THE BUILD-UP OF EPIGENE CHLORINE-36 IN ROCKS
AND ITS RELEASE INTO GROUNDWATER SYSTEMS

by

Laurel J. Izmirian

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Socorro, New Mexico

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ABSTRACT

Equations for calculation of both the build-up of
epigene chlorine-36 with time and of its rate of release due
to weathering are presented in revised form such that they
now take into account chlorine-36 production by muon
reactions, as well as by spallation and neutron activation
reactions.

Wet-chemical methods for the extraction of chloride
from rocks, as a silver chloride precipitate, and for silver
chloride purification are presented. Measured
chlorine-36/total chloride ratios of basalt and rhyolite
samples are compared to theoretically calculated values in
order to determine the reliability of chlorine-36 build-up
as a dating technique. The measured ratios are
significantly lower than expected for the older rocks and
higher than expected for the younger rocks. Measured ratios
are probably representative of a combination of epigene and
meteoric chlorine-36 rather than of epigene chlorine-36
alone.

The rate of release of epigene chlorine-36 as a
function of total and chemical weathering rates is examined,
and it is concluded that although the input of epigene
chlorine-36 to groundwater systems is generally quite small,
it is not necessarily insignificant.

ACKNOWLEDGEMENTS

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INTRODUCTION

Chloride is particularly suited for use in hydrological studies due to its hydrophylic nature and because of the high electron affinity of chlorine. Chlorine has the highest electron affinity of all the elements. Consequently, in nature it is found almost exclusively as the chloride anion, and it experiences little chemical interaction during passage through various systems.

The only unstable isotope of chlorine possessing a half-life greater than one hour is chlorine-36, which has a half-life of 301,000 years. The half-life and build-up rate of chlorine-36 renders it suitable for dating materials ranging in age from 500 to 500,000 years. The virtues of using chlorine-36 in the dating and tracing of old groundwater have recently been explored. However, in utilizing chlorine-36 as a dating tool and/or tracer of groundwater, generally only meteoric chlorine-36 has been considered; it has been assumed that the concentration of epigene chlorine-36 in the groundwater has been negligible. The primary purpose of this study is to explore the viability of this assumption.

Chlorine-36 has not been applied to geological studies to the extent it has been utilized in hydrological applications. Its usefulness for geological studies has been hindered by its low natural abundance and long half-life. Understanding of the epigene chlorine-36 input to groundwater systems has been limited by the paucity of studies examining the build-up of chlorine-36 in geologic materials. The possibility of using the epigene chlorine-36 build-up in establishing the surface-exposure time experienced by rocks, and in studying erosion and weathering rates was first considered in 1955 by Davis and Schaeffer. However, it is only with recent increases in detection sensitivities that application of chlorine-36 techniques to geological studies has become feasible.

Bentley et al. (in press) revised the equations for epigene chlorine-36 build-up with time given by Davis and Schaeffer (1955) in order to take into account chlorine-36 production by spallation of potassium and calcium. This study makes further revisions to the equations, accounting for chlorine-36 production by muon reactions. Measured values of chlorine-36 were obtained from young volcanic rocks and compared to theoretically calculated values, thereby exploring the feasibility of using epigene chlorine-36 build-up as a dating tool, as well as contributing to the heretofore meager understanding of the relative significance of the input of epigene chlorine-36 to groundwater systems. Understanding in regard to the latter

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is further developed by a theoretical examination of the
role of epigene chlorine-36 during erosion and weathering.

BACKGROUND

Mechanisms of Chlorine-36 Production

Chlorine-36 is produced atmospherically (meteoric chlorine-36), epigenically, and hypogenically. There are three principal reactions by which chlorine-36 is produced naturally. These reactions include spallation of heavier nuclei (primarily argon, potassium and calcium) by energetic cosmic rays, neutron activation of argon-36 and neutron activation of chlorine-35. Additionally, chlorine-36 has been produced by certain atmospheric nuclear-weapons tests.

Meteoric chlorine-36 accounts for approximately thirty percent of all near-surface chlorine-36 (Bentley et al., in press). This chlorine-36 is largely produced by two processes: cosmic-ray spallation of argon-40, and neutron activation of argon-36 through the neutron-capture reaction: $^{36}Ar(n,p)^{36}Cl$, with the neutrons arising from cosmic-ray reactions. Contributions from both spallation of potassium and calcium, and from neutron activation of chlorine-35 are extremely slight due to the atmospheric paucity of the parent isotopes. Spallation of argon-40 and neutron activation of argon-36 occur throughout the atmosphere. According to Oeschger et al. (1969) approximately forty percent of the total production takes place in the troposphere, with fifty percent occurring in the stratosphere. Chlorine-36 leaves the stratosphere and

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enters the troposphere during periods of mixing. The
chlorine-36 and stable chloride derived from sea spray are
quickly washed out of the troposphere by precipitation, or
fall out after having become associated with aerosols.
Turekian et al. (1977) report a mean residence time of
approximately one week.

The most significant processes for the production of
epigene chlorine-36 are spallation of abundant potassium and
calcium, and neutron activation of chlorine-35 through the
reaction $^{35}Cl(n,\gamma)^{36}Cl$. Though most rocks contain only a
minor amount of chlorine-35, the relatively large
neutron-activation cross section of chlorine-35 allows
significant chlorine-36 production. Neutrons are primarily
supplied by evaporation neutrons at equilibrium with the
cosmic-ray nucleonic component (Kubik et al., 1984; Bentley
et al., in press). Additional neutrons are supplied by muon
capture reactions (μ^-,n) (Kubik et al., 1984), by
photonuclear reactions of the fast muon component (Zito and
Davis, 1983) and by the release of neutrons from uranium and
thorium decay (Kubik et al., 1984; Bentley et al., in
press). Argon is low in abundance at the surface of the
lithosphere and oceans. Therefore chlorine-36 production by
spallation of argon-40 and by neutron activation of argon-36
is relatively insignificant in these environments.

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Virtually all hypogene chlorine-36 is produced by neutron activation of chlorine-35. Measurable amounts of chlorine-36 can be produced in this manner, even under the modest neutron fluxes of the deep subsurface, because of the relatively large neutron-activation cross section of chlorine-35. Because cosmic rays are generally attenuated by the atmosphere and upper lithosphere, spallation does not commonly occur at depths of more than a few meters below the earth's surface. Neutron activation of argon-36 is also infrequent in the subsurface due to the scarcity of argon-36 in this environment. Neutrons for the $^{35}Cl(n,\gamma)^{36}Cl$ reaction are derived mainly from the uranium and thorium decay series as either secondary neutrons through α,n reactions on light isotopes, or as direct fission neutrons (Bentley et al., in press). Muon capture reactions (μ^-,n) and photonuclear reactions of the fast muon component produce neutrons in this environment just as they do in the upper layers of the earth's surface, but to a much lesser extent (Kubik et al., 1984). Methods for calculation of the subsurface neutron flux were presented by Feige et al. (1968). Kubik et al. (1984) showed calculated chlorine-36/calcium-40 ratios in limestone as a function of depth for various chlorine-36 production processes.

Thermonuclear chlorine-36 was produced in the 1950's by neutron activation of seawater when atmospheric nuclear tests were conducted in the Pacific (Schaeffer et al., 1960). The meteoric chlorine-36 fallout pulse resulting

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from the tests was approximately three order of magnitude
greater than the natural fallout of atmospherically produced
chlorine-36. Enhanced fallout occurred from approximately
1953 to 1963 (Bentley et al., 1982; Elmore et al., 1982).

Calculation of Chlorine-36 Production in Geologic Materials

The half-life of chlorine-36 (301,000 a) and its
build-up rate allow the dating of materials ranging in age
from 500 to 500,000 years. Meteoric chlorine-36 should not
interfere in the dating of fresh, relatively impermeable
rocks (rocks from which all traces of weathering have been
completely removed) provided that meteoric chloride cannot
penetrate the interior of such rocks. The chlorine-36 of
such a rock should consist of that chlorine-36 which is
produced by interaction of cosmic rays with the rock once it
is exposed at the surface, and of that chlorine-36 which is
produced by neutron activation resulting from both uranium
and thorium decay within the rock and from muon
interactions.

Chlorine-36, whether produced by spallation or neutron
activation, accumulates in material at a rate proportional
to the exposure time of the material, while simultaneously
decaying at a rate proportional to its abundance. Bentley
et al. (in press) presented an equation to calculate the
build-up of chlorine-36 with time, but their equation does
not take into account the significance of muon production.

The build-up with time is given by the revised equation:

$$N_{36} = \frac{\psi + \phi_n f + \xi}{\lambda_{36}} (1 - e^{-\lambda_{36}t}) \qquad (1)$$

where N_{36} is the concentration of chlorine-36, in atoms kg^{-1}; ψ is the rate of spallation production, in atoms $kg^{-1}a^{-1}$; ϕ is the neutron flux, in neutrons $kg^{-1}a^{-1}$; f is the fraction of the neutrons absorbed by chlorine-35; ξ is the rate of muon production, in atoms $kg^{-1}a^{-1}$; λ_{36} is the chlorine-36 decay constant ($2.3 \times 10^{-6}a^{-1}$); and t is time, in a.

Yokoyama et al. (1973) treated the method of calculating the spallation production rate (ψ) and representative values were provided by Yokoyama et al. (1977). Spallation of both potassium and calcium must be taken into account; spallation of argon is relatively insignificant. Lal and Peters (1967) calculated a sea-level neutron flux of approximately 3×10^{-2} $kg^{-1}s^{-1}$. More recently, Kuhn et al. (1984) measured the neutron flux (ϕ_n) at various depths in the subsurface. Figure 1 presents representative values from Kuhn et al. (1984), normalized to sea level. The formula used in calculating the fraction of neutrons absorbed by chlorine-35 is:

$$f = \frac{N_{35}\sigma_{35}}{\sum\limits_{i} N_i\sigma_i} \qquad (2)$$

where N_{35} and N_i are respectively, the concentrations of
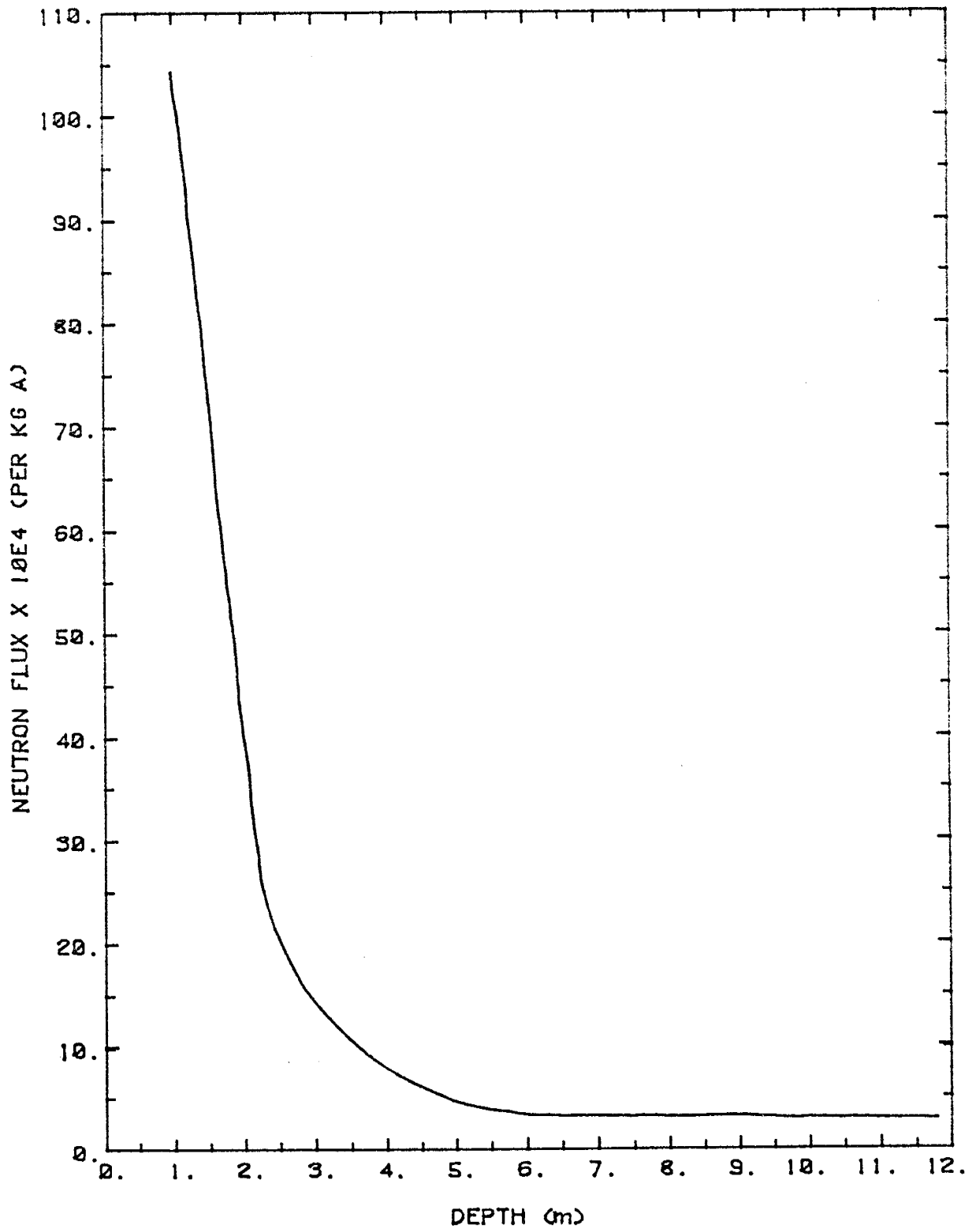
Figure 1. Neutron flux as a function of depth from Kuhn et al. (1984), normalized to sea level.

chlorine-35 and of an isotope, in atoms kg^{-1}; σ_{35} and σ_i are respectively, the neutron-activation cross section of chlorine-35 for chlorine-36 and the neutron-absorption cross section of an isotope, in barns; and the denominator takes into consideration each element contained in the sample. Values of f were calculated for all elements in both a typical basalt and a typical rhyolite. Representative f values indicating the contribution from the elements of greatest significance in basalt and rhyolite are presented in Figure 2. Thermal neutron-absorption cross sections and elemental concentrations in basalt and rhyolite used in calculating the f values are listed in Appendix I. Values for ξ may be obtained using Figure 3 of Kubik et al. (1984), which presents calculated chlorine-36/calcium-40 ratios, as a function of depth, for various production processes of chlorine-36 involving muon reactions. The values of neutron production due to muon capture reactions from Kubik et al. (1984) are of the same order of magnitude as those given by Zito and Davis (1983). Secular equilibrium chlorine-36/calcium-40 ratios, resultant from (μ^-,α) reactions, taken from Kubik et al. (1984) and normalized to sea level are presented in Figure 3 (this paper). Under conditions of secular equilibrium, production rate equals decay rate. Thus the appropriate ratio from Figure 3 may be multiplied by the product of the chlorine-36 decay constant, in a^{-1}, and the calcium-40 concentration of the sample, in atoms kg^{-1}, to obtain the value of ξ.

