COSMOGENIC ^{36}Cl RESEARCH:

CHLORINE EXTRACTION PROCEDURES AND APPLICATION OF DATING TECHNIQUES AT METEOR CRATER, ARIZONA AND BLOODY CANYON, CALIFORNIA

by

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Dedicated to my loving wife,

Jill

Abstract

Rocks which are deeper than 2 meters below the earth's surface are shielded from most cosmic rays. Rocks at the surface or above this depth begin to accumulate cosmogenic radionuclides by several interactions with energetic cosmic rays and secondary thermal neutrons. The buildup of ^{36}Cl and other cosmogenic isotopes is predictable. Knowing the amount of ^{36}Cl in a rock allows calculation of the length of time the rock has been exposed.

This independent study focuses on the application of ^{36}Cl dating to two geomorphic features: Meteor Crater, Arizona, and a group of glacial moraines at Bloody Canyon, in the eastern Sierra Nevada of California. Silver chloride is produced using chlorine extracted from rock samples from these locations. The silver chloride is purified and analyzed for its ^{36}Cl content on a tandem accelerator mass spectrometer (TAMS) at the University of Rochester.

The development of a procedure for extracting chlorine from silicate rocks became a major task of this study. The procedure used with the most success is called the air strip method. Silicate rock is dissolved in a reaction vessel using a mix of hydrofluoric and nitric acids. Air is bubbled through the acid leachate, taking with it the HCl gas produced in the rock dissolution. The air flows into a test tube of solution where silver chloride is precipitated.

Several key parameters in the production rate of ^{36}Cl were re-evaluated during the course of this study. Also, the measurement of low levels of total chlorine in silicate rocks is still undergoing refinement. Results presented here are preliminary due to these factors.

Preliminary calculations give an exposure age for Meteor Crater of 33,500 years. This also dates the time of impact of the meteorite. The calculated age lies between the two values of 25,000 and 50,000 which have been estimated previously by different groups of researchers.

Results from five glacial moraines at Bloody Canyon, California show four age ranges. Tioga moraine samples range in age from 16,300 to 24,300 years old. Tenaya moraine samples range from 16,000 to 91,000 years old. Samples from the upper Tahoe moraine, which is closely related geomorphically to the Tenaya moraine, are bracketed within the Tenaya range. Ages of the upper Tahoe samples range from 50,000 to 90,000 years. A lower Tahoe moraine gives ages of 112,000 to 177,000 years. The oldest glacial feature, the Mono Basin moraine, has ages ranging from 74,000 to 368,000 years old.

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I wish to acknowledge the sacrifice which my family has made for me to obtain this second Master's degree. A loving thanks to my children Valerie, Craig, and Keith. Most of all I thank my wife, Jill, who not only had to endure more graduate school, but as my typist had to learn a whole new computer system for this project.

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I. INTRODUCTION

OBJECTIVE

The primary objective of this study is to apply the buildup of cosmogenic chlorine-36 (^{36}Cl) to the dating of geomorphic features. However, before the ^{36}Cl dating could be accomplished, it was necessary to develop a chlorine extraction technique for carbonate rocks and an improved chlorine extraction technique for silicate rocks. The development of a feasible laboratory process proved complex and very time-consuming, and became a major objective of this project. This report documents the evolution of the laboratory techniques, and presents three viable processes for chlorine extraction.

Two localities were chosen for the application of ^{36}Cl dating techniques. The impact structure at Meteor Crater (Barringer Meteorite Crater) in Arizona was studied to determine the date of impact of an iron meteorite which formed the crater. A sequence of glacial moraines at Bloody Canyon, Mono County, California was also studied with the intention of deriving absolute dates for these moraines.

In each case, samples were collected and processed to extract chlorine which could then be sent to the University of Rochester to be analyzed. Exposure ages were then calculated from the raw data. However, due to uncertainties in the production rate of ^{36}Cl, all exposure ages are preliminary. In addition, not all of the samples from Bloody Canyon were analyzed for ^{36}Cl due to problems with laboratory procedures. Subsequent analyses and calculations will result in a more complete determination of the history of the studied areas.

CHLORINE-36 SYSTEMATICS

Traditional radiometric dating techniques are not well-suited to dating landforms. These methods, e.g. K/Ar, Rb/Sr, measure the time since a geochemical system has become closed. However, ^{36}Cl and other cosmogenic isotopes measure the time since a geologic body which is at or very near the earth's surface has been exposed to cosmic rays. Volcanic rocks are ideal for this dating technique. Magma bodies at depth are shielded from cosmic rays and the lava becomes exposed to cosmic rays at the time of eruption. Glacial terranes also provide a good system for exposure dating. Glaciers scour large fragments from bedrock and deposit them as boulders at the surface upon glacial retreat.

Chlorine-36 builds up in exposed rocks by several types of interactions with cosmic rays. Most of these interactions occur within a few meters of the earth's surface. Below that depth the cosmic rays are attenuated. An important reaction in rocks containing significant chlorine is the thermal neutron activation of ^{35}Cl. A thermal or slow neutron bombards a ^{35}Cl atom, which emits a photon and produces a ^{36}Cl atom. Though the chlorine content in most igneous rocks is fairly low, this reaction may contribute significant amounts of ^{36}Cl because chlorine possesses a large thermal neutron cross-section. This cross-section increases the probability of neutron capture by the chlorine atoms.

In rocks which contain little chlorine, other production mechanisms are important. These are the (direct) spallation of potassium and calcium. These elements are abundant in most igneous rocks and carbonates (in the case of calcium), so spallation is an important ^{36}Cl production reaction. Yokoyama and co-workers (1977) have calculated sea-level production rates of 2670 atoms of ^{36}Cl per kilogram per year per percent K_2O for potassium and 710 atoms of ^{36}Cl per kilogram per year per percent CaO for calcium.

Chlorine-36 can also be produced by the spallation of titanium and iron by high-energy cosmic rays. Such rays only occur in the atmosphere where titanium and iron are not present and thus this production mechanism is insignificant (Phillips et al., 1986). Below the earth's surface ^{36}Cl is produced by negative muon capture by ^{40}Ca but this mechanism can be neglected for surface samples (less than 2 m depth).

There is also a noncosmogenic source of ^{36}Cl which must be accounted for. The natural decay of uranium and thorium in rocks produces neutrons which in turn interact with ^{35}Cl to produce ^{36}Cl. The background level of ^{36}Cl thus varies with U-Th content. The average values have been calculated by Bentley and Davis (1982) for several rock types, including granite, limestone, and sandstone.

Chlorine-36 is also produced in the atmosphere by cosmic ray interactions with argon. The more prevalent reaction is the spallation of ^{40}Ar. Thermal neutron activation of ^{36}Ar also produces ^{36}Cl. This ^{36}Cl washes out of the atmosphere and is termed meteoric ^{36}Cl (Bentley et al., 1986). Steps must be taken to separate the meteoric ^{36}Cl from that which is produced in-situ in the rocks.

The production rate of ^{36}Cl is directly related to the neutron flux. The greater the number of free neutrons in an environment, the higher the production rate of ^{36}Cl and other cosmogenic isotopes. There are three important characteristics of a sample location which affect the neutron flux. These are altitude, geomagnetic latitude, and depth. Each of these must be taken into consideration in determining absolute ages (refer to 'Calculations,' page 11).

Cosmic rays are attenuated by interactions with all forms of matter such as gases, liquids, and solids. The denser the material, the greater its stopping power. The density of the earth's atmosphere decreases with greater distance from the earth's surface. The neutron flux is greater at higher elevations. Based on data from Yokoyama (1977), the production rate of cosmogenic isotopes at 1000 m elevation is twice the rate at sea level. At 2000 m the rate is four times that of the sea level rate.

The position on the earth's surface relative to the earth's magnetic poles also affects the incoming neutron flux. Primary cosmic radiation is comprised mostly of protons. These protons tend to follow the earth's magnetic field thus producing the highest flux at the magnetic pole and the lowest intensity at the magnetic equator. A correction factor must be applied to account for the geomagnetic latitude of a sample location.

Those cosmic rays and associated thermal neutrons which do reach the earth's surface are attenuated or absorbed at a faster rate as they penetrate the earth's surface (Figure 1). This attenuation is produced by the soil and by material above the actual ground surface such as boulders, vegetation, snow, bodies of water, etc. A simplified decay equation describes the attenuation of cosmic rays with depth (Yokoyama, 1977):

$$\phi_d = \phi_0 \, e^{-az} \qquad (1)$$

In this equation, ϕ_d is the cosmic ray flux at depth d. ϕ_0 is the cosmic ray flux at the surface. The attenuation coefficient, measured in $cm^2 g^{-1}$, is represented by a, and z is the depth measured in $g\,cm^{-2}$. A value for a of 1/192 $cm^2 g^{-1}$ is given by Yokoyama (1977) and was used in estimating attenuation depths.

Calculations using this decay equation indicate that primary cosmic rays are mostly attenuated within a depth of 2 m below the earth's surface. At a depth of 2 m in carbonate material, the cosmic ray flux is 5% of the surface flux. At the same depth in granitic material, the cosmic ray flux is 6% of the surface flux. All of the samples selected for this reasearch were at the surface or slightly above it. The portion of samples analyzed

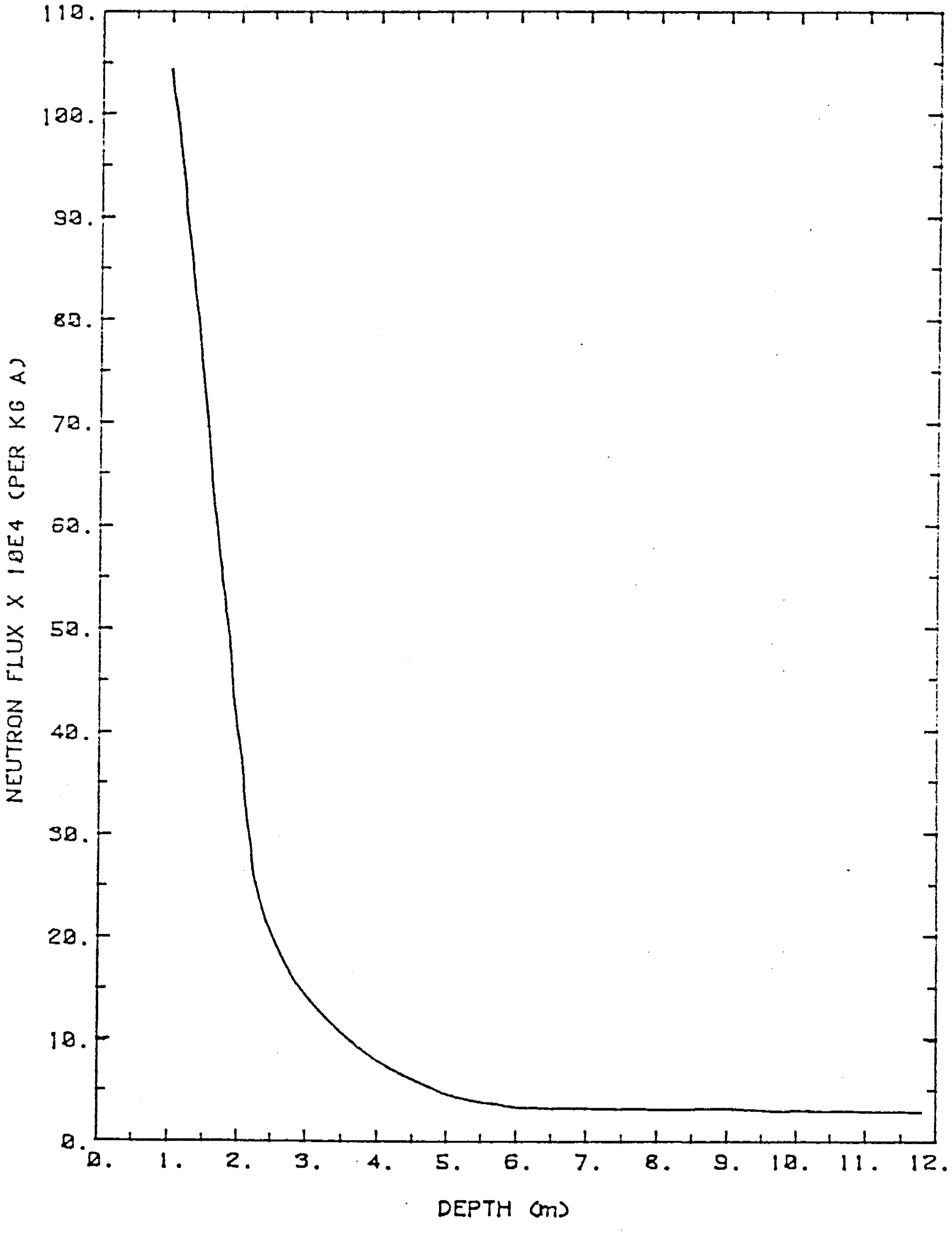


Figure 1. Neutron flux as a function of depth below ground surface, normalized to sea level. From Izmirian (1984) using data derived from Kuhn et al. (1984).

for ^{36}Cl ranged from 0–5 cm depth. At 5 cm in carbonate or granitic material the flux is 93% of the surface flux. No correction for depth has been made in the age calculations for samples at Meteor Crater or Bloody Canyon.

Because ^{36}Cl is radioactive it is decaying at a known rate at the same time that it is being produced. Thus the build–up of ^{36}Cl in a material, caused primarily by interactions of cosmic rays with K, Ca, and Cl, is a regular function of time. Absolute exposure ages can be derived from ^{36}Cl analyses once certain corrections and normalizations are made. The intent of this study is to derive these absolute dates for the Meteor Crater impact and the glacial moraines at Bloody Canyon.

Exposure Assumptions

Since the buildup of cosmogenic ^{36}Cl begins only after a rock has been exposed to cosmic rays, the assumptions at Meteor Crater are that the Kaibab Formation was shielded from cosmic rays prior to the meteor impact. Exposure of these rocks began at the time of impact and has been continuous ever since. It is also assumed that there has been no movement of these boulders once they were initially thrown from the crater to the surrounding ejecta blanket.

In dating glacial moraines the geologic clock starts at the time of moraine deposition. It is assumed that the boulders sampled were a part of the bedrock and shielded from cosmic rays. These rocks were plucked from the bedrock by glaciers and transported. As the glaciers retreated, these rounded boulders were deposited on the crests of lateral and terminal moraines. It is assumed that these boulders have not moved since deposition and have been continuously exposed to cosmic rays since that time. All boulders on a moraine are assumed to have the same exposure age. The cosmic ray flux is also assumed to have been constant within the time frame of these glaciations.

Snow cover, which can strongly attenuate cosmic rays, is a factor to consider for the Sierra Nevada samples. Leavy (1987) presents data from a California snow survey near Mammoth Lake. The average April 1 water content of the snowpack is 51 cm over the period 1928 to 1986. This corresponds to a snow depth of 1 meter given a typical packed snow density of 0.5. The average height of boulders sampled at Bloody Canyon is 1.6 m. The boulders are on ridge crests and would be subjected to wind action during storms. It is probable that snow does not normally accumulate to a depth which would cover these boulders. Thus snow cover is assumed to be negligible and there is no cosmic ray flux correction for snow.

CHLORINE-36 ANALYSIS

The preparation of samples for analysis on TAMS requires a number of laboratory procedures. The chlorine is extracted from the rocks, recovered as AgCl, and the impurities removed while keeping the sample uncontaminated. The actual methods used to accomplish this objective are described in detail in the section "Chlorine Extraction Techniques" (page 16).

The apparatus for measuring ^{36}Cl isotopes is an MP tandem Van de Graff accelerator mass spectrometer. The important features are a cesium sputter ion source, an off-set Faraday cup system, and a 90° magnetic analyzer. This instrument has a time-of-flight detector, and a gas ionization detector. The terminal voltage is approximately 15 MV. Samples are loaded onto wheels which hold 4 unknowns, 1 standard, and 1 blank. The standard can be analyzed between each unknown to detect drift in the equipment. The minimum detection limits for ^{36}Cl are 5×10^5 atoms per sample. This provides a precision of 10% (Kubik, et al., 1988).

The data that is released by the University of Rochester is raw data which has been corrected for variations in the ion source and background readings in the blank.

GEOCHEMISTRY

It is necessary to determine the chemical composition of the rocks sampled since the composition of the rock affects the rate of production of cosmogenic ^{36}Cl. Major element analyses were determined by XRF. Chlorine content was measured using an ion chromatography technique. ICP-ES techniques were used to determine the boron content, and selected rare earth elements, specifically Gd, Sm, and Eu (Walsh et al., 1981). These elements are important in the calculation of the ^{36}Cl production rate because they have very high thermal neutron cross-sections. In an attempt to quantify the contribution of the various ^{36}Cl production methods, a mineral separation was performed on several samples. These mineral separates were analyzed for ^{36}Cl individually.

CALCULATIONS

The equations and relationships used to calculate production rates, normalized ratios, and absolute ages follow.

Sample Location

Altitude, geomagnetic latitude, and depth are all significant factors in determining production rates, normalized ratios, and absolute ages. To convert geographic position to geomagnetic latitude an equation given by Jory (1956) is used:

$$\sin\lambda = \cos\theta_0\ \cos\theta\ \cos(\omega - \omega_0) + \sin\theta_0\ \sin\theta \tag{2}$$

In this equation, λ is the geomagnetic latitude, θ is the geographic latitude, ω is the geographic longitude, θ_0 is 78.6°, and ω_0 is 290.0° corresponding to the position of the 1945 geomagnetic north pole. Once the geomagnetic latitude is known, a correction factor is interpolated using Table 3 in Yokoyama (1977).

Production Rate

Once the geochemical composition is determined it is possible to estimate the rate of production of cosmogenic ^{36}Cl. Phillips et al. (1986) describe the production rate from ^{35}Cl neutron activation as a linear function:

$$\psi_n = \phi_n \frac{\sigma_{35} N_{35}}{\sum_i \sigma_i N_i} \tag{3}$$

The thermal neutron flux at sea level, ϕ_n, is given by Lal and Peters (1967) as roughly 10^6 neutrons $\mathrm{kg}^{-1}\mathrm{yr}^{-1}$. σ_{35} is the thermal neutron capture activation cross-section of ^{35}Cl. The units of σ are barns, with 1 barn = 10^{-24} cm^2 per nucleus. N_{35} is the concentration of ^{35}Cl in atoms per kilogram. σ_i is the thermal neutron absorption cross-section of each element in a sample (in barns). N_i is the concentration of each element in atoms per kilogram. For this study the only elements used are those listed in Table 3, page 40, and Table 5, page 53.

The amount of ^{36}Cl produced by spallation of K and Ca is determined by multiplying the measured amount of each (in percent) by a calculated unit production rate. This yields production rates for that specific sample which are then used in age calculations. The production rates are designated ψ_K and ψ_{Ca} with units of ^{36}Cl atoms $\mathrm{kg}^{-1}\mathrm{yr}^{-1}$ per wt % K_2O and CaO respectively. Yokoyama's values for these unit production rates are further discussed in the "Calculations - Bloody Canyon" section (page 58).

Normalization

Normalization is necessary in order to compare the measured ^{36}Cl ratios because the elevation, geomagnetic latitude, and the concentration of target elements is not identical for all of the samples. It is the normalized values that are used to determine the absolute age of the samples. The computer program used in this research to determine exposure ages calculates normalized ^{36}Cl/Cl ratios for each sample.

