



Carbon Monoxide: Residence Time in the Atmosphere

Author(s): Bernard Weinstock

Source: *Science*, New Series, Vol. 166, No. 3902 (Oct. 10, 1969), pp. 224-225

Published by: American Association for the Advancement of Science

Stable URL: <http://www.jstor.org/stable/1727180>

Accessed: 28/08/2008 13:50

---

Your use of the JSTOR archive indicates your acceptance of JSTOR's Terms and Conditions of Use, available at <http://www.jstor.org/page/info/about/policies/terms.jsp>. JSTOR's Terms and Conditions of Use provides, in part, that unless you have obtained prior permission, you may not download an entire issue of a journal or multiple copies of articles, and you may use content in the JSTOR archive only for your personal, non-commercial use.

Please contact the publisher regarding any further use of this work. Publisher contact information may be obtained at <http://www.jstor.org/action/showPublisher?publisherCode=aaas>.

Each copy of any part of a JSTOR transmission must contain the same copyright notice that appears on the screen or printed page of such transmission.

---

JSTOR is a not-for-profit organization founded in 1995 to build trusted digital archives for scholarship. We work with the scholarly community to preserve their work and the materials they rely upon, and to build a common research platform that promotes the discovery and use of these resources. For more information about JSTOR, please contact [support@jstor.org](mailto:support@jstor.org).

cloud, a variation in radial velocity should be observed on a time scale determined by the orbital period, whereas, for a distributed cloud such as a ring, this would not be the case. The high-velocity features in the W49 spectrum suggest that a cloud with an orbital velocity greater than 100 km/sec would have an orbital period of a few days for a central mass of 1 solar mass and a few years for 100 solar masses. No appreciable shift in radial velocity of the features with high negative velocities in the W49 spectrum has been observed over 2 months' time, an indication that the central mass is probably larger than 10 solar masses if these features are associated with discrete clouds in orbital motion.

S. H. KNOWLES, C. H. MAYER  
W. T. SULLIVAN III

*E. O. Hulburt Center for  
Space Research, Naval Research  
Laboratory, Washington, D.C. 20390*

A. C. CHEUNG

*Department of Physics,  
University of California,  
Berkeley 94720*

#### References and Notes

1. A. C. Cheung, D. M. Rank, C. H. Townes, D. D. Thornton, W. J. Welch, *Nature* **221**, 626 (1969).
2. S. H. Knowles, C. H. Mayer, A. C. Cheung, D. M. Rank, C. H. Townes, *Science* **163**, 1055 (1969); erratum, *ibid.* **164**, 57 (1969).
3. J. Eilder, B. Rönnäng, A. Winnberg, *Nature* **222**, 67 (1969).
4. M. L. Meeks, J. C. Carter, A. H. Barrett, P. R. Schwartz, J. W. Waters, W. E. Brown III, *Science* **165**, 180 (1969).
5. M. S. Cord, J. D. Petersen, M. S. Lojko, R. H. Haas, Eds., *Microwave Spectral Tables (Nat. Bur. Stand. Monogr. 70)* (1968), vol. 4, p. 359.
6. H. Blyussen, A. Dymanus, J. Verhoeven, *Phys. Lett.* **24A**, 482 (1967).
7. E. Raimond and B. Eliasson, *Astrophys. J.* **155**, 817 (1969).
8. H. Weaver, N. H. Dieter, D. R. W. Williams, *Astrophys. J. Suppl.* **16**, 219 (1968).
9. N. H. Dieter, *Astrophys. J.* **150**, 435 (1967).
10. B. Eliasson and J. F. Bartlett, *ibid.* **155**, L79 (1969).
11. M. M. Litvak, A. L. McWhorter, M. L. Meeks, H. J. Zeiger, *Phys. Rev. Lett.* **17**, 821 (1966).
12. Work at the University of California supported in part by NASA. We are grateful to Drs. C. H. Townes and D. M. Rank for valuable discussions and critical comments. We thank J. W. Boland, A. L. Branning, J. H. Nichols, and J. V. Statnick for their assistance with the observations and apparatus. We are grateful to Dr. H. Weaver and the staff of the Radio Astronomy Laboratory at Berkeley for providing calculations of Doppler velocities with respect to the local standard of rest.

