Search for ^{129}Xe in Mineral Grains from Allende Inclusions: An Exercise in Miniaturized Rare Gas Analysis

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*Dedicated to Professor H. Hintenberger on the occasion of his 70th birthday**

A static mass spectrometer, modified by installation of a Baur-Signer (Zürich) ion source and an ion-counting system, was used to detect xenon from single mineral grains from inclusions in the C3 meteorite Allende. The grains were melted in small conical heaters wound from tungsten wire. In almost all cases excess ^{129}Xe from ^{129}I decay was detected, in concentrations varying from < 1000 to 600,000 atoms per microgram. Inferred iodine concentrations increased on the average from pentlandite (0.6 ppb), to hedenbergite (21 ppb), to olivine (92 ppb), to enstatite (203 ppb) to melilite (422 ppb), but vary widely from one grain to another of the same mineral, indicating that the iodine resides in some minor phase which is included "spottily" in the bulk phases over which we had good mineralogical control. About 23,000 atoms of fissiogenic ^{132}Xe, presumably from ^{244}Pu decay, was detected in the largest melilite sample analyzed, but we cannot determine from this study whether the ^{244}Pu is "spotty" like ^{129}I or is uniformly distributed in the melilite. One can foresee that if the samples could be loaded into previously outgassed heater cones, a system such as the one described in this paper would have ^{132}Xe blanks of $\sim 50{,}000$ atoms. It is likely that in such a system the detectability for excess Xe achieved in this paper ($\sim 20{,}000$ atoms) could be substantially improved. We also ran St. Severin troilite, which contains less than $\sim$ 33 atoms of excess ^{129}Xe per microgram, and a single chondrule from Allegan, which contains higher concentrations of radiogenic xenon than were previously reported by Podosek from runs on a pile-irradiated sample.

Introduction

The iodine-xenon method of dating meteorites, which has been practiced since 1960 [1] and has recently showed signs of furnishing useful chronological information [2–4], has always suffered from our ignorance about the iodine sites in the rocks being studied. Since it has been clear that the ultimate sensitivity of the method has never been closely approached in practice, we undertook [as a sabbatical leave project for one of us (JHR)] a search for excess ^{129}Xe in hand-picked mineral grains from inclusions in the Allende C3 carbonaceous chondrite. Essential to the project was miniaturization of the techniques for analysis of traces of xenon from mineral specimens. This report is thus in part a summary of the techniques used and in part a description of results obtained. The experimental work was mostly carried out at the University of Western Australia during the period September 1978 to June 1979.

The Samples

Mineral grains in the 100 – 500 μ size range were hand picked from Allende inclusions under a binocular microscope using stainless steel dental tools. Olivine and enstatite grains were identified optically and confirmed by Scanning Electron Microscopy (SEM) with Energy Dispersive-Analysis of X-ray (EDAX). SEM/EDAX was necessary, e. g., to make the distinction between pentlandite and troilite in sulfide grains from inclusion AI-8. Hedenbergite and melilite grains from inclusion AI-9 were segregated on the basis of color and identified by SEM/EDAX. Sample descriptions are summarized in Table 1.

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* We are pleased to be able to include this paper in a collection in honor of Professor H. Hintenberger, whose work and personal friendship over the years have been held by us in the greatest esteem.

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Table 1. Descriptions and identification data for the Allende samples.

Inclusion No.	Description	Minerals	Description	Method of Identification
AI-1	White inclusion 3.0 × 1.5 mm	Olivine	Colorless, ~ Fo_{90}	Optical, SEM/EDAX
AI-5	Green chondrule 1 mm diameter	Olivine	Pale green, ~ Fo_{85}	Optical, SEM/EDAX
AI-6	Gray inclusion 1.0 × 1.5 mm	Olivine	Gray, ~ Fo_{80}	Optical, SEM/EDAX
AI-8	Dk. gray chondrule	Pentlandite	Bronze-yellow	SEM/EDAX needed to distinguish from troilite
AI-9	Gray inclusion 3 mm diameter	Enstatite	Gray, En_{90-100}	Optical, SEM/EDAX
		Hedenbergite	Dk. gray, nearly pure $CaFeSi_2O_6$	SEM/EDAX
		Melilite	Lt. gray	SEM/EDAX

The SEM/EDAX was performed on a Cambridge Stereoscan 600 scanning electron microscope equipped with a Kevex-Ray energy dispersive spectrometer. Several X-ray energy spectra were taken from each grain by scanning over large areas of the surface. In addition, the grains were examined at high magnification for impurities, with point X-ray analyses taken from any unusual looking areas. The grains were identified by referring to the X-ray spectra of a standard set of mineral samples. Enough standard samples were available to allow composition estimates to be made for olivines and pyroxenes (Table 1).

