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# $^{36}$Cl Studies of Water Movements Deep Within Unsaturated Tuffs

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Measurements of $^{36}$Cl in cuttings from a borehole that was drilled 387 m into unsaturated tuffs indicate the possible detection of significant radioactive decay of cosmogenic $^{36}$Cl in two of the samples. However, the $^{36}$Cl/Cl ratio was found to vary with the amount of pulverization of the cuttings. Work is in progress to separate the $^{36}$Cl/Cl data into cosmogenic and in situ components. The cosmogenic component will be used to trace very slow water movements through the unsaturated zone. Bomb pulse $^{36}$Cl was observed as deep as 153 m, and this identification is not constrained by the problem with pulverization. This work shows the efficacy of $^{36}$Cl measurements for detecting modern water movements deep in the unsaturated zone.

## 1. Introduction

Characterization of water movements in unsaturated zone tuffs at Yucca Mountain, Nevada, is important for predicting the water-borne transport of radioactive nuclides to the accessible environment from a potential nuclear waste repository. The information available prior to the start of this study was compiled by Montazer and Wilson [1]. Data came from laboratory measurements of effective permeabilities utilizing cores from Yucca Mountain boreholes and from measurements in boreholes of geothermal heat flux, hydraulic gradients, and effective permeabilities. The data indicated that the downward flux of water through the potential repository host rock, the moderately to densely welded portion of the Topopah Spring Member of the Paintbrush Tuff formation, may range from 1 × $10^{-7}$ to 0.2 mm/yr. The geothermal heat flux data indicated that the net hydrologic flux may be upward because of vapor phase transport. Measurements of $^{36}$Cl have been undertaken to supplement the information about water movements in the unsaturated zone derived from conventional techniques.

The priniciple of this study derives from the conservative properties of chlorides to trace hydrologic water movements in the liquid phase [2]. Chlorides have been deposited on the arid land at Yucca Mountain by winds that have lofted sea spray into the troposphere. Then rainfall and melted snow have dissolved some of this environmental chloride and transported it into the unsaturated zone. Some of the chlorine in these chlorides is cosmogenic $^{36}$Cl. The radioactive decay of $^{36}$Cl, with its 3 x $10^5$ yr half-life, serves as the timing signal for the rate of water percolation through the unsaturated tuffs. The water need not move downward uniformly for this measurement to be meaningful. For example, a pulse of water could dissolve some chloride, carry the solute some distance underground, then evaporate. The nonvolatile chloride will remain where the water deposited it until moved to a different location by another pulse of water. The cosmogenic $^{36}$Cl measured in a particular sample may result from multiple pulses of water over a period of time, in which case the data would be interpreted in terms of water movement somewhat faster than that of the chloride deposited by the original pulse, but somewhat slower than that of the solute in the last pulse. The rate of solute transport derived from the $^{36}$Cl data, even though it may be an average value, will be useful for calculating transport rates for water-borne nuclides such as $^{99}$TcO$_4^-$ and $^{129}$I$^-$, which are likely to be transported no faster than the average rate derived from the $^{36}$Cl data.

The goal of the work reported below is to observe a decrease in the $^{36}$Cl/Cl ratio as a function of sample depth, where the decrease in the ratio results from the radioactive decay of cosmogenic $^{36}$Cl. The cosmogenic $^{36}$Cl/Cl ratio at the surface of Yucca Mountain was determined to be (519 ± 53) × $10^{-15}$ in a previously published study of infiltration at this site [3]. Obtaining appropriate samples for these analyses has proved to be a problem. First, the solubility of meteoric chloride in water limited the available samples to those from dry-drilled boreholes. Second, the procedure developed for leaching chloride from tuffs at Yucca Mountain that typically contain 2 ppm Cl$^-$ required the use of $\sim$40 kg of material to obtain a sample containing $\sim$20 mg Cl$^-$ for the accelerator mass spectrometry analysis. The only dry-drilled borehole from which cuttings in sufficient quantity had been saved to permit the start of this study was USW UZ-1. Its geographical coordinates are 36°51' N and 116°27' W. The remainder of this paper presents the results of $^{36}$Cl analyses of samples from this borehole, a discussion of the dependence of the measured $^{36}$Cl/Cl ratio on the pulverization of the cuttings, corroborating evidence for the detection of bomb pulse $^{36}$Cl deep underground, and an indication of potential applications of the results of this study.

