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GEOCHEMICAL ABUNDANCES OF IODINE

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BY

JANE EDNA HANISCH BENNETT - 45

A

THESIS

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ABSTRACT

The research reported herein includes unpublished iodine and uranium data on a group of United States Geological Survey standards and on a group of ultrabasic rocks. Data are also included for the major rock types, deep sea sediments, and for graphite and troilite inclusions in iron meteorites. Tellurium data for the troilite are also reported. Appendix I is a literature article (Bennett and Manuel, 1967a) on Canyon Diablo Graphite. Appendix II is a literature article (Bennett and Manuel, 1967b) on deep sea sediments.

The results of this study show that most of the earlier estimates of the crustal abundance of iodine are uniformly too high, except for deep sea sediments. The results also indicate that the apparent "atomic dispersion" theory of iodine was in fact due to rather uniform iodine contamination. The iodine and uranium abundances from this study are used together with terrestrial xenon abundance data recently redetermined by Mr. R. A. Canals in this laboratory to show that the $I^{129}\text{-Xe}^{129}$ formation interval of the earth is similar to that of stony meteorites.

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I. INTRODUCTION

This research was undertaken because the abundances of iodine in many terrestrial materials were unknown, and the available results were widely disputed. The "atomic dispersion" theory of iodine suggested by Goldschmidt (1962) was of particular interest in view of the suspected contamination problems of earlier iodine analyses. At the time this work was undertaken, von Fellenberg's (1924, 1927) iodine determinations for terrestrial samples were still widely quoted although recent neutron activation analyses of meteorites had shown von Fellenberg's iodine data uniformly too high.

Recent studies on the abundance of iodine in meteorites have demonstrated the importance of this element in understanding early geological history (Goles and Anders, 1962; Reed and Allen, 1966; Kuroda et al, 1966; Clark et al, 1967). Using neutron activation analysis, these recent abundance data show excellent agreement and indicate severe contamination problems in many of the earlier analyses. Very few investigations on terrestrial materials have been performed using this superior technique.

As a corollary to this research, the iodine abundances of terrestrial and meteoritic samples are compared with the concentrations of radiogenic Xe^{129} . This comparison permits a calculation of the $I^{129}-Xe^{129}$ formation intervals of the earth and the meteorites. The tellurium abundance of a troilite nodule from the Great Namaqua-

land meteorite was also determined and used with noble gas data (Alexander et al, 1967) to calculate the contribution of iodine and tellurium to the isotopic anomalies of xenon.

II. LITERATURE REVIEW

The need for a systematic study of the abundances of iodine is best illustrated by reviewing the data presently available. It should be noted that much of the early data for terrestrial samples is unreliable but that reliable data for meteorites have been obtained by neutron activation analysis.

For iodine in terrestrial rocks most authors refer to the work of von Fellenberg (1924, 1927) and von Fellenberg and Lunde (1927). The most comprehensive report on iodine is by the Chilean Iodine Education Bureau which relies heavily on von Fellenberg's data. This report covers all iodine determinations published up to 1954. Taylor (1964) refers to Turekian and Wedepohl (1961) who refer to the Chilean Report for their iodine data. Rankama and Sahama (1950) and Goldschmidt (1962) used von Fellenberg's data in the geochemistry of iodine sections of their textbooks. But Goles and Anders (1962) determined iodine in meteorites by neutron activation and showed von Fellenberg's data uniformly too high by factors of 5 to 30 as illustrated in Table I. Kuroda and Crouch (1962) report iodine abundances in igneous rocks by spectrophotometry, which also show von Fellenberg's data somewhat too high as shown in Table I.

Goles and Anders' (1962) values have been found slightly low by Reed and Allen (1966), perhaps due to a high fission yield of iodine from resonance and fast neutron fission of U^{238} and Th^{232} .

Both used neutron activation analysis. In this study an exact correction for interfering fission isotopes is made.

Although most authors find von Fellenberg's data uniformly high, recent iodine determinations in sedimentary rocks are higher than those of von Fellenberg. For instance, note a comparison of Itkina's (1956a) and von Fellenberg's data for iodine in limestone and sandstone in Table I.

The data on iodine indicate a definite enrichment of this element in sediments and organic materials. This is especially exemplified by some of the recent studies by Russian geochemists (Itkina, 1956a; Itkina, 1956b; Gulyayeva and Itkina, 1962). Aside from this and the unexplained concentration of iodine in the Chilean nitrate deposits, presently available data show an unusual uniformity of iodine in rocks. Goldschmidt (1962) points out that contamination may be responsible for the apparent "atomic dispersion" of this element. However this uniform distribution is evident in the best analyses selected by Goldschmidt as shown in Table II.

In Table II recent iodine analyses from stone meteorites by Kuroda et al, 1966, are shown for comparison. These measurements seem to support Goldschmidt's concern for contamination in early iodine analyses. The average abundance of iodine in meteorites is appreciably lower than reported by von Fellenberg (1927) (Table I), and the distribution of iodine in meteorites indicates that this element is not immune to geochemical dispersion.

In summary the iodine abundance data demonstrate a definite need for the application of newer techniques in order to obtain more

reliable abundance information. As more information is obtained on the meteorites, it will be even more necessary that reliable data on terrestrial samples be available in order to compare the early history and geochronology of the earth with the meteorites.

III. PROCEDURE

The procedure used in analyzing for iodine and uranium will be described in detail as several modifications of the various procedures in the literature (eg, Goles and Anders, 1962; Meason, 1964; Kuroda et al, 1966; Clark et al, 1967) have been made.

The reactor used in the work described here is a 200 kilowatt swimming pool reactor located on the campus at the University of Missouri at Rolla. The samples and monitors were encased in polyethylene capsules. These were placed into a large polyethylene vial with the lid covered with paraffin and with a nylon ring around it to which nylon strings were attached. The nylon ring had eight holes, 45 degrees apart. Two strings passed across the top and the bottom of the container intersecting at 90 degree angles, each string being attached to holes 180 degrees apart. This cage-like arrangement of nylon strings was designed to prevent the polyethylene vial from surfacing in the event that the nylon ring slipped from the vial during the irradiation. Lead sinkers were attached at the intersection of the bottom strings and the sample was supported by nylon cord attached at the intersection of the top strings. The polyethylene vial in which the samples and monitors were placed was found to receive a rather constant flux of about 5×10^{12} neutrons per cm^2 second. Most irradiations were for 25 minutes.

The capsules for irradiation were polyethylene tubing closed with a flat tip on a soldering iron. Monitors of 50 lambda each were pipetted into the capsules. Then the pipets were rinsed with H_2O into the capsule. It is thought that the pipetting may be responsible for a great deal of error as an intercontamination of monitors was observed when the pipets were not scrupulously clean. This part of the procedure will be modified in the future.

Monitors of about 0.2 micrograms I^- as NaI or KI per 50 lambda and 0.5 to 1 microgram of U as uranyl nitrate were irradiated. For these it was found necessary to cut the polyethylene capsules open in approximately equal portions of a half inch or less a piece and then add distilled water and squeeze the contents out with tongs into the first separatory funnel. This washing of the monitor from the capsule was repeated several times per half of capsule. This part of the procedure was difficult as it was not possible to determine when all the monitor was washed from the capsules, and it was difficult to handle the capsules with tongs. However when the entire capsule was dumped into the first separatory funnel, iodine contamination (I^{128} activity) was sometimes found up to several parts per billion iodine.

The basic principle of the monitor procedure was an oxidation-reduction cycle using aqueous $NaHSO_3$ as a reducing agent and aqueous $NaNO_2$ in HNO_3 as an oxidizing agent. CCl_4 was used to extract I_2 and H_2O was used to extract I^- . The sample procedure was slightly modified in the first steps of the oxidation-reduction cycle.

The exact monitor procedure is shown in Figure I. Except for monitors and carriers, concentrations were approximate. The amount of reagent necessary depended on volume of water present and the concentration of reagent. The necessary amount of each reagent was determined by observing the color changes between pink I_2 in CCl_4 and clear I^- in H_2O . After the final extraction of I^- into water, the aqueous solution was emptied into a 40 ml centrifuge test tube, acidified with HNO_3 , heated, and precipitated with $AgNO_3$ solution.

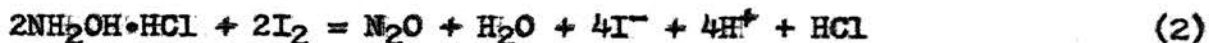
One ml of carrier containing about 20 mg of I^- and one ml of Br^- hold-back carrier containing about 10 mg Br^- were used in all separations. Percentage yield was calculated on the basis of the iodine carrier. All samples and monitors were corrected to 100 per cent yield.

Figure II shows a flow diagram for sample procedure. The initial step was a fusion with $NaOH-Na_2O_2$. One ml I^- carrier was placed on the bottom of a 50 ml nickel crucible, then sample, then $NaOH$ and Na_2O_2 . If the Na_2O_2 comes in contact with the aqueous I^- carrier, the reaction occurs before equilibrium is established between carrier and sample iodine. The fusion was performed under maximum shielding by heating for about 5 minutes at low flame followed by about 10 minutes at high flame of a Meeker burner. The fusion cake was cooled and the nickel crucible placed in a beaker over ice. It was necessary for the fusion cake to be solidified before dissolution or the heat evolved was so intense as to break the Pyrex beaker. After solidification of the fusion cake, the lid was removed from the nickel crucible, and H_2O was squirted onto the fusion cake. The

cake was covered with H_2O and placed into the flame while being held by tongs. The aqueous contents were emptied into the beaker, more water was added, heated, etc. until dissolution was complete. Then a handful of ice was added to the beaker and about 20 ml of 6 M HCl were added, which cleaned the nickel crucible and lid and acidified the solution. More ice was added followed by about 5 ml of HF.

It was extremely important to dissolve the fusion cake as described or the intense heat would cause loss of IO_3^- by vaporization. In early experiments when this procedure was not followed, yields were uniformly low due to the escape of iodine.

The acidified solution was filtered (through coarse filter paper on a plastic Büchner funnel) and the filtrate added to the first separatory funnel (see Figure II). About 0.2 M $NH_2OH \cdot HCl$ was added in slight excess, ie, about 1-2 ml more than needed to completely discolor the $KMnO_4$. This was necessary in order to convert IO_3^- to I^- and to overcome the instability of $NH_2OH \cdot HCl$ to heat. If the exact right amount of $NH_2OH \cdot HCl$ was added, I_2 formed and was extracted into the CCl_4 layer. However in the majority of trials using only $NH_2OH \cdot HCl$, a low yield was obtained due to equation (2).



The procedure described in the literature was therefore altered by adding excess $NH_2OH \cdot HCl$, then 6 M HNO_3 and $NaNO_2$. Sample yields were usually 50-70 per cent using this procedure. The sample procedure beyond the first extraction was like that described for monitors and is shown in Figure II.

The final AgI precipitate was filtered on glass fiber filter paper through a chimney, washed with acetone, then dried 30-60 seconds at 110° C. The filter paper and precipitate were then mounted on a 2 inch stainless steel planchet with 2-sided cellulose tape along the 4 sides. The precipitate was covered with Mylar which was attached to the cellulose tape. The planchet with tape, filter paper and Mylar were weighed before the samples were mounted.

The samples were counted in a gas-flow end window proportional counter having a background of about 12 counts per minute. Except in a few of the standards where the iodine was less than about 20 parts per billion (ppb), there was little trouble separating the 25 minute I^{128} activity from the decay curve of the combined fission products of uranium: I^{131} , I^{132} , I^{133} , I^{134} and I^{135} .

In general frequent 2 minute counts were performed until the activity was less than 100 counts per 2 minutes. The counting of the iodine monitors was then discontinued and the counting time for uranium monitors and samples was lengthened to 5 minutes. All monitors and samples were counted alternately for 2-4 hours following irradiation. Some counting was performed several hours later and several days later. These later counts were necessary for measurement of the long-lived activity in order to validate uranium content, to check on I^{131} activity and to check for contamination.