Larger samples were weighed to within several micrograms on a standard laboratory balance. Smaller samples were weighed on a Perkin Elmer TGS-2 thermogravimetric system which incorporated a sensitive electrobalance. It was found that improved stability resulted from maintaining the weighing cell at a slightly elevated temperature (30 °C). The aluminum disks used to wrap the samples, preformed as tiny cups, had to be tared on a day preceding the final weighing, but a series of permanent standards was weighed each day in order to verify reproducibility of the balance. Later in the research, after it was found that $^{129}Xe_{excess}$ concentrations were highly variable for different grains of the same mineral, there came to be less emphasis on weighings and the weights of very small grains were estimated from the dimensions of the grains as measured with a reticle in a binocular microscope.

The Gas Extraction System

Samples, which varied in size from 1 to 650 micrograms, were usually wrapped under a binocular microscope in disks of 0.00245 cm (1 mil) Al foil 2 mm in diameter. Samples before and after wrapping were easily transported with a slightly sticky (by touch to the tongue) steel needle. For analysis they were vaporized in small conical cups (see Fig. 1) wound from 0.0254 cm (10 mil) tungsten wire through which a heating current of 8 amps was passed. Four such cups were mounted with electrical feedthroughs on a standard 2 inch Conflat flange which constituted the floor of a stainless steel heating cell (see Fig. 2) approximately 38 mm in diameter and 50 mm high. The roof of the heating cell was closed by a 1 inch Varian valve which gave access, when opened, to a viewing window and a fast pumping system. The cups were always observed through the window, before and after vaporization, by a binocular microscope designed for medical applications and thus fitted with an illuminator and optics for long working distances. It was found necessary, in order to prevent samples from jumping out of the heating cups, to tamp a few wisps of fine

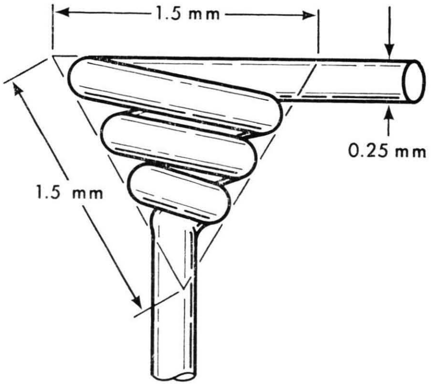

Fig. 1. Detail of tungsten heating coil.

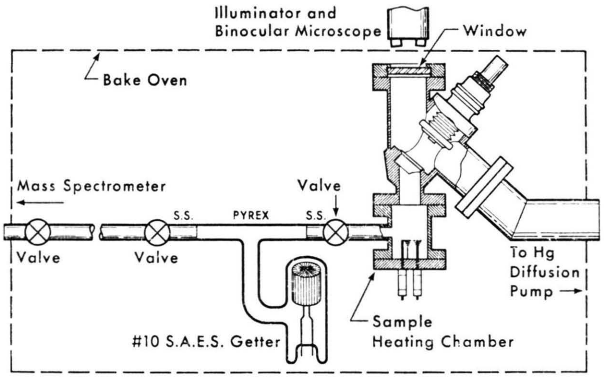

Fig. 2. Gas extraction system.

Pyrex wool into the cups on top of the samples. The gases released were conducted through a simple train of valves and a small, glass-encased S.A.E.S. getter (see Fig. 2) to the mass spectrometer. The sample system up to and including the "spectrometer valve" was baked overnight (until 4 AM) at 200 °C. The standard heating time for the tungsten cups was 3 minutes, followed by 1 minute gettering time, and 5 minutes insertion time (with ion beam off) into the mass spectrometer. The rapidity of these procedures easily permitted the four samples to be run off in a working day, together with the blanks that were always included in such a series of runs in order to monitor the tightness and cleanliness of the system.

During the period of work for this paper, the cold blank for this extraction system averaged 47,000 ^{132}Xe atoms, the hot blanks averaged 250,000 ^{132}Xe atoms, and the samples run averaged 380,000 ^{132}Xe atoms. A filament reheated in the system, when all other filaments had been run and the filament in question had been extensively outgassed, gave a hot blank of the same size as the cold blanks, indicating the blank level that could be achieved if it were possible to load the cups with samples in vacuum after the filaments had been well outgassed.