Normalization allows intercomparisons of completely different rocks. For instance, a volcanic rock from New Mexico can only be compared to a glacial rock from California if the measured ^{36}Cl ratios have been normalized. The raw ^{36}Cl data from the TAMS analysis is normalized to a specified rock composition. The normalization procedure also adjusts for variances in altitude, geomagnetic latitude, and depth. The normalization equation was developed by Phillips et al. (1986). In this equation, the subscripts m and r indicate a measured or reference value, respectively. The f represents the factor used in the calculation. R_0 is the background ^{36}Cl/Cl ratio from U–Th decay. Potassium and calcium values are in percent, and chlorine values are in ppm. ELD is the correction factor which adjusts for elevation, geomagnetic latitude, and depth below ground surface. Each normalized value (Rn) is given by

$$R_n = (R_m - R_o)\,f = (R_m - R_o)\,\frac{Cl_m}{Cl_r}\left[\frac{K_2O_r(\psi_K) + CaO_r(\psi_{Ca}) + Cl_r(\psi_n)_r}{K_2O_m(\psi_K) + CaO_m(\psi_{Ca}) + Cl_m(\psi_n)_m}\right]\frac{1}{ELD} \tag{4}$$

Age Calculation

The several production rates work in a combined fashion through time to build up ^{36}Cl in a rock. Natural radioactive decay of ^{36}Cl is occurring simultaneously. Phillips et al. (1986) give the buildup equation as:

$$R = \frac{ELD(\Psi_K + \Psi_{Ca} + \Psi_n)}{\lambda_{36} N_{Cl}}\left(1 - e^{-\lambda_{36} t}\right) + R_0 \tag{5}$$

R is the ^{36}Cl/Cl ratio. Ψ_K, Ψ_{Ca}, and Ψ_n are the specific production rates for the sample being considered, with units of ^{36}Cl atoms kg^{-1}yr^{-1}. λ_{36} is the decay constant for ^{36}Cl (2.3×10^{-6} yr^{-1}). N_{Cl} is the amount of chlorine (in atoms kg^{-1}) in the rock, and t is time.

The equation in this form can be used to generate a series of ^{36}Cl/Cl ratios through time. Either measured geochemical data or estimated values can be used. Phillips et al. (1986) used the equation to generate a predicted buildup curve against which they tested the validity of the ^{36}Cl exposure dating technique.

Measuring the ratio of ^{36}Cl to stable chloride allows the calculation of the time of exposure to cosmic rays. Exposure age calculations are made by solving this equation (5) for time (t) and using measured ^{36}Cl/Cl ratios (R_m). The equation then takes the form

$$t = \frac{-1}{\lambda_{36}} \ln \left[1 - (R_m - R_o) \frac{\lambda_{36} N_{Cl}}{ELD\,\Psi_T} \right] \tag{6}$$

Ψ_T is the sum of Ψ_K, Ψ_{Ca}, and Ψ_n. The value of the analytical uncertainty of the ^{36}Cl measurement can be entered for R_m, giving an error term for the calculated age.

II. CHLORINE EXTRACTION TECHNIQUES

OVERVIEW

In order to measure the build-up of cosmogenic ^{36}Cl, it was necessary to extract the chlorine from the samples collected at Meteor Crater and on the moraines at Bloody Canyon.

The samples taken at Meteor Crater were of limestone from the Kaibab Formation. An acid–dissolution procedure was developed for these carbonate rocks. This procedure was relatively simple and straight–forward because the rocks could easily be dissolved by nitric acid. A general description of the laboratory process used for dissolving the carbonate rocks of Meteor Crater is included in this section. This process is detailed further in the section "Laboratory Procedures," beginning on page 68.

The extraction of chlorine from the samples collected at Bloody Canyon is significantly more complex. Because these samples are silicate rocks, they are very difficult to dissolve. The best acid for dissolving silicate rocks is hydrofluoric acid. Considerable time and effort were spent developing and documenting a method of acid–dissolution of silicate rocks. A chronology of the laboratory processes developed to extract chlorine from the samples taken at Bloody Canyon are included in this section. These procedures are detailed further in the section "Laboratory Procedures," page 68.

Once the chlorine is extracted from the rocks, whether they are silicate or carbonate rocks, the chlorine is recovered as AgCl. The steps necessary to purify and package uncontaminated AgCl for analysis at the U. of Rochester are discussed in general in this section, and in detail in the section "Laboratory Procedures," page 68.

SAFETY CONSIDERATIONS

The procedure for dissolution of the silicate rocks uses both concentrated hydrofluoric acid (HF) and concentrated nitric acid (HNO_3). Both of these chemicals are toxic and must be used with extreme caution. Hydrofluoric acid is not only hazardous in its liquid form, but also emits toxic vapors. In addition, the acid-rock reaction is strongly exothermic and requires certain safety precautions as well as careful monitoring.

Any worker using this technique should familiarize themselves with HF safety measures. One of the dangers of HF is its subtleness. The HF acid is a weak acid and may contact the skin without a noticeable burn. However, HF is calcium-seeking and will migrate towards bones, possibly taking several hours. When the HF reaches the bone, it dissolves the bone which causes considerable pain and can cause permanent damage. Amputation may be required in severe cases. Thus any possible skin contact with HF should be immediately flushed with water. As a further precaution, calcium in some form such as lime or calcium in glycerine should be applied on the skin so that the HF seeks the surficial calcium rather than migrating down into the bone structures.

Appropriate safety clothing should be worn at all times. This includes a fully-buttoned long-sleeved laboratory coat, acid-resistant gloves, and a face shield. Easy access to a safety shower and eye wash should be ensured. A container of calcium salts should be kept readily accessible for neutralizing small acid spills. For larger spills, one should use appropriate acid spill pillows.

Because of toxic fumes emitted by the HF, particularly during the exothermic reaction with the rock powder, all laboratory procedures should take place under a properly operating fume hood.

SAMPLE PREPARATION

Rock samples collected in the field ranged from 2–10 cm thick. Because of attenuation of the cosmic rays at depth by mineral grains, the uppermost portion of samples was selected for chlorine extraction. The flux of cosmic rays below this depth is greatly reduced. In preparation for acid dissolution, the upper 3–4 cm was removed for crushing.

Prior to acid dissolution, all samples are prepared in the same manner. This preparation includes grinding followed by a meteoric leach. The grinding steps are as follows:

The rock is oriented (refer to 'Field Sample Selection,' page 48). The top 3–4 cm are chiseled off and coarse-crushed using a jaw crusher. The sample is hand-picked to remove lichens and heavily weathered portions. The sample is then crushed to –1/4 inch in a smaller jaw crusher. Samples are pulverized in a Tema tungsten-carbide ring and puck mill. The sample is then sieved through a #20 sieve. The final sample grain size ranges from -20 to -200 mesh. Every piece of crushing equipment and particularly the Tema mill must be carefully cleaned between samples to avoid contamination.

The purpose of the meteoric leach is to remove meteoric chlorine from the sample grains. A 100 gm subsample is agitated for 3-4 minutes in a soil blender with 400 ml deionized water. The sample and water are then poured into a beaker and allowed to settle for 24 hours. The water is then decanted and the sample dried. Dry samples are stored in plastic jars. The blender and beakers must be cleaned and rinsed with deionized water before being used for the next sample.

LABORATORY CONTAMINATION

Because chlorine is pervasive in the environment, extra care must be taken to eliminate contamination. Deionized water should be used to rinse all laboratory equipment and for mixing all reagents. Every piece of laboratory equipment should be meticulously washed and then rinsed with deionized water after each contact with the rock sample. Gloves should be worn at all times to keep body salts from contaminating equipment and samples. The air used in the air strip method should be filtered to remove moisture and particulate matter. Acids used in these procedures should be low in chlorine to maintain chemical purity. The end product of the rock dissolution is silver chloride which degrades in light. Therefore the silver chloride should be stored in darkness.

CHLORINE EXTRACTION FROM CARBONATE ROCKS

OVERVIEW

A system to extract chlorine from carbonate rocks was developed for the Meteor Crater study. Overall, this system is easier to handle and has more flexibility in design than the silicate rock system. This is because the carbonate rocks can be dissolved by nitric acid. A significant cost advantage of the carbonate rock dissolution process is that glassware can be used, whereas Teflon is required for the HF procedures in the silicate rock dissolution.

ACID DISSOLUTION OF CARBONATE ROCKS

Rock dissolution takes place in a filter flask which is placed on a magnetic stir plate. Nitric acid is delivered at a controlled rate from a buret. Several trial runs of this procedure showed that the chlorine is not volatized during dissolution. Thus the chlorine stays in the acid solution and can be recovered by treating the leachate. Chlorine is recovered, concentrated, and purified using the acid–base purification method described in a later section (page 91).

CHLORINE EXTRACTION FROM SILICATE ROCKS

OVERVIEW

The laboratory systems for chlorine extraction have undergone substantial change and improvement during the course of this study. The laboratory system which was used for silicate rocks prior to this research was a sodium hydroxide fusion method (Leavy, 1987). Three systems of chlorine extraction from silicate rocks were developed and refined as part of this project. These three systems are: the distillation method, the diffusion method, and the air strip method. The development of the diffusion method included two generations, the first to be referred to as the experimental diffusion method, and the second as the diffusion method. The air strip method underwent sufficient refinement that a discussion of air strip method I and air strip method II will be presented.

This section will include the theory behind the particular processing technique, a description of the process, a list of significant safety cautions, and a discussion of advantages and shortcomings.

DISTILLATION METHOD

Roman and Fabryka-Martin (1988) described a technique in which HCl was distilled from a reaction vessel into a cold trap. Three samples were processed using a set-up modelled after theirs. These samples were then analyzed on the University of Rochester TAMS.

Up to 50 gm of rock powder and 200–300 ml of HF were reacted in a l–liter open plastic container. The leachate was poured into a 1–liter glass flask connected with 4" glass tubing to a 10" glass cold finger submerged in liquid nitrogen. A vacuum pump was connected at the the top of the cold finger with vacuum tubing to drive the distillation process. Heat was applied to the glass flask. The process was continued for 2–4 hours, with the addition of liquid nitrogen as necessary to keep the finger cold. After the system was disconnected and the liquid nitrogen removed, the cold finger was thawed and the liquid processed by adding 0.1 M silver nitrate to precipitate AgCl. The AgCl recovered was then purified for analysis on TAMS.

Cautions

The acid–rock reaction is violently exothermic. The container must be open to prevent explosions. As a further precaution, a plexiglass cylinder should be place around the reaction vessel.

Shortcomings

The glassware is etched by the HF, at times weakening it and causing breakage. The equipment degrades rapidly and has to be replaced often. For safety reasons, the rock should be dissolved in an open vessel. With an open system, some of the chlorine, in the form of HCl, escapes into the atmosphere and cannot be recovered. Another factor which is critical in the distillation process is a sufficient vacuum. A vacuum pump which can pull 650–700 mm Hg is needed. Siliceous acid is usually precipitated and can sometimes clog the cold finger. The ^{36}Cl data from the samples processed using the distillation method were inconsistent with the ^{36}Cl data from the same rocks prepared using the NaOH fusion method (Jannik, in progress). Table 1 illustrates the discrepancies in ^{36}Cl ratios from samples prepared using the fusion and distillation methods.

DIFFUSION METHOD

The theory underlying the diffusion method is that the acid dissolution releases HCl gas. If the acid dissolution can be performed in a large container with the appropriate fittings, most of the chlorine can be recovered. As the HCl gas which diffuses throughout the sealed system comes into contact with the silver nitrate in the capture cups, a chemical reaction occurs which results in the precipitation of silver chloride.

Experimental Diffusion Method

The experimental diffusion method was an early version of the diffusion method which used a very simplistic laboratory set–up. For this version of the diffusion method the rock was digested in a separate container and only the leachate was processed. The leachate

Table 1: COMPARISONS OF ^{36}Cl DATA

Fusion, Distillation, and Experimental Diffusion Methods

SAMPLE NUMBER	MEASURED RATIO (R) NaOH Fusion Method ^{36}Cl / 10^{15} Cl	MEASURED RATIO (R) Distillation Method ^{36}Cl / 10^{15} Cl
BCM-5B	860 ± 103	125 ± 7
MMT3	3,714 ± 319	12,503 ± 1,880

SAMPLE NUMBER	MEASURED RATIO (R) NaOH Fusion Method ^{36}Cl / 10^{15} Cl	MEASURED RATIO (R) Experimental Diffusion Method ^{36}Cl / 10^{15} Cl
BCM-3A	585 ± 25	476 ± 60
SALT-4		2155 ± 77

was placed in a 2-liter plastic beaker. A plastic cup containing 25 ml silver nitrate solution was placed on a plastic stand near the top of the container or bucket. A lid consisting of Saran Wrap secured with a rubber band was used to seal the system. This bucket was placed in a hot bath and heated for 6-8 hours. After the heating was completed, the silver chloride was recovered and processed in a standard manner using an acid-base purification method.

This method was an experiment. Some of its shortcomings were merely because of its primitiveness. The Saran Wrap seal was not a tight seal, and so recovery was not high. Also, the rubber bands underwent heavy degradation and had to be replaced with each heating cycle.

Only two samples were processed using this method to test its feasibility for further development. Once the samples were analyzed on the University of Rochester TAMS, it was determined that the diffusion method approach should be pursued and so a more durable, efficient apparatus was created. Table 1, page 25, lists ^{36}Cl data from the TAMS analysis of a sample prepared using both the NaOH fusion and experimental diffusion methods. Also listed is a sample composed of table salt (SALT-4) which was run as a test of this method and analyzed on TAMS.

Diffusion Method

The diffusion method was a successful system which provided a method to extract and recover a significant amount of the chlorine present in the rock sample. Seventeen samples have been processed using this method and analyzed on the University of Rochester TAMS.

After the diffusion method approach was deemed feasible, an apparatus was designed which would allow the rock sample to be digested and the chlorine captured in the same container. This apparatus consisted of a two-gallon high-density polyethylene (HDPE) cylindrical container (bucket). Inside the bucket were two shelves which each supported three cups of capture solution. A stirring bar on a vertical rod ran through the center of this container to agitate the rock powder during processing. The entire container was placed in a hot bath and allowed to heat for approximately 24 hours. After heating, the silver chloride was recovered from the six capture cups and combined and treated in the standard manner using an acid–base purification method.

The longer 24–hour heating time was used because it was thought that the reaction progressed too slowly for all of the chlorine to be recovered in the 6–hour heating time initially used in the experimental diffusion method.

Advantages

This system has the advantage of simplicity both in its equipment components, and in the processing steps. Because it is not a fully–sealed system and because the reaction is a slow reaction, there is no chance of a pressure build–up. This makes the reaction safer and so the heating procedure requires very little monitoring.

Shortcomings

The system is not air–tight and thus some HCl gas does escape. This HCl loss into the atmosphere results in a lower silver chloride recovery. The system produces a high volume of liquid which must be treated to recover silver chloride. There are also many pieces which all require thorough cleaning before re-use. The large volume of liquid and the many processing surfaces provide additional opportunities for contamination, which must be avoided. The polyethylene components of this apparatus in contact with hot acid did exhibit signs of serious degradation with repeated use. Teflon components, however, showed no degradation. The optimal heating temperature is 85–90° C. Because of the height of this apparatus, a normal water-bath cover cannot be used. Floating styrofoam packing peanuts on the surface of the water is one method of providing the necessary insulation to produce sufficient temperatures. The long heating time may be considered a shortcoming. However, since the process does not need to be monitored during the heating time, in many instances the long heating time is as much of an advantage as a disadvantage.

AIR STRIP METHOD

The air strip method is the method currently being used for chlorine extraction. The theory behind this method is that it is possible to strip the HCl out of the leachate by bubbling air through it, thus driving the distillation process. The nitric acid used in the leachate keeps the pH of the solution very low thus the HCl is more volatile. There are two generations of air strip methods. Air strip method I alternates the sample between a hot bath and a cold bath to control the violent exothermic reaction of the silicate rock with the HF. In the air strip method II, the HF is delivered into the system by dripping so that the rate of the reaction can be controlled by the rate of drip.

Air Strip Method I

Twenty-four samples were processed for analysis on the University of Rochester TAMS using air strip method I. Step-by-step laboratory procedures describe this process in specific detail. The general air strip I process is as follows: The rock powder (100 g) is placed in a Teflon bottle, and 100 ml conc. nitric acid is added. The bottle is placed in a cold bath and 250 ml cooled HF is added. A lid is placed on the bottle and sealed tightly. This lid has an air loop and carryover tubing in position. The air loop is connected to a filtered air supply. The carryover tubing is connected to a capture tube which has been filled with silver nitrate solution and placed in a second hot bath. The sample is digested by heating for 6 hours, and the silver chloride processed according to the acid-base purification method.

Advantages

This system is very effective in extracting chlorine from rocks.

Shortcomings

This is a sealed system housing a violent exothermic reaction. This means that system explosions can occur. If the system overpressures, the tubing must be disconnected during the heating process. This releases hot, pressurized toxic fumes and spray into the hood area, obviously a hazard to equipment and personnel. The clean-up after such an incident is significant. There is also a chance of contamination to the other samples which are being heated at the same time. This initial exothermic reaction is very unpredictable. Some samples are quite non-reactive, while an occasional sample is so reactive that a pressure build-up becomes acute just moments after the HF is added. The air strip method is very labor-intensive, and must be actively controlled for the first hour or so, and then monitored quite carefully for much of the duration of the digestion process. The optimal reaction is on the threshhold of the dangerous reaction which overpressures, and so it is difficult to maintain the reaction at the optimal point without causing an overpressurization. New holes must be poked in the air-line tubing during each set-up. Nevertheless, the air lines can get clogged and require replacement during the heating process. The carryover tubing often becomes clogged with silicic acid precipitate and can be very difficult to clean. Because of the height of this apparatus a normal bath cover cannot be used; the same "packing peanuts" technique used in the diffusion method can be used to raise and maintain sufficient temperatures.

Quality Control

It is recommended that some quality control procedures be developed to verify that the sample preparation does not introduce contamination. The laboratory procedures used to test for contamination in the air strip I method were conducted in two ways. In each case, laboratory blanks of Week Island halite were processed and submitted for analysis on TAMS. Week Island halite is from a salt dome which is shielded from cosmic rays. It is known to contain no measureable ^{36}Cl. In the first quality control test, a sample of Week Island halite (WIH) was processed through each step of air strip I and acid–base purification, then weighed, packed, and analyzed on the University of Rochester TAMS. The second method of verification involved processing a laboratory blank (Blank A) in which all of the chemicals were used but no sample was present. Reagent volume was one–half of that normally used, in order to conserve expensive reagents. After processing was completed through the early steps of acid–base purification, an aliquoit of Week Island halite was added as a carrier. A processed sample of Week Island halite and Blank A were both analyzed in July, 1988. Results of the analyses of these quality control samples are given in Table 2. Once the measured ratio of Blank A was corrected for machine drift, the ratio was less than zero and thus less than background ^{36}Cl. These data show that no contamination was introduced in the sample processing procedures.

Blank A was also used to examine a worst–case scenario of contamination from the chemical reagents. Several conservative assumptions were made for this calculation. First, Blank A was assumed to have a maximum corrected ratio of 3×10^{-15} ^{36}Cl, higher than the actual analysis. Second, all chlorine from the reagents was assumed to be ^{36}Cl. A 2.99–mg aliquot of Week Island halite containing 1.81 mg of chlorine was added to the sample Blank A. Using the assumed ^{36}Cl ratio gives Blank A a ^{36}Cl content of 92,000 atoms. Thus the reagents used in a normal sample digestion could contain 184,000 atoms of ^{36}Cl.

