

20. M. Xue, D.-H. Wang, J.-D. Gao, K. Brewster, K. K. Droegemeier, *Meteorol. Atmos. Phys.* **82**, 139 (2003).
 21. H. R. Pruppacher, J. D. Klett, *Microphysics of Clouds and Precipitation* (Kluwer Academic Publishers, Dordrecht, Netherlands, 1997).
 22. W. D. Hall, *J. Atmos. Sci.* **37**, 2486 (1980).
 23. M. Z. Jacobson, R. P. Turco, E. J. Jensen, O. B. Toon, *Atmos. Environ.* **28A**, 1327 (1994).
 24. R. List, N. R. Donaldson, R. E. Stewart, *J. Atmos. Sci.* **44**, 362 (1987).
 25. H. P. Meyers, P. J. DeMott, W. R. Cotton, *J. Appl. Meteorol.* **31**, 708 (1992).
 26. E. J. Zipser, in *Cloud Systems, Hurricanes, and the Tropical Rainfall Measuring Mission (TRMM)*, W.-K. Tao, R. Adler, Eds., vol. 29 of *Meteorological Monographs* (American Meteorological Society, Boston, MA, 2003), chap. 5.
 27. R. S. Scorer, *Environmental Aerodynamics* (Wiley, New York, 1977).
 28. D. J. Musil, A. J. Heymsfield, P. L. Smith, *J. Climate Appl. Meteorol.* **25**, 1037 (1986).
 29. T. J. Garrett, H. Gerber, D. G. Baumgardner, C. H. Twohy, E. M. Weinstock, *Geophys. Res. Lett.* **30**, 10.1029/2003GL018153 (2003).
 30. S. C. Sherwood, *Science* **295**, 1272 (2002).
 31. P. K. Wang, *J. Geophys. Res.* **108**, 10.1029/2002JD002581 (2003).
 32. R. G. Knollenberg, K. Kelly, J. C. Wilson, *J. Geophys. Res.* **98**, 8639 (1993).
 33. J. Lelieveld *et al.*, *Science* **298**, 794 (2002).
 34. A. D. Clarke, V. N. Kapustin, *J. Atmos. Sci.* **59**, 363 (2002).
 35. H. B. Singh *et al.*, *J. Geophys. Res.* **107**, 10.1029/2001JD000486 (2002).
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Materials and Methods

References

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Missing OH Reactivity in a Forest: Evidence for Unknown Reactive Biogenic VOCs

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Forest emissions of biogenic volatile organic compounds (BVOCs), such as isoprene and other terpenes, play a role in the production of tropospheric ozone and aerosols. In a northern Michigan forest, the direct measurement of total OH reactivity, which is the inverse of the OH lifetime, was significantly greater than expected. The difference between measured and expected OH reactivity, called the missing OH reactivity, increased with temperature, as did emission rates for terpenes and other BVOCs. These measurements are consistent with the hypothesis that unknown reactive BVOCs, perhaps terpenes, provide the missing OH reactivity.

Emissions of natural or biogenic volatile organic compounds (BVOCs) from vegetation are estimated to exceed all emissions of anthropogenic volatile organic compounds on the global scale and are roughly equal to global emissions of methane (1, 2). They can have a dominant influence on the atmospheric chemistry of forests, rural areas, and some

cities (3). The type of vegetation, solar radiation, and temperature determine the emission rates and species of BVOCs (4).

BVOCs react with hydroxyl radicals (OH) and nitrate radicals (NO₃), and olefinic BVOCs also react with ozone (O₃). A chemical's reaction frequency with OH is the product of its rate-coefficient for reaction with OH times its concentration. The sum of the reaction frequencies with OH for all chemicals is called the OH reactivity, which is the inverse of the OH lifetime. The calculated OH reactivity for the BVOCs that are emitted annually in North America has contributions from isoprene (51%), terpenes (31%), oxygenated BVOCs such as alcohols (16%), and all other known BVOCs (2%) (4). Oxidation of BVOCs by OH in the presence of nitric oxide (NO) is the principal source of tropospheric O₃ (5, 6). At the same time, O₃ reacts with olefinic BVOCs, such as isoprene and terpenes, to produce OH (7–9). Oxidation of some BVOCs by OH, O₃, and NO₃ produces organic acids that have low

vapor pressures and thus condense to form secondary organic aerosols (10–14). Understanding the OH reactivity is key to assessing the importance of these biogenic emissions to O₃ and aerosol formation.

