Reports

Elements 112 to 119: Were They Present in Meteorites?

Abstract. *Chondrites contain a small fission xenon component of unexplained origin. Evidence on the geochemical behavior of this component suggests that it was not derived from an actinide element* ($Z = 89$ *to* 103)*, or from a transition metal between* $Z = 104$ *and* 111*, but from a more volatile progenitor. The most likely candidates are the superheavy elements between* $Z = 112$ *and* 119*, whose lighter congeners* (*mercury, tellurium, lead, and the like*) *are known to be strongly fractionated in meteorites.*

Meteoritic and terrestrial Xe differ in the abundances of isotopes 131 to 136 *(1–6)*. This difference is almost certainly due to spontaneous fission of an extinct transuranium nuclide *(4, 7)*. In some, highly differentiated, meteorite classes (iron meteorites, Ca-rich achondrites), Pu^{244} with a half-life of 82×10^6 years is the most likely source: the proportions of fission-derived Xe isotopes resemble the estimated fission-yield curve of Pu^{244}, and the amounts are no greater than expected from the abundance of Pu^{244} on a model of "continuous" nucleosynthesis for $\sim 10^{10}$ years: $Pu^{244}/U^{238} \approx 0.018$ *(3, 8, 9)*.

The situation in more primitive meteorites (chondrites) is less clear-cut. A fission component is undoubtedly present, but its yield pattern is unlike that of Pu^{244} or, for that matter, of any known heavy element. Instead of peaking out or declining between Xe^{134} and Xe^{136}, the curve rises by a factor of ~ 1.4 *(2, 4, 6)*. Moreover, the amounts of fission Xe (relative to U) are embarrassingly large: up to two orders of magnitude higher than in achondrites, and an order of magnitude higher than expected for Pu^{244}/U^{238} equal to 0.018 *(3)*. A high ratio would imply that a major part of planetary matter was synthesized just prior to the formation of the solar system. This assumption leads to numerous difficulties *(3, 9)*. An alternative parent nuclide is needed, but none of the known transuranic nuclides have the required combination of long half-life and dominant spontaneous-fission decay mode.

One can attempt to infer the nature of the parent nuclide from its geochemical behavior. A useful clue would be the correlation of its Xe^{136} daughter (Xe_f^{136}) with other trace elements. Regrettably, there are only a few meteorites in which Xe_f^{136} and all the trace elements of interest have been determined. We shall therefore plot Xe_f^{136} and the trace elements not against each other but against a common reference standard, Xe^{132}. It is almost entirely nonfission-derived and represents trapped primordial gas *(10)*.

In Fig. 1 Xe_f^{136} is plotted against Xe^{132}. Ten of the points are Berkeley measurements, eight being from Rowe

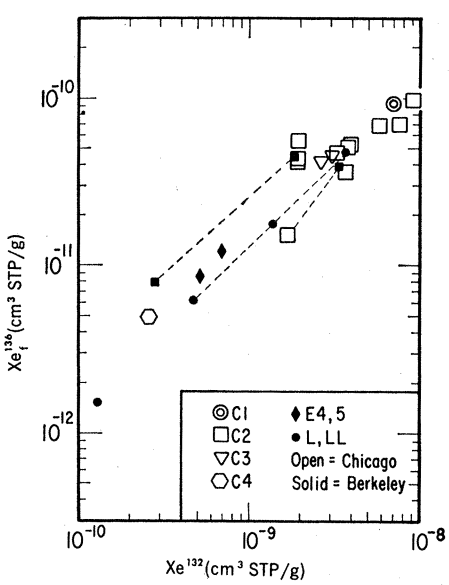

Fig. 1. Fission-derived Xe_f^{136} in chondrites correlates with primordial Xe^{132}. Symbols refer to classification scheme of Van Schmus and Wood *(22)*; C, carbonaceous; E, enstatite; and L,LL, ordinary chondrites. Points connected by dashed lines represent separated chondrule and matrix fractions of the same meteorite, with the matrix (or bulk meteorite) always lying highest. Berkeley data are from *(1, 2, 5, 11)*; Chicago data, from *(12)*.

(5) and two from Krummenacher *et al.* *(11)*. The remaining fifteen are Chicago measurements *(12)*.

Evidently Xe_f^{136} correlates rather well with primordial Xe^{132}, as already noted by Rowe. We can dismiss the most obvious explanation: that the present distribution of Xe_f^{136} was established after decay of its progenitor and hence reflects the geochemical character of Xe, not of its progenitor. Strong evidence for decay *in situ* comes from the Berkeley experiments, where three to ten separate xenon fractions were evolved at successively higher temperatures. The isotopic composition varied from fraction to fraction, with the most fission-derived Xe generally appearing at 600°C or above. Evidently, the xenon has not been isotopically homogenized.

