UC Irvine

UC Irvine Previously Published Works

Title

Oxidation of CS₂ and COS: sources for atmospheric SO₂

Permalink

<https://escholarship.org/uc/item/4mx3n0bk>

Journal

Nature, 281(5728)

ISSN

0028-0836

Authors

Logan, JA
McElroy, MB
Wofsy, SC
et al.

Publication Date

1979-12-01

DOI

10.1038/281185a0

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

magnetic torque induced upon the white dwarf is $T \sim (4\pi/3)B_2r_2^3B_1(r_1/R)^3 \sim 1 \times 10^{37}$, where the subscripts 1 and 2 refer to the primary and to the white dwarf, respectively. The resulting drag force is $F_d = T/R \sim 10^{24}$ dyn, which is the required value. If such coupling is dominant it would imply that SS433 is similar to the model of AM Her suggested by Stockman *et al.*¹⁴. Radio emission can easily arise in the lower regions of the white dwarf magnetosphere, with the X-ray emission being produced by infall onto the stellar surface⁸.

We thank R. L. Brown, J. Liebert, R. O'Connell, S. O'Dell and R. Thompson for helpful discussion, and B. Margon for data. The National Radio Astronomy Observatory is operated by the Associated Universities Inc. under contract with the NSF and Kitt Peak National Observatory by the Association of

Universities for Research in Astronomy Inc. under NSF contract.

Received 21 May; accepted 30 July 1979.

1. Margon, B. *et al. Astrophys. J. Lett.* **230**, L41 (1979).
2. Margon, B. *et al. IAU Circ. No.* 3345 (1979).
3. Liebert, J. *et al. Astrophys. J.* (in the press).
4. Abell, G. O. & Margon, B. *Nature* **279**, 701–703 (1979).
5. Seaquist, E. R. *et al. Preprint* (1979).
6. Terlevich, R. J. & Pringle, J. E. *Nature* **278**, 719 (1979).
7. Fabian, A. C. & Rees, M. J. *Mon. Not. R. astr. Soc.* **187**, 13P (1979).
8. Angel, J. R. A. *Rev. Astr. Astrophys.* **16**, 487 (1978).
9. Liebert, J. *et al. Nature* **279**, 384–387 (1979).
10. Fabian, A. C. *et al. Mon. Not. R. astr. Soc.* **173**, 43 (1976).
11. McGraw, J. *et al. IAU Circ. No.* 3363 (1979).
12. Routh, E. J. *Dynamics of a System of Rigid Bodies*, 340–365 (Dover, New York, 1955).
13. Goldstein, H. *Classical Mechanics*, 182 (Addison, New York, 1950).
14. Stockman, H. S. *et al. Astrophys. J.* **217**, 815 (1977).

Oxidation of CS₂ and COS: sources for atmospheric SO₂

Jennifer A. Logan, Michael B. McElroy, Steven C. Wofsy & Michael J. Prather

Center for Earth and Planetary Physics, Harvard University, Cambridge, Massachusetts 02138

Oxidation of CS₂ and COS initiated by reaction with OH can provide a source of atmospheric SO₂ as large as 12 Mtonnes S yr⁻¹ and may represent the dominant source of SO₂ in remote regions of the marine troposphere.

EMISSION of sulphur associated with combustion of fossil fuel represents a major source of atmospheric pollution^{1,2}, contributing ~65 Mtonnes S yr⁻¹. Although the chemistry of sulphur in polluted atmospheres has been studied extensively, our knowledge of the natural cycle remains rudimentary. Measurements^{3,4} at remote marine locations in the Southern Hemisphere indicate that the atmosphere contains a relatively constant background level of COS and SO₂. We shall argue here that SO₂ is derived at least in part from oxidation of COS, with additional sources due to CS₂ and dimethyl sulphide (DMS).

