Clues in the Rare Gas Isotopes to Early Solar System History

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Those of us who work with rare gases in meteorites and lunar samples have been stimulated by progress in our subject in the Soviet Union. We remember well the work of Gerling, Pavlova, and Rik (refs. 1 and 2) who in 1951 and 1956 initiated potassium-argon dating of meteorites which has become an area of great importance. It was Gerling and Levskiy (ref. 3) in 1956 who made the striking discovery of the existence of gas-rich meteorites, one of the first manifestations of what we now know to be the solar wind. These two results alone have placed Soviet workers in the forefront of my field. We have also been privileged in my laboratory to work with lunar samples returned by the Luna 16 and Luna 20 landers.

Although this paper deals with work dating back as far as 1959, I feel it is still worthy of review, and I intend to present my latest and less tested thoughts on interpretations.

I first want to review the results we have obtained with the extinct radioactivity iodine-129. I remind you that this is a radioactivity which is produced in the r-process of nucleosynthesis and which decays with a half-life of 17 m.y. Consequently, we can expect this radioactivity to have been present in the early years of the solar system, with its concentration relative to normal [127]I changing by a factor of 2 every 17 m.y. In principle, then, it provides a clock sensitive to small time changes even though the events it records took place 4.6 aeons (1 aeon =

10^9 yr) ago. Figure 1 is an old familiar **one**, but it still makes its point. It is a xenon
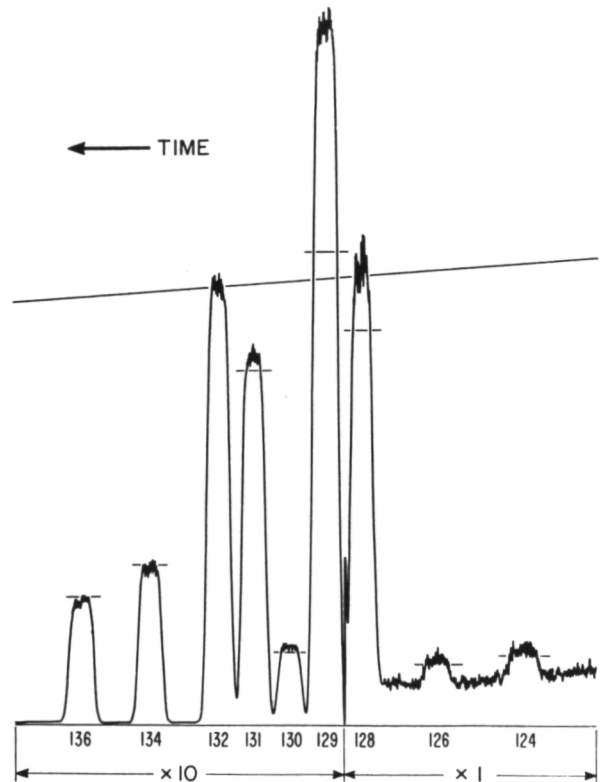

Figure 1.—*Mass spectrum for xenon extracted from the Richardton chondrite. The short horizontal lines mark where the peaks would fall if the sample were xenon from the atmosphere. By far the most marked anomaly is an excess at mass 129 due to radioactive decay of extinct [129]I.*
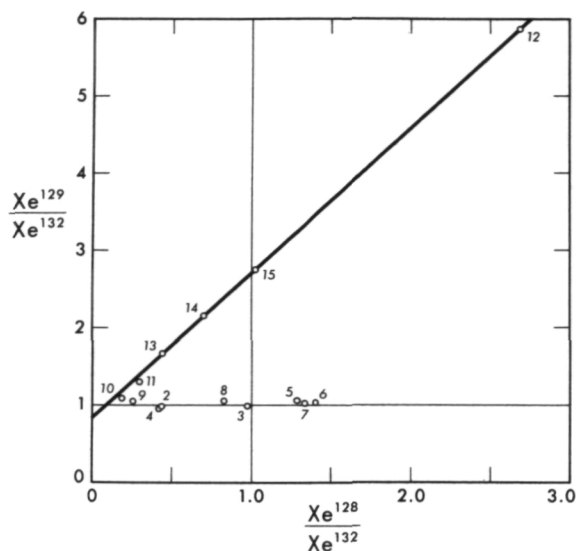
Figure 2.—*An isotope correlation plot for xenon from stepwise heating of a neutron-irradiated sample of the Shallowater achondrite. The numerals marking the points are extraction temperatures in hundreds of degrees. Above 1000°C there is a good correlation between the release of excess Xe^{129} from decay of extinct I^{129} and excess Xe^{128} produced from I^{127} during the irradiation. From diagrams of this type, the initial I^{129}/I^{127} ratio for the meteorite can be determined precisely (ref. 3).*

