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Air Quality**



Donald R. Blake; F. Sherwood Rowland

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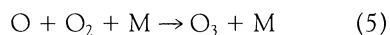
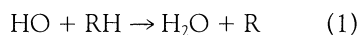
Alkane hydrocarbons (propane, isobutane, and *n*-butane) from liquefied petroleum gas (LPG) are present in major quantities throughout Mexico City air because of leakage of the unburned gas from numerous urban sources. These hydrocarbons, together with olefinic minor LPG components, furnish substantial amounts of hydroxyl radical reactivity, a major precursor to formation of the ozone component of urban smog. The combined processes of unburned leakage and incomplete combustion of LPG play a significant role in causing the excessive ozone characteristic of Mexico City. Reductions in ozone levels should be possible through changes in LPG composition and lowered rates of leakage.

Mexico City lies in a high valley surrounded by mountains capable of holding in pollutants released by its more than 15 million inhabitants and has suffered during the past two decades from increasingly severe smog events with very high ozone (O_3) levels (1, 2). The Mexican 1-hour criterion for O_3 is 0.11 parts per million (ppm; US Environmental Protection Agency, 0.12 ppm; World Health Organization, 0.10 ppm) and was exceeded in Mexico City on 71% of the days in 1986 and 98% in 1992, with values as high as 0.48 ppm on 16 March 1992 (3). Previous investigations of O_3 formation in Mexico City have primarily emphasized the release of hydrocarbons (HCs) from automobiles and trucks, and secondarily in industrial plants (4). Current control mechanisms during periods of high O_3 call for reductions in the use of automobiles and in levels of industrial operation. However, our detailed chemical analysis of the specific HC composition of Mexico City air (5, 6) has consistently shown very high concentrations of the C_3 and C_4 alkanes not usually found as more than very minor components in vehicular or industrial emissions. In most of our air samples, these three alkanes were the dominant nonmethane HCs (NMHC), with concentrations exceeding those of well-known signature compounds for fossil fuel combustion, such as ethylene and acetylene. The source of these alkanes lies in LPG—the major energy source for cooking and heating in urban households in Mexico City—leaking in unburned form into the atmosphere on a massive scale. These reactive HCs, together with the olefinic minor components in

LPG, plus olefinic and acetylenic products from their incomplete combustion, play a major (perhaps the dominant) role in O_3 production in the Valley of Mexico.

Previous studies have recognized the very high NMHC concentration in Mexico City air (7), and that standard emission inventories have fallen short by a factor of 4 in quantitative explanation of their presence (8). No controls on LPG emissions are currently specified in Mexico City, nor have any been specifically proposed (9). Substantial progress toward reduction of urban O_3 formation seems possible if attention is directed toward the problems associated with LPG usage. Although control of O_3 formation by reduction in HC emissions is less effective in areas such as Mexico City with a high ratio of NMHC to nitrogen oxides (NO_x), the overall HC reactivity of LPG is very dependent on its particular composition, especially in olefinic content as discussed below.

The formation of additional O_3 in the troposphere involves a combination of sunlight with excess concentrations of HCs and NO_x as in reactions 1 to 5 (10, 11) (R is an alkyl group; $h\nu$ is a photon; M is a third-body molecule):



Subsequent reactions of the various RO species such as aldehydes and ketones from reaction 3 are also important. A useful approximation to the relative importance of individual HCs in urban O_3 production can be

obtained from the measured HC composition multiplied by the known rate constants for reaction with OH radical in reaction 1 (12). These evaluations require quantitative measurements of ambient HC concentrations, and careful laboratory evaluation of the corresponding rate constants for reaction with each (13). A better approximation for O_3 formation in the urban environment can probably be obtained through the maximum incremental reactivity (MIR) estimates of Carter (14), who takes into account the subsequent reactions which follow the initial OH attack on the HCs.