Sulphurous compounds in the atmosphere

It seems probable that the chemistry of sulphurous compounds in the troposphere should be dominated by reactions involving OH⁵⁻⁷. The hydroxyl radical is formed by reaction of O(¹D) with H₂O, and is removed primarily by reaction with CO and CH₄. Results of model calculations for the concentration of OH are given in Fig. 1. We believe that concentrations shown here should be reliable to within about a factor of 2, and uncertainties of this magnitude should not qualitatively affect the arguments which follow.

Sulphur dioxide may be removed from the atmosphere by various heterogeneous processes⁸, and by gas phase reactions^{5,9} involving OH, HO₂ and CH₃O₂:

and

The products in reactions (2) and (3) have not been measured directly, and these reactions may possibly involve formation of adducts. Reaction (1) has been studied by several groups^{5,10}, using a variety of techniques, and its rate constant is probably known to within about a factor of 2. It constitutes a major, perhaps dominant, path for removal of SO₂. Reaction (3) could be comparable to reaction (1). Considerable uncertainty attaches, however, not only to the mechanism of reaction (3), but also to the concentration of atmospheric CH₃O₂. Reaction (2) is of minor importance.

Studies of SO₂ in polluted air parcels^{11,12} suggest an atmospheric lifetime of about a day. Calculations presented here for the marine atmosphere, using the kinetic data summarised in Table 1 but omitting heterogeneous reactions, indicate a lifetime of about 8 days. The difference may reflect in part the role of heterogeneous chemistry, in part omission of processes in polluted air which might be expected to result in higher concentrations of radicals (RO, RO₂). The calculations presented here were carried out using a one-dimensional photochemical model, as described by Logan *et al.*¹³, with modifications to their chemical scheme as given in Table 1. Vertical profiles for O₃, CO, CH₄ and H₂O were specified using available observational data and calculations were performed for latitudes 45°N, 15°N, 15°S and 45°S.

Significant quantities of SO₂ may be formed during oxidation of COS and CS₂. It appears⁶ that oxidation of COS should be initiated by reaction with OH,

Subsequent steps may involve production and removal of SO:

Rate constants for reactions (5)–(7) have not been determined experimentally. However, it seems reasonable that SH should be oxidised in the atmosphere to SO₂ by reactions (5)–(7) or by some other reaction mechanism. Measurements by Kurylo of the rate constant for reaction (4) and for the corresponding reaction with CS₂ are in conflict with results reported by Atkinson *et al.*¹⁴. Sources of the discrepancies are discussed in detail in ref. 6, and are attributed to complications due to photolysis of COS and to the occurrence of secondary reactions. Kurylo's experiments were performed in conditions designed to minimise these problems and his rate constants have been adopted accordingly. We estimate a global mean lifetime for COS of 200 days. Combining this lifetime with measured concentrations of COS^{4,15}, 0.5 ± 0.1 p.p.b. (parts per 10⁹, by volume) we infer a global destruction rate for COS equivalent to 4 ± 0.8 Mtonnes S yr⁻¹.

Oxidation of CS₂ can provide a significant source of COS^{6,7}, through

Subsequent oxidation of SH, through reactions (5) and (6),

Fig. 1 Altitude profiles for OH and O₃ at 15°S latitude at equinox. *a*, Diurnally averaged concentrations for OH. The model calculations follow the time-dependent variation of short lived chemical species resulting from the diurnally varying radiation field which includes Rayleigh scattering. Calculations are shown for clear sky conditions (A) and a combination of clear sky (70%) and fully reflecting cloud layers at 3 km (17%) and 5 km (13%) (B). Vertical transport is simulated by 'eddy diffusion', with a diffusion coefficient equal to $10^5 \text{ cm}^2 \text{ s}^{-1}$. The chemical model of Logan *et al.*¹³ has been updated as described in Table 1. Fixed profiles for O₃⁴⁸ (see *b*), CO⁴⁹ (0.6 p.p.b.), CH₄⁵⁰ (1.5 p.p.b.) and H₂O (taken from the relative humidity values of Rasmusson⁵¹) were used. The mixing ratio of NO + NO₂ was taken to be 10^{-11} at 0 km, (ref. 52) and a deposition velocity of 1 cm s^{-1} was used for HNO₃. Note that the model implies a value of $1 \times 10^6 \text{ molecules cm}^{-3}$ for the globally averaged concentration of tropospheric OH.

