Argon-36 from Neutron Capture on Chlorine in Nature

D. E. Sinclair and O. K. Manuel

Department of Chemistry, University of Missouri, Rolla, Missouri (USA)

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Argon analysis on samples of sodalite from Dungannon, Ontario reveals an excess of ^{36}Ar from neutron capture on ^{35}Cl and excess ^{40}Ar from the decay of ^{40}K. These results indicate an average production rate of 5.6×10^2 atoms of ^{36}Cl per year per gram of chlorine over the age of the mineral, 3.9×10^8 yrs. The surface residence time of chlorine-rich rocks may be determined from the amounts of ^{36}Ar which accumulate during the time period of exposure to cosmic rays.

Elements in the surface material of the earth are exposed to a natural neutron flux due to the interactions of cosmic rays with matter, to neutron emission in the spontaneous fission of uranium, and to (α, n) reactions in rocks containing elements which emit α-particles. The first studies of this natural neutron flux[1, 2] were undertaken shortly after Chadwick's[3] discovery of the neutron, and recognization of the potential utility for age determinations with radiocarbon from the $^{14}N(n, p)^{14}C$ reaction in the atmosphere[4] resulted in numerous studies of cosmic-ray produced neutrons in the atmosphere. The results of several investigations, showing the dependency of cosmic-ray neutrons on altitude and latitude, are summarized by Lingenfelter[5] and Haymes[6].

Haymes[6] notes that the most of the cosmic-ray produced neutrons are captured in the atmosphere, and only a small fraction of these neutrons are captured by elements of the solid earth. Nevertheless, in surface rocks the neutron production rate from cosmic rays is generally higher than the neutron production rate from natural radioactivity. For example, at $\approx 41°$ N Montgomery and Tobey[7] report the production rate of neutrons in surface rock near sea-level to be about 10^3 neutrons g^{-1} yr^{-1}. This is about 40 times the production rate of neutrons from the radioactivity of a typical granite[8]. At the average continental elevation of 840 m, the production rate of neutrons in surface rock from cosmic rays is approximately one hundred times that of typical granite[8]. Since the neutron-producing component of cosmic rays has an absorption mean free path[9] of 165 g/cm^2, neutron production from cosmic rays exceeds that from the natural radioactivity of average crustal rocks in only the first 2 – 3 m. Quantitative measurements of the integrated neutron flux which has acted on rocks may therefore provide information on their surface residence time.

Chlorine absorbs a major portion of neutrons in rocks containing $\gtrsim$ 0.5% chlorine. The isotope, ^{35}Cl, has a thermal neutron cross-section of 44 barns to produce the 380,000 year half-life chlorine isotope, ^{36}Cl. Davis and Schaeffer[10] and Bagge and Willkomm[11] have measured the activity of ^{36}Cl in chlorine-rich surface samples and compared this with the saturation activity expected from cosmic-ray produced neutrons to calculate the surface residence time. They note that the half-life of ^{36}Cl is convenient for studies of geological processes of the early Pleistocene glacial epoch, including events which occurred 60,000 – 1,000,000 years ago and therefore not convenient for dating by the ^{14}C method.

Previous studies in this laboratory on the isotopic compositions of xenon and krypton in terrestrial ores have revealed neutron capture products ranging in amount from that expected in typical rocks[12] up to $\approx 10^4$ times that expected in typical rocks[13, 14]. It has been suggested by Takagi et al.[15] that the excess ^{129}Xe and ^{131}Xe in tellurium ores may result from violent explosions which occurred in our galaxy as recently as 20 m.y. ago and caused an increased flux of negative muons and their secondary neutrons deep in the earth.

This study on the isotopic composition of argon in sodalite was undertaken in order to see if excess ^{36}Ar could be detected and to compare the integrated neutron flux required to account for any excess ^{36}Ar with the current neutron flux acting on surface rocks.

Reprint requests to Prof. Dr. O. K. Manuel, Department of Chemistry, University of Missouri, 101 Chemical Engr. Bldg., *Rolla, Missouri 65401*, USA.

Measurements

Approximately 75 g of sodalite were made available for this study by the Division of Mineralogy of the National Museum of History, Washington, D.C. This sodalite, catalogued No. 75 980 by the Smithsonian Institute, was taken near the surface of the Princess sodalite mine at Dungannon, Ontario[16]. Thin section examination showed that the sample contained rounded remants of coarse-grained plagioclase, orthoclase and nepheline, which are partly altered to vesuvianite, calcite, and the dominant sodalite.