## 2. Results

Samples for $^{36}$Cl analyses were prepared from USW UZ-1 cuttings collected at nine depths as the borehole was drilled. The samples were prepared by the same procedure as used in the Yucca Mountain infiltration study [3], but with larger apparatus for the first step to accommodate the greater quantities of materials that are required. The resulting AgCl samples were analyzed for $^{36}$Cl at the University of Rochester's accelerator mass spectrometer. The results of the $^{36}$Cl analyses are shown in Table 1. The standard deviations listed in the table are the $\pm 1\sigma$ values based only on counting statistics from the accelerator mass spectrometer.

A second set of $^{36}$Cl measurements was undertaken to determine whether the measured $^{36}$Cl/Cl ratios depended on the size of the particles that were leached. The cuttings from the 76 to 78 m interval were pulverized in a shatterbox for 5 minutes, then releached. A chloride sample for $^{36}$Cl analysis was prepared from the leachate by adding 50.0 mg of NaCl that was measured to contain no $^{36}$Cl. The pulverization and releaching were repeated two additional times. The results of the $^{36}$Cl analyses are shown in Table 2, together with the $^{36}$Cl results from Table 1. When the strong dependence of the measured $^{36}$Cl/Cl ratio on the amount of pulverization was observed, the cuttings from three other intervals were pulverized to prepare additional samples for $^{36}$Cl analyses. The results of these measurements are given in Table 2 also. The decrease in the $^{36}$Cl/Cl ratio for these three samples is not a constant fraction of the original value, even though the pulverization time was the same in each of these three cases. The data, however, may be useful for determining the meteoric $^{36}$Cl component in an end-member analysis.

## 3. Discussion

The purpose of this work was to obtain evidence from $^{36}$Cl data concerning the percolation flux of water through the unsaturated tuffs at Yucca Mountain. The data in Table 1 at the depths of 311 to 312 and 372 to 373 m indicate the possibility of significant $^{36}$Cl radioactive decay at these depths. Had the $^{36}$Cl/Cl ratios been similar to the $519 \times 10^{-15}$ ratio at the surface, further work to develop this technique most likely would not have been justified.

The ratio observed at 364 to 366 m statistically is the same as the $519 \times 10^{-15}$ $^{36}$Cl/Cl ratio observed at the surface. A brief description of the manner in which USW UZ-1 was drilled and why the drilling was terminated should show that the $^{36}$Cl ratio measured at this interval can represent a valid indication of the presence of contemporary water (i.e., less than $10^5$ years for these $^{36}$Cl measurements) without invaliding the results exemplified by the $^{36}$Cl data from the 311 to 312 and the 372 to 373 m intervals. Whitfield [4] states that the first 17.7 m of

USW UZ-1 was drilled using 4,573 l of water. Sufficient water accumulated at the drill bit that it interfered with the drilling operations. A diaphragm pump delivered 1,514 l of water to the surface, but 3,059 l were lost to the formation. The remainder of the hole was drilled using air to cool the drilling bit. Data from drill cuttings and from borehole instrumentation indicated that the water not recovered from the first 17.7 m did not seep below 76 m. The drill hole was planned to terminate in the saturated zone, which starts at a depth of 470 m at the USW UZ-1 location. Drilling actually was discontinued at 387 m, where a large volume of water was encountered. The water was found to contain a chemical polymer with a composition identical to that used in drilling hole USW G-1, which is located 305 m southeast (downdip) of USW UZ-1. Approximately 8.7 × $10^6$ l of polymer drilling fluid was not recovered during the drilling of USW G-1. Whitfield interprets the data in terms of a major fracture zone that provided an hydrologic connection between the two holes or a naturally occurring perched-water zone that is contaminated with the USW G-1 drilling polymer. If a major fracture zone does connect the two holes, then the $^{36}$Cl data observed at the 364 to 366 m interval may indicate that water used to drill USW G-1 reached this interval, as well as the 387 m depth where USW UZ-1 was terminated.

