Reports

Seasonal Variations in the Stable Carbon Isotopic Signature of Biogenic Methane in a Coastal Sediment

Christopher S. Martens, Neal E. Blair, Carol D. Green,
David J. Des Marais

Systematic seasonal variations in the stable carbon isotopic signature of methane gas occur in the anoxic sediments of Cape Lookout Bight, a lagoonal basin on North Carolina's Outer Banks. Values for the carbon isotope ratio ($\delta^{13}C$) of methane range from −57.3 per mil during summer to −68.5 per mil during winter in gas bubbles with an average methane content of 95%. The variations are hypothesized to result from changes in the pathways of microbial methane production and cycling of key substrates including acetate and hydrogen. The use of stable isotopic signatures to investigate the global methane cycle through mass balance calculations, involving various sediment and soil biogenic sources, appears to require seasonally averaged data from individual sites.

We report here the first conclusive evidence for major seasonal variations in the stable carbon isotopic signatures of methane and carbon dioxide gas produced by microbial processes in organic-rich coastal sediments. Such systematic variations have important implications for the use of stable isotopic data to investigate the global methane cycle as well as to elucidate mechanisms and rates of methanogenesis and carbon dioxide generation in natural environments. The observed seasonal isotopic variations are hypothesized to be controlled by changes in pathways of methane production and cycling of acetate and molecular hydrogen within the sediments. Such variations appear to be driven by seasonal temperature changes at our coastal study site (*1*). The direct effect of temperature changes on individual fractionation factors (*2*) for a given methane production mechanism appears to be of secondary importance.

Recent measurements of methane trapped in air bubbles embedded in polar ice suggest that its tropospheric concentration, after more than 25 centuries of relatively constant values (*3*), has increased more than twofold within the past 150 to 400 years. Directly measured concentration changes observed around the world during the late 1970's and 1980's have led to calculated rates of increase ranging from 1 to 2% per year (*4*, *5*). Determinations of tropospheric concentrations of methane in 1951 and 1981 resulting from the analysis of infrared solar absorption spectra yielded an average rate of increase of 1.1 ± 0.2% per year for 1951 to 1981 (*6*). Such concentration changes should have significant environmental consequences including increases in tropospheric temperature, increased tropospheric ozone formation rates, and changes in important stratospheric mixing ratios including those for water vapor and chlorine radicals (*4*, *7*).

Table 1. Cape Lookout Bight sediment gas bubble composition and $\delta^{13}C$ data. Values listed are means ± SD for the number of sample bottles listed. Superscripts indicate the number of samples for which compositional data were obtained when different from the number of sample bottles listed.

Date	Methane sample bottles (no.)	Methane content (%)	$\delta^{13}C$-CH_4 (per mil)	Carbon dioxide sample bottles (no.)	Carbon dioxide content (%)	$\delta^{13}C$-CO_2 (per mil)
6 June 1983	5	97 ± 2	−64.5 ± 0.7	5	2.5 ± 0.1	−6.8 ± 1.1
19 July 1983	6	95 ± 4	−62.2 ± 0.4	6	3.4 ± 0.2^{3}	−8.6 ± 1.2
3 August 1983	5	96 ± 4	−61.7 ± 0.9	5	2.4 ± 0.3	−8.8 ± 1.0
19 August 1983	5	94 ± 2	−57.5 ± 0.3	4	2.4 ± 0.2	−9.4 ± 0.3
15 September 1983	5	97 ± 2	−60.3 ± 0.4	5	2.5 ± 0.1	−8.3 ± 0.5
16 October 1983	6	95 ± 3	−60.0 ± 0.5	5	2.4 ± 0.5^{4}	−7.2 ± 0.6
20 November 1983	4	93 ± 2	−62.2 ± 0.4	4	2.4 ± 0.6	−8.0 ± 0.2
2 February 1984	4	98 ± 3	−63.4 ± 0.6	4	1.6 ± 0.5^{3}	−6.0 ± 1.2
7 April 1984	4	94 ± 3^{3}	−63.8 ± 0.2	4	1.0 ± 0.2^{3}	−5.1 ± 0.7
6 May 1984	4	90 ± 6	−63.8 ± 0.4	3	1.5 ± 0.2	−3.0 ± 0.8
31 May 1984	5	94 ± 5	−68.5 ± 0.7	3	1.8 ± 0.6	−7.0 ± 2.0
14 June 1984	5	94 ± 3	−64.1 ± 0.6	4	2.9 ± 1.0	−6.2 ± 2.4
2 July 1984	4	97 ± 4^{2}	−59.4 ± 1.2	2	2.1 ± 0.1	−10.0 ± 0.7
18 July 1984	4	98 ± 2^{2}	−60.6 ± 1.6	2	2.2 ± 0.2	−10.6 ± 3.2
11 August 1984	5	98 ± 3^{4}	−57.3 ± 0.6	5	2.3 ± 0.2	−7.6 ± 1.2
30 August 1984	4	94 ± 1	−57.9 ± 1.0	3	3.8 ± 1.1	−8.9 ± 1.1
22 September 1984	5	99 ± 0^{2}	−58.0 ± 0.3	5	2.4 ± 1.3	−8.1 ± 1.0

