Carbon in Meteorites

By Gregory T. Shanos

Note: During the past decade, I have been writing and publishing in *Meteorite* the current discoveries on the topic of carbon in meteorites. This review article presents a coherent synopsis of the developments thus far.

[Editors' Note: The references in this article refer back to the author's original papers in *Meteorite* magazine. Please refer to these papers or contact the author directly.]

The element carbon is ubiquitous in nature. Carbon occurs throughout the universe in galaxies, stars, planets, asteroids, and meteorites as well as in all living organisms on Earth. Elemental carbon exists in three fundamental structures, or allotropes. The three allotropes of carbon are graphite, diamond, and fullerene. All three forms of carbon have been detected in meteorites.

Graphite, the most common form of carbon, has molecules that form flat sheets of atoms arranged in a honeycomb-like hexagonal pattern (see Fig. 1a). These sheets can slide over one another, thus making graphite dull, soft, and slippery. Graphite occurs in iron as well as stony meteorites. The Canyon Diablo iron, which formed Meteor Crater in Arizona, contains graphite nodules embedded with nickel-iron veins (see Fig. 1b).

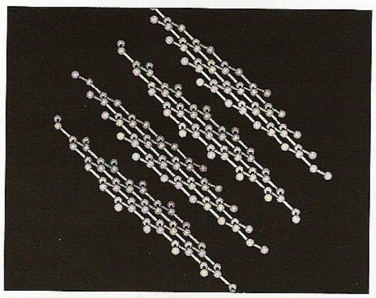

Figure 1a. Carbon as Graphite. Note that the carbon atoms are arranged in a honeycomb-like hexagonal pattern. These sheets can slide over one another, thus making graphite dull, soft, and slippery.

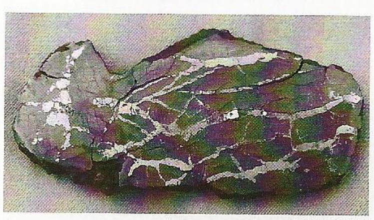

Figure 1b. Graphite Nodule from Canyon Diablo. The black matrix is graphite with embedded veins of nickel-iron. This specimen is from the author's personal collection and weights 57.9 g, measuring 32 mm x 15 mm x 7 mm.

Diamond contains the carbon atoms arranged in a pyramidal structure called a tetrahedron (see Fig. 2a). This rigid structure gives diamond its remarkable hardness. The nature and strength of its chemical bonds make diamond the hardest known substance. The first clue that meteorites may contain diamonds occurred in 1964 when an unusual isotope of xenon was discovered by Edward Anders and colleagues at the University of Chicago. The Allende carbonaceous chondrite contained an isotope called Xe-HL, which means xenon enriched in both the heaviest and lightest isotopes. This exotic component of xenon was so different from that measured extra-terrestrially that researchers believed it must have come from beyond the solar system. Twenty years had elapsed before Lewis and Anders et al. (1988) would be able to separate out the mineral carriers of Xe-HL by subsequent dissolution in strong acids. The resulting mineral was determined to be carbon in the form of diamond!

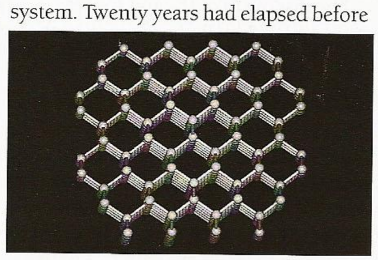

Figure 2a. Carbon as Diamond. Note that the carbon atoms are arranged in a pyramidal structure, or tetrahedron, that gives diamond its remarkable hardness and strength.

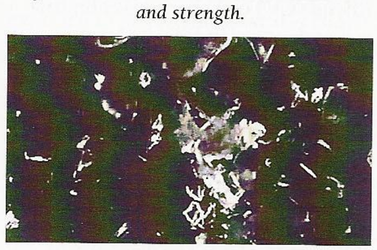

Figure 2b. Photomicrograph of Nanodiamonds. Isolated from the Murchison meteorite.