should provide an additional source for SO₂. We estimate a lifetime for CS₂ due to reaction (8) of 60 days. Observational data for CS₂ are sparse, confined to the UK¹⁵, and indicate a range of mixing ratios between 0.07 and 0.37 p.p.b. Sandalls and Penkett¹⁵ point out that their data are consistent with the view that the ocean and atmosphere are in equilibrium with respect to CS₂. Using marine measurements of CS₂ by Lovelock¹⁶, and solubility data by Seidell¹⁷, they inferred an equilibrium concentration for the atmosphere equivalent to 0.22 ± 0.06 p.p.b. We adopt this value for the mixing ratio of CS₂ to represent global mean conditions. Used in conjunction with the chemical model of Table 1 and with the OH data of Fig. 1, it implies a global destruction rate for CS₂ equal to $12 \pm 3 \text{ Mtonnes S yr}^{-1}$. The associated sources for COS and SO₂ are $6 \pm 1.5 \text{ Mtonnes S yr}^{-1}$ and $12 \pm 3 \text{ Mtonnes S yr}^{-1}$ respectively. Note that the source for COS due to oxidation of CS₂ could account for the bulk of atmospheric COS as discussed by Sze and Ko⁷.

Source rates quoted here are directly proportional to values calculated for the concentration of OH. Studies of CH₃CCl₃^{18,19} suggest that concentrations of OH given in Fig. 1 may be too high by about a factor of 2. If valid, this analysis would require corresponding reduction in source strengths inferred for CS₂ and COS. Relative abundances of CS₂, COS and SO₂ in remote locations are comparatively insensitive to details of the chemical model for OH, and provide a useful test of the hypothesis

proposed here, that is, that oxidation of CS₂ and COS might represent dominant background sources of SO₂. Our model predicts concentration ratios CS₂:COS:SO₂ at 6 km of 0.3:1.0:0.13 which may be compared with observed ratios⁴ of 0.44:1.0:0.17. This is a fairly good agreement, when one remembers that the observational data for COS and SO₂ are uncertain to within about $\pm 30\%$, that our value for the concentration of CS₂ was inferred from measurements of dissolved CS₂, and that the temperature dependencies of the rate constants for the key reactions (1), (4) and (8) are not well defined. In our model, one-half of the SO₂ source is derived from oxidation of CS₂, for which observational data are extremely limited. The mixing ratio for COS is fairly well defined and, given the uncertainties in the rate constants for reactions (1), (3) and (4), oxidation of COS alone might provide the major source for background SO₂.

Results and discussion

Calculated height profiles for SO₂ are shown in Fig. 2, which includes comparison with the observations by Maroulis *et al.*⁴ and Nguyen Ba Cuong *et al.*²⁰. We define a standard model, S, characterised by rate constants and parameters summarised in Table 1. Our choice of rate constant for reaction (1) is based on data reported by Castleman *et al.*²¹ and Cox²². In their studies the rate for reaction (1) was measured relative to the rate for reaction of OH with CO. We applied suitable correction to account for the known pressure dependence²³ of OH + CO.