The Mass Spectrometer

The mass spectrometer for this research was a Nuclide Corporation 6 inch, 60°-deflection apparatus of ancient vintage and large volume (about 5 liters) but extensively modified for the work at hand. These modifications included installation of a Baur-Signer ion source, the fitting of a fast mercury diffusion pump of metal construction which could be substituted for the existing ion pump when desired, the installation of a 50 l/sec water-cooled S.A.E.S. getter, and modification of the detector system for ion counting. The *Baur-Signer ion source*, designed at the Swiss Federal Institute of Technology at Zürich, was selected for this work because of its high sensitivity (we discuss the calibration of the source more fully below) and virtually 100% transmission for the focussed ion beam: almost all ions of the focussed mass which are formed by electron bombardment reach the final collector. The half life for xenon atoms in the apparatus was found to be 1.6 hours. The source is designed to be operated without a source magnet, making for the additional advantages of good stability and low mass discrimination. During sample insertion the pumping action of the ion source was defeated by turning off the high voltage and connecting the draw-out plates to +10 volts, which effectively prevents any positive ions from leaking from the region in the source where they are formed. The *mercury diffusion pump* was employed for pumping the machine prior to xenon runs in order to reduce the rare gas ion background. For the sizes of samples we were handling, the "regurgitation" background for rare gases in an ion pump can be excessive. The *S.A.E.S. getter* was seen as a backup for the small getter in the gas extraction system. With our 5-minute insertion time for samples, there were opportunities for additional cleanup in the mass spectrometer volume even though the getter was operated at room temperature where it best reduced the hydrogen background in the machine. In the *ion counting system* we benefited from the excellent ion counting properties of the Nuclide 20-stage multiplier of box and grid design. With 3000 volts on the multiplier voltage string, we had virtually 100% counting efficiency. With the ion beam disabled, the background counting rate was approximately 0.25 counts per second. The scattered ion counting rate responsible for the remaining "zero" background in the xenon region of the ion spectrum was an additional 0.4 counts per second, or thereabouts. The ion pulses were taken off the last dynode (electrically more quiet than the preceding dynode) and were amplified by "slow" but otherwise effective ORTEC electronics consisting of a Model 142 PC preamp and Model 490 B amplifier-discriminator. Data were taken by improvised manual switching of the high voltage, without altering the draw-out potentials relative to the ion box. Despite this rather clumsy switching method, the mass discrimination of the spectrometer was undetectable ($0 \pm \sim 1$ permil per mass unit) in results for an air xenon sample studied for the purpose. A preexisting counter/line-driver available at Perth recorded the ion counts in contiguous 10-second intervals on paper tape via a teletype. The usual *modus operandi* was to count for 3 10-second intervals and switch to another peak or zero during a 4th, although data blocks of any length could be freely utilized during the run if desired.

Xenon Calibrations

We had two reliable bases for determining the xenon calibration for our microsystem, a direct and an indirect method. The direct method is based upon aluminum foil, from the same roll of 1 mil foil used for wrapping samples, into which fission fragments from a strong ^{252}Cf source had been implanted under controlled conditions. Such foil was prepared in a vacuum box by holding a calibrated point source of ^{252}Cf a known distance above the foil for a known length of time. The "subsolar" point of the irradiated foil having been marked, circles of constant xenon content could then be scribed on the foil. The samples for measurement were obtained from the foil with the same 2 mm diameter punch used to prepare disks of unirradiated foil for the wrapping of samples. Over the period Feb. 14, 1978 to June 3, 1979 in which such irradiated foils were measured, three different strengths of foil were used, containing approximately 15, 9, and 30 thousand ^{132}Xe$_f$ atoms respectively. Figure 3 shows the result of all such foil calibrations and from the Fig. it can be seen that the runs were all carried out during a period when, as far as we know, the ion source had approximately its full "advertised" sensitivity. The runs were considered to be of various degrees of reliability and are so plotted. Most reliable were those runs where both the ratios ^{136}Xe/^{132}Xe and ^{134}Xe/^{132}Xe were measured and where the amounts of ^{132}Xe$_f$ calculated from the two measured ratios were in agreement within experimental error. The next most reliable runs were those where only ^{136}Xe/^{132}Xe ratios were recorded but otherwise the system seemed to be in "top form". The least reliable determinations were those where the 136/132 and the 134/132 calibrations were both obtained but were not in agreement. In all cases the calibration obtained from the 136/132 ratio is that plotted because that ratio changes more rapidly when fission xenon from ^{252}Cf is added to atmospheric xenon. The calibrations are expressed in terms of amps per Torr for xenon atoms. In our direct method they depend upon the percent fission yields for xenon isotopes

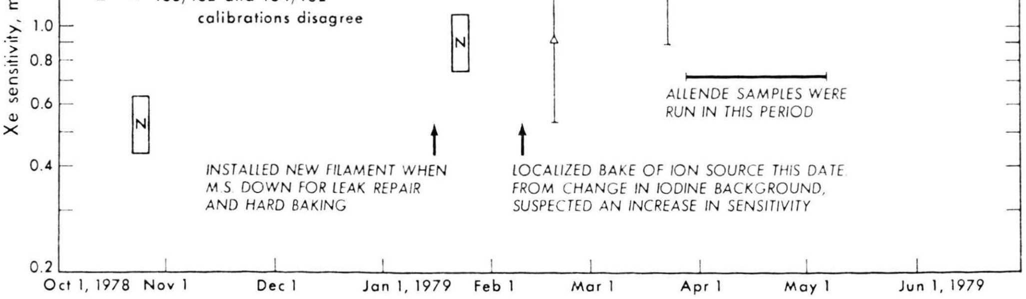

Fig. 3. History of xenon calibrations for the research. For Xe sensitivities based upon Ne measurements, a sensitivity ratio (Xe/Ne) of 11.34 [6] was assumed. For foil calibrations based upon ^{252}Cf we assumed: $Y_f(^{132}Xe) = 1.99\%$; ^{136}Xe and ^{132}Xe to be a mixture of atmospheric and californogenic with $(^{136}Xe/^{132}Xe)_f = 2.04 \pm 0.2$ [5]. The Allende samples were run during a stable period for Xe sensitivity as determined by several methods with reasonable concordance.

tabulated by Rider and Meek [5] and upon calculations we made of the volume of the mass spectrometer.