A normal run consisted of 1 or 2 samples weighing 0.2 to 2 grams and 2 monitors each of iodine and uranium plus an empty capsule as blank. After blanks containing distilled water were shown to give the same activity as empty capsules, the empty capsules were

irradiated as blanks. In most instances blanks gave 50 counts per minute at the beginning of counting, about 40 minutes after termination of the irradiation. By the time all monitors and samples were separated, blanks usually were near background activity. The entire procedure on all samples and monitors normally took 90-120 minutes.

Great Namaqualand troilite was irradiated for 2 hours with iodine and uranium monitors together with monitors of about 1 mg of tellurium as $\text{Te}(\text{NO}_3)_4$. The sample was allowed to sit about an hour after end of irradiation for the 25 minute Te^{131} to decay to I^{131} . Counting was performed every day or two for several days to follow the I^{131} activity ($t_{1/2} = 8$ days). Correction was made for I^{131} from uranium. The tellurium monitors were analyzed by the same procedure as described for other monitors. Except in the case of this troilite, measurable tellurium was not observed for the 25 minute irradiations.

The modifications of sample procedure used to dissolve Canyon Diablo graphite are given in Appendix I.

IV. DATA AND DISCUSSION

The data obtained in the work done for this thesis are shown in Tables III, IV, V and VI. Table III shows the iodine and uranium contents of a group of United States Geological Survey samples. Table IV shows similar data for a group of ultrabasic rocks. Table V shows data for several different rock types and the deep sea sediment data (Bennett and Manuel, 1967b) (see Appendix II). Table VI shows data on Great Namaqualand troilite and Canyon Diablo graphite (Bennett and Manuel, 1967a) (see Appendix I).

In the following discussion, an average crustal abundance of iodine is estimated from the data on terrestrial rocks. This is shown to be similar to the average iodine composition of chondritic meteorites but much less than indicated by von Fellenberg's data (1924, 1927) (see Tables I and II). The wide variations in the iodine abundances are employed to critically examine the theory of "atomic dispersion" of iodine. The average crustal abundance of iodine is combined with the high concentrations of xenon in terrestrial shales (Canalas, 1967) in order to calculate an $I^{129}-Xe^{129}$ formation interval for the earth. The age obtained is shown to be similar to that for chondrites. Finally the abundance data on meteorites are combined with noble gas data by Alexander et al (1967) in order to calculate the contribution of iodine and tellurium to the isotopic anomalies of xenon.

A. Terrestrial Samples

Table III shows average values for iodine and uranium in United States Geological Survey samples on the basis of 2 or 3 trials each. It is interesting to note the low iodine content of basalt, granodiorite and granite. Compare, especially, the granite and basalt values with previous estimates (Tables I and II). Table V compares the uranium results with available data on the same samples taken from different positions. There is sufficient agreement to suggest that differences are perhaps due to the different splits and positions of the other samples.

Table IV shows data on a group of ultrabasic rocks and carbonatites. This group of ultrabasic rocks was analyzed because from the limited information available on the earth's mantle, its composition is thought to be similar to chondrites and ultrabasic rocks (Mason, 1958; Miyake, 1965; Wakita, et al., 1967). Table VIII shows Goles and Anders¹¹ (1962) data on chondrites. The data on ultrabasic rocks show a very wide range of values and sometimes separate analyses for one rock do not agree. This may result from the fact that the pieces of rock were not always of the same mineralogical composition, since small pieces were broken from a large specimen with no attempt being made to pick homogeneous samples or samples of the same composition from one trial to the next. If the rocks shown in Table IV represent mantle material, the iodine content of the mantle is highly variable. Since such wide variations are not observed in meteorites, it appears that the iodine distribution in ultrabasic rocks has been altered by geological processes.

Table V shows abundances in a number of miscellaneous rocks. These analyses were made in an attempt to show what kind of abundance patterns might be expected. With sedimentary rocks, as with ultra-basic rocks, a wide range of values is observed. This is to be expected since iodine is correlated with organic content (Mun and Bazilevich, 1964).

The iodine data in Tables III, IV and V show variations of the iodine abundances in terrestrial material by as much as a factor of 3,000. These results show that von Fellenberg's (1924, 1927) data on iodine were too high for the iodine-poor igneous rocks. Thus it is indicated that the terrestrial distribution of iodine is governed by geochemical principles and that contamination or low sensitivity were responsible for the apparent "atomic dispersion" of this element in early analyses.

In order to estimate a crustal iodine abundance, it is necessary to consider the structure of the earth's crust (Figure III). According to Clarke and Washington (1924) the earth's crust is by weight 95 per cent igneous rocks and 5 per cent sediments. The sediments contain 4 per cent shale, 0.25 per cent limestone and 0.75 per cent sandstone. Using these values together with the iodine abundances for granites and basalts from Table III and for shale, limestone and sandstone from Table IV, the iodine content of the crust is calculated to be approximately 170 parts per billion. This is similar to the chondritic abundances of iodine as shown in Table VIII (Goles and Anders, 1962).

B. Formation Interval of the Earth

Brown (1947) first pointed out that the time interval between formation of the elements and the formation of the earth could be dated if the natural decay products of extinct, short-lived radioactivity could be isolated. Reynolds¹¹ (1960a) discovery of the decay product of extinct I^{129} in stone meteorites ($t_{\frac{1}{2}} = 17$ million years) has been used with meteoritic iodine abundances to rather accurately date the formation time for meteorites (Goles and Anders, 1961; Jeffery and Reynolds, 1961; Manuel and Kuroda, 1964; Merrihue, 1966; Bennett and Manuel, 1967a; Hohenberg et al, 1967; Sabu and Kuroda, 1967) at about $1-3 \times 10^8$ years, depending on the model of element synthesis used for the calculation.

The basis for the calculation can be outlined by the following equations:



$$(I^{129}/I^{127})_{t=c} = (I^{129}/I^{127})_{t=s} e^{-\lambda_{129}(c-s)} \quad (2)$$

$$(I^{129}/I^{127})_{t=c} = (Xe^{129r}/I^{127})_{today} \quad (3)$$

The first equation shows the decay of now extinct I^{129} to form radiogenic Xe^{129r} . If synthesis of the elements in our solar system ceased at some time $t = s$, then the ratio of I^{129} to stable I^{127} would thereafter decrease exponentially with the decay constant λ_{129} . At the time of condensation of planetary bodies, $t = c$, the I^{129}/I^{127} ratio would be as shown in equation (2). During formation of solid bodies, chemical processes would separate the gaseous decay product, Xe^{129r} , from the parent I^{129} . Since the I^{129} behaves chemically as does I^{127} , the decay product of the I^{129} which remained

after time $t = c$ would accumulate at the iodine sites in meteorites. Jeffery and Reynolds (1961) have shown conclusively that this is the site which releases the radiogenic Xe^{129r} . Hence the observed ratio of radiogenic Xe^{129r} to stable I^{127} defines the I^{129}/I^{127} ratio at time $t = c$, as indicated by equation (3). This ratio can be used in equation (2) to calculate the $I^{129}\text{-Xe}^{129}$ formation interval, $\Delta t = c - s$.

Although the above method has been used to calculate $I^{129}\text{-Xe}^{129}$ formation intervals for meteorites, similar calculations for the earth are complicated by the absence of chemical abundance data for the earth's interior and the more complex thermal history of the earth. Since radiogenic Xe^{129} has been trapped in meteorites, the extent of outgassing of this decay product from the earth's interior to the atmosphere is of particular significance in any calculation of the formation interval of the earth. Because such calculations are highly speculative, no exact calculations will be shown here. However the effect of the iodine and xenon data from this laboratory on earlier calculations is illustrated below.

Reynolds (1960b) and Goles and Anders (1961) assumed the earth to be completely outgassed in calculating the $I^{129}\text{-Xe}^{129}$ formation interval for the earth. Their calculations showed that the formation of the earth postdates the formation of the chondrites by 50 to 100 million years. The iodine data shown in Tables III, IV and V indicate that the terrestrial abundance of iodine has been overestimated by a factor of about 2 and Canals (1967) has shown that shales alone

may contain up to 9 times the xenon content of the atmosphere. Thus if the atmosphere contains only one-tenth of the terrestrial abundance of radiogenic Xe^{129r} , and if von Fellenberg's iodine data are uniformly too high by a factor of 2, then the $\text{Xe}^{129r}/\text{I}^{127}$ ratio for the earth has been underestimated by a factor of about 20. Since 4.3 half-lives of extinct I^{129} would be required to increase the $\text{Xe}^{129r}/\text{I}^{127}$ ratio by a factor of 20, the earlier calculations of the $\text{I}^{129}\text{-Xe}^{129}$ formation interval for the earth may have overestimated this time span by 4.3 half-lives of I^{129} , ie 73 million years. Thus this data suggests that the earth and the meteorites are contemporaneous, within limits of the speculative assumptions necessary to estimate an $\text{I}^{129}\text{-Xe}^{129}$ formation interval for the earth.

C. Meteoritic Samples

Two meteorites were analyzed in this work. A detailed discussion of the work on Canyon Diablo graphite will not be given here since this is presented in the published manuscript shown in Appendix I. The results of the iodine and uranium analyses on the graphite are shown in Table VI.

By combining these results with the xenon data of Alexander and Manuel (1967), the $\text{I}^{129}\text{-Xe}^{129}$ formation interval for this iron meteorite was calculated and shown to be similar to the formation intervals reported for chondrites. This is in contrast to Reynolds' (1963) conclusion that the iron meteorites cooled about 200 million years after the chondrites.

A great deal of difficulty was encountered in adapting the analysis procedure for the graphite samples. The major problem

was in quickly dissolving the graphite without loss of iodine. The modifications of the experimental procedure from that used for silicates are shown in Appendix I.

A sample of troilite from the Great Namaqualand iron meteorite was analyzed for iodine, tellurium and uranium. The abundances of iodine and uranium were determined from two samples irradiated for 25 minutes. Due to the relatively small neutron capture cross-section of Te^{130} and the long half-life of I^{131} , the tellurium abundance was determined on a separate sample which had undergone a two hour irradiation.

The iodine, tellurium and uranium abundances in the troilite are shown in Table VI. The iodine and uranium contents in the Great Namaqualand troilite are similar to those in Canyon Diablo troilite, but the tellurium content of the Great Namaqualand troilite is greater than that reported in any troilite phase by Goles and Anders (1962). In spite of the chalcophilic nature of tellurium, Goles and Anders found the abundances of tellurium in troilite to be about equal to the tellurium content of carbonaceous and enstatite chondrites. The tellurium content in the Great Namaqualand troilite, 18 parts per million (ppm), corresponds to an atomic ratio $\text{Te/S} = 1.2 \times 10^{-5}$ if the troilite is assumed to be pure FeS . This value is in close agreement with the cosmic Te/S ratio reported by Suess and Urey (1956).

In an analysis of the abundance and isotopic composition of xenon from the Great Namaqualand troilite, Alexander et al (1967) report no isotopic anomalies except 1.5×10^{-12} cc STP excess Xe^{131} and 8.8×10^{-12} cc STP excess Xe^{129} per gram of troilite. Since fission

would also produce excesses at Xe^{132} , Xe^{134} and Xe^{136} , the anomalies in the troilite are probably the result of nuclear reactions on tellurium and/or the in situ decay of extinct I^{129} .

Thermal neutron capture on tellurium of terrestrial isotopic composition would produce excess Xe^{129} and Xe^{131} in the ratio $\text{Xe}^{129}/\text{Xe}^{131} = 0.63$. Since the anomalous xenon in the troilite occurs in the ratio $\text{Xe}^{129}/\text{Xe}^{131} = 5.9$, this origin of the Xe^{131} would suggest the presence of 7.9×10^{-12} cc STP radiogenic Xe^{129} per gram of troilite or 8.8×10^{-5} cc STP radiogenic Xe^{129} per gram of iodine.

