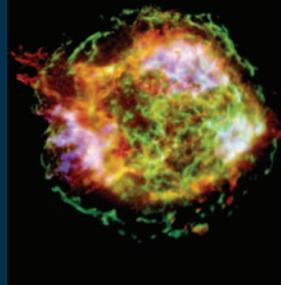


Meteoritic Nanodiamonds: Messengers from the Stars



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This spectacular X-ray image of the supernova remnant Cassiopeia A is the most detailed image ever made of the remains of an exploded star. Colors represent different

X-ray wave lengths. The outer green ring, ten light years in diameter, marks the location of the shock wave generated by the supernova explosion. Inside this shock wave is the ejecta of the supernova, some of which condenses into tiny grains, perhaps including the nanodiamonds discussed in this article.

Scale: Image is 8 arcmin per side.

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Primitive chondritic meteorites contain up to ~1500 ppm of nanometer-sized diamonds. These nanodiamonds contain isotopically anomalous noble gases, nitrogen, hydrogen, and other elements. The isotopic anomalies indicate that meteoritic nanodiamonds probably formed outside our solar system, prior to the Sun's formation (they are thus presolar grains), and they carry within them a record of nucleosynthesis in the galaxy. Their characteristics also reflect the conditions encountered in interstellar space, in the solar nebula, and in the host meteorites.

KEYWORDS: nanodiamond, chondrite, presolar grains, isotopic anomalies, solar nebula

INTRODUCTION

Primitive chondritic meteorites date from the earliest times in solar system history and have survived largely unaltered until today. These meteorites preserve the first objects to form in the solar system, such as calcium–aluminum-rich inclusions, metal grains, and chondrules—the round, millimeter-sized, crystallized melt droplets for which chondrites are named and whose origin is poorly understood. They also preserve dust from the dense, cold, interstellar molecular cloud that collapsed to form the solar system. This presolar dust was the raw material from which the solar system formed. Although scientists had hints in the form of anomalous isotopic compositions in meteoritic components that presolar material was present in chondrites, it was not until 1987 that the first presolar grains were recognized. Diamond was recognized first (Lewis et al. 1987), followed by silicon carbide and graphite. Because presolar diamonds are only a few nanometers in diameter, the term “nanodiamonds” was coined. To date, more than ten different minerals from primitive meteorites have been identified as presolar (e.g., Nittler 2003). Most of these condensed from the ejecta of dying stars that existed long before the solar system formed. Presolar minerals permit us to investigate the stellar nucleosynthetic processes that produced the chemical elements, to study processes in interstellar space, and to probe the events that occurred during the earliest epochs of solar system history.

Nanodiamonds were recognized as presolar because of the isotopically anomalous noble gases that they contain. In general, an element will have the same isotopic composition (within tight limits) anywhere on Earth and in objects formed in the solar system. However, starting in the early 1960s, scientists noticed that xenon in some meteorites had a very strange isotopic composition. It was more than a decade before a group at the University of Chicago determined that the strange xenon was located in a carbonaceous

residue that makes up only a small portion of the host meteorite (Lewis et al. 1975). It took another ten years to determine that the carrier of the strange xenon was nanodiamond (Lewis et al. 1987).

Nanodiamonds were the first presolar component to be recognized, but in many ways they are the least well understood. This is primarily because of their size. Each ~2–3 nm diamond grain contains only a few thousand carbon atoms. No instrument currently available can determine the isotopic composition of a grain this small, and even if such an instrument were available, only carbon is present with enough atoms to give a meaningful composition. The isotopic and trace-element information that we do have comes from samples containing billions of individual nanodiamonds. Unlike μm -sized SiC and Al_2O_3 grains, which provide detailed information about the star around which each grain formed, nanodiamonds provide only a general picture of their source(s).

CHARACTERISTICS OF METEORITIC NANODIAMONDS

Transmission electron microscopy is necessary to determine the characteristics of individual nanodiamonds (e.g., Daulton et al. 1996). The crystal structure of most nanodiamonds is cubic, i.e., true diamond structure, but a few grains show hexagonal symmetry, indicating the carbon polymorph lonsdaleite. Most grains exhibit multiple twins indicative of rapid growth. Meteoritic nanodiamonds have a log-normal size distribution with a median effective diameter of ~2.7–3.0 nm.