Predictions of changes in the atmospheric concentration of methane require a quantitative understanding of its tropospheric sources and sinks. The potential utility of stable carbon isotopic budgets for elucidating these sources has been discussed (*8*). The mass-weighted average isotopic composition of all sources should simply be the mean $\delta^{13}C$ (*9*) of tropospheric methane corrected for a kinetic isotopic fractionation (*10*) during its reaction with free radical hydroxyl and for the less significant effect of non-steady-state concentration increases. The calculated $\delta^{13}C$ value for the sum of these sources in 1980 is given as −49.2 ± 1.5 per mil based on a measured atmospheric value for that year of −47.0 ± 0.3 per mil (*8*). A knowledge of the individual $\delta^{13}C$ signatures of all major sources such as wetlands or cattle (*11*) should allow for budgetary calculations of their relative importance. Factors heretofore proved or assumed to be important in controlling the $\delta^{13}C$ of methane from potentially dominant wetland sources (*4*, *12*) have not included seasonal changes in methane production mechanisms or acetate and hydrogen cycling pathways, or both, which appear to produce the systematic seasonal variations we have observed. This is at least in part due to a paucity of isotopic data for methane produced in wetlands and other environments rich in organic matter.

We conducted a seasonal study by collecting gas bubbles averaging 95 ± 2% (mean ± SD, $n = 17$) methane content from 16 June 1983 through 22 September 1984 from the sediments of a well-characterized coastal marine basin, Cape Lookout Bight, North Carolina (*13*). Decomposition of naturally occurring organic materials in the sediments at this site is dominated by the well-known sequence of bacterial sulfate re-

---

C. S. Martens and C. D. Green, Marine Sciences Program 045A, University of North Carolina, Chapel Hill, NC 27514.
N. E. Blair, Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC 27695.
D. J. Des Marais, NASA-Ames Research Center, Moffett Field, CA 94035.

duction underlain by methanogenesis (*13, 14*). Oxygen and other potentially important electron acceptors supporting decomposition are removed within millimeters to centimeters of the sediment-water interface depending on the rates of microbially mediated reactions that are, in turn, controlled by seasonal variations in organic matter input and temperature. The seasonal temperature variation in the surface sediment in Cape Lookout Bight is illustrated in Fig. 1A.