This correlation is best demonstrated by a plot which is shown in figure 2, where we graph the ratio $^{129}Xe/^{132}Xe$ versus $^{128}Xe/^{132}Xe$. The meteorite in question is the Shallowater enstatite achondrite (ref. 4). The numerals on the points are the temperatures at which the gas was released in hundreds of degrees Centigrade. We see that above 1000°C there is an almost perfect correlation between the release of excess ^{129}Xe and of excess ^{128}Xe. From the slope of this line plus data about the neutron irradiation it is possible to deduce that the initial ratio of ^{129}I to ^{127}I for this meteorite was 1.1×10^{-4}. By exposing different meteorites to the same neutron irradiation it is possible to measure time differences very directly. Figure 3 shows how we infer a difference in time of formation between the petrologic Type-4 Karoonda carbonaceous chondrite and the Peña Blanca Spring enstatite achondrite. Both these meteorites provide a good correlation line, and we infer a difference in the initial $^{129}I/^{127}I$ ratio which corresponds to a time difference of 7.5 m.y. In a study completed in 1970, Podosek (ref. 5) assembled an array
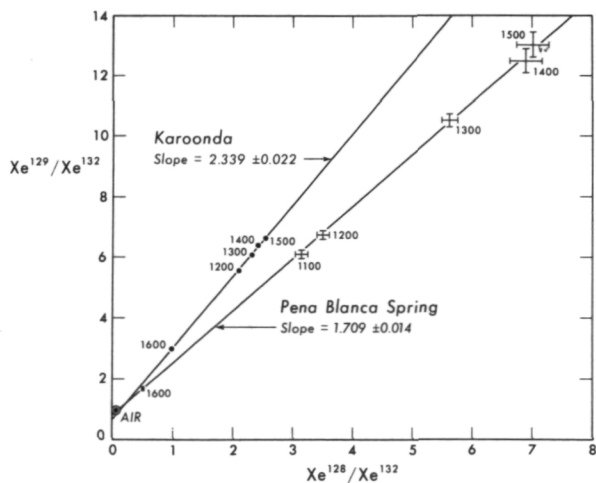
spectrum taken in 1959 from the Richardton chondrite. The small horizontal lines show where the peak tops would fall if we were examining a sample of xenon from the atmosphere. By far the largest deviation from this atmospheric composition occurs at mass 129 where there is a pronounced "spike" of excess gas. Since 1959, this pattern has proved to be a quite general property of meteorites and has led us to explore what we call the iodine-xenon method of dating. In order to carry this method out with some precision, we irradiate the material with slow neutrons, thereby converting part of the ordinary ^{127}I into ^{128}Xe. We follow this irradiation with a stepwise heating of the meteorite, examining the isotopic composition of the xenon given off at successively higher temperatures. Typically, we enter a high-temperature regime in which the release of excess ^{129}Xe correlates with the release of excess ^{128}Xe produced in the pile.

Figure 3.—*Correlations (see caption for fig. 2) for two meteorites having different initial I^{129}/I^{127} ratios as evidenced by the difference in slope. The difference in time of formation inferred for these two meteorites is 7.5 m.y., with the Karoonda carbonaceous chondrite (petrologic Type 4) antedating the achondrite Peña Blanca Spring (ref. 4).*
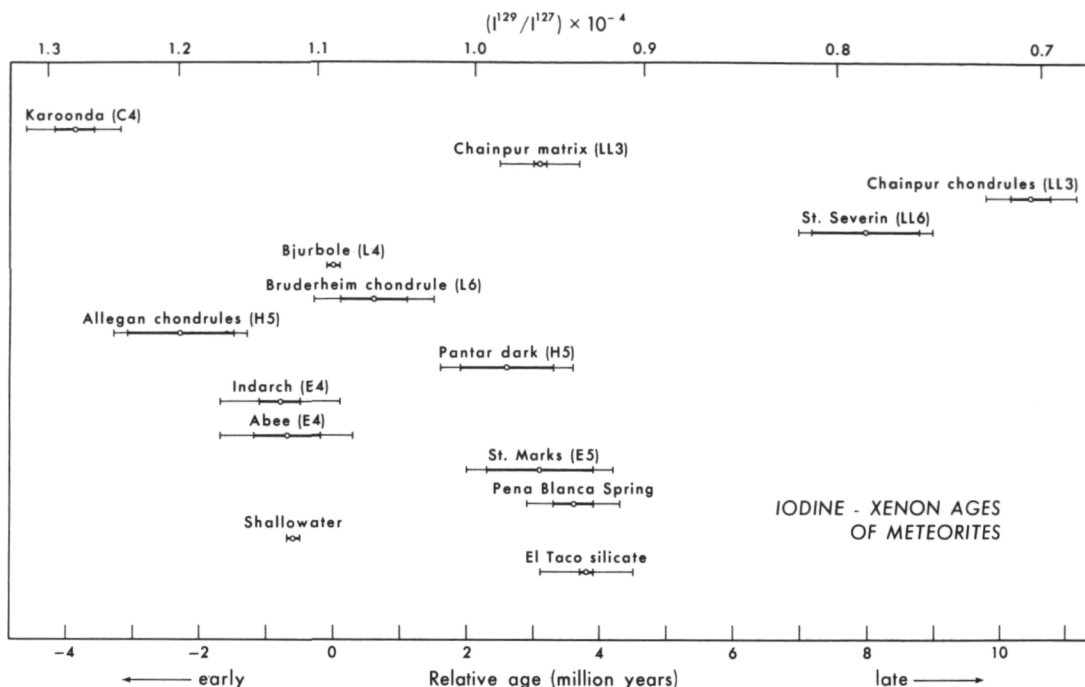
Figure 4.—*An array of I-Xe ages assembled by Podosek (ref. 4) in 1970. The formation times for very diverse meteorites, including a silicate inclusion from the iron meteorite El Taco, all lie within a span of 14 m.y.*

