Xenon in Chondritic Metal

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Dedicated to Heinrich Wänke on the occasion of his 60th birthday.

We report xenon isotopic abundances observed in the stepwise release of noble gases in a high-purity metal separate of the Forest Vale (H4) chondrite. We identify a ^{244}Pu-derived fission component, due to recoils into the metal, a cosmic-ray-produced spallation component and a new trapped component (FVM; ^{132}Xe:^{134}Xe:^{136}Xe = 3.16:1.235:1.000) which is isotopically distinct from known solar system reservoirs. We discuss several processes which might account for observed isotopic shifts and conclude that the signature of FVM xenon may provide clues regarding the origin of chondritic metal.

Introduction

Based on the currently available information on noble gases in meteorites, chondritic metal would appear to be an unlikely material for studies of early solar system processes. It was recognized early that the absence of primordial trapped gases in irons offers the possibility of detailed studies of cosmic-ray-produced spallation components (e.g. Signer and Nier [1]). Twenty-five years ago, the distributions and isotopic signatures of the noble gases in "gas-rich" meteoritic breccias (Suess et al. [2]; Hintenberger et al. [3]) produced the data-base which permitted the identification of the solar wind origin of noble gases in "gas-rich" meteorites (e.g. Wänke [4]). Wänke [4] pointed out the importance of metal phases in these chondrites. The presence of trapped noble gases of solar relative abundances in the surface layers of separated chondritic metal disproved an incorporation based on solubility properties.

In the course of a study of the signatures of fission components in the H4 chondrite Forest Vale [5], we studied this metal for evidence of fission Xe from recoiling fission fragments originating in adjacent phosphates. Along with the fission xenon, we identified distinct xenon isotopic signatures which may shed new light on solar or pre-solar processes. Noonan et al. [6] noted that Forest Vale metal probably cooled rapidly due to the absence of low-Ni zones in kamacite at taenite borders. Lavielle et al. [5] confirmed this evidence in additional metallographic studies. For the present study, Forest Vale metal was first magnetically separated, then etched with concentrated NaOH until all visible adherent silicates were dissolved, and separated into several size fractions. The purity was estimated from microscopic inspection of grain surfaces to be $\gtrsim 99.5\%$, but most of the metal was found to contain minor inclusions of similar composition as the fine-grained matrix [7]. A more detailed characterization of the inclusions is now being carried out.

Xenon in Forest Vale Metal

Lavielle et al. [5] studied the fission Xe record in a phosphate separate of Forest Vale and identified extinct ^{244}Pu as the progenitor of the fission Xe. A limit $^{248}\mathrm{Cm}/^{244}\mathrm{Pu} \leq 1.5 \times 10^{-3}$ was obtained for the fission contribution by extinct ^{248}Cm at the time of Xe retention. Phosphates are frequently observed in contact with metal grains, and we expected to further document the fission progenitors by studying the recoil fragments in adjacent metal. Three grain-size fractions (< 80 μm, 160–280 μm, 280–450 μm) were

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Table 1. Isotopic abundances in the stepwise release of Xe in Forest Vale metal (160–280 μm). Also given are data on other size separates, for temperature steps which reveal FVM-type Xe. Uncertainties in isotope ratios correspond to 95% confidence limits.

Grain size fraction (μm)	Sample weight (g)	Temp. (°C)	^{124}Xe	^{126}Xe	^{128}Xe	^{129}Xe	^{130}Xe	^{131}Xe	^{132}Xe	^{134}Xe	^{136}Xe	[^{136}Xe] ($\times 10^{-12}$ cm^3 STP g^{-1})
160–280	2.0	400	1.057	1.065	22.13	299.1	45.92	240.8	301.7	118.11	=100	0.80
			±.079	.083	.52	2.0	.60	1.5	2.0	.64		.06
		600, P	3.25	5.35	22.7	234.2	36.4	203.1	243.5	109.5	=100	0.066
			±.70	1.00	2.8	8.3	1.9	7.2	6.0	2.9		.005
		600, C	1.80	1.68	24.94	312.8	48.1	247.9	307.9	118.55	=100	0.81
			±.11	.11	.34	1.5	1.0	2.0	2.5	1.00		.06
		800	2.90	4.90	28.1	279.4	43.5	221.2	268.8	117.0	=100	0.053
			±.70	1.00	3.3	7.5	1.6	9.6	7.6	3.4		.004
		900	3.58	4.85	25.3	302.2	45.6	242.4	294.5	119.5	=100	0.101
			±.40	.70	2.0	4.2	1.1	4.8	5.0	3.0		.007
		1000	3.73	3.42	27.2	313.7	47.8	244.5	295.2	119.6	=100	0.116
			±.43	.60	1.9	4.0	1.2	6.5	4.0	1.9		.009
		1100	2.70	2.46	26.9	327.8	50.6	262.6	314.8	123.0	=100	0.136
			±.31	.51	1.4	5.8	1.4	4.3	4.0	2.8		.010
		1200	2.31	1.91	27.35	325.6	50.43	253.0	304.2	119.5	=100	0.254
			±.18	.28	.87	1.0	.94	3.8	3.8	1.5		.019
		1400	2.07	2.33	26.44	335.4	50.60	253.3	311.4	118.7	=100	0.488
			±.16	.22	.71	3.4	.71	3.3	2.8	1.8		.037
		1700	3.13	3.30	27.84	342.5	49.81	252.6	306.7	118.25	=100	0.96
			±.11	.10	.34	2.0	.47	1.8	1.7	.98		.07
<80	0.4	900	4.80	4.73	25.2	298.1	43.2	245.7	282.9	120.1	100	0.491
			±.67	.84	2.1	14.5	1.6	6.8	7.0	2.9		
280–450	0.5	1200	2.40	1.4	26.7	340.6	51.0	257.6	317.2	124.0	100	0.305
			±.80	1.1	3.5	9.1	1.8	9.9	5.8	3.4		
		FVC*	1.457	1.298	26.01	327.03	50.94	257.73	314.49	119.39	100	
			.017	.010	.19	.55	.11	.42	.55	.26		

