Exotic Heavily Ionizing Particles can be Constrained by the Geological Abundance of Fullerenes

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The C_{60} molecule exhibits a remarkable stability that leads to its survival in ancient carbonaceous rocks initially subjected to the elevated temperature requisite for its formation. Elementary particles having a large electronic stopping power can similarly form C_{60} and higher fullerenes in their wake. Combined, these two features point at the possibility of using the C_{60} presence in selected bulk geological samples as a new type of nuclear track detector, with applications in astroparticle physics.

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Sixty carbon atoms, arranged spherically as if on the surface of a soccer ball, form the C_{60} molecule (Buckminster fullerene). Of all possible formations, this peculiar one has the highest symmetry, lowest energy level, no dangling bonds, and is therefore chemically inert much like a noble gas. This leads to an extraordinary photochemical and thermal stability that fueled the expectations for its abundance in the galaxy [1] soon after its discovery. First searches for C_{60} in meteorites and the interstellar medium turned up negative [2,3]; the presence of hydrogen as an abundant coreactant in stellar atmospheres was recognized as an inhibiting factor in its production [3]. In spite of this, there is now growing evidence for C_{60} in interstellar space [4]. On Earth, the confirmation of a natural C_{60} presence followed a similar chronicle: Only particular geological samples having once withstood the high temperature conditions requisite for C_{60} formation have so far shown this evidence. This is the case of precambrian shungite [5], the most highly methamorphosed coal known, or fulgurite [6], the glassy product of a lighting strike. Of particular interest is its presence in shock-produced rubble in the 1.85-billion-year-old Sudbury impact crater [7,8] and in samples from Cretaceous-Tertiary (K/T) boundary clay seams and coals [9]. In the first case, atomic helium encapsulated in the fullerene exhibits an extraterrestrial $^3He/^4He$ ratio, pointing at an origin previous to the impact itself [8]. The high concentration of fullerenes (1–10 ppm) in these samples illustrates the long-term survival of the molecule; the ability to retain extraterrestrial He exemplifies its endurance of extreme conditions such as those accompanying crater formation. The C_{60} presence in concentrations typical of soots from common flames in K/T samples, but not above or below the boundary, is hypothesized to arise from the raging of postimpact sooting wildfires [9].

In the laboratory, fullerenes have been produced by laser ablation, in carbon arcs, by combustion of benzene and lately by ion beam irradiation [10,11]. C_{60} and other polycyclic compounds remain in latent tracks of energetic ions in carbonaceous matter, albeit a minimum of a few eV/Å^3 in transferred electronic energy is needed for this process [10,12,13], so as to permit the completion of chemical formation before the onset of cooling in the particle's hot plasma aftertrack. Given the apparent scarcity of fullerenes in common geological samples, yet its demonstrated ability to survive over long periods, it is natural to wonder if hypothetical highly ionizing and deeply penetrating elementary particles such as magnetic monopoles, nuclearites [14], Q balls [15], etc., should not have left a detectable cumulative signature in ancient carbonaceous rocks. In this Letter, recent models and measurements of C_{60} production under particle irradiation are employed to estimate its yield from such cosmic exotica, comparing it with that from common terrestrial sources of radiation. This geochemical method is appraised judging from the sensitivity of present-day chromatographic techniques and current efficiency in C_{60} extraction from bulk minerals.

A condition for the applicability of this technique is that of good fullerene preservation over the age of the rock. There are several precautions to be taken in this respect for sample selection, a situation similar to that of mica searches [16,17] for weakly interacting massive particles (WIMPs) and monopoles, where the thermal history of the mineral must be such that annealing of latent etch tracks is minimized. While C_{60} integrity under impact and static pressure in the upper layers of the Earth's crust seems assured (it is stable up to 130–170 kbar [18]), there are factors such as exposure to O_3 [19] and UV light [20] to be controlled. An environment low in ozone is imperative since the destruction of fullerenes is 5 orders of magnitude faster in the presence of O_3 than O_2. In fact, the shungite of Ref. [5] is thought to have been protected from O_3 oxidation by the coal in which it was contained [19]. The concentration of hydrogen and sulfur in the rock should also be a criterion for selection, the second preventing C_{60} oxidation when present as sulfide silicates [7]. The thermal decomposition of fullerenes in solid phase, another determining factor, has been measured [21]: The remaining fullerene fraction after a time t at temperature T is

