mountain tuff to possibly shed some light on the issue.

Details of the experiment are provided in Section 5.9. In short, columns containing select samples in specific size fractions were "leached" twice (separately) with distilled water. This was followed by a "spike" of Cl containing a ^{36}Cl/Cl ratio of ~2,500 x10^{-15} and then two additional "washes" with distilled water. The Cl concentration of the spike was ~63 ppm, similar to that found for the ESF seepage. Two hundred mL (~3 rock volumes) was passed through the column at a rate of ~ 1 mL/min (comparable to the seepage drip rate) for each "event". The columns were placed in an oven at ~85°C overnight in between each event and the solutions were analyzed for ^{36}Cl.

As expected the amount of total-Cl and ^{36}Cl decreased significantly with each distilled water application. The initial leach of sample SPC0103205 (12.5-75 mm) yielded a ratio of 1060 ± 110 (1σ) x10^{-15}, whereas the second leach resulted in a lower ratio 290 ± 80 (1σ) x10^{-15} (Tables 11 and 13). However, the ratio after the spike essentially remained the same: 2340 ± 200 x10^{-15} for wash 1 and 2680 ± 170 x10^{-15} for wash 2. This suggests that a bomb-pulse signature in tuffaceous media of these size fractions may require multiple meteoric flow events before the ratio is diminished; however, additional analyses are needed to confirm this hypothesis. This finding seems inherently plausible, given that welded tuff contains significant microporosity (F. Phillips, personal comm. 2006).

Table 13. Cl-36/Cl ratios from a column experiment using ESF rock

Column (#)	SMF ID or UNLV ID	Size Fraction (mm)	Cl-36/(Cl35+Cl37) (E-15)				
			Leach 1	Leach 2	Spike	Wash 1	Wash 2
1	SPC01034200	0.125-2	NA	NA	NA	NA	2772 +/- 222
2	SPC01034201	2-12.5	NA	NA	NA	NA	2882 +/- 135
3	SPC01034205	2-12.5	NA	NA	NA	NA	3987 +/- 261
4	SPC01034205	12.5-75	1057 +/- 108	292 +/-80	2451 +/- 99	2343 +/- 195	2680 +/- 168
5	SPC00557088	0.25-0.5 in	NA	NA	NA	NA	2369 +/- 150
6	RB-1-25-06 (C6-W2)	NA	NA	NA	NA	NA	19.4 +/- 1.5*

DTN: *004JC.006, 004JC.010. Solutions were passed through a glass column containing between 150 and 182 g of ESF rock. Leach (before spike) and wash (after spike) solutions consisted of 200 mL of distilled water. The spike consisted of 200 mL of a standard prepared with a Cl-36/Cl ratio of 2500. Columns were dried overnight between additions of solutions. Flow rates were set at ~ 1 mL/min. The effluent of each column was captured and select samples were analyzed for Cl-36 at PRIME. Because of limited time we were not able to analyze each solution for Cl-36 (NA = Not Analyzed). Instead solutions from an individual sample (top row) and the second wash from every sample (right column) were analyzed. The second wash samples were chosen to reflect a possible scenario where a Cl-36 bomb-pulse passed through the rock, followed by a two washes of similar magnitude containing no bomb-pulse Cl-36. The second wash was analyzed for Cl-36. Blank subtraction was not performed for the leach 2 result because the Cl-36 in the sample was smaller than the blank. Errors are 1SD and include Cl-36 measurement uncertainty and a 2% factor for sample preparation (e.g., weighing, pipetting).

7.2.4 Bromide as an alternative to a Cl carrier

In most cases leachates of ESF rock contain too little Cl to process without the addition of a carrier for mechanical/practical manipulation of the silver chloride precipitate (see section 5.4). In this exploratory study, four samples of Yucca Mountain rock were analyzed without the addition of stable chloride, but with the addition of stable bromide. Chloride isotope measurements by AMS are not compromised by having bromide present (D. Elmore, personal comm., 2006). Enough silver ion was added to partially precipitate the bromide, leaving some natural chloride behind. The ^{36}Cl/Cl ratios in these initial precipitates from the rock samples and three blank samples have highly uncertain (one sigma) ratios: 540 +/- 39%, 1200 +/- 47%, 320 +/- 51%, and 310 +/- 74% for the samples, and 220 +/- 64%, 7000 +/- 57%, and 1400 +/- 36% for the blanks (Table 14). The high uncertainty likely comes from the AMS measurement due to low ion current. Additional silver ion (in excess of what was needed to precipitate the remaining bromide and any chloride leached from the rock) was added to the leachates from three of the rock samples. The results for ^{36}Cl/Cl are: 820 +/- 70, 1250 +/- 90 and 720 +/- 30 (9%, 7%, and 4% one sigma errors, respectively). Thus, there is enough natural chloride in the rock leachates to produce AMS measurements with acceptable uncertainty. As these results are from scoping or exploratory experiments, they are unqualified and are presented for informational purposes only. However, they do suggest that the ^{36}Cl/Cl ratio can be obtained without the addition of stable chloride, which may be advantageous from a contamination and blank subtraction perspective. This procedure may be considered as a task in a new proposal.

Table 14. Cl-36 Accelerator Mass Spectrometry UQ Results for Samples Prepared with Bromide

UNLV Sample ID	PRIME ID	SMF #	Start Date of Leach or Preparation	36Cl/(35Cl+37Cl) (E-15)			Target (mg)
				Measured Ratio	± SD	RSD (%)	
71-1	R06-0670,5A	01034215	2/23/2006	540	210	39	0.9
71-2	R06-0671,5A	01034213	2/23/2006	1200	500	42	1.5
71-3	R06-0672,5A	01034210	2/23/2006	320	150	47	1.3
71-4	R06-0673,5A	01034210	2/23/2006	820	70	9	6.1
71-5	R06-0674,5A	01034215	2/23/2006	310	230	74	2.4
71-6	R06-0675,5A	RB	2/26/2006	220	140	64	1.5
71-7	R06-0676,5A	RB	2/26/2006	7000	4000	57	3.1
16-1	R06-0724,5A	01034215	3/8/2006*	1250	90	7	4.2
16-2	R06-0725,5A	01034210	3/8/2006*	720	30	4	1.2
16-3	R06-0726,5A	RB	3/8/2006*	1400	500	36	4.2

DTN: 004JC.004. *second precipitation (see Section 5.2.4).

7.3 Results for ^{99}Tc and ^{129}I

Iodide, like chloride, is an excellent groundwater tracer and was enriched over background during the above-ground testing of nuclear weapons (Michel et al., 2005). The ^{129}I/^{127}I ratio has a background of about 10^{-12} and a bomb-pulse value of about 10^{-10} (Michel et al., 2005). Another radionuclide associated with the nuclear fallout that can be detected in groundwater is ^{99}Tc. The most commonly found chemical form of ^{99}Tc in groundwater is the pertechnetate anion, a stable species whose generally conservative behavior makes it a useful groundwater tracer (Shroeder et al., 1993). The primary sources for ^{99}Tc in the subsurface are nuclear weapons fallout and natural production through spontaneous fission (6.1% yield) of ^{238}U (Norris, 1979). Elevated ratios of ^{36}Cl/Cl and ^{129}I/^{127}I, and corroborating ^{99}Tc data would provide irrefutable evidence for the presence of bomb-pulse water, although the absence of elevated ^{129}I/^{127}I and ^{99}Tc would not necessarily contradict the presence of bomb-pulse ^{36}Cl.

In our study, ^{99}Tc and ^{129}I were measured in leachates of nine samples of ESF rock and three samples of soil using ICP-MS. The method detection limit (3σ) for ^{99}Tc was 0.26 ng L^{-1} (ppt). Results for ^{99}Tc in three of the rock samples were below the detection limit; however ^{99}Tc was measurable in the other samples, although one of the values had a large uncertainty (Table 15). ^{99}Tc in these samples ranged between 3.4 to 40.5 pg/kg of rock. The highest value was for SPC01034201 (2-12.5 mm), which originates from Sundance fault (ESF 35+93). Excluding this value, the average was 7 ± 2 pg/kg of rock. These values are relatively high compared with 0.09 pg/kg and 0.11 pg/kg reported by Fabryka-Martin et al. (1996) for rock samples collected from Bow Ridge Fault and UZ-N55 cuttings at 53 m depth, respectively; to our knowledge the only two other measurements of Tc-99 in ESF rock. Moreover, in a separate study unrelated to this project, ESF "muck" (rock broken by the TBM and removed to the surface) collected from the pile situated on the ESF pad was pulverized, leached with acid, and analyzed for ^{99}Tc after isolation and preconcentration using resin. That investigation found levels below the detection limit of 13 pg/kg. The unqualified detection limit data is from Cliff Jones and is presented for information purposes only.