A second possibility can also be excluded: that the correlation arose from diffusion loss of both kinds of Xe after the decay of the progenitor. The Berkeley heating experiments show that Xe_f^{136} is released more readily than is Xe^{132}, implying residence in less retentive sites. Hence a partial Xe loss would lead to disproportionate loss of Xe_f^{136}. It could neither create nor maintain a 45° correlation such as that in Fig. 1. We therefore feel justified in assuming that these meteorites have remained closed systems since the decay of the Xe_f^{136} progenitor. The correlation in Fig. 1 then reflects the geochemical behavior of the progenitor.

No correlation of this kind would be expected for an actinide parent nuclide. Figure 2 shows data for the two long-lived actinide elements, U and Th. Their "signature" is altogether different: their abundances remain constant, while Xe^{132} varies by three orders of magnitude. Such constancy is shown by all other nonvolatile elements in chondrites *(13)*. It seems safe to assume that the remaining actinides behave similarly.

On the other hand, volatile elements, such as In, Hg, Bi, Cd, and Kr, do correlate with Xe^{132}. Figure 3 shows the data for In, an element for which a large number of measurements are available. The points scatter considerably, largely because of sampling and experimental errors. Unlike the data in Fig. 1, those in Fig. 3 were determined on separate samples. Variations by factors of 2 to 4 are not uncommon among replicate In and Xe measurements, and so it is not surprising that the correlation is not perfect. Nonetheless, the overall trend is similar to that in Fig. 1.

The correlation between a metal and

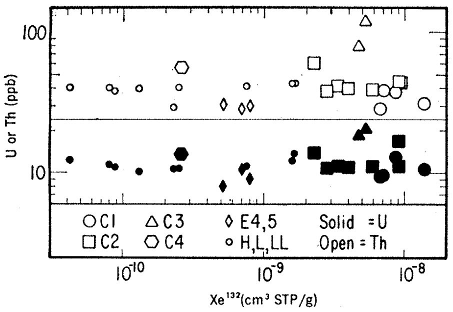

Fig. 2. In chondrites U and Th are virtually constant, and show no correlation with Xe. This behavior is typical of nonvolatile elements, and may be expected of the remaining actinides; U, Th data are from (*23*); Xe data, from (*12, 24*) and references cited therein.

a noble gas is, at first thought, surprising. It has been known for some time, however, that some 2 dozen volatile elements show parallel depletion trends in chondrites (*13*). These trends have been explained by a two-fraction model, according to which chondrites are a mixture of a high-temperature fraction (the chondrules) that has lost its volatiles and a low-temperature fraction (the matrix) that has retained them (*13, 14*). In terms of this model, the decrease from right to left in Fig. 3 may reflect both a smaller matrix content and a higher accretion temperature, leading to less efficient

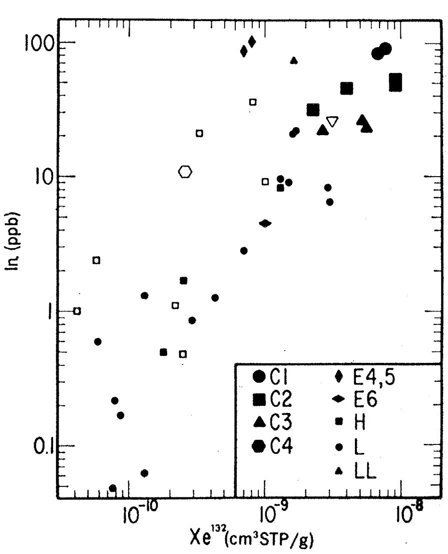

Fig. 3. Indium, like other volatile elements, correlates with Xe^{132}. Since Xe_f^{136} also shows this behavior (Fig. 1), it probably is derived from a volatile progenitor. Open symbols represent In measurements from (*25*); solid symbols, from (*15, 26*). The Xe measurements are from (*12*) and (*24*). The scatter in In data probably represents real differences among classes, but the possibility of systematic errors between the laboratories cannot be ruled out.

trapping of volatiles. Variants of this model, involving a third fraction, have been proposed (*15*).

The fact that Xe_f^{136} correlates with Xe^{132}, while U and Th do not, suggests that the parent nuclide is not an actinide but a more volatile element. This also follows from a second line of evidence: distribution of Xe_f^{136} between chondrules and matrix.

