minutes at 1600°C, yielding a ^{132}Xe blank of 0.48×10^{-12} cm^3 STP. For the samples in Tables 4 and 5, the extraction time was 30 minutes. Blanks at 1600°C (or 25°C) gave the following results, in 10^{-12} cm^3 STP: ^{84}Kr, 3.0 (0.3) and ^{132}Xe, 0.44 (0.10). The background of the mass spectrometer was negligible in the Kr-Xe region, except at masses 78 and 80. Corrections were applied at these masses, and one-half of the correction was included in the error. All isotopic ratios were corrected for mass discrimination, and the uncertainty in this correction was likewise included in the error. The errors in this article are 1 standard deviation.

27. E. Mazor and E. Anders, *Geochim. Cosmochim. Acta* **31**, 1441 (1967); H. W. Weber, H. Hintenberger, F. Begemann, *Earth Planet. Sci. Lett.* **13**, 205 (1971).
28. X-ray diffraction work indicated the presence of spinel and of chromite. The spinel x-ray diffraction pattern matched perfectly with the pattern obtained by R. N. Clayton (private communication) on spinels separated by heavy liquids from Allende's white inclusions. The chromite x-ray diffraction pattern was not as sharp as the spinel pattern, which indicated smaller particle size. Curiously, treatment of the chromite with HNO_3 or aqua regia at ~ 80°C caused a decrease in the spacings by ~1 percent. An extensive but unsuccessful search was made for any additional lines and also for lines removed by the HNO_3 and aqua regia treatments.
29. L. Grossman and J. W. Larimer, *Rev. Geophys. Space Phys.* **12**, 71 (1974).
30. J. Gros, unpublished work.
31. I. A. Breger, P. Zubovic, J. C. Chandler, R. S. Clarke, *Nature (London)* **236**, 155 (1972).
32. D. Virgo, private communication.
33. L. Gmelin, *Handbuch der Anorganischen Chemie*, vol. 52, *Chrom* (Verlag Chemie, Weinheim, ed. 8, 1962), part B.
34. E. R. DuFresne and E. Anders, *Geochim. Cosmochim. Acta* **26**, 251 (1962).
35. E. Vilcsek and H. Wänke, *Z. Naturforsch.* **20a**, 1282 (1965).
36. E. Mazor, D. Heymann, E. Anders, *Geochim. Cosmochim. Acta* **34**, 781 (1970).
37. This archaic term has been restored to active use by D. A. Papanastassiou and G. J. Wasserburg [*Earth Planet. Sci. Lett.* **11**, 37 (1971)]. They use it to designate a minor glassy phase in lunar rocks that is highly enriched in trace elements such as Rb and U.
38. R. S. Lewis, J. Gros, E. Anders, unpublished work.
39. A. G. W. Cameron, *Space Sci. Rev.* **15**, 121 (1973).
40. D. Heymann and A. Yaniv, *Geochim. Cosmochim. Acta Suppl. 1* (1970), p. 1247.
41. K. Marti, *Science* **166**, 1263 (1969).
42. J. W. Larimer and E. Anders, *Geochim. Cosmochim. Acta* **31**, 1239 (1967).
43. M. S. Lancet and E. Anders, *ibid.* **37**, 1371 (1973).
44. D. C. Black and R. O. Pepin, *Earth Planet. Sci. Lett.* **6**, 395 (1969); D. C. Black, *Meteoritics* **4**, 260 (1969); *Geochim. Cosmochim. Acta* **36**, 377 (1972).
45. P. Eberhardt, J. Geiss, H. Graf, N. Grögler, M. D. Mendia, M. Mörgeli, H. Schwaller, A. Stettler, *Geochim. Cosmochim. Acta Suppl. 3* (1972), p. 1821.
46. O. Eugster, P. Eberhardt, J. Geiss, *Earth Planet. Sci. Lett.* **3**, 249 (1967); F. A. Podosek, J. C. Huneke, D. S. Burnett, G. J. Wasserburg, *ibid.* **10**, 199 (1971).
47. R. S. Lewis, *Geochim. Cosmochim. Acta* **39**, 417 (1975).
48. B. Srinivasan and R. S. Lewis, unpublished work.
49. J. W. Larimer and E. F. Holdsworth, private communication.
50. D. L. Phinney, thesis, University of Minnesota (1971).
51. A. G. W. Cameron, in *Proceedings of a Symp. on the Dusty Universe*, Cambridge, Mass., 1973.
52. D. N. Schramm, *Nature (London)* **233**, 258 (1971).
53. L. Grossman and E. Olsen, *Geochim. Cosmochim. Acta* **38**, 1973 (1974).
54. C. M. Gray, D. A. Papanastassiou, G. J. Wasserburg, *Icarus* **20**, 213 (1973); F. A. Podosek and R. S. Lewis, *Earth Planet. Sci. Lett.* **15**, 101 (1972); M. Tatsumoto, D. M. Unruh, G. DesBorough, *Geochim. Cosmochim. Acta*, in press.
55. E. Anders, R. Hayatsu, M. H. Studier, *Science* **182**, 781 (1973).
56. M. Tatsumoto, private communication.
57. P. Signer and H. E. Suess, in *Earth Science and Meteoritics*, J. Geiss and E. D. Goldberg, Eds. (North-Holland, Amsterdam, 1963), p. 241.
58. M. S. Lancet, thesis, University of Chicago (1972).
59. W. B. Lewis, *At. Energy Can. Ltd. AECL Rep. 1402* (1961).
60. H. C. Urey, in *L. Farkas Memorial Volume* (Research Council of Israel, Jerusalem, 1952), p. 3; N. Kokubu, T. Mayeda, H. C. Urey, *Geochim. Cosmochim. Acta* **21**, 247 (1961); E. Anders, *Acc. Chem. Res.* **1**, 289 (1968); K. K. Turekian and S. P. Clark, Jr., *Earth Planet. Sci. Lett.* **6**, 346 (1969).

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Extinct Superheavy Element in the Allende Meteorite

Element 115 (or 114, 113) may have been present in a rare chromium mineral when the meteorite formed.

Edward Anders, H. Higuchi, Jacques Gros,
H. Takahashi, John W. Morgan

Eleven years after Reynolds and Turner (*1*) discovered excess $^{131-136}$Xe in the Renazzo meteorite, the source of the xenon remains unidentified. Presumably it is an unknown transuranium element that decayed by spontaneous fission. But none of the known transuranium elements, including extinct 82×10^6 year ^{244}Pu, produces xenon of this peculiar isotopic composition (*2–4*).

Only one clue to the chemical nature of this element has been available: its volatility. The fission-produced xenon occurs solely in primitive, volatile-rich meteorites, and Anders and Heymann (*5*) therefore suggested that the progenitor of the xenon was to be sought among elements 112 to 119, the only transuranium elements expected to be volatile (*6*). Anders and Larimer (*7*) later revised the range to 111 to 116, after estimating the condensation temperatures of superheavy elements in the solar nebula.

These arguments were based on the distribution of the free element between nebular gas and meteoritic solids, as inferred from the abundance of fission xenon in meteorites of different accretion temperature. The obvious next step (*5, 7*) was to study the distribution of fission xenon among various meteoritic minerals, and compare it with that of other trace elements. This distribution might reveal some further chemical properties of the progenitor, such as oxidation state, ionic radius, and geochemical character (that is, tendency to form oxides, sulfides, or free metal).

This experiment finally became feasible with the isolation of a mineral fraction from the Allende C3 chondrite that was enriched nearly 200-fold in fission xenon, as described in the companion article by Lewis *et al.* (*8*). A mass spectrometric study of the noble gases in this fraction is reported in (*8*). This article describes a radiochemical study of the same fraction.

Results

We have analyzed seven Allende samples for 26 trace elements by radiochemical neutron activation analysis, using

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a procedure developed for lunar samples (*9*). In addition, Cr and Fe were measured by instrumental neutron activation analysis. The elements measured lie mainly in the center and right-hand parts of the periodic table, and include at least one light congener for every superheavy element from 107 to 119, as well as uranium and five lanthanides, which are congeners of the actinide elements 90 to 103. The samples included two chromite or chromite-spinel concentrates (3C1 and 3CS1) that had been separated from Allende by HCl-HF treatment (*8*), four acid-etched portions of these concentrates, and a sample of the bulk meteorite. The data are shown in Table 1; samples with designations ending in 1 (such as 3C1) are unetched, those ending in higher numbers are etched. Etched samples are arranged in order of increasing mass loss.

