Reports

Extinct Superheavy Element in Meteorites: Attempted Characterization

Abstract. *If the unexplained fission xenon component in meteorites is due to a volatile superheavy element, this element must have had a heat of vaporization of 54 ± 3 kilocalories per mole and a normal boiling point of 2500° ± 400°K. The prime candidates are elements 111 and 115, followed by 113, 114, 112, and 116. Elements 105 to 110 are not volatile enough and can therefore be excluded.*

Two types of fission-produced Xe have been found in meteorites (*1, 2*). The first occurs in most meteorite classes and is almost certainly due to ^{244}Pu (half-life 82×10^6 years). It correlates with U and Th, as expected for an actinide parent (*3*), its isotopic pattern matches fission Xe from ^{244}Pu (*4*), and its amount corresponds to an initial ^{244}Pu : ^{238}U ratio of 0.013 (*5*), close to predictions from models of nucleosynthesis.

The second Xe component seems to be due to a volatile parent nuclide, not to an actinide. It is found only in the most primitive, volatile-rich meteorites, for example, carbonaceous and unequilibrated chondrites. It correlates with volatile elements such as In, Hg, and Xe (*1, 6*), not with U and Th. It is much more abundant in the fine-grained matrix than in the coarse-grained chondrules, which are thought to be remelted, degassed matrix (*7*). It has a higher ^{136}Xe : ^{134}Xe ratio, 1.4, than fission Xe from any known actinide (*1, 4, 8*). And it is more abundant, by up to an order of magnitude or more, than the component derived from ^{244}Pu. On the basis of the correlation with volatiles, Anders and Heymann (*6*) suggested that the progenitor of this second Xe component was a volatile transuranium element. The most likely candidates were the superheavy elements of atomic numbers 112 to 119, whose lighter congeners (mercury to francium) are known to be volatile. Other authors independently suggested a superheavy element without, however, specifying a range of atomic numbers (*9*).

Additional data have become available since our previous work that permit a closer characterization of the hypothetical superheavy element in meteorites (hereafter referred to as G). The correlation between the fission Xe daughter (^{136}Xe$_f$) and volatile metals such as In can now be demonstrated directly (inset to Fig. 1), rather than indirectly through plots of ^{136}Xe$_f$ and In against ^{132}Xe (*6*). The numbered subclasses of each chondrite family are the "petrologic types" of Van Schmus and Wood (*10*), which correspond to increasing degree of recrystallization and, approximately, increasing accretion temperature (*11*).

The trend from type 1 to type 6 reflects both increasing accretion temperature and increasing chondrule content (about 0 percent in type 1 and about 75 percent in types 3 to 6), slightly offset by the poor gas retention of the clay minerals in type 1. Given the accretion temperatures, we can estimate the condensation curve of G from the solar nebula. This in turn will enable us to estimate some of its thermodynamic properties.

Accretion temperatures of ordinary chondrites (specifically, the L or "low-iron" group) have been determined from the abundance of volatile metals (Bi, Tl, and In), on the assumption that their condensation was terminated by accretion (*11*). The results ranged from 420° to 500°K, at an assumed total nebular pressure of 10^{-5} atm. These temperatures probably are not grossly in error, as they agree fairly well with independent estimates from the ^{18}O : ^{16}O ratio and Fe^{2+} content of the silicates (*12*).

Let us first consider the possibility that G condensed in elemental form from the solar nebula. This should cover elements 111 and 113 to 115, which are expected to be even more noble than their light congeners, Au,