In three meteorites where chondrules and matrix (or bulk meteorite) were measured separately, Xe_f^{136} was found to be depleted in the chondrules by a factor of up to 10 (Fig. 1). There are no known mineralogical reasons why chondrules should be lower in actinides than is the matrix; in fact, Fleischer (*16*) has shown that chondrules often are *enriched* in uranium. It seems more likely that the depletion of Xe_f^{136} is due to volatility of its progenitor.

The first element beyond the actinide series expected to be slightly volatile is element 111, eka-gold. The next eight elements, 112 to 119, ought to be highly volatile, by analogy to their congeners Hg, Tl, Pb, Bi, Po, At, Rn, and Fr. The first four of these are strongly fractionated in meteorites, and so are the lighter congeners (Te, I, Xe, and Cs) of the last four, radioactive ones (*13*).

There are strong reasons for suspecting an "island of stability" (better, "longevity") near closed neutron shell 184. Seaborg (*17*) has reviewed the evidence and suggests that several relatively long-lived "superheavy" nuclides may exist in the range $Z = 104$ to 124, $N = 174$ to 194. The doubly magic nuclide 114^{298} is an especially promising candidate, since it is also expected to be β-stable (*18*). Half-lives for spontaneous fission are estimated to range all the way up to 10^{19} years and those for α-decay, up to 10^8 years (*17, 19*). In fact at least one cosmic-ray primary particle of $Z = 103 \pm 4$ has apparently been detected (*20*). This suggests that at least one nuclide in this region has a half-life comparable to the age of cosmic rays, several million years.

A superheavy progenitor of fission xenon in chondrites might resolve some of the difficulties mentioned in the introduction. Only a rather small amount of such a superheavy element (which we denote by the symbol G) would be needed to account for the highest observed value of Xe_f^{136}/U^{238}, 6×10^{-5}. The ratio G/U^{238} at the start of Xe_f^{136} retention is

$$G/U^{238})_t = (G/U^{238})_0\, e^{-t(\lambda_G - \lambda_U)} \quad (1)$$

where subscripts 0 and t refer to end of nucleosynthesis and start of Xe_f^{136} retention, while λ_G and λ_U are the decay constants of G and U^{238}. If xenon retention began T years ago, then the present Xe^{136}/U^{238} ratio is related to $(G/U^{238})_t$ by the expression

$$6 \times 10^{-5} = (Xe_f^{136}/U^{238})_{pres} = (G/U^{238})_0\, e^{-t(\lambda_G - \lambda_U)}(1 - e^{-T\lambda_G})e^{T\lambda_U} ys \quad (2)$$

Here y is the fission yield of Xe_f^{136}; s is the fraction of decays by spontaneous fission. The most favorable case is $t = 0$; $y = 0.05$, $s = 1$. With $T = 4.7 \times 10^9$ years, and $\lambda_G >> 10^{-10}$ year^{-1}, we obtain a *minimum* $(G/U^{238})_0$ of 6×10^{-4}. Let P_G and P_U be the production rates of elements G and U^{238} in nucleosynthesis, which we assume to proceed at a constant rate for T years (*9*). At the end of this process

$$(G/U^{238})_{0,min} = 6 \times 10^{-4} = \lambda_U P_G / \lambda_G P_U (1 - e^{-T\lambda}) \quad (3)$$

If we set $T = 10^{10}$ years and $P_G/P_U = 1$, we obtain $\lambda_{G,max} = 3.3 \times 10^{-7}$ year^{-1}, corresponding to a minimum half-life of 2.1×10^6 years. A more realistic, lower production ratio (or a significant delay between end of nucleosynthesis and start of Xe_f^{136} retention) would require a longer half-life.

As far as can be judged, the fission

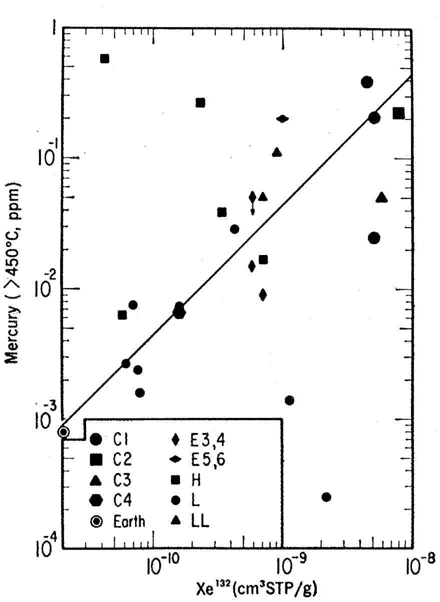

Fig. 4. Mercury (specifically the strongly bound component released above 450°C) (*21*) also shows a correlation with Xe, although several points are grossly discordant. In one respect the fit is better than that for In (Fig. 3), and for Pb, Bi, Tl, I, Xe^{129}, and others: the points for E3 to E5 and C4 chondrites do not fall systematically above the correlation line.

yield curve of a nuclide with mass ~300 should not be inconsistent with the fission-derived Xe spectrum in chondrites. Probably one peak will remain at the 82-neutron shell near mass 140 or 145. The second peak will then be at mass 155 to 160. With a width of some 30 mass units, the two peaks will blend to a large extent. Xe^{134} and Xe^{136} will be on the upward slope of the peak. A yield ratio of ~1.4, as observed in chondrites, is not inconsistent with this picture.