of these iodine-xenon ages which is shown in figure 4. An important observation to be made from these results is that despite the presence on the diagram of very diverse meteorites—including chondrites, achondrites, and a silicate inclusion from an iron meteorite—the total spread in time inferred by this method is quite short, amounting to only 14 m.y. We have referred to this result (ref. 6) as "sharp isochronism" for the formation of the meteorites. We have thus far not been able to determine very meaningfully the detailed time differences occurring in the figure. Nevertheless, there are some individual results which we find significant. Figure 5 shows a recent result obtained in joint work between my laboratory and that of Professor Anders at the University of Chicago (ref. 7). Professor Anders and his coworkers learned how to isolate magnetite from carbonaceous chondrites, and we have found that
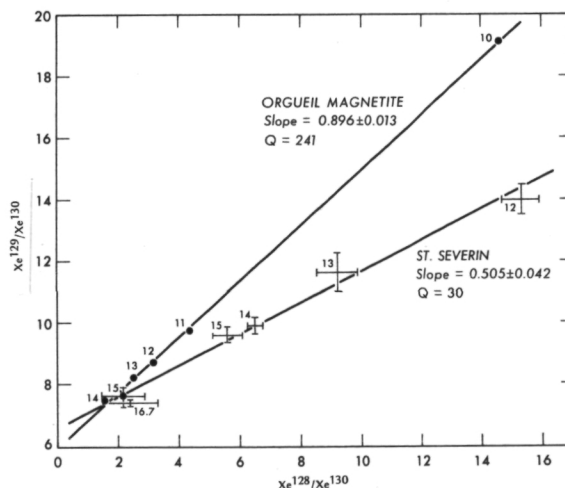

Figure 5.—*Another time difference inferred by the I-Xe dating method. A good correlation was obtained for magnetite from the Type-1 carbonaceous chondrite Orgueil. Orgueil is the most ancient object yet dated by this method, but precedes Karoonda (see fig. 3) by only 1.8 m.y. (ref. 6).*

this mineral is favorable for iodine-xenon dating. You will note that we obtained an excellent correlation for magnetite from the carbonaceous chondrite Orgueil. When placed in the scheme of relative ages that we saw in figure 4, Orgueil magnetite appears to be the earliest or most primitive object dated so far, but separated in time from the Karoonda stone by only 1.8 m.y. There are two important inferences to be made from this result. First, the carbonaceous chondrites are basically contemporaneous with the rest of the meteorites. Secondly, if there is an evolutionary relationship between the petrologic Type-4 chondrites like Karoonda and the more primitive Type-1 carbonaceous chondrites like Orgueil, this evolution took place with rapidity—that is within about 2 m.y. Another detailed result of iodine-xenon dating that appears significant to us is shown in figure 6, where we exhibit the attempt to establish one of these iodine-xenon correlations for the meteorite Manych, a sample of which we received for this purpose through the generosity of Professor Krinov. Manych is an exceptionally unequilibrated meteorite; it is basically an assemblage of fresh chondrules. It is interesting to us that we were not able to ob-

tain an iodine-xenon correlation for this stone (ref. 8), suggesting that the individual chondrites which made it up had different times of origin so that there was not a single event that we could date. The very well defined correlation for the Abee enstatite chondrite is also shown in figure 6 by way of contrast. In Abee we have an almost perfect correlation; in Manych, none at all. Before leaving the topic of iodine-xenon dating, I want to comment that the correlation, when it occurs, seems to be extremely durable. Hohenberg and I (ref. 9) investigated this question in 1969. We took a sample of the Abee stone and heated it to 1200°C in vacuum for 1 hour *before* carrying out the neutron irradiation. We knew from experience that this preheating would drive out about 90 percent of the xenon. We anticipated, therefore, that the iodine-xenon correlation would be largely destroyed. To our surprise, when we examined the preheated sample, even though as anticipated the xenon had been very largely expelled, the residual xenon which came off at temperatures of 1200°C and above exhibited exactly the same correlation as the sample which had received no preheating whatsoever. That result is shown in figure 7. Professor Wasserburg likes to use the word "magic" to describe this durable correlation. Upon reflection, I think we have to say that this durability is not magic at all, but simply a consequence of the fact that wherever the iodine is located in these objects, that part of it that is not disturbed until very high temperatures behaves exactly the way xenon does when similarly located. In other words, the retentively sited iodine appears to be caged in the very durable minerals in such a way that it makes no difference, as to its release, whether it has changed into xenon or not. This supposition is important for interpreting the results of our work because it says that the iodine-xenon date of a meteorite is very little disturbed by heating. This may account for the fact that these dates comprise a compact group: the iodine-xenon clock is very difficult to reset. We could feel more confident of these assertions if we understood
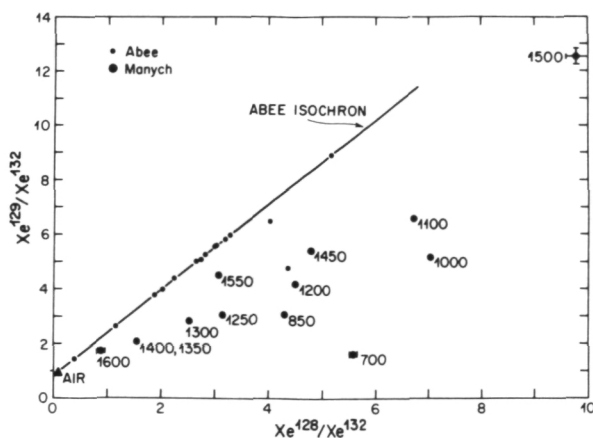