For the continuous synthesis model described by Kohman (1961), Kuroda (1961) has calculated the $\text{I}^{129}/\text{I}^{127}$ ratio at the end of galactic nucleosynthesis to be $(\text{I}^{129}/\text{I}^{127})_s = 3 \times 10^{-3}$. This corresponds to a maximum of 0.52 cc STP radiogenic Xe^{129} per gram of iodine for meteorites which start to retain the gaseous Xe^{129} decay product immediately after nucleosynthesis. Since the Great Namaqualand troilite contains 8.8×10^{-5} cc STP radiogenic Xe^{129} per gram of iodine, this nodule began to retain radiogenic Xe^{129} about 216 million years after an initial $\text{I}^{129}/\text{I}^{127}$ ratio of 3×10^{-3} .

The above is probably a minimum I^{129} - Xe^{129} age for this sample since fast neutrons may produce a larger $\text{Xe}^{129}/\text{Xe}^{131}$ ratio than thermal neutrons. From the presently available cross section data on tellurium (Goldberg et al, 1966), it appears that nonthermal neutrons will produce a maximum $\text{Xe}^{129}/\text{Xe}^{131}$ of about 3. Excesses of Xe^{129} and Xe^{131} have been found in tellurium ores in the ratio $\text{Xe}^{129}/\text{Xe}^{131} = 1.5-3.0$ (Inghram and Reynolds, 1950; Takaoka and Ogata,

1966). These anomalies have been attributed to neutron capture on tellurium and to negative muon reactions (Takagi et al, 1967) on Te^{130} , $\text{Te}^{130}(\mu^-, n)\text{Sb}^{129}(\beta^-)\text{Te}^{129}(\beta^-)\text{I}^{129}(\beta^-)\text{Xe}^{129}$. If the excess Xe^{131} was produced in some reaction which produced $\text{Xe}^{129}/\text{Xe}^{131} \leq 3$, then the radiogenic Xe^{129} in the troilite nodule of Great Namaqualand could amount to as little as 4.3×10^{-12} cc STP/gram. In this case the $\text{I}^{129}\text{-Xe}^{129}$ formation interval would be 231 million years.

Thus the $\text{I}^{129}\text{-Xe}^{129}$ formation interval for the Great Namaqualand troilite appears to be in close agreement with the $\text{I}^{129}\text{-Xe}^{129}$ age of the Sardis troilite (Reynolds, 1963) but appreciably longer than the $\text{I}^{129}\text{-Xe}^{129}$ age of Canyon Diablo graphite. The presence of excess Xe^{129} from neutron capture reactions on tellurium in the troilite phases of both Sardis and Great Namaqualand are consistent with the proposed synthesis of I^{129} in the solar system (Fowler et al, 1962) and $\text{Te}^{128}\text{-Xe}^{129}$ dating of meteorites (Kuroda et al, 1967).

The results from this analysis of Great Namaqualand troilite have been combined with noble gas data from the mass spectrometer laboratory in a manuscript entitled "On Noble Gas Anomalies in the Great Namaqualand Troilite" by Alexander, Bennett and Manuel. This paper was submitted to Zeitschrift für Naturforschung in November, 1967.

V. CONCLUSIONS

The results of this investigation have shown the following:

1. The atomic dispersion theory of terrestrial iodine is inconsistent with the results presented here.

2. Previous estimates of iodine abundance for the earth based on von Fellenberg's data (1924, 1927) were high.

3. Deep sea sediments were found to be highly enriched in iodine over previous estimates.

4. From the iodine abundances in a number of terrestrial materials, fairly concordant I^{129} - Xe^{129} ages are calculated for the earth and for chondrites. Thus it seems likely that the early history of the earth was similar to that for chondrites.

5. A new procedure for analyzing iodine in graphite was developed and a graphite nodule from an iron meteorite was found to have an I^{129} - Xe^{129} age similar to chondrites.

6. A troilite nodule from an iron meteorite was found to be enriched in tellurium and to have started retaining radiogenic Xe^{129} about 100 million years later than chondrites.

TABLE I.

TERRESTRIAL AND METEORITIC ABUNDANCES OF IODINE

Abundances in parts per billion (ppb)

<u>Meteorite</u>	<u>Data by Goles and Anders (1962)</u>	<u>Data by von Fellenberg (1927)</u>
Mocs	50 ppb	1800 ppb
Ergheo	90 ppb	~1200 ppb
Toluca metal	170, 320 ppb	1500 ppb
Canyon Diablo metal	28 ppb	480 ppb
<u>Igneous Rocks</u>	<u>Data by Kuroda and Crouch (1962)</u>	<u>Data by von Fellenberg (1924)</u>
Granite	150 ppb average	440 ppb 200* ppb 380 ppb
Gneiss	40 ppb	380 ppb
<u>Sedimentary Rocks</u>	<u>Data by Itkina (1956a)</u>	<u>Data by von Fellenberg (1924)</u>
Limestone	4,000 ppb	430 ppb 440 ppb
Sandstone	5,700 ppb	320 ppb 700 ppb 1600 ppb

* von Fellenberg and Lunde (1927)

TABLE II.

IODINE ABUNDANCES AND ATOMIC DISPERSION

<u>Rocks (Goldschmidt, 1962)</u>	<u>Iodine (ppb)</u>
Basalt	204
Labradorite rock	230
Barvikite	300
Granite	200
Obsidianite	320
<u>Stone Meteorites (Kuroda et al, 1966)</u>	<u>Iodine (ppb)</u>
Fayetteville Dark	71 \pm 28
Bruderheim	21 \pm 4
Juvinas	35 \pm 4
Stannern	635 \pm 20
Petersburg	83 \pm 25
Cumberland Falls	460 \pm 50
Moore County	81 \pm 8
Shallowater	188 \pm 18
Sioux County	14.0 \pm 0.3
Mt. Padbury	96 \pm 2
Shalka	125 \pm 59
Pena Blanca Spring	29.0 \pm 1.2
Pasamonte	173 \pm 48

TABLE III.

UNITED STATES GEOLOGICAL SURVEY STANDARDS

Sample	Split	Position	ppb I	ppb U
Granite G-2	103	9	43.6 ± 8.3	1505 ± 175
Andesite AGV-1	2	22	119 ± 3	588 ± 35
Peridotite PCC-1	59	19	102 ± 35	27.8 ± 9.4
Dunite DTS-1	26	6	110 ± 5	6.74 ± 0.37
Basalt BCR-1	7	29	18.3 ± 2	676 ± 68
Granodiorite GSP-1	75	25	16.3 ± 2	514 ± 54

TABLE IV.

ULTRABASIC ROCKS AND CARBONATITES

Sample	ppb I	ppb U
Eclogite	32.1	125
California	87.3	60.8
Eclogite	124	463
Germany	245	396
Eclogite	205	35.1
Germany	160	9.22
Dunite	106	4.70
NBS Standard	55.7	22.0
Dunite	153	<10
North Carolina		
Peridotite changing to serpentine	367	<15
Vermont	237	11.6
Carbonatite	798	878
Tanganyika	737	762
Carbonatite with perovskite	<500	4180
Arkansas	<1000	8040
Carbonatite with koppite	<500	3750
Norway	448	2050

Samples from Ward's Scientific Company

TABLE V.

MISCELLANEOUS ROCKS

Sample	ppb I	ppb U
Granite* Pikes Peak	<400	6750 ± 500
Granite* Pikes Peak	<50	1240 ± 200
Granite* Pikes Peak	<50	1140 ± 200
Argillaceous Limestone** New York	137 ± 21	30.6 ± 4.6
Chalk Limestone** England	8000 ± 1600	416 ± 80
Red Sandstone** New York	<20	237 ± 54
Hornblende Schist** North Carolina	<10	87.1 ± 18
Calcareous Shale** New York	3650 ± 720	1710 ± 340
Deep Sea Sediments		
LUS-183	40300 ± 3400	162 ± 22
LUS-212	46400 ± 2400	61 ± 24
LUS-217	49000 ± 1000	250 ± 100
ZEP-23	10900 ± 2200	1500 ± 400

*Samples from United States Geological Survey

**Samples from Ward's Scientific Company

TABLE VI.

METEORITE DATA

Sample	ppb I	ppb U	ppm Te
Canyon Diablo graphite	340 ± 130 637 ± 210* 337 ± 35	129 ± 40 84 ± 40 108 ± 21	----- ----- -----
Great Namaqualand troilite	90 ± 30	2.1 ± 0.5	18 ± 5
Canyon Diablo troilite**	62	3.5	5.0
Sardis troilite**	3590	6.5	7.8
Grant troilite**	24	6.5	2.4
Toluca troilite**	1030	10	1.7
Soroti troilite**	50	17	1.2

*Some troilite inclusion

**Goles and Anders (1962)

TABLE VII.

URANIUM CORRELATIONS

Sample	This work	Hamilton (1966)	Morgan and Heier (1966)
Uranium (ppm)			
Granite G-2	1.5	1.64	2.1, 2.16
Granodiorite GSP-1	0.51	1.80	1.7
Andesite AGV-1	0.59	1.47	1.9, 2.17
Basalt BCR-1	0.68	1.42	1.6, 1.81
Peridotite PCC-1	0.028	~0.005	0.0041
Dunite DTS-1	0.0067	~0.003	0.0032

TABLE VIII.

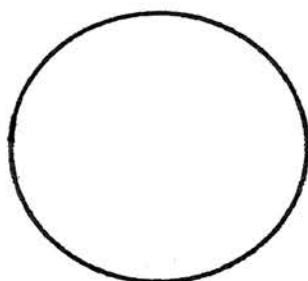
IODINE AND URANIUM IN CHONDRITES

All data from Goles and Anders (1962)

Meteorite	ppb I	ppb U
Beardsley	60, 65	-----
Richardton	31, 21, 33	13
Plainview	47, 50	13, 12
Bruderheim	16, 27, 5	11, 18, 17
Mocs	50	11
Ergheo	90	21
Ställaldalen	570	11
Indarch	210, 300, 300	8, 8, 11
Abee	140, 150	17, 12
St. Marks	64, 100	9, 120
Murray	150, 300, 230	18, 28, 15
Mighei	350, 270	21, 8

FIGURE I.

MONITOR PROCEDURE



represents separatory funnel (SF)

The chemicals inside the circle are initially in the separatory funnel. Above the arrows are reagents added. Below the arrows is the layer drained to the next separatory funnel.