Recent indirect evidence indicates that forests emit unknown, reactive BVOCs, perhaps terpenes (12, 15, 16). In a Michigan forest in 1998, Faloon *et al.* observed unexpected nocturnal OH, late-evening new particle formation, and a dependence of nocturnal OH and hydroperoxy radicals (HO₂) on O₃ (15). In a Sierra Nevada forest in 2000 and 2001, significant chemical loss of O₃ was observed (16). Finally, in the boreal Hyttialä forest (in Finland) in 2000, new particle formation of biogenic origin was observed; ancillary measurements suggest that the particles were produced from oxidation of terpenes (12). We show that forests emit reactive, unmeasured BVOCs with properties similar to those of terpenes.

This evidence comes from the direct measurement of OH reactivity. Measurements were made from 5 July to 3 August 2000, during the Program for Research on Oxidants: Photochemistry, Emissions and Transport (PROPHET 2000) intensive campaign. The site was at the University of Michigan Biological Station (45°30'N, 84°42'W) in the Great Lakes Region in northern Michigan (17). Measurements were made 2 m below the top of a 31-m tall tower, ~10 m above the canopy height. The site is in a mixed, transition forest that consists of northern hardwood, aspen, and white pine. During this period, the site experienced both clean Canadian air from the north and polluted air from cities to the south, such as Chicago and Detroit.

Direct atmospheric measurements of total OH reactivity were made with an instrument called the Total OH Loss-rate Measurement (TOHLM) (18, 19). The TOHLM method is analogous to the discharge-flow technique used in laboratory kinetics studies (20, 21). OH is generated at mixing ratios of a few parts per trillion by volume

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(pptv) by ultraviolet light from a mercury lamp. This light photodissociates water vapor, creating OH and H in a nitrogen flow inside a 1-cm-diameter movable tube. This moveable tube is in the center of a 7.5-cm-diameter glass flow tube, through which ambient air is drawn by a fan. The OH is injected through radially drilled holes at the end of the movable tube, mixed turbulently into the airflow, and detected by an OH detector at the end of the flow tube. The detection technique is low-pressure laser-induced fluorescence (22). OH reacts with trace constituents in the airflow, and as the movable tube is drawn further away from the detector, the observed OH signal decreases. The OH reactivity (s^{-1}) is determined from the slope of the logarithm of the OH signal, as a function of the distance between the OH injector and detector divided by the velocity of the air (23).

The PROPHET 2000 intensive campaign also included meteorological and chemical measurements: temperature, pressure, wind direction and speed, relative humidity, photolysis frequencies, nitrogen dioxide (NO_2), carbon monoxide (CO), isoprene, OH, HO_2 , NO, various nitrates, and anthropogenic hydrocarbons. Missing in 2000 were measurements of BVOCs, such as acetaldehyde, acetone, prominent monoterpenes, formaldehyde (HCHO), methyl vinyl ketone (MVK), methacrolein (MACR), ethanol, and methanol. However, these were measured in summer 1998 (17). The PROPHET 1998 campaign was conducted at the same tower and during a roughly similar period: 11 July to 20 August. The average meteorological conditions—temperature, wind direction, wind speed, and humidity—

Table 1. VOCs and other chemical species measured and used in the OH reactivity calculation. If not otherwise indicated, the species were measured in 2000 with the OH reactivity. Species measured only during the previous PROPHET campaign in 1998 (19) are indicated with an asterisk. Methane (CH_4) was assumed to be 1710 ppbv, although its exact value is not important for PROPHET.

Measured species		
Ethane	m,p-Xylene	HO_2
Ethylene	cis-2-Pentene	CH_4
Propane	o-Xylene	HCHO*
Propylene	Benzene	MACR*
Acetylene	Toluene	MVK*
i-Butane	Ethylbenzene	Acetaldehyde*
n-Butane	Acetone*	Myrcene*
trans-2-Butene	Butanal*	1,8-Cineol*
1-Butene	Propanal*	α -Phellandrene*
cis-2-Butene	NO_2	α -Pinene*
i-Pentane	NO	β -Pinene*
n-Pentane	O_3	d-3-Carene*
1,3-Butadiene	CO	Camphene*
trans-2-Pentene	Isoprene	Limonene*

were nearly identical for that time period in the two years. Furthermore, the mean atmospheric concentrations, diurnal variations, and temperature dependences for CO, NO, NO_2 , O_3 , OH, HO_2 , isoprene, benzene, and toluene were the same to within 1 SD for both years. By assuming that the atmospheric composition at the PROPHET site was the same for both summers, we can combine the data sets to provide complete coverage of the known and previously measured atmospheric constituents in a forest (Table 1).

