

Finally, Ba & Sr accompanying Xe-HL in diamonds from Allende

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Diamonds in primitive meteorites are known to be the carrier of isotopically anomalous Xe-HL and hence must have survived from before the formation of the solar system [1]. Carrying this nucleogenetically distinct xenon, enriched in both the r and p process nuclides, these 20Å diamonds [2] must carry a similar record in other elements. To date, only the 5 noble gases He through Xe, plus C and N, have been isotopically analyzed in this material [3,4,5]. Although Xe-HL suggests a supernova source for the diamonds, no satisfactory model has yet been proposed, in contrast to SiC, where Xe-S and other elements clearly point to low-mass carbon stars [6,7]. The isotopic composition of additional elements might provide the necessary clue but the very low abundance of the other elements expected to accompany Xe-HL makes in-situ measurement by ion probe or by direct loading impossible. The extreme resistance of diamonds to wet oxidation precludes conventional separations. An early negative result [8] in the search for Ba anomalies was inconclusive, because the diamonds never dissolved and may have been lost as a colloid. We have therefore developed a procedure for cold combustion of diamonds in an oxygen plasma, and report here the first results, on Ba and Sr.

A Pyrex vacuum system was filled with 20 torr of high purity oxygen. The sample in an attached high purity quartz finger was combusted with excited atomic oxygen produced by radio-frequency induction. The combustion rate for diamonds was calibrated with terrestrial diamond powder. Recovery of trace elements was checked by drying solutions of radioactive Cr⁵¹ and Rb⁸⁶ on carbon black. After combustion of the carbon black, more than 90% of the activity was recovered into solution by washing the quartz finger with 1N HCl.

Special care was taken to purify the diamonds prior to combustion in order to remove surficial contaminants as well as other meteoritic phases. In several stages, the last ones under clean room conditions in La Jolla, a sample of diamonds from Allende was repeatedly treated with HF, HCl, H₂SO₄ @200C, & HClO₄ @190C, and made colloidal at pH>10. These treatments, respectively, removed the last traces of silicates, fluorides, spinel, and non-diamond carbonaceous material and chromite, as well as any grains substantially larger than the 20Å diamond crystals. Trace element analysis [10] implies that at least one, Ir rich, phase did manage to persist along with the diamonds. After removal of an aliquot for noble gas mass spectrometry, which replicated the known [3] noble gas abundances, 35.8mg of Allende diamonds remained for oxidation.

The sample was oxidized for 82 hours during which the reaction products were removed and fresh oxygen was added several times. By the end of this time the reaction rate was extremely slow and the oxidation was terminated with 0.5mg remaining. The freed elements were dissolved in 1N HCl, leaving a small grayish residue. Following standard procedures, a 9.08% split of the sample solution was spiked to determine the concentration of Ba and Sr (and eventually additional elements), the balance being used to determine the isotopic compositions. The elements were then separated with ion exchange columns for both the spiked and main fractions. Blank corrected Ba and Sr results are given in Table 1 along with Kr and Xe data for comparison.

The first observation is the extremely low concentration of Ba and Sr, comparable to the noble gas abundances and consistent with a nonfractionating ion implantation model [9]. We do need to check if the 1.5% combustion residue has trapped in an insoluble form the major portion of Ba and Sr, possibly confounding the issue.

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The second observation is the slight deviation from normal of some of the ratios. Considering the large changes in the isotopic ratios of the noble gases and the low abundance of Ba and Sr, which precludes heavy dilution with isotopically normal material, we find the small size of the effects odd indeed. Nevertheless, the observed effects for Ba are of the type predicted from the anomalous xenon, small excesses at Ba¹³⁵ and Ba¹³⁷, the isotopes with significant r-process contributions. Comparable enrichments at the p-process isotopes Ba¹³⁰ and Ba¹³² would be buried in the uncertainty.