Figure 6.—*An interesting case where an I-Xe correlation was not observed. The chondrite Manych is essentially an assemblage of fresh chondrules. The I-Xe data suggest that these chondrules were not all formed at the same time. The excellent correlation for Abee is shown for contrast. (ref. 7).*
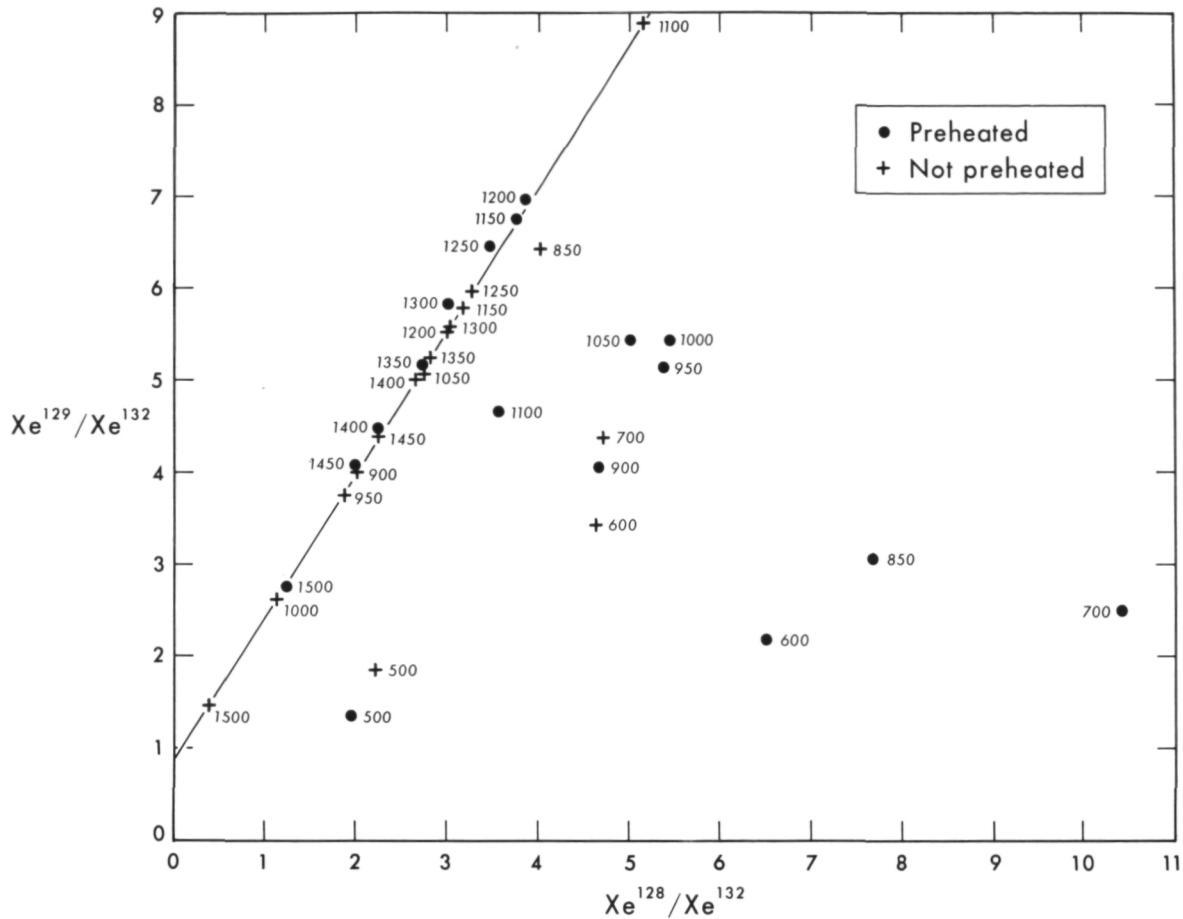
Figure 7.—*Evidence of the durability of the I-Xe correlation in the enstatite chondrite Abee. A preheating of the stone to 1200° C before the neutron irradiation removed 90 percent of the xenon, but did not alter the quality or magnitude of the correlation with iodine for that xenon still remaining in the stone. In the Abee stone the I-Xe clock seems to be almost impossible to reset by simple heating. (ref. 8).*

better the location of the retentively sited iodine in these objects. Unfortunately we still know very little about its location. Possibly the ion microprobe which is beginning to come into use in research will prove useful in this connection.