For the soil samples, results averaged 1.0 ppt, corresponding to ~11 pg/kg of soil (Table 15). The highest concentration (16.3 pg/kg) was found for the deepest interval (30-45 cm). Little data are available in the literature for ^{99}Tc in arid soils for comparison. Uchida et al. (2002) measured ^{99}Tc in rice paddy soils in Japan and estimated total deposition to the northern hemisphere at 6 nBq per kg in the top 25 cm of soil. The researchers reported 6-110 mBq/kg or ~9.5-174 pg/kg in the rice paddy soil. Another paper by Uchida et al. (2000) reported 1.1-14.8 Bq/kg of ^{99}Tc in soil, which corresponds to ~1.8 – 23.6 ng/kg, dry weight, however the samples were collected near the Chernobyl reactor and contained relatively high amounts of organic matter. Closer to Yucca Mountain, Schroeder et al. (1993) measured the migration of ^{99}Tc in the alluvial aquifer at the NTS and concluded that there is low affinity of volcanic tuff for ^{99}Tc, a characteristic of the anion exclusion model.

Although ^{99}Tc was found in leachates of several ESF rock samples, only one sample had results obtained for both ^{99}Tc and ^{36}Cl. This lack of data overlap prevents comparison and correlation between the isotopes, and limits our interpretation of the data. It should be noted in a separate methodology study we found generally poor recoveries for less than ~1 ng of ^{99}Tc, and the concentrations measured in the above samples correspond to an order of magnitude below this level. Therefore the current data should be viewed with caution and additional study is recommended to increase data coverage and improve recovery rates.

Table 15. Tc-99 in Seepage and Leachates of Rock from Yucca Mountain and Soil from Las Vegas Valley

Sample ID	Matrix	Concentration in final extract (ng/L)	Mass of final extract (g)*	Measurement precision (± 1 SD, n=3)	Mass of sample leached (kg)*	Tc-99 pg / kg rock or soil
SPC00557088 (2-12.55mm)	Rock	<DL	10.0145	NA	2.04	NA
SPC01034571	Seep	<DL	10.1088	NA	NA	NA
Silicon Blank (2-12.5)	Silicon	0.29	9.9607	0.106	0.91	3.2
SPC01034568	Seep	0.29	10.1440	0.086	NA	NA
SPC01034205 (2-12.5mm)	Rock	0.49	10.0503	0.72	0.54	9.1
SPC01034208 (2-12.5mm)	Rock	0.56	10.1028	0.116	1.08	5.2
LV1-2 (<2mm)	Soil	0.89	10.3373	0.083	1.1	8.4
SPC01034210 (2-12.5mm)	Rock	0.94	10.2110	0.358	2.79	3.4
LV1-1 (<2mm)	Soil	0.95	10.1502	0.217	1.01	9.5
LV1-3 (<2mm)	Soil	1.21	13.5988	0.383	1.01	16.3
SPC02014361+SPC02014365	Rock	1.53	10.0097	0.373	2.14	7.2
SPC01034201 (2-12.5mm)	Rock	1.7	10.9453	0.04 (RPD)	0.46	40.5
SPC01034201 (12.5-75mm)	Rock	1.89	10.4638	0.524	2.55	7.8

Data are provided for informational purposes only and are considered unqualified. DTNs: 004JC.010, MOL.20060516.0128. RPD = Relative Percent Difference; NA=Not Applicable; data is blank subtracted; Method Blank-5-23-05 yielded 0.452 ± 0.125 ng/L for final extract; SPC01034571 and SPC01034568 are seep samples.

In a related scoping study, five different ESF rock samples (SPC01034206, SPC01034204, SPC01034200, SPC01034201 and SPC01034215) were leached (passive) in distilled water for 24 hours in duplicate. The goal was to examine and compare the surface of leached and unleached samples for ^{99}Tc and ^{129}I by laser ablation (LA) ICP-MS. Each sample consisted of several pieces of rock weighing about 25 g in total. This small sample size was used because the rock needed to fit into a laser ablation (LA) cell. After air drying the samples, a 266 nm laser (Nd:YAG) was used to ablate the surface of the rocks. The ablated material consists of vapors, condensates and particulates generated by the plasma formed by the interaction of the laser light with the solid. The ablation products were swept into a time-of-flight ICP-MS where several masses were monitored, including mass 99 and 129. Results indicate that there was no change in the baseline for the blank (unleached samples) compared with the leached samples.

Although very little sample was leached and no preconcentration was attempted, the above leaches were filtered and analyzed for ^{99}Tc and ^{129}I by ICP-MS. The signals at mass 99 and 129 were compared to the blank to identify (qualitatively) any differences. There were no differences observed between the sample leaches and blanks, so the isotopes were not quantified. The variability in the measurements was ~5% RSD. A crude estimate of the ^{129}I detection limit yielded ~50 ng L^{-1}. It is worth noting that determining iodine by ICP-MS is challenging given its relatively high ionization potential and memory effects. The AMS technique would provide greater sensitivity and superior detection capability; however, we were unable to prepare samples for ^{129}I AMS measurements before the end of the project.

In summary, the presence of ^{99}Tc was detected in leaches of ESF rock, but poor analytical recoveries and lack of data overlap with ^{36}Cl restrict interpretation of these data. Because ^{36}Cl data was acquired late in the project, the bomb-pulse ratio found for sample SPC01034214 could not be corroborated with other isotopes. The ICP-MS detection capability is insufficient for ^{129}I (without incorporating preconcentration measures), and detection by AMS may be preferable.

7.4 Comment on conflicting ^{36}Cl results from prior studies

The conflicting results between USGS/LLNL and LANL were examined but the source or sources of the discrepancy could not be definitively determined. Most of the samples from the validation and prior studies were exhausted and therefore additional data could not be produced for direct comparison. The facility where LANL performed much of the work is no longer accessible and a trailer containing relevant samples was infested by rodents and sprayed with Cl-based bleach rendering the samples useless.

A number of "environmental factors" at the two laboratories have been suggested as possible reasons for the differences. Besides chloride native to the sample, the possibility exists that chloride can be introduced from external sources (contamination) during preparation of the sample for AMS analysis. Given the changes that have occurred in the laboratories over the years we were unable to test if past contamination was responsible for the differences and can not add any new insight to what has already been discussed in the validation study report.

For the most part, the LANL and USGS/LLNL groups used different AMS facilities for ^{36}Cl measurements. LANL primarily submitted samples to PRIME, whereas the USGS/LLNL had samples analyzed at CAMS. The two facilities were compared by providing splits to each laboratory. The samples included standards with ^{36}Cl/Cl ratios that were low (500), medium (2500) and high (10,000), as well as samples with AgCl precipitate masses that were small (~2 mg), average (~6 mg), and relatively large (~ 25 mg). There was no discrepancy between the AMS facilities. On the contrary, samples split and analyzed by CAMS and PRIME were in good agreement.

In summary, we found no errors in calculations used by the two groups and were not able to add any significant new observations or explanations for past data discrepancies. As such we refer to the validation study report, due out latter this year, which presents both sides of the issue. It is worth noting that there are no rock standards available to test the reliability of ^{36}Cl/Cl measurements and obtaining accurate and reproducible ratios from unsaturated rock is a non-trivial matter.

7.5 Size fractions of ESF samples

Portions of the raw (untouched) ESF samples collected during the UNLV study were sieved into size fractions as described in Section 5.2. The size distribution varied as expected with samples described as fault gouge containing higher percentages of the smallest size fractions, whereas samples described as fractured wall rock had greater percentages in the larger size fractions (Table 16). The sieving also allowed selection of a specific size fraction for study. The mid size classes (fines and gravel) were chosen for some of the initial analyses due to the conceptual model for leaching described earlier. However, samples in the latter part of the study (with low blanks) were analyzed without sieving.

Table 16. Size distribution by mass in percent after sieving raw ESF samples*

SMF ID	Fault or General Location	General Description	Size Fraction (mm) "rock flour" <0.125	"fines" 0.125-2.0	"gravel" 2.0-12.5	"large pieces" 12.5-75
SPC01034200	Sundance	Fractured wall rock	1.1	7.3	34.1	57.6
SPC01034201	Sundance	Fractured wall rock	0.3	1.6	15.0	83.1
SPC01034202	Sundance	Fractured wall rock	2.3	16.4	54.1	27.2
SPC01034203	Sundance	Fractured wall rock	0.4	3.9	21.7	74.0
SPC01034204	Sundance	Wall rock within fault zone	1.3	9.5	46.1	43.1
SPC01034205	Alcove 6	Fractured wall rock	0.5	3.7	17.7	78.1
SPC01034206	Alcove 6	Breciatted cooling joint	1.5	10.6	38.8	49.2
SPC01034207	Sundance	Fractured rock/fault gouge	2.4	19.3	53.8	24.4
SPC01034208	Ghost Dance	Fractured wall rock	1.2	7.6	35.0	56.2
SPC01034209	Ghost Dance	Fault gouge	8.2	36.7	45.9	9.2
SPC01034210	Bow Ridge	Fault gouge	5.8	23.6	40.0	30.6
SPC01034214	Drill Hole Wash	Wall rock 0.5-0.8 m	2.0	15.8	38.9	43.3
SPC01034215	Drill Hole Wash	Wall rock 1.08-1.28 m	1.6	15.6	39.1	43.7

Data is unqualified and given for informational purposes only. *not including pieces >75mm

7.6 Results of UNLV leaching experiments

Much work has been done evaluating the effects and implications of different leaching methods and times on ^{36}Cl studies at Yucca Mountain. A peer-reviewed paper by Liu et al. (2003) offers a good overview of the subject. In their conceptual model the probability of detecting a ^{36}Cl/Cl bomb pulse signal is diminished with longer leach times and smaller rock fragments. In our study, leaching conditions were chosen based on literature reviews and a passive leaching study in which we monitored Cl^-, Br^-, SO_4^{-2} and select trace elements as a function of leach time.

