

FULLERENES AND NOBLE GASES IN THE MURCHISON AND ALLENDE METEORITES. Luann Becker¹, Robert J. Poreda² and Ted E. Bunch³, ¹Hawaii Institute of Geophysics and Planetology, University of Hawaii 2525 Correa Rd., (Post Bldg. 602C) Honolulu, HI 96822, email: lbecker@soest.hawaii.edu; ²Department of Earth & Environmental Sciences, Rochester University, Rochester, NY 14626, USA; ³Space Science Division NASA Ames Research Center, Moffett Field, CA 94305

Introduction: Since the synthesis, isolation and characterization of fullerenes more than a decade ago, there has been considerable interest in ascertaining whether or not this new family of carbon (C) molecules occur naturally on the Earth or in the Cosmos (e.g. circumstellar shells, interstellar medium or ISM etc.) [1,2,3]. For example, it has been suggested that the fullerene molecule, C₆₀, might be widely distributed in the Universe, particularly in the outflows of C stars, due to its exceptional thermal stability and photochemical properties [4]. Despite an intense effort carried out by the scientific community to verify this hypothesis, only a few unusual natural occurrences of fullerenes have been reported [5-8]. However, all of the terrestrial discoveries have been limited to the detection of mostly C₆₀, C₇₀ and trace amounts of some higher (H) fullerenes (e.g. C₇₈, C₈₄, C₁₀₀), while extraterrestrial (ET) evidence is limited to trace findings of mostly C₆₀ [9]. The lack of evidence for ET fullerene compounds have thus raised the question of whether or not this form of C is a significant ET carbon phase in meteorites.

In this work we are reporting the identification of naturally occurring fullerenes (C₁₀₀ to C₄₀₀) in two carbonaceous chondrites (Allende and Murchison). We have applied an extraction protocol developed for the isolation of higher fullerenes in arc evaporated soot [2,3] to the carbon-rich acid residues of both meteorites to isolate microgram quantities of fullerene extract. Laser desorption (linear) time-of-flight mass spectrometry (LDMS) was used to confirm the presence of fullerenes in the extracted residue. Because of the unique ability of the fullerene cage structure to encapsulate and retain noble gases for billions of year's (10), we use the isotopic composition of the encapsulated noble gases to identify the source as extraterrestrial.

Data & Results: LDMS analysis of the Murchison C residue extracted with toluene was predominately a kerogen-like C component and revealed only trace amounts of C₆₀ (<1 µg per 60 grams). This toluene extract also contained no anomalous helium above the blank level. Subsequent extraction of the same residue with 1,2,3,5 tetramethylbenzene (TMB) revealed a small peak for C₆₀⁺ and a much more prominent high-mass envelope that dominates the spectrum between C₁₀₀⁺ and C₂₅₀⁺ (Fig. 1a). LDMS analyses of the Allende carbon residue extracted with TMB also revealed a prominent peak for C₆₀⁺ and C₇₀⁺ and some higher fullerenes (C₇₆⁺ to C₉₆⁺) and a similar high-mass envelope (C₁₀₀ to C₂₅₀) to the Murchison TMB extract (Fig. 1b).

Noble Gas Analyses: Measurements of helium (He) in the Murchison residues (~400 µg sample) revealed ³He/⁴He ratios of 2.1 x 10⁻⁴ or about 150 times greater than the air ratio, a value similar to that estimated for the early solar system (11,12; preliminary results for ²⁰Ne/²²Ne ~8.5 and ²¹Ne/²²Ne ~0.027 have also been obtained). The