Sorry to disappoint the ladies, but these diamonds are nanodiamonds measuring approximately 25 angstroms in length and requiring an electron microscope to be seen (see Fig. 2b). Diamonds were found to be the most abundant interstellar grain in a group of meteorites known as carbonaceous chondrites. The diamond concentration in the Allende and Murchison carbonaceous chondrites is approximately 1000 parts per million. The Tagish Lake carbonaceous chondrite has the highest concentration of nanodiamonds to date at 3650-4330 ppm! These nanodiamonds condensed as the carbon-rich outer layers of red giant stars were expelled into space and

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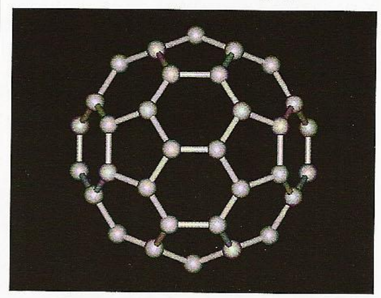

Figure 3. Carbon as Fullerene C_{60}. Fullerene is the third form of carbon discovered only recently in 1985. Fullerene has a structure similar to a hollow soccer ball.

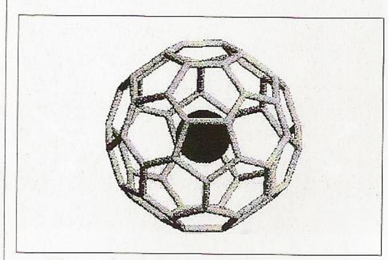

Figure 4. Fullerene C_{60} Entrapping a ^{3}He or ^{40}Ar Atom. These entrapped fullerenes have been found in the Sudbury Crater, the 65 million year old KT boundary, and in meteorites.

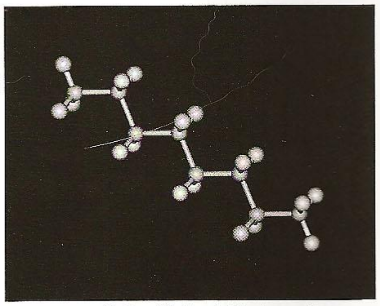

Figure 5. An Aliphatic Hydrocarbon (octane). This is an example of a straight-chain hydrocarbon.

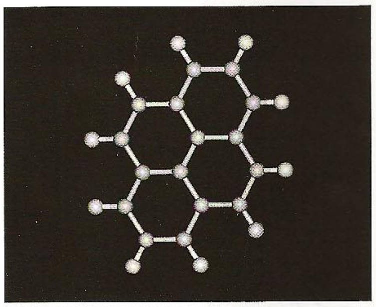

Figure 6. A Polyaromatic Hydrocarbon (PAH). Note the fused aromatic benzene rings.

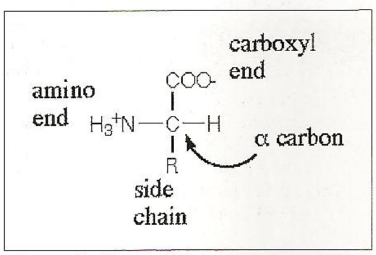

Figure 7. Chemical Structure of an Amino Acid. Note the four different groups around the central alpha carbon. This gives amino acids their chirality, or handedness.

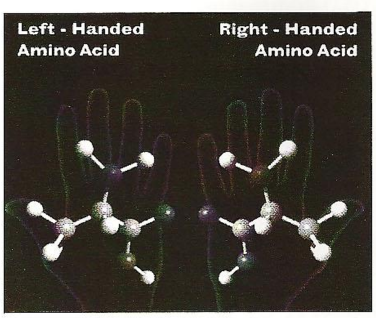

Figure 8. D and L forms of amino acids are mirror images of each other. All living organisms on Earth utilize the L amino acids. Recent research has shown an excess of the L enantiomer in the Murchison meteorite.