This maximum level of contamination could become significant (>1%) for small (< 3.5 mg Cl) samples with ^{36}Cl ratios less than 300 x 10^{-15} ^{36}Cl. Samples of the same mass with ratios of 1000 x 10^{-15} ^{36}Cl could have 0.3% contamination and ratios of 5000 x 10^{-15} ^{36}Cl could have 0.06% contamination. All but one of the glacial moraine samples analyzed had ratios greater than 400 x 10^{-15} ^{36}Cl.

Table 2: QUALITY CONTROL

Air Strip I Method

SAMPLE NUMBER	MEASURED RATIO (R) ^{36}Cl / 10^{15} Cl	BACKGROUND RATIO ^{36}Cl / 10^{15} Cl	CORRECTED RATIO ^{36}Cl / 10^{15} Cl
WIH	0	0	0
Blank A	7.2	9.1	-1.9

Air Strip Method II

Later refinements in the air strip method were implemented in order to minimize the violent exothermic reaction and the subsequent risk of overpressurization. To date, seven samples have been processed and analyzed using the air strip method II. This refinement delivers the HF into the system by dripping. The rate of the reaction is controlled by the rate of drip rather than by alternating between the hot water bath and the ice bath.

Only a small amount of the rock powder is reacting with the HF at any given time, because the amount of HF available for the reaction is limited by the drip rate. However the silica-HF reaction is still exothermic and therefore will heat up the entire solution. The higher heat allows subsequent HF additions to react at a faster rate. The reaction vessel must still be monitored carefully to avoid critical overpressurizing. If the reaction vessel gets very hot and/or the fluid level starts to rise, the HF drip should be turned off until the reaction is stabliized.

Advantages

The drip techniques employed in the current air strip II generation make this system a much safer and more predictable process. Although care must still be taken, the modifications have, in most cases, significantly reduced the risk of overpressurization.

Shortcomings

The air strip method II extends the time during which a critical pressure buildup may occur. A sample which overpressured when processed using air strip method I would, in most cases, reach this critical state within approximately 10 minutes of when the reaction was initiated. One sample which overpressured under the modified drip delivery of HF did so more than an hour and a half after the HF drip was started. So although the frequency of critical overpressurization has been significantly reduced by this modification, the possibility still exists.

ACID–BASE PURIFICATION METHOD

OVERVIEW

The function of the acid–base purification method is to recover, concentrate, and purify the AgCl for analysis. The exact procedures varied slightly according to which dissolution method was used. The methods used here are modified from Conard et al. (1986) who developed their method during research with polar ice samples. The chemical principles which guide this purification are primarily those of solubility. AgCl is soluble in basic solutions and is insoluble in acid solutions. By putting AgCl in solution, it can be separated mechanically from insoluble compounds such as barium sulfate ($BaSO_4$) and silicic acid. Solid AgCl can be recovered at the appropriate steps by acidifying the basic solution.

Once the AgCl is purified, the dried AgCl is packed for analysis on TAMS. The acid–base purification method has three distinct parts, which are described in general in this section. More detail can be found in the section "Laboratory Procedures," beginning on page 68.

Phase 1: AgCl recovery and concentration

The different dissolution methods necessitated some variance in procedures in phase 1 of the process. The purpose of this phase remains constant. Through a series of centrifuging and rinsing of surfaces with ammonium hydroxide, the silver chloride is recovered and concentrated.

Phase 2: Pre-$BaNO_3$ preparations

All samples, regardless of the dissolution method used, are processed in the same manner from this point on. Samples are acidified to re-precipitate the silver chloride, and then dissolved in base. Because of the processing time required in the dissolution and the purification, it is necessary to store the samples at various times. It is important that samples be stored in base, and so this phase takes the samples to the point where they can be stored in darkness until the next phase can be started.

Phase 3: Removal of sulfur.

Sulfur-36 is an interfering isobar in the mass spectrometric analysis of ^{36}Cl, and so steps are necessary to remove the sulfur from the samples. The AgCl is purified of sulfur by solution in ammonium hydroxide followed by the addition of barium nitrate. This precipitates sulfur as barium sulfate. The dried, purified AgCl can then be packed for analysis on the University of Rochester TAMS.

III. METEOR CRATER

OVERVIEW

Meteor Crater is one of the most recent large meteorite craters on earth. It is a very well-preserved late Quaternary impact crater on the Colorado Plateau, 55 km east of Flagstaff, Arizona. Figure 2 illustrates the location of Meteor Crater, also known as Barringer Meteorite Crater. The crater was formed by the impact of an iron meteorite travelling in excess of 11 km per second. The impact event released 15 to 20 megatons of kinetic energy and resulted in a bowl-shaped crater 1.2 km in diameter and 170 m in

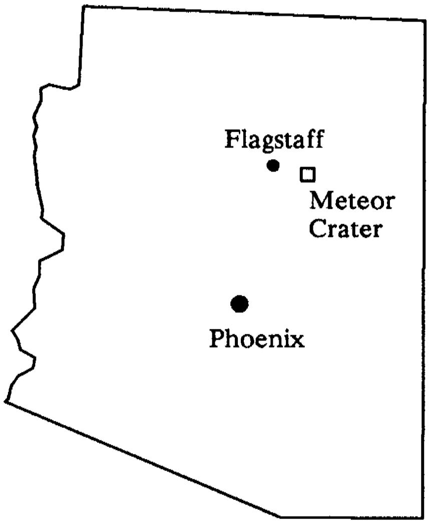


Figure 2. Location map of Meteor Crater, Arizona

depth (D. Roddy, personal communication, 1988). Today the crater walls exhibit steep cliffs composed of approximately 10 m of Moenkopi Sandstone underlain by 90 m of Kaibab Formation (in this location actually a siliceous dolomite). Prior to impact the Kaibab Formation was completely covered by the Moenkopi Sandstone.

The date of the meteorite impact is of considerable interest because such knowledge will enable rates of crater erosion to be quantified. It is also important for the calculation of impact fluxes. The crater was originally estimated to be about 25,000 years old, based on geological correlations and soil development (Shoemaker, 1960). However, thermoluminescense studies indicated an age closer to 50,000 years (Sutton, 1985). The considerable discrepancy between these dates motivated further research into the crater chronology, using measurements and interpretation of cosmogenic ^{36}Cl buildup.

Meteor Crater should be an ideal subject for ^{36}Cl build-up dating because it is possible to identify and sample a geological unit (the Kaibab Formation) that was nearly completely shielded from cosmic rays by 10 m of overlying Moenkopi Sandstone prior to the impact. The Kaibab Formation was virtually instantaneously exposed to cosmic rays at the time of the impact.

FIELD SAMPLE SELECTION

In an attempt to use the build-up of cosmogenic ^{36}Cl as a dating technique, 5 samples were collected from the tops of large boulders thrown from the crater and deposited in the surrounding ejecta blanket. D. Roddy (oral communication, 1987) was unsure of the depth of the original ejecta blanket but postulated that 1–2 m of material has been eroded since impact, principally by wind action. Considering these factors it seems likely that the tall boulders have been continuously exposed to cosmic rays since shortly after impact. The shorter of the sampled boulders may have been briefly covered by fine–grained air fall ejecta. This material would probably have been removed relatively rapidly by wind erosion.

Two boulders on the east rim and one boulder on the west rim were sampled. Two outlying boulders approximately 300 m southeast of the rim were sampled. An average of 700 gm was collected from each of the five boulders. All samples were collected in 1987 and were assigned sample numbers of MC–1 to MC–5. Specific information about these boulders can be found in the section 'Sample Descriptions' (page 124).

SAMPLE PROCESSING

All of the samples collected were carbonate rocks of Kaibab Formation, and so all were processed in an identical manner using the techniques described in the section "Chlorine Extraction of Carbonate Rocks" (page 21). XRF, ion chromatography, and ICP–ES were performed to determine the geochemistry of all 5 of the samples. The chemical compositions of the 5 samples are presented in Table 3, page 40.

Table 3: METEOR CRATER GEOCHEMICAL DATA

	MC-1	MC-2	MC-3	MC-4	MC-5
SiO_2 (%)	28.79	23.96	10.74	27.00	12.95
TiO_2 (%)	0.13	0.13	0.15	0.24	0.14
Al_2O_3 (%)	2.52	2.24	2.38	4.97	2.20
Fe_2O_3 (%)	0.33	0.36	0.73	0.60	0.61
MgO (%)	17.16	17.56	19.36	16.19	18.83
CaO (%)	21.13	23.38	29.21	23.78	28.16
MnO (%)	0.05	0.02	0.07	0.03	0.10
Na_2O (%)	0.16	0.05	0.11	0.17	0.13
K_2O (%)	0.47	0.47	0.43	0.78	0.44
P_2O_5 (%)	0.23	0.28	0.39	0.19	0.48
CO_2 (%)	26.18	27.10	25.84	23.46	27.80
Cl (ppm)	143	131	217	132	259
B (ppm)	3.5	5.3	5.8	7.6	5.6
Nd (ppm)	0	0.3	0.1	0	0
Sm (ppm)	0	0.1	0.1	0.1	0
Gd (ppm)	0.2	0.4	0.3	0.2	0.3

The major element analyses were performed by an XRF fundamental parameters program. The accuracy of these analyses is ±10%. This accuracy is sufficient for calculating thermal neutron capture rates but is insufficient for other geochemical applications. These analyses were made using a pressed powder pellet instead of the fused disc used in standard geochemical analysis.

Chlorine values were measured using XRF. The rare earth data was obtained using ICP-ES analytical techniques.

CALCULATIONS - Meteor Crater

As discussed in a prior subsection (page 13), normalization is necessary before the five measured ^{36}Cl ratios can be compared. For this study, the normalization accounts for elemental composition only, as the other potential variables (elevation, latitude and depth) are essentially constant for all samples. Sample MC–2 was chosen as having an average major element composition and the other samples were then normalized to MC–2. In the normalization equation, the MC–2 value becomes the reference value indicated by the subscript *r*.

This normalized ratio can be used to calculate the time of exposure to cosmic rays, which in the case of Meteor Crater can be presumed to be the date of impact. The measured ratio of ^{36}Cl to stable chloride for each sample, the normalized ratio of ^{36}Cl to stable chloride, and the calculated age for each sample are illustrated in Table 4 (page 42).

The age estimate is calculated using new preliminary values for the thermal neutron flux and the production rate from K spallation. These values are discussed in the subsection "Calculations - Bloody Canyon" (page 58). Research is currently underway to recalculate the production rate of ^{36}Cl from Ca spallation. This new rate will affect the exposure age calculations of carbonate rocks.

Table 4: ^{36}Cl DATA AND CALCULATED AGE

Meteor Crater

SAMPLE NUMBER	MEASURED RATIO (R) ^{36}Cl / 10^{15} Cl	NORMALIZED RATIO (R_n) ^{36}Cl / 10^{15} Cl	AGE years
MC–1	1462 ± 44	1557 ± 47	33,762
MC–2	1194 ± 39	1183 ± 39	25,463
MC–3	1280 ± 57	1552 ± 69	33,705
MC–4	1469 ± 71	1585 ± 77	34,402
MC–1	1207 ± 38	1536 ± 48	33,350

Mean Normalized Ratio: 1483 ± 56 **^{36}Cl / 10^{15}Cl**

CALCULATED AGE: 31,848 ± 1,246 years

Mean Normalized Ratio Excluding MC–2: 1452 ± 56 **^{36}Cl / 10^{15}Cl**

CALCULATED AGE EXCLUDING MC–2: 33,520 ± 1,348 years

CONCLUSIONS

Four out of the five samples analyzed showed very similar normalized ratios. The mean and standard deviation of the normalized ^{36}Cl ratios for the samples MC-1, MC-3, MC-4, and MC-5 was (1452 ± 56) x 10^{-15}. The standard deviation of the four samples, 56 x 10^{-15}, is actually slightly smaller than the mean of the four analytical uncertainties, 59 x 10^{-15}. Inclusion of the sample MC-2 changes the combined result to (1483 ± 56) x 10^{-15}. Although there is no indepedent basis for excluding MC-2, the concordance of the other four samples indicates that the calculated mean excluding MC-2 more accurately reflects the time since the meteorite impact. The exposure age calculated from this mean ratio is 33,500 ± 1350 years.

The preceding results differ significantly from those presented by Phillips et al. (1988). The age of 22,700 presented in their paper was calculated using the thermal neutron flux from Lal and Peters (1967) and the Yokoyama (1977) production rates. The age of 33,500 years is calculated using new preliminary neutron flux and production rate estimates (''Calculations - Bloody Canyon,'' page 58). These values significantly increase the estimated age of Meteor Crater. The calculated exposure age using ^{36}Cl indicates an exposure age between Shoemaker's (1960) original age estimate of 25,000 years and Sutton's (1985) thermoluminescence date of 50,000 years. Estimates of the rates of occurrence of similar impacts over the entire earth continue in the range of once per 25,000 to 50,000 years. This cosmogenic ^{36}Cl exposure data demonstrates that Barringer Meteorite Crater is among the youngest and freshest bowl-shaped large impact craters on the earth.

IV. MORAINES AT BLOODY CANYON

OVERVIEW

There is a disagreement among previous researchers as to the ages and glacial sequences in this area. The intent of this study is to use state-of-the-art dating techniques to determine the absolute ages of the glacial deposition. This information would then shed new light on the glacial history of the Sierra Nevada. The area studied is illustrated in Figure 3.

PREVIOUS WORK AND GEOLOGIC HISTORY

Different researchers have used different nomenclature to describe the geographic features in the Bloody Canyon area. Walker Creek drains generally from the west to the east. In some early studies, 'Bloody Canyon' referred only to the upper reaches of Walker Creek. Sawmill Canyon, which is dry, protrudes from the large, Tahoe right lateral of Walker Creek. In contemporary useage, Bloody Canyon has come to refer to this entire Walker Creek – Sawmill Canyon area. This report will use the term 'Bloody Canyon' to include Sawmill Canyon and the entire Walker Creek drainage.

Evidence of two or three glacial periods was reported by early observers in the late 1800's and early 1900's. Knopf (1918) was the first to map two ages of moraines. This was in

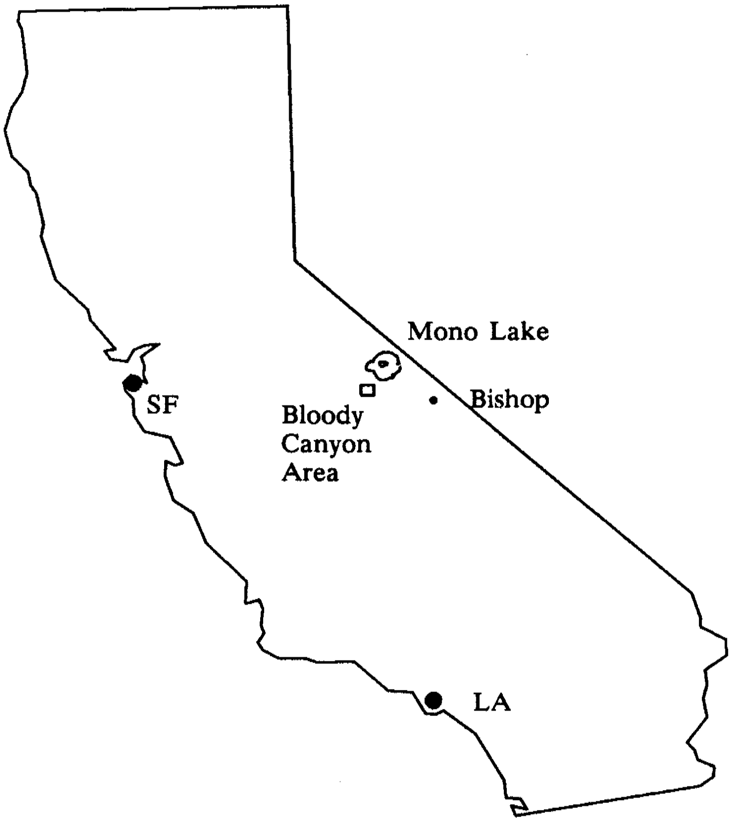


Figure 3. Location map of Bloody Canyon region, California

the Owens Valley section of the eastern Sierra Nevada range. Matthes (1928) and Blackwelder (1928) studied the west and east sides of the Sierras respectively. Each reported evidence of three glaciations.

Blackwelder (1931) named and described four glaciations in the Sierra Nevadas based mainly on exposures on the east side. These four glaciations, listed youngest to oldest, are: Tioga, Tahoe, Sherwin, and McGee. Blackwelder outlined several criteria which he used to justify the age differences. He introduced a granite–weathering ratio which was used in some form by all subsequent investigatiors. Other criteria included boulder frequency, preservation of polished rock surfaces, and the extent of stream–cutting through terminal moraines. The overall size of moraines was also noted as a criterion. The size of moraines increases with increasing age.

Putnam (1949) mapped the June Lake district, concentrating on glacial features. His maps cover part of the Bloody Canyon sequence, all of which he mapped as Tahoe.

Sharp and Birman (1963) added two glacial stages to Blackwelder's sequence. They identified the Tenaya glaciation which they placed between the Tioga and the Tahoe. Moraines within Bloody Canyon were described as examples of the Tenaya. They also added the Mono Basin glaciation, with Sawmill Canyon as their type locality. They determined this stage to be older than the Tahoe and younger than the Sherwin. Criteria used by Sharp and Birman included boulder frequency, a weathering ratio, and a ratio of granitic to non–granitic boulders.

Sharp (1969) also studied the Bloody Canyon moraines while trying to differentiate moraines near Convict Lake. He used semi–quantitative techniques to discern age differences. His techniques included percentages of unweathered abraded boulders and unweathered fretted (pitted) boulders. He also dug soil pits and did a rough grain–size analysis. His theory was that older soils would have a higher percentage of fine–grained material. He found this to be true. At Bloody Canyon he tested only the Tioga and Tahoe moraines and thus did not address the question of the distinctness of the Tenaya and Mono Basin moraines.

Burke and Birkeland (1979) used multi-parameter relative dating techniques to evaluate the glacial sequence in the eastern Sierras. They utilized a total of fourteen techniques, including some previously mentioned. One innovative technique was the hammer-blow weathering ratio in which they evaluated the sound produced when a boulder was struck with a hammer. Their data did not support evidence for a separate Tenaya or Mono Basin glaciation. Thus they suggested that these may be second-order glaciations and so proposed useage of Tahoe and Tioga as the only post-Sherwin glaciations.

Dorn and Turrin (1987) studied moraines at Pine Creek using radiocarbon and cation-ratio techniques on rock varnish. With this method, organic matter extracted from rock varnish was analyzed for ^{14}C with accelerator mass spectrometry. This yielded a minimum age of moraine deposition. The dates for the several Tioga moraines ranged from 19,000 years to 13,200 years. The main Tahoe moraines yielded a minimum age of approximately 150,000 years by cation-ratio dating.

FIELD SAMPLE SELECTION

In selecting rocks to sample, a number of criteria were followed. Only boulders from the crest of a moraine were sampled. This was to ensure that the boulder had not rolled from some other location. This criteria was met on almost every moraine. The largest boulders on a moraine were the primary sampling target. These boulders would provide the greatest exposure to cosmic rays over time. For example, taller boulders would tend to protrude above snow cover and would be less shielded by vegetation. The height of the average boulder sampled was 1.5 to 1.8 m above ground surface.