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RHYOLITE, $f = \dfrac{m_i \sigma_i^{abs}}{6.97}$

Si 17.2%
Cl 4.5%
K 17.4%
Ca 0.5%
Ti 1.1%
Al 6.1%
Na 4.8%
Mn 3.1%
Fe 3.6%
B 14.6%
Sm 2.6%
Li 4.3%
Gd 18.8%
**

BASALT, $f = \dfrac{m_i \sigma_i^{abs}}{7.75}$

Mn 2.8%
Ti 14.8%
Fe 31.4%
Ca 5.6%
K 3.4%
Cl 1.1%
Si 10.6%
Al 5.8%
Na 3.4%
B 2.7%
Li 1.1%
*
Gd 14.1%
Sm 1.2%
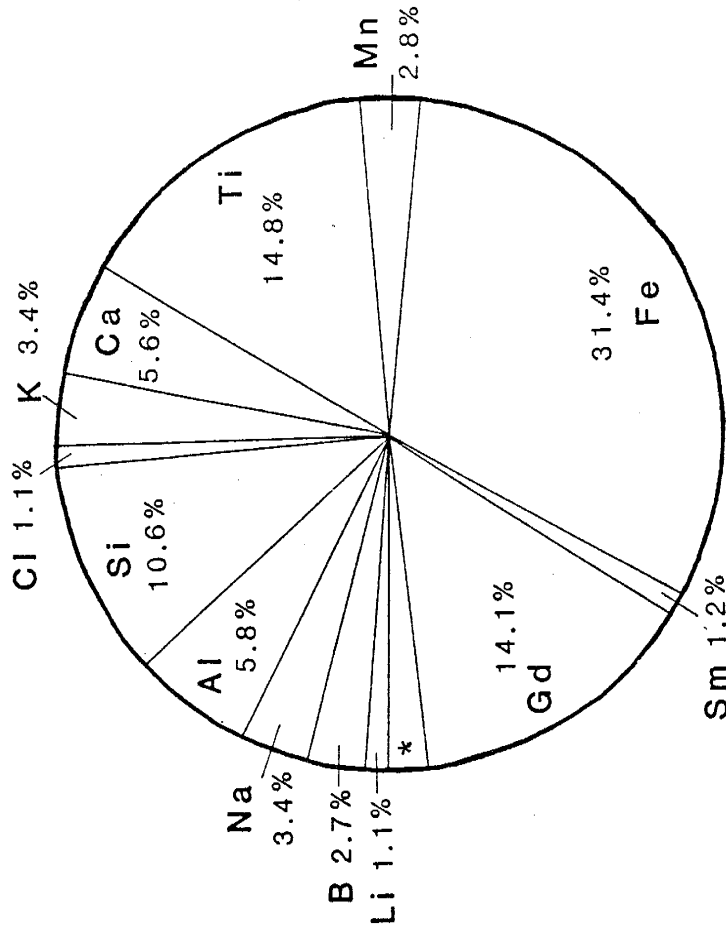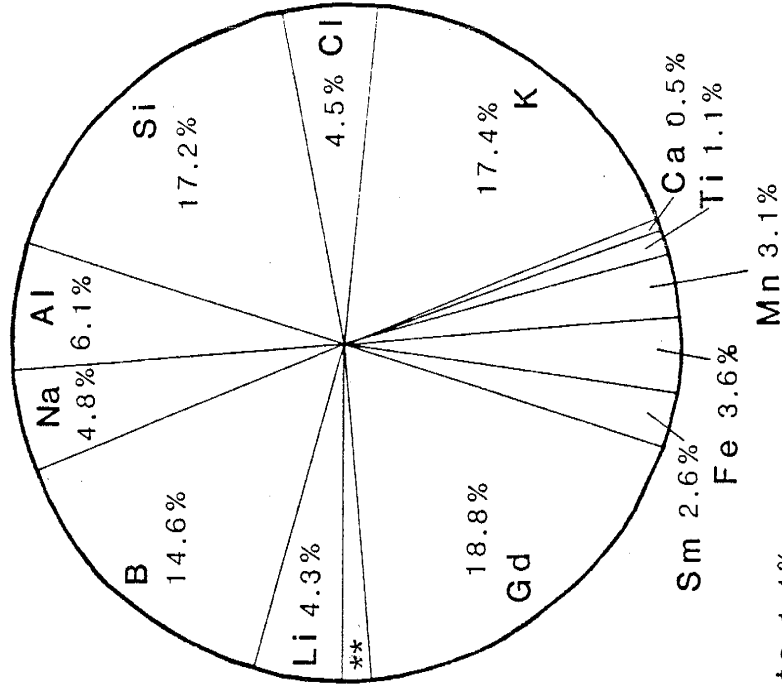
*all other elements 2.0%   ** all other elements 1.4%

Figure 2. Representative f values for the elements in a typical basalt and rhyolite. Elemental concentrations, m_i, were obtained from Wedepohl (1978) and converted to units of $cm^2 kg^{-1}$. Thermal neutron-absorption cross sections, σ_i, in barns, were obtained from Hampel (1968).

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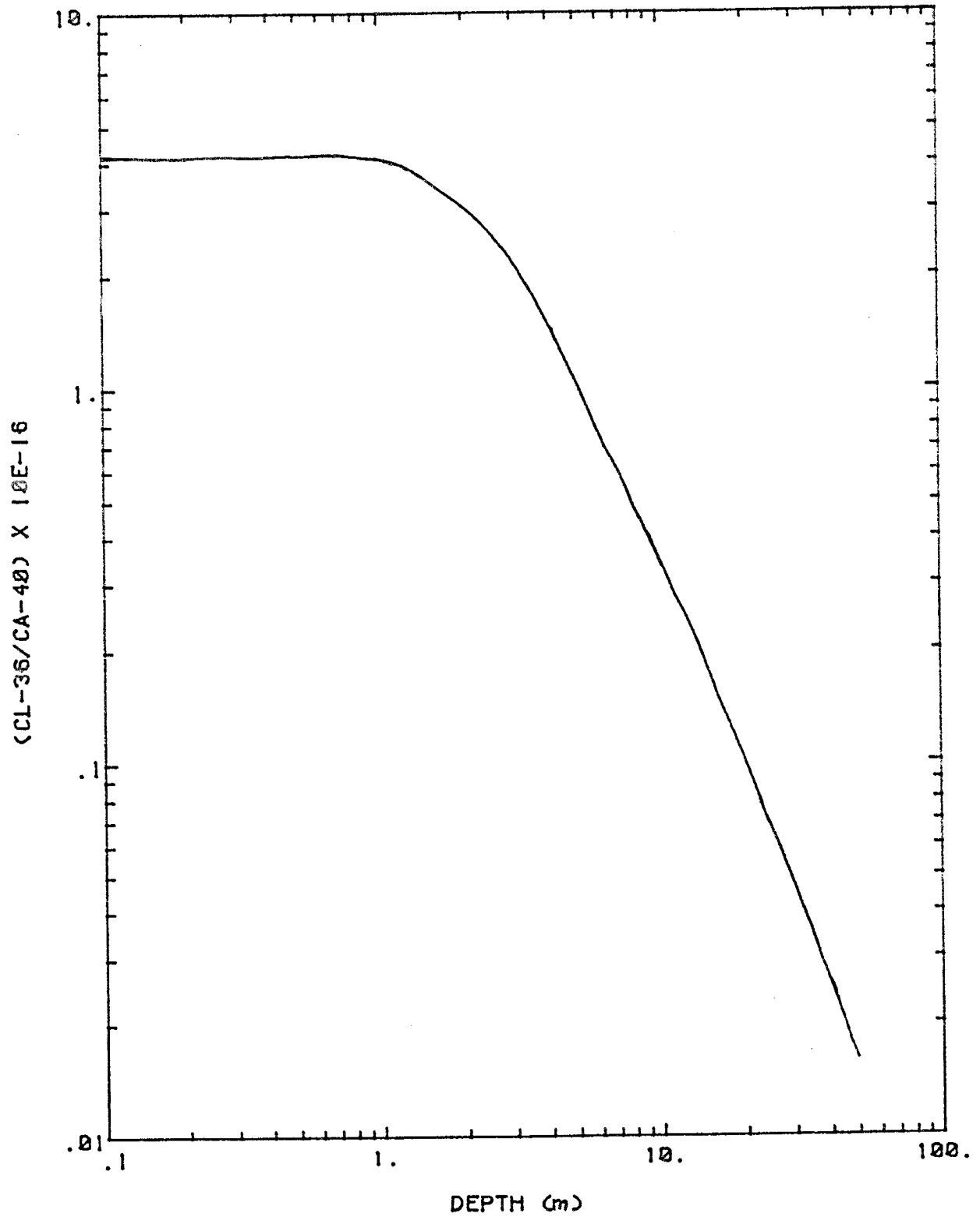
Figure 3. Calculated chlorine-36/calcium-40 ratios resultant from (μ^-,α) reactions, from Kubik et al. (1984), normalized to sea level and presented as a function of depth. Values based on a limestone containing 6.01×10^{24} atoms Ca per kilogram rock.

Rate of spallation, neutron flux and rate of chlorine-36 production from muon reactions are not constant values; the chlorine-36 production rate varies with changes in elevation and depth. Figure 4 shows the relative production rates of cosmonuclides as a function of altitude, from Yokoyama et al. (1977), normalized to sea level. Figure 5 shows the relative chlorine-36 concentration as a function of depth, and was produced by normalizing total chlorine-36/calcium-40 values, for a limestone, to the earth's surface (0 m depth). The total chlorine-36 includes that which is produced by the following methods: (1) spallation of calcium-40, (2) muon capture by calcium-40 and (3) neutron capture reactions with neutrons from a) those neutrons in equilibrium with the cosmic ray nucleonic component, b) muon capture reactions, c) photonuclear reactions of the fast muon component and d) fissioning isotopes. Although the values used are representative of a limestone, it is assumed here that they are indicative of a relative change in chlorine-36 content with depth that is reasonably representative for all rock types. The chlorine-36 content of a limestone is almost exclusively the product of calcium-40 since the potassium content of limestones is extremely low. Therefore the vast majority of the chlorine-36 content of a limestone is accounted for by chlorine-36/calcium-40 ratios, and thus the relative change, with depth, of the chlorine-36 due to calcium-40 is reasonably equal to the relative change, with depth, of the

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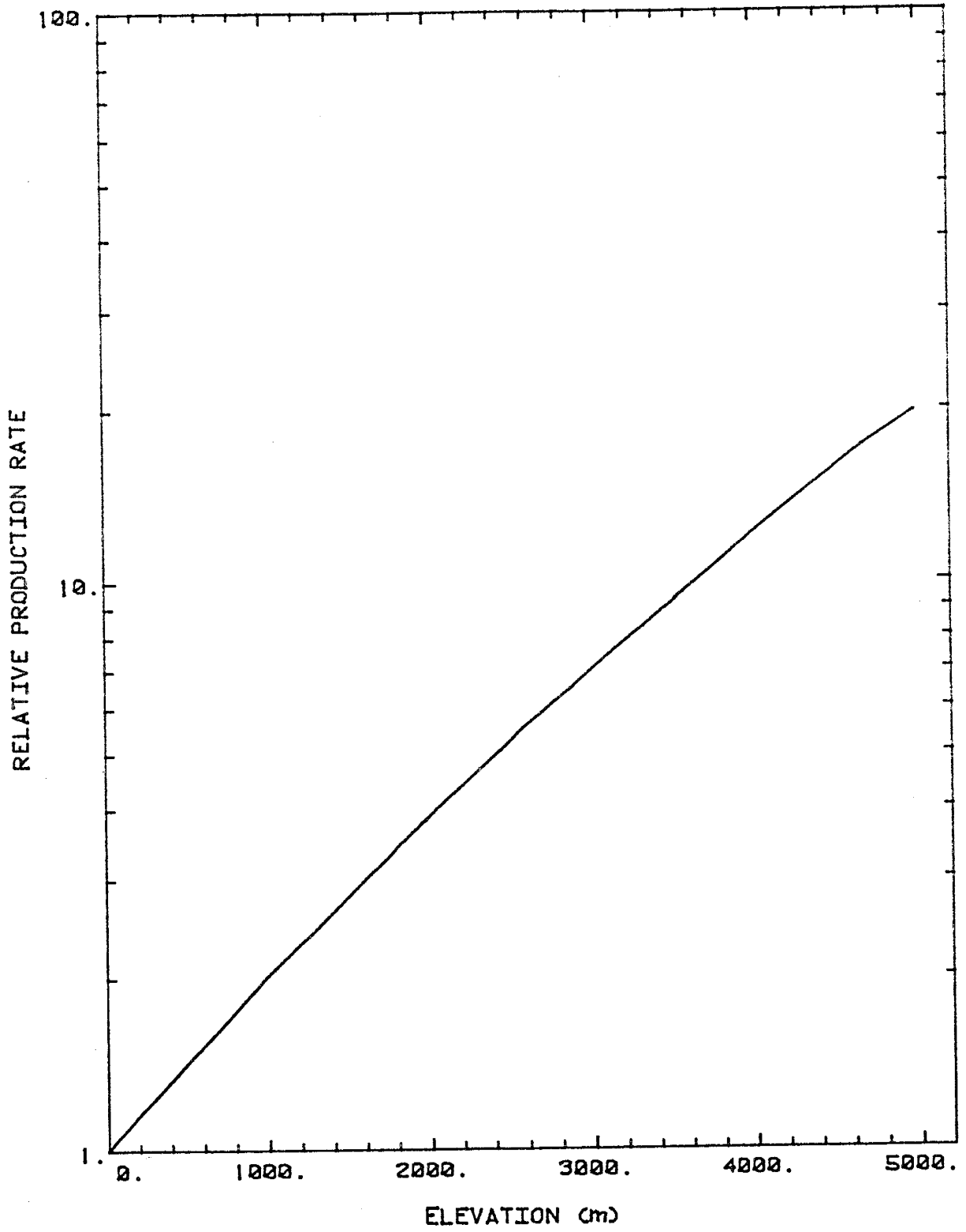
Figure 4. Relative production rate of cosmonuclides as a function of elevation from Yokoyama et al. (1977), normalized to sea level.
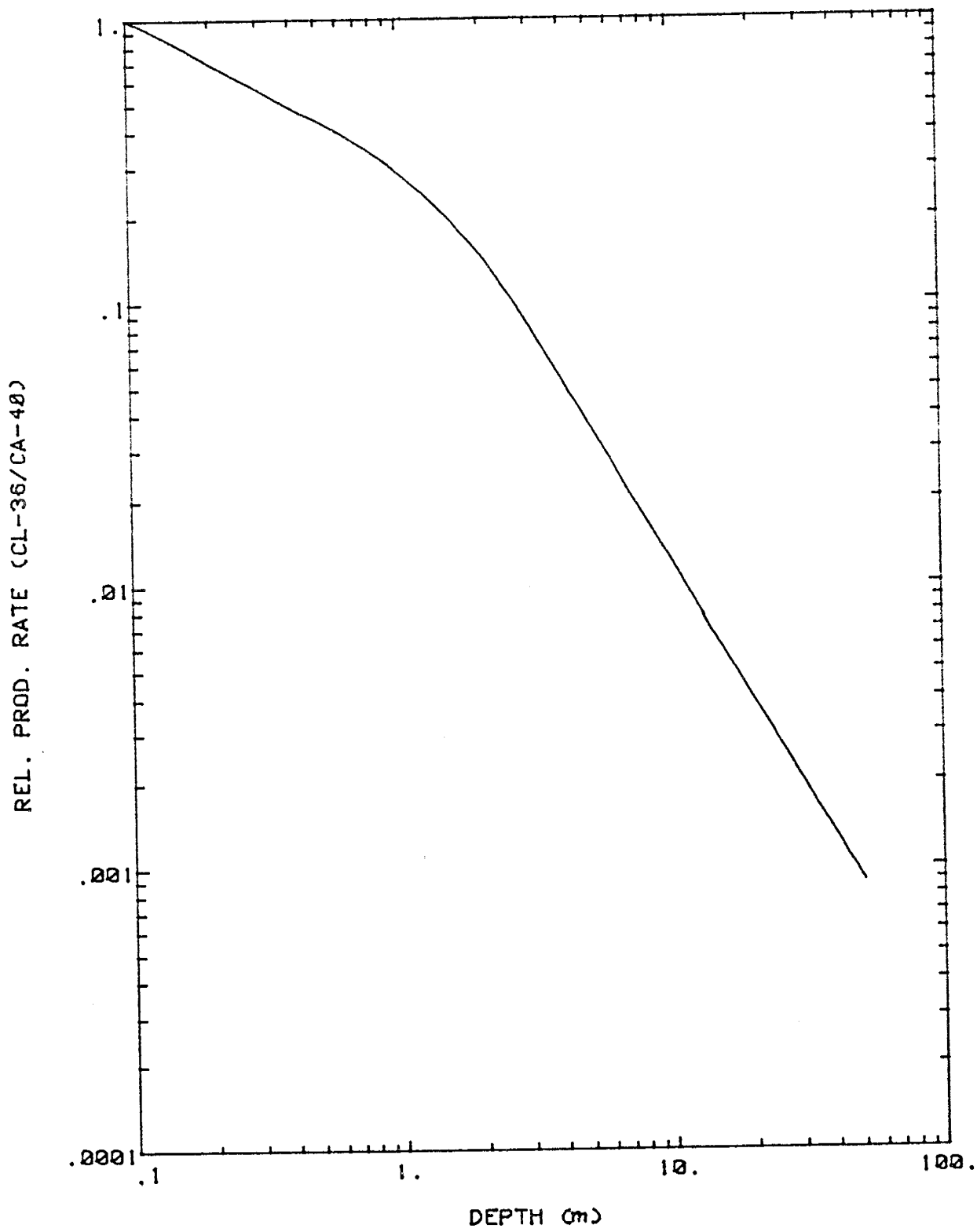
Figure 5. Calculated total chlorine-36/calcium-40 ratios, normalized to the earth's surface (0 m depth) and presented as a function of depth.