If the progenitor of fission Xe in chondrites was indeed a superheavy element, it may be possible to characterize this element more closely by further trace element correlations. Little can be said from the present data except that the correlation of Xe_f^{136} with Xe and Hg is somewhat better than that with Au, In, Tl, Pb, Bi, Te, I, and Cs. Enstatite chondrites, though low in both Xe_f^{136} and Xe^{132}, are high in these eight elements (as well as Xe^{129} from the decay of extinct I^{129}) and hence fall consistently above the correlation line (for example, Fig. 3). Only on Xe_f^{136}-Xe and Hg-Xe plots (Figs. 1 and 4) do they and the C4 chondrites seem to follow the trend of the other meteorites. [The mercury content plotted here is the tightly bound component released above 450°C (*21*), which is more likely to be indigenous than the more abundant, low-temperature component.] The Hg-Xe correlation is badly marred by four aberrant points in the upper left and lower right of the diagram. Possibly these deviant points are due to contamination or to low Hg retentivity in very fine-grained meteorites. We tentatively assume that some explanation of this sort applies and that the correlation is real. But the reverse possibility must be kept in mind.

It is difficult to draw any quantitative conclusions from the apparent correlation of Hg and Xe. The condensation behavior of these two elements is less well understood than that of most others (*13*); little more can be said than that both are outstandingly volatile. The most simpleminded interpretation is that the progenitor was a congener of Hg or Xe. The latter possibility is unlikely, however. Trapping efficiencies of heavy noble gases from the solar nebula seem to have been no greater than 10^{-4} to 10^{-5} (*13*). Even if the efficiency was as high as 10^{-2} for element 118, a rather high abundance in the nebula would be required to account for the observed Xe_f^{136}. This, in turn, would imply a minimum half-life in the range of 10^8 to 10^9 years according to Eq. 3. Moreover, element 118 would presumably be trapped in the same mineralogical sites as Xe, in which case its decay product, Xe_f^{136}, should diffuse at the same rate as Xe^{132}, contrary to observation.

These objections do not apply to eka-mercury, element 112. From the graph given by Nilsson *et al.* (*19*), the half-lives for α decay and spontaneous fission of element 112^{296} can be estimated to be ~10^6 and 10^{13} years, with an uncertainty of several orders of magnitude in either direction. Its α-decay daughter, 110^{292}, would decay predominantly by spontaneous fission ($t_{1/2} \approx 10^5$ years), its half-life for α decay being close to 10^8 years. Nonetheless it would be premature to identify the progenitor of Xe_f^{136} with element 112 on the basis of a simple chemical analogy. We can state with some confidence that the progenitor was highly volatile, but inasmuch as boiling points and heats of vaporization tend to decrease with increasing Z in the right-hand portion of the periodic table, elements 113 to 117 and element 119 cannot be ruled out. A more specific identification of the progenitor must hence be postponed until its geochemical character is established in more detail, from a study of the distribution of Xe_f^{136} among various meteoritic phases (*27, 28*).

