Reports

Atmospheric Noble Gases: Solar-Wind Bombardment of Extratrestrial Dust as a Possible Source Mechanism

Abstract. *A source mechanism for the noble gases in the earth's atmosphere may be the solar-wind bombardment of extraterrestrial dust. Calculations based on estimates of recent influx of dust to the earth, quiet solar-wind intensity, argon abundance in the solar wind, and assumed Poynting-Robertson lifetimes of small particles in space agree within a factor of 5 with the present amounts of argon-36 and argon-38 in the atmosphere.*

Aston, Russell and Menzel, Brown, Suess, and others (*1*) have suggested that the earth has lost all, or all but a very small fraction, of its primitive atmosphere. Shklovskii, Cameron, and Signer and Suess (*2–4*) have proposed the possible accretion of part or all of the noble gases (except helium-4 and argon-40, which are believed to result from the radioactive decay of uranium, thorium, and potassium) in the earth's atmosphere by injection and trapping of ions from the solar wind. Urey (*5*) has discussed possible contributions to the earth's atmosphere of primordial krypton and xenon from cometary debris. The efficiency of injection of solar-wind ions into the earth's magnetosphere is unknown, but is expected to be low. The abundance of primordial noble gases in cometary debris striking the earth is uncertain.

I suggest for the noble gases in the earth's atmosphere an additional source mechanism whose intensity can be estimated from available data; this source is solar-wind bombardment of extraterrestrial grains.

The lifetime in the solar system of small particles that are too large to be rapidly removed by radiation pressure is limited by the Poynting-Robertson effect (*6*); the angular momentum of the particles is gradually reduced, thus causing the particles to spiral into the sun. Lifetimes may also be either shortened or lengthened by several other processes (*7–9*). Whipple and Southworth have shown that it is possible to obtain consistent results for the concentration of zodiacal-cloud material (*7*), for the Fraunhofer corona observations (*10*), and for the estimated amount of dust provided by comets (*8*) if a Poynting-Robertson lifetime is assumed. A cometary origin for most meteoric material within the mass interval from 10^{-3} g to 100 g has been established by fragmentation studies (*11*, *12*), orbital distributions (*13*, *14*), and shower associations (*12*, *14*, *15*) of meteors detectable photographically and with radar. However, the relative contributions by asteroidal and cometary sources are not well established for particles smaller than 10^{-3} g. If a major fraction of the smaller particles is also cometary in origin, then the agreement of estimated cometary input with zodiacal-cloud observations suggests, in fact, that the Poynting-Robertson lifetime is a fairly good approximation.

Let us assume that the lifetimes are limited by the Poynting-Robertson effect, which can be calculated analytically, and that the present dust distribution is a steady state. For a particle of radius *r* cm and density ρ g/cm^3, to go from an initially circular orbit of *a* astronomical units (au) into the sun, the time required is

$$\tau = 7 \times 10^6 \rho r a^2 \text{ year} \qquad (1)$$

If the solar wind flux decreases as a^{-2}, and is W_0 atoms cm^{-2} year^{-1} at 1 au, the total number of solar-wind atoms expected to be stopped by the surface of a particle, which started at A_0 au, by the time it reaches 1 au, is given by

$$n = \pi r^2 \int_0^T \frac{W_0}{a^2}\, d\tau =$$

$$14 \times 10^6 \pi W_0 \rho r^3 \int_1^{A_0} \frac{da}{a} \qquad (2)$$

The number of embedded solar-wind atoms per gram of particles is given by

$$N = 3n/4\pi r^3 \rho = 1.05 \times 10^7\, W_0 \ln A_0 \quad (3)$$

Thus if a mass of *M* g cm^{-2} year^{-1} of extraterrestrial debris arrives at the earth from an average distance of A_0 au, it contributes

$$1.05 \times 10^7\, W_0 M \ln A_0 \qquad (4)$$

atoms of solar-wind material per square centimeter per year to the earth. This expression does not depend on our knowing either the size distribution or the density of the extraterrestrial material—a convenient simplification.