Our standard model assumes that the rate for reaction (1) is independent of temperature. Dependence of results on choice of rate expressions for reaction (1) is shown in Fig. 2*a*, which also includes models allowing modest negative activation energies

Fig. 2 Altitude profiles for SO₂ at 15°S latitude at equinox. The profiles were calculated with the model given in Fig. 1, curve B. The curves labelled S used the standard chemical model of Table 1, with a deposition velocity for SO₂ of 1 cm s^{-1} and a zero-flux boundary condition at the tropopause. The COS mixing ratio was specified at 0.5 p.p.b. Data are from Maroulis *et al.*⁴ (●), aircraft flight over the Pacific Ocean, 0–67° S; and Nguyen Ba Cuong *et al.*²⁰ (x), Indian Ocean cruise, 5–25° S. *a*, The effect of temperature dependent rate constants: curve A, $k_b (\text{OH} + \text{SO}_2) = 5.7 \times 10^{-33} \exp(1,000/T)$; curve B, $k_4 = 3.4 \times 10^{-14} \exp(150/T)$, $k_8 = 1.1 \times 10^{-13} \exp(150/T)$. *b*, Uses the standard model S, but with values for the deposition velocity for SO₂ equal to 2.0, 0.4 and 0.1 cm s^{-1} as noted. *c*, The dashed curve includes loss of SO₂ to aerosols, with a sticking efficiency of 10^{-3} , as described in the text. *d*, The effect of a source of SO₂ from oxidation of DMS. Curve C includes an ocean source of DMS of $2.5 \text{ Mtonnes S yr}^{-1}$, in addition to SO₂ sources from CS₂ and COS oxidation, and may be considered as our best model. The curve labelled 'DMS only' omits all sources of SO₂ except that from DMS oxidation, and allows for a DMS source of $25 \text{ Mtonnes S yr}^{-1}$, the value suggested recently by Nguyen Ba Cuong *et al.*³⁷. The calculated profiles of SO₂ exhibit small (<15%) variations with latitude between 45° N and 45° S.

for reactions (4) and (8). It seems probable that rates for reactions (4) and (8) should be faster at low temperature, given the reaction mechanism proposed by Kurylo^{6,24}. The temperature dependence of k_1 is poorly determined. The rate expression given in Fig. 2a was based on preliminary work by Castleman and Tang²⁵ and Erler *et al.* (ref. 26 and results in ref. 10).

Figure 2b shows the dependence of calculated profiles for SO₂ on the choice of deposition velocity, while Fig. 2c shows the possible influence of heterogeneous loss due to aerosols. The general behaviour of the profiles in Fig. 2a–c is similar. In all cases we find higher mixing ratios at high altitude, consistent with the observational data of Georgii *et al.*²⁷ and Maroulis *et al.*⁴. Uncertainties in loss processes tend to affect mainly concentrations computed for the lowest altitudes. Deposition velocities over land⁸ are reported in the range 0.1–2.0 cm s⁻¹ while Hicks and Liss²⁸ suggest that a value of about 1 cm s⁻¹ should be appropriate for moderate wind conditions at sea.

Results in Fig. 2c imply that loss of SO₂ to aerosols should be relatively unimportant, at least in the marine atmosphere. We used an integrated surface area for aerosols equivalent to 1×10^{-7} cm² per cm³, an estimate based on particle size distributions measured by Meszaros and Vissy²⁹, Blifford³⁰, and Jaenicke *et al.*³¹. We investigated sticking efficiencies for SO₂ as high as 10^{-3} , although experimental data³² suggest efficiencies much lower than this, in the range 10^{-3} – 10^{-6} . Results in Fig. 2 do not allow for transient reductions in SO₂ which might arise due to rainfall.

We assumed a rate constant for reaction (3) equal to 10^{-15} cm³ s⁻¹. With this choice, reaction (3) represents a relatively minor sink for SO₂. Measurements by Kan *et al.*³³ indicate removal of CH₃O₂ by SO₂, with an effective rate constant of 5 – 10×10^{-15} cm³ s⁻¹. If loss of CH₃O₂ observed in the laboratory is associated with the reaction channel (3), concentrations in Fig. 2 could be reduced by about 20%. This estimate assumes, however, an unproven model for oxidation of atmospheric CH₄. It seems unlikely that k_3 should be as large as 10^{-14} cm³ s⁻¹ given the much smaller value, $\leq 10^{-17}$ cm³ s⁻¹ (refs 34, 58), reported for the analogous reaction (2).