The OH reactivity is calculated from the sum of the products of measured or modeled concentrations of atmospheric constituents and their rate coefficients for reactions with OH (5, 19). This method relies on measuring all atmospheric constituents that react with OH. These reactions often produce other constituents, some difficult to measure, that can also react with OH. Models constrained to the measured volatile organic compounds (VOCs) can be used to calculate the OH reactivity due to unmeasured VOCs that are predicted products of the measured VOCs. The OH reac-

tivity that was modeled with the Regional Atmospheric Chemistry Mechanism (24) exceeds that calculated with only measured VOCs by less than 2%, indicating that the predicted products can be ignored in the calculated OH reactivity.

Emissions of isoprene and other BVOCs depend strongly on temperature (1). When both the measured and the calculated OH reactivity are plotted as functions of temperature for times between 4:00 a.m. and 8:00 p.m., the measured OH reactivity is statistically greater than the calculated OH reactivity for temperatures greater than 284 K (Fig. 1A) (25). The mean difference between measured and calculated OH reactivity is $2.6 \pm 1.0 s^{-1}$, and the mean ratio is 1.5 ± 0.1 . The mean measured and calculated OH reactivity are statistically different to a significance level of 0.01, according to the Student's *t* test.

We used the chemical species reported in Table 1 to calculate the OH reactivity for PROPHET (Fig. 1B). Isoprene provides the largest contribution (49%), with contributions from CO and NO_2 (21%), HCHO

Fig. 1. (A) The total OH reactivity measurements (open circles) are shown with the OH reactivity we calculated from the sum of individual chemicals' reaction frequencies (solid squares). Calculated and measured OH reactivity increase with temperature, as expected, because they are both dominated by isoprene emissions, which increase with temperature over this temperature range. Error bars for measurements and calculations are the combination of the total uncertainty in the measurements or calculations and the SEM. (B) The calculated OH reactivity (solid black squares) consists of contributions from OH reactions with isoprene (open orange squares), CO and NO_2 (green diamonds), HCHO (black plus symbols), acetaldehyde (magenta circles), anthropogenic VOCs (red triangles), and terpenes (blue crosses). The data are smoothed with a running mean over 5 K, which smoothes the curves without changing the statistics of the missing OH reactivity.

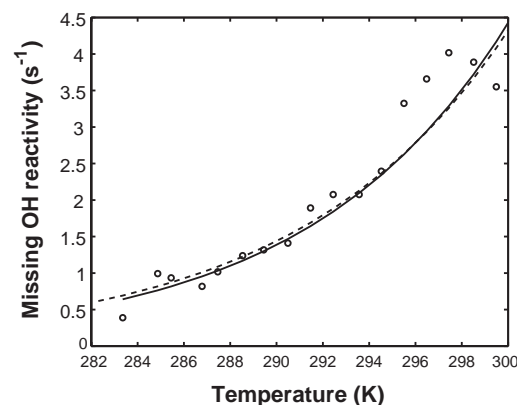
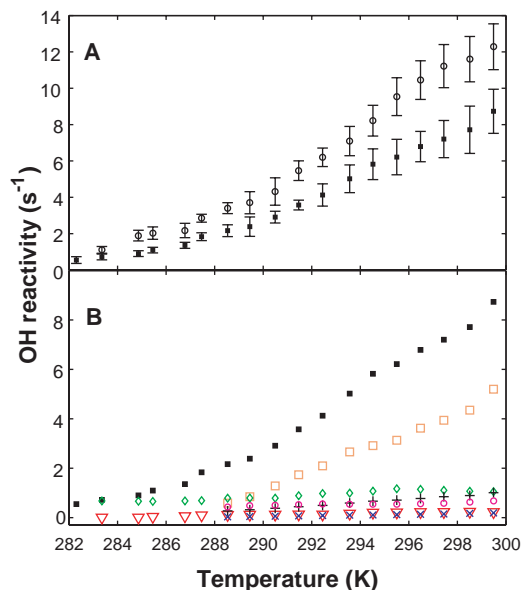