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subsequently cooled. The exotic Xe-HL signature was produced during a type II supernova explosion which ejected the isotope into the diamond stardust. Other interstellar grains have been isolated in Murchison, including graphite (C), silicon carbide (SiC), aluminum oxide (Al_2O_3), and silicon nitride (Si_3N_4). Eventually these implanted grains containing supernova remnants were carried far off into interstellar space where they eventually became trapped in condensing planetesimals of our solar nebula and eventually landed on Earth as meteorites.

The third form of carbon, C_{60} and C_{70}, consists of 60 or 70 carbon atoms bonded to each other and resembles a hollow soccer ball and rugby ball, respectively. The atoms in C_{60} are arranged in a regular pattern of 12 pentagons and 20 hexagons (see Fig. 3). The molecule was named Buckminster Fuller after an American architect who designed a geodesic dome of similar appearance. Scientists have shortened the name to buckyballs or fullerenes. All these names are synonymous with C_{60}. The C_{60} molecule is exceptionally stable, exhibits superconductivity, dissolves in solvents, and has the ability to trap other molecules.

The discovery of C_{60} and C_{70} was made in 1985 by Richard Smalley at Rice University and Harold Kroto of the University of Sussex. These two scientists were studying the effects of carbon vapor heated to a temperature of 8000°C. Unexpectedly, they detected a mysterious new form of carbon. Richard Smalley, Harold Kroto, and Robert Curl were awarded the Nobel Prize in 1996 for their discovery of the fullerene allotrope of carbon.

The discovery of fullerenes in the Allende CV3 carbonaceous chondrite was announced in 1994 by Luann Becker and her team. The discovery of fullerenes in meteorites was rather elusive, possibly due to their very low concentration. The C_{60} content was determined to be only 0.1 ppm. Another form of fullerene containing covalently bonded hydrogenis called fullerane ($C_{60}Hx$). The discovery of fulleranes in Allende was confirmed in 1997.

Fullerenes have also been associated with impact events. Fullerenes were extracted from the shock-produced Onaping Formation breccias of the Sudbury Impact Crater. These breccias, having been formed 1.85 billion years ago, had a concentration of fullerenes ranging from 1 to 10 ppm. In addition, Becker et al. (1996) discovered helium trapped with these fullerenes (He@C_{60}) at the Sudbury Crater (see Fig. 4). Isotopic analysis of the trapped helium indicated that it was extraterrestrial in nature. In addition, the 65 million year old K/T boundary clay was shown to contain fullerenes with entrapped helium isotopes. The K/T boundary fullerenes are believed to be extraterrestrial in origin and to have survived intact.

Higher order fullerenes were discovered by Becker et al. (1996) in the Allende carbonaceous chondrite in 1999, Murchison in 2000, and Tagish Lake in 2001. These higher order fullerenes are remarkably stable and occur in closed caged clusters of C_{100} to C_{400}. Their existence eluded previous detection since they are embedded in the poorly graphitic carbon matrix of the meteorite. Overall, the Allende extracts revealed much more C_{60}, C_{70}, and higher order fullerenes between C_{76} and C_{96} than Murchison. However, both meteorites contain a greater abundance of higher order fullerenes (C_{84} to C_{200}) than C_{60} and C_{70}.

The Tagish Lake higher order fullerenes were between C_{60} and C_{160} as compared to the Murchison distribution of C_{60} to C_{250}. The differing fullerene distributions may be attributed to different compositions of the nebular condensates and/or different aqueous and thermal processing on the asteroid.

The Murchison fullerenes also contained the noble gas helium in a concentration of 1.1x 10^{-8} cm^3/g of fullerenes. The helium was entrapped in the buckyball. Analysis of the isotopic ratio of the helium released by heating indicated that it was extraterrestrial in origin. It was determined that Allende fullerenes released helium one order of magnitude greater than that of the Murchison CM2 meteorite. Tagish Lake was also determined to contain extraterrestrial helium-encased buckyballs.