20 May 1969

## Carbon Monoxide: Residence Time in the Atmosphere

**Abstract.** *A lower limit of 0.1 year for the residence time of carbon monoxide in the atmosphere is derived from radiocarbon measurements. The action of certain microorganisms and atmospheric photochemical reactions are possible mechanisms for the removal of carbon monoxide. This value can be compared with 2.7 years, a value deduced from estimated rates of carbon monoxide production and global measurements of atmospheric concentrations of carbon monoxide.*

Carbon monoxide was first reported in 1949 to be a minor constituent of the atmosphere by Migeotte (1), who assigned certain lines in the 4.7- $\mu$ m region of the solar spectrum to atmospheric carbon monoxide. Bates and Witherspoon (2) estimated that the life of carbon monoxide in the atmosphere is less than 4 years. This estimate was based on a production rate for CO in 1951 of  $8 \times 10^{17}$  molecule  $\text{cm}^{-2}$  year $^{-1}$  ( $1.9 \times 10^{14}$  g year $^{-1}$ ) and a global concentration of 0.1 part per million (the lower of two values observed by Migeotte and Nevin in Switzerland) (3). Although these considerations suggested to them that CO was not accumulating in the atmosphere, they did not feel that the removal mechanism could be identified with certainty at that time.

Of the particular removal mechanisms for CO that they considered, the

action of soil bacteria [in particular, *Bacillus oligocarpophilus* (4)] and the observations of Jones and Scott (5) were deemed the most significant, although the data were not suitable for quantitative analysis. (Jones and Scott, in studying the disappearance of carbon monoxide from sealed-off mine shafts after a coal mine fire, found that many materials from the mine or its vicinity were capable of removing carbon monoxide from air.) A more recent estimate of the lifetime of CO in the atmosphere has been made by Robinson and Robbins (6) who followed the approach of Bates and Witherspoon (2). They estimated the global CO production to be  $2.1 \times 10^{14}$  g year $^{-1}$  in 1966 and the average atmospheric concentration to be 0.1 ppm (based on recent atmospheric measurements in remote areas). They derived a residence time for CO of 2.7

years in agreement with the previous estimate. I report here an independent method for estimating the lifetime of CO in the atmosphere that is related to the radiocarbon-dating method.

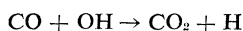
The radiocarbon-dating method (7) is based on the production of  $^{14}\text{C}$  in the atmosphere by the reaction  $^{14}\text{N}(n,p)^{14}\text{C}$  and the subsequent formation of radioactive  $\text{CO}_2$ . Measurements of the  $^{14}\text{C}$  content of samples from the terrestrial biosphere and of contemporary shells, which were independent of latitude and longitude (8), indicated that this radioactive  $\text{CO}_2$  is uniformly distributed over the surface of the earth. That  $^{14}\text{C}$  was in a steady state in nature was indicated by the fact that the specific activity of  $^{14}\text{C}$  measured in living things agreed with that calculated from the  $^{14}\text{C}$  formation rate and the global carbon inventory (9). The success of this method for dating is well established (10).

However, in proposing the method, Libby assumed that the radioactive  $^{14}\text{C}$  atoms would become  $\text{CO}_2$  within a few hours after their formation. Subsequently, Pandow *et al.* (11) studied the chemical fate of  $^{14}\text{C}$  produced in an atomic reactor in the presence of air and found that it was principally fixed as CO. They confirmed this result with  $^{11}\text{C}$  produced in a heavy ion accelerator (12), where the possibility that the radioactive CO might have been produced in the reactor experiment by radiation decomposition was eliminated. Thus, if  $^{14}\text{C}$  is initially fixed as CO, the rate of conversion of radioactive CO to radioactive  $\text{CO}_2$  provides an independent method for determining the lifetime of CO in the atmosphere. MacKay *et al.* did, in fact, report measurements of the specific activity of atmospheric CO (12) from which the lifetime of CO can be estimated.