$\exp[-k(T)t]$, where $k(T) = 1.24 \times 10^9 \exp(\frac{-\tau}{T})$ s^{-1} and $\tau = 3.2 \times 10^4$ K, i.e., a 90% survival probability over 10^9 years even if subjected to a constant 250 °C. Finally, fullerenes exhibit very good stability towards intense irradiation with high-energy electron pulses and gamma rays [22], guaranteeing their resistance to scarce environmental minimum ionizing radiations. In view of these remarkable signs of immunity, the ppm presence (or not) of fullerenes in ancient rocks seems to be less a question of long-term stability and more of sample origin, as experimental findings confirm. If exposure to certain elementary particles over the lifetime of the sample is an abundant source of fullerenes, these should endure to prove the particle's crossing.

It is the ability to efficiently leach fullerenes from bulk mineral and to detect them that ultimately limits this method. In this Letter the state-of-the-art in high-pressure liquid chromatography (HPLC) is conservatively adopted as the detection reference. Similarly, we do not assume a leaching efficiency far beyond what is accomplished nowadays, i.e., that O(1) kg samples can be nearly completely demineralized [9,23] and reduced to ~0.1 ml of liquid containing all organic substances of interest. In essence, this procedure consists of pulverization followed by repeated treatment with HCl/HF to create a C-rich residue, refluxing of this in a small volume of toluene (a good solvent for aromatic compounds), centrifugation and/or filtration, and concentration of the volume to 0.1–1 ml by evaporation under reduced pressure [9,23,24]. The recovery efficiency for thus-treated fullerene-spiked mineral samples has been shown to be ~90% [23]. At a reasonable signal-to-noise ratio, HPLC is currently able to spot ~10^{-10} g of fullerene in 0.1 ml toluene aliquots [9,11]: This is the realistic figure adopted below to estimate the present particle detection ability.

The production of fullerenes in the wake of an energetic particle follows a sequence of events [10–13] that begins with the destruction of all molecular bonds in the track core due to the formation of a short-lived zone of highly excited neutral target atoms by the electronic energy transfer from the projectile. This is followed by the nucleation of one-dimensional C-C complexes via random "sticky" collisions of this gas, coalescing into two-dimensional pentagonal and hexagonal rings that in turn form closed 3D complexes, and among those fullerenes. The concept of a threshold in electronic stopping power for fullerene formation is interchangeable with that of a minimum track temperature above which condensation is facilitated [13]. The dependence of the track temperature $T(r,t)$ on the axial distance r from the particle path and time t after passing is [25]

$$T(r,t) = \frac{T_0}{1 + (4Dt/r_0^2)} \exp\left\{-\frac{(r/r_0)^2}{1 + (4Dt/r_0^2)}\right\}, \quad (1)$$

where D is the thermal diffusivity of the medium and $r_0 \sim 15$ Å is the core radius, which delimits a cylindrical region of plasmalike conditions and highest energy

density [25]. The initial track temperature is given by $T_0 = \alpha S_e/(\pi \rho C_V r_0^2)$, with ρ as the density, C_V the specific heat, S_e the electronic stopping power, and $\alpha \sim 0.1$ as the fraction of energy going into thermal excitation of the Maxwellian gas of carbon atoms. Leaving aside a dependence on the probability of sticky C-C collisions and on the average density of the gas (both temperature independent to first approximation [13,26]), the C_{60} yield is proportional to

$$Y_{60} \propto \iiint \Omega(r,T) 2\pi r\, dr\, dz\, dt \qquad (2)$$

(z denotes the direction along the trajectory). This expression gives the time-integrated volume of material available for fullerene condensation under the favorable conditions described by $\Omega(r,T)$, namely,

