

Fullerenes and the Nature of Planetary Gases Luann Becker¹, Robert J. Poreda² and Joe Nuth³,
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Over the past several decades, two issues have dominated the discussion of planetary noble gas patterns:

- 1) the general resemblance of the noble gas abundances in carbonaceous chondrites to those measured in the Earth's atmosphere and;
- 2) atmospheric inventories of argon and neon that fall off significantly with increasing distance from the Sun

The recognition of the latter has led to the conclusion that the planetary component is not found on planets (Zahnle, 1993). In particular, the inability to explain the missing xenon reservoir, once thought to be sequestered in crustal rocks (Fanale and Cannon, 1972) has been extremely troublesome. Some models have focused on various fractionations of solar wind rather than condensation as the process for the evolution of noble gases in the terrestrial planets. However, these models cannot explain the observed gradient of the gases, nor do they account for the similar Ne/Ar ratios and the dissimilar planetary Ar/Kr ratios. More recent studies have focused on hydrodynamic escape to explain the fractionation of gases, like neon, in the atmosphere and the mantle (Porcelli and Pepin, 1997; Hunten et al., 1988). Escape theory also seems to explain, in part, the isotopically heavy argon on Mars, however, it does not explain the discrepancies observed for the abundances of argon and neon on Venus and the Earth (Pepin, 1991). This has led to the assumption that some combination of solar wind implantation, absorption and escape are needed to explain the nature of planetary noble gases.

It has been suggested that the high xenon abundance of planetary gases may be related to the so-called 'Q' phase (Wieler et al., 1991, 1992). However, Q has only been identified by the stepped release pattern of a bulk meteorite acid residue so it remains unclear whether Q is a discrete phase or a mixture of planetary and solar gases released during analysis. The main outstanding questions still center on the missing xenon and the different Ar/Kr and Ar/Ne ratios for Venus and Earth. The only solutions put forth require either two distinct noble gas reservoirs, one for the fractionation of xenon and the other for the remaining noble gases (Pepin, 1991) or a late cometary veneer

with a composition that reflects a high Kr/Xe ratio and naturally mass fractionated xenon (Hunten, 1988). A potential difficulty for the late veneer is that the Earth's mantle probably degassed quickly (~50 myrs), and the rare gases remaining in the mantle may be consistent with the rare gases in air being the degassed complement of the un-degassed mantle (i.e. no place for a late veneer).

The major focus of our research effort has been to measure the noble gases encapsulated within fullerenes, a new carbon carrier phase (Becker et al., 2000) and compare it to the myriad of components found in the bulk meteorite acid residues. We have focused on the carbonaceous chondrites (Allende, Murchison and Tagish Lake) since they have abundant noble gases, typically with a planetary signature that dominates the stepped-release of the meteorite bulk acid residue. They also contain an extractable fullerene component that can be isolated and purified from the same bulk material.

Several papers have reported on the finding of non-atmospheric He and Ar in the Murchison and Allende meteorites (Becker et al., 2000, 2001) and Tagish Lake (Pizzarello et al., 2001) with ³He/³⁶Ar* ratios that approach the planetary ratio (0.01 vs. a solar ratio of ~ 1) [³⁶Ar* = ³⁶Ar_m (1-(40/36)_m/295.5)]. In addition, the neon isotopic composition (²⁰Ne/²²Ne) of the fullerene fraction was at or below the atmospheric ratio of 9.8 (range 8.9-9.5) and appears to suggest a planetary gas carrier (²⁰Ne/²²Ne = 8) rather than a solar value. Improved techniques for handling and measuring fullerenes has resulted in much lower values (~8.2) lending support to the suggestion that fullerenes are a carrier of the planetary Ne.

Despite these encouraging results some researchers have cast doubt on the possible role of fullerene as a carrier of planetary gases (Buseck, 2002). These criticisms are, in part, due to the inability to obtain a single measurement on the fullerene component and the encapsulated gases. The mass spectrum (Becker et al., 2000) of the larger fullerene cages does not allow for isotopic resolution. Moreover, it has been suggested that minor amounts of other carriers might have survived extraction and may account for the noble gases in our fullerene residues.

In order to test the hypothesis that other carriers may be responsible for the noble gas signatures measured in our fullerene extracted residues, we began a systematic investigation of the low temperature (100-800°C) release of gases from Murchison, Allende and

Tagish Lake fullerenes and the remaining bulk acid residues. Previous research (Weiler et al., 1991, 1992) has demonstrated that digestion of the bulk meteorite acid residues with an oxidizing acid (forming HNO₃) releases copious quantities of “planetary gas” with a unique ²⁰Ne/²²Ne of ~ 10.5 that they named Q.