The concentrations for selected HC compounds found in four representative air samples collected in February 1993 (5, 6) are given in Table 1 in parts per billion by volume (ppbv). Zocalo is in the central part of Mexico City, and canisters were filled there at 6 a.m. and noon during four consecutive days in the Plaza de la Constitución. The Pyramid of the Moon, on the other hand, is ~50 km northeast of the city center and was in an upwind direction from the city on 21 February. The measured HC concentrations there are generally comparable to those expected in locations well separated from local sources, except for those of propane and the two butanes, which are substantially above usual remote levels. Away from urban sources, the concentration of ethane normally exceeds those of propane and each of the butanes, in part because the atmospheric lifetime of ethane is considerably longer. In contrast, the Tlalpan Highway sample was taken in the midst of heavy afternoon traffic, and contains a substantial admixture of gases from vehicular emissions (such as ethylene, acetylene, and isopentane). The decrease in concentration of propane and the butanes between 6 a.m. and noon is a regular occurrence associated with the daylight expansion of the planetary boundary layer from the early morning 100 to 300 m above ground level to late afternoon elevations of about 2000 m above ground level (15).

Very high concentrations of propane, *n*-butane, and isobutane dominate the NMHC molar fractions except in heavy traffic conditions. The molar ratios among these three alkanes are quite similar in the two Zocalo air samples of Table 1, as they were in the other six collected at the same location. These HC ratios and their standard deviations are shown in Table 2 for the eight Zocalo samples and for seven canisters each collected in three other locations around the city. The remaining canisters were filled at various times of day in about 45 locations scattered all over the metropolitan area. For comparison purposes, we note that the reported concentration of propane was 1.6 ppbv for noontime summer measurements in Atlanta (16), and that the median concen-

Department of Chemistry, University of California, Irvine, CA 92717, USA.

tration for propane in 39 U.S. cities was 8 ppbv, with a maximum of 131 (17).

The same C₃-C₄ HC signature appeared in essentially all 75 samples collected during this 6-day period, with the propane concentration exceeding that of ethylene in 66 of them. The correlations of *n*-butane and isobutane with propane were excellent throughout this entire data set, with slopes of 0.458 (correlation coefficient $r^2 = 0.979$) and 0.210 ($r^2 = 0.992$), respectively. In contrast, the correlation with propane of isopentane, a known gasoline combustion and evaporation product, had an r^2 value of only 0.36. The geographical and diurnal constancy of these ratios reflects the very large number of contributing LPG leaks, with no substantial input from any source with a materially different C₃-C₄ composition. Similar patterns emphasizing the C₃-C₄ alkanes were observed in all locations in sample collections made during other time periods (May, July, September, and November). Ten samples collected be-

tween 1 and 4 a.m. on 21 July 1992 showed a similar dominance of these three alkanes, with a propane mixing ratio exceeding 100 ppbv throughout the city. Some samples collected in May 1995 had propane concentrations greater than 600 ppbv.

Fourteen of the February 1993 canisters were collected before 6:30 a.m., prior to most of the morning traffic. In general, these early morning samples had the highest total HC concentrations, particularly for propane and the butanes. The propane concentrations ranged from 52 to 423 ppbv (median 136; average, 174), together with isobutane and *n*-butane concentrations consistent with the ratios shown in Table 2. The maximum total HC concentration observed in any of these samples in February 1993 for C₂ through the C₁₀ HCs was ~4000 ppbC (that is, the sum of observed ppbv mole fraction times the number of C atoms per molecule). These numbers are comparable to the 2000 to 4000 ppbC (maximum 7000 ppbC) reported for total

HC concentration summed over more than 200 individual compounds from C₂ to C₁₃ in 71 samples from six fixed sites in Mexico City. All of the morning samples at these locations were collected gradually over the 3-hour period from 6 to 9 a.m. and therefore always included substantial contributions from morning commuter traffic (18).

Measurements of the composition of the LPG used in Mexico City in February 1993 and May 1995 demonstrated that the same three C₃-C₄ alkanes were the most prominent components in this mixture. Table 3 shows the measured HC composition of a typical LPG sample, M134, collected in February 1993, and of a rounded average composition for all of our 1993 Mexico City LPG samples. The HC composition of LPG is not an established quantity, but the presence of both major amounts of the C₃-C₄ alkanes and significant olefinic material was characteristic of every LPG sample tested. The LPG compositions in Table 3 do not correspond to the alkane ratios recorded in Table 2, the latter being weighted toward the lower boiling propane. Such a deviation is not unexpected because of uncertainties in the mechanisms of vapor-versus-liquid release of LPG to the atmosphere.