The strong dependence of the measured $^{36}$Cl/Cl ratio on the amount of pulverization, as shown by the data in Table 2, resulted in additional analyses to separate the $^{36}$Cl/Cl ratios shown in Table 1 into two components. One component would represent meteoric chloride containing cosmogenic $^{36}$Cl, while the other would represent chloride associated with the tuff that included $^{36}$Cl formed in situ by neutron activation of $^{35}$Cl. The neutrons necessary for the second component are generated in the decay of uranium and thorium series elements in the tuffs, both from spontaneous fission and from $\alpha$,n reactions on light elements that are present in trace quantities [2].

Chemical analyses of the chloride and the bromide compositions of sieved fractions of cuttings were undertaken to help define the end members of the two components. The data are too extensive to present here, and the results still are tentative, but the Cl/Br ratio for the meteoric component appears to be ~130, while the ratio for the tuff component appears to be ~500. When these numbers are used with the $^{36}$Cl data, the values for the meteoric component of $^{36}$Cl do not fall into a consistent pattern It may be that the bromide data are unreliable. Some bromide measurements were close to the 2 part per billion sensitivity limit for the ion chromatograph that is used for the analyses. Consequently, a small analytical error in the bromide concentration can produce a large error in the Cl/Br ratio. Another potential source of error came from the USW UZ-1 drilling operations. The 4,573 l of water used to drill the first 17.7 m was chemically tagged with LiBr [4]. The USW UZ-1 drilling report [5] notes the use of an additional 620 l of water tagged with LiBr to help free a stuck drill string at a depth of 373 m. We presume that the cuttings for the $^{36}$Cl analysis from the 372 to 373 m interval were taken before this water was used. The unambiguous resolution of $^{36}$Cl/Cl ratios into two components may require samples from a borehole drilled without the use of any water and at a location unaffected by the presence of drilling water from surrounding boreholes.

The unanticipated finding in this work is the observation of bomb pulse $^{36}$Cl at a depth as great as 153 m. The origin of the bomb pulse is global fallout from high yield nuclear device testing between 1952 and 1962 that caused $^{35}$Cl in seawater to be activated with neutrons and subsequently injected into the stratosphere. The characteristic that permits a $^{36}$Cl/Cl ratio to be identified as originating from the bomb pulse is a ratio significantly greater than the 519 × $10^{-15}$ cosmogenic ratio. Ratios of $^{36}$Cl/Cl higher than the cosmogenic ratio were observed in saline waters from the Stripa mine in Sweden [6], but these were explained on the basis of in situ neutron irradiation of $^{35}$Cl. The Yucca Mountain tuffs cannot reasonably be expected to generate high $^{36}$Cl/Cl ratios, as at Stripa, because concentrations of chlorine, thorium, and uranium are not high and these trace elements appear to be distributed relatively homogeneously. The geochemical gradients reported by two laboratories [7,8], based on measurements of samples from 166 locations, show chlorine generally below neutron activation analysis detection limits (except in the USW G-1 interval between 402 and 424 m), thorium contents of 20.8 ± 5.3 ppm, and uranium contents of 3.7 ± 1.1 ppm. The thorium and uranium data contain a few points approximately a factor of two or less either above or below the mean elemental contents. There is no evidence for a combination of high values all at one location that might contribute to a high $^{36}$Cl/Cl ratio from in situ production processes. Consequently, the only reasonable source of the high $^{36}$Cl/Cl ratios observed in this work is bomb pulse $^{36}$Cl.

The data in Table 1 show that bomb pulse $^{36}$Cl is present in cuttings from the intervals at 30 to 31, 52 to 54, and 152 to 153 m. The $^{36}$Cl/Cl ratios for these three intervals may represent lower limits, because of the dependence of the $^{36}$Cl/Cl ratio on pulverization, which was noted above. Also, bomb pulse $^{36}$Cl may be present in cuttings from other intervals, but unrecognizable in samples with $^{36}$Cl/Cl ratios of 519 × $10^{-15}$ or lower. The water that transported the bomb pulse $^{36}$Cl from the surface to the depths where the bomb pulse is observed in cuttings collected in 1983 must have been younger than 30 years.