The larger and higher-velocity particles, which melt and ablate during entry, may immediately contribute essentially all of their stopped solar-wind gases to the atmosphere. Whipple (*16*) showed that sufficiently small micrometeorites may survive atmospheric entry without melting. However, because the solar-wind gases will be concentrated close to the surfaces of incoming particles, even very small grains may undergo sufficient surface heating to lose most of their solar-wind gases to the atmosphere; any gases retained should be released in moderate times by weathering and the geologic cycle. In the absence of an atmosphere early in the earth's history, the hypervelocity impacts of the particles on the earth should have vaporized the particles and released their gases. Thus, regardless of the size, velocity, or composition of incoming particles, and regardless of the presence of a preexisting atmosphere, incoming extraterrestrial dust may be expected to deposit most of its solar-wind-accreted volatiles in the atmosphere.

I shall now attempt a quantitative estimate of influx of a particular gas into the atmosphere by this mechanism; I choose argon-36 and argon-38 for the following reasons:

1) There is general agreement that argon cannot have been lost from the earth's atmosphere throughout most of the earth's history. The amount of

argon-40 in the atmosphere, accumulated from the decay of potassium-40 in the earth, is itself direct evidence of at least major retention of argon. This evidence gives an independent experimental confirmation of the difficulty of argon loss from the atmosphere throughout most of the earth's history. Thus estimates of argon retention do not depend only on calculations of exospheric escape, although these calculations also clearly indicate the improbability of major escape of argon.

2) The ratios of argon to helium have been determined separately in planetary nebulae and hot stars (*17*), with good agreement for the average values; agreement is less satisfactory for ratios of neon to helium and neon to argon.

3) Although there are no observational data on the isotopic abundance of argon in the sun or in any other star, theoretical predictions (*18*) suggest that the ratio of argon-40 to argon-36 is about 10^{-4} in stellar objects. Therefore most solar argon is expected to be argon-36 and argon-38.

4) Merrihue (*19*) discovered small amounts of excess argon-36 and argon-38 in magnetic material from deep-sea sediments. He suggested solar-wind bombardment of extraterrestrial dust as one of the possible sources of noble-gas isotopic anomalies in the material. Tilles (*20*) has confirmed the argon observations in sea sediments and observed the presence of similar argon anomalies in a dense fraction of particulate matter from Greenland ice. In each instance, the ratio of excess argon-36 to excess argon-38 is similar to that in atmospheric argon. Each of the samples mentioned, from locations with very low accumulation rates of terrestrial particles, may contain significant amounts of extraterrestrial material.

5) The diffusion constants of argon are generally very much lower than those of either helium or neon, so that argon is far less likely than the light gases to have diffused from the dust grains in space before arrival at the earth.

Available solar wind measurements (*21*) suggest a quiet flux of about 2×10^{8} protons per square centimeter per second ($\sim 6 \times 10^{15}$ protons cm^{-2} year^{-1}), a flux of alpha particles with velocities similar to those of the protons, and an alpha-particle abundance of the order of 5 percent. Using the observed ratio of helium to argon [2.5×10^{4} (*17*)] in hot stars and nebulae, assuming the same abundance in the sun, and assuming no fractionation of the solar wind with respect to this abundance, we have a solar-wind argon flux at 1 au of $W_0 = 12 \times 10^{9}$ atom cm^{-2} year^{-1}.

Estimates of accretion of extraterrestrial dust vary widely. Let us assume as an influx rate the figure of 2×10^{-7} g cm^{-2} year^{-1} obtained by Langway (*22*), which was based on collections of very large volume in a very clean environment. It was based, moreover, only on observation of dark magnetic spherules, and therefore may significantly underestimate influx rates because it does not include any water-soluble compounds, silicates, or volatile compounds that may have vaporized during entry into the atmosphere. Van de Hulst (*10*), on the basis of the diffraction of coronal light by small particles during eclipses, has estimated the space density of small particles near 1 au as 5×10^{-21} g cm^{-3}; from this figure one may estimate the expected mass of material intercepted per year by the earth and have satisfactory agreement with the figure already mentioned.