Fig. 2. The difference between measured and calculated OH reactivity versus temperature (circles). The missing OH reactivity, when fitted with the expression $E(T) = E(293)\exp(\beta(T - 293))$, yields $\beta = 0.11 K^{-1}$ with $R^2 = 0.92$ (solid line). This temperature dependence of the missing OH reactivity is almost identical to that of a derived temperature dependence of terpene emissions (26) (dashed line).

and acetaldehyde (12% each), anthropogenic VOCs (3%), monoterpenes (2%), and O₃, HO₂, SO₂, and NO (<1% combined). At temperatures less than 288 K, only CO and NO₂ contributed significantly to the OH reactivity. BVOCs contribute less at these temperatures, because their concentrations are below the instruments' detection limits (4, 26).

The difference between measured and calculated OH reactivity is temperature-dependent (Fig. 2). This missing OH reactivity is less than 0.5 s⁻¹ when the temperature is less than 284 K, but it increases to 3.7 s⁻¹ when the temperature is 299 K. Terpene emissions typically have a temperature dependence that can be fitted with the expression $E(T) = E(T_s)\exp[\beta(T - T_s)]$, where $E(T_s)$ is the emission rate at T_s , β is the temperature sensitivity factor, and T is the ambient temperature. Terpene emission rates can often be fitted with a β of 0.11 K⁻¹ and a T_s of 293 K (26). When the temperature dependence of the missing OH reactivity is fitted with the same expression, it too has a β of 0.11 K⁻¹, with a correlation coefficient (R^2) of 0.92. This similarity between the fitted curve for typical terpene emissions and the missing OH reactivity provides evidence that the missing OH reactivity results from unmeasured BVOCs with terpene-like temperature dependences.

Unmeasured anthropogenic VOCs are not responsible for the missing OH reactivity. Their mixing ratios depend on their transport to the PROPHET site and not on local emissions that are driven by temperature. They, like the measured anthropogenic VOCs, would show no temperature dependence. Furthermore, known monoterpenes are unlikely to contribute; we measured the most prominent monoterpenes (Table 1), which contributed less than 0.5 s⁻¹ to the OH reactivity. Known but unmeasured sesquiterpenes could be responsible, as could monoterpene reaction products, but their total OH reactivity would need to be 10 times that of the monoterpenes, a large difference.

Some biogenic emissions, such as isoprene and some monoterpenes and alcohols, are sunlight- and temperature-dependent (1, 26). If the missing OH reactivity were due to isoprene or a light-dependent monoterpene or alcohol, or to a short-lived reaction product of these emissions, then it should also depend on light. It does not. First, when the isoprene emission still correlates with light, early before 8 a.m. and late in the day after 5 p.m., the missing OH reactivity is independent of light. Second, between midnight and 4 a.m., when isoprene's contribution to the OH reactivity is much less than 1 s⁻¹, the

missing OH reactivity still depends on temperature. The missing OH reactivity is thus due neither to unmeasured light-dependent terpenes or alcohols, such as 2-methyl-3-buten-2-ol, nor to an error in the measurement of isoprene.

Controversial nocturnal OH measurements at the PROPHET site are consistent with the missing OH reactivity and the presence of unmeasured temperature-sensitive terpene emissions (15). During the daytime, the measured OH was ~2.8 times larger than the modeled OH in both 1998 and 2000 (27). In addition, OH was often seen at night and, depending on the O₃ and temperature, had concentrations in the low-10⁵ molecules cm⁻³ to the mid-10⁶ molecules cm⁻³, whereas models suggest that nocturnal OH should be less than 10⁵ molecules cm⁻³. If the atmospheric constituents that were responsible for the missing OH reactivity were also responsible for the additional OH, they must contain one or more carbon double bonds, react with O₃, and produce OH at a rate of 5 × 10⁶ to 5 × 10⁷ molecules cm⁻³ s⁻¹ (28).