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References and Notes

1. J. H. Reynolds, *Phys. Rev. Lett.* **4**, 8 (1960); *J. Geophys. Res.* **68**, 2939 (1963); C. Merrihue, *J. Geophys. Res.* **71**, 263 (1966); *ibid.* **68**, 325 (1963).
2. J. H. Reynolds and G. Turner, *J. Geophys. Res.* **69**, 3263 (1964).
3. C. M. Hohenberg, M. N. Munk, J. H. Reynolds, *ibid.* **72**, 3139 (1967).
4. R. O. Pepin, in *The Origin and Evolution of Atmospheres and Oceans*, P. J. Brancazio and A. G. W. Cameron, Eds. (Wiley, New York, 1964), pp. 191–234; in *Origin and Distribution of the Elements*, L. H. Ahrens, Ed. (Pergamon, Oxford, 1968), pp. 379–386.
5. H. Funk, F. Podosek, M. W. Rowe, *Geochim. Cosmochim. Acta* **31**, 1721 (1967); M. W. Rowe, *ibid.* **32**, 1317 (1968).
6. K. Marti, *Earth Planet. Sci. Lett.* **3**, 243 (1967).
7. P. K. Kuroda, *Nature* **187**, 36 (1960).
8. M. W. Rowe and P. K. Kuroda, *J. Geophys. Res.* **70**, 709 (1965); M. W. Rowe and D. D. Bogard, *ibid.* **71**, 686 (1966).
9. G. J. Wasserburg, W. A. Fowler, F. Hoyle, *Phys. Rev. Lett.* **4**, 112 (1960).
10. R. O. Pepin and P. Signer, *Science* **149**, 253 (1965).
11. D. Krummenacher, C. M. Merrihue, R. O. Pepin, J. H. Reynolds, *Geochim. Cosmochim. Acta* **26**, 231 (1962).
12. E. Mazor, D. Heymann, E. Anders, in preparation. The data were analyzed by a three-isotope plot as in (*2–5*), but the "primordial" point was set at the average of the nine most primitive isotope ratios measured at Chicago, $Xe^{130}/Xe^{132} = 0.1651$, $Xe^{136}/Xe^{132} = 0.3130$. Pepin's 1968 fission spectrum (*4*) was used instead of that by Reynolds and Turner (*2*). All Berkeley results were recalculated on the same basis.
13. E. Anders, *Space Sci. Rev.* **3**, 583 (1964); J. W. Larimer and E. Anders, *Geochim. Cosmochim. Acta* **31**, 1239 (1967).
14. J. A. Wood, *Icarus* **2**, 152 (1963).
15. S. N. Tandon and J. T. Wasson, *Geochim. Cosmochim. Acta* **32**, 1087 (1968).
16. R. L. Fleischer, *ibid.*, p. 989.
17. G. T. Seaborg, *Annu. Rev. Nucl. Sci.* **18**, 53 (1968).
18. A. G. W. Cameron and R. M. Elkin, *Can. J. Phys.* **43**, 1288 (1965).
19. S. G. Nilsson, S. G. Thompson, C. F. Tsang, *Phys. Lett.* **28B**, 458 (1969); item, *Phys. Today* **22**, No. 2, 63 (1969).
20. P. H. Fowler, unpublished work cited by M. J. Rees and W. L. W. Sargent, *Nature* **219**, 1005 (1968); ———, private communication cited by Nilsson *et al.* (*19*).
21. G. W. Reed, Jr., and S. Jovanovic, *J. Geophys. Res.* **72**, 2219 (1967).
22. W. R. Van Schmus and J. A. Wood, *Geochim. Cosmochim. Acta* **31**, 747 (1967).
23. J. W. Morgan and J. F. Lovering, *Talanta* **15**, 1079 (1968).
24. J. Zähringer. *Geochim. Cosmochim. Acta* **32**, 209 (1968).
25. R. Rieder and H. Wänke, in *Meteorite Research*, P. M. Millman, Ed. (Reidel, Dordrecht, in press).
26. K. F. Fouché and A. A. Smales, *Chem. Geol.* **2**, 5 (1967); R. A. Schmitt and R. H. Smith, in *Origin and Distribution of the Elements*, L. H. Ahrens, Ed. (Pergamon, Oxford, 1968), pp. 183–300.
27. R. Ganapathy, J. W. Larimer, and P. B. Price provided valuable suggestions and criticisms. We are indebted to Dr. E. Mazor for permission to quote his data (*12*). Supported in part by AEC contract AT(11-1)-382, and NASA grant NGR 14-001-010.
28. After this work was submitted for publication, we learned that M. Dakowski (*Earth Planet. Sci. Lett.*, in press) has independently suggested superheavy elements as progenitors of Xe_f^{136} in both chondrites and achondrites.

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Glaciation in Southern Argentina More than Two Million Years Ago

Abstract. *In southern Argentina till beds interbedded with lava flows were deposited by ice that extended at least 40 kilometers east of the present crest of the cordillera. The flow covering the oldest till bed is 3.2 ± 1 million years old. The flow that constitutes the present surface and covers the youngest till bed, is 1.7 ± 0.5 million years old.*

In 1944 Feruglio described an exposure in southern Argentina where till and fluvioglacial material were interbedded with lava flows (*1*). Feruglio noted the great erosion since the volcanism had ceased but, because isotopic dating had not been developed, he was able to describe the glaciation only as "ancient." I visited this exposure in March 1968 and conclude that Feruglio was correct in his identification of till. The material is unsorted, a few of the pebbles are striated, and granitic