Initial results for the fullerenes show the release of a “planetary component” at temperatures from 300-700°C in the Murchison, Allende and Tagish Lake meteorites. Noble gas ratios ³He - ²²Ne - ³⁶Ar - ⁸⁴Kr parallel the “planetary gas” ratios with a ²⁰Ne/²²Ne ratio close to the planetary gas value (Ne-A = 8.2). The ³⁶Ar is > 95% non-atmospheric (⁴⁰Ar/³⁶Ar ≈ 1-10) and the ³⁸Ar/³⁶Ar ratio is atmospheric (~5.31) also consistent with a planetary signature. The stepped-release curve for the bulk meteorite residue is crudely similar to the “pure fullerene” release, providing confirmation that fullerene is likely responsible for the gas release of our meteorite acid residues. Throughout the low temperature step release, the abundances of the noble gases and the planetary signature remained the same, thus, an adsorbed component or gases trapped in other carriers (e.g. silicates, chromites) cannot explain this unique release pattern characteristic of fullerene.

Only at 800°C and above do other gas carriers (e.g. diamond) become dominant in our bulk meteorite acid residue, as the amount of gas released at each temperature step drops dramatically. The overall signature of the high temperature release is dominated by “Ne-A” typified by the diamond carrier (Lewis et al., 1987). The Xe-isotopic ratios at all temperature steps 300°-800°C, resembles the values for AVCC (average carbonaceous chondrites). The δ¹³⁶Xe (‰)_{Air} ≈ -10-12% is clearly consistent with the composition of the Earth’s early atmosphere. Again, the amount of Xe relative to Ar in these low temperature steps is some 20 times lower than the planetary ratio ¹³²Xe/³⁶Ar and at or below the ratio in air. If this finding is confirmed, there would be no need to invoke a “missing Xe” reservoir on Earth (e.g. adsorption on shales, it was simply never there in the first place), rather the Earth’s atmosphere was supplied with noble gases from a fullerene component that was Xe-deficient. Subsequent mixing with “solar type gases” from the interior of the Earth ultimately produced the atmosphere that exists today. This theory would suggest a late veneer (Hunten et al., 1988) that would provide the fullerene planetary component needed instead of invoking two distinct noble gas reservoirs, one for the fractionation of xenon and the other for the remaining noble gases (Pepin, 1991).

To further characterize and evaluate the encapsulation of noble gases in the larger fullerene cages we are developing a new separation method using high performance liquid chromatography;

HPLC). We have begun to carry out experiments on synthetic material “graphitic smokes” to evaluate the noble gases in the larger fullerene cages. Graphitic smokes (GS) are produced by electrically heating a thinned out graphite rod in a noble gas atmosphere (Olsen et al., 2000). The hollow graphite rod allows the C to condense out of the gas more uniformly in comparison to the arc evaporator process used in the synthesis of fullerenes (Kratschmer et al., 1991). Some of these carbonaceous condensates were analyzed for xenon and values as high as 13.7 x 10⁻⁶ cm³ STP/bm of ¹³²Xe were obtained. This is some 2X magnitude greater than typical ¹³²Xe amounts for other synthesized carbonaceous residues (Ott et al., 1981).

We obtained some graphitic smokes synthesized in a noble gas mixture (49% neon, 49% argon, 1% xenon and 1% krypton with the balance of pressure coming from helium) and used our fullerene extraction protocol to determine whether fullerene was a carrier phase for the noble gases measured in the graphitic smoke material. Preliminary measurements of helium and neon in a small amount of toluene extracted graphitic smokes residue (100 μg) indicated that fullerene (mostly C₆₀ and C₇₀) is indeed a carrier phase for the noble gases. Our yield for helium corresponds to one ⁴He per 880,000 fullerene molecules and is similar to the abundances measured in synthetic fullerenes produced in the arc evaporator (Kratschmer et al., 1991; Saunders et al., 1993). The higher fullerenes (up to C₃₀₀) are also present in the graphitic smokes material.

We intend to continue our studies of the graphitic smokes with emphasis on the isolation and separation of the larger cages and direct measurements of the noble gases. The graphitic smokes will be prepared with various mixtures of noble gases of known composition and extracted for fullerenes. The very efficient trapping of Xe in the graphitic smokes strongly suggests a more significant role for the larger fullerene cages to encapsulate the heavy noble gases. A more complete characterization of the larger fullerene cages may well lead to a better understanding of the nature of planetary atmospheres. **Refs:** Becker et al., (2001) *Science* **291**, 1530; Becker et al., (2000) *PNAS* **97**, 2979; Buseck (2002) *EPSL* **203**, 781; Fanale and Cannon, (1972) *GCA* **36**, 319; Hunten et al., (1988) *Meteorites & the Early Solar Sys.* pp. 565; Kratschmer, et al., (1990) *Nature* **347**, 354; Lewis, et al., (1987) *Nature* **326**, 160; Olsen et al., (2000) *LPSC XXXI* Abs.; Ott et al. (1981) *GCA* **45**, 1211; Pepin (1991) *Icarus* **92**, 2; Pizzarello et al., (2001) *Science* **293**, 2236; Porcelli and Pepin (1997) *Orig. of the Earth & Moon* pp. 435; Saunders et al., (1993) *Science* **259**, 1428; Weiler et al., (1991) *GCA* **55**, 1709; Wieler, et al., **56**, 2907 (1992) *GCA* **56**, 2907; Zahnle, (1993); *Planet. Atmos. II* pp. 1305.