ARE FULLERENES RELEVANT TO COSMOCHEMISTRY? A NEW FINDING.

T. L. Wilson[1] and D. W. Mittlefehldt[1], [1]NASA, Johnson Space Center, Houston, Texas 77058 USA.

Introduction: The abundances of noble gases found in primitive, carbonaceous meteorites are unexpected when compared with our Sun. Known as Q-gases (Q for some unknown carrier dubbed "quintessence"), this anomaly has remained a mystery since it was discovered in 1975. Q-gases are characterized by increasing depletions with decreasing atomic number (Z) relative to solar noble gases and normalized to ^{132}Xe (Figure 1). This Q-gas mass fractionation is unexplained, and its investigation is important to understanding the origin of the solar system.

However, the subject is fraught with controversy – in part due to the complex nature of Q and in part due to claims of some researchers that cannot be reproduced by other investigators. The topic is discussed in numerous places [e.g., 1-4], with models of Q falling into two basic categories, both involving carbon entrapment of noble gases. First (Group A), there is the conservative two-dimensional view that Q-gases are adsorbed or sorbed onto a "labyrinth" of graphite or carbon grains [5-9], or they undergo active capture onto growing surfaces [6]. Second (Group B), there is the view holding to the remarkable property of carbon discovered in 1985. Carbon can curl up into closed geometries of hexagon- and pentagon-shaped carbon-ring configurations, a property ignored completely by Group A. Group B thinks of Q as a three-dimensional structure of endohedral carbon cages like fullerenes, carbon onions, or some class of carbon nanotubes [3, 4, 10]. Group B does not exclude Group A effects.

Status: The dismal state of fullerene candidates has been reviewed by Heymann *et al.* [3], while the labyrinth group has been equally unsuccessful. Some are even saying that fullerenes are irrelevant to cosmochemistry, a point of view that is certainly false. A giant fullerene was discovered in the Allende meteorite in 1981 [10, 4, 3] before the advent of fullerene chemistry. If it was not created during or after Allende's terrestrial impact, fullerenes exist in meteoroids in space.

Following a brief investigation into this circumstance, we report here on a new finding that falls into the second group of Q-gas research.

Q-Gas Abundance: In order to discuss the mass-fractionation of Q-gases, their abundance pattern needs to be defined. As mentioned, Q contains a noble-gas abundance pattern that is anomalous compared with the Sun (Figure 1), as well as in comparison with the extra-solar (cosmic or interstellar) abundance. Note that Q may have two substructures, Q1 and Q2, a suggestion dating back to Gros & Anders [11, 5].

Relevance to Cosmochemistry: Noble gas cosmochemistry must necessarily address the subject of endohedral carbon clathrates [12, 13] in view of their importance since the discovery of fullerenes and their fundamental change in our understanding of carbon chemistry. Found originally as the highly stable closed-cage configuration C_{60}, higher stable fullerene allotropes C_n with some having n >100 are known to exist in the carbon soot generated by arc-heating of graphite. They are created by energetic events, and are known to occur naturally and geologically in very low concentrations [4]. When produced in the presence of an ambient noble gas NG, an endohedral carbon-cage clathrate NG@C_n is produced by the reaction NG + C_n → NG@C_n . Figures representing these clathrates can be found elsewhere [4, 12, 13].

This theoretical analysis will focus on C_{60} *per se*. The carbon-cage clathrates NG@C_{60} (NG = He, Ne, Ar, Kr, or Xe) are Van der Waals (VdW) molecules containing entrapped noble gas NG. Since the noble gases are inert and neutral, they interact with matter by means of the classical VdW force. The latter, however, was not understood until it was derived by London [14] as a quantum effect caused by induced multipoles in orbital electron density.

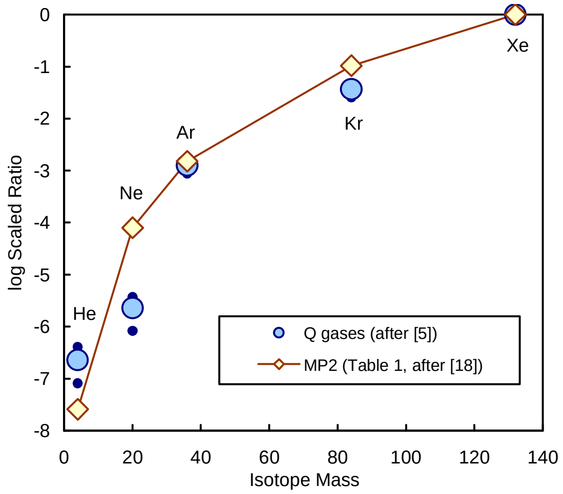

Figure 1. Elemental abundance of Q-gases relative to solar abundance and ^{132}Xe, as a function of mass (from [5]) compared to the London or Van der Waals dispersion energy to the fifth power $F = \bar{E}_{dis}^{5}$ for NG@C_{60}, taken from Table 1. The small dark spots are minimum and maximum values for Q from [5].

Van der Waals Interactions: When studying the behavior of endohedral clathrate systems such as NG + C_{60} ↔ NG@C_{60}, one tends to begin by thinking in terms of VdW radii [e.g., 12] and the Lennard-Jones potential $U(r) = 4\varepsilon\,[(\sigma/r)^{12} - (\sigma/r)^{6}]$ [13]. The VdW contributions ($\sim r^{-6}$) are attractive at large distances r, offset by a repulsive core ($\sim r^{-12}$) as $r \rightarrow 0$. The $-(\sigma/r)^6$ term is the London interaction, giving rise to the London force or dispersion force [14]. Because Xe is a large atom compared to He, one intuitively would argue that Xe@C_{60} is the most unlikely or unstable clathrate in the system – and so on for Kr and Ar. This is opposite to what is observed in Figure 1 for Q.