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total chlorine-36 content. Unless a sample is taken from the earth's surface, at sea level, depth and elevation correction factors, designated D and E respectively, must be introduced. The measured chlorine-36 content of a rock is most conveniently presented as a chlorine-36/total chloride ratio. This requires that the number of chlorine-36 atoms be divided by the number of chloride atoms per kilogram of rock. It is also necessary to take into account the original chlorine-36 content of the rock, thereby yielding the final formula:

$$\frac{^{36}Cl}{Cl} = \frac{ED(\psi + \phi_n f + \xi)}{\lambda_{36}N_{Cl}} (1 - e^{-\lambda_{36}t}) + \left[\frac{^{36}Cl}{Cl}\right]_o \qquad (3)$$

Related Research

Chlorine-36 studies have recently been applied to hydrological problems requiring the dating and/or tracing of old groundwater. But the possibility of using chlorine-36 build-up for the dating of geologic materials and for measuring erosion rates has remained relatively unexplored. This has been due in large to analytical difficulties encountered as a result of the low natural abundance and long half-life of chlorine-36.

The idea that the build-up of epigene chlorine-36 in minerals might be useful in establishing the surface-exposure time experienced by rocks, and in studying

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erosion and weathering rates, was first presented by Davis and Schaeffer (1955). They were also first to actually perform a chlorine-36 measurement on a rock. They obtained a chlorine-36/total chloride ratio of 1.6×10^{-12}, and calculated an exposure time of 24,000 years for a "pre-Wisconsin" phonolite from Bull Cliff near Cripple Creek, Colorado. But in calculating the exposure time, they did not take into account chlorine-36 production by spallation of potassium and calcium. They were unsuccessful, due to insufficient analytical sensitivity, in an attempt to measure the chlorine-36 concentration of a nepheline-sodalite syenite from New Hampshire.

Bonner et al. (1961) attempted to measure chlorine-36 activities of solid salt samples from Dugway Salt Flat, Utah Salt Flat and the Forty Mile Desert in Utah. Their attempts were unsuccessful due to insufficient analytical sensitivity, indicating a chlorine-36/total chloride ratio of less than 10^{-13}. But a measured average chlorine-36/total chloride ratio of 8×10^{-14} in sediments was later obtained by Onufriev and Soifer (1968, as cited by Bentley et al., in press), in conformity with results from other investigations.

Sinclair and Manuel (1974) used a different approach in determining the chlorine-36 concentration of a sodalite from Dungannon, Ontario. They used an indirect approach which enabled determination to be made of a much smaller

chlorine-36/total chloride ratio than that which could have been measured using the direct-detection sensitivity of the time. They measured the argon-36 build-up resulting from chlorine-36 decay, and divided this value by the potassium-argon age of the sodalite thereby obtaining a production rate of 560 ± 210 $(g\ Cl)^{-1} a^{-1}$ -- equivalent to a chlorine-36/total chloride ratio at secular equilibrium of 1.5×10^{-14}.

With recent advances in analytical technique and greatly increased sensitivities, the possibilities of using chlorine-36 build-up as a dating tool are being eagerly reconsidered. Bentley et al. (in press) provided a means of calculating the build-up of chlorine-36 which has been produced by spallation of potassium and calcium as well as by neutron activation. However, their calculations do not take into account chlorine-36 production resultant from muon reactions. Kubik et al. (1984) calculated chlorine-36/calcium-40 ratios as a function of depth for chlorine-36 production processes involving various muon reactions.

Jonte (1956, as cited by Bentley et al., in press) first suggested that chlorine-36 might be produced hypogenically. He obtained a value greatly exceeding those values expected while measuring the chlorine-36 activity of water from Arkansas hot springs. He attributed the difference to analytical difficulties. The difference may

actually have been due to contamination by bomb chlorine-36 (Bentley et al., in press).

Determination of the subsurface neutron flux has remained the major obstacle in calculating the production of hypogene chlorine-36. Procedures for the calculation of this variable were given by Pine and Morrison (1952), Morrison and Pine (1955) and Feige et al. (1968). Additional attempts at determining the subsurface neutron flux were made by Kuroda et al. (1957) and Kuroda and Kenna (1960) who measured the chlorine-36 concentration of uranium ores. Kuroda and Kenna (1960) obtained chlorine-36/total chloride ratios of 9×10^{-11} and 5×10^{-11} for pitchblendes from the Belgan Congo and the Great Bear Lake in Canada, respectively. More recently, Kuhn et al. (1984) used a helium-3 proportional counter to make direct measurements of the neutron flux at various depths.

Analytical Methods

The low natural abundance and long half-life of chlorine-36, and consequently its extremely low specific activity, have always hindered the application of chlorine-36 techniques to geological studies. Natural samples yield chlorine-36 activities in the range of 10^{-5} to 10 disintegrations per minute per gram chloride, corresponding to chlorine-36/total chloride ratios of 10^{-16} to 10^{-10}. Most samples tend toward the lower end of this

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range. Detection sensitivities of previous analytical
methods necessitated that samples selected for the earlier
studies be collected in relatively large quantities, from
rocks of high chlorine content and considerable age, in
order that enough chlorine-36 be present to be measurable.

Chlorine-36 measurements were initially made in the
1950's using screen-wall counters much like those used in
carbon-14 analyses (Davis and Schaeffer, 1955). But
screen-wall counters possessed a sensitivity of only about
one chlorine-36 in 10^{11} chlorine -- a sensitivity incapable
of measuring the chlorine-36 content of most natural
samples. Application of liquid scintillation in the 1960's
increased sensitivity to approximately 10^{-12}
chlorine-36/total chloride (Ronzani and Tamers, 1966; Bagge
and Willkom, 1966, as cited by Bentley et al., in press;
Tamers et al., 1969). Roman and Airey (1981) described some
improvements to the liquid scintillation technique which
further increased sensitivity, raising it to approximately 5
x 10^{-13} chlorine-36/total chloride. This level of
sensitivity is sufficient for analyzing modern waters and
many near-surface rocks, but remains inadequate for analysis
of old groundwater and deep subsurface rocks. The most
significant increase in sensitivity has come with the
relatively recent advent of tandem-accelerator mass
spectrometry (TAMS; Elmore et al., 1979). The sensitivity
level has been raised by TAMS to approximately one
chlorine-36 in 5 x 10^{16} chlorine. This sensitivity is

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sufficient to measure the chlorine-36 of most rocks at all anticipated concentrations.

The TAMS system is composed of a linear accelerator and an inert gas stripper connecting two mass spectrometers. Unlike the older counting techniques, which measured decays of the isotope of interest, the TAMS method actually counts the ions of the particular isotope. Sensitivity is thus increased and analysis time reduced since there exist many more total nuclei of an isotope, at any given time, than there exist decaying nuclei (Elmore et al., 1979; Litherland and Rucklidge, 1981). The first mass spectrometer ionizes the sample and selects atoms and molecules of the desired mass-to-charge ratio. The stripper reduces any molecules to their elemental state through collisions with inert argon gas. Stripped ions are then accelerated, and passed on to the second mass spectrometer where the isotopes of the element of interest are separated out. High velocity acceleration of the ions allows for the measurement of the rate of their energy loss, and consequently, determination of their atomic number (Elmore et al., 1979).

In contrast to the sudden emplacement of some igneous rocks at the earth's surface, most rocks are slowly exposed at the surface by erosion. The erosion rate, if fairly constant, may be used in determining the rate of release of chlorine-36 from rocks, due to weathering. Bentley et al. (in press) presented calculations for determining the rate of release of chlorine-36 due to weathering, assuming a constant erosion rate and approximating the variation in production rate of chlorine-36 with depth by use of an exponential function. Yokoyama et al. (1977, p. 48) presented a similar means of calculation. Revising the calculations of Bentley et al. (in press) to account for muon production of chlorine-36, as was done earlier in calculating the chlorine-36 build-up with time, ultimately yields:

$$\frac{^{36}Cl}{Cl} = \frac{(\psi_o + \phi_{n_o} f + \xi_o)\beta}{(\lambda_{36}\beta + \alpha)N_{Cl}} e^{-\alpha z} \tag{4}$$

where ψ_o, ϕ_{n_o} and ξ_o are the surface production rates, β is the inverse erosion rate, in a m^{-1}, and α is the cosmic-ray attenuation coefficient, in m^{-1}.

Judson and Ritter (1964) calculated rates of regional denudation in the United States ranging from 0.04 m/1000 a to 0.17 m/1000 a. Yokoyama et al. (1977) found the

apparent attenuation coefficient of Mabuchi et al. (1971)
to correspond to a true attenuation coefficient of
1 cm /(192±6) g. This value is in good agreement with the
true attenuation coefficient found earlier by Imamura et al.
(1973).

At 0 meters depth the exponential term of equation (4)
goes to one. Therefore the total chlorine-36/total chloride
at the surface is:

$$R_s = \frac{(\psi_o + \phi_{n_o} f + \xi_o)\beta}{(\lambda_{36}\beta + \alpha)N_{Cl}} + R_{se} \qquad (5)$$

where R_s and R_{se} are, respectively, the chlorine-36/total
chloride at the surface and the secular equilibrium
chlorine-36/total chloride resulting from neutrons produced
by uranium and thorium decay.

METHODS

Sample Selection and Preparation

Chlorine-36 is principally produced by cosmic-ray
spallation of argon, potassium and calcium, and by neutron
activation of argon-36 and chlorine-35. In order to ensure
a chlorine-36 content sufficient for analysis, a sample
should be selected from a rock containing an appreciable
concentration of potassium and calcium. Ideally, the sample
should be taken from a rock at high elevation (for a high
cosmic-ray flux), though even rocks at sea level should have
measurable concentrations of chlorine-36 after a few
thousand years. Selecting a sample of durable and
relatively impermeable rock type from an arid climate should
minimize the potential for loss of chlorine-36 from the rock
due to weathering. The half-life and build-up rate of
chlorine-36 limits dating to 500-500,000 years. In
addition, for the purpose of developing chlorine-36 build-up
as a dating tool, it is essential that the age of the sample
be accurately known. If the sample has not been previously
dated with confidence by some other method, there is no
basis against which to evaluate the accuracy of chlorine-36
as a dating technique.

With conditions for selection of an ideal sample in
mind, it was decided to collect samples of basalts and
rhyolites (both rock types contain substantial

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concentrations of potassium and calcium, and some chloride) of ages spanning as much of the designated age range as possible. Sixteen samples were collected from locales in New Mexico, north central Arizona and central eastern California (Figure 6 and Table 1). Specific locations are listed in Appendix II. The ages of the individual samples and the dating methods used are listed in Table 2. Where possible, samples were collected from different depths at a single location in order to measure the change in chlorine-36 concentration with depth. Surface elevations of the sample sites and the depths from which the samples were collected are listed in Table 3.

The rock samples were prepared for the chloride extraction process following the rock preparation methods for XRF analysis distributed by the Los Alamos National Laboratory, New Mexico (Murphy, unpublished manuscript). All weathered areas and areas of direct surface exposure were removed from the samples. The samples were then fine-crushed, pulverized and reduced to a fine powder in which the dominant size fraction was 100-150 mesh.

Chloride Extraction

Chloride may be extracted from powdered rock samples by a high-temperature digestion process. Using this process, the chloride is ultimately precipitated out in the stable form of silver chloride. Because silver chloride is stable,
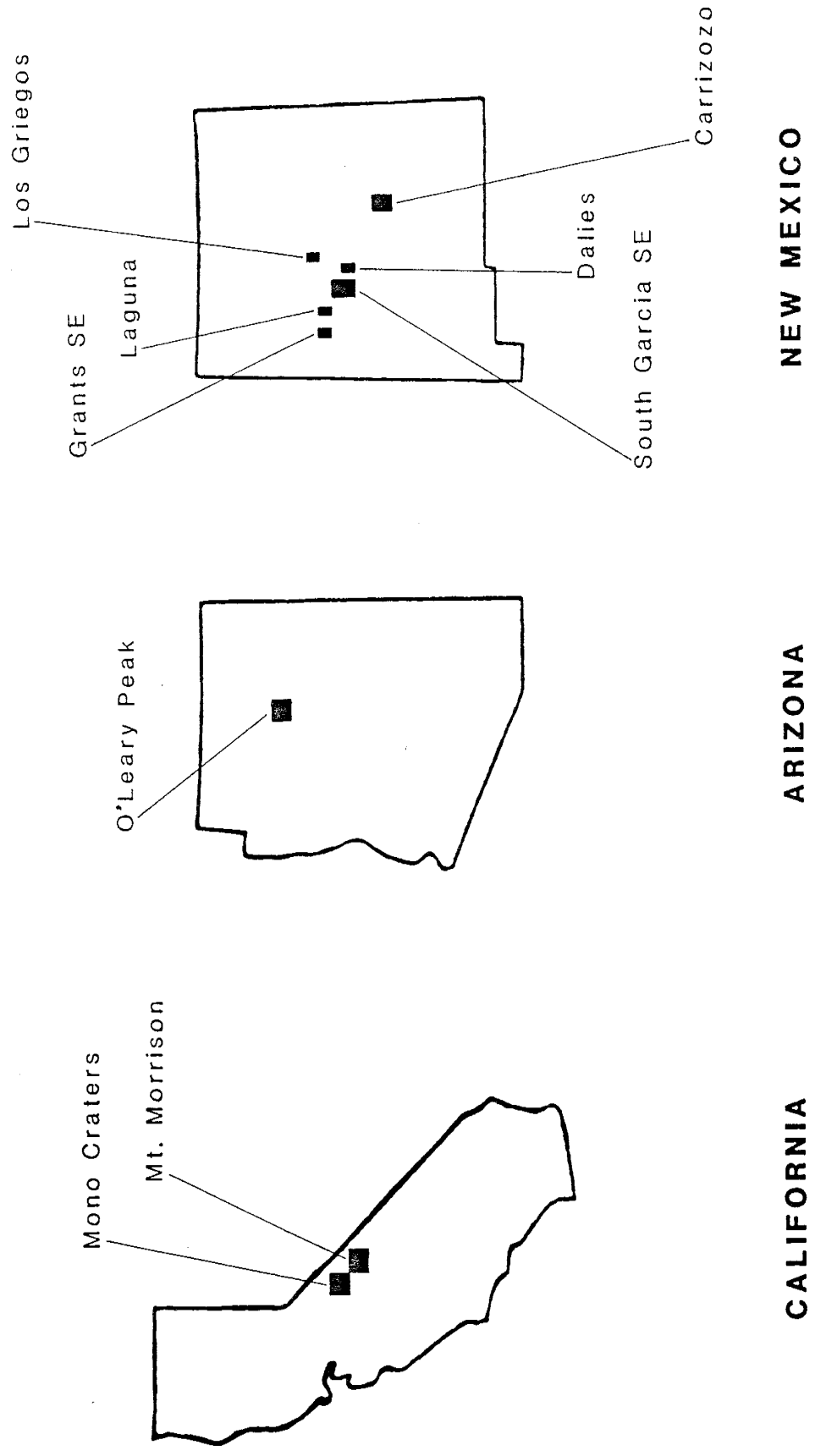
Figure 6. Locations of U.S. Geological Survey quadrangles containing sample sites.