Oxidation of DMS could provide an additional source of SO₂ as suggested by Lovelock³⁵ and discussed further by Maroulis and Bandy³⁶ and Nguyen Ba Cuong *et al.*³⁷. The associated

source of SO₂ would be confined to the lowest 2 km of the atmosphere as the reaction of DMS with OH is exceedingly rapid³⁸. Thus DMS cannot account for the height profile observed for SO₂, a point shown in Fig. 2d. Similar arguments apply to the suggestion that oxidation of H₂S might produce a large source of SO₂. Hydrogen sulphide also reacts very rapidly with OH³⁹, and concentrations as low as a few parts per trillion have been observed in tropical marine air⁴⁰. Most estimates of the contribution of H₂S to the atmospheric sulphur cycle have been derived by subtracting other terms in the budget for sulphur, and are consequently highly uncertain^{1,2}. While biogenic sources of H₂S and DMS may provide significant contributions to the atmospheric sulphur cycle in selected environments (for example, near swamps or salt marshes), these sources cannot account for the observations of SO₂ discussed here.

Liss and Slater⁴¹, using measurements by Lovelock *et al.*³⁵, estimate a net source of 3.7 Mtonnes S yr⁻¹ associated with release of marine DMS, a source whose magnitude should be reduced by about a factor of 1.5 to account for more recent estimates of rates for gas exchange across the air–sea interface⁴².

It seems probable that the concentrations of atmospheric CS₂ and COS should reflect a combination of biogenic and industrial sources^{43,44}. Preliminary measurements of the emission rates of sulphurous gases over salt marshes have shown that fluxes of COS might be comparable to, and in some cases greater than fluxes of H₂S⁴⁵. The relatively uniform distribution^{4,13,46,47} observed for COS suggests a globally distributed source. This apparently argues against a significant industrial component, although there might be important production due to forest fires and combustion associated with land clearance for agriculture. The possibility of a dominant industrial component for CS₂ cannot be excluded, given limitations in the present data base. It seems more likely, however, that diffuse sources should dominate for CS₂ as well as for COS. These sources may include a component due to combustion although thermodynamic considerations suggest that reactions in reducing environments may be more important. It seems probable that these reactions should be microbially mediated: swamps, anaerobic muds and the digestive tracts of various animals offer plausible sites. The relatively uniform distribution observed for SO₂ in the upper marine troposphere⁴ requires a diffuse atmospheric source for

Table 1 Kinetic data

No.	Reaction	Rate expression*	Refs and notes
1	OH + SO ₂ + M → HSO ₃ + M	$k_a = 6.8 \times 10^{-13}$ $k_b = 1.6 \times 10^{-31}$ $1/k = 1/k_a + 1/k_b M$ $k_1 = k \times (k_9/1.4 \times 10^{-13})$	Fit to the data of refs 21, 22
2	HO ₂ + SO ₂ → SO ₃ + OH	2.0×10^{-17}	34
3	CH ₃ OO + SO ₂ → products	1.0×10^{-15}	See text
4	OH + COS → SH + CO ₂	5.66×10^{-14}	6
7	OH + CS ₂ → SH + COS	1.85×10^{-13}	6
8	OH + (CH ₃) ₂ S → products	$6.08 \times 10^{-12} \exp(134/T)$	38
9	OH + CO → CO ₂ + H	$2.10 \times 10^{-13} f(M) \exp(-115/T)$ $f(M) = (1 + 3.7 \times 10^{-20} \times M)$	53 23
10	HO ₂ + O ₃ → OH + 2O ₂	$1.40 \times 10^{-14} \exp(-580/T)$	Zahniser and Howard (personal communication)
11	HO ₂ + NO → OH + NO ₂	$3.3 \times 10^{-12} \exp(254/T)$	54
12	HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	$3.9 \times 10^{-14} f(\text{H}_2\text{O}) \exp(1245/T)$ $f(\text{H}_2\text{O}) = 1 + 2.5 \times 10^{-18} \times [\text{H}_2\text{O}]$	55, 56
13	H ₂ O ₂ + $h\nu$ → OH + OH		57
14	CH ₃ OO + NO → CH ₃ O + NO ₂	8.0×10^{-12}	Estimated
15	CH ₃ OO + HO ₂ → CH ₃ OOH + O ₂	3.0×10^{-12}	Estimated
16	H ₂ O ₂ heterogeneous loss (units, s ⁻¹)	1.16×10^{-5} 0–4 km $1.16 \times 10^{-5} \exp(1.6 - 0.4 z)$ 4–12 km	
17	SO ₂ + aerosol → heterogeneous loss (probability)	0.0	†