The isotopically strange xenon that led to the discovery of nanodiamonds is enriched in both Heavy and Light isotopes compared to “normal” solar system xenon (FIG. 1). It occurs in the diamonds as a trapped gas component, called HL, which also contains isotopically distinct helium, neon, argon, and krypton (Huss and Lewis 1994a). Nanodiamonds also contain two other noble gas components, called P3 and P6 for historical reasons, with isotopic compositions much closer to those of solar system gases. Heating or oxidizing nanodiamond samples in steps can effectively separate these three components. The P3 component is released at low temperatures (FIG. 2A) and has much less

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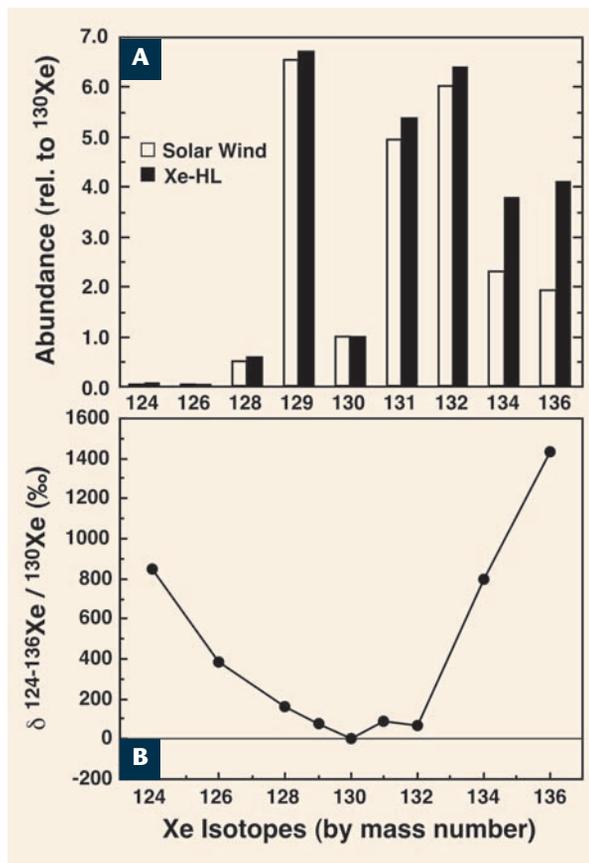


FIGURE 1 Isotopically anomalous xenon in meteoritic nanodiamonds. **A.** Histogram of the abundances of xenon isotopes in Xe-HL and in solar wind. **B.** Xenon isotopes in Xe-HL normalized to the composition of solar wind (the flat line at 0) and plotted as deviations from solar wind composition in parts per thousand (permil = ‰). Note the large excesses of the light and heavy isotopes that give Xe-HL its name.

helium and neon and more argon, krypton, and xenon than the HL component. The P6 component is volumetrically much smaller and is released at higher temperatures than HL (Huss and Lewis 1994a). Although P3 and P6 have isotope ratios similar to solar system xenon, their isotopic compositions are distinct and cannot be produced from solar system xenon by any known process.

The noble gas content of meteoritic nanodiamonds is extremely high, so high that helium and neon from nanodiamonds dominate the helium and neon in the host meteorites, and argon, krypton, and xenon make up several percent of the total budget. This is true even though nanodiamonds comprise only ~0.15% of the fine-grained “matrix” material in primitive chondrites. Yet in spite of the high gas content, only about one diamond in a million contains a xenon atom and only about one in ten contains helium. (For example, nanodiamonds contain about 1.5 ppb of xenon, about 10,000 times more gas than most terrestrial rocks). Thus, there is no such thing as an isotopic composition for the xenon in a single diamond; measured compositions are for the gas extracted from billions of diamonds.

The mean carbon isotopic composition of these billions of nanodiamonds ($\delta^{13}\text{C} = -31\text{‰}$ to -38‰ ; Russell et al. 1996) is within the range of compositions measured in solar system materials, but it is quite different from those of most terrestrial diamonds, which concentrate between -25‰ and $+5\text{‰}$. Chondritic nanodiamonds are rich in nitrogen, the isotopic composition of which is highly enriched in ^{14}N ($\delta^{15}\text{N} = -348\text{‰}$; Russell et al. 1996), and their surface atoms are bonded to hydrogen that is enriched in deuterium

by $\geq 280\text{‰}$ (Virag et al. 1989). The trace elements tellurium and palladium show small excesses of the heaviest isotopes, analogous to, but somewhat smaller than, the anomalies in Kr-H and Xe-HL (Mass et al. 2001).