The indirect method of xenon calibration is based on $\sim 10^{-7}$ ccSTP aliquots of neon which could be introduced into the mass spectrometer from a well-calibrated pipette. The xenon sensitivity of the system was then inferred from the neon sensitivity, using relative ionization probabilities for 100 volts electrons (we used 105 volts in the ion source) tabulated by Dushman [6]. The neon calibrations, four in number, were carried out over a longer period of time. The last two gave xenon sensitivities consistently 28% higher than the average of those measured directly from the foils. In view of our using a sensitivity ratio for xenon and neon which has not been verified in our apparatus, the agreement, or lack thereof, seems reasonable. The first two neon calibrations were during periods of pathologically low sensitivity for the ion source, as discussed in two of the comments appearing in Figure 3. A fact that we find significant is that the xenon calibration for the foils with the largest number (30,000) and the smallest number (9,000) of xenon atoms are in good agreement. This fact appears to rule against the setting in of nonlinearities in xenon calibrations when very small samples are used, as might occur if there were a limited number of specially active sites for xenon adsorption in the system.

General Statement on the Methods

One of the main purposes of this research was to evaluate the potentialities of a microsystem for rare gas studies and it is for that reason that our discussion of methods has been so detailed. The general conclusion reached is that the potentialities of microsystems are great. We find, as mentioned above, that with well outgassed filaments the amounts of rare gases in the blank can be reduced to the level of what is essentially the cold blank that builds up over a period of ten minutes or so in the combined extraction system-spectrometer. Nor were the limits in that "static blank" ever reached in our work. Constrained by an old and quite dirty mass spectrometer, for which long, hard bakes were very likely to lead to the development of leaks, our freedom to work on reducing this blank was quite limited. Moreover excessive halogen contamination and other dirt effects in the mass spectrometer prevented meaningful measurements in small xenon samples of ^{124}Xe, ^{126}Xe, ^{128}Xe, and ^{131}Xe.

Despite these shortcomings of the system, we were able to solve the problem at hand (see below) by detecting significant excesses of ^{129}Xe in individual mineral grains at levels down to 20,000 atoms (Run #80) and significant excesses of $^{132}\mathrm{Xe}_f$ at levels down to 30,000 atoms (Run #62). Every indication is that, with a future method for inserting the grains into the heater cones *after* the heaters have been outgassed and without breaking the vacuum, we can obtain very significant improvements in sensitivity.

It is our intention to prepare a more detailed report on these techniques for private distribution to interested scientists. It can be requested either from P. M. Jeffery or J. H. Reynolds and will be furnished when ready.

Results

The raw data obtained in this study, including hot and cold blanks are set out in Table 2. One sigma errors are appended to the sample weights, when the weights are small, and (in parentheses) to the mass spectrometric data on gas amounts and isotopic ratios. Comparing the results obtained for the blank runs with atmospheric values, one sees that: (a) the ^{129}Xe/^{132}Xe ratios measured in the blank runs always agree with the atmospheric value within 2 σ except for one pathological run where only sparse data were recorded; (b) the same statement can be made for the ^{136}Xe/^{132}Xe, ^{134}Xe/^{132}Xe, and ^{130}Xe/^{132}Xe ratios measured in the blank runs (including discrepant values for the pathological run); nevertheless (c) there appears to be a marginally significant deficiency (0.298 ± 0.018 vs. 0.330) in the average ^{136}Xe/^{132}Xe ratio for the cold blanks. We suppose that the mass spectrometer blank, which contributes appreciably to the cold blanks, is responsible for this effect. Consequently the average cold-blank counts were subtracted from the counts in sample runs in order to compute corrected values of the ratios listed in (b) above. The corrected ratios have not been tabulated but are plotted in the histograms of Fig. 4, where it can be noted that they center upon the atmospheric values.

Referring again to Fig. 4 we note that there is a significant excess in the ratios ^{136}Xe/^{132}Xe and ^{134}Xe/^{132}Xe for run #62 (the largest sample analyzed of

Table 2. Raw data.