CALIFORNIA   ARIZONA   NEW MEXICO

Table 1. Sample identifications and locations.

Sample Number	Sample Name	Rock Type	Lat N Long W
SG-1A SG-1B SG-1C	Suwanee bottom Suwanee top Suwanee center	Basalt	34°50' 107°03'
LG-1A	Albuquerque	Basalt	35°08' 106°43'
DA-1	Cat Hills	Basalt	34°51' 106°50'
CZ-1 CZ-2	Carrizozo cave Carrizozo cave roof	Basalt	33°42' 105°56'
LA-1	Laguna	Basalt	35°02' 107°23'
GR-1	McCartys	Basalt	35°05' 107°46'
NSCB-1	Sunset Crater	Basalt	35°23' 111°32'
SLR-2	Punch Bowl	Rhyolite	37°49' 119°02'
SLR-3	Cone 8060	Rhyolite	37°49' 119°01'
SLR-4	Panum Crater	Rhyolite	37°56' 119°03'
SLR-5	Panum Cone north	Rhyolite	37°56' 119°03'
SLR-6	Wilson Butte	Rhyolite	37°47' 119°01'
SLR-7	Mammoth Lakes	Rhyolite	37°41' 118°59'

Table 2. Sample ages.

Sample Number	Sample Name	Age (yrs BP)	Dating Method and Literature Source
SG-1A SG-1B SG-1C	Suwanee bottom Suwanee top Suwanee center	320,000±200,000	Potassium-argon; Bachman & Mehnert, 1978
LG-1A	Albuquerque	190,000±40,000	Potassium-argon; Bachman & Mehnert, 1978
DA-1	Cat Hills	140,000±38,000	Potassium-argon; Kudo, et. al., 1977
CZ-1 CZ-2	Carrizozo cave Carrizozo cave roof	1,000-1,500	Estimate based on geo- logic field relations; Allen, 1951
LA-1	Laguna	380,000±250,000	Potassium-argon; Lipman & Mehnert, 1979
GR-1	McCartys	1,084-1,284	Estimate based on geo- logic field relations; Nichols, 1946
NSCB-1	Sunset Crater	919 or 920	Dendrochronology; Smiley, 1958
SLR-2	Punch Bowl	11,500±2,900 9,000±1,800 10,900±4,200	Potassium-argon; Dalrymple, 1967
SLR-3	Cone 8060	6,800±1,400 6,100±1,200	Potassium-argon; Dalrymple, 1967
SLR-4 SLR-5	Panum Crater Panum Cone north	1,300 and >1,175±65 but <1,210±55	Obsidian hydration; Friedman, 1968 and Carbon-14; Wood, 1977a
SLR-6	Wilson Butte	1,500±400	Obsidian hydration; Wood, 1977b
SLR-7	Mammoth Lakes	106,000±3,000 94,000±6,000	Potassium-argon; Bailey, et. al., 1976

Table 3. Sample site surface elevations and sample depths.

Sample Number	Sample Name	Surface Elevation (m above sea level)	Sample Depth (m)
SG-1A	Suwanee bottom	1591 ± 3	3.3
SG-1B	Suwanee top		surface
SG-1C	Suwanee center		2
LG-1A	Albuquerque	1606 ± 6	0.25
DA-1	Cat Hills	1626 ± 8	surface
CZ-1	Carrizozo cave	1600 ± 8	4.45
CZ-2	Carrizozo cave roof		1.7
LA-1	Laguna	1783 ± 3	surface
GR-1	McCartys	1945 ± 3	surface
NSCB-1	Sunset Crater	2100 ± 3	surface
SLR-2	Punch Bowl	2304 ± 12	surface
SLR-3	Cone 8060	2438 ± 12	surface
SLR-4	Panum Crater	2121 ± 12	surface
SLR-5	Panum Cone north	2085 ± 12	3
SLR-6	Wilson Butte	2560 ± 12	surface
SLR-7	Mammoth Lakes	2664 ± 12	surface

the samples may easily be stored until purification can be performed. After the samples have been purified, the silver chloride may be analyzed for chlorine-36 using tandem-accelerator mass spectrometry.

The apparatus necessary to perform the digestion process (excepting the gas tank) was set up in a laboratory fume hood. To prevent chloride contamination, clean plastic gloves were worn while handling the apparatus. The general set up of the apparatus is shown in Figure 7. Teflon tubing led from a 60 psi gage flow meter on a tank of prepurified nitrogen gas, to a glass tube. The glass tube was inserted through a teflon stopper and connected, using a sleeve of teflon tubing, to a pyrex coarse fritted gas-dispersion tube (250 mm length, 12 mm cylinder diameter). The gas-dispersion tube was connected so that the frit nearly reached the bottom of the four-liter pyrex sidearm flask it hung in. The four-liter flask (and only the four-liter flask) was situated on a hot plate capable of producing the required 300 °C temperature. Teflon tubing led from the sidearm of the four-liter flask, to a glass tube that was inserted through a black rubber stopper. A silicon or teflon stopper would be preferable to the black rubber stopper used here. It is possible that a trace amount of chloride could be leached from the black rubber. The glass tube extended one-quarter to one-third the way down into a one-liter pyrex sidearm flask. The purpose of this flask was to catch any rock or acid should the system have backed

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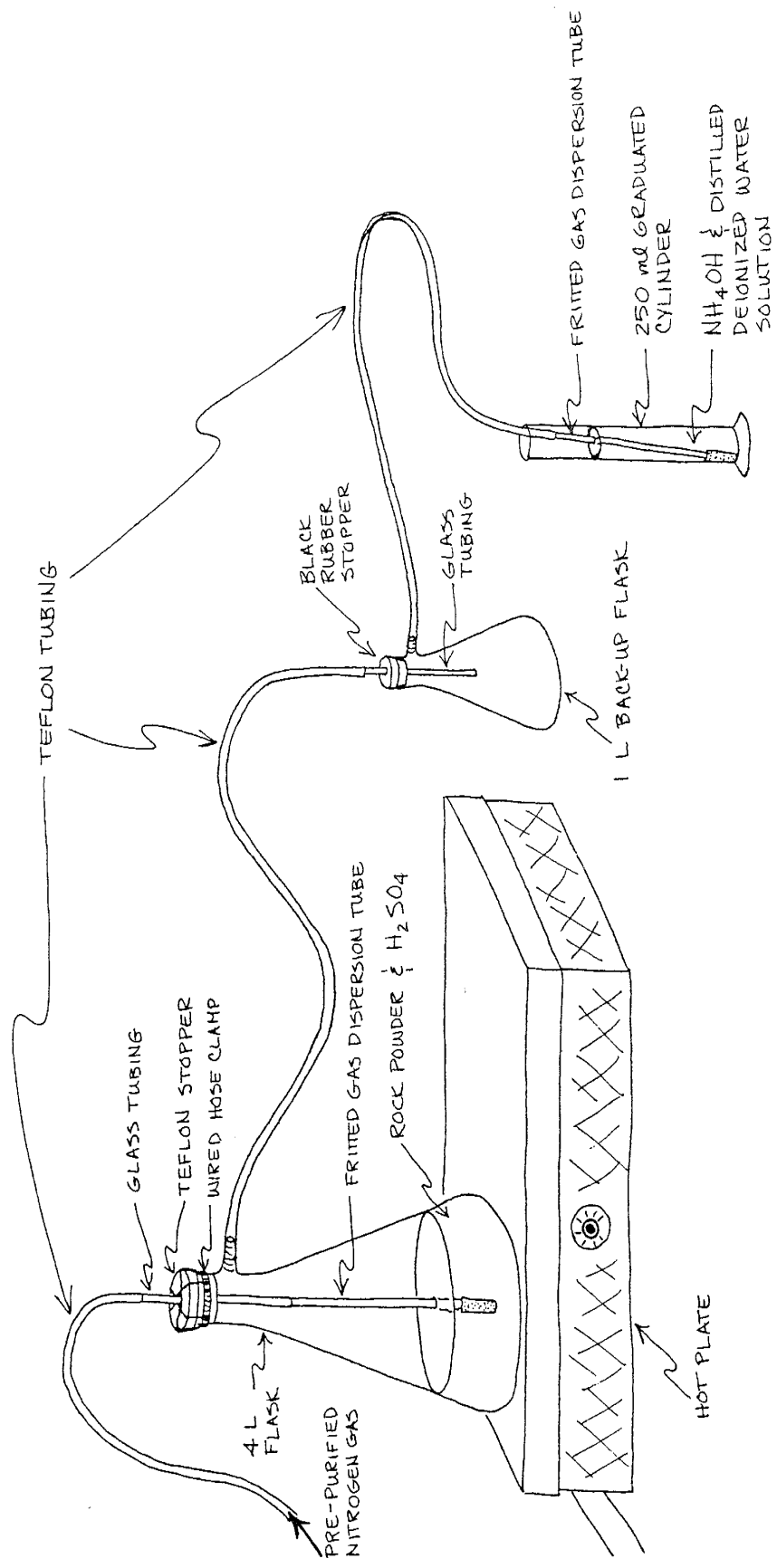
Figure 7. Set-up (within a fume hood, not shown) of the apparatus for the silver chloride extraction process.

The following labels appear in the figure:

- FRITTED GAS DISPERSION TUBE
- 250 ml GRADUATED CYLINDER
- NH₄OH & DISTILLED DEIONIZED WATER SOLUTION
- TEFLON TUBING
- BLACK RUBBER STOPPER
- GLASS TUBING
- 1 L BACK-UP FLASK
- GLASS TUBING
- TEFLON STOPPER
- WIRED HOSE CLAMP
- FRITTED GAS DISPERSION TUBE
- ROCK POWDER & H₂SO₄
- 4 L FLASK
- PRE-PURIFIED NITROGEN GAS
- HOT PLATE

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up (it did not back-up for any of the samples run). Teflon tubing led from the sidearm of the one-liter flask to another fritted gas-dispersion tube identical to the one mentioned previously. This gas-dispersion tube rested on the bottom of a pyrex 250 ml graduated cylinder. All connections were secured with plastic cable-tool ties and/or teflon tape, and during the actual digestion process the silicon stopper was clamped securely to the mouth of the four-liter flask with a hose clamp and wire. Additional equipment used included heat-resistant wool-lined gloves and aluminum foil.

It is worth noting here that simply wrapping the connections actually within the system (ie. those involving the fritted dispersion tubes) with teflon tape was found sufficient to withstand the low gas pressure needed to operate the system. Using plastic cable tool ties only on connections outside the system is preferable for two reasons. First and most important, it eliminates the possibility of leaching trace amounts of chloride into the system from the plastic. Secondly, it simplifies to a degree the cleaning and preparation of the system for the next sample.

Special precaution should be taken to ensure that the black rubber stopper is firmly plugged into the one-liter back-up flask before the gas flow is turned on. Should the stopper pop during the cooking process, the gas flow should

be shut off immediately, the stopper quickly and firmly secured, and the gas flow resumed. Immediate shut off of the gas flow and a quick replugging of the stopper will allow for a minimal loss of chloride from the system.

The digestion procedure was adapted from a procedure obtained via personal communication with Harold Bentley of the University of Arizona, Tucson. The procedure may be found in detail in Appendix III. Each rock powder sample was digested in sulfuric acid to release the chloride of the sample in gas form. The chloride gas was collected in an end cylinder containing a solution of distilled deionized water and ammonium hydroxide. This solution was then acidified with nitric acid, and sufficient silver nitrate was added to precipitate all the chloride as silver chloride. The precipitate was allowed to settle overnight before it was transferred to a dark glass bottle for storage until it could be purified.

The extraction procedure was only partially successful. The amount of chloride extracted from each sample was significantly lower than expected, and it was determined that the sulfuric acid was ineffective in dealing with the highly silicic content of the samples. Hydrofluoric acid is extremely effective in dissolving silicate minerals, and nitric acid attacks metallic minerals in particular. Utilization of a solution combining these two acids might prove a worthwhile alternative to using sulfuric acid.

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Purification

The main objective of the purification process was to reduce the sulfur content of the samples. The presence of sulfur-36 hinders chlorine-36 analysis. Like chlorine-36, the isobar, sulfur-36, forms negative ions. During analysis in the tandem-accelerator mass spectrometer, sulfur-36 ions experiencing the same charge as the chlorine-36 ions, will follow nearly the same path as the chlorine-36 ions in the accelerator beam line system. In order to perform chlorine-36 analysis on a sample of even relatively high chlorine-36 content, the sulfur-36 content must not produce a count of more than approximately one thousand counts per second. Because our total chloride yield from the individual samples was significantly lower than expected, it was absolutely essential that each sample be carefully and repeatedly purified to reduce the sulfur content below the acceptable limit.

Apparatus utilized in the purification process included a fume hood, an oven, a filter/vacuum pump with a hydrophobic microporous membrane and enough Tygon flexible plastic tubing to reach into the fume hood, a hot plate, 47 mm glass filter funnels and 0.45 micron filters. Also used were one-liter pyrex sidearm flasks, 200 ml pyrex culture tubes, size 8 black rubber stoppers, beakers, glass stirring rods and chemical watch glasses (to cover the beakers), parafilm, flat metal spatulas and plastic forceps. In

addition, laboratory squeeze bottles holding distilled
deionized water, dilute nitric acid and reagent grade
ammonium hydroxide were particularly helpful. The stems of
the filter funnels were inserted through the rubber stoppers
and set to rest in the mouths of the flasks.