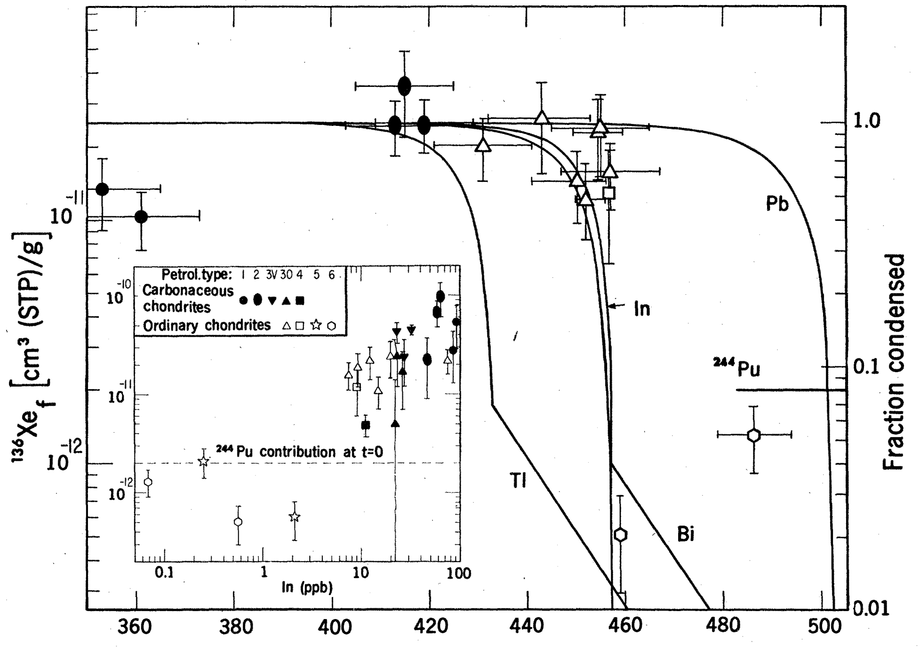
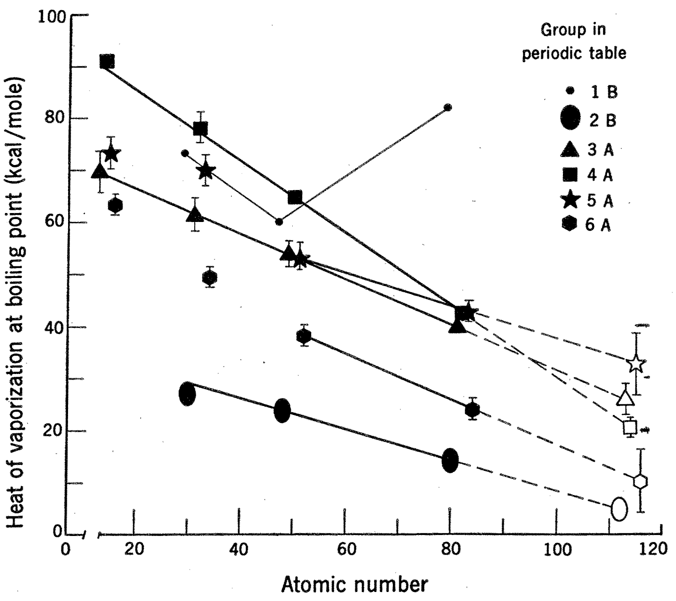


Fig. 1. (Inset) Fission-derived ^{136}Xe$_f$ correlates with a volatile metal, In, and hence probably came from a volatile parent. Both are most abundant in meteorites of lower petrologic type, which accreted from the solar nebula at lower temperatures, where condensation of the volatiles was more complete. The dashed line indicates the maximum contribution from ^{244}Pu at time 0, for an initial ^{244}Pu : ^{238}U ratio of 0.013. The data are largely from (*11, 14, 17*). (Main figure) The content of ^{136}Xe$_f$ in meteorites of known accretion temperature parallels the condensation curves of volatile metals (Tl, Bi, In, and Pb) in the solar nebula. The superheavy progenitor of ^{136}Xe$_f$, therefore, apparently had a similar heat of vaporization, which can be estimated from this graph.

Fig. 2. Extrapolated heats of vaporization of superheavy elements. Where the trend was not linear, only the heaviest two elements were used. The error bars on the extrapolated points (open symbols) represent the highest and lowest linear extrapolations of the experimental points. Numerical values (kcal/mole): 112 (5 ± 2), 113 (26 ± 3), 114 (20.5 ± 1.5), 115 (33 ± 6), and 116 (10 ± 6). Keller *et al.* (*18*) estimated 31 kcal/mole for 113 and 9 to 27 kcal/mole for 114, with row number rather than atomic number as the ordinate.



Tl, Pb, and Bi (*13*). We shall return to elements 112 and 116 to 119 later on.

The basic equation for condensation of a trace element E from a solar gas is

$$\ln(1-\alpha) = -\Delta H_v/RT + [\Delta S_v/R - \ln P_t - \ln(2E/H)] \quad (1)$$

where α is the fraction condensed, ΔH_v is the heat of vaporization, ΔS_v is the entropy of vaporization, P_t is the total pressure, and E and H are the abundances of elements E and H (*11*, *13*).