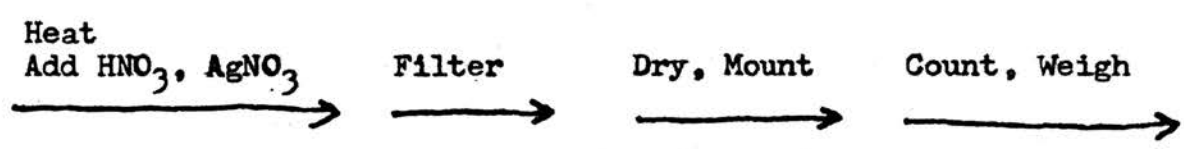
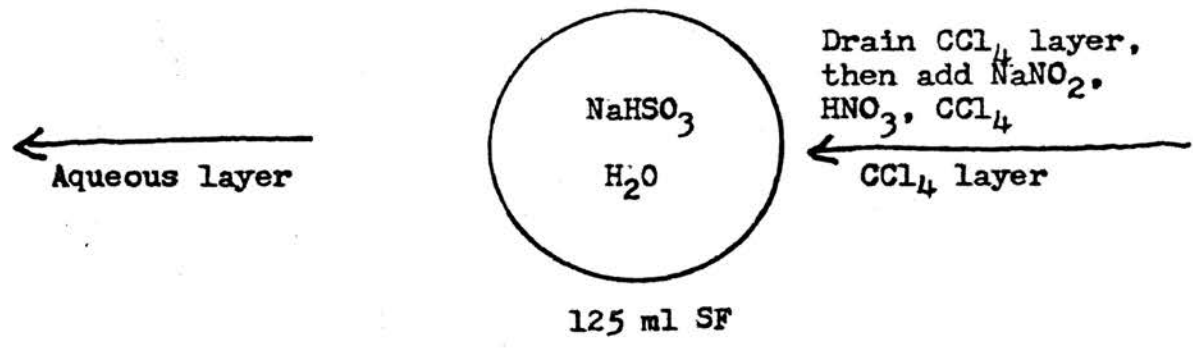
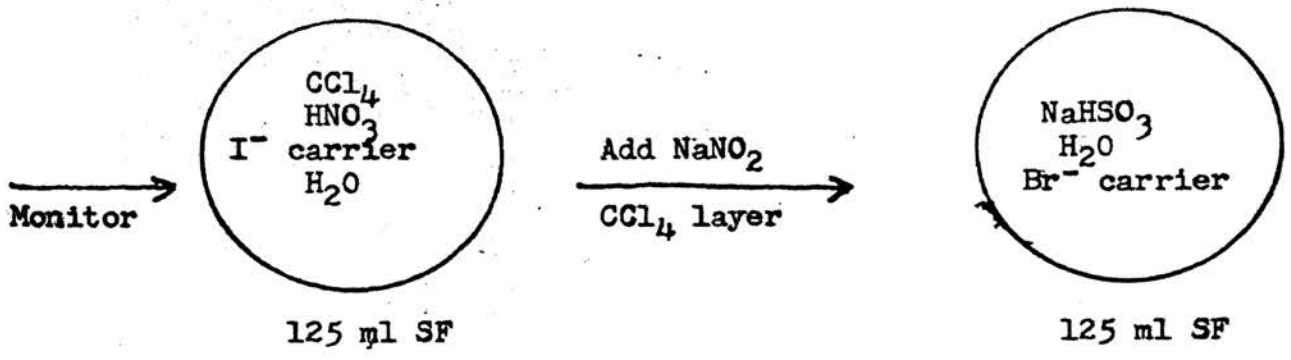
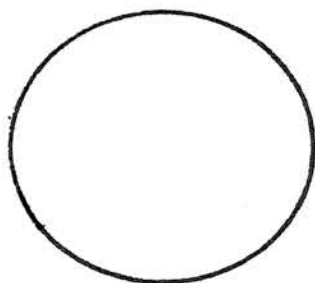


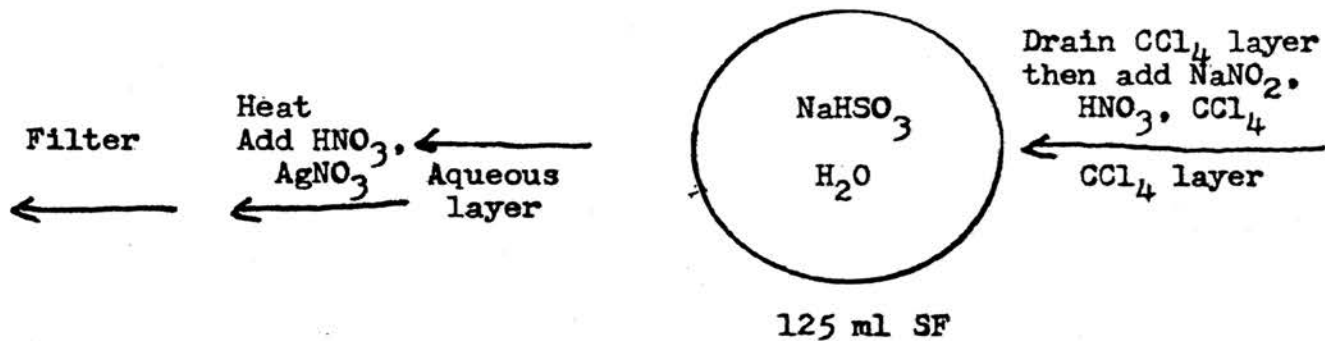
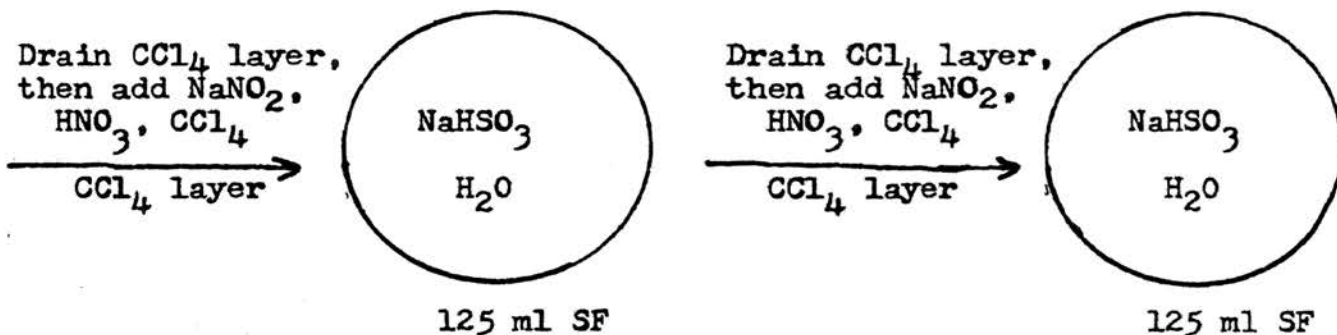
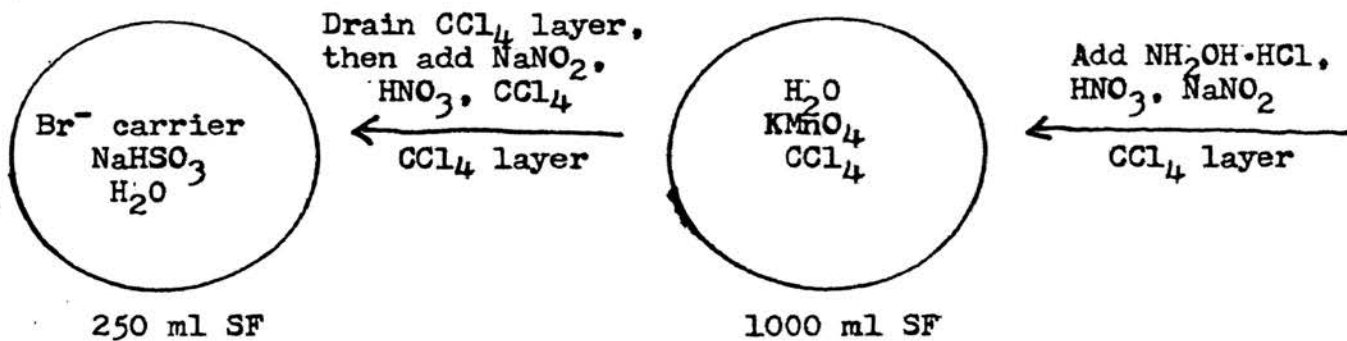
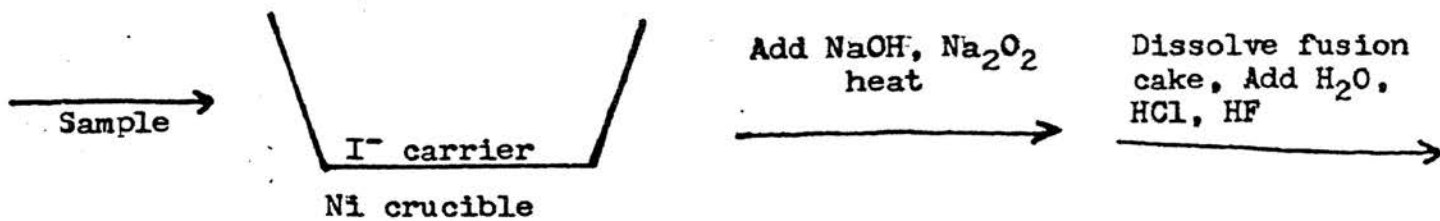
FIGURE II.

SAMPLE PROCEDURE



represents separatory funnel (SF)

The chemicals inside the circle are initially in the separatory funnel. Above the arrows are reagents added. Below the arrows is the layer drained to the next separatory funnel.



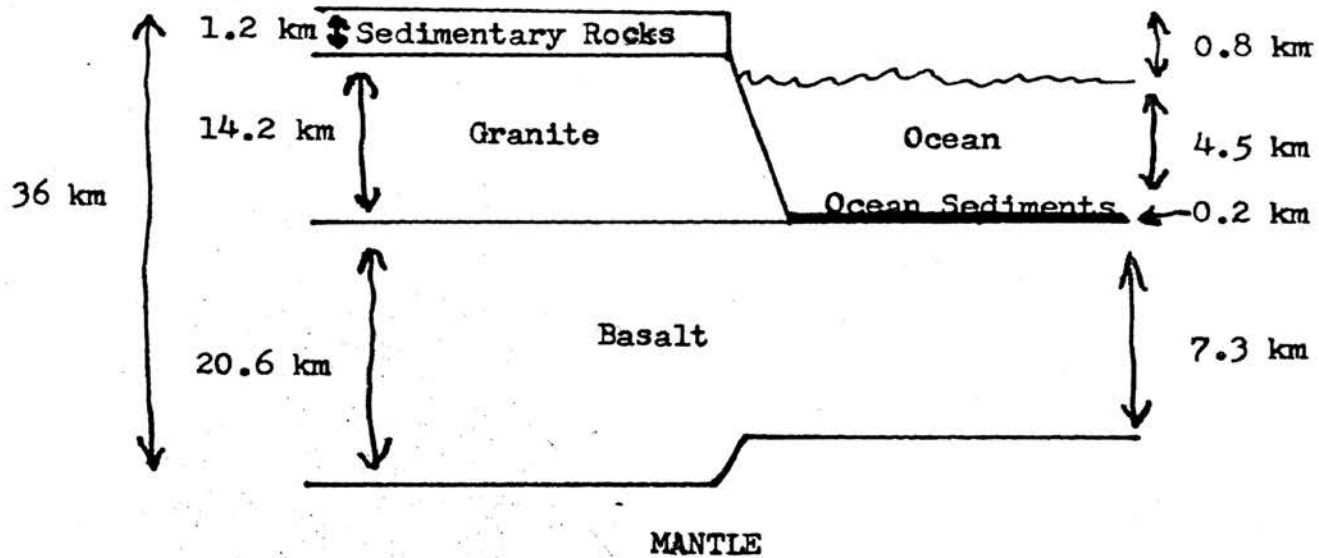
Dry, Mount →

Count, Weigh →

FIGURE III.

STRUCTURE OF THE EARTH'S CRUST

(From Miyake, 1955)



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VITA

Jane E. Hanisch Bennett, daughter of Bessie and Harold Hanisch, was born February 2, 1945 in Cedar Falls, Iowa. She obtained both primary and secondary education at Malcolm Price Laboratory School of University of Northern Iowa in Cedar Falls, Iowa. She entered University of Northern Iowa in September, 1962 in conjunction with her senior year of high school, graduating from Malcolm Price High School in June, 1963. She graduated with a Bachelor of Arts degree in chemistry with honors from University of Northern Iowa in January, 1966. While there, she did research under Dr. James C. Chang on chromium malonate complexes (Chang, 1967). She immediately began her graduate studies at University of Missouri at Rolla.

On September 3, 1966, she was married to Garry A. Bennett. They have no children.

She held a part-time teaching assistantship at University of Missouri at Rolla from January to June, 1966, and from September, 1967 to the present. In June, 1966 she received a research assistantship from National Science Foundation, grant NSF GA-293, which she held until the present time.

APPENDIX I.

"ON THE ORIGIN OF NOBLE GAS ANOMALIES IN CANYON DIABLO GRAPHITE"

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ON THE ORIGIN OF NOBLE GAS
ANOMALIES IN CANYON DIABLO GRAPHITE

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(Received)

ABSTRACT

Activation analyses on Canyon Diablo graphite show an iodine and uranium content of 337 ± 37 ppb and 108 ± 21 ppb, respectively. The $I^{129} - Xe^{129}$ formation interval for the graphite is calculated and found to agree with the formation intervals reported for stone meteorites. During exposure to cosmic rays the Abee enstatite chondrite is shown to be ≈ 25 times more effective than Canyon Diablo in producing epithermal neutrons. The Kr^{86} anomaly in Canyon Diablo graphite and other meteorites is compared to an unexplained Kr^{86} excess reported in pile-irradiated chondrites.