Next, we must select a starting point for the dust-particle orbits; a reasonable guess may be 3 au on the average. Much of the dust and debris lost from comets should originate in the inner solar system, and fine dust from the asteroid belt will also originate near 3 au. Because of the logarithmic dependence of Eq. 4 on A_0, the choice of starting point is not critical.

Finally, we assume a time for accumulation of the terrestrial atmosphere of about 4.5×10^{9} years. Substituting in Eq. 4 and multiplying by this time, we obtain 1.25×10^{20} atoms of argon per square centimeter, or 4.6 cm^3 of argon per square centimeter over the earth's surface at standard temperature and pressure. As I have mentioned, theoretical predictions suggest that this should be mainly argon-36 and argon-38. The current atmospheric abundance of argon-36 and argon-38 is 21 cm^3 per square centimeter of the earth's surface at standard temperature and pressure.

Thus, bombardment of small grains by the current quiet-time solar wind appears to be capable of accounting for about 20 percent of the argon-36 and argon-38 in the atmosphere. Taking into account the higher solar-wind values already observed during geomagnetic storms and periods of great solar activity may increase the 20-percent figure. Furthermore, it is quite possible that the influx rates of dust and debris were higher during earlier periods of the earth's history. The expected ratio of silicates and volatiles to magnetic material in extraterrestrial dust is uncertain; it may well be much greater than 1, and thus further support this mechanism as a source. Considering the uncertainties in (i) average solar-wind flux during the life of the earth, (ii) argon abundance and isotope ratios in solar wind, and (iii) present and past influx rates of dust, the agreement is remarkably close. It is interesting that this estimated source strength is more than four times as strong as the solar wind that would be intercepted by the geometric cross section of the earth with 100 percent efficiency if there were no magnetosphere.

It is also useful to estimate the maximum contribution by meteoritic ablation material to gases of the earth's atmosphere. Hodge *et al.* (*23*) estimate 10^{4} tons of meteoritic ablation material over the earth per year from meteorites larger than 1 g. The highest concentrations of argon observed in gas-rich meteorites (*4, 23*) are lower by more than three orders of magnitude than those already derived. The extremely gas-rich meteorites are certainly less than a tenth of the total meteoritic influx; this source is thus totally negligible when compared with solar wind in small grains, being less than 10^{-6} of our estimates.

Contributions to the atmosphere of radiogenic helium-4 and argon-40 from meteoritic or "cosmic" uranium, thorium, and potassium abundances, accumulated during the entire history of the solar system, seem unimportant when compared with the solar-wind contributions of helium, argon-36, and argon-38, even if they are quantitatively retained in the grains of dust through this entire period.

Since data on the amounts of krypton and xenon in the sun and stars are totally lacking, and the magnitude of possible mass fractionation between the sun and the solar wind is also unknown, it is not considered useful to make direct estimates of the source strength for these gases. However, on the basis of meteorite measurements it may be argued that atmospheric abundances of xenon may be consistent with this source mechanism.

Most of the gas-rich meteorites (*4, 24*) have a ratio of argon-36 to xenon equal to or greater than that in the present atmosphere. The gas-rich meteorites may have acquired their gases from the solar wind (*25*); those with the highest concentrations of helium, neon, and argon should then have ratios of argon to xenon most closely reflecting the solar wind. The meteorite with the greatest abundances of helium, neon, and argon is Fayetteville; its ratio of argon-36 to xenon measures from about 500 to 900, whereas the atmospheric value for this ratio is about 350. If solar-wind gases having the Fayetteville ratio of argon-36 to xenon had been embedded in small grains from which some of the argon had diffused in space, the present relative abundances of argon-36 and xenon in the atmosphere could be reproduced.