In collaboration with L. C. Matsch, they separated three samples of atmospheric CO from liquefied air produced by the Linde Air Products Company in their South Buffalo plant between 21 January and 7 March 1960. The sampling periods comprised 1 to 3 weeks and gave results for the  $^{14}\text{C}$  specific activity of +9.3, -39.3, and -27.9 percent deviation relative to the 95 percent deviation of an oxalic acid sample (National Bureau of Standards) defined as zero age in 1955. The CO content of the air was approximately 0.3 ppm. Although they expected the specific activity of atmospheric CO to

be much greater than that of CO<sub>2</sub>, the data are nevertheless consistent with a relatively short lifetime for CO and with dilution of the radioactive CO by CO produced by combustion. If the radioactive CO is uniformly distributed in the atmosphere like radioactive CO<sub>2</sub>, then we can derive the content of radioactive CO in the atmosphere. If we take the average specific activity of the South Buffalo samples to be 12.3 disintegrations min<sup>-1</sup> g<sup>-1</sup> and the decay constant of <sup>14</sup>C to be 9.6 × 10<sup>12</sup> disintegrations min<sup>-1</sup> g<sup>-1</sup>, the ratio of radioactive CO to stable CO in the samples is 1.3 × 10<sup>-12</sup>. If we use 0.3 ppm for the atmospheric concentration of radioactive CO for these samples, the global concentration of radioactive CO is then 4 × 10<sup>-13</sup> ppm. The mass of the atmosphere is 5 × 10<sup>21</sup> g, which gives 1 kg for the mass of <sup>14</sup>C in the atmosphere as CO. If we assume that the removal mechanism for CO is first-order with respect to CO and that the radioactive CO in the atmosphere is in a steady state, the effective rate constant for the removal of radioactive CO is then 3 × 10<sup>-7</sup> sec<sup>-1</sup> (the rate of formation of <sup>14</sup>C is 1.3 × 10<sup>19</sup> atom sec<sup>-1</sup>) (9). The lifetime of CO in the atmosphere is then 3 × 10<sup>6</sup> seconds or 0.1 year.

This value is probably too low, because radioactive CO, which is principally produced in the stratosphere, may be converted to radioactive CO<sub>2</sub> in significant amounts before it mixes into the troposphere. The same process would have a much smaller effect on the CO produced by combustion on the earth's surface because in that case the total removal would be limited by mass transport of the larger quantity of CO from the troposphere to the stratosphere. A likely process for the conversion to CO to CO<sub>2</sub> in the stratosphere is the reaction (2)

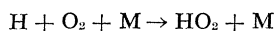


The same reaction could be an effective mechanism for the removal of CO, in the troposphere, but Bates and Witherspoon did not consider it likely. If we assume that CO is in a steady state at a concentration of 0.1 ppm in the atmosphere, we can calculate the concentration of OH required to maintain the steady state from

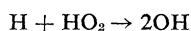
$$[\text{OH}] = P/k[\text{CO}]$$

where  $P$  is the rate of CO production (3.5 × 10<sup>4</sup> molecule cm<sup>-3</sup> sec<sup>-1</sup>) de-

rived from Robinson and Robbins's estimate (6) of 2.1 × 10<sup>14</sup> g year<sup>-1</sup> and an atmospheric volume of 4.1 × 10<sup>24</sup> cm<sup>3</sup>, and  $k$  is the second-order rate constant, 2 × 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup> (13). The concentration of OH required to maintain CO at a concentration of 0.1 ppm is then 7 × 10<sup>4</sup> molecule cm<sup>-3</sup>. This is not unreasonably high but could only be realized by a regenerative chain mechanism for OH because of the large amount of CO involved. The following steps coupled with the previous reaction is one possibility:



and



Thus consideration of the data on radioactive carbon provides additional support for a short lifetime for CO in the atmosphere. This should help to dispel further the concern that CO is accumulating in the atmosphere and represents a longtime hazard to human health. A quantitative assess-

ment of the CO removal processes remains to be worked out, but the action of certain microorganisms and of photochemical processes offer reasonable, possible explanations.

BERNARD WEINSTOCK

Ford Motor Company,  
Scientific Research Staff,  
Dearborn, Michigan 48121

#### References and Notes

1. M. V. Migeotte, *Phys. Rev.* **75**, 1108 (1949).
  2. D. R. Bates and A. E. Witherspoon, *Mon. Notic. Roy. Astron. Soc.* **112**, 101 (1952).
  3. M. V. Migeotte, private communication to D. R. Bates.
  4. M. Stephenson, *Bacterial Metabolism* (Longmans, Green, London, ed. 3, 1949).
  5. G. W. Jones and G. S. Scott, *Ind. Eng. Chem.* **31**, 775 (1939).
  6. E. Robinson and R. C. Robbins, *Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants* (Stanford Research Institute project PR-6755, prepared for the American Petroleum Institute, New York, 1967).
  7. W. F. Libby, *Radiocarbon Dating* (Univ. of Chicago Press, Chicago, ed. 2, 1955).
  8. ———, *ibid.*, p. 15.
  9. ———, *ibid.*, p. 7.
  10. F. Johnson, *ibid.*, chap. 7.
  11. M. Pandow, C. MacKay, R. Wolfgang, *J. Inorg. Nucl. Chem.* **14**, 153 (1960).
  12. C. MacKay, M. Pandow, R. Wolfgang, *J. Geophys. Res.* **68**, 3929 (1963).
  13. G. Dixon-Lewis, W. E. Wilson, A. A. Westenberg, *J. Chem. Phys.* **44**, 2877 (1966).
- 11 June 1969; revised 23 July 1969 ■

## Spectrographic Detection of Topographic Features on Mars

**Abstract.** *Observations of the martian carbon dioxide band at 1.05 microns made with a three-channel multislit spectrophotometer indicate gross height variations in the vicinity of Syrtis Major and surrounding desert regions. Syrtis Major appears to be very high with essentially no detectable carbon dioxide above it. The data appear to confirm local trends and, in magnitude at least, the large variations of height found in earlier radar observations. A one-to-one correlation of height with albedo is not evident in the results. Elevated areas are found in both desert and dark regions. In several regions dark areas are associated with relatively steep slopes.*

The question of the relative altitudes of the dark and bright areas on Mars has been hotly debated in recent years. Traditionally the dark areas are considered to be lowlands. This view is based mainly on the idea that they would be warmer and therefore more likely to support the life forms that were thought responsible for the remarkable regenerative property of the dark areas (1). This supposition received some support when the dark areas were in fact generally found to be some 8°K warmer than the bright regions. Others (2) have shown that the temperature variations have little to do with height differences. They assert that temperature is more closely connected with the local surface albedo. They propose that the regenerative

property is a purely mechanical, wind-driven phenomenon and have concluded that the dark areas are probably higher than the bright deserts. Some quantitative evidence for this view has been provided by early radar data (3) as well as by certain observations of cloud phenomena (4). More recently, radar mapping (5) along a narrow belt at 23°N latitude has indicated very large height variations of some 12 km. However, there does not appear to be any obvious correlation between the radar height contour and albedo changes.

We have devised a three-channel, multislit photometer which, together with the 13.4-m spectrometer of the McMath Solar Telescope of Kitt Peak National Observatory, is capable of de-