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# CHLORINE-36 IN NATURE*

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## Introduction

The isotope chlorine-36 has a half-life of 308,000 years, and decays by the emission of a 0.71 Mev beta ray. Since this half-life falls in a time range of value for geological dating it is of interest to explore its occurrence in nature and consider its possible use for geological dating.

The thermal neutron capture cross section of chlorine-35 is rather high, 32 barns. Consequently a likely process for the formation of chlorine-36 in nature is by neutron capture in the element chlorine. Neutrons are produced at the surface of the earth by the nucleonic component of cosmic radiation. This component is most intense at the surface and falls off with depth with a half thickness of about 40 cm of rock. The intensity of the nucleonic component increases with altitude. At an altitude of 10,000 feet the intensity of this component is eight times as high as the intensity at sea level. Another source of neutrons in nature is from ($\alpha$,n) reactions and spontaneous fission in deposits containing uranium and thorium. The presence of chlorine-36 in deposits high in uranium and thorium has been sought for by Edwards and Jonte at the University of Arkansas.[2] In surface rocks containing a few parts per million of uranium and thorium the neutron production rate from cosmic radiation is much higher than the neutron production rate from ($\alpha$,n) reactions and spontaneous fission. In the present investigation we will consider primarily the formation of chlorine-36 by cosmic radiation. It will be seen in the discussion following that it may be possible to employ cosmic ray induced chlorine-36 radioactivity in surface rocks for geological dating.

The specific chlorine-36 activity A induced by cosmic ray neutrons in a surface rock containing g grams of chlorine per gram of rock in a period of time t is given approximately by the expression[1]

$$A = \frac{Pf}{g}(1 - e^{-\lambda t}) \qquad (1)$$

where P is the cosmic ray neutron production rate per gram of rock and f is the fraction of the neutrons absorbed in the element chlorine. The fraction f can be

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* A more detailed report of these investigations is given in Reference 1. Research performed under the auspices of the U. S. Atomic Energy Commission.

estimated from the thermal neutron capture cross sections, $\sigma$, and the number of atoms present, n, of various species constituting the rock by the ratio

$$f = \frac{n_{Cl}\sigma_{Cl}}{\Sigma n_i \sigma_i} \qquad (2)$$

Similarly one may estimate the specific activity of chlorine in a water body containing $g_s$ grams of chlorine per square centimeter of surface area induced by cosmic ray neutrons in a time t by the equation

$$A = \frac{P_s L f}{g_s}(1 - e^{-\lambda t}) \qquad (3)$$

Here $P_s$ is the cosmic ray neutron production rate at the surface and L is the exponential absorption mean free path of the nucleonic component ($I = I_o e^{-x/L}$).

Chlorine from four natural sources has been examined for chlorine-36 activity. Two of these sources were surface rocks, a nepheline-sodalite syenite from Red Hill, New Hampshire, and a phonolite from Cripple Creek, Colorado. The other two samples were chlorine derived from Great Salt Lake water and Atlantic Ocean water. An estimate of the saturation chlorine-36 activity for each of these samples was calculated using Equations (1), (2) and (3). The result of these calculations and the pertinent factors involved are given in Table I. It may be observed that the specific chlorine activity in ocean water would be expected to be very low, far below detectability with present counting techniques. Also, chlorine from Great Salt Lake water would be expected to be very low in chlorine-36, particularly since this water body is not old enough to reach even one tenth the saturation value. The estimated saturation activities for the rock samples are much higher. Present low level counting techniques are capable of detecting about 0.01 disintegrations $min^{-1}g^{-1}$ of chlorine and it should therefore be possible to observe chlorine-36 in surface rocks that have been exposed on the surface for a period of 30,000 years at sea level or a period of 4000 years at 10,000 feet altitude.