Our time-series leach experiment used two samples, one representing fractured rock (SPC01034203) with a relatively low 24 hr passive Cl^- leachate concentration (0.616 mg/kg rock) and the other consisting of fault gouge (SMF#01034207) with a relatively high Cl^- leachate concentration (23.26 mg/kg rock). The 12.5 – 75 mm fraction was chosen because the gravel fraction (2 – 12.5 mm) had been used for ^{36}Cl measurements. Details of the experiment are provided in Section 5.3.

7.6.1 Leach data for anions

Anion data for the leach experiment are presented in Table 17. Bromide concentrations were near the detection limit and varied little with time, whereas chloride and sulfate concentrations increased with leach time. Concentrations of sulfate and chloride were higher in the fault gouge relative to the fractured rock. For the fault gouge, concentrations of sulfate and, to a lesser extent, chloride tended to level after about 24 hours. In contrast, chloride and sulfate in leaches from the fractured rock seemed to increase steadily over time. We felt it best to treat each sample under the same conditions and decided on a 24 hour passive leach as a compromise between obtaining enough chloride from the samples consisting of mostly fractured wall rock and minimizing the extraction of chloride from the rock matrix. Moreover, this leach time was similar to some earlier work, including 19 hour passive leaches of ECRB cores by the USGS (Paces et al., 2003). In the section below, leachates are further evaluated using rare earth element patterns.

Table 17. Concentration (ppm) of anions in passive leachates for ESF rock

Time (hr)	Fractured rock (SPC01034203)			Fault gouge (SPC01034207)		
	Cl*	Br^-	SO_4^{-2}	Cl^-	Br^-	SO_4^{-2}
0	<MDL	0.026	0.124	<MDL	0.026	0.124
0.75	0.57*	0.020	0.154	0.43	<MDL	1.54
1.5	<MDL	0.029	0.099	1.20	<MDL	2.77
3	0.117	0.027	0.098	2.11	<MDL	4.88
6	<MDL	0.033	0.164	3.16	<MDL	5.84
12	0.119	0.026	0.207	4.79	0.031	6.07
24	0.232	0.029	0.319	9.06	0.070	8.25
48**	0.296	0.032	0.398	12.50	0.45	9.37
MDL	0.11	0.014	0.057	0.11	0.014	0.057

MDL=Method Detection Limit; *for information purposes only ** mean (n=3); DTN:004JC.008

7.6.2 Rare earth element leach and seepage data

Although rare earth elements (REEs) chemically behave differently than chloride, they were studied to learn more about the nature of the rock samples, particularly when elements associated with the rock matrix (rather than sorbed to surfaces) are leached. Whereas the results did not directly impact our leaching experimental design for leaching ^{36}Cl, they are presented because they were part of the work-scope and are of interest scientifically.

Data for REEs were plotted using a log scale for the concentrations (Fig. 2). The concentration data were normalized to Upper Continental Crust (UCC) (Taylor and McLennan, 1985). The solutions appear to reach a state of quasi-equilibrium with the rocks within the first three hours of the passive leaching. This suggests that the labile fraction (i.e., easily exchangeable fraction) is playing a significant role in the case of both the fractured rock and the fault gouge. The labile fraction represents REEs that are weakly adsorbed to surface sites on minerals and/or amorphous phases such as relatively young Fe/Mn/Al oxides/oxyhydroxides.