The Murchison, Allende, and Tagish Lake fullerenes also yielded another surprise during the helium extraction analysis. The noble gas argon was also released in all three meteorites whose isotopic ratio was extraterrestrial in origin. Fullerenes and higher order carbon clusters are formed in the outflows of carbon stars based upon astrophysical models. Their presence in all three carbonaceous chondrites indicates that they can survive passage through space, and then be processed into grains and larger parent bodies such as asteroids. The exceptional stability and survivability of fullerenes with trapped noble gases suggests that exogenous delivery of intact organic material to planetary surfaces is quite favorable.

Carbon as organic refers to carbon being covalently bonded to other elements such as hydrogen, nitrogen, oxygen, etc. When carbon bonds with only hydrogen, the resulting compound is called a hydrocarbon. Each carbon atom forms a tetrahedral arrangement with other surrounding carbon and hydrogen atoms. There are two broad types of hydrocarbons, namely, aliphatic and aromatic. An aliphatic hydrocarbon consists of a long, straight or branching chain of chemically bonded carbon and hydrogen atoms (i.e. CH_3-CH_3-CH_3-CH_3 etc.) (see Fig. 5). An aromatic hydrocarbon consists of carbon arranged in a flat hexagonal ring with one hydrogen bonded to each carbon. The simplest aromatic hydrocarbon is benzene (C_6H_6). Polyaromatic hydrocarbons (PAHs), as the name implies, are poly (many) fused benzene rings (see Fig. 6).

The simplest PAH found in Allende is naphthalene ($C_{10}H_8$), or mothballs! In addition, PAHs have also been confirmed in molecular clouds as well as in interstellar dust particles.

Organic compounds necessary for life have also been detected in meteorites, especially carbonaceous chondrites. Breger and Zubovic (1972) identified formaldehyde (CH_2O), or embalming fluid, in Allende. The formaldehyde exists as a polymer in the matrix of this meteorite HO-(CH_2)-H. In fact, formaldehyde was also detected in the tail of Comet Halley during the 1985/86 apparition. The significance of formaldehyde is that under conditions present in the Earth's primitive atmosphere, this formaldehyde could have been the precursor molecule for carbohydrates.

Early studies by Kvenvolden et al. (1970) have detected organic compounds called amino acids in the Murchison carbonaceous chondrites. To date, over 92 different amino acids have been found in this incredible meteorite. Of these, only 19 are also found on Earth. The remaining amino acids have no apparent terrestrial source. Amino acids are the building blocks for proteins in all living organisms and thus an important class of molecules in the study of exobiology. In addition to amino acids, Murchison also contains fatty acids, sugars, and nucleotides, which are precursor molecules for the formation of proteins, cell membranes, and DNA, respectively.

Amino acids typically contain a central carbon from which four chemical groups, or moieties, are attached. All amino acids contain an amino group (-NH_3), which is a weak base, a carboxylate group (-COOH), which is weakly acidic, and a neutral atom of hydrogen (-H). The other moiety R emanating from the central carbon defines each individual amino acid (see Fig. 7).

Since four different chemical groups originate from the central carbon, amino acids exhibit a property called chirality, or handedness. (Note, glycine is the only amino acid that does not exhibit chirality since the fourth chemical, or R group, is also an atom of hydrogen.) The right-handed version is termed D and the left-handed version is called L. These are mirror images of each other, much like your right and left hands (see Fig. 8a).

The Murchison amino acids were expected to be racemic mixtures containing 50% right-handed (D) and 50% left-handed (L) forms, or enantiomers. By definition, a left-handed molecule will rotate polarized light shone through it to the left and vice versa.

