Chemical effects of large impacts on the Earth's primitive atmosphere

Bruce Fegley Jr, Ronald G. Prinn, Hyman Hartman & G. Hampton Watkins*

Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

Intense bombardment of the moon and terrestrial planets ~3.9-4.0 × 10^{9} years ago[1,2] could have caused the chemical reprocessing of the Earth's primitive atmosphere[3]. In particular, the shock heating and rapid quenching caused by the impact of large bodies into the atmosphere could produce molecules such as HCN and H_2CO[4] which are important precursors for the abiotic synthesis of complex organic molecules[5-7]. Here we model the production of HCN and H_2CO by thermochemical equilibrium and chemical kinetic calculations of the composition of shocked air parcels for a wide range of temperatures, pressures and initial compositions. For atmospheres with C/O ≥ 1, our results suggest that bolide impacts cause HCN volume mixing ratios of approximately 10^{-3} to 10^{-5} in the impact region and global average ratios of 10^{-5} to 10^{-12}. The corresponding H_2CO mixing ratios in the impact region are 10^{-7} to 10^{-9}; no-global mixing can occur, however, as H_2CO is rapidly destroyed or rained out of the atmosphere within days to hours. Rainout to the oceans of 3-15% of the HCN produced can provide ~(3-14) × 10[11] mol HCN per year. This is somewhat larger than other predicted sources of HCN[8] and H_2CO[9] on the primitive Earth.

The atmosphere appeared on Earth very early in its history. Argon and xenon isotope geochemistry[10,11] indicate that the mean age of the atmosphere is 4.4 × 10^{9} yr. The carbonate-bearing sedimentary rocks in the Isua, Greenland supracrustal rocks further suggest the presence of an atmosphere-ocean system 3.8 × 10^{9} yr ago[12]. To evaluate the effects of impacts on this early atmosphere we consider a suite of more than 100 pressure (P) and temperature (T) composition points in the H-C-N-O tetrahedron ranging from chemically reducing to chemically neutral atmospheres, shock pressures from 10^{-3} to 10^3 bar, and shock temperatures from 500 to 5,000 K. Although precise knowledge of the composition of the pre-Archean atmosphere is unavailable, a plausible range of primitive atmosphere compositions can be defined by considering the oxidation states and compositions of present-day volcanic gases, of volcanic gases in equilibrium with metallic iron and of the outgassing from chondritic planets[12-15]. Plausible atmospheres all contain N_2 and small amounts of H_2O in equilibrium with liquid water. Carbon may occur predominantly as CH_4, CO, or CO_2 depending on the assumed oxidation state and H_2 may be present in small amounts conversant with its rapid atmospheric escape.

Thermochemical equilibrium calculations were done using a Gibbs free energy minimization code[16]; thermodynamic data for more than 50 compounds in the H-C-N-O system were taken from standard sources[17,18]. The quenched abundances of HCN and H_2CO in the shock wave were estimated using the relationship

$$t_{chem}(T_Q) \simeq t_{cool}(T_Q) \qquad (1)$$

where t_{chem} is the chemical lifetime of HCN or H_2CO, t_{cool} is the characteristic cooling time of the shock wave and T_Q is the quench temperature. The t_{chem} values for HCN and H_2CO were estimated using kinetic data for the relevant destruction reactions of CN and HCO (see Table 1)[19-27]. This treatment is valid when HCN and CN, and H_2CO and HCO remain in equilibrium (which we verified). Analogous calculations have also been done by previous investigators estimating NO_x production from high

Table 1 Reactions and rate constants used to estimate t_{chem} values for HCN and H_2CO