Date	Run no.	Mineral	Inclusion	Weight (μg)	^{132}Xe amount (ion counts/10 sec)	^{129}Xe/^{132}Xe	^{136}Xe/^{132}Xe	^{134}Xe/^{132}Xe	^{130}Xe/^{132}Xe
Allende samples									
790328	45	Olivine^{a}	5	144^{f}	91 (6)	42.9 (1.1)	0.320 (0.023)	0.399 (0.025)	0.171 (0.016)
790328	46	Enstatite^{a}	9	31^{f}	158 (7)	16.0 (0.2)	0.304 (0.017)	0.401 (0.019)	0.174 (0.012)
790414	62	Melilite^{a}	9	74^{f}	133 (7)	159.7 (1.2)	0.406 (0.021)	0.453 (0.022)	0.184 (0.014)
790425	66	Olivine^{a}	1	64^{f}	278 (10)	13.06 (0.15)	0.352 (0.015)	0.401 (0.015)	0.162 (0.010)
790425	67	Olivine^{a}	6	103^{f}	764 (16)	2.41 (0.02)	0.311 (0.008)	0.394 (0.008)	0.170 (0.005)
790427	69	Hedenbergite^{b}	9	1.5 ± 0.6^{f}	121 (6)	1.01 (0.03)	0.306 (0.011)	0.371 (0.021)	0.169 (0.014)
790427	70	Hedenbergite^{b}	9	2.5 ± 0.6^{f}	104 (6)	1.30 (0.03)	0.298 (0.020)	0.402 (0.023)	0.123 (0.014)
790427	71	Pentlandite^{b}	8	4.4 ± 0.7^{f}	65 (5)	0.998 (0.036)	0.328 (0.028)	0.382 (0.030)	0.147 (0.019)
790502	73	Melilite^{b}	9	7^{f}	236 (9)	11.18 (0.13)	0.334 (0.015)	0.389 (0.016)	0.136 (0.009)
790502	74	Melilite^{b,c}	9	31^{f}	226 (9)	0.970 (0.020)	0.316 (0.015)	0.403 (0.017)	0.145 (0.010)
790502	75	Melilite^{b}	9	$1 + 1.2^{f}$ $- 0.4$	164 (7)	0.991 (0.023)	0.322 (0.018)	0.358 (0.018)	0.132 (0.011)
790507	78	Melilite^{b,c}	9	17 ± 6^{g}	295 (10)	1.54 (0.02)	0.320 (0.013)	0.380 (0.014)	0.151 (0.008)
790507	79	Melilite^{b,c}	9	3.5 ± 1.2^{g}	191 (8)	1.07 (0.02)	0.315 (0.016)	0.362 (0.016)	0.143 (0.010)
790507	80	Hedenbergite^{b}	9	1.8 ± 0.6^{g}	291 (10)	1.02 (0.02)	0.310 (0.012)	0.392 (0.014)	0.163 (0.009)
Cold blanks									
790410	51				23 (3)		0.381 (0.066)		
790411	53				15 (2)		0.269 (0.066)		
790412	56				12 (2)		0.186 (0.069)		
790413	58				30 (3)		0.249 (0.047)		
790414	60				34 (4)		0.350 (0.041)		
790415	63				20 (3)	1.016 (0.112)	0.325 (0.055)		
790425	65				26 (3)		0.375 (0.056)		
790427	68				36 (4)		0.265 (0.040)	0.425 (0.052)	
790502	72				39 (4)		0.339 (0.038)	0.404 (0.043)	
790507	77				23 (3)		0.259 (0.048)	0.356 (0.056)	
790508	81				40 (4)		0.278 (0.030)	0.363 (0.034)	
Average cold blank					27 (3)	—	0.298 (0.018)	0.387 (0.016)	
Hot blanks									
790328	—				171 (5)	0.875 (0.037)^{d}	0.267 (0.023)^{d}	0.324 (0.026)^{d}	0.109 (0.039)^{d}
790414	61				116 (6)	1.024 (0.029)	0.313 (0.020)	0.364 (0.022)	0.162 (0.015)
790503	76				56 (5)^{e}	0.931 (0.047)	0.324 (0.039)	0.395 (0.042)	0.162 (0.029)
Additional samples									
790316	42	St. Severin troilite		425^{f}	117 (6)	1.033 (0.022)	0.366 (0.026)	0.395 (0.026)	0.132 (0.015)
790529	92	Allegan chondrule		650^{f}	312 (10)	12.0 (0.2)	0.405 (0.024)	0.434 (0.024)	0.211 (0.017)
		Atmosphere				0.983 (0.004)	0.330 (0.001)	0.388 (0.001)	0.152 (0.001)

[a] Composite samle. [b] Single grain. [c] Fragment grain from common parent grain. [d] Sparse data reduced by hand.

[e] Reheating of filament in cell where all filaments had been previously heated. [f] Sample weighed on balance.

[g] Weight estimate from size and shape.

Allende melilite). An apparent excess in ^{130}Xe/^{132}Xe for this sample is judged *not* to be significant in view of the histogram for that ratio in Figure 4. The significant excesses of ^{136}Xe and ^{134}Xe we ascribe to spontaneous fission of ^{244}Pu, which usually dominates the production of fissiogenic xenon in primitive chondrites [7]. It is not possible to assign the fissiogenic component to ^{244}Pu *vis à vis* ^{238}U on the basis of the ^{136}Xe/^{132}Xe and ^{134}Xe/^{132}Xe ratios when fission effects are small, but the yields for ^{132}Xe$_{f}$ as