Origin of Meteoritic Nanodiamonds

The origin of meteoritic nanodiamonds is still very much an open issue. A longstanding interpretation of Xe-HL is that the excess light and heavy isotopes were produced in a supernova and were implanted into the diamonds before the solar system formed (e.g., Heymann and Dziczkaniec 1979). On the other hand, because the carbon isotopic composition of nanodiamonds is within the compositional range of solar system materials and because only about one diamond in a million contains a xenon atom, some scientists have suggested that most nanodiamonds formed in the solar system. This view received support from a transmission electron microscope study of interplanetary dust particles (IDPs) (Dai et al. 2002). These authors did not observe nanodiamonds in IDPs thought to have originated from comets, but they did observe them in IDPs thought to be asteroid particles. Because comets probably formed far from the sun from material that was not heavily processed in the solar system, the near absence of diamonds in cometary IDPs suggests that the bulk of the diamonds originated inside, not outside, the solar system.

Although a local origin for meteoritic nanodiamonds is currently popular, I argue that the bulk of the evidence indicates that nanodiamonds formed outside the solar system. The compositions of Xe-HL, Kr-H, tellurium, and palladium show that at least some of the diamonds came from a source where heavy isotopes were preferentially synthesized, probably a supernova. Xe-HL is associated with four other isotopically distinct noble gases, and when all five gases are considered, one out of ~10 diamonds contains a noble gas atom that can reasonably be associated with a supernova source (but see below). The P3 component in nanodiamonds is isotopically distinct from both the major heavy noble gas component in chondrites and from solar wind for all five noble gases (Huss and Lewis 1994a). The P3 gases were probably trapped after nanodiamonds formed, and their distinctive isotopic compositions indicate that they originated outside the solar system. Also, as will be discussed below, the relative abundances of nanodiamonds and other types of presolar grains in chondrites can best be understood in terms of solar system thermal processing of a single mixture; there is no evidence that diamonds are decoupled from other types of presolar grains. The major challenge to this view is the near absence of nanodiamonds in supposed cometary IDPs. However, there is currently no estimate of the abundance of another type of presolar grain in these IDPs to show that other grain types are present at the expected abundances. Without such data, the possibility that we simply do not understand how and from what comets formed cannot be ruled out.

How do nanodiamonds form? We are normally taught that high pressures are required to make diamond, but meteoritic nanodiamonds apparently formed in the low pressures of space. One early idea was that nanodiamonds were produced by high-pressure shock metamorphism of graphite through grain-grain collisions during the passage of interstellar shocks (Tielens et al. 1987). This process is not expected to be efficient, so the diamonds should be accompanied by a large amount of graphite, which has not yet been observed. (The word “shock” has two meanings in this context. An interstellar shock is a discontinuity in gas velocity, pressure, density, etc. Gas atoms typically do not cross the discontinuity, but dust grains can penetrate the shock and collide with other dust grains at high velocity.