ALLENDE CHROMITE 3CI: ENRICHMENTS RELATIVE TO BULK METEORITE

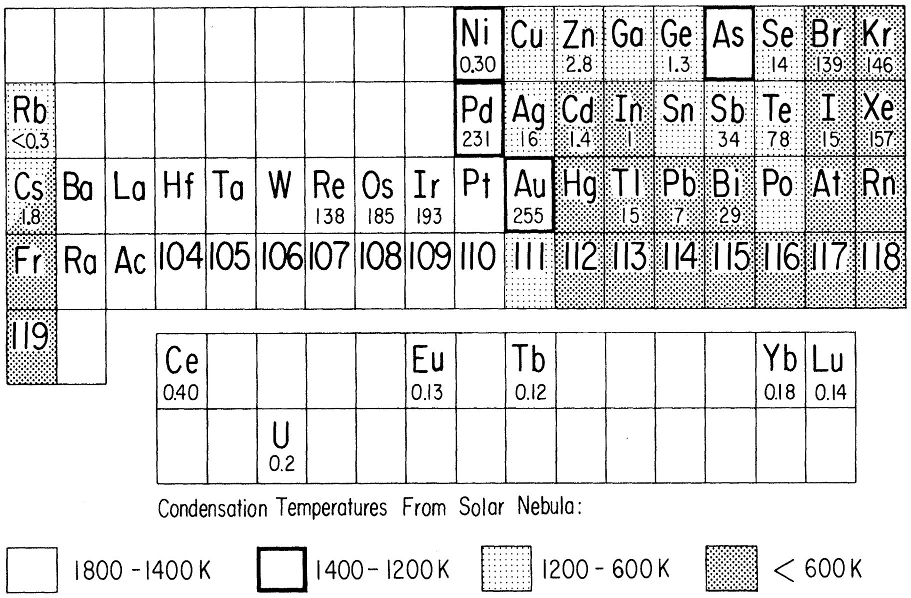


Fig. 1. A chromite-rich fraction that is enriched 180-fold in fission Xe also shows marked enrichments of two groups of trace elements: noble metals (congeners of elements 107 to 111) and volatiles (congeners of elements 113 to 118). It is not enriched in Th, U, and rare earths (congeners of actinides). Presumably the progenitor of fission Xe in primitive meteorites was a noble metal or a volatile element, not an actinide. Data are from Table 1, except for Pb data from Tatsumoto (*10*). Because sample 3C1 was contaminated with U, the U value for 3CS1 has been substituted. The value for I was calculated from the radiogenic ^{129}Xe content.

Table 1. Element abundances in gas-rich mineral fractions of Allende meteorite. All concentrations are in parts per million, except for Xe (10^{-8} cm^3 STP/g) and Cr and Fe (percent). Samples were chromite (C) or chromite-spinel (CS) fractions, comprising 0.17 and 0.31 percent of the bulk meteorite (*8*) and containing about 50 percent carbon. Etching treatment is indicated below sample number. Fum. HNO_3 = red fuming nitric acid. Doubtful values are indicated in italic type. In addition, most values for 3C5 seem somewhat too high, perhaps due to a weighing error on this very small (0.48 mg) sample. Suffixes b (in 3C3b and 3C2b) designate samples prepared for neutron activation analysis.

Element	Allende bulk	3C1	3C3b $HCl-HNO_3$	3C2b HNO_3	3C5 Fum.HNO_3 $HCl-HNO_3$	3CS1	3CS5 Fum.HNO_3 $HCl-HNO_3$
Re	0.0692	9.52	2.94	3.38	4.79	7.91	2.83
Os	0.925	171	42.3	47.4	49.6		30.2
Ir	0.799	154	62	90	84	121	37
Ni	13100	3910	< 1700	< 740	< 1000	2450	< 210
Pd	0.694	160	17.1	180	23.4		5.84
Ag	0.090	1.48	0.08	0.08	0.06	1.66	0.03
Au	0.136	34.7	34.5	27.8	2.17	21.9	0.998
Zn	112	311	371	364	501	694	1040
Cd	0.464	0.650	0.745	*12.2*	≤0.17	0.112	≤0.036
In	0.041	0.04					
Tl	0.058	0.88	0.40	0.056	0.020	0.350	0.011
Ge	29.1	37.1	9.36	34.1	34.3	11.9	7.02
Sb	0.080	2.71	2.57	2.59	*1.97*	1.89	0.685
Bi	0.043	1.23	0.410	0.169	0.083	0.583	0.027
Se	7.4	101	37	18.1	*150*	100	*18.9*
Te	0.995	77.9	12.2	61.9	35.3	41.3	8.56
Br	1.48	206	75.9	37.3	20.9	136	6.76
^{132}Xe	0.192	30.3	14.0	4.20		19.8	
$^{136}Xe_f$	0.0053	1.05	0.73	0.69		0.71	
$^{129}Xe_r$	0.19	2.92	1.28	0.30		1.89	
Rb	0.99	≤0.3	≤1.3	≤0.5	≤2.4	0.246	≤1.0
Cs	0.082	0.15	0.1	≤0.04	≤0.12	0.098	≤0.04
U	0.0134					0.003	
Ce		0.26	1	0.61	3		0.46
Eu		0.009					0.027
Tb		0.01					0.006
Yb		0.03					
Lu		0.007					0.005
Cr		13.0	15.0	14.2	18.6	9.6	10.7
Fe		9	6.5	6	7	9.6	10

Gross Enrichment Pattern

The unetched chromite sample 3C1 shows a remarkably broad enrichment pattern. Sixteen of the 29 elements (*10*) are enriched by more than a factor of 5 over the bulk meteorite (Fig. 1). The enrichment factors are given below the element symbols in Fig. 1. The condensation range from the solar nebula is also indicated, as determined from thermodynamic calculations (*6, 11*), abundance trends in meteorites (*6*), or extrapolations from the periodic table. If such a simple-minded extrapolation holds, the progenitor of fission Xe (hereafter, progenitor) must be sought among the superheavy congeners of these 16 elements.

We can at once eliminate what appear to be leading candidates: the five noble metals Re, Os, Ir, Pd, and Au, which alone have enrichment factors approaching those of primordial or fission Xe (157 and 176). To begin with, we know the principal phases in which these elements reside: Ca,Al-rich inclusions for Re, Os, and Ir (*11*) and nickel-iron for Pd and Au (*12*). Neither the former (*13*) nor the latter (*8*) is enriched in this type of fission Xe. The presence of noble metals in 3C1 is merely a fortuitous consequence of their insolubility in HCl-HF. The sample had been prepared by dissolving > 99 percent of the meteorite in HCl-HF, and so in addition to chromite and the associated Fe,Cr-sulfide, it must have contained a residue of all metals released from the dissolved phases that were too noble to dissolve in HCl-HF.

A more general argument is the volatility of the progenitor, and since it will figure repeatedly in later discussions, some of the evidence will be reviewed here.

Volatility of Progenitor

As stressed in (*5*) and (*7*), fission Xe correlates not with high-boiling elements such as U (or Ir, Re, Au), but only with volatile elements such as In, Bi, Tl, and Hg (Fig. 2) and planetary Xe (*3*). These elements seem to have condensed from a cooling solar nebula between 500° and 400°K (*6, 11, 14, 15*), and the obvious inference is that the progenitor, too, condensed in that range. The more primitive meteorites, designated by lower petrologic type numbers, accreted at lower temperatures and hence collected a proportionately greater share of volatiles.

Some authors (*16*) have contended, however, that the correlation in Fig. 2 reflects the volatility of fission Xe itself, not of its progenitor. In this view (*17*), all chondrites initially had the same amount of volatiles, but then lost them during metamorphic reheating in the meteorite parent bodies. The degree of loss increased with burial depth and peak metamorphic temperature, as indicated by petrologic type. If the progenitor had already decayed by the time of metamorphism, the abundance of fission Xe would reflect the volatility of Xe, not of the progenitor.

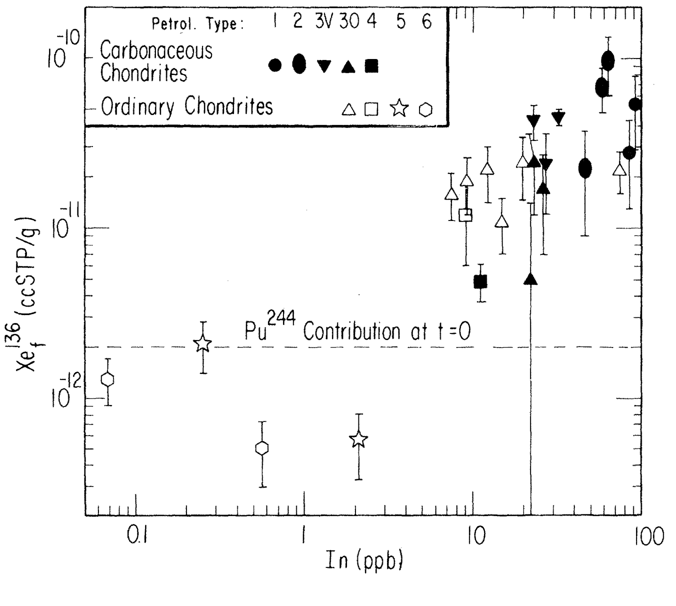
However, there is direct evidence for the volatility of the progenitor: the low abundance of fission Xe in chondrules. Chondrules, millimeter-sized silicate spherules, comprise the major part of most chondrites, and are grossly depleted in volatiles relative to the fine-grained matrix. They apparently represent primary condensate (matrix) that was melted just before accretion (*6, 11*). Volatile elements, from Au and Na on down, were lost during this process. The progenitor seems to have been lost at the same time, because separated chondrules from the Allende (*18*), Chainpur, and Mokoia (*3*) chondrites typically show only one-tenth the planetary and fission Xe content of matrix or the bulk meteorite. (Part of it may actually represent adhering matrix.) The loss definitely occurred before accretion, because chondrules themselves formed before accretion, and metamorphism in these meteorites ranged from slight (Allende, Chainpur) to none (Mokoia).

A tacit assumption in the preceding argument is that the progenitor had not yet decayed when the chondrules formed. This is likely, but not certain. Matrix had condensed from the solar nebula less (probably much less) than 1.8 million years before the chondrules (*19*), and apparently still contained the progenitor in live form. [This follows from the distinctive, highly localized mineralogical siting of fission Xe (*8*).] If the progenitor had been so short-lived that it decayed completely in the ≪ 1.8 million year interval between formation of matrix and chondrules, then it could hardly have reached the solar system in live form in the first place.