* Units cm³ s⁻¹ for bimolecular reactions; cm⁶ s⁻¹ for termolecular reactions. The complete chemical scheme is described in Logan *et al.*¹³.

† The integrated surface area for marine aerosols was taken to be 1.0×10^{-7} cm² per cm³, and a scale height for the aerosol distribution function of 1 km was adopted (see refs 29–31).

this gas. Oxidation of COS and perhaps CS₂ as discussed here can provide a relatively straightforward explanation for the existence of a uniform background level of SO₂.

Received 17 May; accepted 20 July 1979.

1. Friend, J. P. in *Chemistry of the Lower Atmosphere* (ed. Rasool, S. I.) (Plenum, New York, 1973).
2. Granat, L., Rodhe, H. & Hallberg, R. O. *Ecol. Bull.* **22**, 89–134 (1976).
3. Mészáros, E. *Atmos. Envir.* **12**, 699–705 (1978).
4. Maroulis, P. J., Torres, A. L., Goldberg, A. B. & Bandy, A. R. *Trans. Am. geophys. Un* **59**, 1081–1082 (1978); 1082 (1978).
5. Calvert, J. G., Su, F., Bottenheim, J. W. & Strausz, O. P. *Atmos. Envir.* **12**, 197–226 (1978).
6. Kurylo, M. J. *Chem. phys. Lett.* **58**, 238–242 (1978).
7. Sze, N. D. & Ko, M. K. W. *Nature* **280**, 308–310 (1979).
8. Garland, J. A. *Atmos. Envir.* **12**, 349–362 (1978).
9. Cox, R. A. *Phil. Trans. R. Soc. A* **290**, 543–550 (1979).
10. Moortgat, G. K. & Junge, C. E. *Pure appl. Geophys.* **115**, 759–774 (1977).
11. Prahm, L. P., Torp, U. & Stern, R. M. *Tellus* **28**, 355–372 (1976).
12. Nguyen, B. C., Bonsang, B., Lambert, G. & Pasquier, J. L. *Pure Appl. Geophys.* **113**, 489–500 (1975).
13. Logan, J. A., Prather, M. J., Wofsy, S. C. & McElroy, M. B. *Phil. Trans. R. Soc. A* **290**, 187–234, 1978.
14. Atkinson, R., Perry, R. A. & Pitts, J. N., Jr *Chem. phys. Lett.* **54**, 14–18 (1978).
15. Sandalls, F. J. & Penkett, S. A. *Atmos. Envir.* **11**, 197–199 (1977).
16. Lovelock, J. E. *Nature* **248**, 625–626 (1974).
17. Seidell, A. in *Solubilities of Inorganic and Metal Compounds*, Vol. 1 (Van Nostrand, New York, 1940).
18. Singh, H. B. *Geophys. Res. Lett.* **4**, 453–456 (1977).
19. Lovelock, J. E. *Nature* **267**, 32 (1977).
20. Nguyen, B. C., Bonsang, B. & Lambert, G. *Tellus* **26**, 241–248 (1974); Cuong, B. C., Bonsang, B., Pasquier, J. L. & Lambert, G. *J. Res. Atmos.* **8**, 831–844 (1974).
21. Castleman, A. W., Davis, R. E., Munkelwitz, H. R., Tang, I. N. & Wood, W. P. *Int. J. Chem. Kin. Symp.* **1**, 629–640 (1975).
22. Cox, R. A. *Int. J. Chem. Kin. Symp.* **1**, 379–398 (1975).
23. Biermann, H. W., Zetzsch, C. & Stuhl, F. *Ber. Bunsenges. Phys. Chem.* **82**, 633–639 (1978).
24. Kurylo, M. J. & Laufer, A. H. *J. chem. Phys.* **70**, 2032–2033 (1979).
25. Castleman, A. W. & Tang, I. N. *J. Photochem.* **6**, 349–354 (1976).
26. Erler, K., Field, D. & Zellner, R. *4th Int. Conf. on Gas Kinetics Edinburgh* (1975).
27. Georgii, H. W. & Gravenhorst, G. *Pure appl. Geophys.* **115**, 503–511 (1977).
28. Hicks, B. B. & Liss, P. S. *Tellus* **28**, 349–354 (1976).
29. Mészáros, A. & Vissy, K. *J. atmos. Sci.* **5**, 101–110 (1974).