Another important chapter in the study of extinct radioactivities concerns the radionuclide ^{244}Pu. As early as 1960, Kuroda (ref. 10) recognized that if we were correct about our interpretations of the excess xenon-129 found in meteorites we should also expect to find fissiogenic xenon in these objects from the decay of ^{244}Pu, which disintegrates in part by spontaneous fission. Ku-

roda could make this observation with great certainty because ^{244}Pu would undoubtedly be produced in the r-process and would necessarily outlive ^{129}I because of its 82-m.y. half-life. It was Rowe and Kuroda (ref. 11) who then first obtained experimental indications of the validity of Kuroda's assertion. Studying xenon in achondrites, they detected a prominent excess fissiogenic component which had a characteristic isotopic pattern. We now know beyond any doubt that this pattern comes from ^{244}Pu. In 1969, a group of us at Berkeley (ref. 12) succeeded in examining the fission xenon from a sample of ^{244}Pu produced artificially. The results of
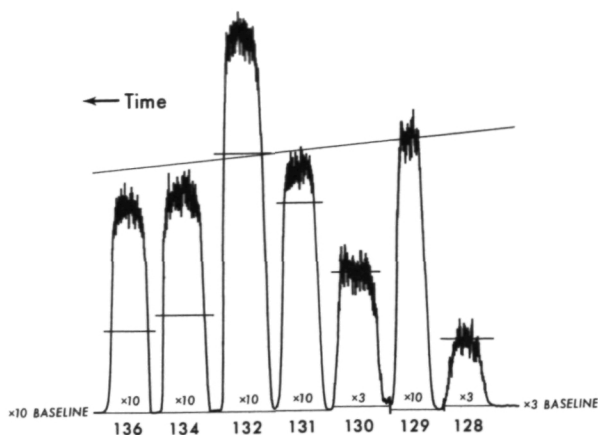
Figure 8.—*Isotopic composition of xenon from spontaneous fission of an artificially prepared sample of* ^{244}Pu. *The short horizontal lines indicate the contributions from air contamination. The small peak from air at mass 128 results from three million atoms. (ref. 11).*

that analysis are shown in figure 8. Again the horizontal lines show where the peaks would fall if only atmospheric xenon were present. The excesses, which is to say the heights of the peaks above these horizontal lines, represent the spectrum of the fissiogenic sample. One notes that it consists of a small amount of ^{131}Xe accompanied by almost equal amounts of ^{132}Xe, ^{134}Xe, and ^{136}Xe. In passing I would like to mention that the smallest peak in this spectrum, the peak at mass 128, corresponds to only three million atoms, which is an indication of how sensitive these techniques can sometimes be. Figure 9 shows how well this isotopic pattern fits the pattern we had previously known from the achondrites. The dark circles are the values from the artificially prepared sample of ^{244}Pu. The open circles and squares are from the achondrites Pasamonte and Kapoeta, respectively. As you can see, the match is virtually perfect and differs considerably from the pattern of fissiogenic xenon from another nuclide at mass 244, ^{244}Cu. It is more difficult to utilize ^{244}Pu in a dating scheme because we lack a reference isotope of Pu which can play the role of ^{127}I. The best we can do at present is to suppose that the Pu when it was extant was

associated in meteorites with uranium. We can then carry out a dating experiment that is somewhat analogous to our procedure for the iodine-xenon method. By irradiating the meteorite with neutrons we produce additional fissiogenic xenon at the uranium locations. If these locations had also been the locations for plutonium, the effect of the irradiation is to revise the isotopic compositions of the fissiogenic xenon released from the uranium sites. A successful experiment of this type is shown in figure 10 where Podosek (ref. 13) plotted the ratio $^{130}Xe/^{132}Xe$ versus the ratio $^{134}Xe/^{132}Xe$ for temperature fractions of xenon from an irradiated sample of the St. Severin meteorite. After correction for spallation effects, which shifted the points from positions designated by the small circles to the positions designated by the crosses (these corrections are quite substantial), the points do lie on a line that is intermediate between one given by fissiogenic xenon from ^{244}Pu and one given by fissiogenic xenon generated entirely by pile neutrons acting on uranium. The detailed position of this line enabled Podosek to
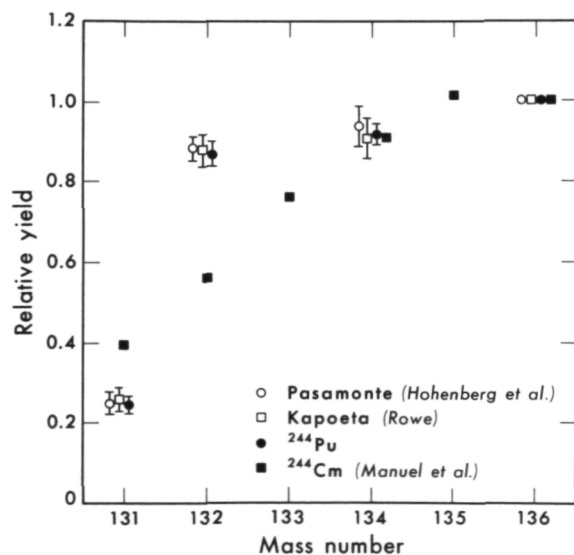