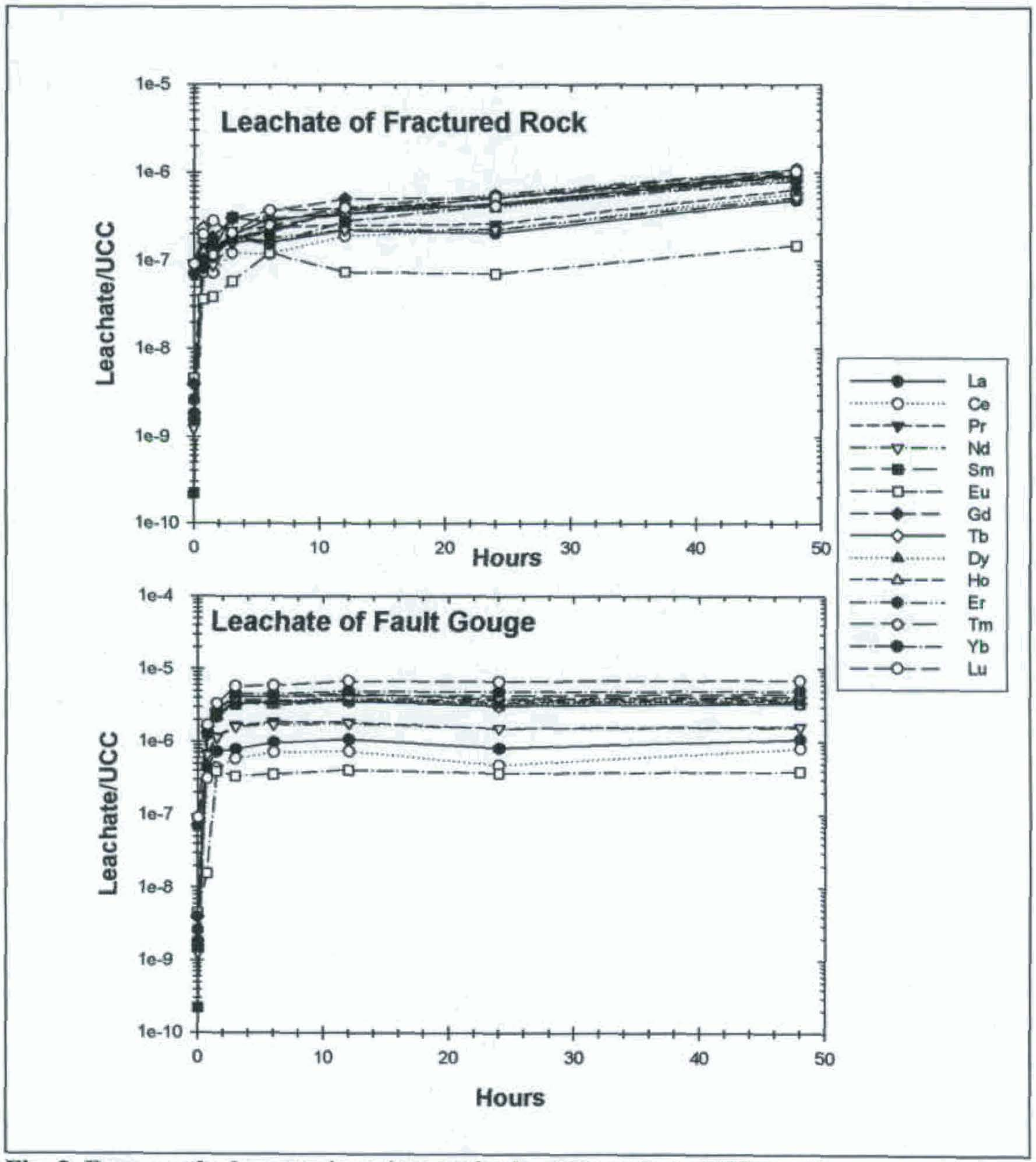


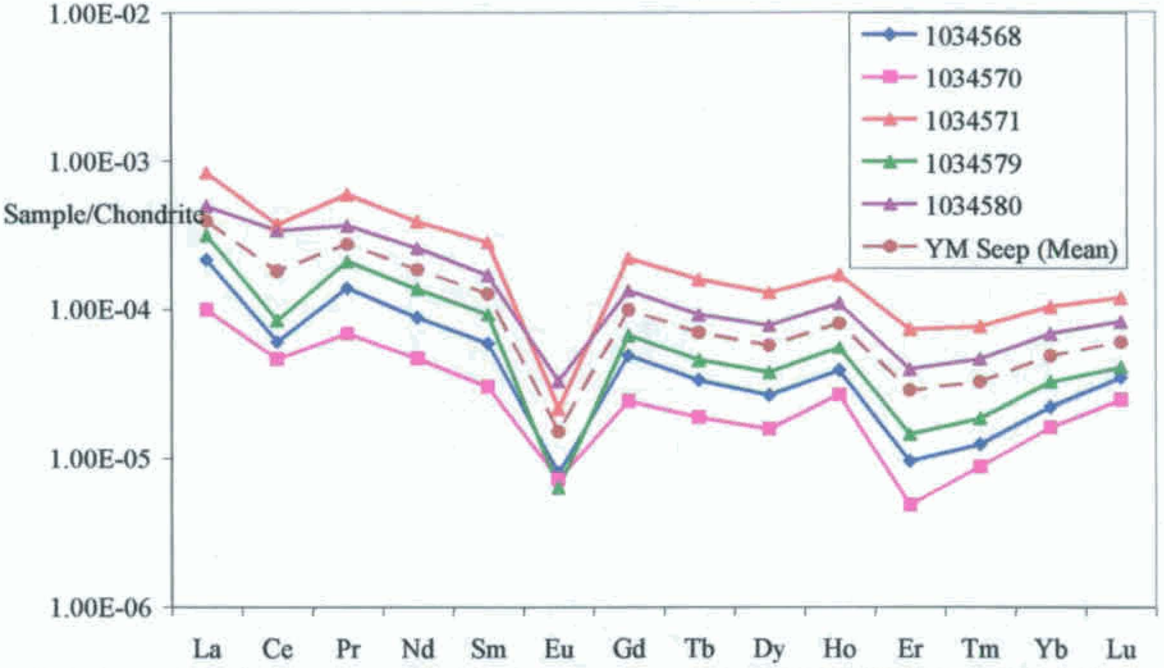
Fig. 2. Rare earth elements in a time-series leach (passive) of ESF rock.
DTN: MO0602UCC004XG.001

The second feature shown in these leach diagrams, is that for the fractured rock leachate, there is a continued, but slower increase in REE concentrations in the leach solution. This suggests either diffusion of REEs out of minerals such as partially hydrated carbonates undergoing dissolution or just slower dissolution of minerals, such as various carbonates, among others, over time. Interestingly, this slow rise in REE concentrations observed for the rock fracture leachates is not apparent in the fault gouge leachates. Moreover, the overall concentrations of REEs in the fault gouge leachates are roughly a factor of 10 greater. This is to be expected as the fault gouge is essentially powdered rock, crushed through fault activity. Thus, REEs within the crystalline mineral structure are more freely able to enter the leach solution as a result of increased surface area.

One interpretation of the data is that adsorption/desorption processes are likely to be most important in contributing dissolved REEs to groundwaters flowing through fractured rocks. If flow through such fractures is sufficiently slow, then diffusion of REEs from hydrated surfaces of carbonate minerals of the carbonate rocks may also contribute. The fractured rock leachate patterns closely resemble, except in an opposite sense, the surface complexation behavior of heavy metals onto carbonate minerals.

Data from the leach study was compared with data collected for natural seepage water from Yucca Mountain. REE concentrations in the seepage were similar to that found for fault gouge leaches. Patterns of REEs in the Yucca Mountain samples (Fig. 3) indicate interaction with volcanic rocks with possibly some contribution from primary or secondary carbonate minerals. Dr. Karen Johannesson (University of Texas at Arlington) and Dr. Zhongbo Yu (UNLV) contributed interpretation to this section.

Fig. 3 Rare Earth Elements in Yucca Mountain Seepage



Data is unqualified and presented for information purposes only; DTN: MO0604UCC004XG.005

7.7 Electron microscopy and imaging analyses

Six samples were examined qualitatively using the SEM to determine the distribution of Cl on the samples, however, identification of the Cl pattern was inconclusive. Most samples were unsuitable for analysis by the Energy Dispersive X-ray Spectroscopy (EDS) detector because they experienced a buildup of charge under the electron beam (charging). Additional carbon coating did not solve this problem. In some instances we were unable to distinguish possible EDS peak for Cl from the background noise, however, Cl was identified in the three samples from Alcove 6 (Table 18). The Cl peaks for these samples tended to cluster around microfractures within the sample.

Polished sections of four rock samples were analyzed using the electron microprobe. Trace amounts of Cl were detected (Table 19) but unlike the SEM the data showed no relationship with fractures, lithophysae, or any other obvious feature. EDS analyses also identified a white mineral at specific points in the sample as Na-Ca chloride. SEM images of these Na-Ca-Cl salts, however, show that the salt is present above the flat and polished surface of the rock sample, indicating that the salts precipitated after the section was polished. At no time did these rock samples come in contact with water after removal from the underground tunnel at Yucca Mountain so their origin is unclear. It is possible that the high intensity of the electron microprobe beam caused formation of these salts, and the source of the Cl may be epoxy used to stabilize the sample for section preparation. A definitive origin cannot be determined without further analyses. Images are included as an attachment to SN# UCCSN-UNLV-059 Vol. 1.

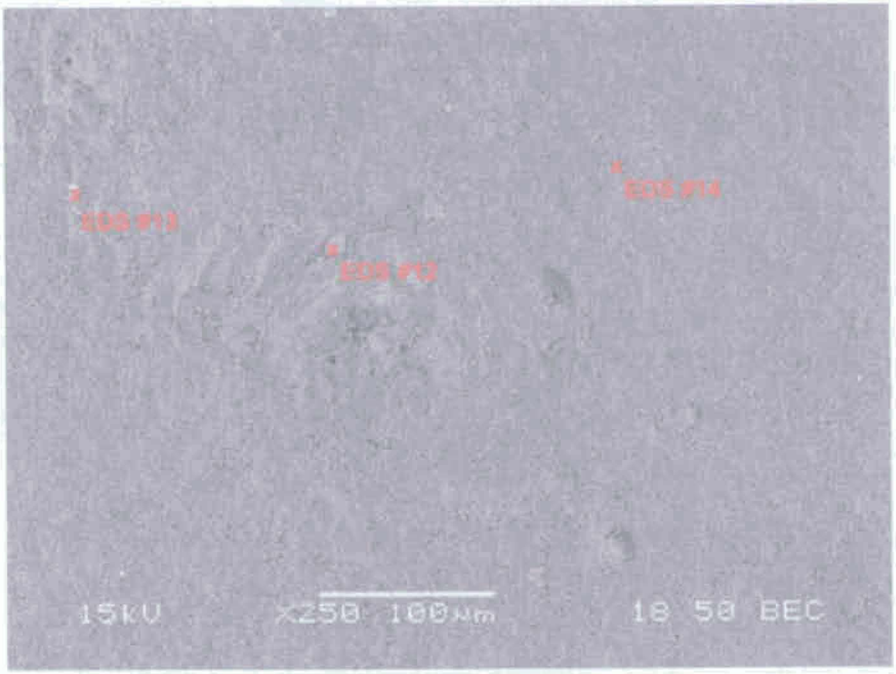


Figure 4 SEM Image of SPC01034207 (for information purposes only).

Figure 5 Macro Image of SPC01034207 (for information purposes only).

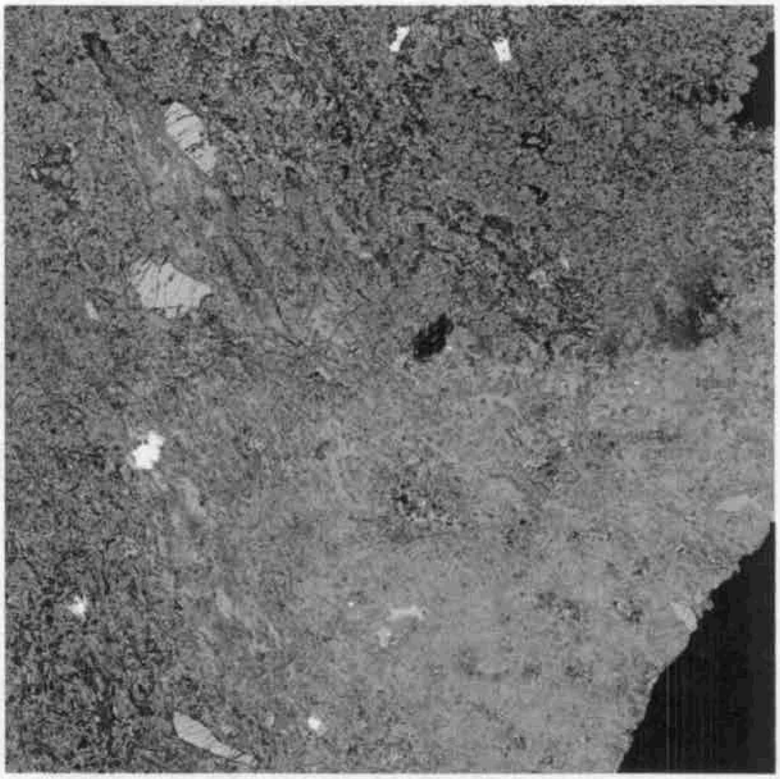


Figure 6 Microprobe Image of SPC01034215 (for information purposes only).