When the trace element forms a solid solution with nickel-iron, the equation becomes

$$\ln\frac{\alpha}{1-\alpha} = \frac{\Delta H_v - \Delta H_s}{RT} - \left[\Delta S_v/R - \ln P_t - \ln\frac{(\mathrm{Fe}+\mathrm{Ni})}{H}\right] \quad (2)$$

where ΔH_s is the heat of solution of E in nickel-iron (*11*, *13*).

Condensation curves of Pb, Bi, Tl, and In are shown in Fig. 1, along with the ^{136}Xe$_f$ contents of 15 chondrites whose accretion temperatures were estimated by means of these curves (*11*) or ^{13}C : ^{12}C, ^{18}O : ^{16}O thermometers (*12*). The scale on the right refers to the condensation curves; that on the left, to the ^{136}Xe$_f$ contents (*14*), recalculated to 25 percent matrix through the Cu and Ga content (*11*).

The lower parts of the curves correspond to condensation as solid solutions (Eq. 2); the upper parts, to condensation as pure elements after the solubility limit in Ni-Fe has been reached (Eq. 1). As the pressure is uncertain by an order of magnitude, the position of the curves is uncertain by ± 30° to 40°K.

Although the ^{136}Xe$_f$ points scatter quite a bit, they seem to define a segment of a condensation curve. Below about 450°K, the trend is roughly asymptotic. The C1's at about 360°K (C refers to carbonaceous chondrites) are too low by a factor of 2, but this may reflect the poor gas retentivity of their fine-grained minerals, as manifested by anomalously low contents of ^{36}Ar, ^{40}Ar, and ^{129}Xe (*14*). Above 450°K, the curve drops precipitously. The two L6's fall below the level expected for ^{244}Pu alone; thus, the curve for G must run below these points. And a number of C3's, although rich in total Xe and volatile elements, contain little ^{136}Xe$_f$ (*14*). This, too, suggests a steep drop of the condensation curve at higher temperatures.

We can now attempt to estimate the heat of vaporization of G. From Fig. 1, it appears that condensation of G was 50 percent complete at about 455°K. From the steepness of the curve above 450°K, G probably condensed as the pure element. With P_t equal to $10^{-5\pm1}$ atm, and a minimum abundance of 6×10^{-4} times that of U (*6*), corresponding to 6×10^{-16} for $2G/H$, we obtain from Eq. 1 for ΔH_v, 43,550 + 455 ΔS_v cal/mole. Trouton's rule seems to hold in this part of the periodic table to better than 10 percent; thus, with ΔS_v equal to 22 ± 2 cal deg^{-1} mole^{-1}, ΔH_v is 54 ± 3 kcal/mole. This corresponds to a normal boiling point, T_b, of 2500° ± 400°K. For a tenfold higher abundance of G (which would imply an improbably low fission yield of ^{136}Xe$_f$, 0.5 percent), ΔH_v is 52 ± 3 kcal/mole and T_b is 2400° ± 350°K.

In the less likely case that G condensed as an alloy near 455°K, Eq. 2 would be applicable. With a value of 3.6×10^{-5} for the ratio (Fe + Ni) : H (*15*), $10^{-5\pm1}$ atm for P_t, and 22 ± 2 cal deg^{-1} mole^{-1} for ΔS_v, we obtain $\Delta H_v - \Delta H_s = 30 \pm 2$ kcal/mole.

We can compare these values with extrapolations from the periodic table, to arrive at a more specific identification of G (Fig. 2).

None of these ΔH_v's agrees with the estimate for G, 54 ± 3 kcal/mole. Element 115, with 34 ± 6 kcal/mole, comes closest. A second prospect is element 111, ekagold. No reliable value could be extrapolated for it, owing to the irregular trend among its lighter congeners Cu, Ag, and Au, but a value somewhere between 40 and 70 kcal/mole seems most likely.

Virtually the same results are obtained for the second alternative, that G condensed as an alloy, with $\Delta H_v - \Delta H_s = 30 \pm 2$ kcal/mole. In order to compare this estimate with our extrapolated ΔH_v's, we must know ΔH_s for each superheavy element. Their lighter congeners have exceedingly small solubilities in Fe-Ni, presumably reflecting differences in size and electronic structure. These differences should be even greater for elements in the seventh row, and we therefore adopt ΔH_s's from the sixth row as lower limits for the seventh row. The values for Tl, Pb, and Bi are 15, 16, and 16 kcal/mole (*13*), which lead to maximum values for $\Delta H_v - \Delta H_s$ of 12 ± 3, 4.5 ± 1.5, and 17 ± 6 kcal/mole. Again, only 115 comes anywhere near the value for G, 30 ± 2 kcal/mole. Element 111 also remains a possibility, having a value for ΔH_s of at least 5 kcal/mole and ΔH_v probably between 40 and 70 kcal/mole.