Table 3 also shows an evaluation of the contributions of each HC in the LPG toward the formation of urban O₃. For this calculation, we have used the MIR estimates given by Carter (14) but adjusted to the per molecule analytical data through multiplication by the molecular weight. For LPG sample M134, only about half of the potential urban O₃ formation is attributable to the alkane components. The remainder results from the less abundant but more reactive olefins. For the average LPG composition in Table 3, the total estimated O₃ formation is increased by a factor of 1.5 through the inclusion of the minor olefins. The atmospheric lifetimes of the various HCs can be approximately estimated for this tropical, high valley location as a few hours in sunlight for the butenes and a few days for the butanes, so that the olefinic composition of the atmosphere should change during the course of each day because of oxidation by reaction with OH.

The concentrations of HCs in LPG available in the Los Angeles area during April 1995 are also shown in Table 3 and are very different from the Mexico City values. The cumulative O₃ productivity in Table 3 for this Los Angeles LPG is less than half as large as that calculated for the Mexico City average and one-third that of sample M134. This reduction in O₃ creation for the Los Angeles LPG stems chiefly from diminution in the total reactive olefinic component, but also benefits from the switch in the C₃-C₄ composition in the direction of the less reactive propane. If the effects of these various composition changes

Table 1. Gaseous composition (in ppbv) of four air samples collected in the Mexico City area, 18 to 21 February 1993, at the times and dates indicated.

Compound	Zocalo I (06:00, 2/21)	Zocalo II (12:00, 2/18)	Pyramid of the Moon (12:30, 2/21)	Tlalpan Highway (16:45, 2/20)
Methane	2980	2300	1776	2122
Ethane	10.4	17.6	1.40	22.5
Propane	220.5	95.5	3.51	38.4
<i>n</i> -Butane	96.5	44.2	1.39	40.5
<i>i</i> -Butane	45.4	20.7	0.68	14.4
<i>n</i> -Pentane	15.3	13.5	0.28	67.5
<i>i</i> -Pentane	21.2	17.7	0.37	90.4
<i>n</i> -Hexane	14.2	10.3	0.12	25.0
2-Methylpentane	6.6	9.6	0.48	32.5
3-Methylpentane	3.9	6.7	0.09	19.7
<i>n</i> -Heptane	2.8	3.9	0.11	10.6
Ethylene	15.5	27.8	0.58	168.2
Propene	5.56	4.44	0.06	39.2
1-Butene	3.22	1.06	<0.005	6.88
<i>i</i> -Butene	2.68	0.92	<0.005	18.4
<i>trans</i> -2-Butene	2.48	0.10	<0.005	5.19
<i>cis</i> -2-Butene	2.22	0.60	<0.005	4.90
1-Pentene	0.46	0.29	<0.005	3.26
1-Hexene	0.50	0.30	<0.005	2.77
Acetylene	19.4	43.7	1.06	213.5
Propyne	0.26	0.57	<0.005	3.56
1,3-Butadiene	0.56	0.24	<0.005	5.68
Isoprene (C ₅ H ₈)	0.20	0.04	<0.005	1.38
Benzene	3.51	5.79	0.28	25.6
Toluene	12.1	29.8	0.37	39.4

Table 2. Molar ratios of propane to butanes in four locations in Mexico City, 18 to 21 February 1993.

Location	Samples	<i>n</i> -C ₄ H ₁₀ /C ₃ H ₈	<i>i</i> -C ₄ H ₁₀ /C ₃ H ₈	<i>i</i> -C ₄ H ₁₀ / <i>n</i> -C ₄ H ₁₀
Zocalo*	8	0.459 ± 0.029	0.213 ± 0.009	0.464 ± 0.010
Parque Popular†	7	0.471 ± 0.050	0.214 ± 0.015	0.457 ± 0.019
A. Lincoln Parque‡	7	0.506 ± 0.054	0.227 ± 0.015	0.451 ± 0.021
Jardin Velarde§	7	0.478 ± 0.028	0.217 ± 0.010	0.455 ± 0.009

*Plaza de la Constitucion. †Between 1st and 2nd Avenues and 17th and 19th Streets. ‡Emilio Castelar/Julio Verne. §Near Centro Medico Metro.

for LPG are calculated directly through initial reactivity of the components with OH radical (13), then the percentage reductions by elimination of olefins or by the change from butanes to propane are even greater.