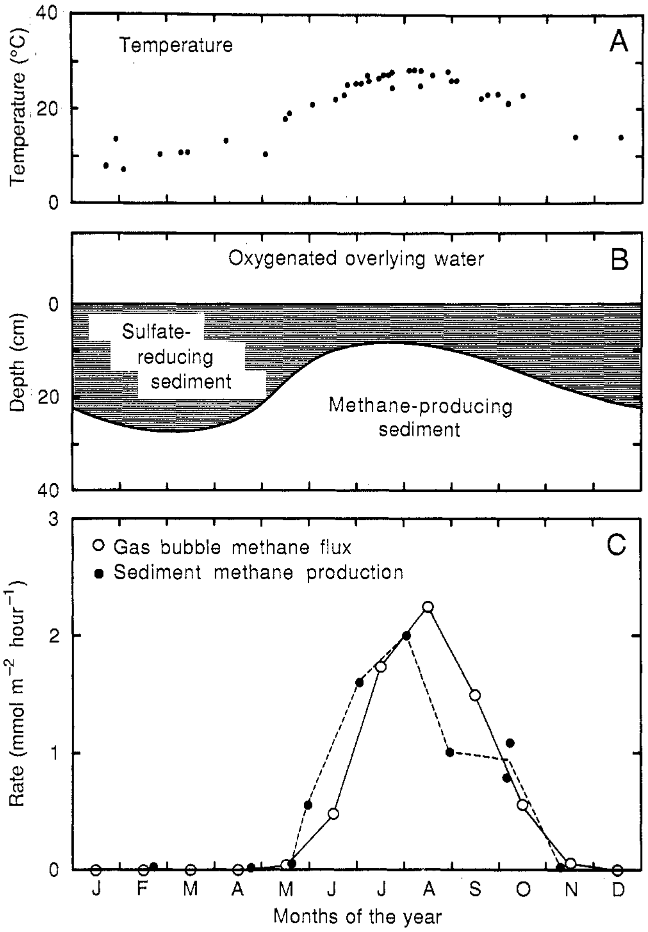

Fig. 1. (A) Temperature variations in the surface sediment in Cape Lookout Bight, North Carolina, during 1983–84. (B) Average seasonal variation in the depth distributions of sulfate-reducing and methane-producing sediments in Cape Lookout Bight during 1976 through 1983 (*13, 15, 16*). (C) Seasonal distribution of methane production rates (*15*) integrated over the sediment column to a depth of 35 cm (●) during 1979 through 1981. Seasonal distribution of monthly averaged methane flux (*13*) out of the sediments via gas bubbles (○) during 1976 through 1978.

The depth distributions of sulfate-reducing and methane-producing sediments observed at our Cape Lookout site during 1976 through 1983 (*13, 15, 16*) are shown in Fig. 1B. Methane production rates greater than 0.01 mmol/liter per day generally occurred between 7 and 35 cm during summer months and between 25 and 35 cm during winter months. Observed seasonal variations in depth-integrated methane production rates (*15*) and upward flux of methane out of the sediments (*16*) are shown in Fig. 1C. The agreement between these independent measurements is not fortuitous since the net methane production rate in the sediment column must equal the flux out under the essentially steady-state conditions observed in Cape Lookout sediments during 1976 through 1983 (*13, 15*). Gas bubbles, which represent the dominant methane transport mode out of the sediment on an annual basis (*13, 16*), directly escape at low tide from the sediments to the troposphere during the warmer months, which generally include May through November. In this study a diver generally stirred the surface sediment to obtain samples. Gas bubbles from the sediments were trapped in a plastic cone (1 m^2) suspended 1 to 2 m above the bottom of the 8-m-deep water column. Four to six sample bottles of 9- or 15-ml volume each were filled on each date. Each bottle was filled by gas displacement through a stopcock mounted at the peak of the cone and immediately sealed in situ with a 1.5-cm-thick (1.0-cm-diameter) black butyl rubber stopper, which was subsequently secured with an aluminum crimp cap on deck. The integrity of each sealed bottle was ensured by reproducibility of methane content between bottles, measurements of nitrogen to check for exchange with air, and the maintenance of the original positive pressure of 1.7 to 1.8 atm resulting from the underwater seal. The procedures used for methane and carbon dioxide isotope measurements have been described (*17*). Carbon isotopic data for methane and carbon dioxide were obtained on 17 dates at our single station (Table 1). Isotopic signatures of the naturally escaping gas match those of gas bubbles collected by stirring the sediments (*18*). Gas bubble signatures also match those of methane dissolved in the sediment pore waters within the methane production zone in both summer and winter (*19*). This agreement between gas bubble and dissolved methane isotopic values suggests that methane oxidation processes (*20*) do not overwhelmingly affect the isotopic signature of gas naturally released to the atmosphere from our site during summer months because of direct and rapid bubble transport through the overlying sediments and shallow water column (*16*).