Is this OH production consistent with the missing OH reactivity? Both O₃ and OH would react with the unmeasured BVOCs. The ratio of the reaction-rate coefficient for reaction with OH (k_{OH}) to that for reaction with O₃ (k_{O_3}) multiplied by the OH yield (Y) of the O₃ reaction, $k_{OH}/(k_{O_3} \cdot Y)$, can be determined from the measured OH loss rate, which is the product of the OH concentration and the total OH reactivity, the calculated OH production rate, and the missing OH reactivity (29). The ratio $k_{OH}/(k_{O_3} \cdot Y)$ determined by this method is 1.2 × 10⁵ to 2.8 × 10⁵ for different temperatures; it is consistent with the measured ratios of some terpenes and sesquiterpenes (30). For example, for highly reactive terpinolene, $k_{OH}/(k_{O_3} \cdot Y) = 1.6 \times 10^5$, which is similar to our calculated ratio, with $k_{OH} = 2.25 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, $k_{O_3} = 1.88 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹, and $Y = 0.74 \pm 0.10$ (31). For terpinolene to produce the average missing OH reactivity of 2.6 s⁻¹, its average mixing ratio would need to be ~500 pptv, a large value compared to the average total measured monoterpene mixing ratio of 50 to 100 pptv. It is more likely that the OH missing reactivity is due to a combination of several highly reactive BVOCs (15, 16, 32). These observations do not provide the identity of the candidate BVOCs, but they do limit the possibilities to candidate BVOCs that have temperature-sensitive but not light-sensitive emissions and at least one carbon double bond.

What about the measured OH reactivity in other environments? TOHLM was deployed a month after PROPHET 2000, from

15 August to 14 September 2000, in the Texas Air Quality Study (TexAQS 2000). The site was located in the urban plume of Houston, Texas. The instrument configuration and operation was identical to that in PROPHET 2000. In this environment, the calculated OH reactivity had contributions from anthropogenic VOCs (35%); CO, NO₂, SO₂, and HCHO (55%); and isoprene (<6%). The average difference between the measured and calculated OH reactivities during the TexAQS is 0.36 ± 1.65 s⁻¹ for a mean OH reactivity of 9.4 s⁻¹, independent of temperature, from 295 K to 313 K. This temperature-independent agreement in an environment dominated by anthropogenic emissions provides additional evidence that the OH missing reactivity observed during PROPHET 2000 is a result of unmeasured temperature-dependent BVOCs.

OH reactivity measurements have been analyzed for only a few locations. In three urban areas—Nashville, Houston, and New York (19, 33)—anthropogenic emissions dominate the OH reactivity and no temperature-dependent missing OH reactivity was observed. However, the combined evidence for unmeasured, temperature-dependent BVOC emissions from the PROPHET site in northern Michigan, the Sierra Nevada forest in California, and the Hyttialä forest in Finland indicates that these BVOCs could be widespread in forests. At the combined concentration required to account for the missing reactivity, these BVOCs would significantly affect the forests' atmospheric chemistry and would be important particle precursors. New, more specific and more sensitive detection techniques will likely be required to determine the identity of the BVOCs responsible for the missing OH reactivity and the reason they have not yet been detected.

References and Notes

1. A. Guenther et al., *J. Geophys. Res.* **100**, 8873 (1995).
2. M. Trainer et al., *Nature* **329**, 705 (1987).
3. W. L. Chameides, R. W. Lindsay, J. Richardson, C. S. Kiang, *Science* **241**, 1473 (1988).
4. J. D. Fuentes et al., *Bull. Am. Meteorol. Soc.* **81**, 1537 (2000).
5. L. I. Kleinman et al., *Geophys. Res. Lett.* **29**, 10.1029/2001GL014569 (2002).
6. T. B. Ryerson et al., *Science* **292**, 719 (2001).
7. S. E. Paulson, A. D. Sen, P. Liu, J. D. Fenske, M. J. Fox, *Geophys. Res. Lett.* **24**, 3193 (1997).
8. N. M. Donahue, J. H. Kroll, J. G. Anderson, K. L. Demerjian, *Geophys. Res. Lett.* **25**, 59 (1998).
9. T. Pfeiffer, O. Forberich, F. J. Comes, *Chem. Phys. Lett.* **298**, 351 (1998).
10. M. O. Andreae, P. J. Crutzen, *Science* **276**, 1052 (1997).
11. Z. Meng, D. Dabub, J. H. Seinfeld, *Science* **277**, 116 (1997).
12. C. D. O'Dowd, P. Aalto, K. Hämeri, M. Kulmala, T. Hoffmann, *Nature* **416**, 497 (2002).
13. I. G. Kavouras, N. Mihalopoulos, E. G. Stephanou, *Nature* **395**, 683 (1998).
14. R. J. Griffin, D. R. Crocker, R. C. Flagan, J. H. Seinfeld, *J. Geophys. Res.* **104**, 3555 (1999).