For Sr, a standard data analysis using $\text{Sr}^{86}/\text{Sr}^{88} \equiv 0.1194$ to remove instrumental fractionation indicates a depletion in Sr^{84} of $-19 \pm 4\%$. However, the actual $\text{Sr}^{86}/\text{Sr}^{88}$ ratio is certainly higher than this. For similar-sized standards run to exhaustion, this ratio changes over the course of the measurement due to fractionation, but the midpoint of the measured ratio is equal to the true value of 0.1194. The midpoint for this identically run sample is 0.1204, yielding the values in table 1, including a large radiogenic component at Sr^{87} . The $\text{Sr}^{84}/\text{Sr}^{88}$ is now normal within error, hence the positive $\delta\text{Sr}^{86}/\text{Sr}^{88}$ is most simply seen as due to an excess at Sr^{86} . In any case, there is no evidence for an enrichment at the (partially) r-process nuclide Sr^{88} , unlike Ba, Xe, and Kr.

We now face a curious dilemma. The noble gases, He through Xe, in these diamonds are fractionated compared to solar abundances, being more depleted in the lighter ones. Now we find that Sr and Ba have the same depletions as Kr and Xe, respectively, in contradiction with any fractionation process based on e.g. volatility, ionic radius, or ionization potential. The near equality of Ba to Xe and Sr to Kr suggests non-selective trapping, but where would we find a reservoir with a (Kr,Sr)/(Xe,Ba) ratio of 1/100 solar? Or, if we compare only the anomalous fractions, those in Sr and Ba are much smaller than those in Kr and Xe. This relative deficiency of the more readily condensed, trapped, and retained Sr and Ba can perhaps be explained by precondensation of solids before trapping of the remaining gases in the diamonds [8]. That Ba but not Sr is enriched in r-process isotopes is not so readily explained away. Sr and Ba are either an exquisite clue, or they are a real joker. Interesting and perhaps puzzling trends also show up in the elemental abundances of other trace elements [10].

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References. [1] Lewis *et al.* (1987) *Nature* **326** 160. [2] Fraundorf *et al.* (1989) *Ultramicroscopy* **27** 401. [3] Huss *et al.* (1991) In preparation. [4] Swart *et al.* (1983) *Science* **220** 406. [5] Lewis *et al.* (1983) *Nature* **305** 767. [6] Lewis *et al.* (1990) *Nature* **348** 293. [7] Gallino *et al.* (1990) *Nature* **348** 298. [8] Lewis *et al.* (1983) *Science* **222** 1013. [9] Lewis and Anders (1981) *Astrophys. J.* **247** 1122. [10] Liu *et al.* (1991) This volume.

Table 1. Isotopic composition of Ba and Xe, Sr and Kr in Allende diamonds.

Ba	ϵ^{130}	ϵ^{132}	ϵ^{135}	ϵ^{136}	ϵ^{137}	Xe	ϵXe^{136}	Sr	δ^{84}	δ^{86}	δ^{87}	Kr	δKr^{86}
14ppb	-14	-50	12.2	-0.6	6.0	6.5ppb	10980	3ppb	0	8.4	120	0.72ppb	146
	± 116	± 130	± 3.8	± 2.8	± 1.5		± 102		± 1	± 1.5	± 1		12

Ba: discrimination corrected to $\text{Ba}^{134}/\text{Ba}^{138} \equiv 0.033715$; ϵ^i = deviation in $\text{Ba}^i/\text{Ba}^{138}$ from normal Ba in parts in 10^4 . Normal ratios: Ba^{130} , 0.001475; Ba^{132} , 0.001413; Ba^{135} , 0.091940; Ba^{136} , 0.109543; Ba^{137} , 0.156545. Xe for comparison: normal $\text{Xe}^{136}/\text{Xe}^{132} = 0.312$.

Sr: corrected for mean instrumental discrimination as measured in standards; δ^i = deviations in $\text{Sr}^i/\text{Sr}^{88}$ from normal Sr in parts in 10^3 . Normal ratios: Sr^{84} , 0.006745; Sr^{86} , 0.1194; Sr^{87} , 0.69897.

Kr for comparison: normal $\text{Kr}^{86}/\text{Kr}^{84} = 0.309$. Two sigma errors in all cases.