Mineral Separation by Selective Etching

Four phases had been detected in the samples by x-ray diffraction or other techniques: spinel, chromite, amorphous carbon, and a minor, elusive Fe,Cr-sulfide, dubbed Q (*8*). In addition, a sludge of noble metals seemed to be present. The spinel could be easily separated by sedimentation, but was probably irrelevant to our study, because the spinel-bearing 3CS samples had consistently lower Xe contents than the spinel-free 3C samples (*8*). The problem thus was to separate the remaining phases. Physical methods were not feasible, because the particles were too small (0.3 μm for chromite) and too intimately associated. Following the example of earlier workers (*20*), we therefore resorted to chemical methods, involving dissolution in appropriate solvents. In the present case, we used aqua regia, HNO_3, and red fuming HNO_3 (*21*).

Procedure. The rationale of the procedure was simple. Chromite and carbon (as well as spinel) are insoluble in any of the acids used, and therefore remained together in the etched residues. Noble metals dissolved in aqua regia. All sulfides are soluble in concentrated HNO_3 or aqua regia, although some, including chromium sulfides, react only slowly, even with fuming HNO_3 (*22*). We therefore subjected one set of samples to a more drastic and prolonged



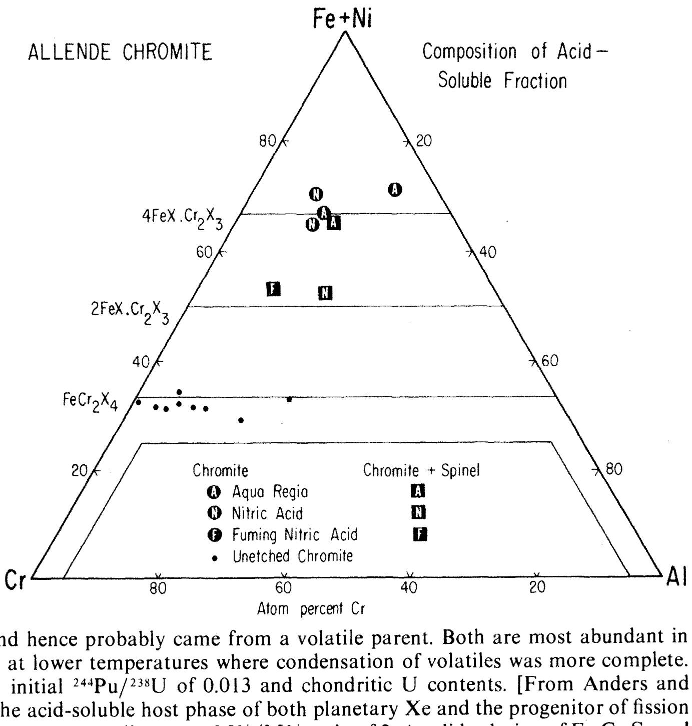


Fig. 2 (left). Fission-derived $^{136}Xe_f$ correlates with a volatile metal, In, and hence probably came from a volatile parent. Both are most abundant in meteorites of lower petrologic type, which accreted from the solar nebula at lower temperatures where condensation of volatiles was more complete. The dashed line indicates the maximum contribution from ^{244}Pu, for an initial $^{244}Pu/^{238}U$ of 0.013 and chondritic U contents. [From Anders and Larimer (*7*)] Fig. 3 (right). Attempted characterization of mineral Q, the acid-soluble host phase of both planetary Xe and the progenitor of fission Xe. Five of the seven samples lie near the highest of the three horizontal lines, corresponding to an M^{2+}/M^{3+} ratio of 2. A solid solution of $Fe_4Cr_2S_7$ and $Fe_4Al_2S_7$ would plot along this line. The remaining two samples fall near the second line, corresponding to a ratio of 1 and a composition $Fe_2Cr_2S_5$-$Fe_2Al_2S_5$. None plot near the original composition of the unetched sample (small dots). Apparently mineral Q is more iron-rich than the original chromite. It may be a sulfosalt such as $Fe_4Cr_2S_7$ or $Fe_2Cr_2S_5$ or a mixture of several minerals containing Fe, Ni, Cr, Al, and S.

treatment with fuming HNO_3, followed by aqua regia.

Trace element data for the etched samples are given in Table 1, and will be discussed later. Of more immediate concern are the dissolved fractions, which were analyzed by atomic absorption for five major elements (*23*) (Table 2).

Composition of Mineral Q

Apparently an Fe,Cr-rich material with lesser amounts of Ni, Al, and Mg was progressively dissolved during etching. This is mineral Q, which contains the bulk of the fission Xe and heavy planetary gases (*8*). It is therefore of greatest interest for this study. We can try to estimate the composition of Q from the data in Table 2. It is obvious on inspection that Ni correlates closely with Fe, while Mg does not correlate with anything and probably represents a residual silicate impurity. [This is also suggested by the electron microprobe analyses in (*8*).] We have therefore plotted the data for the remaining four elements in a ternary diagram, to see whether they correspond to any preferred and meaningful composition (Fig. 3).

Phase	Gas content 10^{-8} cm^3 STP/g	
	$^{132}Xe_p$	$^{136}Xe_f$
Chromite-carbon	1.4	0.36
Mineral Q	310	3.3

Four of the seven samples cluster tightly, at a divalent-to-trivalent element ratio of 2 : 1. A fifth is displaced toward a more Al-rich composition, but again has an M^{2+}/M^{3+} ratio close to 2. The two remaining samples, both from the spinel-bearing 3CS fraction and rather severely etched, are displaced downward and plot near a ratio of 1.

Although these results do not suffice for a conclusive identification, they suggest that Q may be a double sulfide of Fe/Cr ratio between 1 and 2: either the $(Fe,Cr)_{1-x}S$ solid solution (*24*), or a stoichiometric sulfosalt. Iron chromium sulfide minerals of any kind are unknown on the earth (even daubréelite, $FeCr_2S_4$, occurs only in meteorites), but several other double sulfides of M^{2+}/M^{3+} between 1 and 2 are known. They include both sulfosalts of normal stoichiometry such as dufrenoysite ($Pb_2As_2S_5$), cosalite ($Pb_2Bi_2S_5$), lillianite ($Pb_3Bi_2S_6$), and jordanite ($Pb_{14}As_7S_{24}$), and sulfur-poor compounds such as NiAsS, NiSbS, and $Ni_3Bi_2S_2$. And at least two unidentified minerals have been found in association with meteoritic daubréelite (*25*).

The evidence that Q is a sulfide is indirect: there is some unaccounted-for sulfur in the microprobe analysis (nearly enough to convert all elements in the soluble fraction to sulfides); Q, like daubréelite and chromium sulfides, is insoluble in dilute HCl, but slowly soluble in oxidizing acids; and some NO_2 and elemental S were observed during dissolution. We shall therefore assume that Q is an iron-chromium sulfide containing Ni and Al, or a mixture of several minerals containing these elements. For the sake of definiteness, we shall tentatively assign to it the mean composition of the cluster in Fig. 3

$$(Fe_{0.90}Ni_{0.10})_4(Cr_{0.62}Al_{0.38})_2S_7$$

Mineral Q has not yet been found in situ in the meteorite. It may in fact be too fine-grained and disperse for detection by optical microscope or electron microprobe. However, after this work was completed, Larimer and Holdsworth (*26*) found several promising features in thin sections of Allende. They are large, 15- to 20-μm spheres of fine-grained chromite surrounding cores of Ni-rich pentlandite, $(Fe,Ni)_9S_8$. These spheres occur in large (70 to 80 μm) Fe-poor but Cr-rich forsterite crystals, and are always connected to the matrix by fractures.

Amount of Mineral Q

Because of the small size of the samples (2 to 9 mg) and the inevitable mechanical losses on washing (especially for the colloid-prone samples etched with fuming HNO_3), the total amount of dissolved Q could not be accurately determined from the apparent weight loss. We have therefore calculated nominal weight losses, on the assumption that Mg was present as olivine, while all other elements were present as sulfides (Table 2). In the two cases where mechanical losses were small (C2b and C3b), they agree tolerably well with the observed weight losses. The last three samples which had been treated with fuming HNO_3 show larger discrepancies, due to loss of colloidal material and perhaps oxidation of some of the carbonaceous matter. Because Mg seems to be extraneous to Q, we have also calculated the weight loss of the first four elements only (last column in Table 2). It should correspond to the amount of Q dissolved.

In spite of some scatter, the data correlate fairly well with the noble gas data from (*8*). Weight losses and planetary gas losses increase in the order aqua regia < HNO_3 < fuming HNO_3. We attribute this trend to differences in etching rate, not intrinsic solubility. The loss of Q seems to level off at about 8 percent, if we disregard 3C5, which seems to be contaminated with iron and is anomalous in several other respects.

Trace Element Content of Q

We can now try to determine the trace element content of Q, the principal host phase of fission Xe. If the trends are sufficiently clear-cut, they may provide clues to the geochemical character, ionic charge, and atomic number of the progenitor.

A characteristic attribute of Q is its high solubility in aqua regia and particularly HNO_3, on the time scale of our experiments. Elements that reside in Q should show similarly high solubilities. Figure 4

Table 2. Selective etching of Allende samples. Atomic absorption analyses are by D. F. Nava and P. J. Schuhmann of Goddard Space Flight Center, Greenbelt, Maryland. Values in italics seem too high and probably indicate contamination of the solution before analysis. Suffixes a and b in sample designations indicate that samples were prepared independently for mass spectrometry and neutron activation analysis. Treatments were: (aqua regia) aqua regia for 1 hour at 25° to 80°C, CS_2, aqua regia for 2.5 hours at 40° to 80°C; (conc. HNO_3) HNO_3 for 3.5 hours at 80° to 90°C, CS_2 (except 3C2b); (fum. HNO_3) fuming HNO_3 for 24 hours at 80°C, aqua regia for 2 hours at 40° to 80°C, fuming HNO_3 for 2 hours at 70°C.