The purification procedure, like the chloride-
extraction procedure, is a modified version of a procedure
obtained from the University of Arizona at Tucson (H.
Bentley, 1983, written communication). The procedure is
presented in detail in Appendix IV. The silver-chloride
precipitate was washed with distilled deionized water and
then dissolved in concentrated ammonium hydroxide. Barium
nitrate was added and the solution was allowed to stand
overnight in order to precipitate out any sulfate
contaminants as barium sulfate. The solution was filtered
to remove the contaminants, and heated in order to evaporate
the ammonium hydroxide and to reprecipitate the silver
chloride. The silver chloride was washed with distilled
deionized water, redissolved in concentrated ammonium
hydroxide, and reprecipitated out by heating. The samples
were filtered and washed with distilled deionized water,
oven dried, and transferred to dark-glass sample bottles.

After the purification process had been completed, it
was apparent that some of the samples had not yielded
sufficient chloride for analysis using tandem-accelerator
mass spectrometric methods. It was decided that a sodium-

chloride carrier should be added to six of the samples,
SG-1A, SG-1B, DA-1, SLR-2, SLR-3 and SLR-7. These six
samples were redissolved in carefully measured amounts (in
the range of 50 ml) of concentrated ammonium hydroxide, and
an aliquot of approximately thirty milliliters was set aside
from each. These aliquots were later analysed for their
chloride content--the original chloride content, before the
carrier was added. Carefully measured amounts of sodium
chloride (in the range of 35 mg) were added to the six
samples, and they were rerun through the entire purification
process.

It was discovered during a preliminary run of the
tandem-accelerator mass spectrometer that the sulfur content
of some of the samples remained too high for satisfactory
chlorine-36 analysis; additional purification was
necessary. The purification process had been designed for
water samples having a much lower sulfur content than that
of the rock samples. The samples were redissolved, heated
and reprecipitated two more times before finally being
analyzed with a sufficiently low sulfur content.

Analysis

Chlorine-36 analyses were made on the solid (silver
chloride) samples using tandem-accelerator mass
spectrometry. The analyses were performed by Dr. David
Elmore at the Nuclear Structure Research Laboratory of the

University of Rochester, New York.

Chloride analyses were performed on the rock samples by
the Los Alamos National Laboratory using XRF techniques.
The aliquots saved from the six samples to which carrier was
added were analyzed for their chloride content at the New
Mexico Institute of Mining and Technology by Leanna Grossman
of the Chemistry Department, using single column ion
chromatography. An earlier attempt had been made to perform
chloride analyses on the aliquots using chloride titration
techniques, but this method proved futile. Chloride
titration requires the pH of the sample to be lowered to pH
2.3-2.8. As the samples were lowered below pH~7, the
chloride precipitated out as silver chloride.

The chromatograph used in analyzing the aliquots was a
Beckman 110A high performance liquid chromatograph (HPLC)
equipped with a Wescan model conductivity meter. The column
had a pH range of 2-7.5. Our chloride samples (dissolved in
concentrated ammonium hydroxide) were of pH~12. If the pH
of the sample solution was lowered below 7, the chloride
would precipitate out. Thus before the analyses could be
made, it was necessary to bring the sample solutions within
the pH range of 7-7.5. In order to accomplish this 3 ml of
each sample were placed in individual round-bottom flasks.
To evaporate the ammonium hydroxide, the flasks were placed
in a fume hood with a continual stream of air passing over
them for a period of twelve hours. The resulting

precipitate was redissolved in a 4.0 μM buffer (pH = 4.5) yielding a solution of pH 10-11. These solutions were 1/25 diluted using the same 4.0 μM buffer, thereby lowering the pH to ~9. Concentrated phosphoric acid was used to acidify the samples to pH 7.5. It is hoped that very little, if any, silver chloride precipitated out. The sample solutions were filtered through a 0.45 micron millipore funnel and 20 μl of each was injected into the column for analysis (L. Grossman, 1984, written communication).

RESULTS AND INTERPRETATION

Experimental

As noted in the previous section, "Methods", several problems were encountered during the course of laboratory work and analysis of the samples. Most notable of the problems was the extremely low recovery of chloride from the chloride extraction process. The majority of the samples yielded less than 35 mg of silver chloride from an original 0.7 to >1.0 kg of rock. Recovery was so low for samples SG-1C, LG-1A, GR-1, SLR-4 and SLR-6 that analyses of these five samples could not be made.

The measured chlorine-36/total chloride ratios for those samples which were analyzed are listed in Table 4. All of the measured values fall well out of the predicted ranges, and upon first glance the differences between the measured values and the predicted ranges appear quite inconsistent between the individual samples. However, upon closer examination a trend is evident. Figure 8, which plots the measured chlorine-36/total chloride ratios vs. the predicted epigene chlorine-36/total chloride ratios, reveals that the older rocks generally yielded ratios lower than those predicted while the younger rocks yielded ratios higher than those predicted. The one exception is in the case of sample SG-1A, an older rock, which yielded a higher-than-predicted ratio.

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Table 4. Predicted epigene chlorine-36/total chloride ranges and measured chlorine-36/total chloride ratios.

Sample Number	Sample Name	Cl Before Carrier, ppm	Predicted Range ($\times 10^{-15}$)	RATIOS	
				Measured ($\times 10^{-15}$)	Carrier Corrected ($\times 10^{-15}$)
SG-1A	Suwanee bottom	50	113-308	53±19	1,275±457
SG -1B	Suwanee top	39	5,730-16,600	120±11	2,051±188
CZ-2	Carrizozo cave roof	no carrier added	11.5-12.2	≃63	≃63
SLR-2	Punch Bowl	39	333-694	57±16	996±280
SLR-3	Cone 8060	506	252-393	749±200	1,646±440
SLR-5	Panum Cone north	no carrier added	40.4-40.5	465±49	465±49
SLR-7	Mammoth Lakes	134	7,880-9,520	56±7	458±57
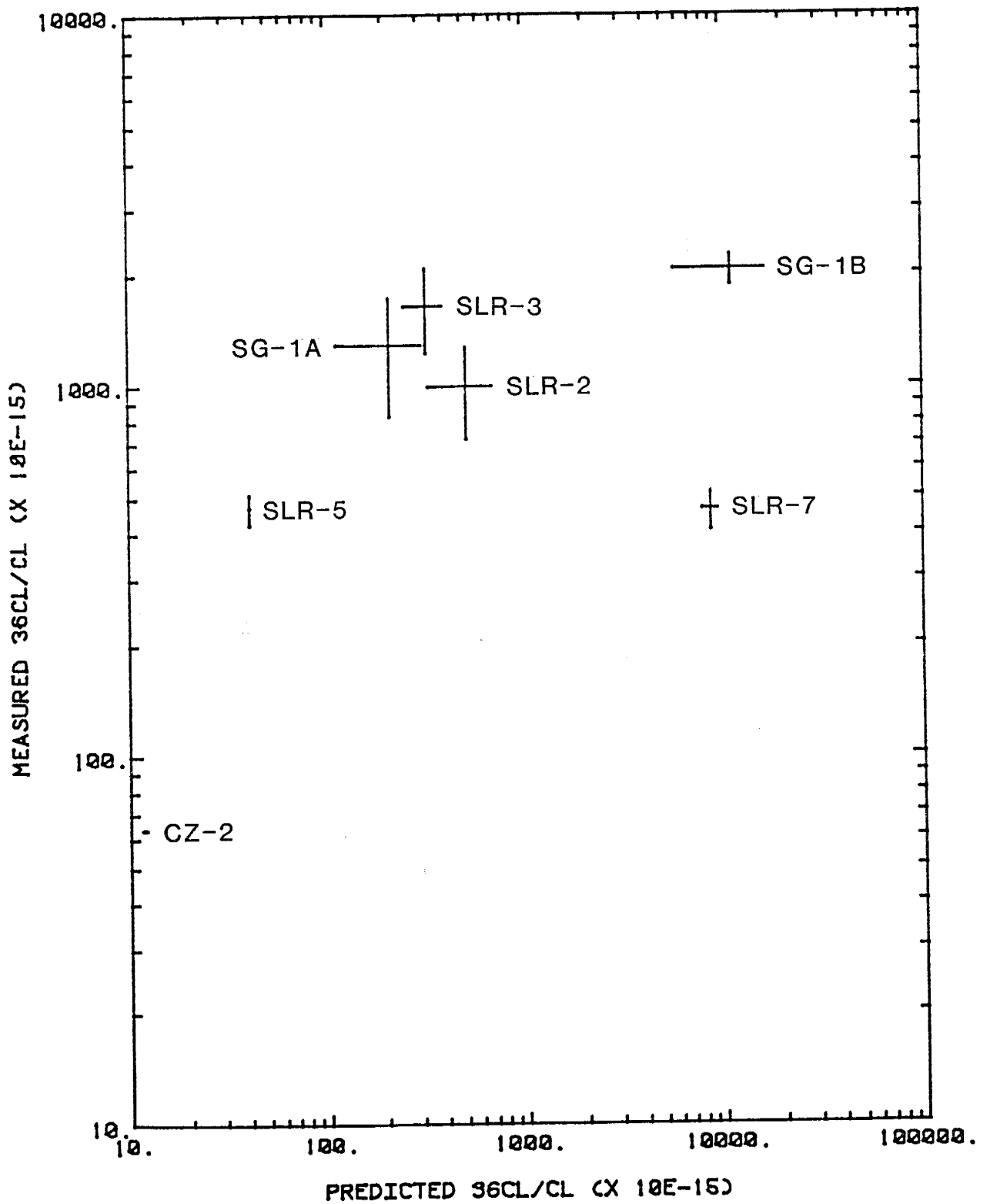
Figure 8. Measured chlorine-36/total chloride ratios plotted against pre-
dicted epigene chlorine-36/total chloride ranges.

It was hoped that by selecting samples of a durable and relatively impermeable rock type, and then carefully ridding the samples of all weathered areas and areas of direct surface exposure, the meteoric chlorine-36 content of the samples would be reduced to a very small and insignificant amount. This may well have been the case had the chloride extraction process produced greater yields. However, the amounts of chloride recovered were so very small that apparently even the extremely low amounts of meteoric chlorine-36 expected to be contained within the rocks proved significant enough to affect the epigene chlorine-36/total chloride ratios. Evidence of the meteoric chlorine-36 having this effect is seen in Figures 9 and 10, which show theoretical meteoric chlorine-36/total chloride ratios for those geographical areas from which the analyzed samples were collected, along with plots of the predicted and measured ratios for the individual samples. A ratio of 280 x 10^{-15} for central eastern California was obtained from Bentley et al. (in press) and a ratio of 700 x 10^{-15} for New Mexico was measured by Phillips et al. (1984). The measured chlorine-36/total chloride ratios for samples SG-1B, CZ-2 and SLR-7 fall inbetween the epigene chlorine-36/total chloride range predicted for the individual samples and the theoretical meteoric chlorine-36/total chloride ratio for the particular geographical area from which each sample was collected. It appears as though the meteoric chlorine-36 content of the
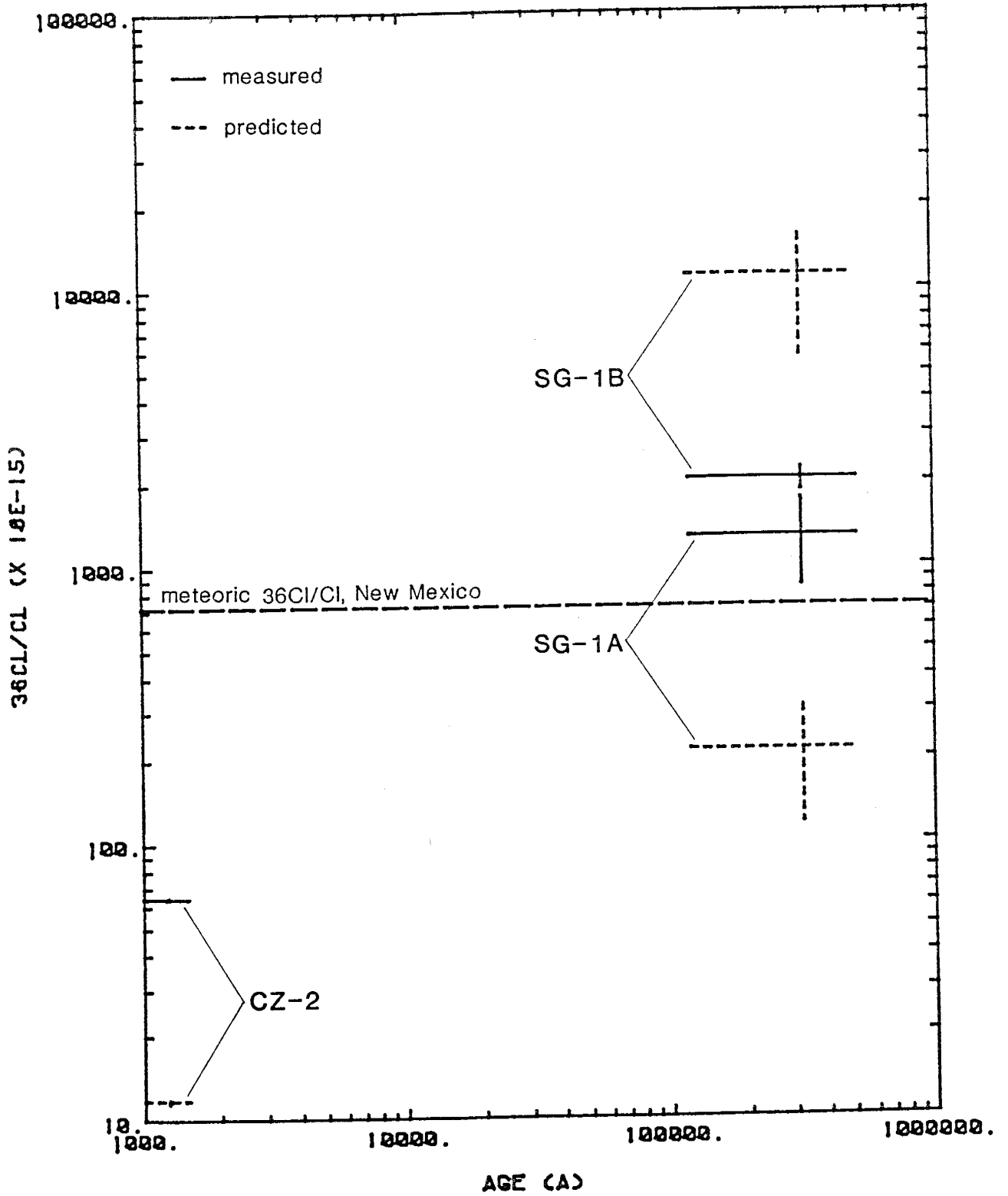
Figure 9. Theoretical, measured and meteoric chlorine-36/total chloride ratios, for New Mexico samples, plotted against age. Meteoric chlorine-36 concentration measured by Phillips et al. (1984).
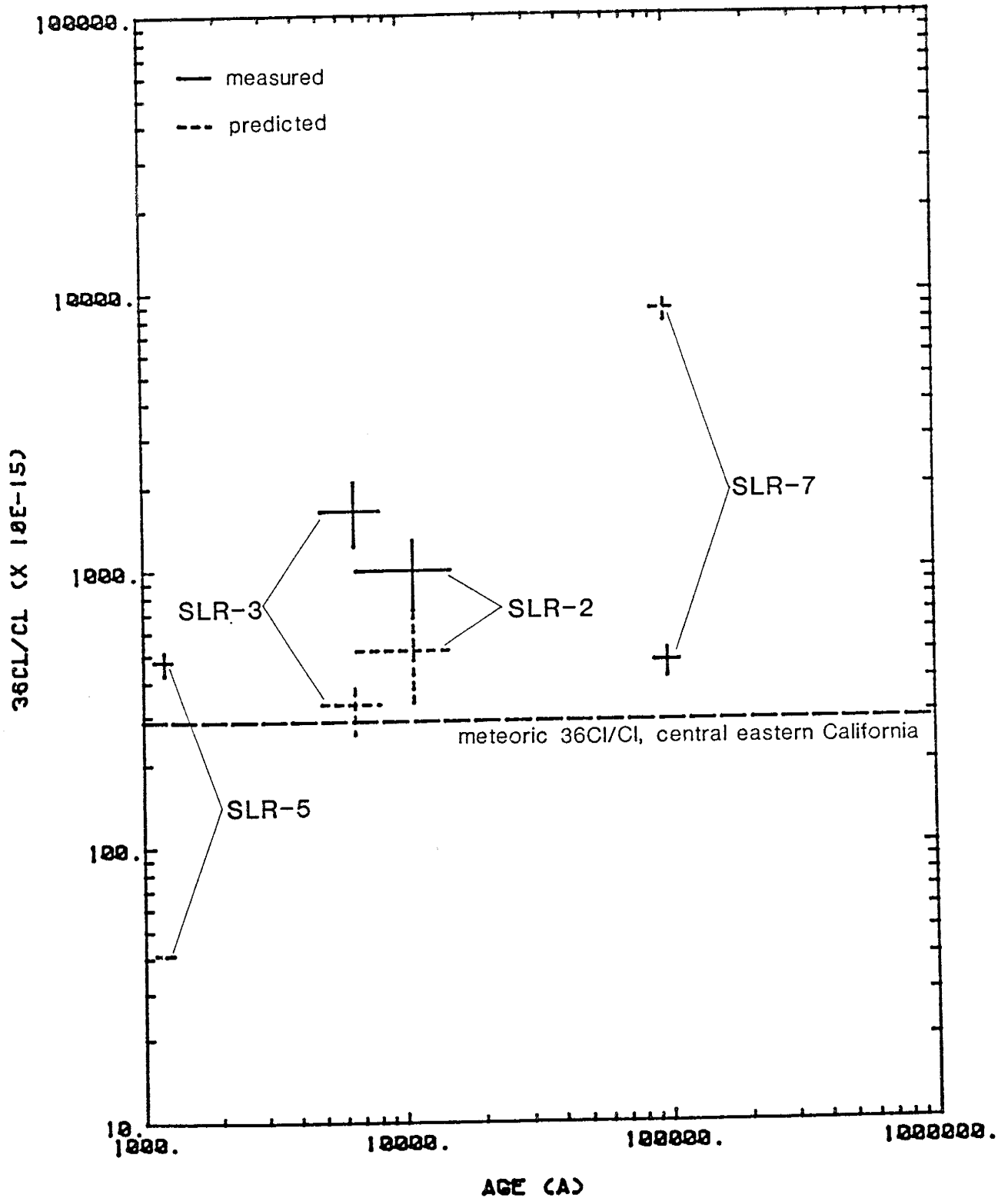
Figure 10. Theoretical, measured and meteoric chlorine-36/total chloride ratios, for California samples, plotted against age. Meteoric chlorine-36 concentration obtained from Bentley et al. (in press).