$$\Omega(r,T) = \begin{cases} 1 \text{ for } T_{\min} < T(r,t) < T_{\max}, & 0 \text{ elsewhere,} \\ 0 \text{ for } r < r_{60}, & 1 \text{ elsewhere,} \end{cases} \qquad (3)$$

where the minimum temperature for fullerene formation is estimated at $T_{\min} \sim 750$–800 K in studies of laser ablation of polymers [12,26], and unconfined C_{60} is seen to readily disintegrate at $T_{\max} \sim 6000$ K. The second condition in $\Omega(r,T)$ imposes that the heated volume must be able to physically accommodate the C_{60} cage within; r_{60} should then naively correspond to the molecule's radius, 3.6 Å. A more adequate phenomenological value $r_{60} \sim 9$ Å [13] is adopted here.

In the present analysis, $T(r,t)$ must be evaluated numerically to compute Y_{60} for different types of radiation. These yields are in arbitrary units until a normalization point is applied; of the handful of recent irradiations of carbonaceous materials with heavy ions, the results of Fink et al. [11] using 3 GeV U^{20+} on thin plates of sucrose ($S_e \sim 2.0 \times 10^4$ keV/μm, ion range ~160 μm) are particularly helpful for this purpose, since the total dissolution of sugar in HPLC reagents guarantees an excellent C_{60} recovery. The found value of 84 ± 31 C_{60} molecules per incident ion should then reflect the actual Y_{60} closely. Equation (2) can be used to assess Y_{60} if the target is instead a carbonaceous rock: The different stopping powers [27] and parameter values for sucrose [$C_V \sim 1.2 \times 10^3$ J/(kg K), $D \sim 2.9 \times 10^{-7}$ m^2/s, $\rho \sim 1.6 \times 10^3$ kg/m^3] and coal-like samples [$C_V \sim 700$ J/(kg K), $D \sim 1.8 \times 10^{-7}$ m^2/s, $\rho \sim 2 \times 10^3$ kg/m^3] translate into an enhancement in Y_{60} by a factor 3.8. The nearly constant S_e over the initial 90% of the ion range in both situations allows one to conclude that, to a good approximation, $\frac{\partial Y_{60}}{\partial z} \simeq 2.5 \times 10^{-4}$ C_{60}/Å at $S_e \simeq 2.4 \times 10^4$ keV/μm for C-rich rocks (the units of S_e and value of ρ are maintained tacitly hereafter). This normalization point anchors our calculation of $\frac{\partial Y_{60}}{\partial z}$ vs S_e (shown in Fig. 1). Fink et al. observed that C_{60} production was a highly inefficient process (36 MeV invested per C_{60} when the molecule's formation energy is 444 eV). An interpretation [11,28] is that the carbon atoms are highly
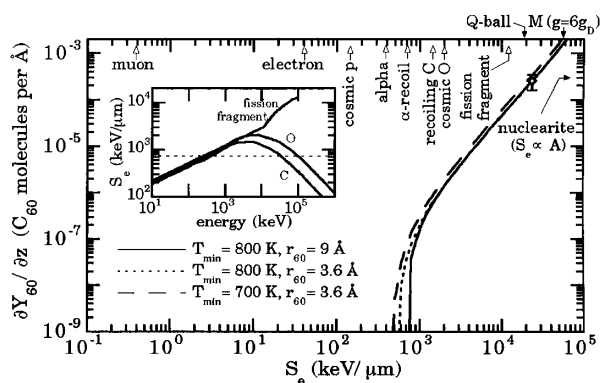
FIG. 1. Estimated C_{60} yield per unit path length vs particle electronic stopping power, in coal-like rocks. The single point corresponds to the overall normalization based on [11]. The dependence on T_{min} and r_{60} is shown; similar variations of r_0 and T_{max} have a comparatively negligible effect. The slope at high S_e is in good agreement with [13]. The *maximum* S_e for common natural sources of radiation is indicated (white arrows) and illustrated in the inset for those above the fullerene production threshold $S_e \sim 750$ keV/μm.