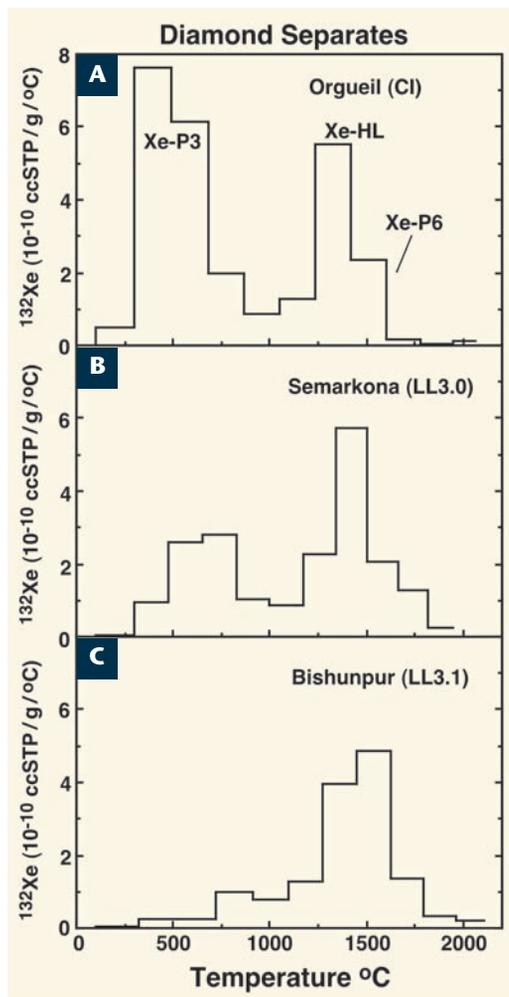


FIGURE 2 Histograms showing xenon released from nanodiamonds from three primitive meteorites as a function of temperature during stepped heating in the laboratory. The ordinate shows the volume of ^{132}Xe released from one gram of nanodiamonds at each temperature step in units of 10^{-10} cubic centimeters at standard T and P. The gas volume for each step has been normalized to the width of the step in $^{\circ}\text{C}$ so that the area under the curve accurately represents the gas volume. The meteorites: Orgueil is a CI chondrite thought to best represent the composition of the early solar system. Semarkona and Bishunpur are LL chondrites, which have matrix compositions very similar to CI except they have lost siderophile elements. These meteorites have experienced very little thermal metamorphism with temperatures increasing from Orgueil to Semarkona to Bishunpur.

Xenon in Orgueil diamonds (A) is released in two distinct peaks. Xenon in the first peak (the P3 component) has an isotopic composition similar to that of solar system xenon. This low-temperature gas is apparently trapped in the surface layer of the diamonds where many of the bonds are C-H, C-O, C-O-O-H, C-N, etc. These bonds break and recombine at relatively low temperature releasing the noble gases. The second peak is dominated by isotopically anomalous Xe-HL. A third component, Xe-P6, is released on the high-temperature tail of the Xe-HL release. Both of these components are sited within the diamond structure and are released when the diamond reacts with the Pt or Ta foil in which the sample is wrapped or with surrounding minerals. Note that the size of the Xe-P3 peak is lower in Semarkona diamond (B) and lower yet in Bishunpur diamond (C). This reflects heating of the LL chondrites that released some of the low-temperature gases on the meteorite parent body (Huss and Lewis 1994b). The petrologic types of the LL chondrites (3.0, 3.1) are derived from measurements of thermoluminescence sensitivity (e.g., Sears et al. 1991), which give the degree of heating each meteorite experienced.

High-velocity collisions generate pressure waves within solid grains, which are also called shock waves. These shock waves can cause pressure excursions into the diamond stability field and convert graphite to diamond.) In recent years, diamonds have been produced industrially at low pressures by a process called chemical vapor deposition

(CVD; see Hemley et al. p. 105). The conditions for optimum diamond growth are remarkably similar to those in stellar ejecta (e.g., Anders and Zinner 1993 and references therein). Industrial CVD synthesis makes use of kinetic factors to stabilize diamond production. However, there may be a thermodynamic reason to expect diamond to form preferentially over other carbon allotropes at very small sizes. Badziag et al. (1990) showed that when the surface bonds are terminated with hydrogen, diamonds smaller than ~ 3 nm in diameter are energetically favored over polycyclic aromatic hydrocarbons (the precursors to graphite). Thus, diamond may well be the stable form of carbon in the nm size range. Other ideas have also been suggested. Graphite grains might be induced to transform to diamond by intense UV irradiation or by intense particle irradiation. However, transmission electron microscope work on meteoritic nanodiamonds and terrestrial analogues strongly indicates that nanodiamonds formed by a vapor-deposition process (Daulton et al. 1996).

The isotopic anomalies in meteoritic nanodiamonds are hard to explain by a single stellar source. This is not surprising, since the measured isotopic compositions represent billions of grains that may have formed in hundreds of different sites. For example, Xe-H and Xe-L are produced in different zones of a supernova (e.g., Heymann and Dziczkaniec 1979), so one might expect that the two components should be separable in the laboratory. Several workers have claimed marginal evidence of separations of Xe-H and Xe-L, but in most cases the effects turned out to be due to additional noble gas components or other experimental artifacts (e.g., Huss and Lewis 1994a). Meshik et al (2001) used a laser and selective optical absorption to extract gases from different populations of nanodiamonds and again found marginal evidence of a separation, but they were unable to demonstrate clearly that Xe-H and Xe-L are separable in the laboratory.