Sample	Treatment (hours)			Amount dissolved (% by weight of unetched sample)					Weight loss (%)		
	Aqua regia	Conc. HNO_3	Fum. HNO_3	Fe	Ni	Cr	Al	Mg	Calc.	Obs.	Q
3CS3	3.5			1.45	0.14	0.44	0.18	0.18	4.3		3.8
3C3a	3.5			2.18	0.27	0.68	0.23	0.09	6.0		5.7
3C3b	3.5			1.63	0.24	0.16	0.28	0.27	4.8	6.3	4.0
3CS2		3.5		1.86	0.19	0.98	0.38	0.09	6.4		6.0
3C2a		3.5		2.60	0.32	0.96	0.26	0.14	7.5		7.1
3C2b		3.5		2.67	0.39	0.77	0.21	0.08	7.1	4.6	6.9
3C5	2		24 + 2	*9.07*	0.12	0.77	0.17	0.26	*16.8*	45	*16.1*
3CS5	2		24 + 2	2.25	0.21	1.58	0.26	0.10	7.8	24	7.5
3CS4*			1	2.0	0.15	1.56				28	

*Instrumental neutron activation analysis by J. Gros. Treatment involved fuming HNO_3 for 1 hour at 80°C, concentrated $HClO_4$ for 1 hour at 80°C, CS_2, and CH_3OH.

compares the solubilities of the trace elements from Table 1. The quantity plotted is the fraction of each element soluble in a given acid. It was found indirectly from the difference between the unetched (C1) and etched (C2 or C3) samples, with an appropriate correction for the weight loss α from Table 2

$$\Delta C2/C1 = [C1 - (1 - \alpha)C2]/C1$$

Six volatile elements in the upper right-hand corner of Fig. 4 indeed have both required characteristics, high overall solubility and preferential solubility in HNO_3. Nickel, a constituent of Q, also falls in the same region. We can specify the position of Q itself on this plot from the weight losses of 3C2 and 3C3, once we know the original Q content of the unetched sample 3C1. Judging from the leveling-off of weight loss with etching time (Table 2), a value near 8 percent seems appropriate. Very similar values, from 7.6 to 8.1 percent, are obtained when plots of residual Br, Bi, Tl, and Ni content against weight loss are extrapolated to zero. Adopting 8 percent for the Q content of 3C1, and using the observed weight losses of 3C2b and 3C3b for $\Delta C2$ and $\Delta C3$, we obtain the point Q8 in Fig. 4. It falls in the middle of the cluster. Higher Q contents would displace this point toward the origin, but even for an improbably high value of 9 percent (Q9), the point would still fall near the cluster.

It appears that six trace elements reside in Q: Bi, Br, I, Se, Tl, and planetary Xe. All are highly volatile, form large ions, and are at least moderately chalcophile (sulfide-seeking) in meteorites. A seventh element, Pb, should be added, because measurements by Tatsumoto (*10*) indicate that it, too, is very soluble in HNO_3. Apparently the progenitor of fission Xe had at least some properties in common with these elements. We shall return to this question in a later section.

In view of the evidence that the progenitor of fission Xe resided in Q, it seems paradoxical that the fission Xe point falls outside the Q grouping. A possible explanation is that some of the fission Xe has recoiled into the chromite, where it is protected from acid attack. Although Q still has a ninefold higher $^{136}Xe_f$ content than the chromite-carbon fraction, the latter is much more abundant (92 percent compared to 8 percent) and so actually accounts for ~60 percent of the fission Xe. Only ~40 percent of the fission Xe has remained in Q, and displays the characteristic solubility in oxidizing acids.

Not much needs to be said about the trace element content of the chromite-carbon fraction. Data for the most heavily etched samples 3C5 and 3CS5 (Table 1) suggest that chromite-carbon contains a substantial fraction of the refractory metals Re, Ir, and Os, and a lesser fraction of the moderately volatile elements Zn, Ge, Te, and Sb. All these elements condense at temperatures above the nebular formation temperature of chromite (< 800°K; see next section), and so it seems that they were present in the parent material of the chromite.

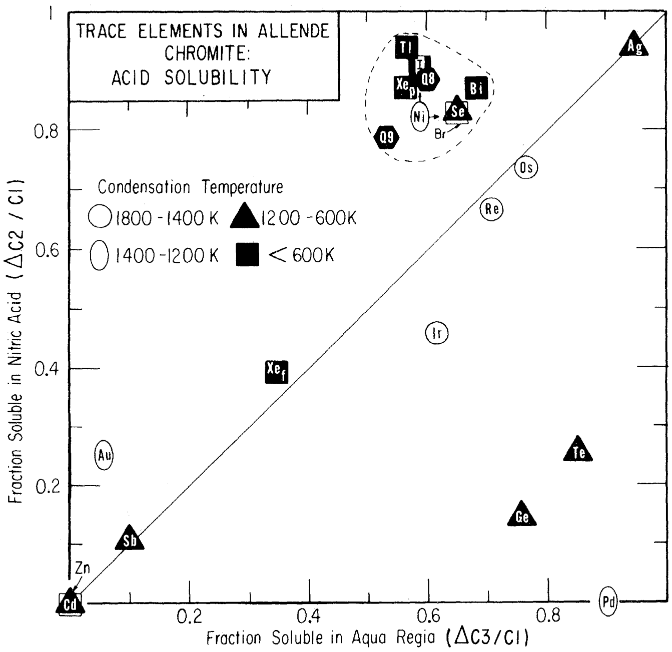


Fig. 4. Trace elements associated with mineral Q. Six volatile elements (Bi, Br, I, Se, Tl, and planetary Xe) dissolve at the same rate as mineral Q: ~60 percent in aqua regia and ~90 percent in HNO_3, in 3.5-hour treatments. All apparently reside in Q. The point Q8 corresponds to the estimated Q content of 8 percent, and Q9, to a conservative upper limit of 9 percent. Although the fission xenon (Xe_f) now plots outside the cluster, because much of the Xe_f has recoiled into chromite, where it is protected from acid attack, the fact that Q still has a ninefold higher fission Xe content per gram than the chromite shows that it, rather than the chromite, is the original host phase of the progenitor. Most of the remaining elements are less soluble overall, and do not show the preferential solubility in HNO_3 that characterizes mineral Q and its associated trace elements. They seem to reside mainly in chromite or in a sludge of noble metals left over after dissolution of the meteorite.

Origin of Chromite and Q

From what is known about the condensation of Cr in the solar nebula, it appears that chromite and Q are not primary condensates, but secondary alteration products of such condensates. According to Grossman and Olsen (*27*), Cr, Co, and Ni condense as alloys with metallic Fe, starting at its condensation point (1374°K at a total nebular pressure of 10^{-4} atm). Such Cr-rich grains have actually been observed in C2 chondrites, where they commonly occur inside crystals of forsterite (Mg_2SiO_4). Forsterite is the next major phase to condense after Fe at all pressures greater than 10^{-4} atm (*11*), and apparently occluded some of the metal grains.

Chromium is somewhat more volatile than Fe, and so some 10 to 20 percent of the Cr still remains in the gas phase at the time all Fe has condensed. This Cr may be able to form small amounts of Cr_2O_3, $MgCr_2O_4$, or $FeCr_2O_4$ as primary condensates (*27*).

Between ~ 800° and 500°K, the metal grains containing the bulk of the Cr react first with H_2O to form FeO (which enters silicates) and then with H_2S to give FeS and $(Fe,Ni)_9S_8$ or Ni-rich metal (*6, 11*). The Cr transforms to $FeCr_2O_4$ at the same time (*28*). It is not known at what point formation of chromium sulfides becomes possible, because thermodynamic data are lacking. Laboratory experiments show, however, that Cr_2O_3 transforms to Cr_2S_3 in an H_2S atmosphere at 450° to 500°C (*29*), and in view of the generally increasing stability of sulfides at lower temperatures, it seems likely that formation of Q will become possible on further cooling.

The noble gas and trace element data for Allende can be explained within the general framework of the condensation model for the formation of meteorites (*6, 11*), at the expense of a few ad hoc assumptions. For the sake of conciseness, we shall present, ex cathedra, a scenario that accounts for the data, rather than try to construct it step-by-step by deductive reasoning.

Between 1400° and 1200°K, Cr,Au,Pd-bearing FeNi grains condensed on Pt-metal nuclei that had previously formed at 1800° to 1500°K. Some were encapsulated in forsterite, others remained free and collected additional siderophile elements on cooling, such as Sb, Ge, and Te. Between 800° and 500°K, the free metal grains reacted to a progressively greater degree with H_2O (*11*), forming FeO and chromite. The chromite (or carbon) trapped He, Ne, and small amounts of the heavy noble gases in anion vacancies, as described by Lancet and Anders (*30*) for magnetite. An isotopic fractionation by an unknown mechanism took place during trapping that enriched the light isotopes of Xe and the heavy isotopes of the other four gases. (No separate roles can yet be assigned to chromite and carbon, because these two phases were not studied separately. The carbon may have formed by decomposition of CO on the surfaces of some catalytically active mineral.)

Below 680°K, the reaction with H_2S commenced, and proceeded alongside the H_2O reaction. In the later stages of this process, probably near 450°K, some part of the chromium formed a sulfide (Q) in intimate association with chromite, which trapped heavy noble gases and volatile-chalcophile elements: Se, Te, Br, I, Bi, Tl, and the progenitor of fission Xe. Possibly the sulfide was formed preferentially from metal grains occluded in forsterite, whose mantles retarded their reaction with the gas at temperatures above 680°K, where chromite alone could form.