	Reaction	Rate constant	Source
(1)	$CHO + H \rightarrow CO + H_2$	$6 \times 10^{13} \exp(-2,500/T)$	19
(2)	$CHO + M \rightarrow CO + H + M$	$7 \times 10^{13} \exp(-7,550/T)$	19*
		$2 \times 10^{13} T^{1/2} \exp(-14,000/T)$	
(3)	$CHO + O \rightarrow CO + OH$	3×10^{13}	19
(4)	$CHO + O \rightarrow CO_2 + H$	3×10^{13}	19
(5)	$CHO + OH \rightarrow CO + H_2O$	6×10^{12}	19*
		3×10^{13}	
(6)	$CHO + O_2 \rightarrow CO + HO_2$	3×10^{13}	19*
		$6 \times 10^{12} \exp(-3,650/T)$	
(7)	$H_2CO + H_2 \rightarrow OH + CH_3$	$1.4 \times 10^{14} \exp(-36,200/T)$	21
(8)	$H_2CO + M \rightarrow HCO + H + M$	$4 \times 10^{12} \exp(-18,500/T)$	22†
(9)	$CN + NO \rightarrow CO + N_2$	8.9×10^{12}	20‡
(10)	$CN + NO \rightarrow NCO + N$	$1.0 \times 10^{14} \exp(-21,190/T)$	23
(11)	$CN + CN \rightarrow C_2 + N_2$	$2.5 \times 10^{17} \exp(-48,000/T)$	20*
		$1.6 \times 10^{15} \exp(-21,700/T)$	
(12)	$CN + O \rightarrow CO + N$	1.0×10^{13}	20
(13)	$CN + O_2 \rightarrow CNO + O$	$2.4 \times 10^{13} \exp(-450/T)$	20
(14)	$CN + C \rightarrow N + C_2$	$3.0 \times 10^{14} \exp(-18,000/T)$	20
(15)	$CN + N \rightarrow C + N_2$	$4.4 \times 10^{14} \exp(-4,600/T)$	20
(16)	$HCN + H_2 \rightarrow CH_2 + NH$	$6.5 \times 10^{15} \exp(-70,456/T)$	24
(17)	$HCN + M \rightarrow H + CN + M$	$1.0 \times 10^{16} \exp(-54,650/T)$	25
(18)	$HCN + O \rightarrow NCO + H$	$7.2 \times 10^{13} \exp(-7505/T)$	26

Units for two-body rate constants are $cm^3 \, mol^{-1} \, s^{-1}$.
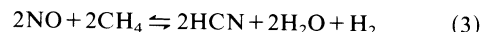* Calculations done with both expressions.
† Also see Bowman[27] for a similar expression.
‡ Average of values given by Baulch *et al.*[20].

temperature shock phenomena (such as nuclear explosions[28-32], lightning discharges[8,33] and large impacts in the atmosphere[34,35]).

The calculated thermochemical equilibrium mixing ratios of important species in the shocked air parcels are illustrated in Fig. 1. These profiles are representative of those obtained by shocking atmospheric compositions which are chemically neutral (Fig. 1a) or chemically reducing (Fig. 1b). The major species produced from a CO_2-rich atmosphere are CO, O_2, H_2 and NO; CO-rich atmospheres yield primarily CO_2, H_2, CH_4, HCN, NH_3 and H_2CO. Graphite precipitation is also possible in CO-rich systems but may be kinetically inhibited if nucleation is slow relative to t_{cool}.

Calculations over a wide range of assumed atmospheric compositions show that the C/O atomic ratio strongly influences the yields of the shock products (see Table 2). Our calculated HCN and NO abundances follow the same pattern first noted by Chameides and Walker[8]. We find that the interconversions between HCN and NO for different major carbon-bearing species are described by the reversible equilibrium reactions:

$$2NO + 2C(gr) + 3H_2 \rightleftharpoons 2HCN + 2H_2O \qquad (2)$$

$$2NO + 2CH_4 \rightleftharpoons 2HCN + 2H_2O + H_2 \qquad (3)$$

$$2NO + 2CO + 5H_2 \rightleftharpoons 2HCN + 4H_2O \qquad (4)$$

$$2NO + 2CO_2 + 7H_2 \rightleftharpoons 2HCN + 6H_2O \qquad (5)$$

The thermochemical equilibrium calculations also show that the HCN volume mixing ratio near T_Q is not sensitive to large changes in the total pressure. It decreases by only two orders of magnitude as P varies from 10^3 to 10^{-3} bar. However, the H_2CO mixing ratio varies as P above the graphite condensation temperature and is pressure independent below this point.