Measurements in 22 U.S. cities have shown median VOC (volatile organic compound)/NO_x ratios in the range from 7.5 to 14.3 (19). In contrast, the mean ratio of NMHC to NO_x for four Mexico City sites was measured to be 34.8 (7), roughly a factor of 4 greater than in the Los Angeles metropolitan area. Evaluations of known emissions from automobiles and industrial sources yielded an NMHC/NO_x ratio of ~3/1 in Mexico City (20). In that previous compilation, the VOC emission sources for the Valley of Mexico were estimated as 625 kilotons (metric) per year, equally divided between mobile sources (317 kilotons/year) and stationary sources [308 kilotons/year: new biogenic emissions (125), solvent use (80), miscellaneous (73), unplanned fires (20) industrial processes (4.5), waste burning (4.4) and residential combustion (0.33)] (21). The last estimate seems very much too small for an area with annual sales of LPG exceeding 2000 kilotons. This identification of LPG as a large, previously unrecognized source of HCs for the Mexico City atmosphere provides a more satisfactory understanding of its O₃ precursor chemistry and moves the emission inventory and NMHC/NO_x ratio closer to the actual observations.

The speciated HC distributions of Table 1 clearly identify unburned LPG gases as major contributors to the HC emissions inventory in the Mexico City atmosphere, ei-

ther on a mass basis or when weighted by OH reactivity. For the initial morning HC composition, ~30% of the O₃ formation arises from the three C₃-C₄ HCs, with another 20% from the C₃-C₄ alkenes. As the morning passes, the relative amounts of ethylene and acetylene increase. A problem arises, however, in assigning the sources of compounds such as the latter two, which are usually attributed in urban situations to the incomplete combustion of fuels used in mobile sources. Indeed, in most urban surroundings, the concept of "incomplete combustion of fossil fuels" is used almost synonymously with "emissions from the vehicular transportation sector." Control strategies toward reactive HCs are then directed toward automobiles and trucks, with industrial emissions next in line for control strategies. However, the incomplete combustion of LPG should also lead to ethylene and acetylene emissions, so that evaluation of the respective contributions from the two fossil fuel sources in Mexico City requires additional information beyond simple molecular identification. The nearly parallel time pattern of usage for LPG and gasoline makes diurnal variations in concentration not immediately useful for discrimination among sources.

Numerous other cities in the world use LPG in significant quantities, and evaluation of its importance for O₃ formation in these urban areas should be carried out. In our laboratory, large propane and butane concentrations have been observed in Taipei, Taiwan; Yerevan, Armenia; Athens, Greece; and several cities in eastern Europe, and O₃ production from these excesses seems probable. Indeed, the survey of HC concen-

trations in 39 U.S. cities showed propane as the fourth most abundant NMHC in ppbC, after isopentane, *n*-butane, and toluene (22), indicating that LPG leakage may play a role in O₃ formation in some American cities. Global estimates of propane emissions have generally substantially underpredicted the amount of propane actually observed (23), but the leakage of LPG has not been properly included in such estimates and may well account for most of the discrepancy.

Although the relative abundance in LPG of the four C₄ olefins was small, their O₃-forming potential can be comparable to the much more abundant alkanes. If the LPG supply for Mexico City were changed to a HC composition consisting mostly of propane (see Table 3), and if the handling procedures for LPG were adjusted to decrease the unburned leakage, our findings suggest that Mexico City O₃ levels could be significantly reduced.

REFERENCES AND NOTES

1. A comprehensive review of air quality studies in Mexico City is given in volume 2 of the five-volume *Mexico City Air Quality Research Initiative (MARI)*. The five volumes are the product of a collaboration between Los Alamos National Laboratory and the Instituto Mexicano del Petroleo (2).
2. *Los Alamos Rep.* LA-12699 (1994).
3. *In (2)*, vol. 2, pp. 22-25.
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5. A total of approximately 180 air samples have been collected and analyzed from five separate trips to Mexico City, including 75 samples collected between 17 and 22 February 1993 in the midst of an extended heavy smog episode (O₃ ~0.30 ppm). All air samples were filled at ground level to ambient pressure (about 0.8 atm at the 2240 meter elevation of Mexico City) in 2-liter stainless steel canisters. The air in these canisters was subsequently analyzed by cryogenic separation of the components condensable at the temperature of liquid nitrogen, followed by multiple-aliquot gas chromatography. Volatile halocarbons were detected by electron capture (ECD) and HCs by flame ionization (FID) (6). Calibrations over the range of detected concentrations showed the FID HC responses to be proportional to concentration within about 2%.