At a specific boulder, the ideal sampling site is the middle of a horizontal surface. This should minimize any edge effect, a factor which is difficult to quantify in the cosmogenic neutron flux. This sampling configuration was rarely encountered. The majority of samples collected were from nearly horizontal surfaces but were usually near the edge of the boulder. Figure 4 illustrates a typical sampling scenario. On a specific moraine the freshest boulders were sought. In general the degree of weathering increases with increasing age of moraine. Thus on the oldest moraines sampled, all boulders were moderately to strongly weathered, but were sampled because they were the best material available on that moraine. The degree of surface degradation of some boulders was evidenced by mafic xenoliths protruding 2–10 cm above the present rock surface. This is interpreted to imply that at least that much weathering or erosion occurred since glacial deposition of the boulder. An additional cause of boulder degradation is forest fires. The heat of these fires can cause boulders to crack possibly spalling pieces off boulder tops. Should such degradation occur the ^{36}Cl date would reflect a complex combination of factors. These factors would include time since moraine deposition, time since fire, and thickness of rock pieces which spalled off.

Figure 4. Typical sample site at Bloody Canyon

At Bloody Canyon, 5 moraine crests of different ages were sampled. Five samples were collected from 5 boulders on each moraine crest. The average sample size was 700 g. Samples were oriented and labelled with respect to top surface and any exposed vertical surface. Field notes included a general rock description with relative biotite, quartz, and feldspar content. An approximate petrographic name was assigned to each rock. The geometry of the boulders was sketched and photographs taken at many sites. Degree of weathering and grain size were also noted.

Samples were collected from moraines in the Bloody Canyon area in 1986 and 1987. Sample numbers, rock descriptions, site descriptions, and other pertinent details are listed in the section "Sample Descriptions" (page 124).

GEOCHEMISTRY

All the rock analyses discussed below were performed by Marek Zreda. Whole rock, major element data for these granodioritic rocks was obtained using a fundamental parameters program on an XRF spectrometer. This method required a pressed pellet made from very fine rock powder. Analytical precision with this method was about ±10% on each element. Total chlorine values were initially obtained using the same pellet on a separate XRF analysis. The calibration curve for the analysis was not well-constrained below 50 ppm Cl. Forty percent of all samples analyzed had values below this detection limit. An ion chromatography technique was recently developed by Marek Zreda which was used to measure the chlorine content of all of the samples.

Rare earth element analysis was performed by Zreda to quanitify concentrations of Gd, Sm, and Eu. These elements can significantly affect the ^{36}Cl production rate because of their high thermal neutron cross-sections. The analytical technique was modelled after that of Walsh et al. (1981). A 1-gm aliquot of rock powder was fused with sodium carbonate. The fusion cake was dissolved and the solution poured on an ion exchange resin. After several elution steps, a solution containing the REE was obtained. This solution was analyzed on an ICP emission spectrometer.

An attempt was made to analyze for boron using ICP-ES. Results of this analysis were not satisfactory due to problems with calibration of the instrument. An assumed boron value was used in the calculations. The value of 15 ppm was used for all glacial moraine samples. This value was obtained from Wedepohl (1978) as an average value for granodiorites.

The chemical compositions of the 19 samples are presented in Table 5, page 53.

Table 5: GEOCHEMISTRY OF BLOODY CANYON SAMPLES

The major element analyses were performed by an XRF fundamental parameters program. The accuracy of these analyses is ±10%. This accuracy is sufficient for calculating thermal neutron capture rates but is insufficient for other geochemical applications. These analyses were made using a pressed powder pellet instead of the fused disc used in standard geochemical analysis. The boron value of all samples is assumed to be 15 ppm.

Chlorine values were measured using ion chromatography and XRF. The rare earth data was obtained using ICP–ES analytical techniques.

	BC86- 1TI	BC86- 3TI	BC86- 5TI
SiO_2 (%)	78.18	74.77	72.32
TiO_2 (%)	0.05	0.31	0.56
Al_2O_3 (%)	12.41	15.42	15.54
Fe_2O_3 (%)	0.80	2.66	4.23
MgO (%)	0.01	1.24	1.99
CaO (%)	0.84	2.12	2.89
MnO (%)	0.03	0.08	0.11
Na_2O (%)	3.21	3.92	3.34
K_2O (%)	5.09	4.38	3.44
P_2O_5 (%)	0.08	0.25	0.34
Cl (ppm)	130	214	106
B (ppm)	15.0	15.0	15.0
Nd (ppm)	28	11	11.20
Sm (ppm)	2.7	1.50	3.90
Eu (ppm)	1.2	0.30	0.60
Gd (ppm)	6	1.8	3.6
Dy (ppm)	3.9	1.50	2.40
Yb (ppm)	2.1	0.60	0.90

	BC86- 6TE	BC86- 8TE	BC86- 9TE	BC86-11TE
SiO_2 (%)	76.88	77.24	65.61	85.21
TiO_2 (%)	0.17	0.25	0.22	0.08
Al_2O_3 (%)	14.18	15.93	14.59	14.84
Fe_2O_3 (%)	1.82	2.58	1.74	1.02
MgO (%)	0.41	1.46	0.68	0.49
CaO (%)	2.14	1.47	1.94	0.98
MnO (%)	0.10	0.11	0.05	0.07
Na_2O (%)	3.37	3.86	3.57	5.16
K_2O (%)	3.75	3.30	4.32	5.34
P_2O_5 (%)	0.09	0.20	0.28	0.02
Cl (ppm)	264	1005	38	199
B (ppm)	15.0	15.0	15.0	15.0
Nd (ppm)	25.6	22.8	13.80	16.80
Sm (ppm)	3.9	4.2		3.9
Eu (ppm)	0.8	0.8	0.90	0.60
Gd (ppm)	3.9	3.6	4.20	4.50
Dy (ppm)	2.4	2.7	2.40	3.00
Yb (ppm)	0.9	0.9	1.80	2.10

The major element analyses were performed by an XRF fundamental parameters program. The accuracy of these analyses is ±10%. This accuracy is sufficient for calculating thermal neutron capture rates but is insufficient for other geochemical applications. These analyses were made using a pressed powder pellet instead of the fused disc used in standard geochemical analysis. The boron value of all samples is assumed to be 15 ppm.

Chlorine values were measured using ion chromatography and XRF. The rare earth data was obtained using ICP-ES analytical techniques.

	BC86–12TA	BC86–13TA	BC86–14TA	BC86–15TA	BC86–16TA
SiO_2 (%)	53.40	67.80	78.00	75.30	72.16
TiO_2 (%)	1.29	0.40	0.20	0.51	0.58
Al_2O_3 (%)	9.41	14.48	14.80	9.40	16.18
Fe_2O_3 (%)	8.56	2.82	1.88	3.41	4.18
MgO (%)	3.95	1.25	1.44	3.13	2.82
CaO (%)	7.37	2.20	1.19	1.46	3.82
MnO (%)	0.25	0.07	0.10	0.06	0.09
Na_2O (%)	3.41	3.77	4.12	3.07	4.38
K_2O (%)	1.06	4.37	3.74	3.85	3.92
P_2O_5 (%)	0.48	0.51	0.33	0.95	0.64

Cl (ppm)	65	165	160	67	84
B (ppm)	15.0	15.0	15.0	15.0	15.0
Nd (ppm)	30.00	47.80	25.60	30.00	33.80
Sm (ppm)	6.00	9.60	4.50	6.00	6.60
Eu (ppm)	1.00	1.80	1.00	1.00	1.00
Gd (ppm)	6.00	8.40	4.00	6.00	5.70
Dy (ppm)	4.00	5.70	2.40	4.00	3.00
Yb (ppm)		2.10	1.20		0.90

The major element analyses were performed by an XRF fundamental parameters program. The accuracy of these analyses is ±10%. This accuracy is sufficient for calculating thermal neutron capture rates but is insufficient for other geochemical applications. These analyses were made using a pressed powder pellet instead of the fused disc used in standard geochemical analysis. The boron value of all samples is assumed to be 15 ppm.

Chlorine values were measured using ion chromatography and XRF. The rare earth data was obtained using ICP–ES analytical techniques.

	SC86–17BMB	SC86–18BMB	SC86–19MB	SC86–20MB	SC86–21MB
SiO_2 (%)	85.20	74.68	75.22	84.68	69.98
TiO_2 (%)	0.15	0.25	0.20	0.10	0.05
Al_2O_3 (%)	11.40	15.27	14.64	14.65	13.17
Fe_2O_3 (%)	1.36	2.15	2.09	1.06	0.47
MgO (%)	0.95	2.08	0.67	0.48	0.50
CaO (%)	0.56	1.22	2.40	1.18	0.71
MnO (%)	0.07	0.13	0.13	0.05	0.04
Na_2O (%)	3.24	2.83	3.51	3.43	3.70
K_2O (%)	3.93	3.90	3.22	5.16	5.62
P_2O_5 (%)	0.94	0.52	0.32	0.17	0.18
Cl (ppm)	146	198	110		
B (ppm)	15.0	15.0	15.0	15.0	15.0
Nd (ppm)	30.00	20.50	31.00	19.20	22.6
Sm (ppm)	6.00	2.85	1.80	3.20	3.8
Eu (ppm)	1.00	0.50		2.40	
Gd (ppm)	5.00	2.23	6.00	3.40	4.4
Tb (ppm)			0.80	0.30	0.4
Dy (ppm)	4.00	1.49	1.20	0.80	2.6
Yb (ppm)		0.62			0.4

The major element analyses were performed by an XRF fundamental parameters program. The accuracy of these analyses is ±10%. This accuracy is sufficient for calculating thermal neutron capture rates but is insufficient for other geochemical applications. These analyses were made using a pressed powder pellet instead of the fused disc used in standard geochemical analysis. The boron value of all samples is assumed to be 15 ppm.

Chlorine values were measured using ion chromatography and XRF. The rare earth data was obtained using ICP–ES analytical techniques.

	BC87- 1TA	BC87- 2TA	BC87- 3TA	BC87- 4TA	BC87- 5TA
SiO_2 (%)	76.44	81.15	74.87	75.62	67.92
TiO_2 (%)	0.20	0.09	0.16	0.18	0.23
Al_2O_3 (%)	14.61	14.31	13.73	13.24	14.75
Fe_2O_3 (%)	1.98	0.80	1.64	1.97	2.26
MgO (%)	1.29	0.25	0.46	0.54	0.95
CaO (%)	2.02	0.85	2.04	2.18	1.84
MnO (%)	0.11	0.05	0.06	0.08	0.11
Na_2O (%)	3.98	4.65	3.51	3.10	3.36
K_2O (%)	4.05	5.64	3.88	2.48	4.32
P_2O_5 (%)	0.58	0.28	0.22	0.36	0.29
Cl (ppm)	175	513	248	75	261
B (ppm)	15.0	15.0	15.0	15.0	15.0
Nd (ppm)	21	16.4	20.6	34.6	17.6
Sm (ppm)	3.3	3.2	3.3	5.4	2.7
Eu (ppm)	0.8	0.2	0.6	1.2	0.6
Gd (ppm)	3.6	3.0	3.0	4.8	3.3
Dy (ppm)	2.4	0.1	1.8	3.6	2.7
Yb (ppm)	1.2	1.0	0.9	0.9	1.5

The major element analyses were performed by an XRF fundamental parameters program. The accuracy of these analyses is ±10%. This accuracy is sufficient for calculating thermal neutron capture rates but is insufficient for other geochemical applications. These analyses were made using a pressed powder pellet instead of the fused disc used in standard geochemical analysis. The boron value of all samples is assumed to be 15 ppm.

Chlorine values were measured using ion chromatography and XRF. The rare earth data was obtained using ICP–ES analytical techniques.

CALCULATIONS - Bloody Canyon

Ages were calculated for a set of rocks which were analyzed for ^{36}Cl in December, 1987. These calculations used the potassium and calcium production rates derived from Yokoyama (1977). The ages obtained were unreasonably young, based on other well-accepted geologic data. Also, the age variation was too small and did not correlate with other paleoclimatic data such as water levels in Searles Lake. Approximate ages obtained in this analysis were: Tioga 6,000 years; Tenaya 8,000 years; Tahoe 20,000 years; Mono Basin 25,000 years.

A means of refining the production rate was sought. In the summer of 1987, moraine boulder samples were collected in the White Mountains (a mountain range along the California-Nevada border). Ronald Dorn (Geography Department, Arizona State University, Tempe) also collected samples with rock varnish from the same moraines for varnish radiocarbon dating. His dates for several of the highest moraines, 9,740, 12,510, and 17,780 years old, provided the opportunity to calibrate the ^{36}Cl production rates.

In an attempt to isolate the several sources of ^{36}Cl, a mineral separation approach was taken. Marek Zreda performed the mineral separations and the subsequent chlorine extractions. The results of the mineral separations were less than ideal due in part to the rock mineralogy, especially the presence of perthitic feldspar. Calcium-rich plagioclase was absent, so a calcium-bearing phase was not available. The fine-to-medium grain size also hindered the separation of pure phases. The following impure phases were obtained from three White Mountain samples: quartz, microcline, and biotite. Each separate was analyzed for major elements and REE.

Chlorine was extracted from the mineral separates using the air strip method II. A whole-rock aliquot of each sample was also processed to extract chlorine. Chlorine-36 analysis was performed in July 1988. Unfortunately, one critical microcline sample was lost in transit. Based on these July 1988 ^{36}Cl ratios and Ronald Dorn's data, new preliminary values for the thermal neutron flux and the production rate from K_2O were established. The new value for the thermal neutron flux (ϕ_n) is 6.5 x 10^5 neutron $kg^{-1}yr^{-1}$. This is a reduction from the value of 1.0 x 10^6 estimated by Lal and Peters (1967) and used in most previous exposure age calculations. This change in the neutron flux is more significant than the change in ψ_K or ψ_{Ca}. The new value for the production rate from K_2O is 900 atoms $kg^{-1}yr^{-1}$ per wt % K_2O, which is considerably lower than that of Yokoyama (1977).

The production rate from calcium could not be refined because no Ca-rich species was analyzed. Future research will test carbonate rocks which have been dated using radiocarbon techniques.

The new preliminary values are used in the exposure age calculations of all Bloody Canyon samples. These calculations give ages which are more consistent with other known geologic data. All 19 samples were normalized to one composition so that comparison is possible amoung all the Bloody Canyon samples.

RESULTS AND CONCLUSIONS

The chlorine content of the sample is critical in the age calculations. At the onset of this research, the importance of the chlorine content was not fully appreciated. Marek Zreda has developed a method using ion chromatography which yielded chlorine contents in samples that had been below the detection level of the XRF method used previously. This improved technique of quantifying low level whole rock chlorine content has substantially altered the preliminary age calculations. The chlorine contents of the rocks sampled closely correlates to the average chlorine values of granodiorites reported in Wedepohl (1978).

Exposure ages were calculated using all samples possible. Exposure ages for all the samples for which ^{36}Cl data and geochemical data are available are presented in Table 6, beginning on page 62. This table lists the measured ratio of ^{36}Cl to stable chloride for each sample, the normalized ratio of ^{36}Cl to stable chloride, and the calculated age for each sample. Table 7, page 64, lists the measured ^{36}Cl ratios for samples which could not have an exposure age calculated because of incomplete geochemical data.

The results for several of the moraines show a considerable spread in exposure ages. This spread could indicate that some of the exposure assumptions detailed previously were not being met. Samples with comparatively low ages have not been continuously exposed since moraine deposition, for one reason or another. The older the moraine, the greater the likelihood of this problem occurring. Perhaps these rocks were originally buried, but as the moraine has been eroded and the top of the moraine lowered, these rocks have become exposed. Although they are currently at the top of the moraine, they do not represent rocks that have been at the top of the moraine since deposition, only since erosion exposed them. Boulders deposited on moraine crests at the time of moraine deposition may have weathered into small fragments. The spread of ^{36}Cl ratios on older moraines represents geologic factors which have shortened the exposure time of the sampled boulders. As the age of the moraines increases, there is a greater variation in the calculated ages due to exposure inconsistencies.

Samples with high ages exhibit another possible problem. It is possible that some of the boulders sampled are reworked boulders which were exposed to cosmic rays prior to the glaciation which deposited them in their current location.

The preliminary results of Bloody Canyon exposure age calculations indicate four fairly distinct glaciations. The Tenaya and upper Tahoe moraines which are closely related geomorphically have similar ranges of exposure ages.

The three Tioga moraine samples give ages of 2,000, 16,300, and 24,300 years respectively. The 2,000 year-old sample is anomalously low. This may reflect an instrument error in the measurement of the raw ^{36}Cl ratio. The sample needs additional TAMS

Table 6: ^{36}Cl DATA AND CALCULATED AGE

Bloody Canyon

SAMPLE NUMBER	MEASURED RATIO (R) ^{36}Cl / 10^{15} Cl	NORMALIZED RATIO (R_n) ^{36}Cl / 10^{15} Cl	AGE years
Tioga moraine:			
BC86- 1TI	59 ± 4	24 ± 2	2,039
BC86- 3TI	536 ± 39	550 ± 25	24,304
BC86- 5TI	443 ± 18	368 ± 15	16,340
Tenaya moraine:			
BC86- 6TE	1350 ± 96	1425 ± 101	63,346
BC86- 8TE	697 ± 38	977 ± 53	44,591
BC86- 9TE	867 ± 32	374 ± 23	15,953
BC86-11TE	1923 ± 60	2003 ± 62	91,151
Tahoe moraine (upper):			
BC87- 1TA	1638 ± 211	1712 ± 220	76,904
BC87- 2TA	3763 ± 133	2008 ± 71	90,593
BC87- 3TA	1308 ± 87	1394 ± 93	61,912
BC87- 4TA	1460 ± 180	1131 ± 139	49,381
BC87- 5TA	1698 ± 94	1871 ± 104	84,761

Table 6: ^{36}Cl DATA AND CALCULATED AGE

Bloody Canyon (cont)

SAMPLE NUMBER	MEASURED RATIO (R) ^{36}Cl / 10^{15} Cl	NORMALIZED RATIO (R_n) ^{36}Cl / 10^{15} Cl	AGE years
Tahoe moraine (lower):			
BC86–12TA	3155 ± 238	2464 ± 186	114,313
BC86–13TA	4313 ± 246	5359 ± 306	302,561
BC86–14TA	5736 ± 256	6748 ± 301	432,496
BC86–15TA	4211 ± 240	3569 ± 203	176,711
BC86–16TA	2793 ± 84	2418 ± 73	112,035
Mono Basin moraine:			
SC86–17MB	3123 ± 223	3302 ± 236	161,216
SC86–18BMB	2001 ± 153	2178 ± 167	100,036
SC86–19MB	1906 ± 77	1662 ± 67	74,221
SC86–20MB*	5365 ± 182	4652 ± 158	244,350
SC86–21MB*	7069 ± 295	6123 ± 256	368,100

* A chlorine value of 150 ppm was assumed in the age calculations listed for these two samples.

Table 7: MEASURED ^{36}Cl RATIOS FOR SAMPLES WITH INCOMPLETE GEOCHEMICAL DATA

These eleven samples were collected by Nancy Jannik and Fred Phillips in 1985 from Bloody Canyon moraines. The samples were analyzed for ^{36}Cl. However, exposure age has not been calculated because most of the necessary geochemical data is unavailable.

SAMPLE NUMBER	MEASURED RATIO (R) ^{36}Cl / 10^{15} Cl
BCM-1A	884 ± 41
BCM-3A	585 ± 25
BCM-4A	761 ± 68
BCM-1B	905 ± 35
BCM-2B	745 ± 33
BCM-5B	860 ± 103
BCM-2C	5061 ± 309
BCM-5C	1352 ± 74
BCM-1D	5061 ± 309
BCM-2D	1519 ± 68
BCM-5D	1857 ± 131

analysis to clarify its exposure age. The ages of the remaining two samples, 16,300 and 24,300 years, correlate with the late Wisconsin glacial period. These sample ages also correlate with the interval of the last high water stand of Mono, Owens, and Searles Lakes which was estimated by Smith and Street–Perrot (1983).