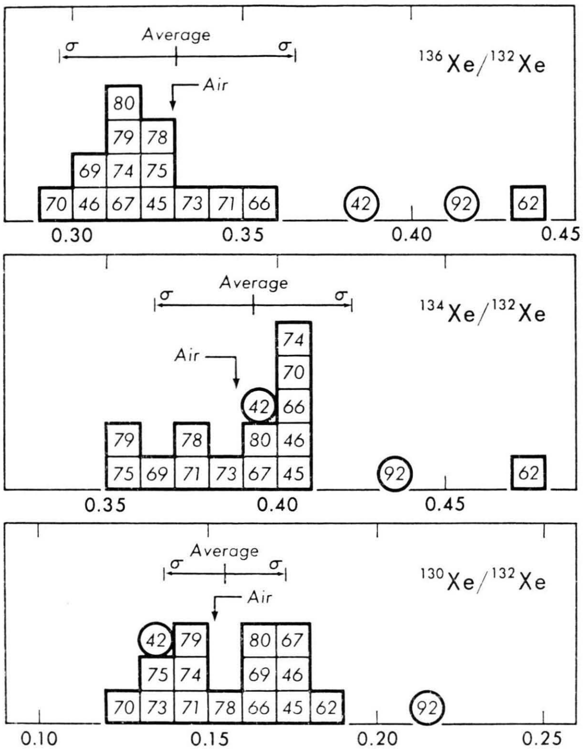

Fig. 4. Histograms for Xe ratios measured in this study· Small blank corrections have been applied (see text) so that values differ somewhat from those set out in Table 2. Standard deviations (σ's) shown are "externally" computed from the distributed values but agree satisfactorily with those "internally" computed from the counting statistics Samples 62 and 92 contain significant amounts of fission xenon. The apparent excess of ^{130}Xe in sample 92 cannot reasonably be attributed to spallation (see text).

calculated separately from the two ratios are in good agreement (within 4%) for the ^{244}Pu hypothesis. The amount so calculated for the 74 microgram melilite sample is 23,000 ± 10,000 atoms (Table 3).

Another sample for which there is a clear excess of the fissiogenic isotopes is the Allegan chondrule measured in run #92. There is also a significant excess of ^{130}Xe in this sample, unlike the Allende melilite, which we at first ascribed to production by spallation from cosmic rays. The chondrule was the only "whole rock" measured in this study and can be expected to contain trace elements which can serve as targets for xenon production by spallation. The sample of St. Severin troilite possibly contains fissiogenic xenon (see Fig. 4) but the amounts inferred from the ^{136}Xe/^{132}Xe and ^{134}Xe/^{132}Xe ratios in this case are in poor agreement, although the errors overlap (see Table 3). We return to further discussion of these auxiliary observations below.

Our principal interest in this study was ^{129}Xe/^{132}Xe ratios, which range widely from the atmospheric value of 0.983 to a value of 160 for the largest melilite sample. The results have been arranged by mineral type in Table 3, where the total number of ^{129*}Xe atoms (the asterisk as usual representing excess amounts of the isotope with respect to atmospheric composition) is listed for each sample, as well as the number of atoms per microgram and the inferred iodine content. To calculate iodine contents we assumed that the excess ^{129*}Xe was iodine correlated and we used a value of 1.37×10^{-4} for the initial ^{129}I/^{127}I ratio. Work by Zaikowski [3] and by Podosek [8] is the basis for this number and it refers specifically to the more abundant and less tightly bound ^{129*}Xe component in Allende inclusions.

From the data in Table 3, we can state a number of conclusions. (a) Sulfides appear to be very iodine-poor, judging from the measurements in Allende pentlandite and St. Severin troilite. Only a single grain of the former was analyzed, weighing 44 micrograms, so that further looking would be worthwhile but the troilite sample was large enough so that its relative lack of ^{129*}Xe (0.04 ± 0.02 ppb) should be fairly conclusive. The paucity of iodine in sulfides is somewhat surprising to us in view of the apparent association of iodine with troilite in iron meteorites [2, 9, 10] – albeit this association has never been verified for individual troilite grains and may, therefore, be considered suspect. (b) The hedenbergite grains studied, which were three in number and all quite small, had average inferred iodine contents of 19 ppb and varied among themselves by about a factor 6. The iodine content in hedenbergite is similar to that which we measured in the single Allegan chondrule. (c) Olivine samples exhibited similarly diverse iodine contents but at a higher level, 80 ppb. The single enstatite run, on a composite sample rather than a single grain – an approach which was abandoned later in the study when use of "large" samples proved to be unnecessary – was higher still (203 ppb) in inferred iodine content. (d) The most diverse iodine concentrations were displayed by the melilite samples with inferred iodine concentrations ranging from zero to 900 ppb. Included were separate runs on three small frag-

Table 3. Reduced data.