The 1993 air samples were initially analyzed with simultaneous passage of aliquots through four combinations of chromatographic columns and detectors. Subsequent reanalysis of some of the 1993 samples divided the chromatographic flow stream through six column-detector combinations, and gave results in close agreement with the earlier measurements. The six combinations included DB-1 and DB-5MS columns with ECD, and DB-1, DB-5MS, PLOT Al₂O₃/Na₂SO₄ and Cyclohex-B columns with FID. All of the 1995 samples were assayed with the six combination procedure. Methane concentrations were measured on a separate analytical apparatus.

Approximately 200 compounds have been observed as clean peaks from the various FID detectors, with more than 70 individual HCs identified and quantitatively measured. In addition to the 26 HCs listed in Table 1, some of the others include (typical 6 a.m. data in parentheses in ppbv): *o*-xylene (2.5), *m*-xylene (6.0), *p*-xylene (2.3), ethylbenzene (4.8), styrene (0.6), 1,3,5-trimethylbenzene (2.8), 1,2,4-trimethylbenzene (2.8), limonene (0.9), *p*-cymene (1.8), and *n*-undecane (0.5). Approximately 75% of the total number of C atoms measured in our experiments are included among the molecules listed in Table 1. Quantitative data were also obtained for more than 25 halocarbons.

6. D. R. Blake *et al.*, *J. Geophys. Res.* **97**, 16559

Table 3. Composition and O₃ production of LPG from Mexico City, February 1993, and Los Angeles, California (LA), April 1995; ROP is relative O₃ productivity and is MIR (14) times molecular weight; O₃ production is the mole fraction times ROP.

Compound	Mole fraction (×10 ²)			O ₃ production		
	Mexico City		ROP	Mexico City		LA mean
	M134*	Mean†		M134	Mean	
<i>Alkanes</i>						
C ₂ H ₆	0.1	0.6	1.1	8	0.01	0.04
C ₃ H ₈	37.0	49.0	95.4	21	7.8	10.3
<i>i</i> -C ₄ H ₁₀	15.9	15.4	1.4	70	11.1	10.8
<i>n</i> -C ₄ H ₁₀	34.9	28.0	0.2	59	20.6	16.5
<i>i</i> -C ₅ H ₁₂	2.1	2.0	0.03	99	2.1	2.0
<i>n</i> -C ₅ H ₁₂	0.9	0.4	<0.01	75	0.7	0.3
Total alkane reactivity:				42.3	39.9	21.2
<i>Alkenes</i>						
C ₃ H ₆	0.7	0.3	1.8	400	2.8	1.2
<i>trans</i> -2-C ₄ H ₈	2.2	1.2	<0.01	560	12.3	6.7
<i>cis</i> -2-C ₄ H ₈	2.2	1.0	<0.01	560	12.3	5.6
<i>i</i> -C ₄ H ₈	2.0	1.0	<0.01	300	6.0	3.0
1-C ₄ H ₈	1.9	1.0	<0.01	500	9.5	5.0
1,3-C ₄ H ₆	0.1	0.1	<0.01	590	0.6	0.6
Total alkene reactivity:				43.5	22.1	7.2
Total HC reactivity:				85.8	62.0	28.4
Alkene/alkane reactivity ratio:				1.03	0.55	0.34

*M134 was collected from a taco stand in Zocalo.

†Average of all LPG samples collected during 1993.

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Polar Standstill of the Mid-Cretaceous Pacific Plate and Its Geodynamic Implications

John A. Tarduno and William W. Sager

Paleomagnetic data from the Mid-Cretaceous Mountains suggest that Pacific plate motion during the Early to mid-Cretaceous was slow, less than 0.3 degree per year, resembling the polar standstill observed in coeval rocks of Eurasia and North America. There is little evidence for a change in plate motion that could have precipitated the major volcanic episode of the early Aptian that is marked by the formation of the Ontong Java Plateau. During the volcanism, oceanic plates bordering the Pacific plate moved rapidly. Large-scale northward motion of the Pacific plate began after volcanism ceased. This pattern suggests that mantle plume volcanism exerted control on plate tectonics in the Cretaceous Pacific basin.