Identity of Progenitor

Two new clues have emerged from this work. The progenitor was chalcophile and condensed from the nebula as (or at least with) a sulfide. And it concentrated in a rare, iron-chromium sulfide (0.04 percent of the meteorite) in preference to the much more abundant iron-nickel sulfides (6 percent of the meteorite). Let us pursue these clues in turn, to see if they further restrict the range inferred from volatility alone, elements 111 to 119. First, we eliminate some unlikely candidates.

Unlikely Candidates: 117 to 119

Of the nine volatile superheavy elements, the last three can probably be dismissed, as in (*7*). However, the arguments are strengthened or modified by the new experimental data.

Element 119. This element is an alkali metal, and is more likely to form an oxide than a sulfide. Indeed, its congeners Rb and Cs have very low abundances in chromite and Q (Table 1 and Fig. 1), and apparently prefer other phases.

Element 118. This element is a noble gas, which, like its lighter congeners, would probably be trapped in Q. But the efficiency of such trapping is low: Allende contains only 1×10^{-8}, 8×10^{-7}, and 1×10^{-5} its cosmic complement of Ar, Kr, and Xe (*8*). The most optimistic extrapolation of this trend predicts a value of 10^{-2} for 118, which in turn requires that the abundance ratio progenitor/^{238}U in the nebula be two orders of magnitude greater than the minimum of 6×10^{-4} (*5*) needed to account for the observed amount of fission Xe. This is not out of the question, because the production ratio in nucleosynthesis may be as high as 1 (*31*), and so enough might be left even after some decay and dilution with older material.

However, the extrapolation of trapping efficiency from Xe to 118 is very long (the intervening noble gas Rn is radioactive), and correspondingly uncertain. It is not at all clear that a linear extrapolation is warranted, because an experimental study of the trapping process (*30*) showed definite limiting size effects. Solubilities in an oxide mineral, magnetite, actually decreased in the order Ar > Kr > Xe. Laboratory data are needed on the solubility of noble gases (including Rn) in Q or similar sulfides. Until such data become available, it seems prudent to assume that 118 is not much more soluble than Xe, and would hence have to be present in the nebula in prohibitively high abundance.

Element 117. At first sight, element 117 seems to be a likely candidate, because its light congeners Br and I are substantially enriched in the chromite concentrate 3C1 (Fig. 1). Presumably their −1 ions substitute for S^{2-}. However, the trend is downward, reflecting the growing disparity in ionic radii (*32*): S^{2-} (1.72 Å), Br^- (1.88 Å), and I^- (2.13 Å). The mismatch would be greater still for element 117.

Moreover, it is doubtful whether element 117 has a stable −1 state (*33*), because its electron affinity is predicted to be only 1.8 ev (*34*). Thus 117 will have to qualify on its own merits, not because of its relationship to Br and I.

The most stable oxidation state of 117 is expected to be +1 (*33*). Astatine, its closest congener, does not seem to form a sulfide in that oxidation state, but since 117 is expected to be more metallic, it may possibly do so. Such a sulfide would be much less stable than Tl_2S, however, because of the higher ionization potential [8.2 versus 6.07 ev (*33*)], larger ionic radius, and smaller electronegativity difference. Although trends are too irregular and data too sparse for a quantitative estimate of the heat of formation, it seems unlikely that 117 will condense as a sulfide.

Condensation of Sulfides

To narrow the range further, we must determine which of the remaining elements 111 to 116 will condense as sulfides rather than as free metals. More specifically, we must look for elements that form sulfides near 400° to 500°K. As shown in (*7*), fission Xe contents drop sharply for meteorites of accretion temperature greater than 460°K, which suggests that the progenitor had a condensation temperature of that order.

Condensation of trace elements from the solar nebula has been discussed by Larimer (*15*). When a trace metal E condenses as a pure phase, the fraction α condensed at a temperature T is given by the relation

$$\log(1-\alpha) = -\frac{\Delta H_s}{2.303RT} + \frac{\Delta S_s}{2.303R} - \log\frac{A(\mathrm{E})}{A(\mathrm{H_2})} - \log P_t \qquad (1)$$

where ΔH_s and ΔS_s are the enthalpy and entropy of sublimation, R is the gas constant, $A(\mathrm{E, H_2})$ are the nebular abundances of E and H_2, and P_t is the total pressure in the nebula.

The equation for a sulfide E_mS_n is similar

$$\log(1-\alpha) = -\frac{\Delta H_c}{2.303RT} + \frac{\Delta S_c}{2.303R} - \log\frac{A(\mathrm{E})}{A(\mathrm{H_2})} - \frac{n}{m}\log\frac{A(\mathrm{H_2S})}{A(\mathrm{H_2})} - \log P_t \qquad (2)$$

except that the ΔH and ΔS terms refer to the reverse of the condensation reaction

$$(1/m)\mathrm{E}_m\mathrm{S}_n(\mathrm{s}) + (n/m)\mathrm{H_2(g)} \longrightarrow \mathrm{E(g)} + (n/m)\mathrm{H_2S(g)}$$

The enthalpy ΔH_c may be expressed in terms of the standard enthalpies of formation of H_2S and E_mS_n, ΔH_h and ΔH_f, and the enthalpy of sublimation of the element

$$\Delta H_c = \Delta H_s + \Delta H_h - (1/m)\Delta H_f$$

Actually, trace elements tend to condense as solid solutions in major minerals rather than as pure phases, if a suitable host mineral is available. If the host phase is nickel-iron, the condensation equation becomes

$$\log\frac{\alpha}{1-\alpha} = \frac{\Delta H_s - \Delta H_a}{2.303RT} - \frac{\Delta S_s}{2.303R} + \log\frac{cA(\mathrm{Fe}) + A(\mathrm{Ni})}{A(\mathrm{H_2})} + \log P_t \qquad (3)$$

where $A(\mathrm{Fe, Ni})$ are the nebular abundances of these two elements, c is the fraction of the Fe in metallic form, and ΔH_a is the heat of solution.

For a trace element sulfide E_mS_n condensing as a solid solution with an iron-chromium sulfide $Fe_pCr_qS_r$, the condensation equation is similar

$$\log\frac{\alpha}{1-\alpha} = \frac{\Delta H_c - \Delta H_a}{2.303RT} - \frac{\Delta S_c}{2.303R} + \log\frac{cA(\mathrm{Cr})}{NA(\mathrm{H_2})} + \frac{n}{m}\log\frac{A(\mathrm{H_2S})}{A(\mathrm{H_2})} + \log P_t \qquad (4)$$

Here c is the fraction of the total Cr present as the sulfide, and N is $q/(p+q)$, the atom fraction of Cr in the sulfide.

There is no easy way to calculate ΔH_s or ΔH_f from first principles. Extending our efforts from (*7*), we have therefore resorted to simple extrapolations from the periodic table (Fig. 5). In contrast to Keller *et al.* (*35*), we used atomic number rather than period number as the abscissa.

The heats of vaporization were converted to heats of sublimation by applying small corrections for heat of fusion and heat capacities. We assumed that the superheavy elements had the same melting points and heats of fusion as their sixth period congeners. For heat capacities in the solid, liquid, and gaseous states we used 6.7, 7.2, and 5 cal mole^{-1} deg^{-1} (*36*). Our results agreed with those of Keller *et al.* (*35*) within ± 5 kcal/mole, except for 114, where their ΔH_s is lower by 13 kcal/mole.

The heats of formation of sulfides showed less regular trends, and the extrapolations hence are less certain, particularly for groups 1B, 3A, and 6A (Fig. 5). Indeed, it is not at all clear that linear extrapolations are warranted, because the properties of valence electrons in the seventh period are strongly influenced by relativistic effects (*35*). However, we did not succeed in finding a satisfactory alternative. Calculations based on Born-Haber cycles for sixth period sulfides (with corrections for interatomic distance, ionization potential, and repulsive potential) gave plausible results in some but not all cases, and in view of the uncertainties in the corrections, the results seemed less reliable than plain extrapolations.

Element 115 is expected to form a stable +1 state, owing to the exceptionally low first ionization potential [(5.9 volts (*33*); 5.2 volts (*35*)]. No other element in group 5A forms a sulfide E_2S, and we therefore had to estimate its heat of formation rather circuitously from that of Tl_2S, using a Born-Haber cycle. The low ionization potential is partly offset by the higher heat of sublimation and larger interatomic distance, resulting in an enthalpy of −33 kcal/mole, only 10 kcal/mole more negative than that of Tl_2S.

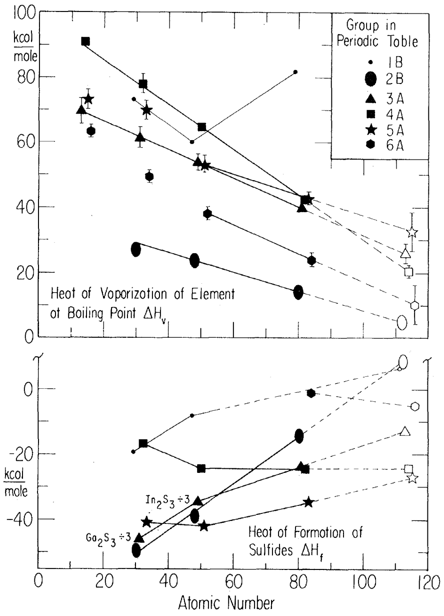


Fig. 5. Extrapolated thermodynamic properties of superheavy elements. Where the trend was not linear, only the heaviest two elements were used. No meaningful extrapolations were possible for element 111, but the values chosen (ΔH_v = 70 kcal/mole and ΔH_f = 7 kcal/mole) are consistent with the low volatility of Au and the low stability of Au_2S [see also (*35*)].

Entropies were extrapolated from experimental data, or from additivity relations (*36*). Trends were much more regular than for enthalpies, and so the results should be more reliable.