Measured variations in the $\delta^{13}C$ signature of gaseous methane observed during 1983–84 are illustrated in Fig. 2A. The range in values is from light (^{13}C-depleted) wintertime values averaging approximately −64 per mil to heavy summertime values approaching −57 per mil. Corresponding $\delta^{13}C$ data for carbon dioxide, which makes up 1 to 3% of the total gas bubble composition, are presented in Fig. 2B. The carbon dioxide results essentially mirror those for methane, with lighter carbon dioxide exiting the sediment during warmest summer months. The agreement between $\delta^{13}C$ values of methane in gas bubbles and dissolved in surrounding pore water in the methane production zone (*19*) also suggests that the isotopic composition is controlled primarily by production as opposed to oxidation processes. Changes in the proportion of methane production from acetate fermentation versus carbon dioxide reduction (*1*) and in pathways of acetate cycling (*21*) in Cape Lookout Bight sediments coincide with the observed rapid changes in $\delta^{13}C$ values for gas bubble methane during June to August. This coincidence leads us to hypothesize that the isotopic variations are due, in part, to changes in methanogenic and acetate cycling pathways. Seasonal variations in methane hydrogen isotopes (δD) measured in subsamples from this study (*22*) further support this hypothesis in that lightest values occur during summer months, a result expected if the fraction of methane production from acetate fermentation increases (*23*).

We can estimate the mean annual $\delta^{13}C$ value of methane escaping from Cape Lookout Bight sediments by natural bubble ebullition through use of the Fig. 1C gas flux data and $\delta^{13}C$-CH_4 results in Table 1. Methane-rich gas bubbles only escape the sediments by natural low-tide ebullition during May to November of a typical year (Fig. 1C) (*16*). Mean gas flux data (*13*) used to construct Fig. 1C are presented in Table 2. Also listed are the percentage of the total annual gas bubble flux ascribable to each month as well as an average $\delta^{13}C$ value for each. The

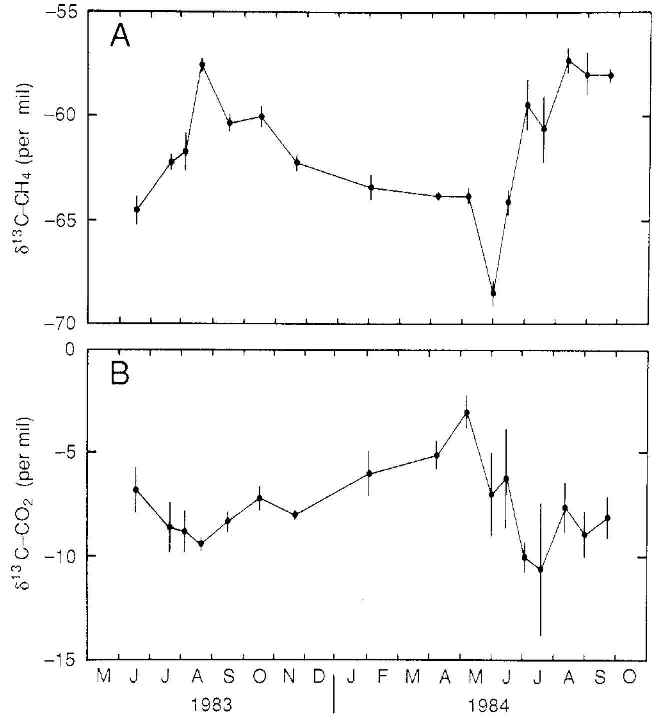

Fig. 2. (A) The $\delta^{13}C$ signature of methane in gas bubbles collected during 1983–84 from the sediments of Cape Lookout Bight, North Carolina. (B) The $\delta^{13}C$ signature of carbon dioxide in gas bubbles. The error bars (mean ± SD) are based on measured isotopic variations among four to six bottles from each sampling date.

averages are calculated from the 4 to 19 individual methane sample $\delta^{13}C$ values available for a given month. The percentage of the total gas flux for each month and average $\delta^{13}C$ value for each are then used to calculate a weighted average value of −60.0 ± 1.0 per mil (1 SD, $n = 72$) for methane escaping Cape Lookout sediments by natural ebullition. Only one of the mean $\delta^{13}C$-CH_4 values from the 17 sampling dates (Table 1) equals this −60.0 ± 1.0 per mil value.