P: pyrolysis; C: combustion in 10 torr O_2. * Lavielle and Marti (1989), to be published.

studied for an expected surface correlation of fission recoils. The metal separates were wrapped in Al foil and stored in vacuum for several days before they were first heated to remove adsorbed atmospheric gases. In the sample of 160–280 μm grains, atmospheric contamination was successfully desorbed at 400 °C, and it was possible to monitor a low temperature release of fission and spallation gas; the other separates were heated to 600 °C. After the pyrolysis step at 600 °C, samples were heated in ~10 Torr O_2, in order to combust organic contaminants and carbonaceous trace phases. The trapped gases were then released by stepwise pyrolysis and finally the metal was melted at 1700 °C. Re-extractions showed that $\gtrsim 98\%$ of the gas was released. The noble gases were cleaned on getters in three steps, and Xe and Ar were separated cryogenically and analysed separately.

In Table 1, we report the isotopic abundances observed in the stepwise release of Xe in the Forest Vale 160–280 μm metal fraction. As expected, the 400 °C data show atmospheric isotopic abundances due to air contamination, while the relatively large release in the combustion step (600°,C) indicates a mixture of air and trapped Xe of the type observed in Forest Vale combustion (FVC) steps [8]. Table 1 and Fig. 1 show that the pyrolysis steps 600°,P and 800° contain significant amounts of chiefly ^{244}Pu-derived fission xenon, since the amounts of Xe_F from ^{238}U spontaneous fission are much smaller ($< 4\%$ Xe_F in phosphate, [5]). This component is most abundant in the small (< 80 μm) and least abundant in the large (280–450 μm) grain separates and is consistent with a recoil origin of fission fragments in adjacent phosphates [5]. Below 1200°, the mixing ratios of fission Xe decrease with increasing temperature. The inferred trapped Xe component is not compatible with FVC xenon. Figure 1 shows the observed correlation of the ratios $^{134}Xe/^{136}Xe$ and $^{132}Xe/^{136}Xe$ which are little affected by cosmic-ray-induced spallation Xe and represent primarily mixtures of trapped and fission components.

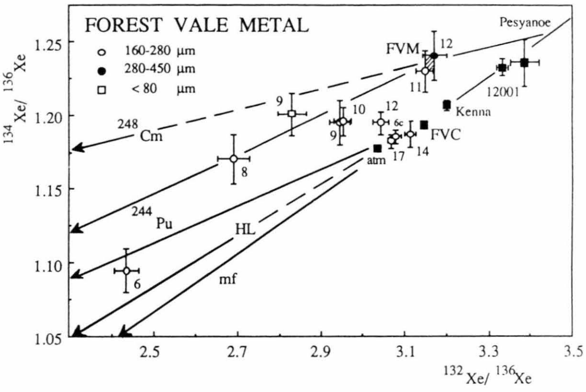

Fig. 1. In Fig. 1, we display the ratios $^{134}Xe/^{136}Xe$ vs. $^{132}Xe/^{136}Xe$, as observed in temperature fractions of Forest Vale metal separates (1 σ uncertainties are shown). Temperatures are indicated in hundreds of degrees. The 900 °C, 160–280 µm data may indicate the presence of a minor air-like component in the metal, in excess of applied blank corrections. The line labeled mf indicates mass-fractionation of the FVC-reservoir. The plotted isotope ratios of FVM- and the FVC-reservoirs could possibly have formed from a common precursor, the FVM-reservoir by addition of fission Xe (see text), the FVC-reservoir by either adding HL-Xenon or by mass-fractionation. Sources of data: FVC-Xe [8], Kenna-Xe [17], Pesyanoe-Xe [18], lunar soil 12001-Xe [19], ^{248}Cm fission Xe [20], HL-Xe [13], ^{244} Pu fission Xe [21].