From these data, we have calculated the temperatures at which elements 111 to 115 would be 50 percent condensed as metals or sulfides (Table 3). The numerical constants used and their sources are given in (*37–40*). The only value requiring comment is the H_2S/H_2 ratio. During condensation, this ratio is normally controlled by the equilibrium $Fe + H_2S \rightleftarrows FeS + H_2$, which commences at 680°K. In the Allende meteorite, 88 percent of the total Fe is present as FeO, and the remaining Fe and Ni can tie up no more than 25 percent of the solar complement of S. We therefore assumed that the H_2S/H_2 ratio was 75 percent of the solar ratio (*38*), or 2.36×10^{-5}. Although this appeared to be the most reasonable choice, we must note that it definitely favored the condensation of sulfides. The alternative assumption, that the system was buffered by the Fe-FeS equilibrium (*15*), would have given temperatures up to 100°K lower.

Table 3. Condensation of elements 111 to 116, Tl, Pb, and Bi. Symbols: ΔH = enthalpy, kcal/mole; ΔS = entropy, cal mole^{-1} deg^{-1}. Subscripts refer to the following processes: s, sublimation; a, solution; f, formation; c, condensation.

Element	Metal (alloy with FeNi)			Sulfide (solid solution in $Fe_4Cr_2S_7$)				Temperature for 50 percent condensation			
								Solid solution		Pure phase	
	ΔH_s	ΔH_a	ΔS_s	ΔH_f	ΔS_f	ΔH_c	ΔS_c	Metal	Sulfide	Metal	Sulfide
111	79	5	32	7	43	69	32	900	740	630	520
112	5		19	9	24	−9	37	72		76	
113	29	13	28	−12	39	38	34	200	320	240	230
114	23	14	25	−24	25	42	36	120	370	190	270
115^{+3}	38	14	31	−27	52	44	47	300	330	300	250
115^{+1}	38	14	31	−33	44	69	33	300	520	300	370
116	18		31	−5	21	18	44	220	150	140	110
Tl	43.9	13	28.6	−23.2	36	64.6	34.2	390	520	430	440
Pb	46.2	14	24.9	−24.0	21.8	65.3	38.0	430	570	500	510
Bi	47.3	14	30.5	−34.2	47.9	57.0	47.6	410	420	460	370

Elements 111, 112, and 116

It would seem that these three elements can be excluded. Element 111 condenses as a metal rather than as a sulfide, as shown by the higher condensation temperature (Table 3). Although the extrapolations for element 111 are exceedingly uncertain, because of the irregular trend in ΔH_v's and the lack of data for Au_2S, no plausible change will make the sulfide the stable condensation form. Gold (I) sulfide is even less stable than HgS, decomposing at 240° compared to > 600°C. And our etching experiments show that the congeners of element 111, Ag and Au, do not reside in Q.

Element 112 is both too volatile and too noble. Again, no plausible change in the extrapolations will raise its condensation temperature into the range 400° to 500°K. It is possible that 112 will be trapped in anion vacancies like a noble gas, because it resembles noble gases in inertness and volatility. [Its predicted first ionization potential, 11.2 volts (*33*), actually exceeds that of Rn.] But as argued for element 118, the trapping efficiency is likely to be much less than 1, requiring a very large abundance of the progenitor in the nebula (*41*).

Another possibility is that 112, like Hg, forms a compound with Ni (*7*). But to offset the volatility of 112, this compound would have to have a very large heat of formation, if the condensation temperature is to be raised into the range 400° to 500°K.

The etching experiments do not favor 112. Although we did not measure the nearest congener Hg, the other two congeners Zn and Cd are not enriched in the chromite concentrate (Fig. 1) and are not located in Q (Fig. 4).

Element 116 is not very amenable to predictions, because its immediate congener Po is a short-lived radioactive element, and its lighter congeners S, Se, and Te are much less metallic. Its extrapolated heat of vaporization is only 11 kcal/mole (Fig. 5). Among its congeners only Po forms a sulfide, with $\Delta H_f^0 = -1$ kcal/mole (*39*). Although sulfides generally become less stable with increasing atomic number (Fig. 5), we have optimistically assumed a value of -5 kcal/mole for 116S. Nonetheless, it appears that 116 will condense as a metal rather than as a sulfide (Table 3).

As pointed out in (*7*), element 116 may form a stable Ni (or Fe) compound in the solar nebula. Extrapolation of the trends for lighter congeners predicts ΔH_f^0 of -4 ± 6 and -8 ± 3 kcal/mole for Fe116 and Ni116. These values are much too low to raise the condensation temperature into the range 400° to 500°K.

The evidence from etching experiments is weak but again unfavorable. Whereas the lightest congener Se is located largely in Q, the next congener Te is not.

Elements 113 to 115

These three elements look more promising than any we have discussed thus far. They condense as sulfides, their congeners Tl, Pb, and Bi are enriched in the chromite concentrate 3C1 (Fig. 1), and their congeners reside in Q (Fig. 4).

None of the calculated temperatures fall near 460°K, the tentatively estimated condensation temperature of the progenitor (*7*). In one case (115_2S) we have slightly overshot the mark, obtaining a condensation temperature of 520°K. This is no problem, because a solid solution with Q could not form until Q itself had appeared (at 450° to 500°K?).

In all remaining cases, temperatures are too low. In order to raise the condensation temperature of the sulfide solid solution to 460°K, the heat of vaporization or heat of formation, or both, would have to be increased. Specifically, the difference $\Delta H_s - \Delta H_f - \Delta H_a$ (for +2 ions), or $\Delta H_s - 0.5\,\Delta H_f - \Delta H_a$ (for +1 and +3 ions) must be enlarged by the following amounts, in kilocalories per mole

113	14
114	10
115 (+3)	18
115 (+1)	-6

All of these changes are within the nominal uncertainties of the extrapolations, even if we continue to ignore the heat of solution and the propriety of linear extrapolations. Thus there is no clear reason at present to prefer one element over the other, although 115 (in the +1 state) looks best, and 113 worst.

It may be possible to extend this approach further when data on additional meteorites become available. Condensation from a sulfur-rich gas has not received much attention in recent years, and it seems that both the thermodynamic data and the parameters in the condensation equations need to be further checked for self-consistency. The data in Table 3 should not be taken too literally; for example, we suspect that the condensation temperature of Tl_2S is too high by some tens of degrees, while that of Bi_2S_3 is too low.

Table 4. Enrichment of volatile elements in 3C1 and 3CS1.

Element	3C1 / Bulk	3CS1 / Bulk	Fraction of total
$^{136}Xe_f$	175	118	0.66
^{132}Xe	161	105	0.60
Br	139	92	0.52
Bi	28.6	13.6	0.090
Tl	15.2	6.0	0.066
Se	13.6	13.5	0.065
$^{129}Xe_r$	15.4	10.0	0.057
^{204}Pb (*10*)	6.5	2.8*	0.02

*Estimated from ratio 3CS1/3C1 for Bi and Tl.

Enrichment of Elements 113 to 115 and Their Congeners in Mineral Q

If the progenitor indeed was a congener of Tl, Pb, or Bi, then it is necessary to explain why these elements are not as strongly enriched in Q and associated chromite as are fission (and planetary) Xe. Whereas 66 percent of the total Xe in the meteorite resides in fractions 3C1 and 3CS1, only 2 to 9 percent of the Tl, Pb, and Bi does (Table 4).

The reason may be the high volatility of the superheavy elements. Not only is their intrinsic volatility greater, but their low abundance [6×10^{-4} that of ^{238}U, or $\sim 10^{-4}$ that of their sixth period congeners (*5*)], further depresses the condensation temperature of pure phases, according to Eqs. 1 and 2. The net effect is that each superheavy element in Table 3 has only a single chemical state with a condensation temperature even approaching 460°K: a solid solution of the sulfide in Q. Each of their congeners, on the other hand, has three to four states available, including at least one pure phase (Table 3). Thus, when Q first began to form at some temperature between 500° and 450°K, elements 113 to 115 (and other largely uncondensed elements such as Br and Xe) would concentrate mainly in this mineral. Slightly less volatile elements, such as Tl, Pb, and Bi, would not concentrate so exclusively in Q because they had several other condensation states available. The proportion condensed in Q would depend both on the fraction condensed prior to the appearance of Q and on the relative rates of condensation on the several substrates.

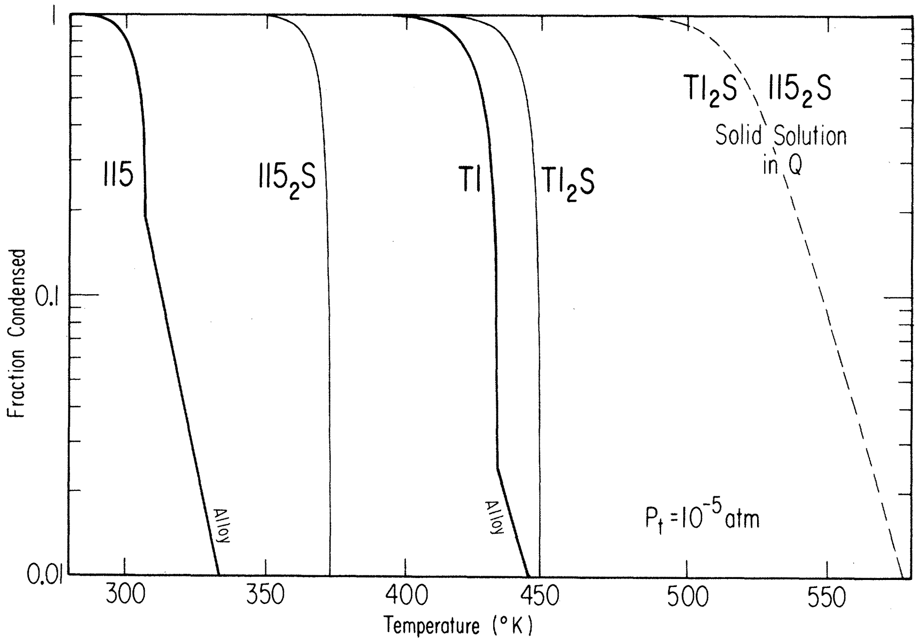


Fig. 6. Condensation curves of Tl and element 115. Both elements can, in principle, condense as solid solutions in the chromium sulfide mineral Q at 580° to 500°K. Nothing happens, however, until Q itself begins to appear, at some temperature between 500° and 450°K. Upon further temperature drop to 430°K, Q must compete for Tl atoms with several other stable condensation states—that is, the pure phases Tl_2S and Tl. Because substrates for these two states (FeS and FeNi) are more abundant than Q, a substantial part of Tl will condense as surface coatings on FeS and FeNi, rather than as a solid solution in Q. Element 115, on the other hand, must condense entirely in Q, because its remaining condensed states are not stable in the temperature range where C3 chondrites accreted, 400° to 450°K.