These arguments are based on the tacit assumption that the extrapolations in Fig. 2 are reliable, which is not to be taken for granted. The assigned error limits merely reflect scatter and experimental error in the data for the light congeners. They make no allowance for the possibility that the linear trend does not extend into the superheavy region. With all due respect to Mendeleev, there is no theoretical reason why the trends in Fig. 2 should be linear. The irregularities in families 5, 6, and especially 1 underscore the possibility that the ΔH_v's may remain constant or rise rather than fall between rows 6 and 7. A flat trend would give ΔH_v's of 40 to 45 kcal/mole for elements 113 to 115, approaching the required value for G.

Of the remaining volatile elements, 112 and 116 to 119, the last three can probably be excluded. Elements 117 and 118 can be ruled out because $^{136}Xe_f$ does not correlate either in abundance or in thermal release pattern with ^{129}Xe (from the decay of extinct ^{129}I), or with primordial ^{132}Xe (*1, 14*). Thus its progenitor apparently was not a halogen or noble gas, otherwise it would have been trapped at the same sites. Element 119, ekafrancium, cannot be excluded on chemical grounds because its heaviest stable congener, Cs, has an abundance pattern in meteorites similar to that of other volatile elements (*11*). No calculations are possible, because the host phase and solid-solution behavior of Cs are not known. The principal argument against element 119 thus is its short predicted α-decay half-life, about 1 second.

The remaining two elements, 112 and 116, probably form stable Ni compounds in the solar nebula, by analogy with their lighter congeners Hg and Po. Judging from the meteoritic abundances of Hg, Te, and Se (*16*), their condensation temperatures seem to have been raised into the 400° to 700°K range, probably by compound formation. Significantly, these elements do not show the steep drop of abundance with accretion temperature that is characteristic of $^{136}Xe_f$ and the insoluble metals of groups 3B to 5B, In, Tl, Pb, and Bi (Fig. 1). Presumably the 2B and 6B elements are more soluble in major meteoritic phases, such as Ni-Fe or FeS. If this trend extends into the region of superheavy elements, 112 and 116 must be rated among the less likely choices.

Thus the principal candidates are 111 and 115, followed by 113, 114, 112, and 116 in that order. This choice is based on the apparent volatility of the free element; to narrow the range further, it will be necessary to establish its oxidation state and chemical behavior, by appropriate studies on meteorites.

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15 October 1971; revised 20 December 1971 ■

Infrared Spectral Emittance in Geological Mapping: Airborne Spectrometer Data from Pisgah Crater, California

Abstract. *Measurements of spectral emittance in the infrared region from 6.8 to 13.3 micrometers were made with an airborne spectrometer at a rate of six spectra per second, on flights 650 meters above the olivine basalt flows at Pisgah Crater in the southern Californian desert. The spectra show chemical and mineralogical differences that can be related to differences in the terrain below the aircraft.*

At a recent symposium (*1, 2*), two presentations were made of the techniques of independently performed geological mapping from the air, over the same terrain. This report emphasizes the nonimaging technique involving spectral measurements in the infrared from 6.8 to 13.3 μm taken while flying at 650 m (2000 feet) above the olivine basalt flows and alluvium and dry lake beds (Lavic Lake) at Pisgah Crater, near Barstow, California. The instrumentation (*3*), includes a boresight camera by which one can relocate the ground track of the (7 mrad, 0.4°) circular field of view of the spectrometer (*4*).

A total of 514 of the 4300 spectra were collected (*4*) in four flight lines of total length 28 km (*5*). They were separated into 31 geological groupings, located as black and white bands on the large-scale photographs (Fig. 1) taken at the same time along the flight line F–F' (*6*).

The raw radiance spectra from the rock and soil surfaces were ratioed by an average "water body" spectrum (average of 50 spectra) obtained by flying at the same altitude over a nearby lake (*7*). The emittance spectra were then inverted (*8*) and normalized for statistical studies, by setting their means at 0.0 and their standard deviation (S.D.) at 1.0. By this transform all the spectra have the same amplitude range, which permits more precise comparison of their information content. Care should be taken in using these normalized spectra, as they are no longer numerically the same as absolute emittance (used for calculating temperatures from radiance levels).

These selected spectra are then analyzed in two formats. In the first, emittance values for 10 to 50 spectra [mean