Calculated chemical lifetimes for HCN and H_2CO are compared with the radiative cooling time for the shocked air column in Fig. 2. The HCN quench temperatures vary from 1,560 to 2,100 K depending on the specific HCN destruction reactions. The H_2CO quench temperatures are in contrast <1,110 K. If reaction (2) in Table 1 is relatively fast, H_2CO may remain in equilibrium below 650 K. The corresponding mixing ratios for HCN ($T_Q \approx 1,600$ K) and for H_2CO ($T_Q \approx 1,000$ K) from Fig. 1b are 10^{-4} and 10^{-8}, respectively. For the range of reducing atmospheres studied we calculate HCN mixing ratios of 10^{-3} to 10^{-5} at T_Q and H_2CO mixing ratios of ~10^{-7} to 10^{-9} at T_Q in the impact region.
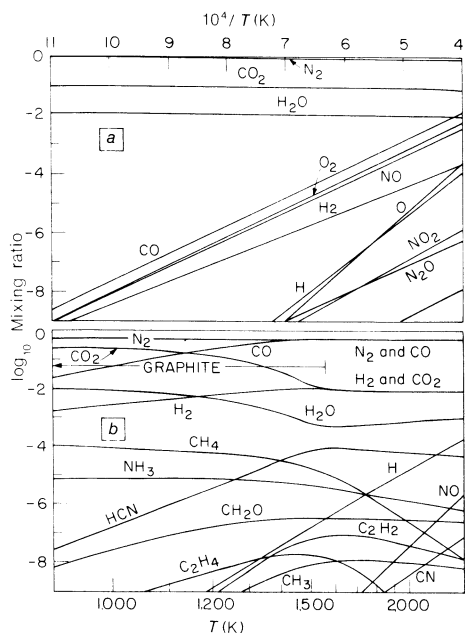
Fig. 1 Equilibrium abundances of important species in a cooling parcel of shocked air. *a*, Neutral atmosphere of 90% N_2, 9% CO_2, 1% H_2O at a shock pressure of 10 bar. HCN, H_2CO, NH_3 and many other species with mixing ratios $<10^{-9}$ are not shown here. *b*, Reducing atmosphere of 49.5% N_2, 49.5% CO, 1% H_2O at a shock pressure of 100 bar. Graphite precipitation occurs at 1,556 K; it is a major carbon sink by 1,000 K. All hydrocarbons (except C_2H_2 and C_2H_4) have mixing ratios $<10^{-9}$. In both cases increasing dissociation of molecules to radicals, atoms, and ions occurs with increasing temperature.

Fig. 2 Calculated chemical lifetimes for H_2CO (*a*) and HCN (*b*) for the reducing atmosphere shown in Fig. 1*b*. The numbers refer to the reactions in Table 1; reaction 16 has a t_{chem} very similar to those for reactions 12, 13, 15 and is not shown. The radiative cooling time is calculated from the Stefan–Boltzman law. For $T > T_Q$, $t_{chem} < t_{cool}$ and the HCN and H_2CO remain in equilibrium, while for $T < T_Q$, $t_{chem} > t_{cool}$ and the HCN and H_2CO are quenched at their mixing ratios established at $T = T_Q$ where $t_{chem} = t_{cool}$. The T_Q values used for HCN and H_2CO in our discussion are 1,600 K and 1,000 K respectively. However, H_2CO may remain in equilibrium below ~650 K if reaction (2) is fast.