procedure used in [11,12] (closed system etching with nitric acid or CSSE) would destroy fullerenes and release the encapsulated noble gases. Unlike other carriers (diamond, SiC) fullerene is the only identifiable and "extractable" phase that would react with nitric acid. The ³He/⁴He ratios are most likely attributed to a He-A component often regarded as the prototype for the "planetary" noble gas component. Our measured He concentrations for the (H) fullerene fraction are much lower than the CSSE extract [11,12]. Preliminary measurements of the remaining bulk residue after extraction with solvents also demonstrated that a large fraction of ³He (15 ncc/g) remained in our acid residue. This suggests that we are either not completely successful at extracting the fullerenes from the meteorite C residues or that there exists other caged carbonaceous carriers (e.g. giant fullerenes) that are readily oxidized by nitric acid but are not very soluble in TMB. The high temperature release steps for Murchison also yielded argon with a non-atmospheric ⁴⁰Ar/³⁶Ar of 35. After correction for an atmospheric blank, the ⁴⁰Ar/³⁶Ar ratio dropped to 10, clearly reflecting the formation of the Murchison fullerenes in an extraterrestrial (presolar?) environment. We should expect the ⁴⁰Ar/³⁶Ar ratio in this ET component to be less than 1, however the use of an organic solvent such as TMB produces a residue that may effectively trap some atmospheric gases. More importantly, the ratio of ³He/³⁶Ar clearly identifies the trapped noble gas as "planetary" rather than solar, consistent with the findings of Weiler et al., [11,12] for the CSSE extracts.

The isotopic composition of the He contained within the Allende fullerene extract is more than an order of magnitude greater than the values found in Murchison. This unexpected result contrasts with the He observed by Weiler et al. [11] for Allende, but is similar to the He found in other meteorites which have been interpreted as 'implanted' or He produced by 'spallation' processes [7]. Due to the high temperatures and partial pressures of He needed (1000 atm. at 1000°C) for incorporation into the fullerene caged molecule, it seems unlikely that the ratios measured in the Allende fullerenes could have originated from implantation or spallation processes. Measurements of noble gases (Ne and Ze) are underway and should reveal the source of this unique signature. The Allende extracts also contained argon with a mixture of an atmospheric and non-atmospheric component that was slightly higher than Murchison (⁴⁰Ar/³⁶Ar ~ 50), but is consistent with the formation of the fullerene carrier in an extraterrestrial environment.

Discussion: The correlations between "planetary" He and Ar in the fullerene fraction of carbonaceous chondrites have important implications for the origin of the atmospheres of terrestrial planets. After Signer and Suess [13] proposed the term "planetary noble gases" for the meteoritic gas component that displays elemental abundances similar to those in the terrestrial atmosphere, it was widely accepted that meteoritic planetary noble gases were the precursors for

terrestrial atmospheres. Some workers still favor scenarios where planets acquire most of their volatiles by degassing of the chondrite-like building blocks during accretion [14]. Others favor mass dependent fractionation of a partly "solar", partly "planetary" noble gas mixture after accretion of the terrestrial planets [15]. Here we suggest that fullerene be considered as a carrier phase for the planetary noble gases. The strong link between fullerenes and a planetary noble gas spectrum suggests that the conditions existing in the nebula at the time included a reservoir of these gases with an environment that favored fullerene formation (i.e. low H/C ratio). Alternatively a planetary pattern for the fullerene component would more likely form and encapsulate these noble gases in a circumstellar or interstellar environment.

Previous work on synthetic fullerenes have demonstrated that the light noble gases (He, Ne and Ar) are incorporated into C₆₀ molecules in proportion to their partial pressure in the gas phase. No elemental fractionation during the incorporation has been documented for any of the synthetic fullerene experiments. We cannot, however, rule out the possibility that elemental and isotopic fractionation of the noble gases could occur during fullerene formation and noble gas encapsulation in certain stages of nebular condensation. As an example, one could envision that high-energy plasma might create conditions favorable to fullerene genesis and provide for a mechanism that creates a planetary noble gas pattern from a dominantly solar one. Alternatively, because of the unique Ne, Ar and Xe isotopic ratios found in the CSSE experiments of Weiler, a presolar origin for both the fullerenes and the noble gas anomalies must be explored.

A fullerene carrier phase for noble gases resolves some of the issues concerning the trapping of these gases in meteorites. Experimental work carried out by Wacker (15), resulted in a model where noble gases are physically adsorbed on the interior surfaces of amorphous C grains containing a network of micropores of 20 Å or less.

The network or *pore labyrinth* is formed by the gaps between graphite crystallites within the C grains or by fullerene-type structures. Interestingly, Weiler et al., (11,12) noted that the size of the 'Q' phase carrier need only be a few angstroms in diameter to sufficiently trap He and Ne for billions of years, maintaining its gases in the laboratory up to temperatures of 1000°C. Thus, the results presented in this study support the notion that fullerene is an important new carrier phase for noble gases in meteorites.

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