1. INTRODUCTION

The isotopic composition of xenon and krypton in Canyon Diablo graphite has been reported in an earlier article in this journal [1]. In addition to a large excess of Xe^{129} , the graphite was reported to contain excess Xe^{128} , Kr^{80} , Kr^{82} and Kr^{86} . These anomalies were attributed to the decay of extinct I^{129} and to neutron capture reactions on iodine, bromine and rubidium. The iodine and uranium abundances in Canyon Diablo graphite are reported in this article and used together with the recently determined electron-capture branch of Rb^{86} [2] to discuss the origin of the noble gas anomalies.

2. EXPERIMENTAL TECHNIQUE

The iodine and uranium content of Canyon Diablo graphite were determined by neutron activation analysis. The chemical procedure was almost identical to that reported by Goles and Anders [3] and Clark, Rowe, Ganapathy and Kuroda [24]. The samples were irradiated with two aqueous monitors of each of the following salts: NaI , $\text{Te}(\text{NO}_3)_4$ and $\text{UO}_2(\text{NO}_3)_2$. The irradiation was conducted in a local reactor for 25 minutes at a flux of $\approx 5 \times 10^{12}$ n/cm²/sec.

The irradiated graphite samples were dissolved in a hot solution of conc. H_2SO_4 and conc. H_3PO_4 containing an excess of CrO_3 . Conc. HCl was leaked into this solution during the dissolution process to oxidize

I_2 gas to IO_3^- . After the graphite was dissolved, an excess of hydroxylamine hydrochloride was used to reduce IO_3^- to I_2 and to destroy the excess CrO_3 . The I_2 was extracted into carbon tetrachloride, then cycled into an aqueous solution of $NaHSO_3$, extracted into carbon tetrachloride using acidic $NaNO_2$, and this cycle repeated three times. The I^- was precipitated from an acidic aqueous solution by the addition of $AgNO_3$. The AgI precipitate was filtered, dried and mounted on 2 inch stainless steel planchets for proportional counting. Approximately 20 mg of I^- carrier which passed through the entire procedure with the graphite gave yields of 20-40% for the graphite samples.

The monitors together with 20 mg of I^- carrier were subjected to two cycles of the above described extraction, precipitated as AgI and mounted in the same fashion as sample AgI . Yields of 75-90% were observed for the monitors.

The samples and monitors were counted for gross β -activity in a gas-flow end window proportional counter having a background 12 counts per minute. The initial activity of I^{128} in the sample was about an order of magnitude greater than the other iodine activities and therefore easily distinguished. The iodine from the uranium and tellurium monitors were subjected to the first CCl_4 extraction within 2 minutes of the separation time for the sample iodine. No tellurium was detected in the graphite.

3. RESULTS AND DISCUSSION

3.1 Uranium and Iodine Content of Canyon Diablo Graphite

The results of our iodine and uranium measurements are shown in Table 1 together with earlier measurements of iodine and uranium in Canyon Diablo. The errors shown for our measurements were estimated from the variation in activity of monitors and their yields relative to sample yields. The smaller errors on sample No. 146 reflect an improvement in our procedure for removing the total monitor activity from the polyethylene vials. The abundances of iodine and uranium for sample No. 146 will be used in all calculations shown later.

The enrichment of iodine in graphite supports the suggestion of Alexander and Manuel [1] that the excess Xe^{128} and Xe^{129} in the graphite originates from iodine. Uranium shows an even greater enrichment in graphite. Although there have been no other measurements of uranium in meteoritic graphite reported in the literature, Kim, Hwang and Sang [5] report high uranium abundances in terrestrial graphite.

3.2 $I^{129} - Xe^{129}$ Formation Interval

The Canyon Diablo graphite has been reported to contain 8.52×10^{-10} cc STP excess Xe^{129} per gram [1]. Combining this value of the decay product of I^{129} with the iodine abundance shown in Table 1, the formation interval for the Canyon Diablo graphite can be calculated from the equation [6],

$$\Delta t_{129} = (17/0.693) \ln (I^{127}/Xe^{129}) (I^{129}/I^{127})_0 \text{ Million years.} \quad (1)$$

The value of the I^{129}/I^{127} ratio at the end of nucleosynthesis, $(I^{129}/I^{127})_0$, depends on the model of element synthesis. For sudden synthesis the ratio will be near unity and for continuous synthesis the longer the duration of nucleosynthesis, the smaller will be the $(I^{129}/I^{127})_0$ ratio. Many of the recent calculations of $I^{129} - Xe^{129}$ formation intervals for stone meteorites use either $(I^{129}/I^{127})_0 = 3 \times 10^{-3}$ [7] or $(I^{129}/I^{127})_0 = 1.25 \times 10^{-3}$ [6]. These values of $(I^{129}/I^{127})_0$ in equation (1), together with the iodine and radiogenic Xe^{129} abundances mentioned above, yield $I^{129} - Xe^{129}$ formation intervals of $\Delta t = 131$ and 110 million years, respectively.

Kuroda et al [4] have measured xenon and iodine in twelve stone meteorites. Using $(I^{129}/I^{127})_0 = 3 \times 10^{-3}$, they calculate $I^{129} - Xe^{129}$ formation intervals with the range of 127-300 million years. Hohenberg et al [8] calculate a somewhat different $I^{129} - Xe^{129}$ formation interval by analyzing for xenon from neutron-irradiated meteorites. By comparing the release of radiogenic Xe^{129} with pile-produced Xe^{128} , the latter have shown that the high temperature minerals of the chondrites began to retain radiogenic Xe^{129} about 61 million years after an initial $(I^{129}/I^{127})_0 = 1.25 \times 10^{-3}$. However, the same chondrites show appreciably longer formation intervals for the low temperature minerals [9]. Thus, our value of $\Delta t = 110$ million years for the graphite is difficult to relate to the $I^{129} - Xe^{129}$ formation interval calculated by Hohenberg et al [8].

Since the $I^{129} - Xe^{129}$ formation intervals calculated by Kuroda et al [4] are based on the same method used here (ie comparing the total iodine and radiogenic Xe^{129} abundances in the sample), any difference in the

formation time for stone and iron meteorites will be best illustrated by comparing the formation interval of the graphite ($\Delta t = 131$ m. y.) with the range of formation intervals which Kuroda et al [4] obtain for stone meteorites ($127 \text{ m. y.} \leq \Delta t \leq 300 \text{ m. y.}$). This indicates that there is no appreciable difference in the formation time for iron and stone meteorites.

In contrast to the above conclusion, Reynolds [10] reports a total of 1.3×10^{-10} cc STP excess Xe^{129} in Sardis troilite. Comparing this with an iodine content of 3.59 ppm reported by Goles and Anders [3], Reynolds suggested that cooling of the troilite postdates the cooling of the chondrites by about 200 m. y. To compare Reynolds' results with the formation intervals calculated by Kuroda et al [4], the above values and $(\text{I}^{129}/\text{I}^{127})_0 = 3 \times 10^{-3}$ were used in equation (1). This yields an $\text{I}^{129} - \text{Xe}^{129}$ formation interval of $\Delta t = 234$ m. y. for the troilite.

3.3 Neutrons in Canyon Diablo

Marti, Eberhardt and Geiss [11] have shown that the Kr^{80} , Kr^{82} and Xe^{128} in the Abee and Mezo["]-Madaras chondrites are due to neutron capture of intermediate or fast neutrons. They note that the relative abundances of these neutron-capture products and the abundances of bromine and iodine in chondrites are in excellent agreement with the neutron capture cross sections for 30-300 ev neutron energies. Although the excess Kr^{80} and Kr^{82} in Canyon Diablo graphite are 5-10 times larger than the excess Kr^{80} and Kr^{82} in Abee or Mezo["]-Madaras, the ratio of excess Kr^{80} to Kr^{82} in the graphite is 2.5 [1], in close agreement with the cross-section of bromine for 30-300 ev neutrons [11].

By comparing the cosmic ray exposure ages, the iodine abundances and the excess Xe^{128} in Canyon Diablo graphite and in Abee, the relative production rates of Xe^{128} from iodine can be calculated for these two meteorites.

Fisher and Schaeffer [12] have measured the abundances of the light noble gases in the metal phase of Canyon Diablo. They calculate an $\text{Ar}^{36}/\text{Cl}^{36}$ exposure age of 160 million years. Table 2 compares the abundances of the light noble gases in the graphite and the metal regions of Canyon Diablo. The low abundance of cosmogenic helium in the graphite is probably due to selective loss of helium from this sample. This may have occurred at the time of impact or during the twelve hour preheating of the sample to $\approx 100^\circ\text{C}$ prior to gas analysis [1]. We interpret the close agreement in the abundance of cosmogenic neon in the metal and graphite regions to indicate that the samples were exposed to essentially the same total cosmic ray flux.

The neutron flux, f , of 30-200 ev neutrons acting on Abee and Canyon Diablo during their cosmic ray exposure age, t , is

$$f_{\text{Abee}}/f_{\text{C.D.}} = \frac{[\text{Xe}^{128*}]_{\text{Abee}} [\text{I}^{127} \times t]_{\text{C.D.}}}{[\text{Xe}^{128*}]_{\text{C.D.}} [\text{I}^{127} \times t]_{\text{Abee}}}, \quad (3)$$

where Xe^{128*} is excess produced by neutron capture on iodine. For Abee, Marti et al [11] list an exposure age of 6 million years, 145 ppb iodine, and 2.5×10^{-12} cc STP excess Xe^{128} per gram. For Canyon Diablo graphite we use an exposure age of 160 million years [12], 337 ppb iodine and

7.2×10^{-12} cc STP excess Xe^{128} per gram [1]. These values in equation (3) indicate that the cosmic ray flux on Abee during its exposure age was approximately 25 times more effective than the cosmic ray flux on Canyon Diablo in the production of Xe^{128} from iodine. This difference results from many causes, eg., the depth of the sample in the meteorite, the slowing down density of the neutrons, and the cross sections for other neutron reactions in the meteorite. The contribution of these factors in chondrites has been described by Eberhardt, Geiss and Lutz [13].

From the iodine abundance shown in Table 1, the excess Kr^{80} and Xe^{128} [1] and the neutron cross-sections of bromine and iodine for 30-300 ev neutrons [11], the bromine content of Canyon Diablo graphite is estimated to be 15 ppm.

3.4 The Kr^{86} Anomaly

Alexander and Manuel [1] reported a small excess of Kr^{86} in Canyon Diablo graphite and pointed out that neutron capture on Rb^{85} followed by an electron capture branch in the decay of Rb^{86} might be responsible for the Kr^{86} anomaly. Excess Kr^{86} has also been reported in Fayetteville [14], Abee, Canyon Diablo troilite [15], Richardton and Orgueil [16]. In the following discussion it is shown that Rb^{86} is not responsible for the excess Kr^{86} in meteorites, but that a neutron irradiation of meteoritic material will produce an excess of Kr^{86} from some source other than fission of U^{235} .