The pathways by which the $^{36}$Cl bomb pulse was transported to the locations where it is observed should be determined to help understand water flow in unsaturated tuffs. Our previous work near this location [3] showed a $^{36}$Cl bomb pulse profile that reached a maximum about 0.5 m below the surface, with no evidence for the bomb pulse below 2 m. Observation of the bomb pulse at significantly greater depths at the USW UZ-1 location could have resulted from the use of water to drill the first 17.7 m. The water used for this drilling came from well J-13. A sample of water from well J-13 was collected around the time of the drilling operations and analyzed for $^{36}$Cl. The $^{36}$Cl/Cl ratio was measured to be (531 ± 41) × $10^{-15}$. Thus, the drilling water is unlikely to be the source of the bomb pulse. The drilling water could have washed the bomb pulse down from the alluvium near the surface. However, the large volume of water that was used (4,573 l) had practically no contact with the top two meters of alluvium. It is more likely that this volume of water would tend to dilute any entrained bomb pulse to undetectable levels. The absence of a distinct $^{36}$Cl bomb pulse at three intervals above that at 152 to 153 m, including the interval at 150 to 152 m, indicates that lateral water flow is involved in the transport of the bomb pulse, but some downward flow is possible. The profile of the bomb pulse below 153 m could not be determined, because the next interval where cuttings were available was at 183 m. If lateral water flow did transport the $^{36}$Cl bomb pulse to the locations where it has been detected, then cuttings from a borehole drilled without water at a location updip from USW UZ-1 also should show the presence of the bomb pulse deep in the unsaturated zone.

Recently reported analyses of tritium performed by the U. S. Geological Survey [9] support the interpretation of the $^{36}$Cl data in terms of lateral water flow. The tritium was measured in moisture from cores collected at two Yucca Mountain locations, UE-25 UZ#4 and UE-25 UZ#5. High tritium values, indicating the presence of modern water, were found to decrease rapidly to a low value at 10 to 12 m in UE-25 UZ#4. Then spikes of high tritium were observed at 25 m and at 46 to 50 m in this same borehole and at 28 m and at 34 m in UE-25 UZ#5. The tritium spikes were taken to indicate recent water movement in fractures or bedded units in the unsaturated tuffs at Yucca Mountain. Another observation from this work is that moisture pulses penetrate only to a depth of ~10 m.

Additional evidence has been obtained for the presence of bomb pulse $^{36}$Cl deep in unsaturated tuffs. Cuttings from dry drilling operations conducted in the Nevada Test Site's G-Tunnel, located ~45 km northeast of Yucca Mountain, were analyzed for $^{36}$Cl. The results are shown in Table 3. The horizontal distances shown in the table are relative to a vertical fault visible in the welded, unsaturated tuff in a drift near some of the drilling. The fault is not thought to go to the surface, which is some 400 m overhead. The first two $^{36}$Cl measurements with cuttings from G-Tunnel were undertaken with the expectation that the $^{36}$Cl/Cl ratios would be significantly less than 519 × $10^{-15}$. Observation of the $^{36}$Cl bomb pulse in one of the two samples was a complete surprise. Additional measurements have confirmed the presence of the bomb pulse, as is evident in Table 3. The high $^{36}$Cl values appear to be nearly symmetric in a northeast-southwest plane that is centered around the fault near DH-1. Additional drilling was planned to define the $^{36}$Cl bomb pulse in three dimensions, but the U. S. Department of Energy closed G-Tunnel to all further work in December, 1989, before this additional drilling could be started. These G-Tunnel data confirm the observations from the USW UZ-1 cuttings that the $^{36}$Cl bomb pulse can be detected deep within unsaturated zone tuffs. The G-Tunnel data are insufficient to define the transport path or paths to the location where the bomb pulse is observed. The two lowest $^{36}$Cl/Cl ratios are significantly lower than the cosmogenic ratio. They provide additional evidence that the radioactive decay of cosmogenic $^{36}$Cl may serve to trace the percolation of water through unsaturated zones over long times.

## 4. Applications

The determination of the meteoric component of the $^{36}$Cl/Cl ratio in unsaturated zone water flow, if accomplished successfully, combined with the observation of the $^{36}$Cl bomb pulse deep within the unsaturated zone, offers the potential for discriminating between matrix flow and fracture flow in a complex hydrologic regime. This information is important for calculating the future performance of a nuclear waste repository located in the unsaturated zone, as proposed for Yucca Mountain.