All living organisms on Earth utilize L-amino acids for the synthesis of proteins. Recent studies by Cronin and Pizzarello (1997) investigated

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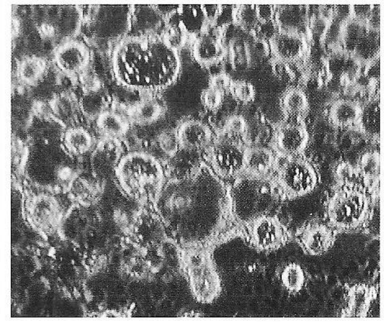

Figure 9. Boundary structures are fatty acids isolated from the Murchison meteorite that form closed vesicles in an alkaline solution. Could these simple vesicles have enclosed other molecules forming a primitive chemical "cell" in the Earth's primordial soup?

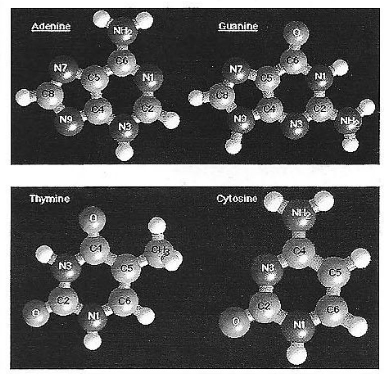

Figure 10a and 10b. The nucleotide bases adenine, guanine, thymine, cytosine, and uracil (not pictured) have all been detected in the Murchison meteorite. These bases form the structure of the DNA and RNA molecules.

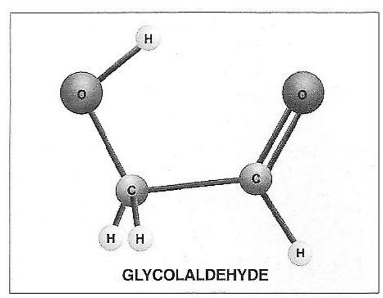

Figure 11. Glycoaldehyde, a simple sugar, has been detected in the Murchison meteorite as well as the interstellar cloud Sagittarius B2.

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extraterrestrial amino acids in the Murchison meteorite that are not incorporated into proteins and are thus extremely rare in the terrestrial biosphere. These authors discovered an excess of the L form of up to 9% in non-biological amino acids. A hypothetical mechanism would be that the L form preference may have been imposed on the interstellar cloud out of which the solar system formed by circularly polarized light such as synchrotron radiation from a neutron star. This polarized light may have thus catalyzed the preferential synthesis of L-amino acids.

This recent conformational discovery of an excess of left-handed (L) amino acids in the Murchison meteorite raises the possibility that a similar excess was present in the early inventory of organic compounds on the Earth. The excess L-form of amino acids was produced in space and thus preordained by Nature. Evolutionary processes selected for the most abundant materials available, namely, the left-handed amino acids, to form peptides for incorporation into proteins. The utilization of L amino acids in living organisms was once believed to be a purely terrestrial fingerprint. Recent evidence of L amino acid abiotic synthesis in space raises the possibility that organisms evolving on planets elsewhere in the universe may also be utilizing L amino acids in their biological systems.

A recent paper by Meierhenrich and Muñoz Caro (2004) noted the identification of diamino acids in the Murchison meteorite. As the name implies, there are two amino (NH3) groups attached to the central alpha carbon. The amino acid inventory continues to increase.

The organic component of carbon in the Murchison meteorite continues with the discovery of fatty acid molecules. Fatty acids are hydrocarbons containing a terminal carboxylic acid (i.e., $CH_3CH_2CH_2COOH$). The hydrocarbon portion is non-polar and lipophilic (fat-loving), whereas the carboxylic acid (-COOH) is polar and hydrophilic (water-loving). Deamer (1985) noted that isolated fatty acids were able to assemble in membranes. In an alkaline aqueous environment, the carboxylic acid ionizes and the fatty acids can self-assemble and encapsulate, forming a type of membrane, or boundary structure (see Fig. 9). A review of the literature shows that Murchison contains over 100 carboxylic fatty acid type compounds! The importance of these membranous boundary structures is that they could encapsulate other molecules to form a type of primitive "cell." This encapsulation would provide a micro-environment wherein molecular reactions can occur, ultimately leading to replication of this simple structure.