The neutron production rates from (α,n) reactions and spontaneous fission were calculated for these rocks and saline waters from their uranium and thorium contents. These calculations were based upon the estimated (α,n) yields of Morrison and Pine[3] modified for the composition of the rock. The results of these calculations are given in Table I along with the corresponding saturation chlorine activity from neutrons arising from this source. These yields are higher than those given in Reference 1 because the earlier calculations assumed that all the alphas in the natural series have the same (α,n) yield as for polonium alphas. When account is taken of the fact that a number of alphas in the natural series have higher energies, and consequently higher (α,n) yields the results listed in Table I are obtained. The authors would like to thank Professor Morrison for pointing out the error in the earlier calculation. It may be observed that the phonolite has a relatively high uranium and thorium content, but the neutron production rate from (α,n) reactions and spontaneous fission is about 100 times lower

## TABLE I

### Calculated $Cl^{36}$ Radioactivities in Surface Rocks and Saline Waters

| | Nepheline-sodalite syenite Red Hill, N. H. | Latite phonolite Cripple Creek, Colorado | Great Salt Lake, Utah | Ocean water |
|---|---|---|---|---|
| Cosmic ray neutron production at the surface,[4] neutrons $g^{-1}\,min^{-1}$ | $5.0 \times 10^{-3}$ | $27 \times 10^{-3}$ | $12 \times 10^{-3}$ (total production $1.7\ n/cm^2$) | $3.1 \times 10^{-3}$ (total production $0.43\ n/cm^2$) |
| Altitude, feet above sea level | 960 | 10,700 | 4200 | 0 |
| Fraction of neutrons absorbed in chlorine, f, calculated from Equation (2) | 0.30 | 0.30 | 0.77 | 0.32 |
| Percent chlorine | 0.35 | 0.35 | 11 | 1.9 |
| Saturation $Cl^{36}$ activity induced by cosmic rays estimated by Equation (1) or (3), disintegrations $g^{-1}\,min^{-1}$ | 0.44 | 2.3 | 0.028 | $2.6 \times 10^{-5}$ |
| Uranium content | 0.6 ppm | 11 ppm | $5.0 \times 10^{-9}$ g/ml | $2.5 \times 10^{-9}$ g/ml |
| Thorium content | 8 ppm | 110 ppm | -- | -- |
| Total neutron production from uranium and thorium by (α,n) reactions and spontaneous fission** | $1.9 \times 10^{-5}$ $g^{-1}\,min^{-1}$ | $2.9 \times 10^{-4}$ $g^{-1}\,min^{-1}$ | $6 \times 10^{-6}$* $cm^{-2}\,min^{-1}$ | $1.1 \times 10^{-3}$* $cm^{-2}\,min^{-1}$ |
| Saturation $Cl^{36}$ activity induced by (α,n) reactions and spontaneous fission, disintegrations $g^{-1}\,min^{-1}$ | 0.002 | 0.025 | $1 \times 10^{-7}$* | $7 \times 10^{-8}$* |

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* Based on uranium content only.

** The following (α,n) yields were used, neutrons per α-particle: rocks, $2 \times 10^{-6}$ for Th series, $1 \times 10^{-6}$ for U series; ocean water $2 \times 10^{-7}$ and Great Salt Lake water $5 \times 10^{-7}$ for U series.

than the cosmic ray neutron production rate. The total neutron production rate in Great Salt Lake and the ocean arising from their uranium contents is very much lower than the total neutron production rate from cosmic radiation.

## Experimental Results

Samples of these rocks were selected from the surface at a location considered to be free from vigorous erosion. The rocks were crushed and ground to about 100 mesh and extracted with hot 20:1 nitric acid. The chlorine was isolated from the solution by precipitation as silver chloride. The silver chloride was dissolved in concentrated ammonium hydroxide, and the silver removed as silver sulfide. The resulting solution was evaporated to yield ammonium chloride. Hydrochloric acid gas was evolved from this ammonium chloride by addition of sulfuric acid in a closed system. The evolved HCl was caught in ammonium hydroxide prepared from gaseous ammonia and distilled water contained in a plastic container. The resulting ammonium hydroxide solution was evaporated to dryness. The purification by HCl evolution was found to remove small amounts of radioactive contaminants. One must be particularly careful to remove potassium. Great Salt Lake salt and Atlantic Ocean salt were purified directly by the HCl evolution procedure.