The excess Kr^{86} in Canyon Diablo graphite is 6.2% of the excess Kr^{80} . To demonstrate that Rb^{86} is not responsible for the Kr^{86} anomaly, we use the following equation to calculate the rubidium abundance necessary to produce the excess Kr^{86} .

$$(\text{Kr}^{86}/\text{Kr}^{80})_{\text{excess}} = (\lambda_{\text{E. C.}}/\lambda_{\beta^-}) [\text{Rb}^{85}] \sigma_{85} / [\text{Br}^{79}] \sigma_{79} \quad (4)$$

Alexander, Manuel and Ganapathy [2] have measured the isotopic composition of krypton from an irradiated rubidium salt and shown that $\lambda_{\text{E. C.}}/\lambda_{\beta^-} \approx 5 \times 10^{-5}$ for Rb^{86} . For thermal neutrons $\sigma_{85}/\sigma_{79} = 0.067$ [17]. For epithermal neutrons the σ_{85}/σ_{79} ratio is appreciably smaller due to the large epithermal resonances in bromine and their absence in rubidium [17]. Thus the minimum rubidium content necessary to produce the Kr^{86} anomaly will result from the use of thermal neutron cross sections in equation (4). Using 15 ppm for bromine and thermal neutron cross sections of Br^{79} and Rb^{85} , equation (4) indicates that the graphite would have to contain a minimum of 21% rubidium by weight in order to account for the Kr^{86} anomaly. By a similar calculation it can be shown that all reports of excess Kr^{86} in meteorites would necessitate unreasonably large rubidium abundances to produce the excess Kr^{86} from electron capture of Rb^{86} .

Although neutron capture on Rb^{85} is not responsible for the excess Kr^{86} in meteorites, Merrihue [18] has reported an excess of Kr^{86} in neutron-irradiated samples of Abee and Bruderheim chondrules. An integrated flux of 5.59×10^{18} n/cm² [8] on the chondrules, IBC-21, produced $2.0 \pm 0.5 \times 10^{-12}$ cc STP excess Kr^{86} per gram and an integrated

flux of 1.15×10^{19} n/cm² [8] on Abee resulted in $20 \pm 3 \times 10^{12}$ cc STP excess Kr⁸⁶ per gram. The fission produced krypton, Kr^{86f}, can be calculated from the following equation.

$$\text{Kr}^{86f} = f \sigma_f [\text{U}^{235}] Y^{86} \quad (5)$$

In this equation f is the integrated neutron flux, σ_f is the cross section for neutron-induced fission of U²³⁵, and Y^{86} is the fission yield at mass 86.

The uranium content of the Bruderheim chondrules IBC-21 has been calculated to be 17 ppb from the amount of fissiogenic xenon produced by the irradiation [18]. This value avoids any contamination or inhomogeneity problems since the excess Kr⁸⁶ and fissiogenic xenon were measured from the same sample. The spectrum for heavy xenon isotopes in the irradiated Abee sample has not been published. Other investigators report the uranium in Abee as 17 ppb [3], 12 ppb [3] and 11 ppb [19]. Using an average of these uranium values for Abee together with $\sigma_f = 580$ barns and $Y^{86} = 2.02\%$ [20], equation (5) yields

$$[\text{Kr}^{86f}]_{\text{Abee}} = 1.2 \times 10^{-12} \text{ cc STP/gm, and}$$

$$[\text{Kr}^{86f}]_{\text{IBC-21}} = 0.76 \times 10^{-12} \text{ cc STP/gm.}$$

The excess Kr⁸⁶ from some source other than U²³⁵ amounts to $19 \pm 3 \times 10^{-12}$ cc STP per gram in Abee and $1.2 \pm 0.5 \times 10^{-12}$ cc STP per gram in the Bruderheim chondrules.

The amount of krypton, Kr^{86*}, which comes from the electron capture branch of Rb⁸⁶ can be calculated from the following equation.

$$[\text{Kr}^{86*}] = f \sigma_{85} [\text{Rb}^{85}] (\lambda_{\text{E.C.}} / \lambda_{\beta^-}) \quad (6)$$

Here f is the integrated flux, σ_{85} is the thermal neutron cross section of Rb^{85} and $\lambda_{\text{E.C.}}/\lambda_{\beta^-}$ is the branching ratio in the decay of Rb^{86} . Gast [21] found 3.45 and 3.41 ppm rubidium in Abee. The rubidium content of the Bruderheim chondrules has not been reported. For a whole sample of Bruderheim, Shields [22] found 2.79 ppm rubidium. This rubidium value will be used for the Bruderheim chondrules in the following calculations.

For the above rubidium contents, $\sigma_{85} = 0.76$ barns [17], $\lambda_{\text{E.C.}}/\lambda_{\beta^-} = 5 \times 10^{-5}$ [2], and the integrated neutron fluxes given earlier, equation (6) yields

$$[\text{Kr}^{86*}]_{\text{Abee}} = 2.8 \times 10^{-13} \text{ cc STP/gm, and}$$

$$[\text{Kr}^{86*}]_{\text{IBC-21}} = 1.1 \times 10^{-13} \text{ cc STP/gm.}$$

Thus, aside from the production of Kr^{86} from U^{235} and Rb^{85} , the irradiation of Abee and Bruderheim chondrules produced an excess of Kr^{86} amounting to $19 \pm 3 \times 10^{-12}$ cc STP/gm and $1.1 \pm 0.5 \times 10^{-12}$ cc STP/gm, respectively.

The larger excess Kr^{86} in Abee is probably due to the greater flux on Abee and to a greater abundance of the target nuclei which produce Kr^{86} during the irradiation. If the difference in flux on the two samples is eliminated, then the Bruderheim sample is found to be depleted in the target nuclei by a factor of 8.4 ± 4 relative to Abee. By comparison Larimer and Anders [23] report Ag, Ga, Ge, I and Te in ordinary chondrites to be depleted relative to Type I enstatite chondrites by factors of 7.8, 4.2, 5.6, 6.8 and 5.4, respectively. This suggests that the element

responsible for the excess Kr^{86} in the irradiated samples may follow the chemistry of the elements intermediate between metals and nonmetals in the right-hand side of the periodic table.

We do not understand the origin of the excess Kr^{86} produced in pile-irradiated meteorites. The krypton spectra have been reported for only three irradiated meteorite samples [17], Abee, Bruderheim and Bruderheim chondrules. Each shows an excess of Kr^{86} above that produced from U^{235} or Rb^{85} . The whole sample of irradiated Bruderheim contained about the same excess Kr^{86} as the irradiated Bruderheim chondrules, but the statistical error on Kr^{86} in the whole sample is larger than the excess Kr^{86} . From the data available it is not possible to determine if this excess Kr^{86} is accompanied by excess Kr^{84} and Kr^{83} , as would be expected from fission. The neutron irradiation of a meteorite sample produces all the krypton isotopes except Kr^{78} , which Merrihue [17] does not report. In the above calculations we have used the excess Kr^{86} values reported by Merrihue, who normalized the krypton spectrum to Kr^{84} . Since fission contributes to Kr^{83} , Kr^{84} and Kr^{86} , this normalization gives a lower limit of the excess Kr^{86} .

The excess Kr^{86} in the unirradiated meteorites is apparently not due to fission of extinct Pu^{244} , since Hohenberg, Munk and Reynolds [26] note that the excess Kr^{86} in Pasamonte is so large that "our lower limit for fission krypton exceeds that estimated from Pu^{244} by a factor of 12". Thus

an unexplained excess of Kr^{86} has been reported in seven unirradiated meteorites [1, 14, 15, 16, 26] and produced in all reports of krypton analyses from pile-irradiated meteorites. It therefore seems likely that neutron-induced reactions are responsible for the excess Kr^{86} observed in Canyon Diablo graphite and six other meteorites.

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We are grateful to Drs. E. Anders, R. Ganapathy, G. G. Goles, P. K. Kuroda and M. W. Rowe for advise on the activation analysis, to Mr. A. Elliott and Mr. M. Little for assistance with the irradiations and to Dr. P. W. Gast and Mr. E. Alexander, Jr. for unpublished data. This work was supported by the National Science Foundation grant NSF-GA-293.

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TABLE 1
IODINE AND URANIUM IN CANYON DIABLO

Sample	Run	Sample Wt. (mg.)	I (p. p. b.)	U (p. p. b.)	Investigator
Graphite	82	169	340 \pm 130	129 \pm 40	This work
	102*	93	637 \pm 210	84 \pm 40	This work
	146	157	337 \pm 35	108 \pm 21	This work
Metal	27A	1060	28 \pm 4	<0.6	Goles and Anders [3]
Troilite	25A	3000	62 \pm 8	3.5 \pm 0.4	Goles and Anders [3]

*Small troilite inclusion noticed in sample after irradiation.

TABLE 2
 HELIUM, NEON AND ARGON IN CANYON DIABLO
 ($\times 10^{-8}$ cc STP/gram)

	GRAPHITE	METAL
He ³	2.5	94
He ⁴	94	320
Ne ²⁰	1.83	----
Ne ²¹	1.37	0.97
Ne ²²	1.77	1.05
Ar ³⁶	----	2.7
Ar ³⁸	----	4.3
Investigator	Alexander [25]	Fisher and Schaeffer [12]

APPENDIX II.

"ON IODINE ABUNDANCES IN DEEP SEA SEDIMENTS"

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ON IODINE ABUNDANCES IN DEEP SEA SEDIMENTS

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Iodine abundance in deep sea sediments have been estimated at 0.05 ppm by Turekian and Wedepohl [1961] from the I/Cl ratio of the sea. However, chlorine and bromine are greatly enriched in deep sea sediments whereas an iodine abundance of 0.05 ppm is less than that found in igneous rocks.

Neutron activation analysis for iodine and uranium was conducted using a flux of $\approx 5 \times 10^{12}$ n/cm²sec from the reactor on campus. The chemical separation was similar to that used by Goles and Anders [1962] and Clark, et. al. [1967]. Samples weighing about 0.3 grams were irradiated with monitors for 25 minutes and the resulting iodine activities were counted for gross β -activity in a gas-flow end window proportional counter having a background of 12 counts per minute. The huge I^{128} activity was easily distinguishable from the longer lived iodine isotopes from uranium. No I^{131} activity from tellurium was observed.

The data obtained on deep sea sediments are shown in Table 1 along with data for Bruderheim, a meteorite whose iodine abundance is well-known. The Bruderheim data agrees well with literature values [Goles and Anders, 1962; Kuroda et. al., 1966], although Bruderheim contains appreciably less iodine and uranium than the sediments. Several blank analyses were conducted by irradiating distilled water in the polyethylene capsules as used for monitors and samples. The resulting activities were less than 1% of the activities observed in the samples. Each of the values shown in Table 1 are the average of two determinations. The errors represent the differences between the two trials and encompass the errors due to technique and measurement.

The deep sea sediments were obtained from Professor E. D. Goldberg and are described by Goldberg et. al. [1964] and by Goldberg and Griffin [1964]. The locations, depths and mineral constituents of each sample are shown in Table 1. From this data no conclusions can be made about the association of iodine with any one mineral or with the calcium carbonate content. The exact iodine content may depend on organic content, as Gulyayeva and Itkina [1962] have emphasized, or on sorption of iodine on clays [Vinogradov, 1939; 1957]. Although no data are available on the organic carbon content of the sediments analyzed, the rather uniform iodine abundances and the absence of any correlation with clay or carbonate content may reflect uniform amounts of organics in these sediments. Since ZEP 23 was taken considerable north of the other samples, this might be an area of local iodine depletion and uranium enrichment.

On the basis of the LUS samples primarily, it is concluded that deep sea sediments can contain up to 50 ppm iodine. Thus Turekian and Wedepohl's [1961] estimate of 0.05 ppm is drastically low. The iodine in deep sea sediments appears to be higher than in shales or igneous rocks. Using the deep sea sediment data reported by Turekian and Wedepohl together with the iodine values obtained in this work, the Br/I and Cl/I ratios in the deep sea sediments are calculated to be 1.4 and 420, respectively, for the three sediments from the Lusiad Expedition and 7 and 2100, respectively, for the Zephyrus sample ZEP-23. These ratios are much lower than found in sea water but about the same as in igneous rocks [Turekian and Wedepohl, 1961].