If no neon were lost from the grains in space, this source mechanism would provide a surplus of neon. The need for great depletion of neon exists in one form or another with all source mechanisms proposed for the noble gases in the atmosphere (*1, 3*); the source discussed here is no exception.

Depletion may have resulted from corpuscular heating of the atmosphere, if the earth's magnetic field was frequently much weaker than it is now. The evidence for field reversals of the earth, with a time scale of about 10^6 years, is quite strong (*26*). However, if additional atmospheric heating during periods of little or no magnetic field is insufficient to provide an adequate escape rate for helium, it could not have caused major loss of neon (*27*).

Perhaps the most promising way to account for the required depletion of neon is to assume that, at the temperature of the grains in space, helium and neon have substantially higher diffusion constants than has argon; such differences almost surely exist. The large (many orders of magnitude) differences in apparent room-temperature diffusion constants of both helium and neon relative to argon, which have been observed in meteorites (*28*), seem quite consistent with the loss of a large fraction of the neon and retention of a large fraction of the argon while the dust grains are in space. Since the detailed composition and structure of the extraterrestrial material are unknown, the diffusion constants of noble gases near or below room temperature are very poorly determined, and solar wind abundances are also uncertain, one cannot say whether differential diffusion is in fact quantitatively adequate to account for the necessary depletion and the observed isotope ratios. However, this source appears to provide a mechanism for neon depletion that does not contradict the currently available, uncertain, observational evidence.

Loss of helium-4 from the surfaces of the grains in space is probably great. With the solar-wind parameters previously used, and assuming no loss of helium from the grains while in space, we would calculate a helium-4 influx from this source of the order of 7×10^{14} atom $\text{cm}^{-2}\text{yr}^{-1}$. This figure is about an order of magnitude greater than the estimated flux of radiogenic helium-4 into the atmosphere (*29*); this estimate itself is quite uncertain. In view of the severe uncertainties concerning the actual loss of helium from the grains in space, I shall not discuss the effect of expected contributions of helium from this source upon the apparent discrepancies between inventory, production, and escape rates of helium-4 (*27*).

If the contemporary ratio of helium-3 to helium-4 in the solar wind is as high as the ratio measured in gas-rich meteorites (about 3×10^{-4}), and if some helium is retained, this source could provide an important amount of the helium-3 in the atmosphere, with little effect on the atmospheric abundance of helium-4. This might help to bring into closer agreement the escape conditions apparently required for helium-3 and helium-4.

The estimated contribution of nitrogen to the atmosphere by this solar-wind mechanism is about 0.1 percent of atmospheric nitrogen (*30*). The complexities of the chemically active gases in the earth, in the atmosphere, and in the extraterrestrial dust, and the uncertainties in chemical composition of the dust, restrict my discussion of the possible contributions by extraterrestrial dust to these gases. Such contributions may be important for some gases.

Other inner planets (Mars and Venus, for example) also should have received noble gases from this source. The expected source strength is proportional to the planet's geometric cross section and to the dust intensity at the orbit of the planet. The strength could possibly be modified by differing amounts of diffusive fractionation corresponding to the different final distances from the sun of the dust grains at the orbit of the planet. However, the observability of contributions from this source compared with those from others depends on the existence and completeness of the planet's loss of atmosphere early in the history of the solar system.