Figure 9.—*Agreement between the isotopic pattern for xenon from spontaneous fission of* ^{244}Pu *(see fig. 8) and fissiogenic xenon found in achondrites. By this comparison, existence of* ^{244}Pu *as a bona fide extinct radioactivity was confirmed (ref. 11).*
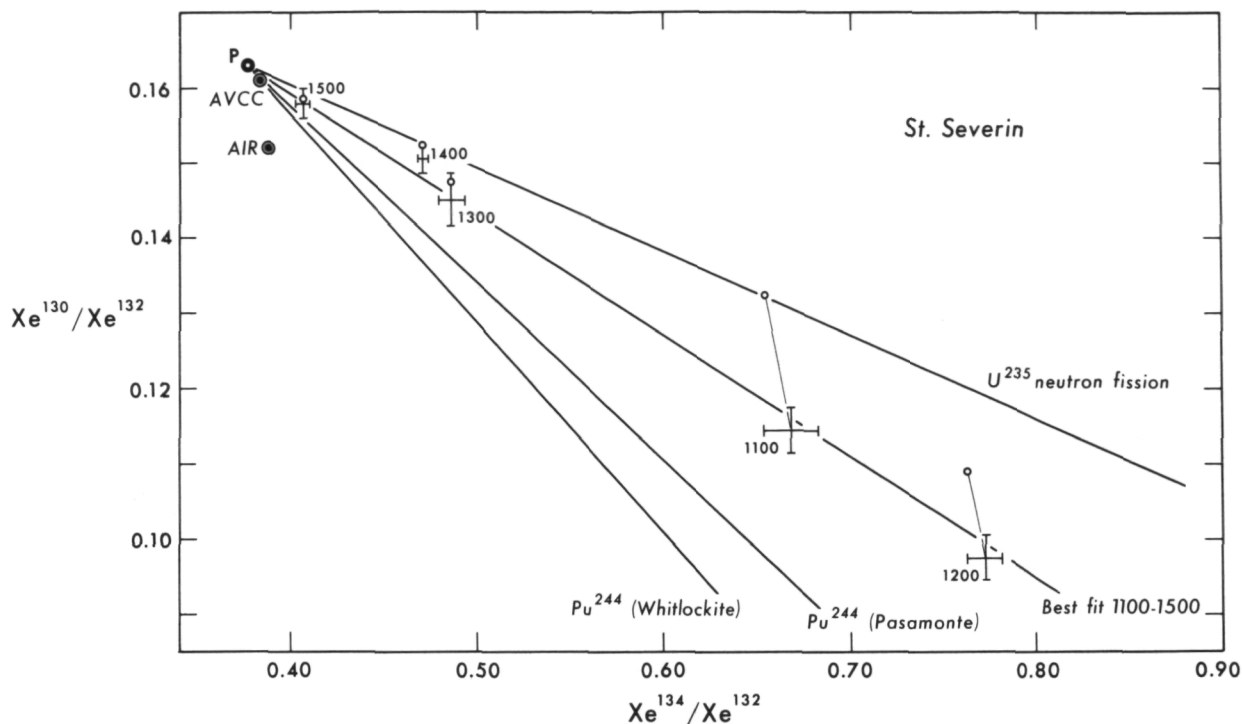
Figure 10.—*Evidence for an association between uranium and Pu²⁴⁴ in the chondrite St. Severin. The correlation plot is for xenon extracted in stepwise heating from a neutron-irradiated sample. The points have been corrected as indicated for spallation xenon resulting from galactic cosmic rays. The correlated high temperature points define a line intermediate between the lines obtained by mixing trapped xenon with (1) xenon from Pu²⁴⁴ fission and (2) xenon from neutron-induced fission of U²³⁵. The position of the intermediate line fixes the initial Pu²⁴⁴/U²³⁸ ratio in the sample at 0.013 (ref. 12).*

calculate an initial ratio ²⁴⁴Pu/²³⁸U of 0.013 for a bulk sample of St. Severin. Tentatively, we view that number as our best determination up until now of the ratio for the solar system at the time the meteorites commenced to retain xenon. So far it has not been possible to obtain quantitative results of this type for as many meteorites as would be needed for dating. The few cases where success has been obtained do support the idea of general contemporaneity of meteorites. There is no known contradiction between the iodine-xenon and the plutonium-xenon dating schemes.

One of the important applications of these results has been to the subject of cosmochronology. If one were provided with a sufficiently large array of radioactive nuclides, both extinct and extant, produced in r-process nucleosynthesis, one could in prin-

ciple deduce in detail the chronological history of that mode of nucleosynthesis. Figure 11 shows how such a chronology might be displayed. If we say that the galaxy was born at $t = 0$ and that the nucleosynthesis which contributed to our solar system went on up until the time, T, we could represent the production rate as a function of time by the function p (t). In the model I have illustrated in the figure there is shown a large amount of early nucleosynthesis, followed by a modest amount of continuous nucleosynthesis, and terminated by a late spike. I should emphasize that this model is only illustrative and many others are possible, although they must be, as we shall see, bound by the constraints imposed from abundance measurements for the array of radioactivities. Following the end of nucleosynthesis there is a dormant period, Δ, during which
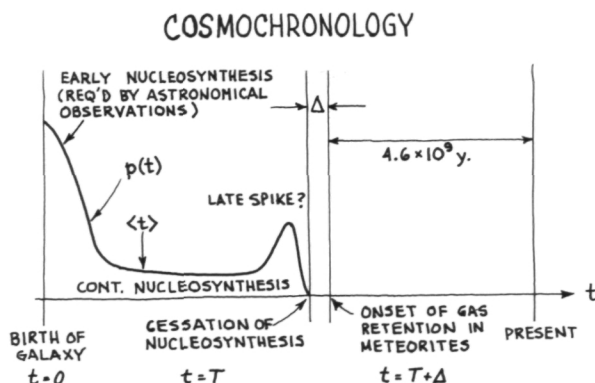
COSMOCHRONOLOGY