Globally averaged HCN mixing ratios were estimated using a simple model developed to describe NO_x production by the putative Cretaceous/Tertiary impactor[34]. We take the HCN production efficiency as 10^7 molecules erg^{-1} (for a $CO + N_2$ atmosphere) from Chameides and Walker[8]. This efficiency is strongly composition-dependent ranging from ~10^{10} molecules erg^{-1} ($CH_4 + N_2$) to ~10^3 molecules erg^{-1} ($CO_2 + N_2 + H_2O$)[8]. From Lewis *et al.*[34] we take the energy deposited in the atmosphere by a 10^{17} g metal-rich impactor (vertical entry angle ~12 kms^{-1}) as ~$10^{25.8}$ erg and the energy deposition by a 10^{18} g cometary impactor (grazing entry angle ~65 km s^{-1}) as ~$10^{30.3}$ erg. The estimated HCN yields are in the range of 10^{33}–10^{37} molecules per impact and the fraction of the atmosphere shocked per impact is in the range 10^{-8}–10^{-3} (assuming HCN mixing ratios of ~10^{-3} to 10^{-5} at T_Q and the present atmospheric mass of 5.1×10^{21} g). Corresponding globally-averaged HCN and H_2CO mixing ratios would be from 10^{-5} to 10^{-12} and from 10^{-10} to 10^{-16}, respectively. However, these globally-averaged values are relevant only if the chemical lifetimes of the species are longer than the global atmospheric mixing time of 1–3 yr.

Several potential loss mechanisms for HCN and H_2CO are possible; we qualitatively discuss these by analogy with these processes in the present-day terrestrial atmosphere. Precipitation can transport HCN and H_2CO to the primitive oceans where abiotic syntheses of complex organic molecules may occur[5-7,12]. Cicerone and Zellner[36] deduced that HCN has a long rainout lifetime of about 34 yr; H_2CO is much more soluble (it polymerizes in aqueous solution) and has a rainout lifetime[37] of about 10 days. Both species are also destroyed by solar ultraviolet photolysis and by reaction with OH. The HCN and H_2CO chemical lifetimes in the present day atmosphere are ~1-5 years[37] and ~3 hours[38], respectively. However, the latter value refers to the sunlit troposphere at 30° N and at noon; a diurnal average is probably 3-4 times longer. These general considerations suggest that isolated impacts are a negligible global H_2CO
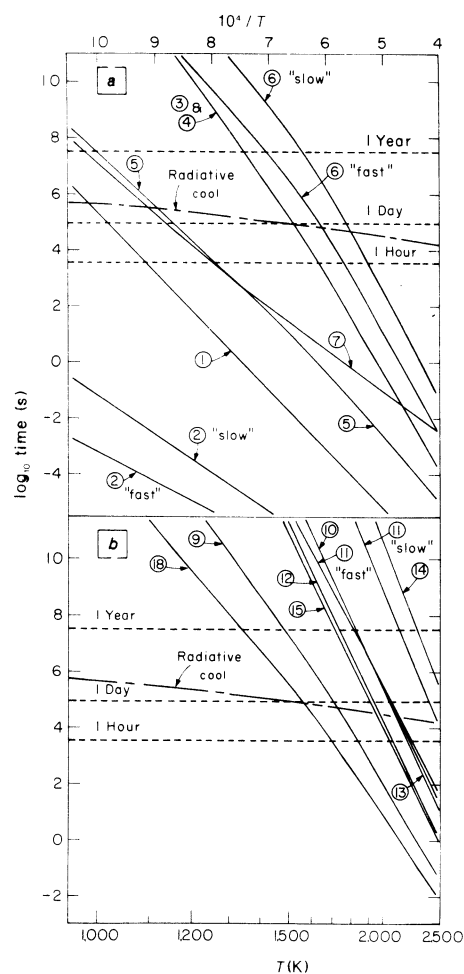
source relative to possible photolytic sources[y]; only small, temporally and spatially localized production may occur. However, these considerations are consistent with a significant global source of HCN from isolated impacts.