Table 2. Averaged methane gas flux and isotopic data. The full year weighted average (WA) value incorporates data from May through November (1983 and 1984) when natural gas bubble ebullition occurs.

Month	Monthly methane bubble flux* (mmol m^{-2})	Annual flux† (%)	$\delta^{13}C$-CH_4‡ (per mil)
January	0	0	
February	0	0	−63.4 ± 0.6
March	0	0	
April	0	0	−63.8 ± 0.2
May	38	0.8	−66.4 ± 2.5
June	350	7.2	−64.3 ± 0.7
July	1270	26.2	−61.0 ± 1.6
August	1643	33.9	−58.7 ± 2.0
September	1095	22.6	−59.1 ± 1.4
October	409	8.4	−60.0 ± 0.5
November	47	1.0	−62.2 ± 0.4
December	0	0	
Full year	4582 ± 1277	100.0	−60.0 ± 1.0 WA§

*Uncertainty in methane bubble flux for each month is ±53% [1 SD (*13*)]. †Uncertainty in annual flux percentage or flux fraction (F_i) for each month is ±59% (1 SD). ‡Values for $\delta^{13}C$-CH_4 for each month (X_i) calculated as described in text from Table 1 data. §The uncertainty in the WA $\delta^{13}C$ value determined for May through November was calculated as the square root of the variance

$$SD_{WA}^2 = \sum_i SD_{F_i}^2 (X_i - \delta^{13}C_{WA})^2 + \sum_i SD_{X_i}^2 \cdot F_i^2$$

The major implication of our results is that isotopic data for methane produced at any single site will probably vary seasonally over a significant range, which is controlled by the balance among processes occurring within the sediment column. The observed range should reflect changes in methane production mechanisms and substrates, production rates, transport modes, and consumption reactions, such as anaerobic and aerobic oxidation. At our Cape Lookout site the systematic change in the isotopic signature of methane gas emitted to the troposphere appears to be, at least in part, controlled by changes in methane production mechanisms (*1*) and rates (*15*) or by changes in acetate- and hydrogen-cycling pathways or by some combination. At other sites where transport to the troposphere from production zones is slower or involves greater exposure of the migrating gas to oxidizing environments prior to escape from the sediments or overlying waters, the roles of both anaerobic and aerobic oxidation processes (*20*) should be enhanced. Gas sampling programs that do not consider seasonal variations in all of these processes may yield systematically biased results. No single set of measurements for one date can accurately characterize the isotopic signature of biogenic methane annually escaping to the troposphere from our site and presumably from most other locations.