The Tenaya moraine samples give an age range of 16,000 to 91,000. These samples show no clustering and exhibit the wide age spread mentioned earlier. Field evidence suggests that the Tenaya glaciation is fairly closely related to the Tahoe glaciation. The Tenaya lateral moraine which was sampled appears from a distance to be pasted onto the Tahoe lateral moraine. These two lateral moraines merge together toward the terminus. It is probable that the Tenaya represents a late pulse of the Tahoe glaciation. The probable age of the Tenaya moraine is 40,000–90,000 years old.

Samples from the upper part of the Tahoe moraine range in age from 50,000 to 90,000 years old. This group of samples does not seem to contain anomalously high or low values. There is fairly good correlation with the early period of the Wisconsin glaciation which is estimated to range from 60,000 – 100,000 years ago. The lower values on this moraine probably represent boulders exposed subsequent to deposition.

The '86TA' samples were collected from what was thought to be the main Tahoe moraine. After closer inspection of aerial photos this moraine was re–evaluated as a ridge extending from beneath the main Tahoe moraine at a low angle, rather than part of the main moraine. The sampled ridge is south of Walker Creek. To the north of Walker Creek there is a matching moraine with similar morphology. Both exhibit a greater degree of rill formation on their flanks than do the higher, main Tahoe laterals. The '86TA' moraine represents an early Tahoe glaciation. The later Tahoe glaciation which produced the high, prominent moraines seen today obliterated or covered all but the ends of the early Tahoe laterals. In fact, had the later Tahoe event not terminated just upstream of the '86TA' moraine, it would have eroded and/or covered it also. The sampled boulders have been exposed over time as this ridge has been eroded. The ^{36}Cl dates indicate an age of 112,000 - 177,000 years old, older than the main Tahoe.

Two samples from the '86TA' set have ages of 300,000 and 430,000 years. These samples appear to have high total chlorine values which would increase the calculated exposure age. Additional chlorine analysis is needed to confirm the chlorine values and thus the age calculations.

Mono Basin moraine boulders show a large spread in exposure ages. This is to be expected because field relationships indicate that the Mono Basin moraines are the oldest glacial feature at Bloody Canyon. As the age of the moraines increases, there is a greater variation in the calculated ages due to exposure inconsistencies.

Two of the five Mono Basin samples have unknown total chlorine values. These two samples also have the highest measured ^{36}Cl ratios of the set. Thus the upper value of the exposure age range is difficult to quantify. Exposure age calculations were performed using different assumed values for the unknown total chlorine.

The three samples with known chlorine values give exposure ages of 74,000 - 161,000 years. These samples represent boulders exposed subsequent to moraine deposition by erosion of the moraine ridge crest. Using 50 ppm Cl for the unknown values extends the age range to 163,000 years which is still within the age range of the younger '86TA' moraine. Assumed values of 100 ppm Cl gives ages of 191,000 and 282,000 years. This pushes the minimum age of the Mono Basin glaciation into the pre–Illinoisian period. Field relationships indicate that there was a considerable time gap between the Mono Basin glaciation and the glaciation which deposited the lower Tahoe moraines. The time gap is increased by assuming values of 150 ppm Cl, a reasonable assumption based on other measured chlorine values. Ages of 244,000 and 368,000 years are obtained with the 150 ppm Cl values. The Searles Lake sediment record (Jannik, in progress) shows high water stands at about 420,000 years and 350,000 years. It is probable that the Mono Basin glaciation correlates with these high water periods.

V. LABORATORY PROCEDURES

OVERVIEW

This section on laboratory procedures is intended to thoroughly describe the laboratory processes developed as part of this research. The acid–dissolution method for carbonate rocks and the three feasible methods of extracting chlorine from silicate rocks will be detailed. In addition to listing the various steps in carbonate rock dissolution, the diffusion method, and air strip methods I and II, this section will also include the steps necessary for the acid–base purification method used to concentrate and purify the AgCl recovered during the dissolution process, and the final weighing and packing necessary to prepare the samples to be analyzed at the University of Rochester. As the laboratory procedures were being developed it became desireable to design worksheets for various parts of the process. If such a worksheet was designed, this section will include a sample worksheet which has been filled out with representative values to illustrate both how to complete the worksheet and also a typical process. In the 'Worksheets' section (page 102) there are blank worksheets which can be used in the future to record information as the various steps are being performed.

INITIAL PREPARATIONS

All equipment must be thoroughly cleaned before beginning any of these processes. At the onset and during the course of processing the samples, it is necessary to make additional preparations. These are listed below.

Capture solution

Capture solution is made with 1 part 0.1 M silver nitrate to 2 parts dilute nitric acid. The dilute nitric acid is made with 1 part conc. nitric acid to 10 parts deionized water. The mixing of capture solution takes approximately 20 minutes, and new solution must be mixed every 10–12 heatings.

Silver nitrate solution

The preparation of silver nitrate solution takes approximately 30 minutes, and new solution must be mixed every 50 samples.

Barium nitrate solution

The shelf life of barium nitrate is approximately 3 months, after which the barium nitrate should be discarded and new solution prepared. This author found no quantitative description of how to prepare the barium nitrate solution. The methods described by Conard et al. (1986) mention only a saturated barium nitrate solution. Thus the proportion of ingredients is flexible to produce the desired solution. The following preparation method was used in this project:

> Place 6 gm of barium carbonate powder in a jar or other container which can be sealed well. **Caution: barium carbonate is extremely toxic and should be handled with gloves and a dust mask.**
>
> 35–40 ml of concentrated nitric acid is added to the barium carbonate. This should be added in small increments until all sputtering stops, at which time the remaining nitric acid can be added. The approximate ratio of barium carbonate to nitric acid is thus 1 gm to 6 ml.
>
> The key criteria in determining the correct mixture is that some solid barium carbonate should still remain. This ensures that the nitric solution is saturated with barium. The barium carbonate should be allowed to settle and only clear solution should be pipetted off the top to add to the sample.

Tantalum sample holders

The University of Rochester supplied tantalum sample holders, each of which had to be engraved with a number. A hole of an appropriate size must be drilled in each holder. Each hole is drilled with a depth equal to its width. The University of Rochester specifies 3 sizes of holes: 1 mm in diameter by 1 mm deep, 1.5 mm x 1.5 mm, and 2 mm x 2 mm. The drill speed should be set for drilling stainless steel, and drilling oil used.

After the holes are drilled and the numbers engraved, it is necessary to clean these sample holders thoroughly in the following manner:

Wash the sample holders in acetone to remove all of the drilling oil.

Wash the sample holders in a 5:1 mixture of concentrated nitric acid and HF for 30–60 seconds.

Wash the sample holders with distilled water 3 times.

Dry the sample holders thoroughly in the oven.

V–vials

Small plastic v–vials (vials which have a conical bottom) are used to store and transport the filled tantalum holders. These v–vials must also be cleaned and dried thoroughly in the oven before use.

CLEAN–UP

Neutralize acid and dispose of waste

After each digestion, the acid must be neutralize and disposed of. This process is done under the fume hood. The neutralization process is strongly exothermic, and sputtering of the acid is common. Protective laboratory clothing including a face shield should be worn. The used acid from each reaction vessel is poured into its own 1–gallon polyethylene bucket. About a half-cup of dry lime is added to the acid. This causes a very strong reaction which produces steam and a considerable amount of heat. After the reaction has stopped sputtering, another scoopful of lime is added. The mixture should be stirred after several scoops are added to ensure complete mixing. This mixture becomes thicker as more lime is added. At the desired pH the mixture is similar to a very thick paste. Dry lime is added until the acid is neutral and has a pH above 5. Typically, 300-400 gm of dry lime are required to neutralize the acid from each reaction vessel. After the mixture cools it is double-bagged and disposed of.

ACID DISSOLUTION OF CARBONATE ROCKS

Equipment Used

1000 ml filter flask

100 ml buret

magnetic stirrer and stir bars

600 ml glass beaker

300 ml 5.3 M nitric acid

18 ml 0.1 M silver nitrate

40 ml DI water

plastic tubing

Detailed Procedures

A 100–gm aliquot of finely–crushed rock is placed in the flask with a stirring bar. The sample is then wetted with 40 ml of DI water. The flask is placed on the stir plate and connected to the buret which is positioned above the flask and delivers acid at a controlled rate. The 5.3 M nitric acid is dripped into the flask at the desired rate. Rock dissolution begins as soon as acid is added, causing considerable bubbling. As the acid level in the buret drops, the flow rate will decrease. If this is the case the buret should be refilled to keep a higher head on the acid. Early in this process the stir bar may be immobilized because of the thick mud. As soon as possible the stir bar should be running at a moderate speed to help with mixing and dissolution of the sample. Acid should be added until no reaction is visible. Approximately 300 ml was required to fully digest the carbonate samples from Meteor Crater.

The acid leachate is treated to recover chlorine. To accomplish this recovery, the acid leachate and sample residue are poured into a 600 ml beaker and allowed to settle for several hours. Deionized water in a wash bottle is used to rinse the flask and obtain a more complete transfer. The supernatant leachate is then decanted into another beaker and 18 ml of 0.1 M silver nitrate is added to precipitate the AgCl. Due to the high density of the leachate the silver nitrate must be stirred well to ensure reaction with the entire sample. The sample is allowed to sit overnight to settle the silver chloride. The acid leachate is decanted and the silver chloride is transferred to a glass centrifuge tube by dissolving in base. When siliceous dolomites are processed using these techniques, a silicic acid precipitate is formed when the silver chloride is dissolved in base. This sediment is removed by centrifuging and decanting the basic solution into a clean tube.

The silver chloride is then further processed according to the steps beginning with 'phase 2: pre-$BaNO_3$ preparations' (page 93) of the acid-base purification method detailed in a later subsection.

ACID DISSOLUTION OF SILICATE ROCKS

DIFFUSION METHOD

Equipment Used

1 2–gal HDPE bucket with lid

Teflon stirrer – fabricated from Teflon rod and bar

6 HDPE cups, 9.5 cm in diameter by 4 cm in height

2 HDPE shelves, 18 cm in diameter, as described below

1 hot water bath

Laboratory Set–Up

The following photograph and sketch (Figure 5, next page) indicate the laboratory set–up.

Detailed Procedures

1. React the sample and assemble the apparatus.

The stirring rod is positioned in the bucket. The rock powder is then placed in the bottom of the bucket. Concentrated nitric acid (100 ml) is added and mixed in order to thoroughly wet the sample. The HF is then added without mixing. The lower shelf is in-

Figure 5. Diffusion method apparatus

stalled. This shelf has a central hole through which the stirring rod is placed and large wedge-shaped openings which allow the HCl gas to circulate in the system. Three capture cups each containing 35 ml silver nitrate are placed on this shelf. Care must be taken not to spill silver nitrate into the acid solution. If such spillage occurs, the chlorine derived from the rock dissolution would not be recovered because it would remain in the leachate as silver chloride instead of evaporating as HCl. The top shelf is then installed and three more capture cups are positioned on it. These upper three capture cups should be offset so that they do not directly overlap the lower cups. The lid is then placed on the entire system and vacuum grease applied around the protruding stirring rod to help seal it. To minimize HCl loss, this apparatus should be assembled quickly once the HF has been introduced into the system.

2. Digest the sample by heating 24 hours.

The whole bucket is then placed in a hot bath. The sample should be stirred fairly frequently at the onset of the procedure and can be stirred less frequently as the sample is digested.

3. Recover and concentrate the silver chloride.

After heating, the bucket can cool down to facilitate handling while recovering silver chloride. The capture solution in the six cups is combined into a clean plastic container. Because this solution contains some HF it should not be stored in a glass container.

4. Rinse the capture cups with base to recover additional silver chloride.

After emptying the solution the cups are rinsed with ammonium hydroxide into a separate clean container to recover any fine silver chloride coating the surfaces. The silver chloride dissolves in the ammonium hydroxide. The pH change caused by the basic rinse results in the precipitation of silicic acid, a white colloidal substance. This can be removed by centrifuging and decanting the basic solution. This basic solution is set aside to combine with the other solution later.

5. Centrifuge the capture solution.

The capture solution is poured into 6–8 centrifuge tubes to spin down the silver chloride. After decanting the acid solution the silver chloride is dissolved in ammonium hydroxide and combined into one centrifuge tube.

6. Combine the capture solution and the rinse solution; acidify.

If volume allows, the basic rinse solution can be combined with the capture solution at this point. This combined solution is then acidified, centrifuged and decanted as detailed in phase 2 of the acid–base purification method (page 91). Should the volume of rinse solution be too large to allow the two solutions to be combined, the rinse solution must be acidified separately and centrifuged to produce a silver chloride pellet. This pellet is dissolved in base and then added to the silver chloride from the capture solution.

AIR STRIP METHOD I

The set-up used in the air strip method I could accomodate four samples. Digesting several samples together is more efficient, but also very intensive because so much has to be monitored so carefully. Originally, a second capture tube was used in order to recover any silver chloride which did not collect in the primary capture tube. When two capture tubes were used, the maximum number of samples that could be efficiently processed at one time was three because of the size of the centrifuge used during the acid-base purification process. However, the amount of silver chloride collected in the secondary capture tube was exceedingly small, and did not warrant the extra time and effort necessary to retrieve it. The following procedures are based on digesting four samples at a time.

EQUIPMENT

4 1-liter Teflon reaction bottles

4 tightly fitting reaction bottle lids, each with three 1/8" holes drilled for tubing

4 50-ml Teflon centrifuge tubes

4 centrifuge tube lids, each with two 1/8" holes drilled for tubing

4 60"-lengths of 1/8" OD Teflon tubing

4 HDPE tee connectors (size for 1/4" ID tubing)

magnetic stirring bars

funnels

test tube rack

deionized water

2 hot water baths

1 ice bath

filtered compressed air supply

LABORATORY SET-UP

The following photograph and sketch (Figure 6) indicate the laboratory set-up.

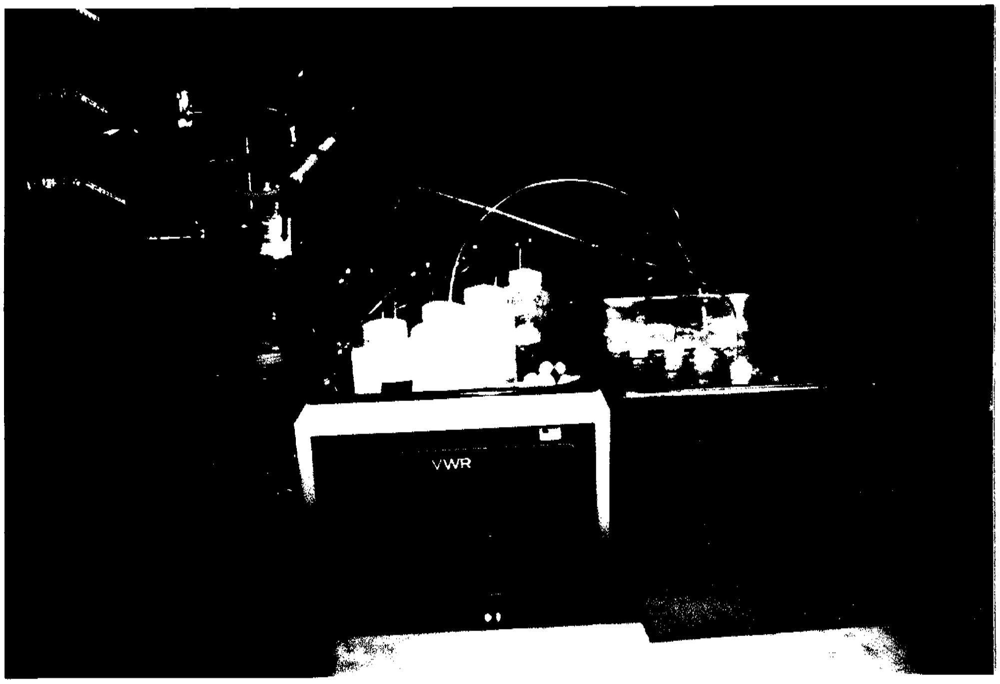


Figure 6. Apparatus, air strip I method

ASSEMBLING THE APPARATUS

Gloves should be worn while assembling the apparatus. An air loop which will be inserted inside the reaction bottle is made of 31" of 1/8" OD Teflon tubing. In order to keep the loop submerged in the acid, the tubing is tied together above the loop with Teflon beading. Each end of the tubing protrudes 3" above the lid. These ends are then wrapped with 2" of Teflon tape and inserted into a 1/4" HDPE tee connector. The tee is later connected to the air supply. About 20 holes should be poked in the air loop using a sewing needle. These holes should be poked near what will be the bottom of the loop. The best pattern of holes is unknown. Several patterns were tried which resulted in equal amounts of clogging. The carryover tubing which goes from the reaction vessel to the capture tube is made of 20" of 1/8" OD Teflon tubing. This should not have any holes poked in it. The carryover tubing is connected to the capture tubing by a 2" piece of 1/8" ID Tygon tubing.

The capture loop which will be inside the capture tube is made from 13" of 1/8" OD Teflon tubing. The loop is assembled by inserting each end of the tubing through the two holes in the lid so that it forms a loop inside the centrifuge (capture) tube when the lid is affixed. The loop should extend to the bottom of the tube. The ends of tubing which protrude from the lid should be about 2" in length. One end of the tubing is crimped over and tied off with a twist tie. The other end will be attached to the carryover tubing. Approximately 10 holes should be poked in the loop of tubing using a sharp sewing needle. This is best done while holding the needle with pliars or a similar gripping device.

PREPARATION

Position the two water baths inside the properly functioning fume hood. The position will be influenced by the fume-hood manufacturer's recommendations for operation. Turn the hot water baths on. Allow about 2 hours for them to reach the necessary temperature of 85-90° C.

Wearing gloves, assemble the apparatus.

Suit up in protective clothing.

Fill the centrifuge tubes with silver nitrate. Fasten the lids loosely so that air pressure may be released. Place these capture tubes in the hot water bath.

Connect the carryover tubing to the capture tubes.

Prepare the ice bath.

Make sure that a container of calcium powder is in the hood work area.

DISSOLUTION PROCESS

1. React the sample.

Place rock powder and a magnetic stirring bar in a 1-liter Teflon bottle.

Add 100 ml conc. nitric acid. Mix so that the sample is thoroughly wetted. Place bottle in cold bath. Allow to settle several minutes.

Add 250 ml cooled HF (approximately -2° C or lower). The HF should be added slowly and carefully so that minimal mixing occurs. Some reaction with very fine rock powder will occur and cannot be avoided.

2. Connect the air system.

Place the lid with an air loop on the reaction bottle and seal tightly. Connect the air supply. Connect the carryover tubing to the capture tube. Flow rate should be adjusted so that moderate bubbling is occuring in both the reaction bottle and the capture tube.

3. Control the reaction.

The Teflon bottle can now be placed in the hot bath and monitored carefully for a violent exothermic reaction. The hood sash should be partially down at this point to add extra facial protection but still allow manual access. The bottle is alternated between the ice bath and the hot water bath in order to control the reaction. With the hot water bath at 80° C, the strong reaction takes approximately 5-7 minutes to initiate. As the sample is warming in the bath, orange bubbles begin to form within the rock powder. This orange hue may be due to iron filings in the sample. As the temperature rises, the bubbles increase in number. When these bubbles begin to erupt from the sample, it is time to quickly place the sample back into the cold bath to dampen the strong reaction. If the strong reaction proceeds, the space above the acid will fill with orange fumes and the acid itself with froth. The ideal reaction is one in which some frothing of the acid occurs, but the acid level in the bottle only rises approximately 1" at most. Should the level rise beyond that point, there is a real danger of overpressuring. If the acid level rises 3" or more the lid will have to be loosened or the carryover tubing removed to release the excess pressure. This will send toxic hot acid vapors and liquid spraying around the hood area.