To a first order, 1/34 to 5/34 of the HCN produced in a single impact event will be rained out of the atmosphere based on the lifetimes quoted above. Taking the present globally averaged rainfall rate[37] of 3.3×10^{-6} g cm^{-2} s^{-1}, a Henry's law constant[36] of 4×10^3 and a HCN global mixing ratio of 10^{-6} we derive a HCN rainout rate of 3 to 14×10^{11} mol yr^{-1}. This is somewhat larger than predicted H_2CO (from photolysis)[9] and HCN (from lightning)[8] rainout rates on the primitive Earth of ~10^{11} mol yr^{-1}.

Impactor fluxes on the primitive Earth are not well constrained. However, a few large impacts every 1-5 yr will maintain the globally averaged HCN mixing ratios and rainout rates calculated above. More frequent impacts will lead to increasing HCN abundances.

Table 2 Equilibrium mixing ratios of HCN, NO and H_2CO for different assumed atmosphere compositions at 2,000 K and shock pressures of 10 and 100 bar

$p = 10$ bar Starting composition	$\log_{10}$ mixing ratios HCN	NO	H_2CO
44.4% N_2, 44.4% CO, 11.1% H_2*†	−2.6	−9.3	−6.6
14.3% N_2, 57.1% CO, 22.6% CH_4†	−2.6	−9.6	−6.0
9% N_2, 90.1% CO, 1% H_2O	−5.0	−7.5	−7.2
49.5% N_2, 49.5% CO, 1% H_2O	−5.2	−7.0	−7.5
1% N_2, 98% CO, 1% H_2O	−5.4	−8.1	−7.2
70% N_2, 26.4% CO_2, 2.6% CO, 1% H_2O	−9.9	−4.1	−10.4
80% N_2, 17.3% CO_2, 1.7% CO, 1% H_2O	−10.0	−4.1	−10.6
80% N_2, 19% CO_2, 1% H_2O	−12.2	−3.2	−12.3

$p = 100$ bar Starting composition	$\log_{10}$ mixing ratios HCN	NO	H_2CO
10% N_2, 80% CO, 10% H_2*	−3.2	−8.8	−6.3
9% N_2, 90% CO, 1% H_2O	−4.0	−8.0	−6.2
49.5% N_2, 49.5% CO, 1% H_2O	−4.1	−7.4	−6.5
1% N_2, 98% CO, 1% H_2O	−4.4	−8.5	−6.2
70% N_2, 26.4% CO_2, 2.6% CO, 1% H_2O	−8.9	−4.6	−9.4
80% N_2, 17.3% CO_2, 1.7% CO, 1%H_2O	−9.0	−4.6	−9.6
80% N_2, 19% CO_2, 1% H_2O	−12.0	−3.4	−11.9

* High H_2 mixing ratio cannot be sustained for long periods. This case is shown for illustrative purposes only.

† Graphite saturated system. This case is shown for illustrative purposes only.