Table 18. Samples analyzed by the SEM for Chlorine.

SMF #	Geologic Split	Location	Surface	Scientific Notebook	Excavated or Hand Sampled	# of EDS Points	Results
SPC01034200	-1	ESF 35+93	Rough	UCCSN-UNLV-059 Vol. 1	Excavated	0	Charging No Analysis
SPC01034200	-2	ESF 35+93	Rough	UCCSN-UNLV-059 Vol. 1	Excavated	0	Charging No Analysis
SPC01034200	-3	ESF 35+93	Rough	UCCSN-UNLV-059 Vol. 1	Excavated	0	Charging No Analysis
SPC01034200	-4	ESF 35+93	Rough	UCCSN-UNLV-059 Vol. 1	Excavated	0	Charging No Analysis
SPC01034206	-1	Alcove 6 1+60	Rough	UCCSN-UNLV-059 Vol. 1	Hand Sampled	3	Possible small Cl peak
SPC01034206	-2	Alcove 6 1+60	Rough	UCCSN-UNLV-059 Vol. 1	Hand Sampled	0	Charging No Analysis
SPC01034206	-3	Alcove 6 1+60	Rough	UCCSN-UNLV-059 Vol. 1	Hand Sampled	1	No Cl Detected
SPC01034206	-4	Alcove 6 1+60	Rough	UCCSN-UNLV-059 Vol. 1	Hand Sampled	0	Charging No Analysis
SPC01034207	-1	Alcove 6 0+93	Polished	UCCSN-UNLV-059 Vol. 1	Hand Sampled	26	Possible small Cl peak
SPC01034210	-1	ESF 1+99.8	Rough	UCCSN-UNLV-059 Vol. 1	Hand Sampled	0	Charging No Analysis
SPC01034210	-2	ESF 1+99.8	Rough	UCCSN-UNLV-059 Vol. 1	Hand Sampled	4	No Cl Detected
SPC01034210	-3	ESF 1+99.8	Rough	UCCSN-UNLV-059 Vol. 1	Hand Sampled	0	Charging No Analysis
SPC01034210	-5	ESF 1+99.8	Polished	UCCSN-UNLV-059 Vol. 1	Hand Sampled	1	No Cl Detected/Charging
SPC01034214	-1	ESF 19+33	Polished	UCCSN-UNLV-059 Vol. 1	Excavated	0	Charging No Analysis
SPC01034229	-1	Alcove 6 1+68	Polished	UCCSN-UNLV-059 Vol. 1	Excavated	40	small Cl peak (identified by instrument)

Data are qualitative in nature and are unqualified and presented for information purposes only. Samples that were charging under the SEM could not be analyzed using the EDS detector. "Possible small chloride peak" may reflect the presence of chloride or may be background.

Table 19. Samples analyzed by the Electron Microprobe for Chlorine.

SMF #	Geologic Split	Location	Surface	Scientific Notebook	Excavated or Hand Sampled	Results
SPC01034201	N/A	ESF 35+93	Polished	UCCSN-UNLV-059 Vol. 1	Excavated	Cl Detected
SPC01034202	N/A	ESF 35+93	Polished	UCCSN-UNLV-059 Vol. 1	Excavated	Cl Detected
SPC01034204	N/A	ESF 35+93	Polished	UCCSN-UNLV-059 Vol. 1	Excavated	Not Analyzed
SPC01034206	-5	Alcove 6 1+60	Polished	UCCSN-UNLV-059 Vol. 1	Hand Sampled	Not Analyzed
SPC01034210	-4	ESF 1+99.8	Polished	UCCSN-UNLV-059 Vol. 1	Hand Sampled	Cl Detected
SPC01034214	-2	ESF 19+33	Polished	UCCSN-UNLV-059 Vol. 1	Excavated	Not Analyzed
SPC01034215	-2	ESF 19+33	Polished	UCCSN-UNLV-059 Vol. 1	Excavated	Cl Detected
SPC01034229	-2	Alcove 6 1+68	Polished	UCCSN-UNLV-059 Vol. 1	Excavated	Not Analyzed

Chloride was detected in post-polish salts that accumulated on the polished surfaces of some samples; the location of the salts does not correlate with any obvious rock features and the source of the chloride may be epoxy that was damaged during the analyses.

7.8 Inventory of remaining (unleached) samples

Much effort was expended to collect relevant samples in a manner that would minimize contamination (see Section 5). Despite having to analyze more sample than anticipated, there remains rock that has been untouched and available for further study (Table 20). Indeed a follow-up study is recommended to take advantage of these valuable remnants to provide additional information and confirmatory results.

Table 20. Inventory of Remaining (Unleached) ESF Rock Samples. Data are unqualified and presented for information purposes only.

Sample ID	Collection Date	Sample Details	~Weight (kg)
SPC01034200	3-2-2005	Sundance Fault ESF 35+93	1.6
SPC01034201	3-2-2005	Sundance Fault ESF 35+93	2.6
SPC01034202	3-2-2005	Sundance Fault ESF 35+93	9.6
SPC01034203	3-2-2005	Sundance Fault ESF 35+93	2.3
SPC01034204	3-2-2005	Sundance Fault ESF 35+93	4.3
SPC01034205	3-21-2005	Alcove 6, 1+60	1.4
SPC01034206	3-21-2005	Alcove 6, 1+60	1.1
SPC01034207	3-21-2005	Alcove 6, 0+93	2.6
SPC01034209	3-21-2005	Alcove 6, 1+52	1.1
SPC01034210	3-21-2005	Bow Ridge Fault, 1+ 99.8	4.0
SPC01034214	3-31-2005	Drill Hole, 19+33	8.6
SPC01034215	3-31-2005	Drill Hole, 19+33	9.8
SPC01034229	7/19/2005	Alcove 6, 1+68	>10
SPC00557088	3-31-2005	EVAL-1, 1/4" -1/2"	1.1

7.9 CONCLUSIONS AND RECOMMENDATIONS

^{36}Cl, ^{99}Tc and ^{129}I are three long-lived radionuclides that can be associated with radioactive fallout, which peaked during the above-ground tests of thermonuclear weapons conducted in the late 1950's and early 1960's. This bomb-pulse signature has been used to date young groundwater and trace infiltration patterns in soil and rock. The isotopes can be used as hydrologic tracers because of their solubility and generally conservative behavior. LANL scientists used ^{36}Cl data to demonstrate the presence of fast-path percolation in ESF tunnel samples. An attempt to obtain similar results by an independent laboratory failed to produce ^{36}Cl/Cl ratios indicative of ~50 year old water flow at repository depths. However, the two groups followed somewhat different procedures and sometimes produced conflicting results. This project was tasked to determine the source of the discrepancy and obtain additional data on bomb-pulse isotopes in the ESF. To that end we have collected rock from inside the ESF, soil from the surface of Yucca Mountain, and seepage from the south portal, and analyzed the samples for ^{36}Cl and, in some cases, ^{99}Tc and ^{129}I. AMS and ICP-MS were used to measure extremely low concentrations of the isotopes. The following list highlights UNLV's main findings and recommendations.

- Results for rock samples collected in the UNLV study were generally lower than those found by LANL for comparable samples, but were still in agreement with the range of data produced from the area. Only one sample, welded tuff with rare breccia from near the Drill Hole Wash fault, yielded a ^{36}Cl/Cl bomb-pulse ratio: 1590 ± 80 (1σ) $\times 10^{-15}$. These few results should be viewed with caution until replicated.

- Data for soil samples collected above the ESF were consistent with that typically found for desert soils leached with meteoric water and showed that we are able to measure a bomb-pulse ^{36}Cl signal from a relevant environmental sample.

- Seepage collected from the ESF near the south portal yielded ^{36}Cl/Cl ratios ($\times 10^{-15}$) that ranged between 680 ± 40 to 1110 ± 40 and averaged 800 ± 80, consistent with modern meteoric water with perhaps a small bomb-pulse component.

- Results for ^{36}Cl standards prepared from NIST reference material showed that the procedures for target preparation and analysis were reliable and served as an independent calibration check for PRIME data.

- Samples split and analyzed by CAMS and PRIME were in good agreement.

- A column experiment indicated that a bomb-pulse ^{36}Cl/Cl ratio in tuffaceous rock may require multiple meteoric flow (leaching) events before the ratio is significantly diminished.

- Scoping studies using bromide as an alternative carrier suggest that the ^{36}Cl/Cl ratio can be obtained without the addition of stable chloride, which may eliminate a potential source of uncertainty in the analysis.

- ^{99}Tc was measured in ESF rock but poor analytical recoveries and lack of data overlap with ^{36}Cl limit interpretations of these data. The detection capability of the ICP-MS was insufficient for measuring ^{129}I without incorporating preconcentration, and detection by AMS may be preferable.