Figure 11.—*An illustrative model for r-process nucleosynthesis.*

radioactivities decayed but were no longer replenished, and which terminated with the formation of our contemporaneous array of meteorites. Following that event by 4.6 aeons is the present. Turning to figure 12, one sees the equations for the abundance of radionuclides at the time of formation of the meteorites, $t = T + \Delta$. The equation in the top line simply says that the amount left at $T + \Delta$ will be the sum of the amounts produced at various times, t, after taking into account the extent to which radioactive decay will have diminished those amounts. We use $p(t)$ as before to designate the general rate of nucleosynthesis and P_i to represent the production factor for the particular radionuclide in question. Rearranging that equation in the second line, one sees that the ratio of the abundance N_i to P_i, multiplied by a simple exponential factor, is equal to a quantity which is a single value of the function that is essentially the Laplace transform of the production rate $p(t)$. This tells us that a large number of radionuclides, well distributed as to mean life, would provide us with the Laplace transform of the production function. But from the Laplace transform we could deduce the production function as its inverse. In reality, the number of nuclides available for this purpose is quite limited—the radioactive isotopes of uranium, thorium, rhenium, and the extinct nuclides [129]I and [244]Pu that we have discussed earlier in this report. Thus we can only deduce

a few features of the production function. The principal results obtained on a relatively firm basis are shown at the bottom of figure 12. As Schramm and Wasserburg (ref. 14) were first to point out, one of the important results is a value for the average time for nucleosynthesis, which is to say the center of gravity of the production function. We know from the uranium and thorium isotopes that the average age for r-process material is at least 8 aeons ago. In addition, the results for iodine and plutonium taken together give quite a firm value of Δ, 150 m.y. And, finally, our best value (discussed above) for the initial abundance in the solar system of [244]Pu relative to uranium suggests that there was *not* a late spike in the production function. There has recently been proposed by Reeves (ref. 15) an interesting speculation as to what might have led to the 150-m.y. interval of dormancy. Reeves points out that this period is about the time between successive passages of our pre-solar cloud of dust and gas through the dense spiral arms of our galaxy where fresh radioactivities would preferentially be added. He suggests that the last nucleosynthesis coincided with the passage of our cloud through the next to last spiral arm. The measurements of Δ, according to this model, are then measurements of the time we spent cruising between the spiral arm which last put radioactivities into our cloud and the following spiral arm wherein the condensation of our Sun was triggered.

$$N_i(T+\Delta) = P_i \int_0^T p(t)\, e^{-\lambda_i(T+\Delta-t)}\, dt$$

$$\frac{N_i(T+\Delta)}{P_i} e^{+\lambda_i(T+\Delta)} = \int_0^T p(t)\, e^{-\lambda_i t}\, dt \equiv f(\lambda_i)$$

IF THERE WERE MANY SPECIES WITH DIFFERENT λ_i's
$p(t)$ COULD BE OBTAINED AS ESSENTIALLY THE INVERSE LAPLACE
TRANSFORM OF THE FUNCTION $f(\lambda)$.

FIRM RESULTS: $\langle t \rangle \sim 9$ b.y. AGO (U, Th CONSIDERATIONS)
                $\Delta \sim 150$ m.y.   (BASED ON I[129])
                LATE SPIKE? - PROBABLY NOT (BASED ON Pu[244])

Figure 12.—*Equations for the abundances in newly formed meteorites of radioactive nuclear species produced in the r-process. Some inferences about solar system cosmochronology are also stated.*

I have two final topics I want to touch upon. First, I want to mention that the products of extinct radioactive decay have somewhat surprisingly been detected in both terrestrial and lunar samples. I am not referring here to the examples of in-situ decay of ^{244}Pu which have been detected both by nuclear tracks and by xenon measurements in lunar rocks. These results were fully to be expected simply because of the great antiquity of the lunar rocks in question. What I am referring to here is the observation of amounts of ^{129}Xe and fissiogenic xenon from ^{244}Pu in certain Apollo 14 breccias where the abundance of these gases is much higher than can be accounted for by in-situ production. This result was discovered by Drozd et al. (ref. 16) in St. Louis, and has been confirmed in our laboratory at Berkeley. Somehow accumulations of xenon that originated in decay of extinct radionuclides were stored in the Moon before being implanted in certain special Apollo 14 breccias,
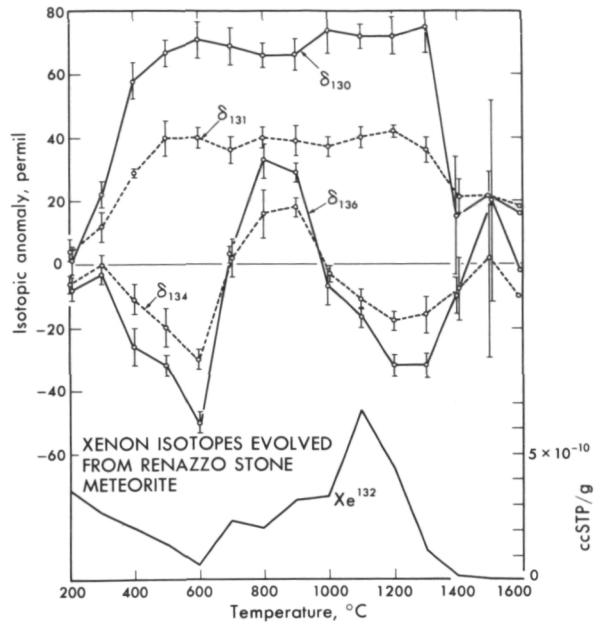