samples pulled the relatively low epigene chlorine-36/total chloride ratios of the younger rocks up and the relatively high epigene chlorine-36/total chloride ratios of the older rocks down.

The difference between the predicted range of ratios and the measured ratio for sample SG-1A cannnot be accounted for in the same manner, or else the measured ratio would have been lower than the predicted range rather than higher as it is. Sample SG-1A was collected from a depth of 3.3 meters below the earth's surface. It seems possible that the higher-than-expected ratio might be accounted for by the downward infiltration of meteoric chlorine-36, accompanied by chlorine-36 (in an amount greater than that of the meteoric chlorine-36) released from the overlying rocks by weathering. Release of chlorine-36 from the overlying rocks may also account for the high ratio given by sample SLR-5, collected from a depth of approximately 3 meters.

Measured ratios for samples SLR-2 and SLR-3 are also high relative to predicted ranges and to the meteoric concentration. However, these samples were collected from the earth's surface; no chlorine-36 could have been contributed by overlying rocks. The high chlorine-36/total chloride ratios for these samples are probably the result of bomb-chlorine-36 contributions.

Tandem accelerator mass spectrometric analyses of samples DA-1, CZ-1, LA-1 and NSCB-1 had not yet been completed at the time of this writing.

Theoretical

There are three principal factors that determine the relative significance of the release of epigene chlorine-36 into the groundwater at a given locale. These factors include: 1) weathering rates (both the total weathering rate and the chemical weathering rate), 2) chloride content of the rock and 3) geomagnetic latitude. In general, as the rate of weathering increases, the epigene chlorine-36/total chloride ratio decreases, due to the shorter time available for chlorine-36 build-up. In regard to the significance of epigene chlorine-36 release into groundwater, this decrease in the amount of chlorine-36 available for release, due to increased weathering rate, is somewhat countered by an increase in the amount released at any given time. Figures 11 and 12, respectively, present the rate of release of chlorine-36 from a typical basalt (low chloride content) and from a typical rhyolite (relatively high chloride content), at the surface, calculated as a function of weathering rate using equation (5). Figure 13 presents the meteoric chlorine-36 fallout rate as a function of latitude (Bentley et al., in press).
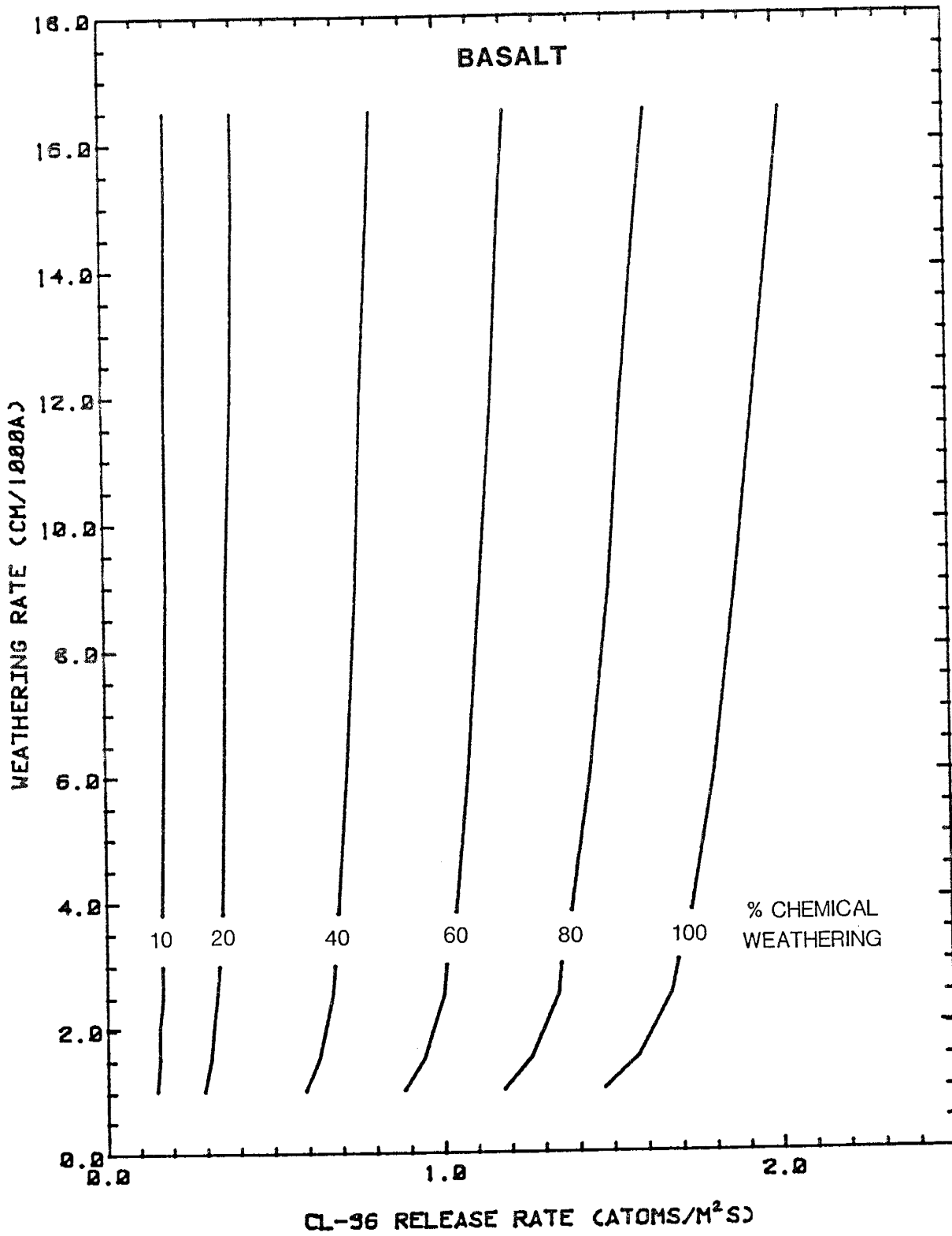
Figure 11. Calculated rates of release of epigene chlorine-36, as a function of total and chemical weathering rates, from a typical basalt at the earth's surface.
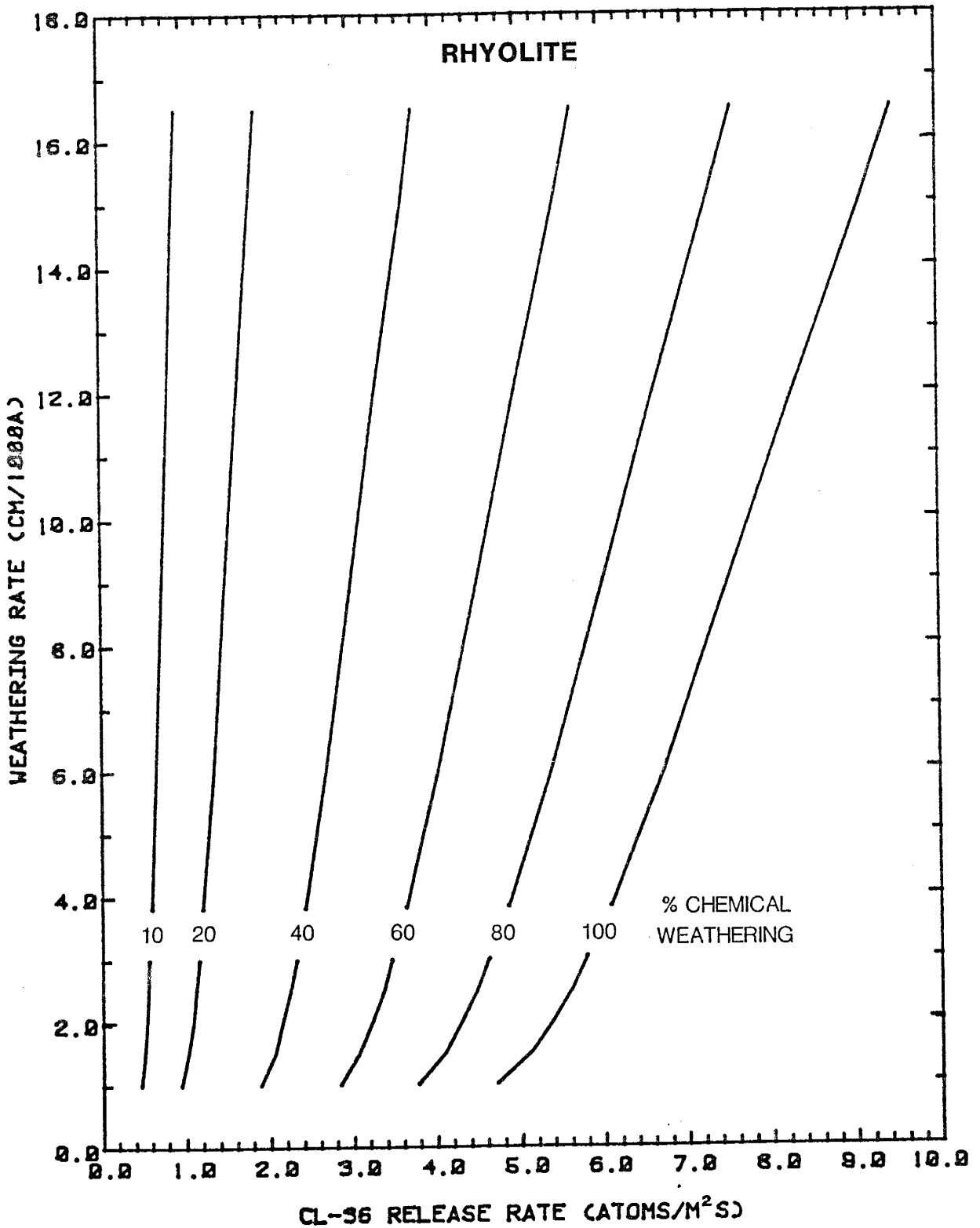
Figure 12. Calculated rates of release of epigene chlorine-36, as a function of total and chemical weathering rates, from a typical rhyolite at the earth's surface.
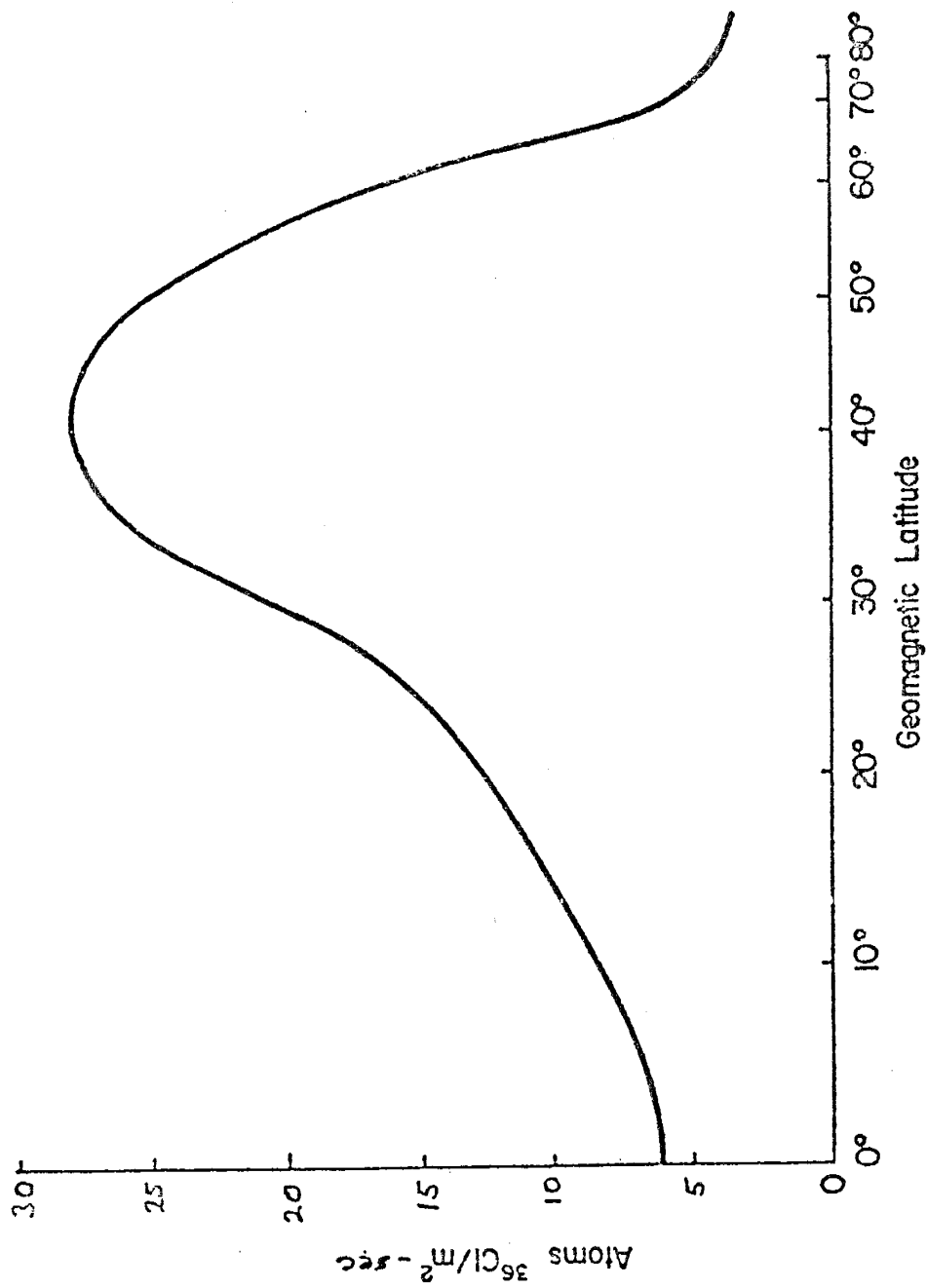
Figure 13. Meteoric chlorine-36 fallout as a function of geomagnetic latitude (from Bentley et al., in press).