1. Noble Gas Analyses

In order to determine the presence and approximate release temperature of excess ^{36}Ar, argon was extracted by stepwise heating of a single piece of sodalite. The sample used for this initial study, Sample 1, weighed 11.917 g. The concentration and isotopic composition of argon released at progressively increasing extraction temperatures of 600°, 800°, 1200° and 1400 °C were analyzed statically in a glass 60° mass spectrometer with a 4.5 inch radius of curvature[17]. The gas extraction and cleanup procedures have been described earlier[18].

The isotopic spectrum was measured 10 times for each analysis. The mass spectrometer was calibrated before and after each sample by analyzing small volumes of air ($\approx$ 0.01 cc STP). The spectrometer showed no background peaks in the 35 – 39 mass range, and the small background signal at mass 40 was always negligible relative to the ^{40}Ar signal from the samples. During the analyses, no extraneous peaks were observed at masses 35, 37, 39, or 41, peaks which might indicate the presence of hydrocarbons.

Anomalous isotope ratios in argon from the sodalite gradually approached the composition of atmospheric argon[19] during spectrometric analysis, as expected for a spectrometer memory of atmospheric standards. The rate of change in the isotope ratios during analysis is greater for the more anomalous ratios. The maximum variations observed in the ^{36}Ar/^{38}Ar ratios during analysis occurred for the argon released from Sample 1 at 1200 °C where the measured ^{36}Ar/^{38}Ar ratios varied from 5.87 to 5.65 during the time of the analysis. The isotopic spectrum was calculated to the time of sample introduction into the analyzer tube, and the errors reported in the isotope ratios are one standard deviation (σ) from the least squares line through the observed ratios as a function of residence time in the mass spectrometer.

Approximately 15 grams of sodalite were crushed in a mortar and pestle to -50 mesh size and an aliquot of this weighing 7.266 g was used as Sample 2. The argon was extracted in two steps, at 800 °C and 1400 °C, and analyzed in the manner employed for Sample 1. In order to determine the K-Ar age, the integrated neutron flux, and the neutron flux expected from natural radioactivity, other aliquots were analyzed for chlorine, potassium and uranium.

2. Chlorine Analysis

Duplicate aliquots of the crushed sodalite sample, weighing approximately 1 g each, were analyzed for chlorine gravimetrically using the method of Koltoff and Sandell[20]. Briefly, the method consists of a $NaCO_3$ fusion followed by precipitation of the chloride using $AgNO_3$. The precipitate was redissolved with NH_4OH, filtered and the filtrate acidified. The resultant precipitate was filtered on tared filter paper, dried and weighed.

3. Potassium Analysis

An aliquot of crushed sodalite weighing 0.1000 g was analyzed for potassium by atomic absorption. The aliquot was mixed with 2 ml HF and the mixture was heated to dryness. The residue was dissolved in 10 ml of 5 N HCl and diluted to 100 ml by the addition of a 1% solution of $(NH_4)_2HPO_4$. This solution was analyzed, together with potassium standards in the range of 0.5 to 10 ppm, on a Perkin Elmer 305 A atomic absorption unit operated in the emission mode. A reagent blank consisting of 10 ml of 5 N HCl and 90 ml of 1% $(NH_4)_2HPO_4$ was used to zero the instrument.

4. Uranium Analysis

An aliquot of the crushed sodalite weighing 0.3611 g was analyzed for uranium by neutron activation. The method consists of irradiating the sample with uranium monitors for 30 minutes at a flux of $\approx 2 \times 10^{12}$ n/cm^2 sec and beta counting $^{131-135}$I from neutron induced fission of uranium. Becker et al.[21] give the experimental details.

Results and Discussion

The results of our analyses are given in Table 1. The amounts of excess ^{36}Ar and excess ^{40}Ar, shown as ^{36r}Ar and ^{40r}Ar, respectively, were calculated from the following equation:

$$[{}^{ir}\mathrm{Ar}] = [({}^{i}\mathrm{Ar}/{}^{38}\mathrm{Ar})_{\mathrm{sod.}} - ({}^{i}\mathrm{Ar}/{}^{38}\mathrm{Ar})_{\mathrm{air}}]\,[{}^{38}\mathrm{Ar}]_{\mathrm{sod.}} \tag{1}$$

Table I. Argon, Chlorine, Potassium and Uranium in Sodalite from Dungannon, Ontario.