1. Tera, F., Papanastassiou, D. A. & Wasserburg, G. J. *Earth planet. Sci. Lett.* **22**, 1-21 (1974).
2. Wetherill, G. W. *Proc. 6th lunar Sci. Conf.* 1539-1561 (1975).
3. Hochstim, A. R. *Proc. natn. Acad. Sci. U.S.A.* **50**, 200-208 (1963); in *Chemical Evolution and the Origin of Life* (eds Buvet, R. & Ponnamperuma, C.) 96-113 (North-Holland, New York, 1971).
4. Fegley, B., Hartman, H. & Prinn, R. G. *EOS* **63**, 1018 (1982).
5. Oro, J. & Kimball, A. P. *Archs biochem. Biophys.* **94**, 217-227 (1961).
6. Cairns-Smith, A. G. *Genetic Takeover and the Mineral Origins of Life*, 21-31 (Cambridge University Press, 1982).
7. Abelson, P. H. *Proc. natn. Acad. Sci. U.S.A.* 1365-1372 (1966).
8. Chameides, W. L. & Walker, J. C. G. *Origins Life* **11**, 291-302 (1981).
9. Pinto, J. P., Gladstone, G. R. & Yung, Y. L. *Science* **210**, 183-185 (1980).
10. Sarda, P., Staudacher, Th. & Allegre, C. J. *Earth planet. Sci. Lett.* **72**, 357-375 (1985).
11. Staudacher, Th. & Allegre, C. J. *Earth planet. Sci. Lett.* **60**, 389-406 (1982).
12. Holland, H. D. *The Chemical Evolution of the Atmosphere and Oceans* (Princeton University Press, 1984).
13. Holland, H. D. in *Petrologic Studies: A Volume to Honor A. F. Buddington* (ed Engel, A. E. J., *et al.*) 447-477 (Geological Society of America, Boulder, 1962).
14. Gerlach, T. M. & Nordlie, B. E. *Am. J. Sci.* **275**, 353-410 (1975).
15. Lewis, J. S. & Prinn, R. G. *Planets and their Atmospheres Origin and Evolution*, 225-238 (Academic, New York, 1984).
16. Gordon, S. & McBride, B. J. *NASA SP273* (1976).
17. *JANAF Thermochemical Tables* (eds Stull, D. R. & Prophet, H.) NSRDS-NBS-37 (US Government Printing Office, Washington, 1971).
18. Glushko, V. P. *et al.* (eds) *Thermodynamic Properties of Individual Substances* Vols 1-4 (High-Temperature Institute, Moscow, 1978-1982).
19. Baulch, D. L., Drysdale, D. D., Duxbury, J. & Grant, S. J. *Evaluated Kinetic Data for High Temperature Reactions* Vol. 3, 337-361 (Butterworths, London, 1976).
20. Baulch, D. L., Duxbury, J., Grant, S. J., Montague, D. C. *Evaluated Kinetic Data for High Temperature Reactions* Vol. 4, 576-635 (*J. phys. Chem. Ref. Data* **10**, Suppl. 1, 1981).
21. Prinn, R. G. & Barshay, S. S. *Science* **198**, 1031-1034 (1977).
22. Chen, C. J. & McKenney, D. J. *Can. J. Chem.* **50**, 992-998 (1972).
23. Colket, M. B. *Int. J. Chem. Kinet.* **16**, 353-369.
24. Prinn, R. G. & Fegley B. Jr. *Astrophys. J.* **249**, 308-317 (1981).
25. Szekely, A., Hanson, R. K., and Bowman, C. T. *J. phys. Chem.* **88**, 666-668 (1984).
26. Higashihara, T., Salto, K. & Murakami, I. *J. phys. Chem.* **87**, 3707-3712 (1983).
27. Bowman, C. T. *Symp. 15th Int. Combust. Proc.* 869-882 (Combustion Institute, Pittsburgh, 1974).
28. Foley, H. M. & Ruderman, M. A. *J. geophys. Res.* **78**, 4441-4450 (1973).
29. Gilmore, F. R. *J. geophys. Res.* **80**, 4553-4554 (1975).
30. Goldsmith, P., Tuck, H. F. Foot, J. S., Simmons, E. L. & Newson, R. L. *Nature* **244**, 545-551 (1973).
31. Johnston, H., Whitten, G. & Birks, J. *J. geophys. Res.* **78**, 6107-6135 (1973).
32. Zeldovich, Ya. B. & Raizer, Ya. *Physics of Shock Waves and High Temperature Phenomena* Vol. 2, 566-571 (Academic, New York, 1967).
33. Chameides, W. L. *Nature* **277**, 123-125 (1977).
34. Lewis, J. S., Watkins, G. H., Hartman, H. & Prinn, R. G. *Geol. Soc. Am. Spec. Pap. 190*, 215-221 (1982).
35. Park, C. *Acta astronautica* **5**, 523-542 (1978).
36. Cicerone, R. J. & Zellner, R. *J. geophys. Res.* **88**, 10, 689-10, 696 (1983).
37. Giorgi, F. & Chameides, W. L. *J. geophys. Res.* **90**, 7872-7880 (1985).
38. Lowe, D. C. & Schmidt, U. *J. geophys. Res.* **88**, 10, 844-10, 858 (1983).