The unambiguous identification of bomb pulse $^{36}$Cl deep underground establishes a new technique for detecting where modern water has flowed in hydrologic studies of unsaturated zones. The most likely pathways for such flow is through faults and fractures. Evidence for the presence of modern water wherever it occurs in the unsaturated zone is important not only for studies pertaining to high level nuclear waste disposal, such as this one, but also for low level nuclear waste and hazardous waste sites, which frequently are underlain by unsaturated zones.

## 5. Summary

The original purpose of this work was to determine fluxes of water percolating through unsaturated zone tuffs as traced by the radioactive decay of $^{36}$Cl. The USW UZ-1 data indicate that the decay of cosmogenic $^{36}$Cl may have been detected, but the observed dependence of the measured $^{36}$Cl/Cl ratios in cuttings on the amount of pulverization requires additional work to separate the meteoric component of the $^{36}$Cl/Cl ratio from the in situ ratio.

The unexpected finding in this work was the observation of bomb pulse $^{36}$Cl as deep as 152 to 153 m below the ground surface. The absence of recognizable bomb pulse $^{36}$Cl between 250 and 500 m is interpreted as evidence for lateral water flow, in accord with the interpretation provided by the U. S. Geological Survey of tritium data from two nearby boreholes. Confirmation that the $^{36}$Cl bomb pulse can be detected deep underground is provided by data from G-Tunnel, about 45 km away, where the bomb pulse was observed in samples from borehole cuttings that were collected ~400 m underground. Applications of this work include the potential for discriminating between matrix and fracture flow in the unsaturated zone and for detecting recent water movements as traced by the $^{36}$Cl bomb pulse at hazardous materials disposal sites.

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Table I. Results of $^{36}$Cl Analyses of USW UZ-1 Cuttings

| Depth Interval Below Surface (m) | $^{36}$Cl/Cl ($\times 10^{15}$) |
|---|---|
| 30–31 | 11400 ± 360 |
| 52–54 | 2498 ± 198 |
| 76–78 | 436 ± 25 |
| 120–122 | 390 ± 48 |
| 150–152 | 403 ± 42 |
| 152–153 | 2046 ± 103 |
| 311–312 | 245 ± 38 |
| 364–366 | 454 ± 61 |
| 372–373 | 102 ± 11 |

Table 2. Decrease of $^{36}$Cl/Cl Ratio with Pulverization Time

| Depth Interval Below Surface (m) | Shatterbox Time (min) | Added NaCl (mg) | $^{36}$Cl/Cl ($\times 10^{15}$) |
|---|---|---|---|
| 76–78 | 0 | 0 | 436 ± 25 |
| | 5 | 50 | 193 ± 7 |
| | 10 | 50 | 91 ± 4 |
| | 15 | | 36 ± 11 |
| | 20 | | 25 ± 5 |
| 152–153 | 0 | | 2046 ± 103 |
| | 3 | | 1885 ± 150 |
| 311–312 | 0 | | 245 ± 38 |
| | 3 | | 159 ± 12 |
| 364–366 | 0 | | 454 ± 61 |
| | 3 | | 340 ± 15 |

Table 3. Results of $^{36}Cl$ Analyses of G-Tunnel Cuttings

| Sample | Distance from Fault (m) | Direction from Fault | $^{36}Cl/Cl$ ($\times 10^{15}$) |
|---|---|---|---|
| AC-2 | 70.9 – 73.9 | Northeast | 306 ± 22 |
| AC-2 | 55.0 – 57.6 | Northeast | 845 ± 76 |
| DH-1 | 5.3 | Southwest | 1539 ± 101 |
| DH-1 | 5.3 | Southwest | 1964 ± 75 |
| DH-2 | 7.8 | Southwest | 1709 ± 70 |
| AC-1 | 43.1 – 44.8 | Southwest | 1243 ± 87 |
| AC-1 | 44.8 – 47.4 | Southwest | 3044 ± 360 |
| AC-1 | 56.0 – 58.3 | Southwest | 412 ± 18 |