This point is illustrated in Fig. 6, for the specific cases of Tl and 115. Both elements can, in theory, begin to condense as solid solutions in Q as soon as the temperature has dropped to 580°K, but since no Q is available yet, nothing happens. Once Q begins to appear below 500°K, it starts to take up some Tl_2S and 115_2S, but on further temperature drop to ~450° to 430°K, three more condensation states become available for Tl: pure sulfide, pure metal, and NiFe alloy. The distribution of Tl among these states will depend on kinetic factors, and since substrates for the last three are more abundant than chromite (7 percent versus 0.7 percent), a substantial part of the Tl may condense as a surface coating on NiFe or FeS (*15*), rather than as a solid solution in Q. The equivalent states for 115 have much lower condensation temperatures, owing to the $\log A(E)/A(H_2)$ term in Eqs. 1 and 2, and so 115 can condense only as a solid solution of its sulfide in Q.

There exist data that support this picture. Ikramuddin and Lipschutz (*42*) have found that most of the Tl and Bi in Allende is very loosely bound, and is volatilized at 400° to 600°C. Such volatility would be expected for a surface coating. Only 7 percent of the Tl and 12 percent of the Bi persist to > 1000°C. These percentages agree rather well with the percentages in Q, as determined in the present study: 7 and 9 percent (Table 4).

A disappointing implication of these data is that Allende is not the ideal meteorite in which to study the distribution of the progenitor and its congeners among meteoritic phases. Most of the Tl and Bi is labile, and the small fraction that is not resides almost entirely in one phase, Q. Although it is suggestive that Pb^{2+} and other divalent chalcophile ions such as Cd^{2+} and In^{2+} are less enriched in Q than are the two ions of odd ionic charge, Bi^{3+} and Tl^{+}, it would be premature to argue that the progenitor must have been an element of odd ionic charge—that is, 115 or 113. Much of the difference may reflect volatility rather than crystal chemical factors, and it may take some well-planned experiments on well-chosen meteorites to learn something about the crystal chemistry of the progenitor.

Half-Life of Progenitor

Our data permit us to set an upper limit to the amount of a long-lived superheavy element that might still be present in the meteorite. Because a superheavy element can be expected to undergo fission under thermal neutron bombardment, we measured a short-lived fission product (^{140}Ba) in the irradiated sample 3CS1, to see whether an excess over the amount expected from ^{235}U was present.

The amount of ^{140}Ba corresponded to a uranium content of 3 parts per billion, a value consistent with the abundance of other lithophile elements. If we instead attribute the ^{140}Ba entirely to a superheavy element, then this element must have the same product of abundance, fission cross section, and fission yield of ^{140}Ba as ^{235}U, or $5.5 \times 10^{10} \times 580 \times 0.063$ atom barn/g. There is no way of estimating the fission cross section of the superheavy element, but if we assume for illustrative purposes the same value as for ^{235}U, and the same fission yield of ^{140}Ba, then the upper limit for the present abundance of a superheavy element is 5.5×10^{10} atom/g.

This is appreciably less than the 3.2×10^{12} atom/g that must have decayed to produce the fission Xe in this sample. An upper limit to the half-life thus is $< 770 \times 10^6$ years. Of course this value is illustrative only, being based entirely on an assumed thermal neutron fission cross section of the element.

A better estimate is that of Schramm (*43*). Using a plausible range of values for all parameters and two alternative models of nucleosynthesis, he obtained upper and lower limits of 68 and 16 million years, on the assumption that the element was 110. Production rates for 113 to 115 might be lower, which would raise the upper limit.

Summary

We have tried to identify the extinct superheavy element that was present in meteorites and decayed to $^{131-136}Xe$ by spontaneous fission. To characterize its chemical properties, we have measured 26 trace elements in six mineral fractions from the Allende C3 chondrite that were enriched up to 180-fold in fission Xe. The superheavy element turned out to reside mainly in a rare mineral associated with chromite (probably a Fe,Ni,Cr,Al-sulfide), comprising only 0.04 percent of the meteorite. It is accompanied by volatile, sulfide-seeking elements such as Tl, Bi, Pb, Br, I, and the heavy noble gases Ar, Kr, and Xe, all of which apparently condensed with this mineral when it formed in the solar nebula at some temperature between 400° and 500°K. Of the nine volatile superheavy elements 111 to 119, only 115, 114, and 113 are expected to condense as sulfides in that temperature interval. Presumably at least one of these elements has an isotope with a half-life in the range 10^7 to 10^8 years: too short to survive to the present day, but long enough to leave detectable effects in meteorites.

References and Notes

1. J. H. Reynolds and G. Turner, *J. Geophys. Res.* **69**, 3263 (1964).
2. R. O. Pepin, in *Origin and Distribution of the Elements*, L. H. Ahrens, Ed. (Pergamon, Oxford, 1968), p. 379; O. Eugster, P. Eberhardt, J. Geiss, *Earth Planet. Sci. Lett.* **3**, 249 (1967); K. Marti, *ibid.*, p. 243; J. H. Reynolds, in *Recent Developments in Mass Spectroscopy*, K. Ogata and T. Hayakawa, Eds. (Univ. of Tokyo Press, Tokyo, 1970), p. 594; P. Eberhardt, J. Geiss, H. Graf, N. Grögler, M. D. Mendia, M. Mörgeli, H. Schwaller, A. Stettler, *Geochim. Cosmochim. Acta Suppl. 3* (1972), p. 1821.
3. M. W. Rowe, *Geochim. Cosmochim. Acta* **32**, 1317 (1968).
4. E. C. Alexander, Jr., R. S. Lewis, J. H. Reynolds, M. C. Michel, *Science* **172**, 837 (19 B. Srinivasan, E. C. Alexander, Jr., O. K. Manuel, D. E. Troutner, *Phys. Rev.* **179**, 1166 (1969).
5. E. Anders and D. Heymann, *Science* **164**, 821 (1969).

J. W. Larimer, *Geochim. Cosmochim. Acta* **31**, 1215 (1967); ___ and E. Anders, *ibid.*, p. 1239; E. Anders, *Acc. Chem. Res.* **1**, 289 (1968); in *Nobel Symposium 21, From Plasma to Planet*, A. Elvius, Ed. (Almqvist & Wiksell, Stockholm, 1972), p. 133; in *l'Origine du Système Solaire*, H. Reeves, Ed. (Centre National de la Recherche Scientifique, Paris, 1972), p. 179.

7. E. Anders and J. W. Larimer, *Science* **175**, 981 (1972).

R. S. Lewis, B. Srinivasan, E. Anders, *ibid.* **190**, 1251 (1975).

9. R. R. Keays, R. Ganapathy, J. C. Laul, U. Krähenbühl, J. W. Morgan, *Anal. Chim. Acta* **72**, 1 (1974).
10. Lead, uranium, and thorium were determined by M. Tatsumoto on 3Cl and a similarly prepared sample 4Cl. The former appeared to be contaminated, and hence gave only upper limits. The latter also showed some U and Th contamination, but gave a reasonable amount of Pb of primitive isotopic composition (Pb, 8.53 ± 0.18 part per million; ^{204}Pb, 127 ± 4 parts per billion). The latter value was used to calculate the enrichment factor in Fig. 1. The U value for Fig. 1 was taken from 3CS1 (Table 1).
11. L. Grossman and J. W. Larimer, *Rev. Geophys. Space Phys.* **12**, 71 (19 L. Grossman, *Geochim. Cosmochim. Acta* **36**, 597 (1972).
12. K. F. Fouché and A. A. Smales, *Chem. Geol.* **2**, 105 (1967).
13. F. A. Podosek and R. S. Lewis, *Earth Planet. Sci. Lett.* **15**, 101 (1972).

J. C. Laul, R. Ganapathy, E. Anders, J. W. Morgan, *Geochim. Cosmochim. Acta* **37**, 329 (1973).

15. J. W. Larimer, *ibid.*, p. 1603.
16. M. N. Rao and K. Gopalan, *Nature (London)* **245**, 304 (1973); W. M. Howard, M. Arnould, J. W. Truran, *Astrophys. Space Sci.* **36**, L1 (1975).