- The source or sources of the conflicting results between the USGS/LLNL and LANL, as discussed in the draft USGS validation study report, could not be definitively determined. Our experience with apparent ^{36}Cl contamination of some blanks and samples, from an undetermined, but laboratory-related source, underlined the difficulty of ^{36}Cl measurements on very small samples.

- Despite having gained valuable experience, most of the quality results presented in this report were generated late in the study and could not be replicated because of lack of time.

- A follow-up study is recommended to deliver additional and confirmatory information on the remaining unleached and possibly a few new samples. Full resolution of the issue of the presence/absence of bomb-pulse is within reach.

8. INPUTS AND REFERENCES

8.1 Inputs

004JC.002. Chlorine-36 Bomb Pulse Study of Chlorine-36/Chlorine and Chlorine-35/Chlorine-37 Isotope Ratios Measured in Leachates from Rock Collected from the Yucca Mountain Exploratory Study Facility. CAMS, Non-Q

004JC.004. Chlorine-36 Bomb Pulse Study of Chlorine-36/Chlorine and Chlorine-35/Chlorine-37 Isotope Ratios Measured in Leachates from Rock Collected from the Yucca Mountain Exploratory Study Facility. PRIME, Non-Q

004JC.008. Concentrations of Chloride, Sulfate and Bromide in Leachate Samples Collected for Cl-36 Studies from April 2005 through February 2006.

004JC.006. Chlorine-36 Bomb Pulse Study of Chlorine-36/Chlorine and Chlorine-35/Chlorine-37 Isotope Ratios Measured in Leachates from Rock Collected from the Yucca Mountain Exploratory Study Facility. PRIME, Q, Measured Ratios

004JC.007. Chlorine-36 Bomb Pulse Study of Chlorine-36/Chlorine and Chlorine-35/Chlorine-37 Isotope Ratios Measured in Leachates from Rock Collected from the Yucca Mountain Exploratory Study Facility. PRIME, Q, Blank-Corrected Ratios

004XG.001. Rare Earth Elements (REEs) concentrations in Passive Leachates of Fractured Rock and Fault Gauge analyzed by a Time-Series Experiment.

004XG.004. Technetium-99 (Tc-99) Concentrations From Leachates Of Rock Collected From The Exploratory Studies Facility (ESF) at Yucca Mountain and Soil From The Las Vegas Valley.

004XG.005. Rare Earth Element concentrations for seep collected in the south ramp of the Exploratory Studies Facility (ESF) at Yucca Mountain.

007AB.002. Yucca Mountain Precipitation Data, 01/01/03-12/31/03.

007AB.003. Yucca Mountain Precipitation Data, 01/01/04-12/31/04.

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LAJF831222AQ98.009. Chlorine-36 Analyses of Salts Leached from ESF Niche 3566 (Niche #1) Drillcore. Submittal date: 09/09/1998.

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LL030605223121.030. Cl Abundance and Cl Ratios of Leachates from ESF Core Samples. Submittal date: 06/13/2003.

MO0603UCC004JB.001. Concentrations of Chloride, Sulfate and Bromide in Leachate Samples Collected for Cl-36 Studies from April 2005 through February 2006.

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UN020SPA030AB.001. Yucca Mountain Precipitation Data, 12/12/00-12/31/01.

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APPENDIX 1 Summary Table of Anion Data (DTN 004JC.008)

Summary Table of Anions in Samples Associated with Cl-36 Study Task ORD-FY04-004

Sample ID	Start Leach Date	Analysis Date	Cl (ppm)	SO4 (ppm)	Br (ppm)	Notes
SPC00557088 (4/25/05)	4/25/2005	4/28/2005	R	0.709	0.569	Also referred to Eval. #1
SPC01034200 (4-21-05)	4/21/2005	4/28/2005	R	1.58	0.0891	2-12.5 mm fraction
SPC01034202 (4-21-05)	4/21/2005	4/28/2005	R	0.726	UD	2-12.5 mm fraction
SPC01034203 (4/25/05)	4/25/2005	4/28/2005	R	1.60	0.137	2-12.5 mm fraction
SPC01034204 (4-21-05)	4/21/2005	4/28/2005	R	0.563	UD	2-12.5 mm fraction
SPC01034206 (4-21-05)	4/21/2005	4/28/2005	R	1.51	0.432	2-12.5 mm fraction
SPC01034207 (4-21-05)	4/21/2005	4/28/2005	R	20.3	0.271	2-12.5 mm fraction
SPC01034208 (4-21-05)	4/21/2005	4/28/2005	R	2.84	0.192	2-12.5 mm fraction
SPC01034209 (4-21-05)	4/21/2005	4/28/2005	R	9.95	0.202	2-12.5 mm fraction
SPC01034210 (4-21-05)	4/21/2005	4/28/2005	R	4.39	0.0798	2-12.5 mm fraction
SPC01034214 #1 (4-21-05)	4/21/2005	4/28/2005	R	0.945	UD	2-12.5 mm fraction
SPC01034214 #2 (4-21-05)	4/21/2005	4/28/2005	R	1.03	UD	2-12.5 mm fraction
SPC01034215 #1 (4-21-05)	4/21/2005	4/28/2005	R	0.932	UD	2-12.5 mm fraction
SPC01034215 #2 (4-21-05)	4/21/2005	4/28/2005	R	1.03	UD	2-12.5 mm fraction
Blank Silicon 2-12.5 mm (4-21-05)	4/21/2005	4/28/2005	R	0.484	UD	2-12.5 mm fraction
DI 0hr (5-7-05)	5/7/2005	6/2/2005	R	0.124	0.0256	Time Series Blank
DI .75hr (5-7-05)	5/7/2005	6/2/2005	R	0.0700	0.0158	Time Series Blank
DI 1.5 hr (5-7-05)	5/7/2005	6/2/2005	R	0.0928	0.0302	Time Series Blank
DI 3hr (5-7-05)	5/7/2005	6/2/2005	R	0.0698	0.0341	Time Series Blank
DI 6hr (5-7-05)	5/7/2005	6/2/2005	R	0.0783	0.0330	Time Series Blank
DI 12hr (5-7-05)	5/7/2005	6/2/2005	R	0.0712	0.0326	Time Series Blank
DI 24hr (5-7-05)	5/7/2005	6/2/2005	R	0.0487	0.0540	Time Series Blank
DI 48hr (5-7-05)	5/7/2005	6/2/2005	R	0.0721	0.0424	Time Series Blank
SPC01034203 .75hr (5-7-05)	5/7/2005	6/2/2005	R	0.154	0.0198	Time Series Fractured Rock
SPC01034203 1.5hr (5-7-05)	5/7/2005	6/2/2005	R	0.0989	0.0290	Time Series Fractured Rock
SPC01034203 3hr (5-7-05)	5/7/2005	6/2/2005	R	0.0982	0.0273	Time Series Fractured Rock
SPC01034203 6hr (5-7-05)	5/7/2005	6/2/2005	R	0.164	0.0328	Time Series Fractured Rock
SPC01034203 12hr (5-7-05)	5/7/2005	6/2/2005	R	0.207	0.0259	Time Series Fractured Rock
SPC01034203 24hr (5-7-05)	5/7/2005	6/2/2005	R	0.319	0.0286	Time Series Fractured Rock
SPC01034203 48hr (1) (5-7-05)	5/7/2005	6/2/2005	R	0.384	0.0349	Time Series Fractured Rock
SPC01034203 48hr (2) (5-7-05)	5/7/2005	6/2/2005	R	0.396	0.0246	Time Series Fractured Rock
SPC01034203 48hr (3) (5-7-05)	5/7/2005	6/2/2005	R	0.414	0.0365	Time Series Fractured Rock
SPC01034207 .75hr (5-7-05)	5/7/2005	6/2/2005	R	1.54	UD	Time Series Fault Gouge
SPC01034207 1.5hr (5-7-05)	5/7/2005	6/2/2005	R	2.77	UD	Time Series Fault Gouge
SPC01034207 3hr (5-7-05)	5/7/2005	6/2/2005	R	4.88	UD	Time Series Fault Gouge
SPC01034207 6hr (5-7-05)	5/7/2005	6/2/2005	R	5.84	UD	Time Series Fault Gouge
SPC01034207 12hr (5-7-05)	5/7/2005	6/2/2005	R	6.07	0.0309	Time Series Fault Gouge
SPC01034207 24hr (5-7-05)	5/7/2005	6/2/2005	R	8.25	0.0705	Time Series Fault Gouge
SPC01034207 48hr (1) (5-7-05)	5/7/2005	6/2/2005	R	10.2	0.460	Time Series Fault Gouge
SPC01034207 48hr (2) (5-7-05)	5/7/2005	6/2/2005	R	9.04	0.509	Time Series Fault Gouge
SPC01034207 48hr (3) (5-7-05)	5/7/2005	6/2/2005	R	8.86	0.389	Time Series Fault Gouge
SPC01034201 2-12.5 mm (5-23-05)	5/23/2005	6/2/2005	R	1.04	0.0627	
SPC01034201 12.5-75mm (5-23-05)	5/23/2005	6/2/2005	R	0.315	0.0350	
SPC01034205 2-12.5mm (5-23-05)	5/23/2005	6/2/2005	R	1.11	0.142	
SPC01034211 (5-23-05)	5/23/2005	6/2/2005	R	0.428	0.0134	Field Silicon Blank
SPC01034212 (5-23-05)	5/23/2005	6/2/2005	R	0.358	0.0141	Field Silicon Blank
SPC01034213 (5-23-05)	5/23/2005	6/2/2005	R	0.283	0.0216	Field Silicon Blank
SPC01034216 (5-23-05)	5/23/2005	6/2/2005	R	0.272	0.0102	Field Silicon Blank
SPC2014361+SPC2014365 (5-23-05)	5/23/2005	6/2/2005	R	0.739	UD	
SPC2014661 (5-23-05)	5/23/2005	6/2/2005	R	0.185	0.00752	
SPC1004844 (5-23-05)	5/23/2005	6/2/2005	R	0.192	0.0130	
SPC2016028 (5-23-05)	5/23/2005	6/2/2005	R	0.146	0.0239	
LV1-1 <2mm (5-23-05)	5/23/2005	6/2/2005	R	0.487	0.0109	Las Vegas Soil
LV1-2 <2mm (5-23-05)	5/23/2005	6/2/2005	R	0.313	0.0160	Las Vegas Soil
LV1-3 <2mm (5-23-05)	5/23/2005	6/2/2005	R	0.632	0.00948	Las Vegas Soil
Reagent Blank (5-23-05)	5/23/2005	6/2/2005	R	0.112	0.0220	