The samples were counted in a screen wall Geiger-Müller counter containing two liners coated with ammonium chloride. On one liner was placed ammonium chloride derived from Atlantic Ocean water which served as a reference standard, because the arguments above show that chlorine from the ocean should be extremely low in chlorine-36 activity. The other samples were placed on the second liner in succession and counting measurements performed comparing them to the reference liner. The ammonium chloride was placed on the inside of the cylindrical liners by drying an alcohol-water slurry of the salt as the slurry was centrifuged to the wall by spinning the liner on a lathe. Following the series of measurements, the sensitivity of the counter was calibrated with ammonium chloride containing a known amount of chlorine-36 activity. The results of these measurements are summarized in Table II. It may be observed that the only sample that contained a measurable amount of chlorine-36 was the chlorine extracted from the latite phonolite from Cripple Creek, Colorado. This sample was purified further by an additional HCl evolution and again counted. Since the specific activity did not change it was concluded that the activity observed was chlorine-36 and did not arise from contamination. From the level of activity observed in the phonolite one would deduce from Equation (1) that the sample had been exposed for a period of 24,000 ± 4000 years. The surface sample of nepheline-sodalite syenite from Red Hill, New Hampshire, has less than 1/40 the estimated saturation activity which suggests this rock has been on the surface for less than 10,000 years.

## Discussion of Results

It is possible to use the rate of production of chlorine-36 in a surface rock to measure the time of exposure of the rock to cosmic radiation. For example, a flow of lava suddenly exposes a fresh rock surface to cosmic ray bombardment. By assaying the chlorine-36 activity in the lava at the present time,

## TABLE II

### Results of Counting Measurements on Samples of Chlorine from Surface Rocks and Saline Waters

| Origin of the chlorine | Weight $NH_4Cl$ on liner, g | Counting rate above Atlantic Ocean reference standard* cts/min | Specific activity dis/min/g Cl |
|---|---|---|---|
| 1. Atlantic Ocean | 15.0 | -0.06 ± 0.03 | -0.02 ± 0.01 |
| 2. Latite phonolite, Cripple Creek, Colo. | 19.8 | 0.37 ± 0.05 | 0.12 ± 0.02 |
| 3. Nepheline-sodalite syenite, Red Hill, N. H. | 34.6 | 0.01 ± 0.04 | 0.00 ± 0.01 |
| 4. Nepheline-sodalite syenite, Red Hill, N. H., sample from 8 feet below the surface | 36.1 | -0.06 ± 0.03 | -0.01 ± 0.01 |
| 5. Latite phonolite, sample 2 re-evolved | 11.3 | 0.28 ± 0.04 | 0.12 ± 0.02 |
| 6. Atlantic Ocean, sample 1 re-evolved | 26.6 | -0.03 ± 0.04 | -0.01 ± 0.01 |
| 7. Great Salt Lake, Utah | 41.4 | 0.02 ± 0.04 | 0.00 ± 0.01 |

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* Reference liner contained 16.4 g of ammonium chloride.