15. I. Faloon *et al.*, *J. Geophys. Res.* **106**, 24315 (2001).
16. M. R. Kurpius, A. H. Goldstein, *Geophys. Res. Lett.*, **30**, 1371, 10.1029/2002GL016785 (2003).
17. M. A. Carroll, S. B. Bertman, P. B. Shepson, *J. Geophys. Res.* **106**, 24275 (2001).
18. T. A. Kovacs, W. H. Brune, *J. Atmos. Chem.* **39**, 105 (2001).
19. T. A. Kovacs *et al.*, *J. Environ. Monit.* **5**, 68 (2003).
20. N. M. Donahue, J. S. Clarke, K. L. Demerjian, J. G. Anderson, *J. Phys. Chem.* **100**, 5821 (1996).
21. F. Kaufmann, *J. Phys. Chem.* **88**, 4909 (1984).
22. P. S. Stevens, J. H. Mather, W. H. Brune, *J. Geophys. Res.* **99**, 3543 (1994).
23. Each decay takes 4.3 min, with 20 s at each of 13 steps, a 10-s measurement of OH plus the background signal, and a 10-s measurement of the background signal alone. The OH signal decreases a factor of 10 to 20 over the 13 steps. The OH reactivity, k_{OH} , is the slope of the logarithm of the OH signal, S_{OH} , as a function of the time (the distance divided by the velocity) minus the OH loss to the flow tube's walls, k_{wall} : $k_{OH} = -\Delta \ln(S_{OH}) / \Delta \text{time} - k_{wall}$. The OH wall loss, which was determined by flowing ultrahigh-purity zero air down the flow tube, was $2.2 \pm 0.4 \text{ s}^{-1}$ for PROPHET 2000 and five subsequent field studies. We calibrated the TOHLM by adding known quantities of CO and some hydrocarbons and comparing the slope of the OH reactivity with the accepted reaction-rate coefficient (18). In the presence of ambient NO, HO₂ reacts with the NO to reform OH, changing the observed slope of the decay. The HO₂ recycling was insignificant during the PROPHET 2000 campaign, when NO was never more than 0.2 ppbv.
24. W. R. Stockwell, F. Kirchner, M. Kuhn, *J. Geophys. Res.* **102**, 25847 (1997).
25. The absolute uncertainty of TOHLM measurement is $\pm 10\%$, with 1σ confidence level, and the wall loss uncertainty is $\pm 0.4 \text{ s}^{-1}$. For an OH reactivity of 10 s^{-1} , the combined uncertainty is $\pm 1.05 \text{ s}^{-1}$, with 1σ confidence level. The total uncertainty in the calculated OH reactivity [14% on average (1σ confidence level)] is based on the uncorrelated errors of the measurements of the atmospheric constituents and their reaction-rate coefficients and the SEM for each temperature (19). The gas chromatography-flame ionization detector measurements of V.Y. and co-workers in 2000, using the Al₂O₃/KCl porous layer open tubular (PLOT) column, indicate no significant hydrocarbon-like molecules were unaccounted for. In single-ion gas chromatography-mass spectrometry measurements that were tuned to measure monoterpenes, made by D.R. and E.A. in 1998, the peaks of all VOCs in the monoterpene region were identified and quantified above an equivalent mixing ratio of 1 pptv; less than 1% of the total peak area was unidentified (17).
26. G. W. Schade, A. H. Goldstein, M. S. Lamanna, *Geophys. Res. Lett.* **26**, 2187 (1999).
27. D. Tan *et al.*, *J. Geophys. Res.* **106**, 24407 (2001).
28. R. Atkinson, J. Arey, *Atmos. Environ.* **37** (suppl 2), 197 (2003).
29. The ratio of the reaction rate of the constituent with OH to the product of the reaction rate with O₃ and its OH yield is given by $k_{OH}/(k_{O_3} \cdot Y) = (OH_{\text{reac, meas}} - OH_{\text{reac, calc}}) / (OH_{\text{loss}} - OH_{\text{source, calc}} / [O_3])$, where $OH_{\text{reac, meas}}$ is the OH reactivity measured; $OH_{\text{reac, calc}}$ is the OH reactivity calculated (the difference is the missing OH reactivity); OH_{loss} is the OH loss rate, the product of the OH concentration and the measured OH reactivity; $OH_{\text{source, calc}}$ is the OH production from all known OH sources, both photolytic sources and those involving O₃ plus known alkenes; and $[O_3]$ is the measured concentration of ozone.
30. R. Atkinson, *J. Phys. Chem. Ref. Data* **26**, 215 (1997).
31. S. M. Ashmann, J. Arey, R. Atkinson, *Atmos. Environ.* **36**, 4347 (2002).
32. A. C. Lewis *et al.*, *Nature* **405**, 778 (2000).
33. X. Ren *et al.*, *Atmos. Environ.* **37**, 3639 (2003).
34. We thank J. Bassis and J. Simpasa, G. Yip for assistance with the CO data, G. Visconti for support, A.