In summary, a new source of atmospheric noble gases is proposed, consisting of bombardment by solar wind of fine-grained dust and particles in space which later arrive at the earth. The source intensity is calculable; its strength, if Poynting-Robertson particle lifetimes are assumed, depends only weakly or not at all on several of the unknown quantities of interest. There is fair agreement between the estimated source strength of argon and the present atmospheric abundances of argon-36 and argon-38. A mechanism for neon depletion is required; this may be diffusive losses from the surfaces of the dust grains in space. The source strength does depend directly on (i) overall solar-wind intensity, which has been fairly well determined already over part of the solar cycle; (ii) solar-wind abundances of the noble gases and their isotopes, which are not yet directly determined; (iii) total influx of extraterrestrial material to the earth; (iv) particle lifetimes in space; and (v) noble-gas loss rates from the grains in space. As the values for these quantities are refined, it should be possible to ascertain more precisely the relative importance of this source of the atmosphere's noble gases in comparison with other sources.

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Vanillin, Cis-Terpin Hydrate, and Cis-Terpin as Ice Nucleators

Abstract. *Vanillin,* cis-*terpin hydrate, and* cis-*terpin cause ice nucleation at relatively high threshold temperatures. Trace quantities of these substances should exist in the natural atmosphere and may act as ice nuclei.*

Many organic crystalline substances can nucleate ice formation in supercooled water (*1*), and some act at relatively high threshold temperatures, for example, α-phenazine at −3.5°C, *l*-leucine at −4.5°C.

We have tested, for nucleating activity, a number of crystalline organic compounds which occur among essential oil substances. Testing was done in a 110-liter cold box. Small crystals of the test substances were allowed to settle onto a supercooled soap film suspended in the box. Any ice nucleation produced is readily observed from the rapid formation and growth of ice crystals in the film (*2*).

Vanillin crystals (recrystallized from water) act as ice nuclei on the soap film at a threshold of −4.5°C; when obtained by recrystallization from ethyl alcohol, the ice nucleation temperature is reduced to −6°C. Sublimed vanillin crystals act at −9°C. It is interesting that vanillin is produced photochemically by the action of ultraviolet light on vapors of isoeugenol, presumably through oxidation of the isoeugenol by ozone produced by the radiation (*3*).

Terpin hydrate shows a threshold temperature of action of −3.5°C on a soap-film detector. However, crystals supported on a glass slide in the cold chamber show no overgrowth of ice crystals above −6°C, and they act at this temperature only when exposed in a cloud of supercooled droplets.

When terpin hydrate is heated it loses water at 100°C and sublimes. The sublimed crystals have a melting point of 103°C and are presumably anhydrous *cis*-terpin. We find that sublimed terpin crystals nucleate a soap film at −2.5°C. Since *cis*-terpin readily absorbs water to re-form terpin hydrate, it is an interesting point whether the sublimed crystals act in the anhydrous form or as the hydrate to freeze the water.

The following substances were found to be inactive above −11°C: thymol, benzyl cinnamate, cinnamic alcohol, and terpineol.

Went (*4*) has estimated the mass of essential oils released annually by the biosphere to the atmosphere at 1.5×10^{11} kg. Two of the most widely distributed substances among the essential oils are the terpenes dipentene (*dl*-limonene) and α-pinene (*5*). Dilute mineral acids readily convert these substances into terpineols, terpinolene, terpin hydrate, cineole, and a number of other substances, depending on the exact conditions of the reaction, such as temperature, acidity, agitation, and others (*5*).

The oxidation of SO_2, a constituent of the natural atmosphere, to SO_3 can proceed either photochemically (*6*) or in solution in cloud droplets (*7*). The bulk of the resulting H_2SO_4 is apparently neutralized rather quickly by traces of atmospheric ammonia. However, the *p*H of rain water is 4 to 6 (*8*), and cloud droplets may likewise be assumed to be acidic. When cloud droplets evaporate the *p*H will fall sharply, so that in theory trace quantities of crystalline reaction products could be formed from pinene, dipentene, and other plant vapors adsorbed onto acidic cloud droplets and condensation nuclei in the atmosphere.

We have exposed drops of 10 and 25 percent H_2SO_4 to saturated atmospheres of both pinene and dipentene at room temperature and at −5°C. Very small quantities of crystalline reaction products are quite readily produced, but we have not positively identified them.

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