The measured Xe-HL and Kr-H compositions are also significantly less extreme than compositions from nucleosynthetic models (Heymann and Dziczkaniec 1979; Clayton 1989). This implies that an isotopically "normal" component is intimately intermixed with the isotopically anomalous gas. To calculate the supposedly pure end-member isotopic composition from the stellar source, the "normal" component is typically removed by assuming that all of the ^{130}Xe , which is not produced by the processes that generate Xe-H or Xe-L, is in the "normal" component, usually assumed to have the composition of solar wind. Several ideas for the production of Xe-H in a supernova setting have been suggested. An early idea invokes the classical r-process, in which large numbers of neutrons released from deep in the exploding star are captured by seed nuclei on a timescale that is short with respect to their lifetime against β -decay, to produce large excesses of heavy xenon isotopes (Heymann and Dziczkaniec 1979). Clayton (1989) suggested that when a massive star collapses to become a type II supernova, the neutrino burst generated in the core would release enough neutrons from the helium shell of the pre-supernova star to produce large excesses of neutron-rich isotopes. Ott (1996) suggested that classical r-process nucleosynthesis accompanied by separation of xenon from iodine and tellurium precursors within a few hours after termination of the process could produce Xe-H. Each model has its problems, and none has been generally accepted.

A recent experimental study in which noble gas ions were implanted into nanodiamonds produced a remarkable result. A single component was implanted, but when the sample was measured by stepped heating, the gases were released in two peaks that were almost identical to the bimodal release shown in Fig. 2a (Koscheev et al. 2001).

This suggests that the isotopically “normal” component intimately mixed with the HL component might be P3, and if so, then calculations of the pure Xe-HL composition have been done incorrectly in the past. A calculation subtracting P3 gases produces a Xe-HL composition not too different from previous ones but suggests that Kr-H is accompanied by Kr-L. Direct evidence for Kr-L has not been seen before. This calculation also suggests that the exotic component was implanted and then largely outgassed before the P3 component was implanted (Huss et al. 2000).

NANODIAMONDS AS PROBES OF SOLAR SYSTEM PROCESSES

The noble gases in nanodiamonds and the abundances of nanodiamonds and other presolar materials among chondrites are sensitive probes of thermal processing, both in the solar nebula and in the meteorite parent bodies (Huss and Lewis 1994b, 1995; Huss et al. 2003). The P3 component is released at low temperatures, and the release temperature seems to be largely independent of the surroundings in which the diamonds are located. Because of this, the P3 abundances from diamond separates provide a relatively precise measure of the temperature to which the meteorites were heated during their history (cf. Fig. 2). This P3-based “metamorphic” scale can be calibrated to give a quantitative estimate of the maximum temperature experienced by the diamonds and associated material, and this calibration seems to be consistent across the chondrite classes. The abundances of diamonds in chondrite matrices can be reliably determined by measuring the amount of Xe-HL in meteorite residues (Huss and Lewis 1995; Huss et al. 2003). Among presolar materials whose abundances in the host meteorite are easily determined (diamond, SiC, and graphite), nanodiamond is among the most resistant to thermal processing. Within a meteorite class, the relative and absolute abundances of presolar grains can establish the relative amount of heating each meteorite experienced

(Huss and Lewis, 1995). Among the essentially unmetamorphosed members of the various meteorite classes, the relative abundances of presolar materials and the amount of P3 gas in diamonds seem to reflect the nebular thermal processing that produced the chemical classes of chondrites (Huss et al. 2003). Thus, nanodiamonds are potentially powerful probes of both nebular and parent-body processes in the early solar system.

FUTURE RESEARCH

Future research on meteoritic nanodiamonds should address the following questions:

1. How many different kinds of diamonds are present in bulk nanodiamond samples and how can they be recognized?
2. Are the diamonds dominantly presolar or were they mostly produced in the solar system?
3. How did the diamonds form?
4. What nucleosynthetic source or sources are reflected in the isotopically anomalous noble gases and trace elements in the diamonds?
5. Can these sources be identified and characterized effectively from the diamond samples?

These are essentially the same questions that scientists have been working on since the diamonds were discovered. But because of the small size of individual diamonds, we do not currently have the tools to address them effectively. Instrumentation is improving rapidly, however, and detection limits are getting better. So I am confident that eventually the tools will be developed that will permit us to answer these basic questions about meteoritic nanodiamonds.

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