Element	Sample 1				Sample 2	
	600 °C	800 °C	1200 °C	1400 °C	800 °C	1400 °C
Argon Isotopes						
^{36}Ar	5.43 ± 0.02	5.38 ± 0.06	5.89 ± 0.06	5.63 ± 0.10	5.35 ± 0.01	5.61 ± 0.01
^{38}Ar	$\equiv 1.00$	$\equiv 1.00$	$\equiv 1.00$	$\equiv 1.00$	$\equiv 1.00$	$\equiv 1.00$
^{40}Ar	1712 ± 13	7314 ± 26	$25{,}500 \pm 1{,}100$	$32{,}100 \pm 1{,}100$	2598 ± 5	5856 ± 40
Argon Content (cc STP/g)						
$^{38}\mathrm{Ar} \times 10^{10}$	2.41 ± 0.48	17.4 ± 3.5	3.24 ± 0.65	1.26 ± 0.25	17.3 ± 3.5	8.13 ± 1.63
$^{36r}\mathrm{Ar} \times 10^{10}$	0.19 ± 0.07	0.52 ± 1.05	1.75 ± 0.37	0.35 ± 0.14	0.00 ± 0.21	2.11 ± 0.43
$^{40r}\mathrm{Ar} \times 10^{7}$	0.32 ± 0.07	100 ± 20	77 ± 16	38 ± 8	17.6 ± 3.5	34.8 ± 7.0
Chlorine Content	— — — — —				$2.6 \pm 0.2\%$	
Potassium Content	— — — — —				$0.31 \pm 0.01\%$	
Uranium Content	— — — — —				1.6 ± 0.1 ppm	

where i is the mass number of the isotope and the concentration of ^{38}Ar per gram of sodalite is represented by $[^{38}\mathrm{Ar}]_{\mathrm{sod.}}$. Due to variations in the sensitivity of the mass spectrometer, the $[^{38}\mathrm{Ar}]_{\mathrm{sod.}}$ values are reliable to within $\pm 20\%$, and the errors shown on the isotope ratios represent one standard deviation ($\pm \sigma$) due to statistical variations in the spectrometer signal and in the mass discrimination correction.

Atmospheric-type argon[19] was selected to represent the trapped component because the ^{36}Ar/^{38}Ar ratios observed in argon from the sodalite are $0-10\%$ higher than the ^{36}Ar/^{38}Ar ratio in atmospheric argon, and the ^{40}Ar/^{38}Ar ratios are higher than the ^{40}Ar/^{38}Ar ratio in the atmosphere by factors of 1.08 to 20.30. Therefore all the ^{36}Ar/^{38}Ar ratios and all the ^{40}Ar/^{38}Ar ratios in argon from the sodalite can be resolved in terms of mixtures of atmospheric argon with excess ^{36}Ar and with excess ^{40}Ar. Further, the lowest values observed for the ^{36}Ar/^{38}Ar and ^{40}Ar/^{38}Ar ratios in the sodalite are close to atmospheric values[19], as would be expected if the nonradiogenic argon in sodalite were atmospheric in composition.

Although one cannot totally rule out the possibility that part of the excess ^{36}Ar might be due to mass fractionation effects of argon diffusing into the rock, there are three reasons to doubt that this mechanism is responsible for the high ^{36}Ar/^{38}Ar ratios observed in sodalite. Firstly, the highest ^{36}Ar/^{38}Ar ratio observed in the argon from sodalite is 10% greater than the ^{36}Ar/^{38}Ar ratio in air. A study[22] on the isotopic composition of argon in 27 rocks revealed some variations due to fractionation, but the largest ^{36}Ar/^{38}Ar ratio observed in these rocks was only 2% higher than the average ^{36}Ar/^{38}Ar ratio observed in air, and only 1% higher than the ^{36}Ar/^{38}Ar ratio observed in one of the air standards. Secondly, there have been no reports of such high ^{36}Ar/^{38}Ar ratios in any other terrestrial samples, and there is no reason to believe sodalite possesses some unusual ability to fractionate the argon isotopes. Finally, the isotope, ^{36}Ar, is the decay product of ^{36}Cl, an isotope which has been detected[10, 11] earlier in samples of chlorine-rich surface rocks, such as sodalite. Therefore the results of these earlier studies[10, 11] predict the presence of excess ^{36}Ar by a very plausible mechanism: neutron-capture on ^{35}Cl to produce ^{36}Cl, and the subsequent β-decay of ^{36}Cl to produce an enrichment of ^{36}Ar.

The results of our initial noble gas analysis on sodalite, Sample 1, demonstrated the presence of excess ^{36}Ar and indicated that the bulk of this ^{36r}Ar is released at extraction temperatures >800 °C. Therefore, only two gas extraction temperatures were used for the aliquot of crushed sodalite, Sample 2. The argon released at 800 °C appeared to be primarily atmospheric-type argon plus some radiogenic ^{40}Ar. At 1400 °C, where the sample melted, a prominent enrichment of both ^{36}Ar and ^{40}Ar was observed. The total amounts of ^{36r}Ar in Sample 1 and Sample 2 $(2.81 \pm 1.63) \times 10^{-10}$ cc STP/g and $(2.11 \pm 0.64) \times 10^{-10}$ cc STP/g, respectively, agree within the error limits of the measurements. However, Sample 1 contained about 4 times as much ^{40r}Ar as did Sample 2. This difference may be due to differences in the relative amounts of potassium-rich feldspathoids in the two samples[23]. Since we have analyzed for potassium, chlorine and uranium in other aliquots of Sample 2, but have no quantitative information on the content of these elements in Sample 1, we will use the argon data from Sample 2 to calculate the K-Ar age and the integrated neutron flux for the sodalite.