4. Digest the sample by heating for 6 hours.

Soon after the frothing subsides and the reaction has been controlled beyond the strong reaction, the sample can be placed in the hot bath for the duration of the digestion process and requires only moderate attention. In rock samples processed using air strip method I, the strong reaction did not occur a second time.

At this point the second sample can be reacted using a second set–up. Once the second reaction is controlled, the third sample can be reacted, and so on.

Periodically the sample bottles should be vigorously shaken to re–mix the sample. The air lines must be checked periodically for bubbling rate. Heating continues for approximately 6 hours, or until the sample has been digested. Often, the carryover tubing becomes clogged with silicic acid precipitate as the heating finishes. Adding more HF during the heating process alleviates this clogging problem. This clogging seems to correspond with fairly complete digestion, indicated by the bleached appearance of the sample residue. The silicic acid precipitate is very difficult to clean, however, and must be dissolved with HF once the heating process is completed. The air loop in the reaction bottle may become clogged with sludge. This can occasionally be overcome by increasing the air pressure. At times, the air loop must be replaced during the digestion process.

5. Disassemble and secure.

When the sample is finished heating, disconnect the carryover tubing and the air supply. Remove the reaction bottle from the hot bath, cover, and allow to cool. Remove the capture tube from its bath. Place each capture tube and its tubing in a clean, covered container and store in darkness until ready to process the silver chloride. The initial processing of the silver chloride should be accomplished within a few days. Once the AgCl has been processed through phase 2 of the acid-base purification method, it can be stored for longer periods of time as long as it is stored in darkness.

This completes the digestion process.

Once the acid in the reaction bottle has cooled, the acid can be neutralized and all equipment washed, then rinsed in DI water.

HF DISSOLUTION WORKSHEET (Air Strip Method)

Read sequence vertically.

Date: WED 6-22-88

S1 BEGIN-END	S2 BEGIN-END	S3 BEGIN-END	TASK DESCRIPTION
LMC87-3SH2	LMC86-18SH	LMC86-20SH	Sample numbers
			acquire ice
10:30 AM	11:25 AM - :28	1:05 PM - :12	fill capture cups for s1
10:44 - :47	11:36 - :41	1:17 - :20	prepare ice bath
10:37	11:28	1:12 - :14	transfer S1 to reaction bottle
10:40 - :44	11:32 - :36	1:14 - :17	add HNO_3
67 ml	67 ml	67 ml	amount of HNO_3
10:47 - :51	11:41 - :44	1:20 - :23	add HF
220 ml	220 ml	220 ml	amount of HF
10:56	11:47	1:27	connect air system
:58	11:48; 11:55	1:28; :33; :38	sample to hot bath
11:09	12 NOON - 12:02	1:42	strong reaction, sample to cold bath
11:15	12:07 PM	1:45	reaction stable in hot bath
	11:53	1:32; :36	SAMPLE INTO COLD BATH
	2:45 NEW CARRYOVER TUBING	3:20	
4:20 PM	3:50 PM	4:25 PM	out of bath, cooking finished
			disassemble reaction bottle
			cover and secure capture tubes

AIR STRIP METHOD II

The set-up used in the second generation air strip method is very similar to that of air strip method I. This subsection will concentrate on the modifications rather than the entire set-up.

Additional Equipment For Each Set-up

tightly-fitting reaction bottle lids each containing 5 holes for 1/8" tubing

500 ml polyethylene separatory funnel

separatory funnel lid with a hole drilled for 1/8" tubing

24" of 1/8" OD Teflon tubing

8" of 1/8" OD Teflon tubing

magnetic stirring plate

straight HDPE connector (size for 1/4" ID tubing).

capture solution made with HF

Laboratory Set-Up

The following photograph (Figure 7, page 88) illustrates the laboratory set-up.

Additional Assembly

Two additional holes are needed in the lid of the reaction vessel, one through which to drip the HF acid, and another to equalize pressure between the reaction vessel and the

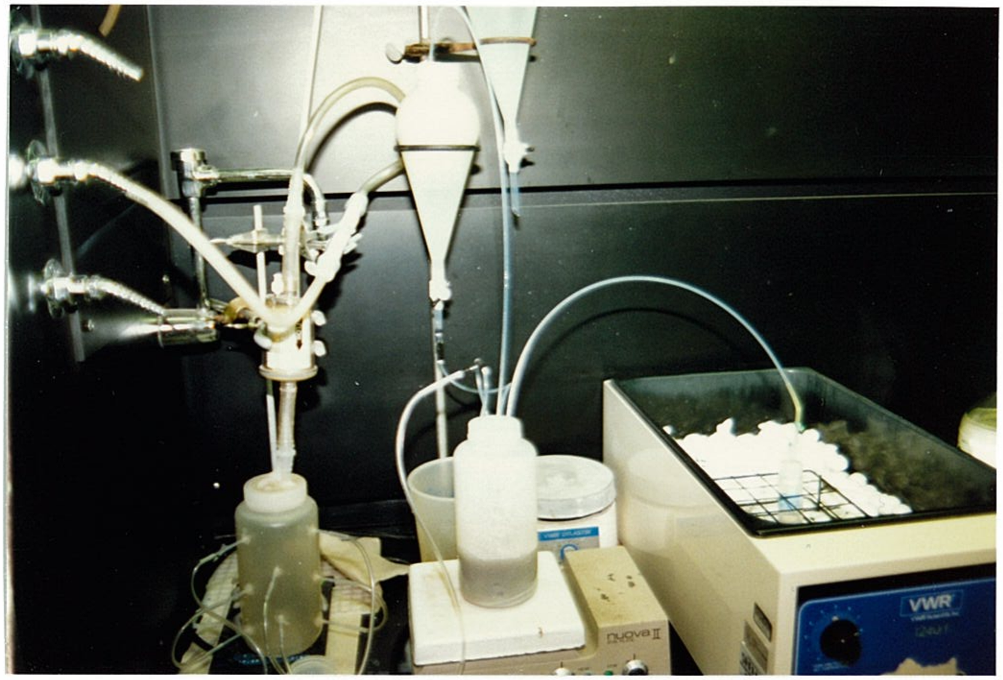


Figure 7. Apparatus, air strip II method

separatory funnel. The 8” length of tubing is connected to the bottom of the separatory funnel containing the HF with a straight HDPE connector (1/4” ID tubing size). The 24” length of tubing connects the top of the separatory funnel to the reaction vessel. The purpose of this pressure equalization is to keep the HF flowing. Without this equalization, the pressure buildup in the reaction vessel causes a stoppage in the flow of HF.

Additional Preparations

Make HF capture solution by combining 5 parts HF, 5 parts deionized water, 1 part conc. nitric acid, and 5 parts 0.1 M silver nitrate. Each capture tube is filled with 25 ml of this HF capture solution.

Place 250 ml of HF in the separatory funnel. For samples significantly smaller than 100 g (such as mineral separates) the amount of HF used would be based on 25 ml for each 10 g of sample.

DISSOLUTION PROCESS

1. Mix the reagents.

Place the rock powder and a magnetic stirring bar in a 1-liter Teflon bottle. Add 100 ml conc. nitric acid and mix so that the sample is thoroughly wetted. Allow to settle several minutes. The reaction bottle is now placed on the magnetic stirring plate. If possible the stir plate is turned on at this point to start mixing the sample. At times the mixture is too thick and the stir bar cannot turn freely.

2. Connect the air system.

Place the lid with the air loop on the reaction bottle and seal tightly. Connect and start the air supply. Connect the carryover tubing as in air strip method I. Connect the HF supply tubing from the separatory funnel to the reaction vessel. Connect the pressure equalization tubing from the separatory funnel to the reaction vessel.

3. Control the reaction.

Start the flow of HF at a rate which allows individual drops to be visible. The sample will begin to react almost immediately. As the temperature of the solution increases due to the exothermic reaction, some faint orange fumes may be emitted. If the stir bar has not been started, it should be started as soon as possible. The reaction must be monitored during the entire drip process. If the reactions gets quite vigorous, the HF drip should be stopped and the reaction allowed to proceed and stabilize. After all of the HF has been added, the reaction vessel should remain on the stir plate for several minutes to ensure that no critical reaction takes place. Once this has been determined, the reaction bottle is placed in the hot bath and heated for the remainder of the six hours.

4. Digest the sample by heating for 6 hours.

From this point on, air strip methods I and II are the same.

ACID - BASE PURIFICATION METHOD

OVERVIEW

Once the chlorine has been extracted, the captured silver chloride is processed according to an acid-base purification method. Phase 1 of this method as described below is specifically for dissolution using the air strip method. Phases 2 and 3 are used for all three feasible extraction techniques developed for carbonate and silicate rocks, and so will be described in significant detail.

EQUIPMENT

deionized water

nitric acid

ammonium hydroxide

barium nitrate

centrifuge

4 standard lids for the centrifuge tubes

4 250 ml beakers

4 pipettes

4 glass centrifuge tubes

aluminum foil

Phase 1: AgCl recovery and concentration

1. Centrifuge capture solution and rinse bubble tubing.

The bubble tubing from the capture tube is placed in a clean 250 ml beaker. This tubing is coated with fine silver chloride which must be recovered by dissolving in base. Put a standard lid (without holes) on the capture tube and then centrifuge to consolidate the silver chloride. While the tube is centrifuging, rinse the tubing with ammonium hydroxide and collect the solution in the beaker. Set this solution aside to combine with the silver chloride in the capture tube at a later time.

2. Pipette and dissolve in base.

Pipette off the supernatant which is in the centrifuge tube, being careful not to remove any of the silver chloride in the bottom of the tube. The inside of the capture tube is also coated with silver chloride. To recover this silver chloride, add 1–2 ml ammonium hydroxide to the capture tube. Seal tightly and rinse the inside by shaking.

3. Combine the tube and tubing portions of the sample; transfer to a glass test tube.

Combine the basic solutions from the capture tube and the beaker into a glass centrifuge tube.

4. Remove silicic acid if necessary.

If silicic acid is present an additional centrifuge step is necessary to remove this material. Centrifuge and decant the clear, basic solution into a clean centrifuge tube. The silicic acid adheres well to the bottom of the tube thus decanting is preferable to pipetting. This decanted solution contains the silver chloride and is ready for the subsequent processing steps.

Phase 2: Pre-$BaNO_3$ Preparations

5. Acidify to re-precipitate the silver chloride.

Nitric acid is added to this basic solution to re-precipitate the silver chloride. Centrifuge to spin down the silver chloride and then decant.

6. Dissolve in base.

Add 3 ml conc. ammonium hydroxide. It is at this point that the samples can be stored in darkness until the next phase can be started.

Phase 3: Removal of sulfur

7. Add barium nitrate.

Using a pipette, add 1 ml barium nitrate. Add the barium nitrate carefully as sputtering does occur. The solution is now allowed to sit 8 hours or overnight to allow the formation of barium sulfate. Not all samples will show a visible precipitate at this point, but pipetting is still preferable to decanting because contamination can be minimized. This step removes sulfur which is a major contaminant in the ^{36}Cl analysis.

8. Remove barium sulfate; precipitate the silver chloride.

The sample is centrifuged and the solution pipetted into a clean tube leaving behind the barium sulfate. Acidify the solution to precipitate silver chloride. Centrifuge and decant the acid solution. Rinse the silver chloride with DI water. Centrifuge and decant the water.

9. Dry.

The centrifuge tube is now wrapped in foil to prevent exposure to light and placed in the oven to dry overnight.

AgCl PROCESSING WORKSHEET (Acid–Base Purification Method)

Read sequence horizontally.

Date: THURS 6-23-88

S1 BEGIN–END	S2 BEGIN–END	S3 BEGIN–END	TASK DESCRIPTION
LMC87-3SH2	LMC86-18SH	LMC86-20SH	Sample numbers
10:57AM	11:00	11:02 - :05	put tubing into beakers
11:05 - :14			centrifuge 3 tubes
11:16 - :23	11:23 - :29	11:29 - :35	pipette / tubes
			DI rinse pipettes
11:10AM - :14	11:44 - :49	11:49 - :54	rinse tubing with basic solution
11:55 - 12N	12N - 12:03	12:03PM - :07	transfer basic solution to glass
12:09 - :18			centrifuge 3 to remove F–Si acid
12:11 - :15			DI RINSE PIPETTES
12:18 - :23			transfer solution to another tube ALL 3
12:23 - :30			acidify ALL 3
		LOW AgCl	
12:30 - :42			centrifuge ALL 3
12:42 - :46			decant acid ALL 3
12:46 - 12:51			add 2 ml base (NH_4OH) ALL 3
12:51 - :56	12:56 - 1PM	1:02PM - :06	add 1 ml $BaNO_3$
			let stand 8 hours

POST-BaNO$_3$ WORKSHEET (Acid-Base Purification Method)

Read sequence horizontally. Date: MON 7-11-88

S1	S2 BEGIN-END	S3	S4	TASK DESCRIPTION	S5	S6
LMC87-3SH2	LMC86-18SH	LMC86-20SH		Sample numbers	SC86 18MB	LMC86-16SH
	9:20AM - :29			centrifuge 3 \ 2 samples	4:10 - :20 PM	
S1 & S2 CONTAIN SOME SMALL WHITE CRYSTALS						
S3 CONTAINS NO CRYSTALS						
9:30 - :38	9:38 - :41	9:41 - :44		pipette into clean test tube	4:20 - :26	
	9:44 - :52			acidify	4:26 - :30	
	9:53 - 10:02 AM			centrifuge	4:30 - :40	
18SH APPEARS TO BE VERY LOW IN AgCl, SO IT WILL						
BE WRAPPED IN FOIL AND SET ASIDE TO TREAT						
LATER WITH CARRIER						
10:02		10:05		decant acid solution	4:40	4:42
10:05		10:09		rinse AgCl with DI water	4:42	4:45
	10:09 - 10:18			centrifuge		
				INTERRUPTED BY VWR SALESMAN FROM		
				4:45 - 5:15 PM		
10:18		10:20		decant water	5:15	
10:21		10:22		wrap test tube in foil	5:17	
10:24		10:24 AM		put in oven	5:20 PM	
				Dry overnight		

WEIGHING AND PACKING DRIED SAMPLES

For analysis on the TAMS the silver chloride is loaded into small tantalum cylinders (5 mm high and 6 mm diameter) which have a small hole drilled in them. Holes are drilled with different dimensions (please refer to the subsection describing the initial preparations, page 69) to accomodate samples of different sizes, since the sample should completely fill the hole. Using a metal spatula, the dried silver chloride sample is scraped from the bottom of the glass centrifuge tube to loosen it (Figure 8). Based on the quantity of scraped material an appropriate size holder is chosen. The holder is weighed to the nearest tenth of a milligram. The holder is then secured in a 4" diameter aluminum disk. The silver chloride is carefully transferred from the tube to the tantalum sample holder using the spatula. A tamping device such as a cleaned drill bit, wire, or paper clip is used to compact the silver chloride into the hole. If the sample is too small to completely fill the hole, the University of Rochester recommends mixing the sample with silver bromide or gold powder that has little or no sulfur content. Tweezers are needed to lift the tantalum holder out of the aluminum disk. The filled tantalum holder is then weighed and the sample weight can be derived. Sample sizes usually range from 2–7 mg, with 4 mg being an average sample weight.

The packed tantalum holder is then placed upside-down in a v-vial. A small tissue is placed on top as cushioning and the vial closed. It is then wrapped in aluminum foil to

Figure 8. Scraping the dried AgCl from the centrifuge tube

ensure darkness, and labeled. Any extra sample should be placed in a separate vial, labeled, and wrapped in aluminum foil.

As with other processes, gloves should be worn at all times.

Before the next sample can be packed, every tool must be carefully cleaned. The disk is washed with dilute NH_4OH to dissolve any silver chloride remnants from the preceding sample. It is then rinsed with DI water and blown dry with compressed air. After it has air-dried for several additional minutes it can be used for the next sample. The spatula, the tamping device, and the tweezers must all be cleaned between samples also. The same method of washing with dilute NH_4OH and rinsing with DI water is necessary. If a watch glass is used to carry the sample holder to the scale for weighing, it should be rinsed with DI water before being used again.

PACKING AND WEIGHING WORKSHEET (Read sequence vertically)

S1 BEGIN-END	S2 BEGIN-END	S3 BEGIN-END	TASK DESCRIPTION
			DATE WED 7-27-88
LMC87-7TI	BLANK A	BC86-7TE	Sample numbers
10:05 PM			clean area
10:10	10:57PM 7/28 AM	11:25 PM	prepare to pack samples
10:16	TOO WET, BACK INTO ↓	11:35	scrape AgCl from bottom of test tube
10:20	OVEN 11:04	11:41	select appropriate Ta holder, make labels
10:27	11:05 AM	11:43	weigh sample holder
10:28 - :44	11:06 - :23	11:45 - 12:02	pack sample holder
10:45	11:25	12:03 AM	re-weigh filled sample holder
10:47		12:05	final preparation for storage
	11:30		store extra AgCl, separate dark vial
10:51 - :56	11:34 AM - :40	12:08 - :15	clean Al disk
	11:11 PM - 11:16		clean ~~3~~ 2 sets of utensils
			DATE THURS 7-28-88
LMC86-4TI	LMC86-11TA		Sample numbers
			clean area
12:17 AM	1:40 PM		prepare to pack samples
TOO WET, INTO → 11:50AM	1:42		scrape AgCl from bottom of test tube
OVEN 11:53	1:45		select appropriate Ta holder, make labels
11:54	1:46 break		weigh sample holder
11:56 - 12:10	1:55 - 2 PM		pack sample holder
12:11 PM	2:01		re-weigh filled sample holder
12:13	2:02 - :05		final preparation for storage
[illegible]			store extra AgCl, separate dark vial
12:17			clean Al disk
12:24 - :30			clean 3 sets of utensils

SAMPLE WEIGHING LOG

Sample Number	Tantalum Holder No.	Empty Holder Wt. g	Sample & Holder Wt. g	AgCl Sample Wt. mg	Notations	Hole Size mm	Date
BC86-12TA	1712	2.6096	2.6161	6.5	-1/2 filled	1.6x1.0	6/10
BC86-13TA	1705	2.6086	2.6155	6.9		1.6x1.0	6/12
BC86-15TA	1637	2.6104	2.6134	3.0	ext vial, 1.0mg	1.6x1.0	6/14
LMC86- 1TI	1641	2.6020	2.6065	4.5	ext vial, 5.7mg	1.6x1.0	6/14
BC86- 6TE	1707	2.5951	2.6002	5.1		1.6x1.0	6/14
BC86-10TE	1711	2.6129	2.6189	6.0	ext vial, 2.1mg	1.6x1.0	6/19

VI. WORKSHEETS

OVERVIEW

During the development of the laboratory procedures it became necessary to design a number of worksheets. Some of these worksheets are helpful in the actual laboratory processes, whereas others are used to record more general information or to keep track of the sample processing progress.

Some worksheets that had been filled out with representative values were included in a prior section. The first part of this section has any sample worksheets which were not presented previously. These sample worksheets have been filled out with representative values to illustrate how to complete the worksheets. The second part of this section includes blank copies of all of the worksheets designed during this project. They are available for future use.

A list of the available worksheets follows.