We thank N. Dak Sze for helpful discussions, and acknowledge support from NASA, grant NSG-2031, and the NSF, grant ATM 78-09712.

30. Blifford, I. H. *J. geophys. Res.* **75**, 3099–3103 (1970).
31. Jaenicke, R., Junge, C. & Kanter, H. J. *Met. Forsch. Ergebn.* **87**, 1–54 (1971).
32. Judeikis, H. S., Stewart, T. B. & Wren, A. G. *Atmos. Envir.* **12**, 1633–1641 (1978).
33. Kan, C. S., McQuigg, R. D., Whitbeck, M. R. & Calvert, J. G. *Int. J. Chem. Kin.* (in the press).
34. Burrows, J. P., Cliff, D. I., Harris, G. W., Thrush, B. A. & Wilkinson, J. P. T. *W.M.O. Tech. Not. No.* **511**, 25–28 (1978).
35. Lovelock, J. E., Maggs, R. J. & Rasmussen, R. A. *Nature* **237**, 452–453 (1972).
36. Maroulis, P. J. & Bandy, A. R. *Science* **196**, 647–648 (1977).
37. Nguyen, B. C., Gaudry, A., Bonsang, B. & Lambert, G. *Nature* **275**, 637–639 (1978).
38. Kurylo, M. J. *Chem. phys. Lett.* **58**, 233–237 (1978).
39. Perry, R. A., Atkinson, R. & Pitts, J. N. *J. chem. Phys.* **64**, 3237–3239 (1976).
40. Slatt, B. J., Natusch, D. F. S., Prospero, J. M. & Savoie, D. L. *Atmos. Envir.* **12**, 981–991 (1978).
41. Liss, P. S. & Slater, P. G. *Nature* **247**, 181–184 (1974).
42. Broecker, W. S. & Peng, T. -H. *Tellus* **26**, 21–35 (1974).
43. Crutzen, P. J. *Geophys. Res. Lett.* **3**, 73–76 (1976).
44. Peyton, T. O., Steele, R. V. & Mabey, W. R. *Stanford Res. Inst. Rep. No.* 68–01–2940 (1976).
45. Aneja, V. P., Overton, J. H., Cupitt, L. T., Durham, J. L. & Wilson, W. E. *Tellus* **31**, 174–178 (1979).
46. Hanst, P. L., Spiller, L. L., Watts, D. M., Spence, J. W. & Miller, M. F. *J. Air Pollut. Contr. Ass.* **25**, 1220–1226 (1975).
47. Maroulis, P. J., Torres, A. L. & Bandy, A. R. *Geophys. Res. Lett.* **4**, 510–512 (1977).
48. Chatfield, R. & Harrison, H. J. *geophys. Res.* **82**, 5969–5976 (1977).
49. Heidt, L. E., Kransnec, J. P. *Trans. Am. geophys. Un* **59**, 1077 (1978).
50. Ehhalt, D. H., Schmidt, U. *Pure appl. Geophys.* **116**, 452–464 (1978).
51. Rasmusson, E. M. in *The General Circulation of the Tropical Atmosphere and Interactions in the Extraterrestrial Latitudes* (ed. Newall, R. E., Ch. 5. MIT Press, 1972).
52. McFarland, M., Kley, D., Drummond, J. W., Schmeltekopf, A. L. & Winkler, R. H. *Geophys. Res. Lett.* **6**, 605–608 (1979).
53. Greiner, N. R. *J. chem. Phys.* **51**, 5049–5051 (1969).
54. Howard, C. J. & Zahniser, M. S. *J. chem. Phys.* (submitted).
55. Cox, R. A. *W.M.O. Tech. Note No.* 511, 17–27 (1978).
56. Hamilton, E. J. & Lii, R.-R. *Int. J. chem. Kin.* **9**, 875–885 (1977).
57. Molina, L. T., Schinke, S. D. & Molina, M. J. *Geophys. Res. Lett.* **4**, 580–582 (1977).
58. Graham, R. A., Winer, A. M., Atkinson, R. & Pitts, J. N. *J. Phys. Chem.* **83**, 1563–1567 (1979).