New Developments: Computational quantum chemistry research has made tremendous advances in recent years, with much attention paid to endohedral fullerenes NG@C_{60}. That work includes exchange repulsion and electron correlation effects omitted in first-order Hartree-Fock (HF) theory in quantum mechanics. Higher-order nonlinear perturbation theory takes the form of density functional theory (DFT) and second-order Møller-Plesset theory (MP2) [15]. Scuseria [16] and Thiel [17] have made some of the first calculations of NG@C_{60} binding energies derived from DFT and MP2.

A more recent calculation of London dispersion interactions for NG@C_{60} has been performed by Pyykkö [18] using MP2. It will be examined here, noting that MP2 always lowers the first-order HF state. This results in bound states and attractive (negative) London terms in Pyykkö's work. The dispersion energies E_{dis} (kJ/mol) are given in Table 1 for Pyykkö's Case 0.

Table 1

Noble Gas	E_{dis}(kJ/mol)	$\bar{E}_{dis}$	$F = \bar{E}_{dis}^{\,5}$
He	-7.5	0.030303	2.56E-08
Ne	-22.0	0.151515	7.99E-05
Ar	-71.2	0.272727	0.001509
Kr	-95.7	0.636364	0.104358
Xe	-124.9	1.0	1.0

The first thing to observe is that MP2 has lowered the dispersion energies E_{dis} as expected, making the heavier gases more stable and reversing the trend to be compatible with the Q-gas abundance in Figure 1. Next one needs to normalize E_{dis} to Xe, as $\bar{E}_{dis}$. Since the functional relationship between mass fractionation and noble-gas mass in Figure 1 is totally unknown, one can ask if there is a straightforward functional dependence similar to the Q abundance data. One finds that $F = \bar{E}_{dis}^{\,5}$ gives such a relationship. This is graphed in Figure 1. Except for Ne there is a strong resemblance to the Q abundances.

The same functional relationship used in Table 1 can be applied to Thiel's work on MP2 interaction energies (without counterpoise corrections) for NG@C_{60} bound states (-1.0, -5.3, -7.5, -16.1, -17.1 kcal/mol) in [17], and one arrives at a similar graph as Figure 1. As pointed out by Thiel, the inclusion of a single set of polarization functions for the noble gas involved can affect the relative energies dramatically. This might be relevant to the behavior of He, Ne, and Kr.

Conclusions: This study does not intend to say that the comparison in Figure 1 is a compelling argument that fullerenes exist in meteorites or that NG@C_{60} is Q. Nevertheless, the resemblance is appealing and deserves further investigation at a much more comprehensive level, including cases for NG@C_n where $n > 60$. The result is the first of its kind in cosmochemistry, derived mathematically from computational quantum chemistry. A fifth-order function of the London dispersion energies and clathrate binding energies for NG@C_{60} bears a strong resemblance to Q-phase abundances.

Acknowledgement: The authors would like to thank Gustavo Scuseria of Rice University for pointing out the relevance of Ref. [18] to the Q-Phase mass fractionation problem.

References: [1] Ozima M. and Podosek F. A., *Noble Gas Geochemistry* (Cambridge Univ. Press, 2nd ed., 2002). [2] Ott U. (2002), in *Noble Gases in Geochemistry and Cosmochemistry*, D. Porcelli et al., eds. *Rev. Mineral. Geochem. 47***,** 71-100. [3] Heymann D. *et al.* (2003), *Fullerenes, Nanotubes, and Carbon Nanostructures 11*, 333-370. [4] Buseck P. R. (2002), *Earth Planet. Sci. Lett. 203*, 781-792. [5] Busemann H. *et al.* (2000), *Meteoritics & Planet. Sci. 35*, 949-973. [6] Hohenberg C. M. *et al.* (2002), *Meteoritics & Planet. Sci. 37*, 257-267. [7] Wacker J. F. (1989), *Geochim. Cosmochim. Acta 53*, 1421-1433. [8] Zadnik M. G., Wacker J. F., and Lewis R. S. (1985), *Geochim. Cosmochim. Acta 49*, 1049-1059. [9] Wacker J. F., Zadnik M. G., and Anders E. (1985), *Geochim. Cosmochim. Acta 49*, 1035-1048. [10] Smith P. P. K. and Buseck P. R. (1981), *Science 212*, 322-324. [11] Gros J. and Anders E. (1976), *Earth Planet. Sci. Lett. 33*, 401-406. [12] Mittlefehldt D. W. and Wilson T. L. (2007) *LPS XXXVIII*, 2194. [13] Wilson T. L. and Mittlefehldt D. W. (2006) *LPS XXXVII*, 1386. [14] London F. (1930), *Z. Physik 63*, 245-279. [15] Møller Chr. and Plesset M. S. (1934), *Phys. Rev. 46*, 618-622. [16] Darzynkiewicz R. B. and Scuseria G. E. (1998), *J. Phys. Chem. A 102*, 3458; *ibid 101*, 7141-7144. [17] Thiel W. *et al.* (1997), *Chem. Phys. Lett. 275*, 14-18. [18] Pyykkö P. *et al.* (2007), *Phys. Chemistry Chem. Phys. 9*, 2954-2958.