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Evidence of Hominin Control of Fire at Geshar Benot Ya'aqov, Israel

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The presence of burned seeds, wood, and flint at the Acheulian site of Geshar Benot Ya'aqov in Israel is suggestive of the control of fire by humans nearly 790,000 years ago. The distribution of the site's small burned flint fragments suggests that burning occurred in specific spots, possibly indicating hearth locations. Wood of six taxa was burned at the site, at least three of which are edible—olive, wild barley, and wild grape.

Archaeological research suggests that the association between hominins and fire (1, 2), including hominins' use (3) and control (4) of fire, dates far back; however, the question of how long ago hominins gained control of fire has been an ongoing debate. By Upper Pleistocene times, cultural data include hearths, burned flint artifacts, and burned bones in Africa [e.g., (5)], the Levant (6, 7), and Europe (8). Several Middle Pleistocene sites (~500,000 years ago) in Europe [e.g., (9, 10)] and the Levant (11, 12) seem to exhibit human exploitation and control of fire. Earlier periods have yielded only fragmentary evidence, interpreted as stemming from natural bush fires (13) or taphonomic disturbances (14). Several Early Pleistocene sites in Africa offer data that consist primarily of sediment coloration (15, 16). We present here archaeological and paleobotanical evidence—burned organic and inorganic materials—that indicates the presence of fire at the Acheulian site of Geshar Benot Ya'aqov (GBY) during the Lower and Middle Pleistocene (17) and suggests that the burning of these materials resulted from hominin activities rather than natural phenomena.

GBY, a waterlogged site on the shores of the paleo-Lake Hula, is located in the northern Dead Sea Rift. Situated on a plate boundary, the site is tectonically disturbed (18). It contains a depositional sequence

~34 m thick, in which Acheulian archaeological horizons are embedded. We excavated archaeological horizons above the Brunhes-Matuyama (B-M) chron boundary (0.79 million years ago), where we uncovered extensive assemblages of artifacts.

Burned flint artifacts (longer than 20 mm) and microartifacts (2 to 20 mm in length) occur in all the excavated archaeological horizons, including the eight levels of Layer II-6 (table S1), which is located some four meters above the B-M chron boundary. The time span represented by these horizons is tens of thousands of years (17). Flint artifacts were present in the entire sequence, including the unexcavated areas, but we found burned flint items only in the areas that we excavated. This report presents the lithic assemblage from Area C, which is in the upper part of the stratigraphic sequence. The base of layers V-5 and V-6 of Area C (17) is located slightly more than 13 m above the B-M chron boundary.

Layers V-5 and V-6 contain two sediment types—coarse (coquina), in layer V-5, and fine (clay), in layer V-6; the shift between these sediment types indicates a change in the water level of the lake [figure 1 in (17)]. Layer V-5, with an excavated volume of 2.25 m³, and layer V-6, with an excavated volume of 1.39 m³, yielded large enough samples for lithic analysis. Of the three rock types used by the Acheulian hominins—flint, basalt, and limestone—flint is the most abundant in these layers, whereas in the other areas of the site, basalt is the most common type of rock. At temperatures of about 350° to 500°C, fire visibly alters and damages flint, as evidenced by typical macrofracture deformations such as pot lids, crazing, shrinkage,

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