and knowing the cosmic ray neutron production rate in the rock, and the fraction of the neutrons absorbed in chlorine, the time of exposure of the lava may be determined. The neutron production rate and the fraction of neutrons absorbed in chlorine may be determined by independent nuclear measurements. There are numerous geological events that lead to the sudden exposure of rocks on the surface. Exposure of underlying rock by vigorous glacial scouring of rock surfaces, exposure of rock as glacial boulders quarried out by an active glacier and deposited on the terminal moraine, wave erosion of a rocky shoreline, exposure of a fresh rock surface by faulting, and rock exposed by the flow of water in a stream or river channel that is later abandoned are a few examples of geological processes suddenly exposing rock surfaces to cosmic ray neutrons. In order to date the time of exposure it is necessary to insure that the rock surface has not been eroded more than a few inches since its exposure. This is a difficult requirement but one that can be met in many instances, for example, in the case that glacial striae appear on the surface. Another requirement is that the rock contain a workable amount of chlorine. It may be observed from Equations (1) and (2) that the specific activity is independent of chlorine concentration. Large amounts of rock must be extracted if the chlorine content is below 0.05% in order to obtain a large enough sample of chlorine for a sensitive measurement. The average chlorine content of igneous rocks is about 0.02%,[5] according to the most recent survey.

The sensitivity of the dating procedure suggested is illustrated in Figure 1, and compared with the well established carbon-14 dating method. On the figure is plotted the increase in counting rate of a counter, against the age of the sample measured. A curve is given for an acetylene filled proportional counter for carbon-14 assay. The counter reported by Suess[6] and currently used by the U. S. Geological Survey for carbon-14 dating was selected because this counter is approximately the same size and has the same background as the counter used in these studies. Two curves are given for chlorine derived from surface rocks at sea level and at 10,000 feet elevation. The shaded areas indicate the magnitude of the statistical counting error of one and four times sigma. At 10,000 feet the chlorine activity reaches the $4\sigma$ level at 4000 years, and at sea level reaches the $4\sigma$ level at 30,000 years. The carbon-14 method reaches the $4\sigma$ level in about 40,000 years which represents the limit of sensitivity for this counter. The two methods have a large area of overlap at mountain altitudes, from 4000 to 40,000 years. It would then be particularly interesting to check the chlorine-36 method suggested against carbon-14 dates in this time range. From such a comparison one may also check the reasonable assumption of constant cosmic ray intensity with time.

The expressions (1) and (2) may be used to estimate the amount of other radioactive isotopes induced in surface rocks by cosmic ray neutron capture. Of the elements of high neutron capture cross section that occur in igneous rocks, cobalt appears particularly interesting. Cobalt-60 has a short half-life, 5.7 years, and would therefore be at equilibrium in any carefully chosen surface rock. The observed saturation cobalt-60 activity should be useful to determine the cosmic ray neutron production rate in a surface rock. A means of testing the expressions used in estimating these neutron induced activities is to prepare artificial rock