Worksheets Included In This Section

*Air Strip Dissolution / Cooking Process

*Acid-Base Purification Method - AgCl Process

*Acid-Base Purification Method - Post-BaNO3 Steps

*Packing and Weighing Samples

*Sample Weighing Log

Status of Samples Collected

Sample Inventory Detail

Sample Inventory Summary

Sample Number / Tantalum Holder Cross-Reference

Tantalum Holder / Sample Number Cross-Reference

Raw ^{36}Cl Data

*Blank copies only. Sample copies included in "Laboratory Procedures."

STATUS OF SAMPLES COLLECTED

Because of numerous scheduling, laboratory, and coordination problems, a number of samples were collected that do not have the complete data required for an age calculation. In order to calculate an exposure age, there must be ^{36}Cl analysis and geochemical data - major element, chlorine, and REE. Every sample that was collected at the moraines of Bloody Canyon is listed below, with a ✓ to indicate the stages that have been completed. If more than two stages have been completed, a ☐ indicates the missing stage(s) which prevent(s) an exposure age calculation. Those samples with sufficient information for age calculations are indicated by boldfaced sample numbers.

SAMPLE NUMBER	CRUSHED	LEACHED	HF DIGESTION	^{36}Cl ANALYSIS	MAJOR ELEMENT	Cl XRF	REE ICP
BC86- 2TI	✓	✓	✓	☐	✓	✓	✓
BC86- 3TI	✓	✓	✓	✓	✓	✓	✓
BC86- 4TI	✓	✓	✓	☐	✓	✓	✓
BC86- 5TI	✓	✓	✓	✓	✓	✓	✓
BC86- 6TE	✓	✓	✓	✓	✓	✓	✓
BC86- 7TE	✓	✓	✓	☐	✓	✓	✓
BC86- 8TE	✓	✓	✓	✓	✓	✓	✓
BC86- 9TE	✓	✓	✓	✓	✓	✓	✓
BC86-10TE	✓	✓	✓	☐	✓	✓	✓
BC86-11TE	✓	✓	✓	✓	✓	✓	✓
BC86-12TA	✓	✓	✓	✓	✓	✓	✓
BC86-13TA	✓	✓	✓	✓	✓	✓	✓
BC86-14TA	✓	✓	✓	✓	✓	✓	✓
BC86-15TA	✓	✓	✓	✓	✓	✓	✓
BC86-16TA	✓	✓	✓	✓	✓	✓	✓

STATUS OF SAMPLES COLLECTED (cont)

SAMPLE NUMBER	CRUSHED	LEACHED	HF DIGESTION	^{36}Cl ANALYSIS	MAJOR ELEMENT	Cl XRF	REE ICP
SC86-17MB	✓	✓	✓	✓	✓	✓	✓
SC86-18BMB	✓	✓	✓	✓	✓	✓	✓
SC86-19MB	✓	✓	✓	✓	✓	✓	✓
SC86-20MB	✓	✓	✓	✓	✓	✓	✓
SC86-21MB	✓	✓	✓	✓	✓	✓	✓
BC87- 1TA	✓	✓	✓	✓	✓	✓	✓
BC87- 2TA	✓	✓	✓	✓	✓	✓	✓
BC87- 3TA	✓	✓	✓	✓	✓	✓	✓
BC87- 4TA	✓	✓	✓	✓	✓	✓	✓
BC87- 5TA	✓	✓	✓	✓	✓	✓	✓
SG86- 1SH							
SG86- 2SH							
SG86- 3SH							
SG86- 4SH	✓	✓	☐	☐	✓	✓	✓
SG86- 5SH							
SG86- 6SH							
LMC86- 1TI	✓	✓	✓	✓	☐	☐	☐
LMC86- 2TI	✓	✓	✓	☐	✓	✓	✓
LMC86- 3TI	✓	✓	✓	☐	✓	✓	✓
LMC86- 4TI	✓	✓	✓	✓	✓	✓	✓
LMC86- 5TI	✓	✓	✓	☐	✓	✓	✓
LMC86- 6TI	✓	✓	✓	☐	☐	☐	☐

STATUS OF SAMPLES COLLECTED (cont)

SAMPLE NUMBER	CRUSHED	LEACHED	HF DIGESTION	^{36}Cl ANALYSIS	MAJOR ELEMENT	Cl XRF	REE ICP
LMC86- 7TI	✓	✓	☐	☐	✓	☐	☐
LMC86- 8TI	✓	✓	✓	☐	☐	☐	☐
LMC86- 9TI	✓	✓	✓	☐	✓	✓	☐
LMC86-10TI	✓	✓	✓	✓	✓	✓	✓
LMC86-11TA	✓	✓	☐	☐	✓	✓	✓
LMC86-12TA	✓	✓	☐	☐	✓	✓	✓
LMC86-13TA	✓	✓	✓	☐	☐	☐	☐
LMC86-14TA	✓	✓	✓	☐	✓	✓	✓
LMC86-15TA	✓	✓	✓	✓	☐	☐	☐
LMC86-16SH	✓	✓	✓	☐	☐	☐	☐
LMC86-17SH	✓	✓	✓	☐	☐	☐	☐
LMC86-18SH	✓	✓	✓	☐	✓	✓	✓
LMC86-19SH							
LMC86-20SH	✓	✓	✓	☐	✓	✓	✓
LMC87- 1SH2	✓	✓	✓	☐	✓	✓	✓
LMC87- 2SH2	✓	✓	✓	☐	✓	✓	✓
LMC87- 3SH2	✓	✓	✓	☐	✓	✓	✓
LMC87- 4SH2	✓	✓	☐	☐	✓	✓	✓
LMC87- 1NG	✓	✓	☐	☐	✓	✓	✓
LMC87- 2NG	✓	✓	☐	☐	✓	✓	☐
LMC87- 3NG	✓	✓	☐	☐	✓	✓	☐
LMC87- 1ML	✓	✓	☐	☐	☐	☐	✓

STATUS OF SAMPLES COLLECTED (cont)

SAMPLE NUMBER	CRUSHED	LEACHED	HF DIGESTION	^{36}Cl ANALYSIS	MAJOR ELEMENT	Cl XRF	REE ICP
LMC87- 2ML	✓	✓	☐	☐	☐	☐	✓
LMC87- 3ML	✓	✓	☐	☐	☐	☐	✓
LMC87- 1SM	✓	✓	☐	☐	✓	✓	☐
LMC87- 2SM	✓	✓	☐	☐	✓	✓	☐
LMC87- 3SM	✓	✓	☐	☐	✓	✓	☐
LMC87- 1TM1	✓	✓					
LMC87- 2TM1	✓	✓					
LMC87- 3TM1	✓	✓					
LMC87- 1TM2	✓	✓	☐	☐	✓	☐	✓
LMC87- 2TM2	✓	✓	☐	☐	✓	☐	✓
LMC87- 3TM2	✓	✓	☐	☐	✓	☐	✓
LMC87- 1X	✓	✓	☐	☐	✓	✓	✓
LMC87- 1Y	✓	✓	☐	☐	✓	✓	✓

SAMPLE INVENTORY DETAIL - PAGE______

LEACHED

DIGESTED

Date # Dte # Dte # Dte
Date # Dte # Dte # Dte
Date # Dte # Dte # Dte

AgCl

Phase 1: AgCl recovery and concentration, then stored in base

LMC87 # 2ML Date 7-16 # Dte # Dte # Dte
Date # Dte # Dte # Dte
Date # Dte # Dte # Dte

Phase 2: Pre-$BaNO_3$ Acidify, then add base

Date # Dte # Dte # Dte
Date # Dte # Dte # Dte
Date # Dte # Dte # Dte

$BaNO_3$ ADDED TO SAMPLE

LMC86 # 16SH Date 7-10 # SC86 18MB Dte 7-10 # Dte # Dte
" # 17SH Date 7-10 # LMC87 1SH2 Dte 7-11 # LMC4TI Dte 7-17 # Dte
" # 14TA Date 7-10 # 2SH2 Dte 7-11 # BC7TE Dte 7-18 # WIH-2 Dte 7-19

POST $BaNO_3$ ACIDIFY

LMC87 # 1SH2 Date 7-16 # Dte # Dte # Dte
2SH2 Date 7-16 # Dte # Dte # Dte
Date # Dte # Dte # Dte

IN OVEN DRYING

LMC87 # 3SH2 Date 7-11 # SC18MB Dte 7-11 # 1SH2 Dte 7-18 # Dte
LMC86 # 20SH Date 7-11 # 16SH Dte 7-18 # 2SH2 Dte 7-18 # Dte
17SH Date 7-18 # LM14TA Dte 7-18 # WIH-2 Dte 7-20 # Dte

DRIED, READY TO WEIGH AND PACK

3SH2 Date 7-12 # 16SH Dte 7-19 # Dte # Dte
20SH Date 7-12 # LMC4T2 Dte 7-26 # Dte # Dte
Date # 2SH2 Dte 7-19 # Dte # Dte

SAMPLE INVENTORY SUMMARY - COVERING:

DATE

LEACHED

DIGESTED

AgCl

Phase 1:

Phase 2:

$BaNO_3$ ADDED

POST $BaNO_3$

IN OVEN

DRIED

TOTALS:

LEACHED

IN PROGRESS

PACKED

READY FOR Cl-36 ANALYSIS

SAMPLE NUMBER / TANTALUM HOLDER CROSS-REFERENCE

SAMPLE NUMBER	TANTALUM HOLDER NO.	SAMPLE WEIGHT-mg
BC86- 6TE	1707	5.1
BC86-10TE	1711	6.0
BC86-12TA	1712	6.5
BC86-13TA	1705	6.9
BC86-14TA	1645	2.0
BC86-15TA	1637	3.0
SC86-17MB	1708	4.1
SC86-18BMB	1703	3.2
BC87- 1TA	1646	2.2
LMC86- 1TI	1641	4.5
LMC86- 2TI	1701	6.1
LMC86- 5TI	1647	1.9
LMC86- 8TI	1710	4.9
LMC86-13TA	1638	2.2
LMC86-14TA	999	1.8
LMC86-15TA	1648	1.7
LMC86-16SH	993	2.1
LMC86-17SH	1214	4.6
LMC86-20SH	992	1.2
LMC87- 1SH2	996	1.3
LMC87- 2SH2	1659	2.6
LMC87- 3SH2	995	1.9

TANTALUM HOLDER / SAMPLE NUMBER CROSS-REFERENCE

TANTALUM HOLDER NO.	SAMPLE NUMBER	SAMPLE WEIGHT-mg
992	LMC86-20SH	1.2
993	LMC86-16SH	2.1
995	LMC87- 3SH2	1.9
996	LMC87- 1SH2	1.3
999	LMC86-14TA	1.8
1214	LMC86-17SH	4.6
1637	BC86-15TA	3.0
1638	LMC86-13TA	2.2
1641	LMC86- 1TI	4.5
1645	BC86-14TA	2.0
1646	BC87- 1TA	2.2
1647	LMC86- 5TI	1.9
1648	LMC86-15TA	1.7
1659	LMC87- 2SH2	2.6
1701	LMC86- 2TI	6.1
1703	SC86-18BMB	3.2
1705	BC86-13TA	6.9
1707	BC86- 6TE	5.1
1708	SC86-17MB	4.1
1710	LMC86- 8TI	4.9
1711	BC86-10TE	6.0
1712	BC86-12TA	6.5

RAW ^{36}Cl DATA

SAMPLE NUMBER	DATE OF ^{36}Cl ANALYSIS	^{36}Cl /10^{15} Cl
BC86- 1TI	DEC, 1987	59± 4
BC86- 3TI	DEC, 1987	536± 39
BC86- 5TI	DEC, 1987	443± 18
BC86- 6TE	JULY, 1988	1350± 96
BC86- 8TE	DEC, 1987	697± 38
BC86- 9TE	DEC, 1987	867± 32
BC86-11TE	DEC, 1987	1923± 60
BC86-12TA	JULY, 1988	3155± 238
BC86-13TA	JULY, 1988	4313± 246
BC86-14TA	JULY, 1988	5736± 256
BC86-16TA	DEC, 1987	2793± 84
SC86-18BMB	JULY, 1988	2001± 153
SC86-19MB	DEC, 1987	1906± 77
SC86-20MB	DEC, 1987	5365± 182
SC86-21MB	Dec, 1987	7069± 295
BC87- 1TA	JULY, 1988	1638± 211
BC87- 2TA	DEC, 1987	3763± 133
BC87- 3TA	DEC, 1987	1308± 87
BC87- 4TA	DEC, 1987	1460± 180
BC87- 5TA	DEC, 1987	1698± 94

HF DISSOLUTION WORKSHEET (Air Strip Method)

Read sequence vertically. Date:__________

S1 BEGIN-END	S2 BEGIN-END	S3 BEGIN-END	TASK DESCRIPTION
			Sample numbers
			acquire ice
			fill capture cups for s1
			prepare ice bath
			transfer S1 to reaction bottle
			add HNO_3
			amount of HNO_3
			add HF
			amount of HF
			connect air system
			sample to hot bath
			strong reaction, sample to cold bath
			reaction stable in hot bath
			out of bath, cooking finished
			disassemble reaction bottle
			cover and secure capture tubes

AgCl PROCESSING WORKSHEET (Acid-Base Purification Method)

Read sequence horizontally. Date:__________

S1 BEGIN-END	S2 BEGIN-END	S3 BEGIN-END	TASK DESCRIPTION
			Sample numbers
			put tubing into beakers
			centrifuge tubes
			pipette tubes
			DI rinse pipettes
			rinse tubing with basic solution
			transfer basic solution to glass
			centrifuge to remove F-Si acid
			transfer solution to another tube
			acidify
			centrifuge
			decant acid
			add 2 ml base (NH_4OH)
			add 1 ml $BaNO_3$
			let stand 8 hours

POST-BaNO_3 WORKSHEET (Acid-Base Purification Method)

Read sequence horizontally. Date:

S1	S2	S3	S4		S5	S6
	BEGIN-END			TASK DESCRIPTION		
				Sample numbers		
				centrifuge samples		
				pipette into clean test tube		
				acidify		
				centrifuge		
				decant acid solution		
				rinse AgCl with DI water		
				centrifuge		
				decant water		
				wrap test tube in foil		
				put in oven		
				Dry overnight		

PACKING AND WEIGHING WORKSHEET (Read sequence vertically)

S1 BEGIN-END	S2 BEGIN-END	S3 BEGIN-END	TASK DESCRIPTION
			DATE
			Sample numbers
			clean area
			prepare to pack samples
			scrape AgCl from bottom of test tube
			select appropriate Ta holder, make labels
			weigh sample holder
			pack sample holder
			re-weigh filled sample holder
			final preparation for storage
			store extra AgCl, separate dark vial
			clean Al disk
			clean 3 sets of utensils
			DATE
			Sample numbers
			clean area
			prepare to pack samples
			scrape AgCl from bottom of test tube
			select appropriate Ta holder, make labels
			weigh sample holder
			pack sample holder
			re-weigh filled sample holder
			final preparation for storage
			store extra AgCl, separate dark vial
			clean Al disk
			clean 3 sets of utensils

SAMPLE WEIGHING LOG

Sample Number	Tantalum Holder No.	Empty Holder Wt.	Sample & Holder Wt.	AgCl Sample Wt.	Notations	Hole Size	Date
		g	g	mg		mm	

STATUS OF SAMPLES COLLECTED

SAMPLE NUMBER	CRUSHED	LEACHED	HF DIGESTION	^{36}Cl ANALYSIS	MAJOR ELEMENT	Cl XRF	REE ICP

SAMPLE INVENTORY DETAIL - PAGE______

LEACHED

_______ _______ _______ _______ _______ _______ _______ _______ _______ _______
_______ _______ _______ _______ _______ _______ _______ _______ _______ _______
_______ _______ _______ _______ _______ _______ _______ _______ _______ _______

DIGESTED

#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______
#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______
#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______

$AgCl$

Phase 1: $AgCl$ recovery and concentration, then stored in base

#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______
#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______
#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______

Phase 2: Pre-$BaNO_3$ Acidify, then add base

#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______
#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______
#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______

$BaNO_3$ ADDED TO SAMPLE

#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______
#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______
#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______

POST $BaNO_3$ ACIDIFY

#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______
#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______
#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______

IN OVEN DRYING

#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______
#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______
#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______

DRIED, READY TO WEIGH AND PACK

#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______
#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______
#_______Date_______#_______Dte_______#_______Dte_______#_______Dte_______

SAMPLE INVENTORY SUMMARY – COVERING:____________________

DATE ____ ____ ____ ____ ____ ____ ____ ____

LEACHED ____ ____ ____ ____ ____ ____ ____ ____

DIGESTED ____ ____ ____ ____ ____ ____ ____ ____

AgCl

Phase 1: ____ ____ ____ ____ ____ ____ ____ ____

Phase 2: ____ ____ ____ ____ ____ ____ ____ ____

$BaNO_3$ ADDED ____ ____ ____ ____ ____ ____ ____ ____

POST $BaNO_3$ ____ ____ ____ ____ ____ ____ ____ ____

IN OVEN ____ ____ ____ ____ ____ ____ ____ ____

DRIED ____ ____ ____ ____ ____ ____ ____ ____

TOTALS:

LEACHED____

IN PROGRESS____

PACKED ____

READY FOR Cl-36 ANALYSIS

________ ________ ________ ________ ________ ________ ________ ________ ________ ________

________ ________ ________ ________ ________ ________ ________ ________ ________ ________

________ ________ ________ ________ ________ ________ ________ ________ ________ ________

________ ________ ________ ________ ________ ________ ________ ________ ________ ________

________ ________ ________ ________ ________ ________ ________ ________ ________ ________

________ ________ ________ ________ ________ ________ ________ ________ ________ ________

SAMPLE NUMBER / TANTALUM HOLDER CROSS-REFERENCE

SAMPLE NUMBER	TANTALUM HOLDER NO.	SAMPLE WEIGHT-mg

TANTALUM HOLDER / SAMPLE NUMBER

CROSS-REFERENCE

TANTALUM HOLDER NO.	SAMPLE NUMBER	SAMPLE WEIGHT-mg

RAW ^{36}Cl DATA

SAMPLE NUMBER	DATE OF ^{36}Cl ANALYSIS	^{36}Cl /10^{15} Cl

VII. SAMPLE DESCRIPTIONS

OVERVIEW

Six samples were collected at Meteor Crater in the summer of 1987. The sample numbers assigned to these carbonate rocks were MC-1 through MC-6.

Eighty samples were collected from moraines at Bloody Canyon, Little McGee Creek, and Sawmill Canyon in 1986 and 1987. The sample numbers assigned indicate the location of the moraine sampled (Bloody Canyon samples begin with the prefix ‘BC’, Little McGee Creek samples are designated ‘LMC’, Sawmill Canyon sample numbers start with ‘SC’, Sherwin Grade begin with ‘SG’) followed by the year sampled. Samples are then numbered sequentially, with a suffix to indicate the specific glaciation as mapped by Sharp and Birman (1963) at Bloody/Sawmill Canyons and Bateman (1965) at Little McGee Creek. These glaciations are: Tioga (TI), Tenaya (TE), Tahoe (TA), Mono Basin (MB), and Sherwin (SH).

At the time of sampling a general petrographic name was assigned to each sample. Various notations were made as to degree of weathering, location, and significant observations. The samples were oriented, and most boulders were sketched and/or photographed.

There are complete field notes for all samples collected at Bloody Canyon, Sawmill Canyon, Little McGee Creek, and Sherwin Grade in 1986. In addition, field notes for all samples collected in 1986 and 1987 for which ^{36}Cl data is available are presented. Field notes for all other samples collected in 1986 and 1987 are available from Fred Phillips or myself but are not included in this report. Sketches of all and photographs of most of the sample sites are also available upon request.