The effects of past variations of the Earth's rotation rate on climate

B. G. Hunt

Australian Numerical Meteorology Research Centre, PO Box 5089AA, Melbourne, Australia 3001

Palaeological evidence indicates that the rotation rate of the Earth during the late Precambrian was 2–2.5 times faster than now. Typically high rotation rate in a fluid system reduces the characteristic size of dynamic features, their associated transport processes and the overall intensity of the motions. The climatic consequences of the high rotation rate during the Precambrian are outlined. In particular, it is hypothesised that variations in the rotation rate imposed an important, and possibly dominant, effect on the genesis and termination of the Precambrian ice age. Other possible implications of the high rotation rate to oceanography, life forms and geology are briefly noted.

POTENTIAL mechanisms for producing climatic variations include solar perturbations owing to orbital variations of the Earth¹, volcanic activity², tectonic movements³, fluctuations in solar output⁴, glacier surgings⁵ and oceanic feedback⁶. On a time scale of hundreds of millions of years a further factor, which has received relatively little attention⁷, is the increase in the rotational period of the Earth. This increase is very small (~2.5 ms per century) and is still taking place. However, since the atmospheric and oceanic circulations are known to be critically influenced by the Earth's rotation rate it follows that climate should also be affected. Hence it is of value to consider what

impact past variations in the rotation rate might have had on the evolution of the Earth's palaeoclimate, and to see how well the deductions fit the known facts.

This assessment will be obtained by interpreting the results of a numerical model of the atmospheric circulation. This general circulation model of the atmosphere was hemispheric in extent, devoid of topography and thus oceanic influences, and was set up for fixed annual mean conditions⁸. Despite these apparently serious omissions the model is capable of a remarkable simulation of many features of the atmosphere^{8,9}, which encourages the belief that its application to problems concerned with variations in the rotation rate of the Earth has merit. This model has now also been run with the rotation rate increased and decreased by a factor of 5 as part of a separate study¹⁰, and it is this data base of three experiments which will be used here.

Prehistorical perspective

The rotational history of the Earth can be traced back to the late Precambrian era, about 1.5×10^9 yr ago. Based on growth patterns from shells and corals the Earth then had at least 800–900 solar days per yr, implying a rotation rate 2–2.5 times greater than the present value¹¹. MacDonald¹² has calculated the past variation of the rotation rate and his results for one set of assumptions are shown in Fig. 1. This illustrates a possible increase in rotation rate with decreasing time up to about