volumetrically diluted in sucrose (one in four), reducing the probability of C-C collisions; this is aggravated by the presence of hydrogen, which can lead to aromatic hydrocarbons rather than fullerenes as stable end products [3]. There should then be an additional enhancement in Y_{60} for rocks primarily composed of C. For these the overall normalization of Fig. 1 is probably largely conservative and not a substitute for calibrations using ions of stopping power similar to that of the particle of interest (calibrations that should also determine the leaching efficiency for a specific rock type).

Do natural backgrounds give rise to a significant fullerene presence in shallow-mined carbonaceous rocks? Isolated minimum ionizing radiations cannot play a role (Fig. 1). However, recoiling carbon nuclei with energies ≥ 30 MeV ($Y_{60} \simeq 0.1$) can be induced by underground muons, albeit the cross section for this process [29] is small at $< 10^{-3}$ mb. With a muon flux 10^{-3} cm^{-2} s^{-1} at a modest 150 m depth, these recoils should produce a meager $< 10^{-21}$ (g C_{60}/kg rock)/yr. A comparable contribution, if any, is expected from O(1) MeV recoils ($Y_{60} \simeq 10^{-3}$) originating in elastic scattering of the 2×10^{-7} cm^{-2} s^{-1} fast neutron flux typical below this depth. Similarly, recoiling daughters from (n, p), (n, α), (α, p), and (α, n) reactions in C can be shown to contribute negligibly, and the same applies to the scarce penetrating medium- and large-mass cosmic ray nuclei. The biggest offenders are, by far, spontaneous fission fragments ($Y_{60} \simeq 5$) which result in 2.8×10^{-18} (g C_{60}/kg rock)/yr per ppm ^{238}U, making a low U concentration necessary if ancient samples of age ~ 1 Gyr are to be utilized (US coals exist with < 0.02 ppm U). This is again reminiscent of WIMP mica searches, where $\leq 10^{-4}$ ppm U are desirable.

The central result of our analysis is that heavily ionizing particles energetic enough to maintain a constant $S_e >$

10^3 through the Earth's upper crust should produce at least $\sim 2.05 \times 10^{-26} S_e^{2.1}$ g C_{60} per cm traversed in C-rich rock. Assuming a spherical rock geometry, with average trajectory length equal to its radius, the limit on their flux attainable by processing a rock mass $M(kg)$ of age $t(yr)$ is then

$$\Phi(\text{cm}^{-2} \text{ s}^{-1} \text{ sr}^{-1}) < \max[8.2 \times 10^3 \varepsilon/(MtS_e^{2.1}),$$
$$8.3 \times 10^{-12} M^{-2/3} t^{-1}], \quad (4)$$

where $10^{-10}\varepsilon$ g is the minimum chromatographically detectable C_{60} mass ($\varepsilon_{\text{HPLC}} = 1$). The first term judges the ability of the particles to produce enough fullerenes during the lifetime of the sample, whereas the second imposes that at least one such particle must have crossed it (i.e., dictates the minimum exposure Mt necessary for the first term to apply). For magnetic monopoles, this method is essentially applicable only to those with $\beta > 10^{-1}$, for which the main mode of energy loss is via ionization. In this sense, this proposal is complementary to mica searches [17], where the sensitivity decreases rapidly above $\beta \sim 10^{-3}$. For $\beta = 1$, monopole energy losses in C-rich rock depend on their magnetic charge $g = ng_D$ via $S_e \simeq 1.6 \times 10^3 n^2$ [30] ($g_D = $ Dirac charge). Inspection of Eq. (4) shows that, for $n > 3$, $t \sim 10^9$, and $M < 50$, an improvement of the best current limits [31] in this velocity range is already within reach. For $n = 1, 2$, a decrease in ε must be awaited: Using a reasonable $M < 100$, future or alternative C_{60} detection techniques can ameliorate the present experimental limits for grand unified theory fast monopoles ($\Phi < 3 \times 10^{-16}$) by several orders of magnitude before running into the limitations expressed by the second term in Eq. (4), with the attainable radiopurity of the rock as the only constraint.