The Murchison carbonaceous chondrite also contains all five nucleic acid molecules, namely, adenine, guanine, cytosine, thymine, and uracil. These molecules are found in RNA and DNA of all biological organisms (see Fig. 10)!

Copper et al. (2001) announced the discovery of sugar molecules in the Murchison meteorite. Chemically, sugars are a group of compounds with a number of hydroxyl (-OH) groups attached to a carbon skeleton. Sugars and related compounds are thus known as polyhydroxylated compounds, or polyols. The most abundant sugars extracted from both meteorites were the three-carbon polyols dihydroxy-acetone, glycerol, and ethylene glycol. Living organisms on Earth utilize sugars as a source of energy and also in forming the backbone of the DNA molecule. One of the sugar alcohols, glycerol, is used by living organisms to build cell membranes. Sugar molecules such as glycoaldehyde were recently discovered in the interstellar cloud

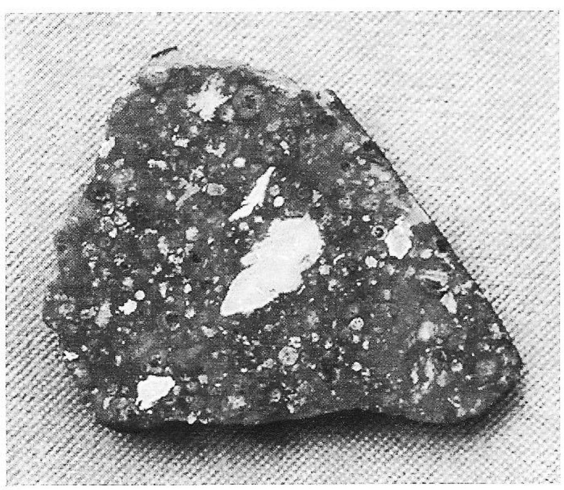


Figure 12. Photo of the Allende CV3 carbonaceous chondrite. Fell on February 8, 1969, in Chihuahua, Mexico. Note the abundant round chondrules and irregular, white refractory inclusions set in a dark gray matrix. This meteorite contains an aggregate of objects that once were suspended in the solar nebula. Allende also dated the solar system at 4.56 billion years. Specimen is from the author's personal collection (9.5 g and measures 37 mm x 25 mm x 4 mm).

Figure 13. Photo of the Murchison CM2 carbonaceous chondrite. Fell on September 28, 1969, in Victoria, Australia. Note the chondrules in a black phyllosilicate matrix containing the organic-rich carbon. The matrix of Murchison contains approximately12% water! The carbon in this meteorite has yielded a wealth of information regarding the possible origins of life on Earth. Specimen from the author's personal collection (20 g wedge measuring 33 mm x 29 mm x 14 mm).

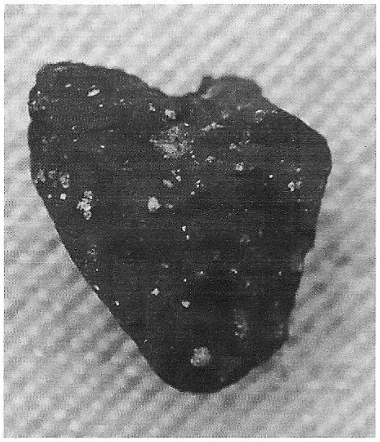
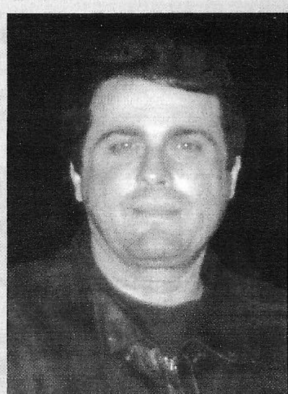


Figure 14. Photo of the Tagish Lake (CI2) carbonaceous chondrite. Fell on January 18, 2000, in the Yukon Territory, British Columbia. Carbon as graphite, diamond, fullerene, and organics has also been discovered in this recent arrival to our planet. Specimen from the author's personal collection (0.28 g and measures 10 mm x 7 mm x 4 mm).