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TABLE 1
IODINE AND URANIUM
IN DEEP SEA SEDIMENTS

	Samples				Investigator
	LUS-183	LUS-212	LUS-217	ZEP-23	
I (ppm)	40.3 ± 3.4	46.4 ± 2.4	49 ± 10	10.9 ± 2.2	This work
U (ppb)	162 ± 22	61 ± 24	250 ± 100	1500 ± 400	This work
Water Depth (m)	3500	4360	3340	5214	Goldberg and Griffin[1964] and Goldberg et. al. [1964]
Core Depth (cm)	33-37	70-74	60-64	65-70	ibid.
Location					ibid.
latitude	19°44'S	6°47'N	3°56'N	26°14'N	
longitude	12°55'W	19°18'W	34°04'W	26°27'W	
CaCO ₃ Content	89%	54%	62%	61%	ibid.
Minerals					ibid.
montmorillonite	24%	16%	23%	16%	
illite	40%	18%	30%	44%	
kaolinite	21%	52%	35%	27%	
chlorite	13%	14%	12%	13%	

ON IODINE ABUNDANCES IN DEEP-SEA SEDIMENTS

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A Reprint from



On Iodine Abundances in Deep-Sea Sediments

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Iodine abundance in deep-sea sediments has been estimated at 0.05 ppm by *Turekian and Wedepohl* [1961] from the I/Cl ratio of the sea. Chlorine and bromine are, however, greatly enriched in deep-sea sediments, but an iodine abundance of 0.05 ppm is less than the iodine abundance found in igneous rocks.

Neutron activation analysis for iodine and uranium was conducted using a flux of $\approx 5 \times 10^{12}$ n/cm² sec from the reactor on campus. The chemical separation was similar to the method used by *Goles and Anders* [1962] and *Clark et al.* [1967]. Samples weighing about 0.3 gram were irradiated with monitors for 25 min, and the resulting iodine activities were counted for gross β activity in a gas-flow end-window proportional counter having a background of 12 counts/min. The huge I¹²⁸ activity was easily distinguishable from the longer-lived iodine isotopes from uranium. No I¹³¹ activity from tellurium was observed.

The data obtained from deep-sea sediments

are shown in Table 1 along with data for Bruderheim, a meteorite whose iodine abundance is well known. The Bruderheim data agree well with values from the literature [*Goles and Anders*, 1962; *Kuroda et al.*, 1966], although Bruderheim contains appreciably less iodine and uranium than the sediments. Several blank analyses were conducted by irradiating distilled water in the polyethylene capsules as used for monitors and samples. The resulting activities were less than 1% of the activities observed in the samples. Each of the values shown in Table 1 is the average of two determinations. The errors represent the differences between the two trials and encompass the errors due to technique and measurement.

The deep-sea sediments were obtained from E. D. Goldberg and are described by *Goldberg et al.* [1964] and by *Goldberg and Griffin* [1964]. The locations, depths, and mineral constituents of each sample are shown in Table 1. From these data no conclusions can be made

TABLE 1. Iodine and Uranium in Deep-Sea Sediments

	Samples			
	LUS-183	LUS-212	LUS-217	ZEP-23
I,* ppm	40.3 ± 3.4	46.4 ± 2.4	49 ± 10	10.9 ± 2.2
U,* ppb	162 ± 22	61 ± 24	250 ± 100	1500 ± 400
Water depth, † m	3500	4360	3340	5214
Core depth, † cm	33-37	70-74	60-64	65-70
Location †				
Latitude	19°44'S	6°47'N	3°56'N	26°14'N
Longitude	12°55'W	19°18'W	34°04'W	26°27'W
CaCO ₃ content †	89%	54%	62%	61%
Minerals †				
Montmorillonite	24%	16%	23%	16%
Illite	40%	18%	30%	44%
Kaolinite	21%	52%	35%	27%
Chlorite	13%	14%	12%	13%

* This work.

† *Goldberg and Griffin* [1964] and *Goldberg et al.* [1964].

ON THE ORIGIN OF NOBLE GAS ANOMALIES IN CANYON DIABLO GRAPHITE

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Activation analyses on Canyon Diablo graphite show an iodine and uranium content of 337 ± 35 ppb and 108 ± 21 ppb, respectively. The $^{129}\text{I} - ^{129}\text{Xe}$ formation interval for the graphite is calculated and found to agree with the formation intervals reported for stone meteorites. During exposure to cosmic rays the Abee enstatite chondrite is shown to be ≈ 50 times more effective than Canyon Diablo in producing epithermal neutrons. The ^{86}Kr anomaly in Canyon Diablo graphite and other meteorites is compared to an unexplained ^{86}Kr excess reported in pile-irradiated chondrites.

1. INTRODUCTION

The isotopic composition of xenon and krypton in Canyon Diablo graphite has been reported in an earlier article in this journal [1]. In addition to a large excess of ^{129}Xe , the graphite was reported to contain excess ^{128}Xe , ^{80}Kr , ^{82}Kr and ^{86}Kr . These anomalies were attributed to the decay of extinct ^{129}I and to neutron capture reactions on iodine, bromine and rubidium. The iodine and uranium abundances in Canyon Diablo graphite are reported in this article and used together with the recently determined electron-capture branch of ^{86}Rb [2] to discuss the origin of the noble gas anomalies.

2. EXPERIMENTAL TECHNIQUE

The iodine and uranium contents of Canyon Diablo graphite were determined by neutron activation analysis. The chemical procedure was almost identical to that reported by Goles and Anders [3] and Clark, Rowe, Ganapathy and Kuroda [4]. The samples were irradiated with two aqueous monitors of each of the following salts: NaI , $\text{Te}(\text{NO}_3)_4$ and $\text{UO}_2(\text{NO}_3)_2$. The irradiation was conducted in a local reactor for 25 min at a flux of $\approx 5 \times 10^{12}$ n/cm²/sec.

The irradiated graphite samples were dissolved in a hot solution of conc. H_2SO_4 and conc. H_3PO_4 containing an excess of CrO_3 . Conc. HCl was leaked into this solution during the dissolution process to oxidize I_2 gas to IO_3^- . After the graphite was dissolved, an excess of hydroxylamine hydrochloride was used to reduce IO_3^- to I_2 and to destroy the excess CrO_3 . The I_2 was extracted into carbon tetrachloride, then cycled into an aqueous solution of NaHSO_3 , extracted into carbon tetrachloride using acidic NaNO_2 , and this cycle repeated three times. The I^- was precipitated from an acidic aqueous solution by the addition of AgNO_3 . The AgI precipitate was filtered, dried and mounted on 2 in. stainless steel planchets for proportional counting. Approximately 20 mg of I^- carrier which passed through the entire procedure with the graphite gave yields of 20-40% for the graphite samples. It should be noted that this procedure may contain an inherent error if there is loss of iodine before the carrier equilibrates with the sample.

The monitors together with 20 mg of I^- carrier were subjected to two cycles of the above described extraction, precipitated as AgI and mounted in the same fashion as sample AgI . Yields of 75-90% were observed for the monitors. Several blank analyses on distilled water enclosed in the same polyethylene capsules as used for the samples and monitors produced

Table 1
Iodine and uranium in Canyon Diablo.

Sample	Run	Sample wt. (mg)	I (ppb)	U (ppb)	Reference
Graphite	82	169	340 ± 130	129 ± 40	This work
	102	93	637 ± 210	84 ± 40	This work
	146	157	337 ± 35	108 ± 21	This work
Metal	27A	1060	28 ± 4	< 0.6	Goles and Ande
Troilite	25A	3000	62 ± 8	3.5 ± 0.4	Goles and Ande

* Small troilite inclusion noticed in sample after irradiation.

activities which would correspond to less than 5 ppb iodine for a 100 mg sample.

The samples and monitors were counted for gross β -activity in a gas-flow end window proportional counter having a background 12 counts per min. The initial activity of ^{128}I in the sample was about an order of magnitude greater than the other iodine activities and therefore easily distinguished. The iodine from the uranium and tellurium monitors was subjected to the first CCl_4 extraction within 2 min of the separation time for the sample iodine. Due to the relatively long half-life of ^{131}I and the small cross section of ^{130}Te , this procedure is not very sensitive for tellurium. From the absence of excess ^{131}I activity in these samples we estimate an upper limit of 2 ppm for tellurium.

3. RESULTS AND DISCUSSION

3.1. Uranium and iodine content of Canyon Diablo graphite

The results of our iodine and uranium measurements are shown in table 1 together with earlier measurements of iodine and uranium in Canyon Diablo. The high iodine abundance shown for sample 102 may result from the troilite inclusion. Goles and Anders [3] report 3590 ppb iodine in the troilite phase of Sardis. The errors shown for our measurements were estimated from the variation in activity of monitors and their yields relative to sample yields. The smaller errors on sample No. 146 reflect an improvement in our procedure for removing the total monitor activity from the polyethylene vials. The abundances

of iodine and uranium for sample No. 146 will be used in all calculations shown later.

The enrichment of iodine in graphite supports the suggestion of Alexander and Manuel [1] that the excess ^{128}Xe and ^{129}Xe in the graphite originate from iodine. Uranium shows an even greater enrichment in the graphite. Although there have been no other measurements of uranium in meteoritic graphite reported in the literature, Kim, Hwang and Sang [6] report uranium abundances in terrestrial graphite.

3.2. ^{129}I - ^{129}Xe formation interval

The Canyon Diablo graphite has been reported to contain $8.52 \times 10^{-10} \text{ cm}^3 \text{ STP excess } ^{129}\text{Xe}$ per gram [1]. Combining this value of the decay of ^{129}I with the iodine abundance shown in table 1, the formation interval for the Canyon Diablo graphite can be estimated from the equation [7],

$$\Delta t_{129} = (17/0.693) \ln \left(\frac{^{127}\text{I}/^{129}\text{rXe}}{^{129}\text{I}/^{127}\text{I}} \right) \times (129\text{I}/^{127}\text{I})_0 \text{ million years}$$

It should be noted that the formation intervals calculated by eq. (1) are based on a generic relationship between iodine and excess ^{129}Xe , although this relationship has not been experimentally established for iron meteorites. Many of the recent calculations of ^{129}I - ^{129}Xe formation intervals for stony meteorites use either $(^{129}\text{I}/^{127}\text{I})_0 = 3 \times 10^{-3}$ [8] or $(^{129}\text{I}/^{127}\text{I})_0 = 1.25 \times 10^{-3}$ [7]. These values of $(^{129}\text{I}/^{127}\text{I})_0$ in eq. (1), together with the iodine and radioactive ^{129}Xe abundances mentioned above, yield 1

^{129}Xe formation intervals of $\Delta t = 131$ and 110 million years, respectively.

Kuroda, Rowe, Clark and Ganapathy [5] have measured total xenon and iodine in twelve stone meteorites. Using $(^{129}\text{I}/^{127}\text{I})_0 = 3 \times 10^{-3}$, they calculate $^{129}\text{I} - ^{129}\text{Xe}$ formation intervals with the range of 127-300 million years. Hohenberg, Podosek and Reynolds [9] calculate a somewhat different $^{129}\text{I} - ^{129}\text{Xe}$ formation interval by analyzing for xenon from neutron-irradiated meteorites. By comparing the release of radiogenic ^{129}Xe with pile-produced ^{128}Xe , the latter have shown that the high temperature minerals of the chondrites began to retain radiogenic ^{129}Xe about 61 million years after an initial $(^{129}\text{I}/^{127}\text{I})_0 = 1.25 \times 10^{-3}$. However, the same chondrites show appreciably less radiogenic ^{129}Xe associated with iodine in the low temperature minerals.

Since the $^{129}\text{I} - ^{129}\text{Xe}$ formation intervals calculated by Kuroda, Rowe, Clark and Ganapathy [5] are based on the same method used here (i.e. comparing the total iodine and radiogenic ^{129}Xe abundances in the sample), any difference in the formation time for stone and iron meteorites will be best illustrated by comparing the formation interval of the graphite ($\Delta t = 131$ m.y.) with the range of formation intervals which Kuroda, Rowe, Clark and Ganapathy [5] obtain for stone meteorites ($127 \text{ m.y.} \leq \Delta t \leq 300 \text{ m.y.}$). This indicates that there is no appreciable difference in the formation time for iron and stone meteorites. In contrast to this conclusion, Reynolds [10] has suggested that the cooling of Sardis troilite postdates the cooling of chondrites by about 200 m.y.