REFERENCES AND NOTES

1. P. M. Crill and C. S. Martens, *Geochim. Cosmochim. Acta*, in press.
2. L. M. Games *et al., ibid.* **42**, 1295 (1978).
3. R. C. Robbins, L. A. Cavanagh, L. J. Salas, *J. Geophys. Res.* **78**, 5341 (1973); H. Craig and C. C. Chou, *Geophys. Res. Lett.* **9**, 477 (1982); R. A. Rasmussen and M. A. K. Khalil, *J. Geophys. Res.* **89**, 1563 (1984); B. Stauffer, G. Fischer, A. Neftel, H. Oeschger, *Science* **229**, 1386 (1985).
4. W. Seiler, in *Current Perspectives in Microbial Ecology*, M. J. Klug and C. A. Reddy, Eds. (American Society for Microbiology, Washington, DC, 1984), p. 468.
5. R. A. Rasmussen and M. A. K. Khalil, *J. Geophys. Res.* **86**, 9826 (1981); P. J. Fraser, M. A. K. Khalil, R. A. Rasmussen, A. J. Crawford, *Geophys. Res. Lett.* **8**, 1063 (1981); D. R. Blake *et al.*, *ibid.* **9**, 477 (1982); M. A. K. Khalil and R. A. Rasmussen, *J. Geophys. Res.* **88**, 5131 (1983); D. H. Ehhalt, R. J. Zander, R. A. Lamontague, *ibid.*, p. 8442; P. J. Fraser, M. A. K. Khalil, R. A. Rasmussen, L. P. Steele, *J. Atmos. Chem.* **1**, 125 (1984); G. I. Pearman, D. Etheridge, F. de Silva, P. J. Fraser, *Nature (London)* **320**, 248 (1986).
6. C. P. Rinsland, J. S. Levine, T. Miles, *Nature (London)* **318**, 245 (1985).
7. W. C. Wang, Y. L. Yung, A. A. Lacis, T. Mo, J. E. Hansen, *Science* **194**, 685 (1976); A. Lacis, J. Hansen, P. Lee, T. Mitchell, S. Lebedeff, *Geophys. Res. Lett.* **8**, 1035 (1981); V. Ramanathan, R. J. Cicerone, H. B. Singh, J. T. Kiehl, *J. Geophys. Res.* **90**, 5547 (1985); R. E. Dickinson and R. J. Cicerone, *Nature (London)* **319**, 109 (1986).
8. C. M. Stevens and F. E. Rust, *J. Geophys. Res.* **87**, 4879 (1982). The uncertainties listed by these authors are described as "estimated absolute accuracies."
9. Values of $\delta^{13}C$ (per mil) relative to that for the Pee Dee belemnite carbonate (PDB) standard are defined by the equation $\delta^{13}C = [(R_{sample}/R_{PDB}) - 1] \times 10^3$, where $R = {}^{13}C/{}^{12}C$ and $R_{PDB} = 0.0112372$.
10. The correction for methane oxidation by hydroxyl radical used by Stevens and Rust (*8*) was based on the 2.8 ± 1.3 per mil ($k_{12}/k_{13} = 1.0028$) kinetic isotope effect reported by F. Rust and C. M. Stevens [*Int. J. Chem. Kinet.* **12**, 371 (1980)]. J. A. Davidson *et al.* [*Trans. Am. Geophys. Union* **67**, 245 (1986)] have recently reported a much larger kinetic isotope effect ($k_{12}/k_{13} = 1.025$) for which a total methane source significantly more depleted in ^{13}C would be calculated.
11. F. Rust, *Science* **211**, 1044 (1981).
12. D. M. Ehhalt, *Tellus* **26**, 58 (1974); ——— and U. Schmidt, *Pure Appl. Geophys.* **116**, 452 (1978); J. C. Sheppard, H. Westburg, J. F. Hopper, K. Ganesan, P. Zimmerman, *J. Geophys. Res.* **87**, 1305 (1982).
13. C. S. Martens and J. V. Klump, *Geochim. Cosmochim. Acta* **48**, 1987 (1984).
14. C. S. Martens and R. A. Berner, *Science* **185**, 1167 (1974).
15. P. M. Crill and C. S. Martens, *Limnol. Oceanogr.* **25**, 564 (1983); P. M. Crill, thesis, University of North Carolina, Chapel Hill (1984).
16. C. S. Martens and J. V. Klump, *Geochim. Cosmochim. Acta* **44**, 471 (1980).
17. D. J. Des Marais, J. H. Donchin, N. L. Nehring, A. H. Truesdell, *Nature (London)* **292**, 826 (1981); G. Yuen, N. Blair, D. J. Des Marais, S. Chang, *ibid.* **307**, 252 (1984); D. E. Matthews and J. M. Hayes, *Anal. Chem.* **50**, 1465 (1978).
18. Isotopic signatures of gas samples collected during natural low-tide bubbling in summer months differ by approximately +1 per mil from those of gas collected by stirring the sediment. This difference is presumably due to oxidation of the naturally released bubbles, which must migrate up through more oxidized sediments before escaping to overlying waters and the troposphere [see (*20*)].
19. N. E. Blair, C. S. Martens, D. J. Des Marais, unpublished data. The $\delta^{13}C$ of pore water methane in the zone of active methane bubble formation (Fig. 1A) at our site was −63.01 ± 0.13 per mil on 2 February 1984, and −58.27 ± 0.50 per mil on 30 August 1984, matching the signature of methane in gas bubbles sampled on those dates (Fig. 2A).
20. Our results indicate that anaerobic [W. R. Reeburgh, *Earth Planet. Sci. Lett.* **47**, 345 (1980)] or aerobic [for example, J. W. M. Rudd and R. D. Hamilton, *Limnol. Oceanogr.* **23**, 337 (1978)] methane oxidation, or both, have not significantly frac-