An extraordinary episode of volcanism that was marked by the creation of several large oceanic plateaus affected the Pacific Ocean basin during the Cretaceous (1–4). In some models, the plateaus represent sites where mantle plumes first impinged on the oceanic lithosphere (5). The bulk of volcanism is represented in the Earth's largest oceanic plateau, the Ontong Java Plateau (OJP), which formed in the early Aptian (3). The relation between this large-scale volcanism and the tectonic development of the Pacific basin is unclear. Anderson (6), for example, suggested that changes in Pacific basin plate motion drove Cretaceous volcanism, negating the need for a deep mantle plume source. To examine the relation between early Aptian volcanism and plate tectonics, we examined the absolute motion of the Pacific plate from recent paleomagnetic data available through deep sea drilling in the Mid-Pacific Mountains (MPM) [Ocean Drilling Program (ODP) sites 865 and 866] (7) (Fig. 1). At site 866, an altered basaltic basement sequence was recovered beneath a thick (1622 m) sequence of shallow water limestone. Down the section, the basalts grade from submarine pillows to subaerial flows separated by

weathered horizons (boles) (Fig. 2). Strontium and carbon isotopic (8) and paleontologic dating (9) of the basal sediments suggest that the basalts are of at least Hauterivian age [127 to 132 million years ago (Ma)] (10). $^{40}\text{Ar}/^{39}\text{Ar}$ radiometric age dating yields two age groups (123 Ma and 127.8 Ma) (11) that are broadly consistent with the other age estimates.

These data suggest that a paleolatitude estimate for the Pacific plate during the period before plateau-building volcanism might be available from the site 866 basalts. If the magnetization of the boles was ac-

quired during weathering, they might provide an internal average of paleosecular variation (PSV). To test this hypothesis, three boles were sampled, in addition to the least altered basalts, for paleomagnetic analysis (12).

A large percentage of magnetization was lost between 550° and 580°C, which is characteristic of a magnetite carrier and a chemical remanent magnetization (13) (Fig. 3). In addition, most samples displayed a small remanence with unblocking temperatures >580°C, which is characteristic of hematite. In the basalt samples in which a clear hematite component was isolated (~30%), it was colinear with the magnetite magnetization. The sequence was of reversed polarity (positive inclination, Southern Hemisphere), with a reversed-to-normal polarity transition near the base of the hole. Thermal demagnetization of bole samples displayed similar unblocking characteristics but with a larger hematite contribution (Fig. 3).

If undetected, large-volume short-duration volcanism can bias the time-averaged field value derived from any lava sequence (14). A plot of inclination versus the basalt stratigraphy reveals several important clues to the origin of the magnetizations (Fig. 2). Although directions from bole B-2 are scattered, the three boles do not appear to

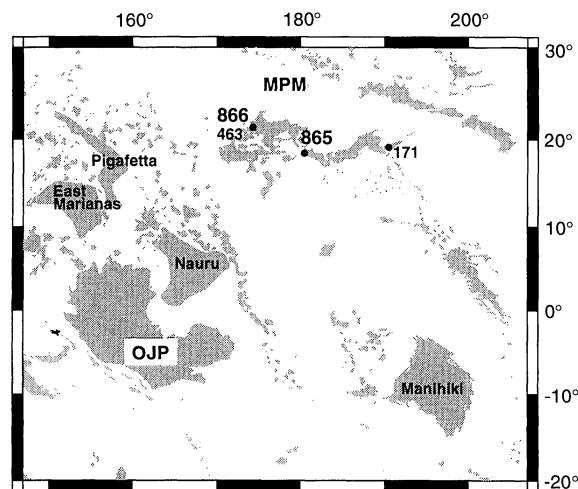


Fig. 1. Early Cretaceous (Aptian) volcanism represented on Manihiki Plateau and in the Nauru, Pigeffeta, and East Marianas basins has been linked to a mantle plume that formed the OJP (3). Alternatively, this volcanism is thought to result from a change in plate motions (6). Also shown are the MPM and the Deep Sea Drilling Project (DSDP) and ODP drill sites.

J. A. Tarduno, Department of Earth and Environmental Sciences, University of Rochester, Rochester, NY 14627, USA.

W. W. Sager, Department of Oceanography, Texas A&M University, College Station, TX 77843, USA.