The K-Ar age of the crushed sodalite sample can be calculated from the concentrations of potassium and ^{40r}Ar given in Table 1. Assuming the potassium to be of normal isotopic composition and using the decay parameters given by Beckinsale and Gale[24], we obtain an age equal to $(0.39 \pm 0.07) \times 10^9$ yr.

If all of the ^{36r}Ar is due to neutron capture reactions on chlorine, the above age can be used with the chlorine and ^{36r}Ar content of Sample 2 to obtain the average production rate of ^{36r}Ar. From the total argon in Sample 2 we find that $[^{36r}\mathrm{Ar}]_{\mathrm{sod.}} = (2.11 \pm 0.64) \times 10^{-10}$ cc STP/g, which requires an average production rate of 560 ± 210 atoms of ^{36r}Ar per gram of chlorine per year over the past 390×10^6 yr. Since gas loss over geologic time would reduce the content of both ^{40r}Ar and ^{36r}Ar, this process would cause very little error in the calculated production rate for ^{36r}Ar.

The neutron flux acting on the sodalite can be obtained from the production rate of ^{36r}Ar and the cross-section of ^{35}Cl for neutron capture. If the bulk of the neutron capture reactions on ^{35}Cl in the sodalite occurs for thermal neutrons, then the data shown in Table 1 for Sample 2 indicates an average neutron flux of $(1.0 \pm 0.4) \times 10^3$ neutrons/cm^2 yr. Alternately we can estimate the average neutron density directly from the amount of ^{36r}Ar and the age of the sodalite. For this calculation we use the model of Davis and Schaeffer[10], where the number of neutrons absorbed per gram of material is assumed to be equal to the number of neutrons produced by cosmic rays per gram. In chemically pure sodalite[23], $Na_4(AlSiO_4)_3Cl$, the chlorine content is 7.3% but this element captures 91% of all thermal neutrons according to the neutron capture cross-sections given by Lederer et al.[25]. Davis and Schaeffer[10] have shown that chlorine captures 30% of the neutrons in nepheline-sodalite syenite containing only 0.35% chlorine. Lacking complete analytical data on all elements in our samples, we assume that $\approx 75\%$ of all thermal neutrons are captured by chlorine and that the density of our sodalite samples are ≈ 2.5 g/cm^3. These assumptions and the data in Table 1 indicate a specific neutron production rate of 480 ± 180 neutrons/g yr. By comparison, a uranium concentration of 1.6 ppm is expected to produce ≈ 0.8 neutrons/g yr from spontaneous fission and ≈ 16 neutrons/g yr from (α, n) reactions[10]. Thus, the ^{36r}Ar observed in this experiment appears to be the product of cosmic-ray produced neutrons.

The results of our measurement of the average number of neutrons acting on sodalite over the past 390×10^6 yr are generally lower than estimates of the present-day neutrons acting on surface rock. For example, the work of Montgomery and Tobey[7] indicates a neutron production rate of ≈ 950 neutrons/g yr at sea level, and the production rate of radiocarbon near sea-level, 4.75×10^{-27} ^{14}C per sec per ^{14}N atom[26], is equivalent to 8.2×10^4 neutrons/cm^2 year if the cross-section for the $^{14}N(n, p)$ ^{14}C reaction is 1.81 barns[25]. The lower average neutron flux indicated by the amount of ^{36r}Ar in sodalite may result from partial shielding by a rock overburden during part of the 390×10^6 yr history of the samples. However, our results show no indication of any great increase in the neutral neutron flux during the past 390×10^6 yr. This interval includes the 90×10^6 yr age of one of the tellurium ores where neutron capture products have been attributed to a high neutron flux from explosions in our galaxy[15].

Conclusions

The major objectives of this work was to detect excess ^{36}Ar arising from capture of cosmic-ray produced neutrons in surface rock and to compare the integrated neutron flux over the age of the rock with the current neutron flux acting on surface rocks. Our results can be summarized as follows:

a) Neutron-capture produced ^{36}Ar can be detected in chlorine-rich surface rocks. Therefore, measurements of ^{36r}Ar and chlorine can be used with information on the surface neutron flux to measure the surface residence times of rocks.

b) The average neutron flux, 1×10^3 neutrons/cm^2 yr, acting on the sodalite used in this study shows no evidence for the high neutron flux proposed by Takagi et al.[15] to account for the high concentrations of neutron-capture products in tellurium ores.

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