

CHEMISTRY OF FULLERENES ON THE EARTH AND IN THE SOLAR SYSTEM: A 1995 REVIEW, D. Heymann, *Department of Geology and Geophysics, Rice University, Houston, TX 77251. e-mail: dieter@owl.net.rice.edu.*

Fullerenes C_{60} and C_{70} , the all-carbon molecules with closed-cage structures were discovered in 1990 in shungite from the Kola peninsula [1]. Subsequent discoveries in terrestrial materials include a fulgurite from Colorado [2], clays and marls from several locations on the Cretaceous-Tertiary boundary [3,4], and carbon-rich breccias from the Sudbury impact structure [5]. A search for fullerenes in the carbon-rich materials anthraxolite, shungite, and thucholite, however, failed to find them [6].

It was suggested in 1986 [7] that helium and other inert gases in chondritic meteorites might be trapped in C_{60} . While this idea has been neither proven nor disproven, it is interesting to note that He atoms have been introduced artificially into fullerene cages [8]. Early searches for fullerenes in carbonaceous chondrites failed to find them [9-11], but in 1994 it was reported that a sample of Allende contained 100 ppb C_{60} [12]. A report that fullerenes $C_{60}H_n$ with $n > 4$ had been found in Allende [13] was puzzling in light of the poor stability of these compounds in the Earth's atmosphere. An attempt to confirm the presence of fullerenes in Allende failed [14].

Extraterrestrial fullerenes have been discovered in and around a micrometeorite impact pit on the skin of the LDEF (Long Duration Exposure Facility) spacecraft with C_{60} contents of the carbon-rich matter up to 5% reported [15]. This work prompted a search for fullerenes in Apollo 11 and Apollo 12 lunar fines; but none were found [16,17].

Only a few of the fullerene syntheses discovered in laboratories are likely to be applicable. Formation by the condensation of elemental carbon in a circumstellar gasphase has been suggested as the source for fullerenes in meteorites [12,18]. Pyrolysis of PAH's such as naphthalene [19] may play a role in the hot atmospheric plume of impact processes [5,15]. Discovery of the formation of fullerenes in flames [20-23] prompted the suggestion that the KT boundary fullerenes had been formed by wildfires [3,4]. It was later argued that the presence of oxygen in the KT atmospheres at levels comparable to today would have prevented the formation of fullerenes by wildfires [13], but that is a weak argument because oxygen is essential for the formation of fullerenes in flames.

Fullerenes are quite stable in the Earth's atmosphere, but, like all forms of carbon, will burn when heated to sufficiently high temperatures. At temperatures in the range 200 to 250 °C C_{60} and C_{70} decompose in a matter of hours to oxygen-rich substances of unknown composition and structure, but it is not clear whether the reaction occurs with O_2 or O_3 [24]. C_{60} in solution was destroyed photochemically with UV [25]; in that case it is all but certain that the reaction occurred with O_3 formed from O_2 by the UV irradiation. The very swift reaction of C_{60} and C_{70} with ozone was directly studied [26]. It was found that a series of epoxides and, ultimately, very oxygen-rich substances formed, and that C_{60} decomposed about 1.4 times faster than C_{70} [27]. The rates of reaction with O_2 , N_2 , H_2O , and CO_2 in the atmosphere are still unknown.

Atmospheric conditions following a large crater-forming impacts such as Sudbury and Chicxulub are transiently so extreme that it is safe to say that fullerenes will neither form, nor be able to survive, except perhaps at the very fringes of the atmospheric plume. Once the plume-phase is past, the atmosphere is still hot and greatly enriched in SO_2 and O_2 from sulfates [28], O_3 , CO , CO_2 , H_2O , NO , NO_2 [29]. As the atmosphere cools below 1000 °C, SO_2 and O_2 react to form SO_3 and, eventually, H_2SO_4 and aerosols of the acid. At room temperature, fullerenes C_{60} and C_{70} appear to be quite stable in the presence of SO_2 [30]. However, it is known that SO_2 in the presence of O_2 and ultraviolet light is capable of rapid oxidation and sulfonation [31] and these are conditions likely to occur in the Earth's atmosphere after large crater-forming impacts.

That H₂SO₄ (40%) + HNO₃ (40%) as well as 'oleum' attack fullerenes very swiftly, even at room temperature, was known since 1992 [32-34]. The products, OH-rich fullerols are brown powders, slightly soluble in water. It was not known that C₇₀ reacts significantly faster than C₆₀ [35]. Perhaps the reaction of fullerenes with SO₃ or hydrated forms of SO₃ can explain the absence of C₇₀ from the clays of Woodside Creek, a KT site in New Zealand [3,4].

The solubilities of C₆₀ and C₇₀ in pure water at room temperature are less than 0.04 ng/ml and possibly as small as 10 molecules per ml [36].

With regards to laboratory procedures, one must remember that fullerenes are usually present in terrestrial and extraterrestrial matter in such small amounts that these can easily dissolve in almost every organic solvent and in CS₂. The traditional destruction of silicates with HF-HCl does not attack fullerenes, but heating in perchloric acid does destroy them [37]. Generally speaking, fullerenes should not be exposed to strongly oxidizing chemicals.

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