It seems reasonable to assume that epigene chlorine-36 is released solely by chemical weathering (ie. if mechanical weathering was to account for 100% of the total weathering rate and chemical weathering was to account for 0%, no epigene chlorine-36 would be released). It is logical then that for any given total weathering rate, the rate of release of epigene chlorine-36 will increase as the percentage of chemical weathering increases. Likewise, with chemical weathering accounting for a given percentage of the total weathering rate, the epigene chlorine-36 release rate will increase as the total weathering rate increases. These two trends are displayed in Figures 11 and 12, though the latter relationship is far less distinctive for the basalt, with its lower chloride content, than it is for the rhyolite.

Comparison of Figures 11 and 12 shows that with all other factors being constant, the rhyolite, with its chloride content of 4.5%, produces higher epigene chlorine-36 release rates than does the basalt of 1.1% chloride. This is expected since chlorine-36 content is generally proportional to total chloride content. However, for any given chloride content, the epigene chlorine-36 release rate will increase as the chlorine-36/total chloride ratio increases.

Figure 13, in conjunction with Figures 10 and 11, makes evident the influence that geomagnetic latitude may have on the significance of the release rate of epigene chlorine-36. Meteoric chlorine-36 fallout peaks at a latitude of approximately 40°. The fallout rate drops at latitudes lower and higher than 40°, dropping at a slightly quicker rate for the higher latitudes. As the fallout rate of meteoric chlorine-36 decreases, epigene chlorine-36 accounts for an increasing percentage of the total chlorine-36 present in the groundwater, and release of small amounts of epigene chlorine-36 into the groundwater increases in significance. In other words, the release of epigene chlorine-36 is significantly more important at the lower and higher latitudes than it is at the middle latitudes.

Table 5 is based on information provided by Figures 11, 12 and 13. It presents the general conditions, under the four most extreme weathering situations, for which the rate of release of epigene chlorine-36 into the groundwater might be considered significant. In summary:

(1) For rocks having a low chloride content (using a basalt of 1.1% chloride as a guide),

- if the chemical weathering percentage is high, the release of epigene chlorine-36 will be significant at the lower and higher latitudes, regardless of the total weathering rate.

- if the chemical weathering percentage is low, the release of epigene chlorine-36 will not be significant, regardless of latitude and regardless of the total weathering rate.

- the release of epigene chlorine-36 will be insignificant at the middle latitudes regardless

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Table 5. General geographic areas (designated by geomagnetic latitude and based on information from Figures 11, 12 and 13) in which the amount of epigene chlorine-36 released into the ground-water systems under different weathering conditions might be considered significant. This study considers the rate of release of epigene chlorine-36 to be significant if it is approximately equal to 10% or greater of the meteoric chlorine-36 fallout rate.

WEATHERING RATES, WR

	LOW TOTAL WR LOW CHEMICAL WR	LOW TOTAL WR HIGH CHEMICAL WR	HIGH TOTAL WR LOW CHEMICAL WR	HIGH TOTAL WR HIGH CHEMICAL WR
LOW CHLORIDE CONTENT ROCK:	NO LATITUDES	LATITUDES < 30° LATITUDES > 60°	NO LATITUDES	LATITUDES < 30° LATITUDES > 55°
HIGHER CHLORIDE CONTENT ROCK:	LATITUDES > 70°	ALL LATITUDES	LATITUDES < 15° LATITUDES > 65°	ALL LATITUDES

LOW TOTAL WR $\equiv$ 3.81 cm/1000 a
HIGH TOTAL WR $\equiv$ 16.51 cm/1000 a

LOW CHEMICAL WR $\equiv$ 10%
HIGH CHEMICAL WR $\equiv$ 100%

LOW CHLORIDE CONTENT: Based on a basalt of 1.1% Cl.
HIGHER CHLORIDE CONTENT: Based on a rhyolite of 4.5% Cl.

of the chemical and total weathering rates.

(2)   For rocks having a higher chloride content (using a rhyolite of 4.5% chloride as a guide),

- if the chemical weathering percentage is high, the release of epigene chlorine-36 will be significant at all latitudes, regardless of the total weathering rate.

- if the chemical weathering percentage is low but the total weathering rate is high, the release of epigene chlorine-36 will be significant at the lower and higher latitudes.

- if the chemical weathering percentage is low and the total weathering rate is low, the release of epigene chlorine-36 will be significant only at the higher latitudes.

SUMMARY

A revision of the equation, from Bentley et al. (in press), for calculation of epigene chlorine-36 build-up with time was presented. The revised equation takes into account chlorine-36 production by 1) spallation of potassium and calcium, 2) neutron activation of chlorine-35 and 3) muon reactions. A similar revision was presented of the equation, from Bentley et al. (in press), for calculation of the rate of release of epigene chlorine-36 due to weathering.

Sixteen basalt and rhyolite samples, of ages spanning the chlorine-36 dating range, were run through a chloride extraction process. The amount of chloride recovered from the rocks, as silver chloride precipitate, was significantly lower than expected, and it was determined that a solution of hydrofluoric and nitric acids would probably be more effective in dissolving the rock powder than was the sulfuric acid utilized in this study. After having been purified, five of the silver chloride samples were analyzed for chlorine-36 concentration. The measured chlorine-36/total chloride ratios were compared to theoretical epigene chlorine-36/total chloride ratios calculated using the revised equation for chlorine-36 build-up with time. It was determined that the measured chlorine-36 concentrations were representative of a

combination of epigene chlorine-36 and meteoric chlorine-36 rather than of epigene chlorine-36 alone.

The rate of release of epigene chlorine-36 as a function of total and chemical weathering rates was considered. It was determined theoretically that the amount of epigene chlorine-36 released into groundwater systems as a result of weathering may be significant in some cases. More specifically, it was determined that with chemical weathering accounting for a high percentage of the total weathering rate, though the total weathering rate may be low, even rocks of low chloride content can yield chlorine-36 in amounts that will be significant in areas of low or high geomagnetic latitude. With a low percentage of chemical weathering, though the total weathering rate may be high, even the amount of chlorine-36 released from rocks of higher chloride content will only sometimes be significant; the amount of chlorine-36 released will be significant, in groundwater systems, only at the lower and higher geomagnetic latitudes.

SIGNIFICANCE AND RECOMMENDATIONS

This study is significant in that it presents revised
equations which take into account chlorine-36 production by
muon reactions for calculation of both epigene chlorine-36
build-up with time and release rate of epigene chlorine-36
due to weathering. It is an early step in the development
of epigene chlorine-36 build-up as a dating tool for
relatively young near-surface rocks. As accuracy and
confidence in utilization of epigene chlorine-36 build-up as
a dating tool increases, so will understanding in regard to
the role of epigene chlorine-36 during weathering and the
relative significance of its release into groundwater
systems.

In addition, this study presents a very general but
comprehensive theoretical examination of the rate of release
of epigene chlorine-36 as a function of total and chemical
weathering rates at the earth's surface. This examination
revealed that release of epigene chlorine-36 into
groundwater systems is indeed significant in some instances,
and should therefore be taken into consideration during the
dating and tracing of groundwater, and not simply ignored as
negligible, as generally has been assumed in the past.

Future studies might include refining the chloride
extraction process for recovery of chloride from rocks,
determination of the rate of release of epigene chlorine-36

as a function of total and chemical weathering rates at various depths, and the use of epigene chlorine-36/total chloride ratios in determining erosion rates.

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APPENDICES

APPENDIX I

	Element	Thermal Neutron-Absorption Cross Section (barns)	Elemental Concentration (mole kg^{-1})		Elemental Thermal Neutron-Absorption Cross Section per Kg Rock (cm^{2}kg^{-1})	
			Basalt	Rhyolite	Basalt	Rhyolite
1	H	0.332	$<6.25 \times 10^{-8}$		$<2.64 \times 10^{-10}$	
2	He	0.007	2.02×10^{-3}	7.06×10^{-3}	8.61×10^{-2}	3.02×10^{-1}
3	Li	71±1	7.77×10^{-5}	6.66×10^{-4}	4.21×10^{-7}	3.61×10^{-6}
4	Be	0.0090	4.62×10^{-4}	2.22×10^{-3}	2.11×10^{-1}	1.02
5	B	760	2.00×10^{-2}	3.08×10^{-2}	4.09×10^{-5}	6.32×10^{-5}
6	C	0.0034	1.57×10^{-3}	1.21×10^{-3}	1.79×10^{-3}	1.38×10^{-3}
7	N	1.9	2.63×10^{1}	2.98×10^{1}	$<3.17 \times 10^{-3}$	$<3.59 \times 10^{-3}$
8	O	<0.0002	1.89×10^{-2}	2.53×10^{-2}	1.14×10^{-4}	1.52×10^{-4}
9	F	0.01	1.61×10^{-7}	3.61×10^{-6}	3.88×10^{-9}	8.67×10^{-8}
10	Ne	0.04	8.70×10^{-1}	1.09	2.64×10^{-1}	3.31×10^{-1}
11	Na	0.505	1.85	7.94×10^{-2}	7.68×10^{-2}	3.30×10^{-3}
12	Mg	0.069	3.26	3.07	4.51×10^{-1}	4.25×10^{-1}
13	Al	0.23	8.55	1.25×10^{1}	8.24×10^{-1}	1.20
14	Si	0.16	5.50×10^{-2}	1.83×10^{-2}	6.62×10^{-3}	2.20×10^{-3}
15	P	0.20	1.35×10^{-2}	8.86×10^{-3}	4.23×10^{-3}	2.78×10^{-3}
16	S	0.52	4.20×10^{-3}	1.55×10^{-2}	8.43×10^{-2}	3.12×10^{-1}
17	Cl	33.3	1.65×10^{-4}	5.96×10^{-4}	6.38×10^{-5}	2.29×10^{-4}
18	Ar	0.64	2.12×10^{-1}	9.72×10^{-1}	2.64×10^{-1}	1.21
19	K	2.07	1.67	1.50×10^{-1}	4.32×10^{-1}	3.88×10^{-2}
20	Ca	0.43	8.45×10^{-4}	1.11×10^{-4}	1.22×10^{-2}	1.60×10^{-3}
21	Sc	24.0±1.0	3.29×10^{-1}	2.13×10^{-2}	1.15	7.46×10^{-2}
22	Ti	5.8	4.63×10^{-3}	1.41×10^{-3}	1.40×10^{-2}	4.24×10^{-3}
23	V	5.00±0.01	5.39×10^{-3}	3.85×10^{-5}	1.01×10^{-2}	7.16×10^{-5}
24	Cr	3.1	2.73×10^{-2}	2.68×10^{-2}	2.17×10^{-1}	2.13×10^{-1}
25	Mn	13.2	1.54	1.61×10^{-1}	2.43	2.54×10^{-1}
26	Fe	2.62	7.30×10^{-4}	7.47×10^{-5}	1.64×10^{-2}	1.68×10^{-3}
27	Co	37.4	2.47×10^{-3}	$<1.02 \times 10^{-4}$	6.68×10^{-3}	2.76×10^{-4}
28	Ni	4.5	1.00×10^{-3}	9.44×10^{-5}	2.29×10^{-3}	2.16×10^{-4}
29	Cu	3.8				

Appendix I

Element		Thermal Neutron-Absorption Cross Section (barns)	Elemental Concentration (mole kg^{-1})		Elemental Thermal Neutron-Absorption Cross Section per Kg Rock (cm^{2}kg^{-1})	
			Basalt	Rhyolite	Basalt	Rhyolite
30	Zn	1.1	1.36×10^{-3}	1.62×10^{-3}	9.03×10^{-4}	1.07×10^{-3}
31	Ga	3.1	2.44×10^{-4}	2.73×10^{-4}	4.55×10^{-4}	5.09×10^{-4}
32	Ge	2.4	1.93×10^{-5}	1.38×10^{-5}	2.79×10^{-5}	1.99×10^{-5}
33	As	4.3	1.33×10^{-5}	4.67×10^{-5}	3.44×10^{-5}	1.21×10^{-4}
34	Se	11.8	1.27×10^{-6}	6.33×10^{-8}	9.03×10^{-6}	4.50×10^{-7}
35	Br	6.7 ± 0.3	9.10×10^{-6}	1.01×10^{-4}	3.64×10^{-5}	4.08×10^{-4}
36	Kr	23.9	2.33×10^{-6}	1.40×10^{-6}	3.35×10^{-5}	2.02×10^{-5}
37	Rb	0.73	3.04×10^{-4}	1.25×10^{-3}	1.34×10^{-4}	5.50×10^{-4}
38	Sr	1.21	6.32×10^{-3}	4.57×10^{-4}	4.60×10^{-3}	3.33×10^{-4}
39	Y	1.31 ± 0.08	3.60×10^{-4}	4.27×10^{-4}	2.84×10^{-4}	3.37×10^{-4}
40	Zr	0.18	1.92×10^{-3}	7.47×10^{-3}	2.08×10^{-4}	8.07×10^{-4}
41	Nb	1.15 ± 0.05	8.18×10^{-4}	3.01×10^{-4}	5.66×10^{-4}	2.08×10^{-4}
42	Mo	2.5	1.15×10^{-5}	2.71×10^{-5}	1.73×10^{-5}	4.08×10^{-5}
43	Tc					
44	Ru	2.6				
45	Rh	156	1.94×10^{-7}		1.82×10^{-5}	
46	Pd	8	3.29×10^{-7}	$<2.82\times10^{-8}$	1.58×10^{-6}	$<1.36\times10^{-7}$
47	Ag	63 ± 1	9.27×10^{-7}	4.64×10^{-7}	3.52×10^{-5}	1.76×10^{-5}
48	Cd	2,500	4.00×10^{-7}	4.45×10^{-7}	6.02×10^{-4}	6.68×10^{-4}
49	In	190 ± 10	6.97×10^{-7}	3.74×10^{-7}	7.95×10^{-5}	4.28×10^{-5}
50	Sn	0.625	7.58×10^{-6}	3.03×10^{-5}	2.85×10^{-6}	1.14×10^{-5}
51	Sb	5.7 ± 1.0	1.23×10^{-6}	1.64×10^{-6}	4.22×10^{-6}	5.63×10^{-6}
52	Te	4.7 ± 0.1	1.57×10^{-8}	1.57×10^{-8}	4.44×10^{-8}	4.44×10^{-8}
53	I	6.2	6.46×10^{-7}	2.05×10^{-7}	2.41×10^{-6}	7.65×10^{-7}
54	Xe	25	3.04×10^{-7}	9.64×10^{-8}	4.58×10^{-6}	1.45×10^{-6}
55	Cs	29	9.03×10^{-6}	3.84×10^{-5}	1.58×10^{-4}	6.68×10^{-4}
56	Ba	1.2	1.79×10^{-3}	8.21×10^{-3}	1.29×10^{-3}	5.93×10^{-3}
57	La	8.9	4.39×10^{-5}	3.96×10^{-4}	2.35×10^{-4}	2.12×10^{-3}
58	Ce	0.6	1.14×10^{-4}	7.42×10^{-4}	4.12×10^{-5}	2.68×10^{-4}
59	Pr	11.6	1.92×10^{-5}	8.52×10^{-5}	1.34×10^{-4}	5.95×10^{-4}