Run	Inclusion	Weight (μg)	^{129*}Xe (10^4 atoms)[d]	[^{129*}Xe] (10^4 atoms/μg)	Inferred $\overline{[\mathrm{I}]}$ (ppb)[e]	^{132}Xe$_f$ (10^4 atoms)[f]	Inferred $\overline{[^{244}\mathrm{Pu}]}$ (ppb)[g]
Olivine samples							
45	5	144[a]	659 (17)	4.6 (0.1)	70.8 (1.5)		
66	1	64[a]	580 (7)	9.1 (0.1)	140 (2)		
67	6	103[a]	188 (3)	1.83 (0.03)	28.2 (0.5)		
Enstatite sample							
46	9	31[a]	410 (5)	13.2 (0.2)	203 (3)		
Hedenbergite grains							
69	9	1.5 (0.6)[b]	0.56 (0.63)	0.4 (0.4)	6 (6)		
70	9	2.5 (0.6)[b]	5.7 (0.5)	2.3 (0.6)	35 (9)		
80	9	1.8 (0.6)[b]	1.86 (1.01)	1.0 (0.6)	15 (9)		
Pentlandite grain							
71	8	4.4 (0.7)[b]	0.17 (0.41)	0.04 (0.09)	0.6 (1.4)		
Melilite samples							
62	9	74[a]	3650 (30)	49.3 (0.4)	759 (6)	2.3 (1.0)	1.9 (0.8)
73	9	7[b]	416 (5)	59.4 (0.7)	914 (11)		
74	9	31[b]	−0.51 (0.78)	−0.02 (0.02)	−0.3 (0.3)		
75	9	$1^{+1.2}_{-0.4}$[b, c]	0.23 (0.65)	0.2 (0.7)	3 (11)		
78	9	17 (6)[b, c]	28.4 (1.0)	1.7 (0.6)	26 (9)		
79	9	3.5 (1.2)[b, c]	2.87 (0.66)	0.82 (0.34)	13 (5)		
St. Severin troilite							
42	—	425	1.0 (0.4)	0.0024 (0.0009)	0.036 (0.015)	0.6 (0.8)	0.09 (0.12)
Allegan chondrule							
92	—	650	592 (11)	0.91 (0.02)	14.0 (0.3)	4.4 (1.7)	0.42 (0.16)

[a] Composite sample. [b] Single grain. [c] Fragment grain from common parent grain.

[d] $[N(132) \times 10^{-4}][^{129}\mathrm{Xe}/^{132}\mathrm{Xe} - 0.983]$. [e] $[\mathrm{I}] = [^{129*}\mathrm{Xe}]/(1.37 \times 10^{-4})$, see text.

[f] Assuming ^{136}Xe and ^{132}Xe to be a mixture of atmospheric and plutonogenic with $(^{136}\mathrm{Xe}/^{132}\mathrm{Xe})_f = 1.142 \pm 0.040$ [14].

[g] Assuming: $Y_f(^{136}\mathrm{Xe}) = 6\%$, $T_{1/2}(^{244}\mathrm{Pu}) = 8.18 \times 10^7$ y, $T_{1/2}(\mathrm{SF\ of\ }^{244}\mathrm{Pu}) = 6.55 \times 10^{10}$ y.

ments of the same grain; even there, varying iodine concentrations were seen (3, 13 and 26 ppb).

It seems clear from these facts that the more abundant ^{129}I-bearing phases are not the bulk mineral phases over which we had good control in this miniaturized study, but rather are some sort of inclusions or "micro-nuggets" which are associated with the bulk minerals in a "spotty" fashion. There may indeed be preferred minerals for association with the iodine inclusions, in which case from our observations the affinity for inclusions seems to descend from melilite (472 ppb weighted average for iodine) and enstatite (203 ppb for a single analysis) through olivine (92 ppb) and hedenbergite (21 ppb) to the singularly impoverished sulfides (0.6 ppb in Allende pentlandite and 0.04 ppb in troilite from a meteorite, St. Severin, of another class).

Discussion

Zaikowski [3, 4] has determined I-Xe ages for a number of single inclusions in Allende, working of course with neutron-irradiated samples. What he finds in all of 3 inclusions analyzed to date is that there is a "low temperature" regime (900 – 1150 °C) in which most of the ^{129*}Xe is released and in which an iodine-xenon correlation is displayed. He finds, further, that there is a "high temperature" regime ($\geqq$ 1200 °C) in which much less ^{129*}Xe is released and in which a *different* iodine-xenon correlation is seen, corresponding to an age which is older by about 4 m.y. than the age for the low temperature isochron. If samples are etched with nitric acid, the low temperature behavior is affected much more (i. e. substantial Xe loss occurs) than the high temperature behavior. Zaikowski notes that chlorine appears in the solution when acid is applied and that ^{38}Ar produced during the pile irradiation by the ^{37}Cl$(\eta, \gamma\beta)^{38}$Ar reaction is selectively removed by the treatment. These observations led Zaikowski to suggest that the minerals nepheline and sodalite may contain most of the ^{129*}Xe. Our results are certainly not incompatible with those of Zaikowski, but we would say that the iodine-rich phases, which may indeed include nepheline and sodalite, are in part associated with other minerals as inclusions. It would be interesting to examine melilite grains more closely in hopes of actually observing the iodine micronuggets. It would also be useful to see what is the effect on the melilite grains of treatment with nitric acid. In Zaikowski's work, the iodine-rich minerals were accessible to the acid. Nepheline and sodalite, if separable, should clearly be studied by the microtechnique in the future.