Appendix 1 cont.

Reagent blank 1 (9-27-2005)	9/27/2005	10/24/2005	0.0105	ND	ND	
Reagent blank 2 (9-27-2005)	9/27/2005	10/24/2005	0.00829	ND	ND	
Reagent blank 3 (9-27-2005)	9/27/2005	10/24/2005	0.0114	ND	ND	
Reagent blank 4 (9-27-2005)	9/27/2005	10/24/2005	0.0108	ND	ND	
Reagent blank 5 (9-27-2005)	9/27/2005	10/24/2005	0.0155	ND	ND	
Reagent blank 6 (9-27-2005)	9/27/2005	10/24/2005	0.0150	ND	ND	
Reagent blank 1 (12-13-2005)	12/13/2005	12/22/2005	0.0342	ND	ND	
Reagent blank 2 (12-13-2005)	12/13/2005	12/22/2005	0.0336	ND	ND	
Reagent blank 3 (12-13-2005)	12/13/2005	12/22/2005	0.0279	ND	ND	
Reagent blank 4 (12-13-2005)	12/13/2005	12/22/2005	0.0325	ND	ND	
SPC01034204(12-27-05)	12/27/2005	1/5/2006	0.166	ND	ND	
SPC01034206 (12-27-05)	12/27/2005	1/5/2006	0.513	ND	ND	
SPC00557088 (12-27-05)	12/27/2005	1/5/2006	1.11	ND	ND	
SPC01034210 (12-27-05)	12/27/2005	1/5/2006	2.37	ND	ND	
SPC01034214 #1 (12-27-05)	12/27/2005	1/5/2006	0.472	ND	ND	
SPC01034215 #1 (12-27-05)	12/27/2005	1/5/2006	0.264	ND	ND	
Reagent blank 1 (12-27-05)	12/27/2005	1/5/2006	0.0349	ND	ND	
Reagent blank 2 (12-27-05)	12/27/2005	1/5/2006	0.0367	ND	ND	
SPC01034207 (12-27-05)	12/27/2005	1/9/2006	14.3	ND	ND	
SPC01034209 (12-27-05)	12/27/2005	1/9/2006	7.43	ND	ND	
C1 (1-30-06)	1/30/2006	2/8/2006	0.756	ND	ND	Column experiment, wash 2
C2 (1-30-06)	1/30/2006	2/8/2006	0.980	ND	ND	Column experiment, wash 2
C3 (1-30-06)	1/30/2006	2/8/2006	0.412	ND	ND	Column experiment, wash 2
C4 (1-30-06)	1/30/2006	2/8/2006	0.763	ND	ND	Column experiment, wash 2
C5 (1-30-06)	1/30/2006	2/8/2006	0.661	ND	ND	Column experiment, wash 2
C6 (1-30-06)	1/30/2006	2/8/2006	0.0244	ND	ND	Column experiment, wash 2
C1-L1	1/25/2006	2/8/2006	1.79	ND	ND	Column experiment, leach 1
C2-L1	1/25/2006	2/8/2006	0.144	ND	ND	Column experiment, leach 1
C3-L1	1/25/2006	2/8/2006	0.343	ND	ND	Column experiment, leach 1
C4-L1	1/25/2006	2/8/2006	1.23	ND	ND	Column experiment, leach 1
C5-L1	1/25/2006	2/8/2006	0.127	ND	ND	Column experiment, leach 1
C6-L1	1/25/2006	2/8/2006	0.0313	ND	ND	Column experiment, leach 1
C1-L2	1/26/2006	2/8/2006	0.0627	ND	ND	Column experiment, leach 2
C2-L2	1/26/2006	2/8/2006	0.0615	ND	ND	Column experiment, leach 2
C3-L2	1/26/2006	2/8/2006	0.0200	ND	ND	Column experiment, leach 2
C4-L2	1/26/2006	2/8/2006	0.884	ND	ND	Column experiment, leach 2
C5-L2	1/26/2006	2/8/2006	0.0592	ND	ND	Column experiment, leach 2
C6-L2	1/26/2006	2/8/2006	0.0238	ND	ND	Column experiment, leach 2
C1-W1	1/29/2006	2/8/2006	10.6	ND	ND	Column experiment, wash 1
C2-W1	1/29/2006	2/8/2006	1.82	ND	ND	Column experiment, wash 1
C3-W1	1/29/2006	2/8/2006	1.98	ND	ND	Column experiment, wash 1
C4-W1	1/29/2006	2/8/2006	0.978	ND	ND	Column experiment, wash 1
C5-W1	1/29/2006	2/8/2006	1.57	ND	ND	Column experiment, wash 1
C6-W1	1/29/2006	2/8/2006	0.145	ND	ND	Column experiment, wash 1
C1-S1	1/27/2006	2/8/2006	62.9	ND	ND	Column experiment, spike 1
C2-S1	1/27/2006	2/8/2006	63.9	ND	ND	Column experiment, spike 1
C3-S1	1/27/2006	2/8/2006	63.7	ND	ND	Column experiment, spike 1
C4-S1	1/27/2006	2/8/2006	65.7	ND	ND	Column experiment, spike 1
C5-S1	1/27/2006	2/8/2006	64.3	ND	ND	Column experiment, spike 1
C6-S1	1/27/2006	2/8/2006	64.6	ND	ND	Column experiment, spike 1

Appendix 1 cont.

Reagent blank 1 (1-31-06)	1/31/2006	2/9/2006	0.0305	ND	ND
Reagent blank 2 (1-31-06)	1/31/2006	2/9/2006	0.0404	ND	ND
SPC01034230 1-31-06	1/31/2006	2/9/2006	0.125	ND	ND
SPC01034231 1-31-06	1/31/2006	2/9/2006	0.130	ND	ND
SPC01034232 1-31-06	1/31/2006	2/9/2006	0.423	ND	ND
SPC01034233 1-31-06	1/31/2006	2/9/2006	0.117	ND	ND
SPC01034233 duplicate 1-31-06	1/31/2006	2/9/2006	0.106	ND	ND
SPC01034234 1-31-06	1/31/2006	2/9/2006	0.0831	ND	ND
SPC01034235 1-31-06	1/31/2006	2/9/2006	0.340	ND	ND
SPC01034236 1-31-06	1/31/2006	2/9/2006	0.206	ND	ND
SPC01034237 1-31-06	1/31/2006	2/9/2006	0.327	ND	ND
SPC01034238 1-31-06	1/31/2006	2/9/2006	0.203	ND	ND
SPC01034239 1-31-06	1/31/2006	2/9/2006	0.190	ND	ND
SPC01034240 1-31-06	1/31/2006	2/9/2006	0.541	ND	ND
DL			0.11*	0.057	0.014

IC = Ion Chromatography
ND=Not Determined
DL = Detection Limit
DI = Deionized Water
UD = Undetected
R=Rejected Data (possible Cl contaminaiton)