Coherent states of squarks and sleptons, predicted by supersymmetric generalizations of the standard model and dubbed Q balls [15], are also expected to be highly penetrating and to have a flux of $\sim 1.25 \times 10^3 Q_B^{-3/4}(1 \text{ TeV}/m)$ cm^{-2} s^{-1} if they play a significant role as galactic dark matter [32]. Their mass, m, is assumed to be in the 0.1–100 TeV range, and their baryon number must respect $Q_B > 10^{15}$ ($m/1$ TeV)^4. Their stopping power in matter of density ρ should be $\sim 10^4 \frac{\rho}{1 \text{ g/cm}^3}$ keV/μm, but the energy loss mechanism depends on their being charged or neutral [32]. Here it is conservatively assumed that only charged Q balls are able to provide a dense enough energy transfer to form fullerenes. In that case, a modest reduction in ε would bring about a challenge to the Q ball sensitivity of large underground detectors such as super-Kamiokande (surface area $= 7.5 \times 10^7$ cm^2).

Stable or metastable condensates of up, down, and strange quarks (a.k.a. strange quark matter or "nuclearites"), with mass numbers ranging from small nuclei to neutron stars ($A \sim 10^{56}$), may constitute the ground state of hadronic matter [14,33]. If they make up an important fraction of the galactic dark matter halo, their local

flux should be $\Phi_{SDM} = 6 \times 10^5 A^{-1}$ [14]. Their stopping power in rock [$4 \times 10^{-6} A^{2/3} (\frac{v}{300 \text{ km/s}})^2$ keV/μm for $A > 10^{15}$] is so enormous that the associated shock wave could in some cases create a visible scar of melted material, an "astroblem" [14] (for large A the electronic and nuclear temperatures in the shock wave are assumed to balance out, making S_e a sizable fraction of the total stopping power). An interesting peculiarity of the method proposed here becomes evident in searches for nuclearites: Other techniques (mica, plastic track detectors, scintillators) rely on the principle "one particle, one event," and therefore their flux limits are blind to the value of A (i.e., of S_e). In contrast to this, Eq. (4) improves as $A^{-2.1 \times (2/3)}$ for nuclearites. Keeping in mind that $\Phi_{SDM} \propto A^{-1}$, this means that a negative C_{60} search could, in principle, exclude nuclearites as the galactic dark matter for *all* values $A > 10^{13}$ ($A > 10^{25}$ being not yet ruled out). Needless to say, this ability is maimed by the second term in Eq. (4). All the same, such a search can immediately improve the existing sensitivity to these particles (a limit of $\Phi < 10^{-20}$ for $A > 10^{14}$) by 2 orders of magnitude after processing a realistic $M \sim 100$. The possibility that lighter aggregates of strange matter ("strangelets") may reach deeply into the atmosphere [34], a hypothesis put forward to explain several anomalous ("Centauro") events in detectors, can also be tested in this way (strangelet stopping power in rock is expected to weigh in at $\sim 3.5 \times 10^4$ keV/μm [14]).

In conclusion, an ubiquitous abundance of C_{60} in rocks could be the signature of *any* new family of energetic highly ionizing elementary particles. Its absence would allow in most cases to further push existing experimental limits, no small feat given their severity. In view of the incipience of studies of fullerene production by ion beams, our conservative estimates should be taken at face value [e.g., temperature- and material-dependent effects [13,35] can increase the exponent of S_e in Eq. (4), resulting in an enhanced signal-to-(fission)noise ratio for this search]. Irradiations of C-rich rocks to measure the production/recovery of fullerenes are then in order, together with searches for a natural fullerene presence correlated to spontaneous fission of ^{238}U (possibly a new tool in geological dating).

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