tionated the bubble gas sample through preferential consumption of ^{12}C-CH_4. Such fractionation may occur to dissolve methane transported more slowly through the 7- to 25-cm-thick sediment cover overlying the methane production zone via molecular diffusion or to methane bubbles that become lodged in overlying sulfate-reducing sediments between low-tide bubbling episodes. Gas bubble methane transport in our site accounts for approximately 84% of the total annual methane flux of 5.7 ± 2.6 mol m^{-2} (*13*). The potential importance of carbon isotopic fractionation of methane during its transport up through an oxidizing sediment column has been discussed by Stevens and Rust (*8*).

21. F. J. Sansone and C. S. Martens, *Geochim. Cosmochim. Acta* **46**, 1575 (1982) and references therein.
22. R. A. Burke, thesis, University of South Florida (1985).
23. I. Woltemate, M. J. Whiticar, M. Schoell, *Limnol. Oceanogr.* **29**, 985 (1984); M. J. Whiticar, E. Faber, M. Schoell, *Geochim. Cosmochim. Acta* **50**, 693 (1986).

24. We thank J. P. Chanton for assistance with sample collection. We thank M. Bevis and L. K. Benninger for discussions concerning error analysis. Research supported by NASA grant NAGW-593 and NSF grants OCE 82-08666 and OCE 84-16963 to C.S.M. and NASA Planetary Biology funding to D.J.D. Laboratory and boat facilities were provided by the University of North Carolina's Institute of Marine Sciences, Morehead City.

23 December 1985; accepted 19 June 1986

Eclogites, Pyroxene Geotherm, and Layered Mantle Convection

ASISH R. BASU, JENNIFER S. ONGLEY, IAN D. MACGREGOR

Temperatures of equilibration for the majority (81 percent) of the eclogite xenoliths of the Roberts Victor kimberlite pipe in South Africa range between 1000° and 1250°C, falling essentially on the gap of the lower limb of the subcontinental inflected geotherm derived from garnet peridotite xenoliths. In view of the Archean age (>2.6 × 10^9 years) of these eclogites and their stratigraphic position on the geotherm, it is proposed that the inflected part of the geotherm represents the convective boundary layer beneath the conductive lid of the lithospheric plate. The gradient of 8 Celsius degrees per kilometer for the inflection is characteristic of a double thermal boundary layer and suggests layered convection rather than whole mantle convection for the earth.

IN A STUDY OF UPPER MANTLE PETROLOGY, Boyd (*1*) estimated the equilibration conditions of ultramafic xenoliths containing the assemblage garnet, orthopyroxene, clinopyroxene, and olivine from kimberlites in northern Lesotho. Temperature and pressure estimates of the Lesotho xenoliths defined a curvilinear trend ranging in temperature from 900° to 1400°C corresponding to depths of 100 to 200 km. Boyd interpreted this trend as the segment of a fossil geotherm at the time of kimberlite eruption. The lower temperature-pressure end of this xenolith trend coincided essentially with the continental shield geotherm of Clark and Ringwood (*2*), although the trend showed an inflection, beginning at 1100°C, and extending to 1400°C and a depth of 200 km (Fig. 1).