Figure 14.—*Evidence for an anomalous fission-like component in the Renazzo carbonaceous chondrite. The component is released in a mid-temperature range (ref. 18).*
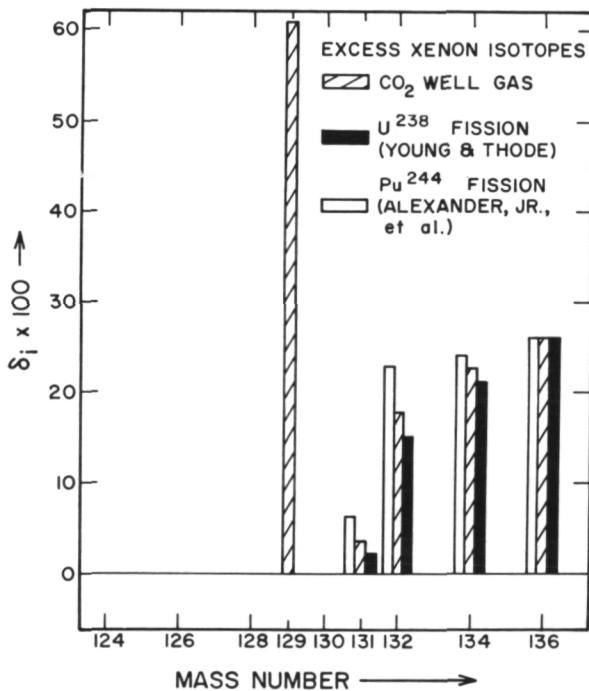

Figure 13.—*Isotopic composition of xenon from a Co$_2$ gas well in New Mexico. The excess Xe^{129} is unambiguous. The fissiogenic xenon may be in part from Pu^{244} (ref. 17).*

the implantation presumably having been accomplished by shock. An analogous result for the Earth was the observation of anomalous xenon in certain CO_2 gas wells in the state of New Mexico. First observed at Berkeley in 1963 (ref. 17), this result was beautifully confirmed in 1971 by Boulos and Manuel (ref. 18) at the University of Missouri at Rolla. Their result is shown in figure 13. The excess abundance of ^{129}Xe is completely unambiguous in their work. In addition, they see a fissiogenic component which may be in part from ^{244}Pu. More measurements are needed before we can be sure about the plutonium fossil. Again the place of storage for these xenon samples is unknown.

Finally, let me refer to the anomalous fissiogenic xenon we have seen in the carbonaceous chondrites Renazzo and Murray. In the middle range of temperatures in a stepwise heating extraction, a pronounced fission-like component was seen in both these meteorites. We see in figure 14 that for Renazzo (ref. 19) the effect takes the
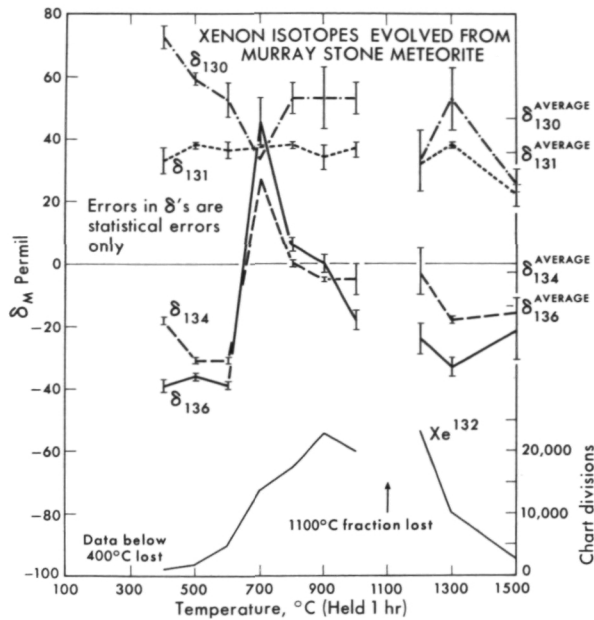
Figure 15.—*Occurrence of the anomalous fission-like component of xenon in the Murray carbonaceous chondrite. Again the component is released in a mid-temperature range.*

form of simultaneous increases in the relative abundances of ^{134}Xe and ^{136}Xe. A similar result is seen for Murray in figure 15. We have known for many years now that the isotopic pattern for this fission-like component differs in these carbonaceous stones from other fissiogenic patterns. The origin of this component is still unknown. For a time it was attractive to attribute it to fission of a super-heavy element. Such an element could be both fissiogenic and volatile and therefore might be selectively concentrated in the carbonaceous chondrites as suggested by Heymann and Anders (ref. 20) and on other grounds by Dakowski (ref. 21). Theorists who study the likelihood that such a super-heavy nuclide could be produced in the r-process seem lately to be very doubtful (ref. 22). It may be that the anomalous xenon component in the carbonaceous chondrites is somehow related to the anomalous oxygen that Clayton and his coworkers (ref. 23) have recently detected in nonhydrous minerals in carbonaceous chondrites. They have convinced us that the anomalous oxy-

gen is of a nuclear and not a chemical origin; it may represent material from interstellar grains which were not mixed isotopically with the rest of the solar system. If this indeed was the case, these grains may have contributed anomalous xenon as well. Clearly these unanswered questions are much in our minds in the ongoing research.

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