Appendix I

Element		Thermal Neutron-Absorption Cross Section (barns)	Elemental Concentration (mole kg^{-1})		Elemental Thermal Neutron-Absorption Cross Section per Kg Rock (cm^{2}kg^{-1})	
			Basalt	Rhyolite	Basalt	Rhyolite
60	Nd	46	9.71×10^{-5}	3.26×10^{-4}	2.69×10^{-3}	9.03×10^{-3}
61	Pm					
62	Sm	5,600	2.86×10^{-5}	5.32×10^{-5}	9.63×10^{-2}	1.79×10^{-1}
63	Eu	4,600	9.87×10^{-6}	7.24×10^{-6}	2.73×10^{-2}	2.00×10^{-2}
64	Gd	46,000	3.94×10^{-5}	4.71×10^{-5}	1.09	1.31
65	Tb	46	6.92×10^{-6}	6.92×10^{-6}	1.91×10^{-4}	1.91×10^{-4}
66	Dy	1,100	3.63×10^{-5}	3.82×10^{-5}	2.40×10^{-2}	2.53×10^{-2}
67	Ho	64	8.49×10^{-6}	9.09×10^{-6}	3.27×10^{-4}	3.50×10^{-4}
68	Er	166	2.15×10^{-5}	2.51×10^{-5}	2.15×10^{-3}	2.51×10^{-3}
69	Tm	118±6	3.55×10^{-6}	4.08×10^{-6}	2.52×10^{-4}	2.90×10^{-4}
70	Yb	37	1.85×10^{-5}	2.48×10^{-5}	4.12×10^{-4}	5.53×10^{-4}
71	Lu	108	3.14×10^{-6}	3.89×10^{-6}	2.04×10^{-4}	2.53×10^{-4}
72	Hf	105	2.69×10^{-5}	2.24×10^{-5}	1.70×10^{-3}	1.41×10^{-3}
73	Ta	21.3±1.0	4.97×10^{-6}	$\approx5.53\times10^{-5}$	6.38×10^{-5}	$\approx7.10\times10^{-4}$
74	W	19.2±1.0	5.44×10^{-6}	1.31×10^{-5}	6.26×10^{-5}	1.52×10^{-4}
75	Re	86	1.93×10^{-9}	6.12×10^{-9}	9.99×10^{-8}	3.17×10^{-7}
76	Os	15				
77	Ir	440	2.08×10^{-7}	1.04×10^{-7}	5.51×10^{-5}	2.76×10^{-5}
78	Pt	9	1.38×10^{-7}	2.56×10^{-8}	7.46×10^{-7}	1.38×10^{-7}
79	Au	98.8	1.73×10^{-8}	2.54×10^{-9}	1.03×10^{-6}	1.51×10^{-7}
80	Hg	370	3.49×10^{-8}	1.94×10^{-7}	7.77×10^{-6}	4.32×10^{-5}
81	Tl	3.7	1.47×10^{-6}	6.36×10^{-6}	3.28×10^{-6}	1.41×10^{-5}
82	Pb	0.17	1.54×10^{-5}	1.16×10^{-4}	1.58×10^{-6}	1.19×10^{-5}
83	Bi	0.034	7.18×10^{-7}	5.74×10^{-7}	1.47×10^{-8}	1.17×10^{-8}
84	Po					
85	At					
86	Rn					
87	Fr					
88	Ra					
89	Ac					

Appendix I

Element	Thermal Neutron-Absorption Cross Section (barns)	Elemental Concentration (mole kg^{-1})		Elemental Thermal Neutron-Absorption Cross Section per Kg Rock (cm^{2}kg^{-1})	
		Basalt	Rhyolite	Basalt	Rhyolite
90 Th	7.4	8.45×10^{-6}	1.12×10^{-4}	3.76×10^{-5}	4.99×10^{-4}
91 Pa					
92 U	11.78	2.23×10^{-6}	2.10×10^{-5}	1.58×10^{-5}	1.49×10^{-4}

APPENDIX II

Sample Locations

SG-1A,1B,1C, Suwanee basalt flow, New Mexico; U.S.
     Geological Survey South Garcia SE 7.5' Quadrangle,
     lat 34°50'N., long 107°03'W. The samples were taken
     from the southernmost portion of the Suwanee flow, from
     the east side of the road approximately 45 meters
     beyond the point at which Route 6 first cuts the
     southern end of Black Mesa.

LG-1A, Albuquerque volcanic field, New Mexico; U.S.
     Geological Survey Los Griegos 7.5' Quadrangle,
     lat 35°08'N., long 106°43'W. The sample was obtained
     from the point at which the road crests the cliff top.

DA-1, Cat Hills volcanic field, New Mexico; U.S.
     Geological Survey Dalies 7.5' Quadrangle, lat 34°51'N.,
     long 106°50'W. The sample was collected from a small
     roadcut, on the north side of the road, approximately
     0.8 km into the Isleta reservation.

CZ-1,2, Carrizozo malpais, New Mexico; U.S. Geological
     Survey Carrizozo 15' Quadrangle, lat 33°42'N.,
     long 105°56'W. The samples were taken from a cave in
     an embankment on the northern side of Route 380. The
     embankmment is adjacent to a small turnout
     approximately 1.6 km west of the Valley of Fires park
     entrance.

LA-1, Mount Taylor volcanic field, New Mexico; U.S.
     Geological Survey Laguna 7.5' Quadrangle, lat 35°02'N.,
     long 107°23'W. The sample was collected from a small
     roadcut/rest stop on the south side of Interstate 40,
     approximately S50°E from Laguna church.

GR-1, McCartys basalt flow, New Mexico; U.S. Geological
     Survey Grants SE 7.5' Quadrangle, lat 35°05'N.,
     long 107°46'W. The sample was obtained from the
     eastern end of a roadcut on the south side of
     Interstate 40, across from Stuckeys.

NSCB-1, Bonita lava flow, Arizona; U.S. Geological Survey
     O'Leary Peak 7.5' Quadrangle, lat 35°23'N.,
     long 111°32'W. The sample was collected from an area
     of lava squeeze-up at the western edge of the Bonita
     flow, within the Sunset Crater National Monument. An
     aspen tree that was scarred with a rock hammer marks
     the locale.

Appendix II

SLR-2, Mono craters, California; U.S. Geological Survey
    Mono Craters 15' Quadrangle, lat 37°49'N.,
    long 119°02'W. The sample was taken from the summit of
    the small cone within Punch Bowl.

SLR-3, Mono craters, California; U.S. Geological Survey
    Mono Craters 15' Quadrangle, lat 37°49'N.,
    long 119°01'W. The sample was taken from the cone just
    northeast of Punch Bowl. It was procured from a minor
    peak immediately south of the highest point of the
    cone.

SLR-4, Mono craters, California; U.S. Geological Survey
    Mono Craters 15' Quadrangle, lat 37°56'N.,
    long 119°03'W. The sample was obtained from the
    interior dome of Panum Crater, from a site
    approximately 100 meters south of the highest point on
    the west side.

SLR-5, Mono craters, California; U.S. Geological Survey
    Mono Craters 15' Quadrangle, lat 37°56'N.,
    long 119°03'W. The sample was collected from the south
    side of the dome of Panum Cone (north). It was taken
    from underneath an overhang, measuring approximately 3
    meters in thickness, located approximately 20 meters
    above the trail's end.

SLR-6, Mono craters, California; U.S. Geological Survey
    Mono Craters 15' Quadrangle, lat 37°47'N.,
    long 119°01'W. The sample was obtained from Wilson
    Butte. It was procured from the southernmost pinnacle
    of those alongside U.S. Route 395.

SLR-7, Long Valley caldera, California; U.S. Geological
    Survey Mt. Morrison 15' Quadrangle, lat 37°41'N.,
    long 118°59'W. The sample was collected from the south
    side of the cone located approximately 4 kilometers
    north-northwest of the town of Mammoth Lakes.

APPENDIX III

Chloride-Extraction Procedure

The 4 L flask, the 1 L back-up flask, the 250 ml graduated end cylinder and the fritted gas dispersion tube that hangs in the 4 L flask must be replaced with clean apparatus each time the process is run. All should be thoroughly washed with laboratory soap and water. They should then be rinsed several times with distilled water, followed by a couple of rinses with distilled deionized (DD) water. None of the apparatus should ever be "sterilized" using HCl.

1. Measure 180 ml of DD water and 20 ml of reagent grade NH_4OH into the 250 ml graduated end cylinder. This should result in a solution having a pH of 10-12.

2. Measure out 1 L of reagent grade H_2SO_4. Pour the H_2SO_4 and the rock powder into the 4 L flask, alternating between the two but beginning and finishing with acid, and being careful not to get any acid or rock in the arm of the flask. Swirl the flask after each new introduction of acid or rock.

3. Press the black rubber stopper (or preferably a silicon or teflon stopper) tightly into the 1 L back-up flask, and secure the silicon stopper to the 4 L flask with the wired hose clamp.

4. Carefully open the gas flow until the sample first begins to bubble. Then adjust the flow to a pressure of ~5-6 psi. Watch to see that the solution in the 250 ml graduated end cylinder begins to gently bubble (this may take 30 seconds or 10 minutes depending on the sample).

5. Cook the sample at 250°C-300°C for 2 hours. Swirl the 4 L flask every half-hour or so during this time. (Note that the 2 hours does not include the time it takes for the hot plate to heat to 250°C. In order to save time the hot plate may be warming up while the other preparations are being made.)

6. Turn off the hot plate. Swirl the 4 L flask for one or two minutes. Shut off the gas flow, and immediately after the 250 ml graduated end cylinder ceases bubbling remove the silicon stopper with the fritted gas dispersion tube from the 4 L flask. This will prevent matter from being sucked up into the gas dispersion tube and into the tubing.

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7. Remove the fritted gas dispersion tube from the 250 ml graduated end cylinder, and rinse it with a small amount of DD water so that any chloride which might have accumulated on it is washed into the graduated cylinder.

8. Unstop the black rubber stopper from the 1 L back-up flask, and remove the teflon tubing from the side arms of both the 1 L back-up and the 4 L flasks. Rinse the insides of the teflon tubes with DD water and set the tubes aside being careful to keep all connecting portions clean (ie. cover the ends with plastic).

9. To catch any chloride that may have remained in the 1 L back-up flask, use solution from the 250 ml graduated end cylinder to twice rinse the flask, pouring the solution back into the end cylinder each time.

10. Use reagent grade HNO_3 to bring the solution in the 250 ml graduated cylinder down to a pH of 2-3. Transfer this solution to a clean pyrex 1 L flask, and add 150 ml of 0.1 N $AgNO_3$. The solution should now be cloudy with precipitate. Cover and wrap the flask with aluminum foil and let it stand overnight in a dark, cool place.

11. Decant the excess supernatant, using some of it to rinse out a 60 ml dark glass bottle several times. Pour the AgCl precipitate into the bottle. Seal the bottle tightly and store it in a dark, cool place.

APPENDIX IV

AgCl Purification Procedure

The entire purification process is performed in a laboratory
fume hood. Great care to avoid contamination during the
purification process is crucial. Clean plastic or rubber
gloves should be worn at all times, and all equipment should
be washed and treated each time it is used. Laboratory
squeeze bottles holding distilled deionized (DD) water,
dilute HNO_3 and reagent grade NH_4OH are extremely helpful.
- Glassware should first be washed with water and laboratory
  soap, and rinsed with distilled water. Next it should be
  rinsed with dilute HNO_3 followed by DD water, then rinsed
  with reagent grade NH_4OH, and then rinsed several times
  again with DD water.
- The metal bases of the filter funnels, holding the plastic
  support screens, should not be rinsed with HNO_3. These
  can be rinsed with DD water, followed by reagent grade
  NH_4OH, and then rinsed again in DD water.
- The metal spatulas and plastic forceps may be washed in
  the same manner as the filter funnel bases.
- The sample bottle caps should simply be washed with
  laboratory soap and water, and rinsed with distilled water
  followed by DD water.

1. Decant the supernatant and filter the AgCl precipitate
    to near dryness.

2. Leaving the precipitate in the filter funnel, wash it
    thoroughly with DD water, filtering the water through.
    Discard the solution.

3. Dissolve the precipitate by adding approximately 50 ml
    reagent grade NH_4OH to the filter funnel. Filter this
    into a clean flask. Discard any precipitate remaining
    on the filter paper.

4. Add 1 ml $Ba(NO_3)_2$ to the flask (To make the $Ba(NO_3)_2$
    solution, place a good amount of solid $Ba(CO_3)_2$ in a
    flask. Add sufficient HNO_3 to dissolve some of the
    $Ba(CO_3)_2$, but leaving some solid $Ba(CO_3)_2$ in the bottom
    of the flask. When using the $Ba(NO_3)_2$ solution, draw
    off the liquid at the top). Cover the flask with
    parafilm and let it stand overnight.

5. Transfer the solution to the filter apparatus and
    filter into a culture tube standing in a flask (lower
    and raise the culture tube into and out of the flask
    with plastic forceps). Then transfer the solution to a
    600 ml beaker (smaller beakers may be used, but the 600
    ml beaker is more efficient during the heating
    process). Discard any precipitate remaining on the
    filter paper.

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6. Lay a glass stirring rod across the top of the beaker and cover the beaker with a chemical watch glass (concave side up). Evaporate the NH_4OH and reprecipitate the AgCl by heating the beaker at 50°C–65°C. As the precipitate approaches very near the bottom of the beaker, it may be buoyed up with a squirt of DD water to prevent it from sticking to the beaker bottom.

7. Using DD water, rinse the precipitate from the beaker into the filter apparatus. Wash the precipitate thoroughly with DD water, and filter it to near dryness.

8. Redissolve the AgCl precipitate by adding approximately 50 ml reagent grade NH_4OH to the filter funnel. Filter into a clean culture tube standing in a flask and transfer to a 600 ml beaker. Discard any precipitate remaining on the filter paper.

9. Cover and heat the beaker as in step 6.

10. Wash and filter the precipitate as in step 7.

11. Crumple and then flatten a blue filter-cover paper (found between the individual 0.45 micron filters), and lay it on a chemical watch glass. Using a clean metal spatula, place the filter paper holding the AgCl precipitate atop the blue filter-cover paper. Then place the chemical watch glass in an oven, allowing the precipitate to dry overnight at 45°C (if time is particularly short, a drying time of 45 minutes at 65°C should be sufficient).

12. Transfer the dry powder sample to a 30 ml dark-glass sample bottle. Wrap parafilm around the bottle cap.