An interesting intimation from our work is that one of the most primitive constituents of Allende, as evidenced by its ^{129}Xe content, is a minor phase whose properties and history it would be important to explore. There is a general tendency lately in cosmochemical research for certain special phases to assume importance in the meteoritic record. Our work has, without being so planned, fallen into that pattern. One must note however, that the mixing of ^{127}I and ^{129}I was evidently very uniform in the early solar system despite its possible concentration in special minor phases. In this respect it would differ from aluminum where anomalous concentrations of radioactive ^{26}Al accompany ^{27}Al in inclusions but only sporadically so.

Because our data on fission xenon are so limited, it is not possible to say whether ^{244}Pu occurs spottily in a minor, included phase, as ^{129}I does, or is uniformly present in certain minerals. The only Allende sample where fission xenon was seen was the large, composite melilite sample which had almost the highest ^{129*}Xe concentration as well. But for the next largest melilite sample, a 31 microgram grain analyzed in run #74, the same level of fission xenon concentration would be obscured by the "noise" (see Figure 4). Further work on melilite grains is obviously necessary in order to settle this interesting question.

A final point of contact with previous research is our measurements on the Allegan chondrule which can be compared with studies of a neutron-irradiated sample of these chondrules by Podosek [8]. Quite different ^{129}Xe/^{132}Xe ratios were seen in the two cases. Both in run #92 and in an earlier run not tabulated in this paper because it followed a lower temperature heating step in which an unknown amount of xenon was lost, we saw a ratio of about 14, whereas Podosek's values for that ratio were (totally) 1.45 and (maximally in a 1600 °C heating step) 2.25. The concentration of ^{129*}Xe in Podosek's work was 1200 atoms per microgram, neglecting a small fission correction in ^{132}Xe. Our value is 9100 atoms per microgram, so that the difference seems to be one of ^{129*}Xe concentration rather than differing amounts of trapped gas. Podosek's data do not enable us readily to compute the amount of fission xenon from ^{244}Pu decay, since there is a pile-induced fission component which implants xenon with a ^{136}Xe/^{132}Xe ratio which varies from one irradiation to another because second order reactions are involved and which appears not to be determined for the irradiation in question. Using ^{134}Xe/^{132}Xe ratios, where second order complications do not occur, we can only put an upper limit on $(^{132}\mathrm{Xe})_f$ from ^{244}Pu decay of 84 atoms per microgram in Podosek's sample. If, as Podosek supposes, the fissiogenic xenon from ^{244}Pu is greatly overwhelmed in the sample by pile-induced fission xenon, his data point to a considerably lower concentration of $(^{132}\mathrm{Xe})_f$ from plutonium decay than that. Our observed value of fission ^{132}Xe from plutonium decay is 68 ± 26 atoms per microgram which again suggests that our sample is richer in radiogenic xenon from extinct sources than Podosek's. It is possible that the pile irradiation of Podosek's sample had some effect on these concentrations. Finally, there is a discrepancy in the inferred contents of excess ^{130}Xe produced in spallation. Podosek finds 0.9 atoms per microgram; we found 55 ± 15 atoms per microgram. In this instance our concentration is certainly unreasonably large. We made a rough measurement of the ^{21}Ne content in the Allegan chondrule and obtained 1.8×10^{-8} ccSTP/g. This ^{21}Ne content can be assumed to be mostly cosmogenic and a cosmic ray exposure age of 4.6 m.y. obtained, using a chondritic production rate for ^{21}Ne of 0.4×10^{-8} ccSTP/g-m.y. [11]. This age is near the maximum in the sharply peaked distribution of exposure ages for bronzite chondrites and as such is quite convincing for the H 5 chondrite Allegan. Srinivasan [12] has developed a lunar production rate for spallogenic ^{126}Xe in samples of known barium and rare earth element ($\mathrm{REE} \equiv \mathrm{La} + \mathrm{Ce} + \mathrm{Pr}$) content, which can reasonably be applied to the production of ^{130}Xe in chondrites by multiplying by a factor 2 in order to compensate for the $4\pi/2\pi$ irradiation factor. Using Srinivasan's formula and average chondritic values for barium and rare earth contents (3.5 ppm Ba, 1.3 ppm REE) [13] one predicts a spallogenic content of 1.3 atoms/microgram in a chondrite with an exposure age of 4.6 m.y., in reasonable agreement with Podosek's value of 0.9. Our large value must, therefore, be spurious – a circumstance which appears unlikely but certainly not impossible in view of the spread displayed by the histogram for ^{130}Xe/^{132}Xe in Figure 4.

Conclusions and Acknowledgements

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* *Note added in proof:* Just after fiinishing this paper we read a preprint of a paper submitted to the Review of Scientific Instruments by C. M. Hohenberg entitled "High sensitivity pulse-counting mass spectrometer for noble gas analysis". That paper, which includes an independent evaluation of the Baur-Signer source will be of interest to many readers of this one. We wish to thank Prof. Hohenberg for sending us his results before publication.

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