R. T. Dodd, *Geochim. Cosmochim. Acta* **33**, 161 (1969); J. T. Wasson, *Meteorites* (Springer, New York, 1974).

18. E. L. Fireman, J. DeFelice, E. Norton, *Geochim. Cosmochim. Acta* **34**, 873 (1970).
19. R. S. Lewis and E. Anders, *Proc. Natl. Acad. Sci. U.S.A.* **72**, 268 (1975).
20. E. Vilcsek and H. Wänke, *Z. Naturforsch.* **20a**, 1282 (1965); P. M. Jeffery and E. Anders, *Geochim. Cosmochim. Acta* **34**, 1175 (1970).
21. Care was taken to minimize contamination during etching. Samples were handled only in fused silica ware. Reagents were specially purified (deionized distilled water, triple distilled acetone and carbon disulfide, Ultrex high-purity HCl and HNO_3). Some contamination became inevitable, however, when the samples (especially C5 and CS5) developed a tendency to become colloidal at *p*H values greater than 2. The final washings had to be done with 0.01*M* HCl, and so any impurities from the HCl remained in the samples.
22. L. Gmelin, *Handbuch der Anorganischen Chemie*, vol. 52, *Chrom* (Verlag Chemie, Weinheim, ed. 8, 1962), part B.
23. Results for Cr, Fe, and Ni were checked by instrumental neutron activation analysis (J. Gros, unpublished data). They were systematically higher (by 10 to 20 percent) than the atomic absorption values, but otherwise consistent with them.
24. A. El Goresy and G. Kullerud, in *Meteorite Research*, P. M. Millman, Ed. (Reidel, Dordrecht, Netherlands, 1969), p. 638.
25. P. Ramdohr, *The Opaque Minerals in Stony Meteorites* (Elsevier, New York, 1973).
26. J. W. Larimer and E. F. Holdsworth, private communication.
27. L. Grossman and E. Olsen, *Geochim. Cosmochim. Acta* **38**, 173 (1974).
28. J. W. Larimer, private communication.
29. E. Hertel and H. von Holt, *Z. Phys. Chem. B* **28**, 393 (1935).

→ M. S. Lancet and E. Anders, *Geochim. Cosmochim. Acta* **37**, 1371 (1973).
31. D. N. Schramm and E. O. Fiset, *Astrophys. J.* **180**, 551 (1973); D. N. Schramm, private communication.
32. E. J. W. Whittaker and R. Muntus, *Geochim. Cosmochim. Acta* **34**, 945 (1970).
33. B. Fricke and J. T. Waber, *Actinides Rev.* **1**, 433 (1971).
34. J. T. Waber, D. T. Cromer, D. Liberman, *J. Chem. Phys.* **51**, 664 (1969).
35. O. L. Keller, Jr., J. L. Burnett, T. A. Carlson, C. W. Nestor, Jr., *J. Phys. Chem.* **74**, 1127 (1970); O. L. Keller, Jr., C. W. Nestor, Jr., B. Fricke, *ibid.* **78**, (1974); O. L. Keller, Jr., C. W. Nestor, Jr., T. A. Carlson, *ibid.* **77**, 1806 (1973); G. T. Seaborg and O. L. Keller, Jr., in *The Chemistry of the Actinide Elements*, J. Katz and G. T. Seaborg, Eds. (McGraw-Hill, New York, in press).
36. O. Kubaschewski, E. LL. Evans, C. B. Alcock, *Metallurgical Thermochemistry* (Pergamon, Oxford, ed. 4, 1967).
37. Numerical constants and their sources are given below. Pressure: $P_t = 10^{-5}$ atm (*14, 15*); this value is uncertain by about an order of magnitude. Elemental abundances: solar-system abundances are from (*38*). Heats of solution: estimates are from Larimer (*15*) for LL-chondrites, whose metal comes closest in Ni content to that of Allende. Thermodynamic data: (*39*) or (*15*). H_2S/H_2 ratio: 2.36×10^{-5}, or 0.75 of solar-system ratio (*38*). $[cA(\mathrm{Fe} + A(\mathrm{Ni})]/A(\mathrm{H}_2) = 1.03 \times 10^{-6}$, based on the actual metal content of Allende (*40*). $[cA(\mathrm{Cr})]/[NA(\mathrm{H}_2)] = 6.57 \times 10^{-8}$, based on $c = 0.017$, the ratio (Cr in Q)/(total Cr in meteorite), and $N = 0.207$, the mole fraction of Cr in Q according to the adopted formula.
→ A. G. W. Cameron, *Space Sci. Rev.* **15**, 121 (1973).
39. D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, R. H. Schumm, *Nat. Bur. Stand. (U.S.) Tech. Note 270-3* (1969); *ibid., Note 270-4* (1969). The ΔG_f^0 value for PoS given in the first printing of *Note 270-3* (+52 kcal/mole) is in error, and should be −1 kcal/mole (D. D. Wagman, private communication). The standard entropy change based on extrapolated values for Po and PoS was close to zero, and so $\Delta H_f^0 \approx \Delta G_f^0$.
40. R. S. Clarke, Jr., E. Jarosewich, B. Mason, J. Nelen, M. Gomez, J. R. Hyde, *Smithson. Contrib. Earth Sci. No. 5* (1970).
41. Mercury, the congener of 112, is overabundant in meteorites by one or two orders of magnitude, compared to neighboring elements or interpolated "cosmic" abundan → [G. W. Reed and S. Jovanovic, *J. Geophys. Res.* **72**, 2219 (1967)] and one might be tempted to postulate a similar overabundance for 112. However, stepwise heating experiments have shown that most of this Hg is very loosely bound, and probably represents terrestrial contamination. The tightly bound Hg retained above 450°C, which is most likely extraterrestrial, is present in much more reasonable abundances, and so there is little reason to assume an overabundance of 112.
42. M. Ikramuddin and M. E. Lipschutz, *Geochim. Cosmochim. Acta* **39**, 363 (1975).
43. D. N. Schramm, *Nature (London)* **233**, 258 (1971).

44. We are indebted to D. F. Nava and P. J. Schuhmann for the atomic absorption analyses, to M. Tatsumoto for the Pb and Th analyses, and to J. W. Larimer and E. F. Holdsworth for permission to quote their electron microprobe data. We thank Rudolph Banovich for preparation of the drawings. This work was supported in part by grant NGL-14-001-167 from the National Aeronautics and Space Administration.

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NEWS AND COMMENT

The Haemmerli Affair: Is Passive Euthanasia Murder?

A lot has happened in medicine during the past 25 years to change the very nature of what is so romantically called the "healing art." There are respirators for persons who cannot breathe and pacemakers for those whose hearts do not work. For persons laid low by serious infection, there are antibiotics. For those who cannot eat, there is artificial feeding.

Because of these and other advances in medical technology, some individuals, who in an earlier era would have died, today are alive and well. Others who would have died are now condemned to exist as living corpses. Most of us can agree that medical technology has created as many problems as it has solved. What we cannot agree on is what to do about it. The issues often are posed as ones requiring new definitions of life and death, and we are caught in a semantic web from which we cannot get free. Technology seems to have the upper hand because people have not learned how to cope with it. For very practical reasons it must be brought under control.

In the United States, the dilemma technology presents has been forced on the public consciousness by the case of Karen Ann Quinlan, whose life is being relentlessly maintained by a respirator. Some persons, including her parents and her priest, believe that she has a "right to die" and that her respirator should be turned off. A court has ruled that to do so could be considered murder. The machine breathes on.

On the other side of the Atlantic, the right to die is being debated in the press, in national governments, and in the Council of Europe in the context of an unprecedented legal case that is forcing people to think about the difference between passive euthanasia and murder. One of Switzerland's most prominent physicians has been accused of murder in the deaths of elderly, hospitalized patients. His crime, if it is one, lies in not maintaining heroic measures to prolong the lives of patients in irreversible coma. The case raises in concrete terms a question that is new to medicine: Are there times when a physician has a duty to do nothing?

The accused is Urs Peter Haemmerli, 49 years old. During a recent visit to New York, he told his side of the story during a lengthy interview with Science. *His accuser is Regula Pestalozzi, a Swiss politician who, according to accounts in the European press, will not comment on the case.*

This is a story about a murder case in which there is no victim, or at least no corpse. And it is a story about politics and medicine and the law. It is happening in Switzerland; it could happen elsewhere.

Early on the morning of 15 January, Urs Peter Haemmerli was arrested at his home in Zurich, having been accused of murder. Two policemen came knocking at seven o'clock. Haemmerli recalls that they politely waited for him to dress before taking him off to jail. At first he thought it was a bad joke. "After all," he reasons, "if I had murdered someone, I would be the first to know it."

As it turned out, Haemmerli was not accused of murdering "someone." He was accused of murdering by starvation an unspecified number of unnamed elderly patients at Triemli City Hospital, where he is chief of medicine. The alleged murders are said to have taken place during a period of four years. For months, lawyers have been combing the hospital's records in search of a victim. No formal charges can be pressed and the case cannot proceed unless he can be accused of murdering someone in particular. Haemmerli optimistically bets that no murder victim will ever be found and that his case will never come to trial. But the fact that it has come up at all sets a precedent for cases involving passive euthanasia.

As the accused recounts it, this is how the "Haemmerli affair" came about.

In the spring of 1974, a woman named Regula Pestalozzi was elected to the Zurich city council and named as the city's chief health officer, a position that put her in charge of the municipal hospital system. Haemmerli was pleased. During her campaign, Pestalozzi, a layperson, had called for improved care for the elderly and the chronically ill. At Triemli, described as Zurich's newest and most modern municipal hospital, there were many such patients. Haemmerli thought that he would have a friend in court in the new health officer. He invited her to visit Triemli. Months passed but she never came. Then, in December, she asked him to visit her, and one day the doctor and the politician had a long conversation in her office. Haemmerli remembers it as a very pleasant occasion.

Among other topics, Haemmerli and Pestalozzi talked about the care of the ter-