Sagittarius B2 (North) (see Fig. 11).

Thirty years after its arrival, the Murchison meteorite continues to astound the scientific community with new and exciting discoveries from the interstellar to the origins of life on Earth. The four types of carbon (graphite, diamond, fullerene, and organic) found in meteorites continue to rewrite the textbooks as research in this area is ongoing.

Email: gshanos@yahoo.com



Gregory T. Shanos is a pharmacist by profession, an avid amateur astronomer, and meteorite collector. He holds a Doctorate of Pharmacy and resides in Longboat Key, Sarasota, Florida.

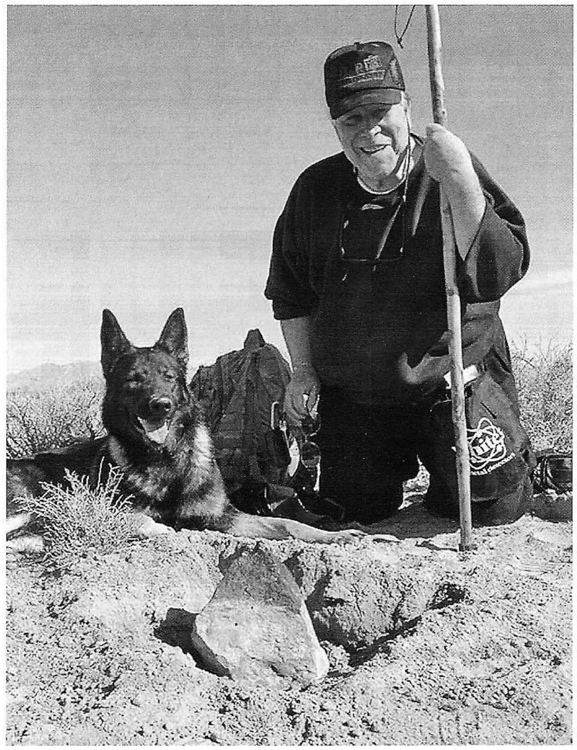


Figure 1. The author with Sonny Clary's dog Brix overlooking the find.

A Year of Study Results in a Record First Find!

By Count Guido Deiro

[Editors' note: This article originally appeared in the March issue of *Meteorite-Times Magazine* (www.meteorite-times.com), in its "Meteorite People" column.]

I have lived and worked in the Great Basin and Mohave Desert all my life. For dozens of years and thousands of hours, I worked as a commercial airplane and helicopter pilot providing contract services to government agencies and scientific laboratories, most associated with the Nevada Atomic Proving Grounds (87% of the State of Nevada is government land).

After the death of Howard Hughes, (yes, I did know and fly with him), I left my position at the Hughes Tool Co. as Director of Aviation Services and began brokering ranch properties, public land grazing rights, and patented water rights, which put me "boots on ground" throughout the state.

I began to study meteorites about a year ago as a diversion to take my mind off the two years of radiation and chemo treatments I had been undergoing for stage IV metastasized cancer. I had responded well for a seventy-two year old and was in remission. I needed some new pursuit to get my mental and physical health back. Little did I know that I was about to catch another disease – and this one incurable – an obsession with meteorites.

After purchasing some 60 different types and classifications, a stereo scope, and a cabinet for comparison purposes – and after reading numerous posts on Meteorite Central's Meteorite Mailing List and dozens of papers, attending the Tucson Gem and Mineral Show, putting faces on all whom I had met online – I decided I was ready to go into the field and find my own meteorites.

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