3.3. Neutrons in Canyon Diablo

Marti, Eberhardt and Geiss [11] have shown that the ^{80}Kr , ^{82}Kr and ^{128}Xe in the Abee and Mezö-Madaras chondrites are due to neutron capture of intermediate or fast neutrons. They note that the relative abundances of these neutron-capture products and the abundances of bromine and iodine in chondrites are in excellent agreement with the neutron capture cross sections for 30-300 eV neutron energies. Although the excess ^{80}Kr and ^{82}Kr in Canyon Diablo graphite is 5-10 times larger than the excess ^{80}Kr and ^{82}Kr in Abee or Mezö-Madaras, the ratio of excess ^{80}Kr to ^{82}Kr in the graphite is 2.5 [1], in close agreement with the cross section of bromine for 30-300 eV neutrons [11].

Table 2
Helium, neon and argon in Canyon Diablo
($\times 10^{-8} \text{ cm}^3 \text{ STP/g}$).

	Graphite	Metal
^3He	2.5	94
^4He	94	320
^{20}Ne	1.83	—
^{21}Ne	1.37	0.97
^{22}Ne	1.77	1.05
^{36}Ar	—	2.7
^{38}Ar	—	4.3
$^3\text{He}/^{21}\text{Ne}$	1.8	97
Investigator	Alexander [26]	Fisher and Schaeffer [12]

By comparing the cosmic ray exposure ages, the iodine abundances and the excess ^{128}Xe in Canyon Diablo graphite and in Abee, the relative production rates of ^{128}Xe from iodine can be calculated for these two meteorites.

Fisher and Schaeffer [12] have measured the abundances of the light noble gases in the metal phase of Canyon Diablo. They calculate an $^{36}\text{Ar}/^{36}\text{Cl}$ exposure age of 160 million years. Table 2 compares the abundances of the light noble gases in the graphite and the metal regions of Canyon Diablo. The low $^3\text{He}/^{21}\text{Ne}$ ratio in the graphite may be due to selective loss of helium from this sample, either at the time of impact or during the twelve hour preheating of the sample to $\approx 100^\circ\text{C}$ prior to gas analysis [1]. Heymann, Lipschutz, Nielsen and Anders [13] list the abundances of some of the light noble gases in 61 fragments of Canyon Diablo. The ^3He content varied from $\leq 0.03 \times 10^{-8}$ to $294 \times 10^{-8} \text{ cm}^3 \text{ STP per gram}$, but the neon and argon contents were only reported for samples with at least $10 \times 10^{-8} \text{ cm}^3 \text{ STP } ^3\text{He/g}$. These gas-rich samples displayed $^3\text{He}/^{21}\text{Ne} = 77-110$ and cosmic ray exposure ages clustering near 170 and 540 m.y.

The neutron flux, f , of 30-300 eV neutrons acting on Abee and Canyon Diablo during their cosmic ray exposure age, t , is

$$f_{\text{Abee}}/f_{\text{C.D.}} = \frac{[^{128}\text{Xe}^*]_{\text{Abee}} [^{127}\text{I} \times t]_{\text{C.D.}}}{[^{128}\text{Xe}^*]_{\text{C.D.}} [^{127}\text{I} \times t]_{\text{Abee}}}, \quad (2)$$

where $^{128}\text{Xe}^*$ is excess produced by neutron capture on iodine. For Abee, Marti, Eberhardt and Geiss [11] list an exposure age of 6 m.y., 145 ppb iodine, and $2.5 \times 10^{-12} \text{ cm}^3 \text{ STP excess } ^{128}\text{Xe}$ per gram. For Canyon Diablo graphite we use an exposure age of 170-540 m.y. [13], 337 ppb iodine and $7.2 \times 10^{-12} \text{ cm}^3 \text{ STP excess } ^{128}\text{Xe}$ per gram [1]. These values in eq. (2) indicate that the cosmic ray flux on Abee during its exposure age was approximately 23-73 times more effective than the cosmic ray flux on Canyon Diablo in the production of ^{128}Xe from iodine. This difference results from many causes, e.g., the depth of the sample in the meteorite, the slowing down density of the neutrons, and the cross sections for other neutron reactions in the meteorite. The contribution of these factors in chondrites has been described by Eberhardt, Geiss and Lutz [14].

From the iodine abundance shown in table 1, the excess ^{80}Kr and ^{128}Xe [1] and the neutron cross sections of bromine and iodine for 30-300 eV neutrons [11], the bromine content of Canyon Diablo graphite is estimated to be 15 ppm.

3.4. The ^{86}Kr anomaly

Alexander and Manuel [1] reported a small excess of ^{86}Kr in Canyon Diablo graphite and pointed out that neutron capture on ^{85}Rb followed by an electron capture branch in the decay of ^{86}Rb might be responsible for the ^{86}Kr anomaly. An excess of ^{86}Kr is also observed when the krypton spectra of Fayetteville [15], Abee, Canyon Diablo troilite [16], Richardton and Orgueil [17] are normalized to ^{84}Kr and compared with atmospheric krypton. In the following discussion it is shown that ^{86}Rb is not responsible for the excess ^{86}Kr in meteorites, but that neutron irradiation of meteoritic material will produce an excess of ^{86}Kr from some source other than fission of ^{235}U .

The excess ^{86}Kr in Canyon Diablo graphite is 6.2% of the excess ^{80}Kr . To demonstrate that ^{86}Rb is not responsible for the ^{86}Kr anomaly, we use the following equation to calculate the rubidium abundance necessary to produce the excess ^{86}Kr .

$$\begin{aligned} \left(\frac{^{86}\text{Kr}}{^{80}\text{Kr}}\right)_{\text{excess}} &= (\lambda_{\text{E.C.}}/\lambda_{\beta^-}) \\ &\times [^{85}\text{Rb}] \sigma_{85}/[^{79}\text{Br}] \sigma_{79}. \quad (3) \end{aligned}$$

Alexander, Manuel and Ganapathy [2] have measured

the isotopic composition of krypton from an irradiated rubidium salt and shown that $\lambda_{\text{E.C.}}/\lambda_{\beta^-} = 10^{-5}$ for ^{86}Rb . For thermal neutrons $\sigma_{85}/\sigma_{79} = 0.067$ [18]. For epithermal neutrons the σ_{85}/σ_{79} ratio is appreciably smaller due to the large epithermal resonances in bromine and their absence in rubidium [18]. Using 15 ppm for bromine and thermal neutron cross sections of ^{79}Br and ^{85}Rb , eq. (3) indicates that the graphite would have to contain a minimum amount of rubidium by weight in order to account for the ^{86}Kr anomaly. By a similar calculation it can be shown that all reports of excess ^{86}Kr in meteorites would require an unreasonably large rubidium abundance to produce the excess ^{86}Kr from electron capture.

Although neutron capture on ^{85}Rb is not responsible for the excess ^{86}Kr in meteorites, Merritt [18] has reported an excess of ^{86}Kr in neutron-irradiated samples of Abee and Bruderheim chondrites. The integrated flux of $5.59 \times 10^{18} \text{ n/cm}^2$ [9] on the Bruderheim chondrite, IBC-21, produced $2.0 \pm 0.5 \times 10^{-12} \text{ cm}^3 \text{ STP excess } ^{86}\text{Kr}$ per gram and an integrated flux of 10^{19} n/cm^2 [9] on Abee resulted in $20 \pm 3 \text{ cm}^3 \text{ STP excess } ^{86}\text{Kr}$ per gram.

Neutron-induced fission of ^{235}U may be responsible for part of this excess ^{86}Kr produced in irradiation. The uranium content of the Bruderheim chondrite IBC-21 has been calculated to be 17 ppm from the amount of fissionogenic xenon produced during the irradiation [19]. The spectrum for heavy isotopes in the irradiated Abee sample has not been published. Other investigators report the uranium content of Abee as 17 ppb [3], 12 ppb [3] and 11 ppb [3]. Using an average of these uranium values together with a fission cross section of 580 barns and a 2.02% yield at mass 86 [21], it can be shown that neutron-induced fission of ^{235}U would produce only $10^{-12} \text{ cm}^3 \text{ STP } ^{86}\text{Kr}$ per gram of Abee and $10^{-12} \text{ cm}^3 \text{ STP } ^{86}\text{Kr}$ per gram of chondrite.

The amount of ^{86}Kr produced in these irradiated samples from electron-capture of ^{86}Rb can be calculated from the rubidium contents. Gast [22] reports 3.45 and 3.41 ppm rubidium in Abee. The rubidium content of the Bruderheim chondrite has not been reported, but Shields [23] reports 2.79 ppm in a whole sample of Bruderheim. Using a neutron capture cross section of 0.76 barns for ^{85}Rb and 5×10^{-5} for the electron-capture branching of ^{86}Rb , it can be shown that the above rubidium

dances would produce only 2.8×10^{-13} cm³ STP ⁸⁶Kr per gram of Abee and 1.1×10^{-13} cm³ STP ⁸⁶Kr per gram of IBC-21. Thus, aside from the production of ⁸⁶Kr from ²³⁵U and ⁸⁵Rb, the irradiation of Abee and Bruderheim chondrules produced an excess of ⁸⁶Kr amounting to $19 \pm 3 \times 10^{-12}$ cm³ STP/g and $1.1 \pm 0.5 \times 10^{-12}$ cm³ STP/g, respectively.

The larger excess ⁸⁶Kr in Abee is probably due to the greater flux on Abee and to a greater abundance of the target nuclei which produce ⁸⁶Kr during the irradiation. If the difference in flux on the two samples is eliminated, then the Bruderheim sample is found to be depleted in the target nuclei by a factor of 8.4 ± 4 relative to Abee. By comparison Larimer and Anders [24] report Ag, Ga, Ge, I and Te in ordinary chondrites to be depleted relative to type I enstatite chondrites by factors of 7.8, 4.2, 5.6, 6.8 and 5.4, respectively. This suggests that the element responsible for the excess ⁸⁶Kr in the irradiated samples may follow the chemistry of the elements intermediate between metals and nonmetals in the right-hand side of the periodic table. Since the irradiation did not produce xenon in excess of the amounts expected from fission of ²³⁵U, symmetrical neutron-induced fission of lighter elements seems to be the only mechanism which could produce the ⁸⁶Kr anomaly.

The krypton spectra have been reported for only three irradiated meteorite samples [18], Abee, Bruderheim and Bruderheim chondrules. Each shows an excess of ⁸⁶Kr above that produced from ²³⁵U or ⁸⁵Rb. The whole sample of irradiated Bruderheim contained about the same excess ⁸⁶Kr as the irradiated Bruderheim chondrules, but the statistical error on ⁸⁶Kr in the whole sample is larger than the excess ⁸⁶Kr. From the data available it is not possible to determine if this excess ⁸⁶Kr is accompanied by excess ⁸⁴Kr and ⁸³Kr, as would be expected from fission. The neutron irradiation of a meteorite sample produces all the krypton isotopes except ⁷⁸Kr, which Merrihue [19] does not report. In the above calculations we have used the excess ⁸⁶Kr values reported by Merrihue, who normalized the krypton spectrum to ⁸⁴Kr. Since fission contributes to ⁸³Kr, ⁸⁴Kr and ⁸⁶Kr, this normalization gives a lower limit of the excess ⁸⁶Kr.

The excess ⁸⁶Kr in the unirradiated meteorites is apparently not due to fission of extinct ²⁴⁴Pu, since Hohenberg, Munk and Reynolds [25] note that the

excess ⁸⁶Kr in Pasamonte is so large that 'our lower limit for fission krypton exceeds that estimated from ²⁴⁴Pu by a factor of 12'. Thus an unexplained excess of ⁸⁶Kr has been reported in seven unirradiated meteorites [1, 15-17, 25] and produced in all reports of krypton analyses from pile-irradiated meteorites. It therefore seems likely that neutron-induced reactions are responsible for the excess ⁸⁶Kr observed in Canyon Diablo graphite and six other meteorites.

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