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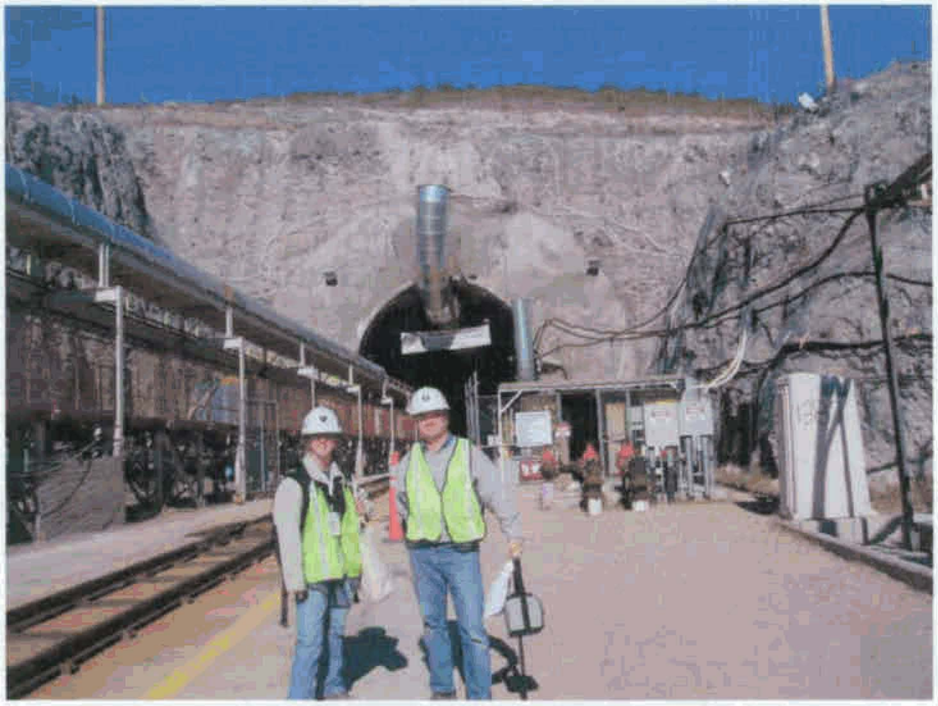
* The chloride detection limit of 0.11 ppm determined on 4/11/05 is likely not appropriate for samples analyzed in fall of 2005 and spring of 2006 when a new source of water (distilled, purchased from Walgreen's Corporation) was used leach samples. Using leaching process blank results during the later period, we estimate the DL (3σ criteria) to be 0.008 ppm from 9-27-05 through 10-27-05 and 0.011 ppm from 12-13-05 through 2-9-06. The latter two periods are separated because leaching of samples occurred in stainless steel buckets and plastic containers, respectively. The chloride IC detection limit for samples analyzed during the period 9-27-05 and 10-27-05 was calculated from the six reagent blanks dated 9-27-2005. The chloride IC detection limit for samples analyzed during the period 12-13-05 and 2-9-06 was calculated from the eight reagent blanks collected on 12-13-06, 12-27-06, 1-31-06.

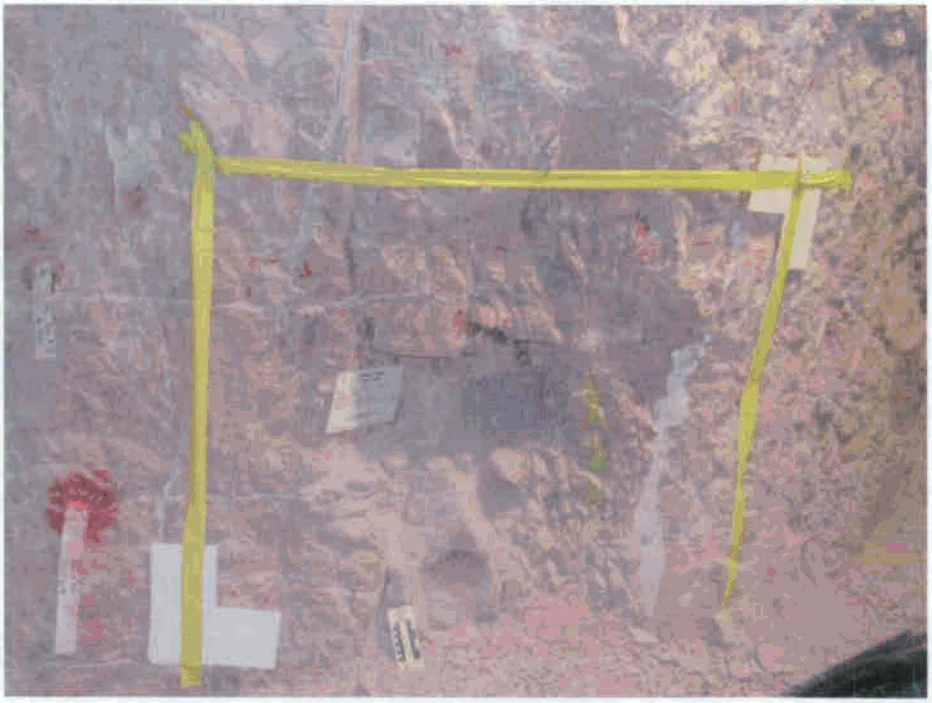
APPENDIX 2 Calculations used for determining background corrected ^{36}Cl/Cl ratios

Source data used in the calculating corrected ^{36}Cl/Cl ratios from the AMS measured ^{36}Cl/Cl ratios were DTNs: 004JC.008 (ion chromatography data), 004JC.006 (^{36}Cl/Cl ratios measured at PRIME). Other information can be found in scientific notebook number UCCSN-UNLV-065, vols. 1 and 4. Specifically, the measured ratios were background corrected for chloride in the leach water and ^{36}Cl determined process blanks as follows. Chloride in the reagent blank and chloride added as carrier were subtracted from the total chloride determined in the final leachate. The resultant value was used as the denominator in the ^{36}Cl/Cl corrected ratio calculation. The numerator was determined by multiplying the measured ratio by the total chloride (mg) in the final leachate, and subtracting the amount of ^{36}Cl stemming from reagents/process, which was in turn calculated by multiplying the measured ratio for the process blank by the amount of chloride (mg) added from the blank. If more than one process blank was used for a leaching run, mean blank results were employed in the calculation. Propagation of the measured ^{36}Cl/Cl uncertainty through the calculations followed standard error propagation techniques and included a 2% factor for sample preparation.

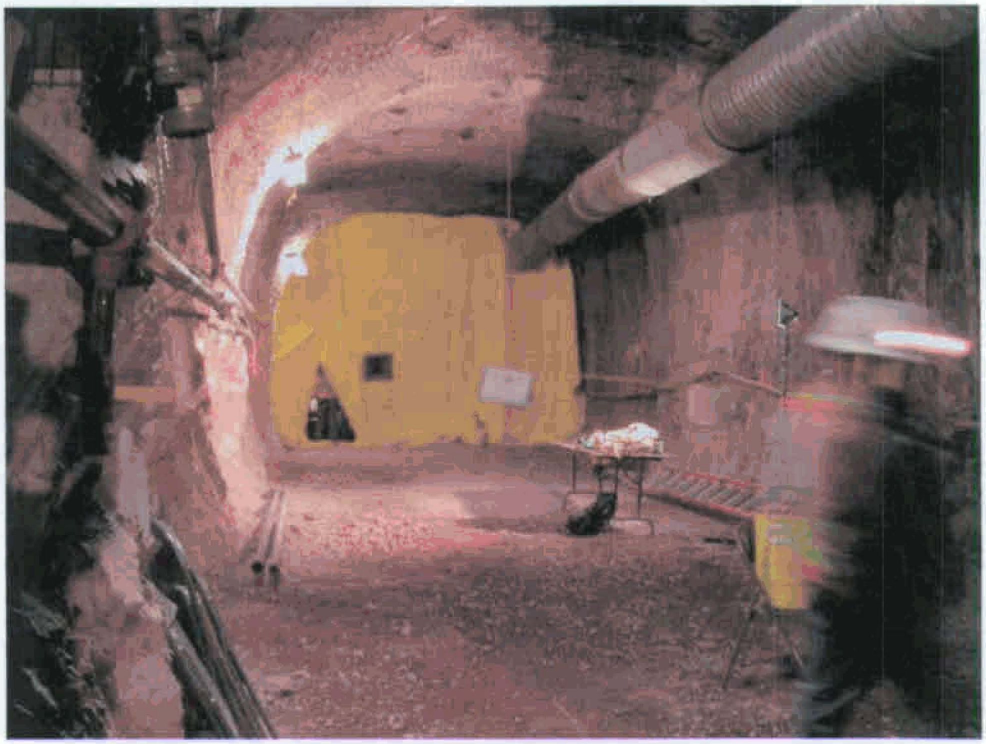
APPENDIX 3 Select photos from sampling



R. Howley & J. Cizdziel at north portal



Alcove 6 (1+68) Excavation Site



Alcove 6 Dust Protection Device

Bobcat excavation Alcove 6 (1+68)

Drill Hole Wash Sample Site

Rock collection onto plastic sheet

South ramp surface dig site

North ramp surface dig site