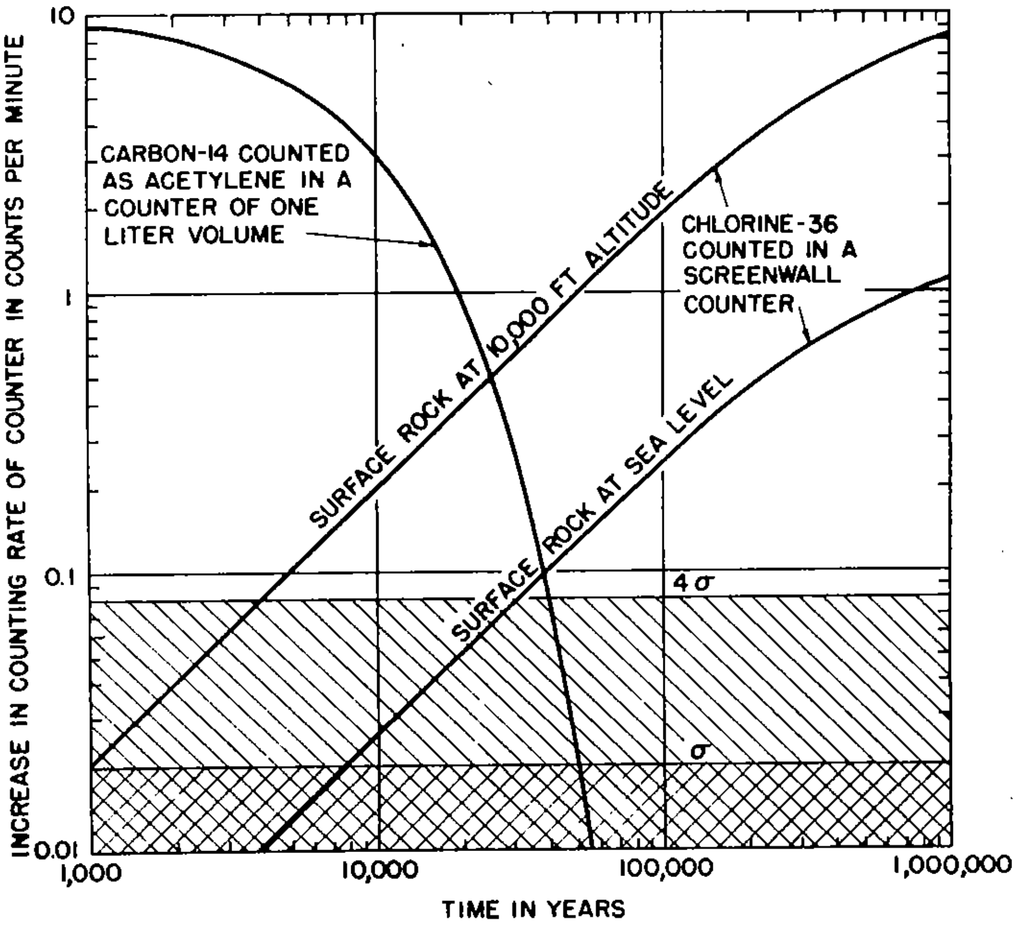

Figure 1. Comparison of $C^{14}$ and $Cl^{36}$ dating.

samples with elements of high neutron capture cross sections diluted with elements of low neutron capture cross section. Some preliminary experiments along these lines have been performed with mixtures of gold and silica. The $Au^{198}$ activity induced has a 2.7 day half-life and therefore reaches the saturation value in a reasonable time for laboratory experiments.

## References

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## Discussion

CRAIG: What do you use for the amount of chlorine for the ocean, just the amount within two or three mean free paths?

DAVIS: The total amount of chlorine per square centimeter of surface.

REYNOLDS: Why is the saturation activity for Great Salt Lake so low?

DAVIS: The Lake has an average depth of 13 feet, and is high in chlorine. The activity is therefore diluted with a large amount of salt. This is true for most bodies of saline water. There could be some shallow bodies of water that are low in chlorine, if so, the saturation activity might get up to 0.1 counts per minute per gram of chlorine.

UREY: Were you able to determine the age of Great Salt Lake?

DAVIS: No, we did not observe a measurable amount of chlorine-36 activity. However, the lake basin has been filled and evaporated to dryness several times, so that even if we had observed some activity it would be impossible to set a meaningful date on the lake.

CRAIG: There are lakes in the far west that have been evaporating steadily and you could compare these with radiocarbon. You could date the end of alluvial and the beginning of the evaporation and tie this in with carbon-14 in places like Borax Lake.

DAVIS: The difficulty with these lakes is that the chloride content is very high. This makes the specific chlorine-36 activity low.

CRAIG: In these lake deposits there is a little salt in a large amount of sodium carbonate.

DAVIS: To date such a deposit one must be certain that the salt is not mixed up when it rains, so that the salt observed on the top has always been there.

WASSERBURG: Isn't there a lot of boron in that deposit? I would like to ask you to comment on the possibility of using chlorine gas at high pressure in a counter to increase the sensitivity.

DAVIS: Chlorine has a high electron attachment tendency so that the counter would not behave correctly. It would be hard to get 3 grams of chlorine in the gas phase in a counter and have it count. To my knowledge no one has ever made a chloride crystal count. I do not know whether an organic chloride in a scintillating liquid would work. Ammonium chloride on a liner is quite sensitive and is the best thing we have thought of.

EDWARDS: There is no reason why you could not use an organic chlorine compound scintillator.