Another characteristic of this geotherm is that the xenoliths plotting on the shallow limb of the geotherm displayed a coarsely granular texture whereas those that defined the inflected limb were intensely sheared. Boyd also interpreted the point of inflection on this geotherm as marking the top of the low-velocity zone beneath Lesotho at the time of kimberlite eruption around 90 million years ago. In addition to this Lesotho geotherm, inflected geotherms based on the pyroxene geothermometry-barometry approach (*1*) have also been established from other regions in southern Africa (*3–5*). The overall patterns of these geotherms are broadly similar—that is, the temperature-depth profiles of the xenoliths show agreements with the theoretical (4.2 × 10^{-2} W m^{-2} heat flow) continental geotherm up to 1100°C, with a perturbation at higher temperatures. This deviation has been interpreted (*6*) as a perturbed geotherm associated with the convective movements, possibly diapiric (*7*), during the eruption of the kimberlites.

Although the above thermal, chemical, and stress distribution (rheology) structure is constructed mostly on the basis of garnet lherzolite xenoliths, many other varieties of mantle-derived xenoliths, including eclogites, harzburgites, dunites, and megacrysts of pyroxene, ilmenite, garnet, phlogopite, and diamond and graphite, are also present in the xenolith population of kimberlites. Because of the lack of reliable geothermometers and geobarometers, assignment of relative depths of origin for these xenoliths are more ambiguous, but it is clear that they must lie somewhere along the ambient mantle geotherm.

We focused on the eclogite xenoliths in kimberlites, particularly those from the Roberts Victor Mine in the Orange Free State of South Africa, to evaluate the temperatures of equilibration and the depths of origin of the eclogites and the implications of these data on the thermal evolution of the subcontinental mantle. This study was also prompted by several developments: (i) oxygen isotope systematics have been used to indicate that an ancient oceanic crust altered by seawater was the original source rock for the Roberts Victor eclogites (*8, 9*); (ii) samarium-neodymium study of the eclogites indicates an Archean age (*10*); (iii) an improved experimentally determined geothermometer (*11*), based on Mg-Fe exchange between garnet and clinopyroxene, allows reasonable estimates of the temperature of equilibration; (iv) computation (*12*) of seismic velocities as a function of temperature and pressure in the upper mantle is most consistent with an olivine and orthopyroxene-rich lithosphere extending to 150 km beneath the shield areas, followed by a high-temperature gradient or change in mineralogy, or both, that serves to decrease the velocities beneath the lithosphere; and (v) proof of mantle heterogeneity by various radiogenic isotopes and geochemical data has been combined with laboratory and numerical experiments on mantle convection to suggest that convection is restricted to discrete layers (*13*).

The partition of Fe^{2+} and Mg^{2+} between coexisting garnet (gt) and clinopyroxene (cpx), expressed as $K_d = (Fe^{2+}/Mg^{2+})_{gt}/(Fe^{2+}/Mg^{2+})_{cpx}$, is strongly temperature-dependent, and coupled with the mole fraction of calcium in garnet assemblages (*11*) provides a sensitive thermometer for eclogitic rocks. With this thermometer, temperatures of equilibration have been calculated for 62 eclogite xenoliths from the Roberts Victor kimberlite pipe. The eclogites include examples of both types previously defined on the basis of textural, isotopic, and chemical criteria (*8, 14, 15*) and we assume no Fe^{3+} in either the garnet or the clinopyroxene. These estimated temperatures are shown in Fig. 1 and compared with the Lesotho geotherm based entirely on the garnet lherzolite xenoliths. In Fig. 1 the geotherm of Boyd (*1*) has been corrected for the presence of FeO and CaO in enstatites and garnets by the method of Wood and Banno (*16*). The histogram indicates that 81% of the analyzed Roberts Victor eclo-

---

A. R. Basu and J. S. Ongley, Department of Geological Sciences, University of Rochester, Rochester, NY 14627.
I. D. MacGregor, Division of Earth Sciences, National Science Foundation, Washington, DC 20550.