METEOR CRATER

SAMPLES MC-1 TO MC-6

These samples were collected on July 1, 1987 with Dave Roddy of the USGS in Flagstaff, AZ and Fred Phillips of New Mexico Institute of Mining and Technology in Socorro, NM. MC-6 was collected as a backup sample and was not analyzed.

MC-1

Location: N66W to visitor center; due S of major boulder on east rim of crater.

Petrographic name: Kaibab Formation (dolomite)

Boulder size: about 2.5 m high

MC-2

Location: top of largest boulder on east side

Petrographic name: Kaibab Formation (dolomite)

Boulder size: 9+ m high

MC-3

Location: S80E from crater, 250 m from rim crest

Petrographic name: Kaibab Formation (dolomite)

Boulder size: 1.3 m high

Comments: outlier boulder of Kaibab; sample is a single large piece; boulder is partly covered with shrub growth

MC-4

Location: S45E from crater, 300 m from rim crest; farther SE outlier of Kaibab, right at a fence corner

Petrographic name: Kaibab Formation (dolomite)

Boulder size: 1.3 m high

MC-5

Location: west side of crater, boulder is -35 m west of rim proper

Petrographic name: Kaibab Formation (dolomite)

Boulder size: 12 m high

Comments: known to USGS staff as 'tall pinnacle rock,' this boulder tilts toward the rim (eastward)

MC-6

Location: adjacent to west rim, 40 m NE of pinnacle rock (MC-5)

Petrographic name: Kaibab Formation (dolomite)

Condition: more pitted and weathered than any other sample

Boulder size: 1.5-2.0 m high

Comments: back-up sample

BLOODY CANYON

SAMPLES BC86-1TI TO BC86-5TI

All of the samples on this moraine were taken from the crest of the ridge. There was some sage cover but few trees.

BC86-1TI

Petrographic name: granodiorite

Condition: fresh

Boulder size: 1.4 m high, 1.2 m wide, 1.2 m deep

Comments: relict glacial polish and striae on this surface

BC86-2TI

Location: 15 m up nose (SW)

Petrographic name: granodiorite, coarse-grained

Condition: fractures with iron stains

Boulder size: 1.0 m high, 1.2 m wide, 1.0 m deep

BC86-3TI

Location: 90 m SW from BC86-2TI

Petrographic name: granodiorite

Condition: minor alteration, slightly crumbly

Boulder size: 1.0 m high at sampling site, 1.8 m wide, 1.0 m deep

BC86-4TI

Location: 6 m NW of BC86-3TI

Petrographic name: granodiorite, fine-grained; biotite - poor

Condition: friable - some weathering?

Boulder size: 0.8 m high, 1.0 m wide, 0.6 m deep

Comments: glacial polish

BC86-5TI

Location: 60 m S30W from BC86-4TI

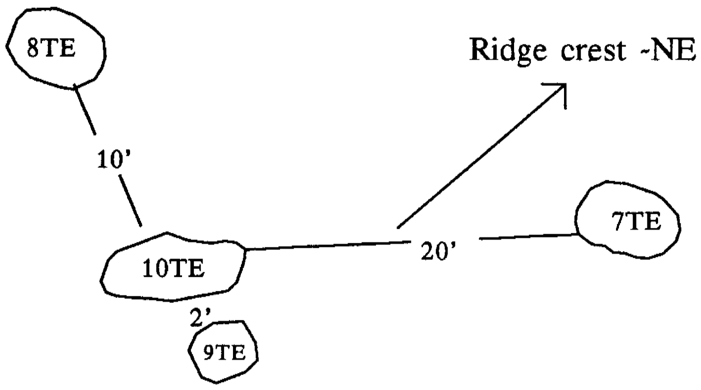
Petrographic name: granodiorite, biotite - rich

Boulder size: 0.6 m high, 1.0 m wide, 0.6 m deep

Comments: taken from edge of boulder with a vertical face

SAMPLES BC86-6TE TO BC86-10TE

This Tenaya moraine is south of the Tioga moraine sampled and at an elevation of about 2400 m. The ridge crest trends approximately northeast. The sample pattern has the following relationships:



BC86-6TE

Location: adjacent to burned tree

Petrographic name: granodiorite

Condition: fresh, massive

Boulder size: 1.1 m high, 1.5 m wide, 1.0 m deep; sample site at 1.0 m

Comments: remains of polished surface protrudes 1-2 cm above most of rock surface, indicating boulder erosion or exfoliation

BC86-7TE

Location: 60 m NE of BC86-6TE

Petrographic name: granodiorite

Condition: weakly weathered; moderate Fe-staining

Boulder size: 1.2 m high, 1.0 m wide, 1.5 m deep

Comments: moderate forest; boulder selected for low Fe-staining

BC86-8TE

Location: 9 m N of BC86-7TE

Petrographic name: medium-grained granodiorite with some coarse (1.5 cm) feldspars

Condition: moderately weathered

Boulder size: 1.0 m high, 1.2 m wide, 0.8 m deep

BC86-9TE

Location:	3.6 m SW of BC86-8TE
Petrographic name:	granodiorite, biotite poor. Some aplite and quartz veining near sample site
Condition:	fresh
Boulder size:	1.0 m high, 0.6 m wide, 1.0 m deep
Comments:	'Ts' marking top surface but dips 40° to SW

BC86-10TE

Location:	3 m SW of BC86-8TE
Petrographic name:	granodiorite
Condition:	fresh
Boulder size:	0.6 m high, 1.2 m wide, 1.0 m deep
Comments:	sample taken from top of a tabular, flat boulder, near horizontal surface, 'good' neutron flux

BC86-11TE

Location: 75 m NE of BC86-7TE

Petrographic name: fine-grained granite, pinkish

Condition: weathering rind uniformly 4 mm thick, well-developed; light gray rind contrasts with pink rock

Boulder size: 1.0 m high, 1.2 m wide, 0.6 m deep

Comments: site currently at 0.6 m; sample believed to be at top once (polish)
possible Burke and Birkeland soil pit 2.4 m NE

SAMPLE BC86-12TA

This Tahoe sample was taken from a low ridge about 300 m south of Walker Creek. The elevation at the sample site was approximately 7440 ft.

BC86-12TA

Petrographic name: amphibole - rich, probably a metamorphic rock

Condition: moderately weathered

Boulder size: 2.1 m high, 1.5 m wide, 1.8 m deep

Comments: large boulder. Sample at 1.5 m high.
Boulder has slumped to west but site seems to be original top.
Rock very fractured.

SAMPLES BC86-13TA TO BC86-15TA

These Tahoe samples were taken south of the ridgecrest, and so exposure may not be as long. The boulders sampled were quite large and somewhat weathered.

BC86-13TA

Location: 30 m due S of BC86-12TA

Petrographic name: medium-grained granite

Condition: weakly weathered

Boulder size: 2.7 m high, 1.8 m wide, 1.8 m deep

Comments: thin pieces sampled. Sloped face dips 35° to SW.
Sample site 2.1 m high from ground directly underneath.

BC86-14TA

Location: 30 m E of BC86-13TA

Petrographic name: granodiorite, coarse to medium-grained

Condition: fresh

Boulder size: 2.0 m high, 2.4 m wide, 1.8 m deep

Comments: sample site 1.8 m high

BC86-15TA

Location: 150 m E of BC86-14TA, 25-30 m S of ridgecrest

Petrographic name: coarse to medium-grained granodiorite

Condition: moderately to strongly altered but upper 4 cm of sample are weak to moderately weathered

Boulder size: 3 m high, 1.8 m wide, 1.2 m deep

Comments: sampled near fracture with heavy Fe-staining;

sample site is 3 m high, so elevation may be same as ridgecrest

BC86-16TA

Location: about 250 m west of dirt road, elevation about 7240 ft

Petrographic name: granodiorite, coarse-grained with xenoliths

Boulder size: 5.5 m high, 6 m wide, 3 m deep

Comments: on boulder surface, xenoliths protrude ~3 cm; this much exfoliation of granodiorite has taken place. Sample taken from place where flat top begins to curve down

SAMPLES SC86-17MB TO SC86-21MB

These Mono Basin samples were taken on the southern lateral moraine of Sawmill Canyon in the central portion of Section 8, T1S, R26E.

SC86-17MB

Location: on ridgecrest at about 7800 ft elevation

Petrographic name: granodiorite, coarse-grained

Condition: strongly weathered, feldspars altered. Strong Fe-stain in spots. Well-jointed.

Boulder size: 1.8 m high, 1.2 m wide, 2.4 m deep

Comments: Burke and Birkeland soil pit 30 m E along crest

SC86-18MB

Location: 60 m E of SC86-17MB

Petrographic name: granodiorite

Condition: moderately weathered, boulder has pegmatitic phase and a 1 cm dike or vein

Boulder size: 1.2 m high, 1.0 m wide

SC86-19MB

Location: about 800 m E of SC86-18MB at about 7600 ft

Petrographic name: granodiorite

Condition: moderately to strongly weathered

Boulder size: 1.0 m high, 1.0 m wide, 0.6 m deep

Comments: sample site 1.0 m high

SC86-20MB

Location: about 50 m E of section line between Sections 7 and 8; elevation about 7860 ft

Petrographic name: granodiorite

Condition: moderately to strongly weathered, feldspar altered, boulder contains xenoliths and veinlets

Boulder size: 1.8 m high, 3 m wide, 1.8 m deep

Comments: sample site is 1.6 m high. Sample has a smooth side which was exposed at crack. It is thought that the crack is not a geometry problem (timing of crack?)

SC86-21MB

Location: 60 m W of SC86-20MB

Petrographic name: granite, fine-grained - felsic igneous

Condition: moderately weathered. Polished surface and well-developed weathering rind 3–4 mm thick.

Boulder size: 1.0 m high, 1.2 m wide, 1.0 m deep

SAMPLES BC87-1TA TO BC87-5TA

These Tahoe samples were collected in 1987 on the highest right lateral moraine of Bloody Canyon. The moraine has a forested crest at the top of a sharp ridge. This flat-topped crest was 5-20 m across in most places. Five boulders were sampled from 5 sites working from the NE (low) end of the ridge to the SW (higher) portion of the moraine. The moraine continues to climb to higher elevations. The samples are all from the NW 1/4 of Section 5, T1S, R26E.

BC87-1TA

Location: about 7700 ft elevation

Petrographic name: quartz monzonite?, coarse-grained

Condition: moderately weathered

Boulder size: 1.6 m high

BC87-2TA

Location: 60 m SW of BC87-1TA

Petrographic name: quartz monzonite?, medium-grained

Condition: somewhat weathered

Boulder size: 1.2 m high

Comments: smoother surface

BC87–3TA

Location:	60 m SW of BC87–2TA
Petrographic name:	quartz monzonite?, fine–grained
Condition:	weathered
Boulder size:	1.5 m high

BC87–4TA

Location:	60 m SW of BC87–3TA
Petrographic name:	quartz monzonite?, fine–grained
Condition:	fresh
Boulder size:	1.4 m high

BC87–5TA

Location:	60 m SW of BC87–4TA, at about 7840 ft
Petrographic name:	quartz monzonite?, fine–grained
Condition:	fresh
Boulder size:	1.5 m high

LITTLE McGEE CREEK

SAMPLES LMC86-1TI TO 10TI

LMC86-1TI

Location: south of McGee Creek at 2900 m elevation

Petrographic name: mafic plutonic - diorite? Biotite and amphibole - rich

Boulder size: 1.5 m high, 1.8 m wide

Comments: boulder contains inclusions which are even more mafic than boulder; jointed

LMC86-2TI

Location: 1.0 m E of LMC86-1TI

Petrographic name: granodiorite, coarse-grained

Condition: fresh to weakly-weathered

Boulder size: 1.1 m high, 1.8 m wide, 1.0 m deep

LMC86-3TI

Location: 1.5 m E of LMC86-2TI

Petrographic name: granodiorite, coarse to medium-grained

Boulder size: 1.0 m high, 1.2 m wide, 1.2 m deep

Comments: sample taken from a square edge, facing SE. Sample consists of 10+ pieces, 1–2 cm thick, taken along a 0.6 m interval of edge, top not marked

LMC86–4TI

Location: 10 m E of LMC86–3TI

Petrographic name: granodiorite

Condition: fresh

Boulder size: 1.0 m high, 0.6 m wide, 0.6 m deep

LMC86–5TI

Location: 60–80 m NW of LMC86–4TI

Petrographic name: granodiorite

Condition: fresh to weakly-weathered

Boulder size: 1.2 m high, 1.5 m wide, 1.2 m deep

Comments: sample is from a nearly vertical surface facing SE. Uncertain whether this moraine is the same as the moraine of LMC86–1TI through 4TI

LMC86-6TI

Location: 90+ m E of fault scarp, elevation 3000 m

Petrographic name: granodiorite, medium to coarse-grained

Condition: moderately weathered

Boulder size: 1.2 m high, 0.6 m wide, 2.4 m deep

Site: 0.6 m high from uphill side; 1.2 m high from downhill side

Comments: mafic clasts protruding 1-2 cm indicate degradation of boulder

LMC86-7TI

Location: 15 m W of LMC86-6TI

Petrographic name: granodiorite

Condition: fresh

Boulder size: 1.0 m high, 1.0 m wide, 1.0 m deep

Comments: sample marked with S for side - a steep face facing SE

LMC86-8TI

Location: 80 m SE (along crest) from LMC86-6TI

Petrographic name: granodiorite

Condition: weakly to moderately weathered

Boulder size: 1.0 m high, 2.1 m wide, 2.4 m deep

Comments: sample taken from a nearly horizontal surface, with material chipped away on all sides

LMC86-9TI

Location: 24 m SE of LMC86-8TI

Petrographic name: granodiorite

Condition: fresh to weakly weathered

Boulder size: 1.5 m high, 1.2 m wide, 1.5 m deep

LMC86-10TI

Location: 15 m SE of LMC86-9TI

Petrographic name: granodiorite

Condition: weakly weathered

Boulder size: 1.2 m high, 1.8 m wide, 1.0 m deep

Comments: some coarse feldspars (plagioclase)

SAMPLES LMC86-11TA TO 15TA

These samples were taken from a Tahoe moraine that was lower in elevation and NE from the crest of the previously sampled Tioga crest. The sampling area ressembles a bench on the flank of the high Tioga moraine. The elevation is 2940 m.

LMC86-11TA

Location: 200 m NE of LMC86-6TI

Petrographic name: granodiorite, medium to fine-grained

Condition: weakly to moderately weathered

Boulder size: 1.8 m high, 1.2 m wide, 1.8 m deep

Comments: sample is a 1+ cm thick exfoliation piece, top not noted. Boulder weathered; clasts protrude 2-4 cm in relief and indicate exfoliation of granodiorite

LMC86-12TA

Location: 6 m N of LMC86-11TA

Petrographic name: granodiorite, coarse-grained

Condition: moderately weathered

Boulder size: 1.2 m high, 3 m wide, 1.2 m deep

LMC86-13TA

Location: 30 m W of LMC86-12TA

Petrographic name: mafic xenolith which is a fine-grained inclusion in granodiorite. Xenolith is biotite-rich and contains quartz and feldspar

Boulder size: 1.2 m high, 1.2 m wide

Comments: sits 10 cm above rest of boulder surface

LMC86-14TA

Location: 1.5 m S of LMC86-13TA

Petrographic name: granodiorite, medium to coarse-grained

Condition: moderately weathered

Boulder size: 1.5 m high, 2.1 m wide, 1.2 m deep

LMC86-15TA

Location: 90 m E of LMC86-12TA

Petrographic name: granodiorite, medium to coarse-grained

Condition: moderately weathered

Boulder size: 1.8 m high, 3 m wide, 1.8 m deep

SAMPLES LMC86-16SH TO 20SH

This Sherwin moraine is very broad with no discernable crest, considerable deflation is likely. The moraine is 60-90 m across and is located in the south-central part of Section 31. Elevation is about 2460 m. Most boulders on this moraine are moderately to strongly weathered. Samples 17SH and 18SH are part of a group of 6 boulders which are 1.2 m or more in height.

LMC86-16SH

Petrographic name:	granodiorite, medium to coarse-grained
Condition:	moderately to strongly weathered
Boulder size:	1.8 m high, 2.4 m wide, 1.8 m deep

LMC86-17SH

Location:	60 m NE of LMC86-16SH
Petrographic name:	intermediate to mafic plutonic rock - diorite? Fine-grained matrix with coarse plagioclase phenocrysts
Condition:	moderately weathered
Boulder size:	1.8 m high, 2.4 m wide, 1.2 m deep
Comments:	boulder well-fractured

LMC86-18SH

Location:	10 m N of LMC86-17SH
Petrographic name:	granodiorite, medium to coarse-grained
Condition:	strongly weathered
Boulder size:	1.5 m high, 1.5 m wide, 1.2 m deep

LMC86-19SH

Location:	45 m N of LMC86-18SH
Petrographic name:	granodiorite
Condition:	moderately to strongly weathered
Boulder size:	2.4 m high, 2.4 m wide, 1.2 m deep
Comments:	site at 1.8 m

LMC86-20SH

Location:	120 m NE of LMC86-19SH
Petrographic name:	granodiorite, medium to coarse-grained
Condition:	strongly weathered
Boulder size:	2.4 m high, 1.8 m wide, 1.8 m deep
Comments:	one piece marked with 'S' for side

SAMPLES SG86-1SH TO 4SH

Samples were collected at the top of the Sherwin grade (SG) which is the type locality of the Sherwin till. This area is on the Casa Diablo 15' quadrangle. The boulder density is very sparse, perhaps 1 or 2 large boulders over 1.2 m in height in a square area 150 m on a side.

SG86-1SH

Location: Approximately 300+ m from repeater station. Bearing is S70W from SW corner of repeater station. Reading taken from pile of concrete rubble toward boulder.

Petrographic name: granodiorite, medium to coarse-grained; many coarse feldspars

Condition: strongly weathered

Boulder size: 1.8 m high, 3 m wide, 1.8 m deep

Comments: VS on sample - a vertical face which is a joint face opposing slab on ground, therefore not exposed as long as top surface

SG86-2SH

Location: 60 m NW of SG86-1SH

Petrographic name: granodiorite, some biotite, coarse feldspar

Condition: strongly weathered

Boulder size: 1.2 m high, 2.4 m wide, 1.2 m deep

Comments: at a boulder 24 m SW of SG86–2SH, a smooth (polished?) surface sits 3–4 cm above the rest of the boulder suggesting 3–4 cm of erosion

SG86–3SH

Location: 60 m S70W of repeater station

Petrographic name: granodiorite

Condition: moderately weathered, minor Fe–staining

Boulder size: 1.2 m high, 1.8 m wide, 1.0 m deep

Comments: VS surface is a joint face with little exposure

SG86–4SH

Location: 60 m due N of SG86–5SH; S60E from repeater station (from same concrete rubble)

Petrographic name: granodiorite, medium to coarse–grained

Condition: moderately weathered

Boulder size: 1.1 m high, 1.5 m wide, 1.2 m deep

SG86-5SH

Location: 150–180 m S60E of repeater station

Petrographic name: granodiorite?, biotites totally altered

Condition: strongly weathered, rock is crumbly

Boulder size: 4.1 m high, 3.0 m wide, 2.4 m deep

Comments: sample is for quartz separation only

SG86-6SH

Location: west side of US 395 on south end of 'morainal' hill; bearing 080° to repeater station;

Petrographic name: granodiorite, coarse feldspar

Condition: strongly weathered, rock is crumbly

Boulder size: 2.7 m high, 3.6 m wide, 1.5 m deep; site 2.1 m high at a joint

Comments: candidate for quartz separation for ^{10}Be, 15–20 cm of possible rock erosion above sample site

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