Inspection of Fig. 1 reveals that data obtained after the combustion step (600°,C) do not plot on or near the tie-line FVC-Xe$_F$ (^{244}Pu). The $^{134}Xe/^{136}Xe$ ratios are shifted upwards in the figure. In Table 1 and in Fig. 1, we report recent data on other grain-size fractions which confirm this isotopic shift (900° step in < 80 µm and 1200° step in 280–450 µm). It is interesting to note that the largest shifts in the three grain-size fractions are observed at different temperatures, reflecting a grain-size dependence in the Xe release. For the present discussion it is useful to introduce a new isotopic Xe signature FVM,

$$^{132}Xe : ^{134}Xe : ^{136}Xe = 3.16 : 1.235 : 1.000,$$

corresponding to the average of the two largest shifts (the 1100 °C in 160–280 µm and 1200 °C in 280–450 µm grain-size fractions). The 160–280 µm Xe data (Table 1) of temperature steps 800°, 900° and 1100° plot near the tie-line FVM – Xe$_F$(^{244}Pu), but $^{134}Xe/^{136}Xe$ ratios of the 1000°, and especially the 1200°, steps appear to be lower, indicating that an additional component is present. We note from Fig. 1 that the 1400° and 1700° temperature fractions do not plot close to the above tie-line. These temperature steps show signature close to FVC, but shifted toward a ^{136}Xe-rich component. It is not clear at this time whether these Xe components are released from the inclusions in the metal, but we note (Table 1) that a significant fraction of the total Xe is released in the melt (1700°) step.

Nuclear Reactions

Figure 1 reveals an ~ 3.4% shift in the ratio $^{134}Xe/^{136}Xe$ of FVM-Xe when compared to that of FVC. On the other hand, the $^{132}Xe/^{136}Xe$ and $^{130}Xe/^{136}Xe$ ratios agree within error limits. The question arises as to whether this shift might be due to nuclear reactions. Lavielle et al. [5] observed abundant cosmic-ray-produced spallation components and recoil tracks in Forest Vale phosphates produced during the long 72 Ma exposure time. Spallation Xe components are also observed in the metal data (Table 1). The isotopes ^{124}Xe and ^{126}Xe are good monitors of such reactions. Spallation effects in $^{134}Xe/^{136}Xe$ can be evaluated from available cross-sections. Relative yields of $^{130}Xe_c$ are larger than those of $^{134}Xe_c$ for Ba and REE targets [9], and also for heavy metal targets [10]. Data on proton induced reactions with Th show that fission reactions compete with spallation reactions [11]. In this case, the excitation functions for $^{130}Xe_c$ and $^{134}Xe_c$ are similar. Therefore, we can rule out the possibility that the observed shift in the $^{134}Xe/^{136}Xe$ ratio is due to cosmic-ray reactions, since the predicted shift in the $^{130}Xe/^{136}Xe$ ratio is not observed.

Another type of nuclear reaction which needs to be assessed are thermal neutron induced reactions, followed by fission recoil implantation. The ratio $(^{134}Xe/^{136}Xe)_{nF} = 1.246$ of neutron induced fission reactions on ^{235}U [12] is identical within error with the value observed in FVM. A shift, due to addition of Xe$_{nF}$(^{235}U) would correspond to a horizontal displacemenet in Fig. 1 and could explain the FVM signature if the trapped (unshifted) Xe was similar to solar-type. The concentration of FVM-Xe obtained by summing the 800° to 1100° temperature fractions is $^{136}Xe = 0.36 \times 10^{-12}$ cm^3 STPg^{-1}. This calculation assumes that the observed data in the 800° to 1100° steps represent mixtures of FVM and Xe$_F$(^{244}Pu). The amount of $^{136}Xe_F(^{235}U)$ required to produce the FVM-Xe shift from solar Xe (lunar soil 12001) is 1.9×10^{-14} cm^3 STPg^{-1}. On the other hand, the results of Forest Vale phosphates show no evidence of ^{235}U-derived fission Xe [5]. Also, we noted that stepwise release of FVM xenon differes from that of ^{244}Pu-derived fission recoils. If a neutron irradiation of metal took place before accretion of the meteorite, the release systematics of FVM-Xe and ^{244}Pu-derived Xe_F would not necessarily be identical. For illustration purposes, if we assume the presence of 0.1 ppb ^{235}U in the metal (corresponding to ~1% silicate inclusions), a neutron fluence of 3.4×10^{15} n cm^{-2} is required to produce the FVM shift. In this scenario, chondritic metal would display a remarkable neutron record either in early solar system or in presolar history.

Relation to Other Solar System Xenon Components

Figure 2 shows some of the well-established Xe components in solar system materials: Solar-type Xe (as observed in solar wind containing "gas-rich" meteorities and on the lunar surface), ureilitic Xe (Kenna), FVC-Xe, carbonaceous chondritic Xe, terrestrial atmospheric Xe and FVM-Xe. From Figure 1, we see that FVM-type Xe cannot be obtained from any of the other reservoirs by either mass dependent fractionation (line mf) or by the addition of HL-type Xe [13]. We will now discuss other possible relationships to solar system Xe components.

First FVM may represent a xenon reservoir which already contains a ^{244}Pu-derived fission component. If so, the signature of a fission-free trapped component will plot on the extended $Xe_F(^{244}Pu)$ – FVM tie-line, labelled T_{244} in Fig. 2, which extends in the direction of U-Xe [13, 14]. The only direct observation of U-type signature was in an irradiated and H_2O_2-etched Murray anti-colloid sample in a temperature step which released only 2% of its xenon [15].

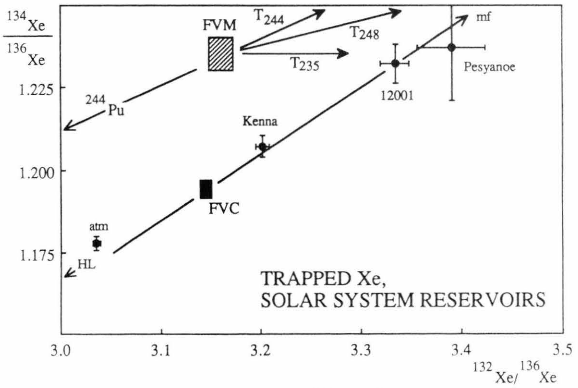

Fig. 2. Figure 2 shows the ratios $^{134}Xe/^{136}Xe$ and $^{132}Xe/^{136}Xe$ in several solar system components and reservoirs (see ref. in Figure 1). We note that solar-type-Xe (Pesyanoe, 12001), Kenna-Xe and FVC-Xe define a trend-line. In this figure, shifts are consistent with either the addition of HL-Xe to FVC-Xe or mass fractionated (mf) xenon, indicated by the dashed line. FVM-Xe is clearly not on this trend-line. For a discussion of the lines labeled T_{244}, T_{248}, and T_{235}, see text.

^{248}Cm-derived fission xenon was not observed in phosphates of Forest Vale [5]. However, we cannot rule out the possibility that ^{248}Cm fission fragments recoiled into metal grains or precursors thereof during the presolar history of the metal. The fission branching ratio is much larger for ^{248}Cm than for ^{244}Pu, and the cooling time of supernovae may be appropriate to condense metal and permit ^{248}Cm recoil implantation. In this scheme, FVM xenon would represent a mixture of a trapped component and $Xe_F(^{248}Cm)$. The "fission-free" trapped component would plot on the extension of the $Xe_F(^{248}Cm)$-FVM tie-line, indicated by T_{248}, and its isotopic signature would be intermediate between solar-type and U-Xe components. This scenario has obvious implications regarding the origin of chondritic metal.

The possible presence of a $Xe_F(^{235}U)$ component was already discussed earlier. In principle, any trans-bismuth nuclides which decayed by a fission-branch and in proximity to metal would produce recoiling fission fragments and Xe reservoirs shifted in the direction of FVM-Xe. It is interesting to note that the calculated concentrations of FVM xenon also may suggest a grain-size dependence with the largest concentration in the smallest grains. However, the location of FVM-xenon within the grains needs to be further documented.

Finally, we need to consider the possibility that FVM-Xe represents a distinct solar system or presolar component that was incorporated at an early stage in the history of metal grains. As pointed out above, the grain-size dependence, as well as the release characteristics, favor a near-surface location of FVM-Xe. This evidence might suggest ion implantation much in the same way that a solar wind origin was inferred for noble gases in gas-rich meteorites [4]. However, the elemental abundances are clearly not solar, since the trapped $^{36}Ar/^{132}Xe$ ratios in the 800° to 1100 °C steps are ~100. An origin by implantation of either solar or stellar wind ions appears unlikely. The nature and origin of FVM-Xe appear to be closely related to the origin of Forest Vale metal itself. Additional recent Xe data obtained from the Ste. Marguerite (H4) metal separate [16] and preliminary data on Estacado (H6) metal show that FVM-Xe is present in H4, but not in H6 chondrites. We need to further assess its occurrence in lower petrologic types as well as the distribution of FVM xenon within metal grains.

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