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**Formation of Secondary Organic Aerosols Through
Photooxidation of Isoprene**

Magda Claeys, *et al.*

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total surface. Second, near the tops of the barriers to isomerization, where isomerization is slow, the potential for vibrationally mode-specific effects exists if the SEP process deposits energy in modes that are closely associated with the reaction coordinate(s). Third, if isomerization involves H atom tunneling, it may be possible to use these methods to explore the conformational mixture of the tunneling levels as a function of vibrational level and energy relative to the classical barrier height. Finally, there may be circumstances where the spectra will provide evidence for competing pathways turning off certain open channels for isomerization as other more efficient pathways open up.

References and Notes

1. D. A. Evans, D. J. Wales, *J. Chem. Phys.* **118**, 3891 (2003).
2. D. J. Wales, *Energy Landscapes* (Cambridge Univ. Press, Cambridge, 2003).
3. T. Ebata, K. Kouyama, N. Mikami, *J. Chem. Phys.* **119**, 2947 (2003).
4. B. C. Dian, A. Longarte, P. R. Winter, T. S. Zwier, *J. Chem. Phys.* **120**, 133 (2004).
5. D. Evans, D. Wales, B. C. Dian, T. S. Zwier, *J. Chem. Phys.* **120**, 148 (2004).
6. B. C. Dian, G. M. Florio, A. Longarte, T. S. Zwier, *J. Chem. Phys.*, in press.
7. M. Silva, R. Jongsma, R. W. Field, A. M. Wodtke, *Annu. Rev. Phys. Chem.* **52**, 811 (2001).
8. T. Burgi, T. Droz, S. Leutwyler, *Chem. Phys. Lett.* **246**, 291 (1995).
9. Y. D. Park, T. R. Rizzo, L. A. Peteanu, D. H. Levy, *J. Chem. Phys.* **84**, 6539 (1986).
10. L. A. Philips, D. H. Levy, *J. Chem. Phys.* **89**, 85 (1988).
11. Y. R. Wu, D. H. Levy, *J. Chem. Phys.* **91**, 5278 (1989).
12. L. L. Connell, T. C. Corcoran, P. W. Joireman, P. M. Felker, *J. Phys. Chem.* **94**, 1229 (1990).
13. J. R. Carney, T. S. Zwier, *J. Phys. Chem. A* **104**, 8677 (2000).
14. J. R. Carney, T. S. Zwier, *Chem. Phys. Lett.* **341**, 77 (2001).
15. B. C. Dian, J. R. Clarkson, T. S. Zwier, data not shown.
16. Studies of this type can be used to test statistical theories of isomerization rates which assume that intramolecular vibrational redistribution is fast compared to the rate of isomerization. See D. M. Leitner, B. Levine, J. Quenneville, T. J. Martinez, P. G. Wolynes, *J. Phys. Chem. A* **107**, 10706 (2003).
17. J. C. Keske, B. H. Pate, *Annu. Rev. Phys. Chem.* **51**, 323 (2000).
18. T. M. Korter, N. V. Tri, J. T. Yi, D. W. Pratt, personal communication (2003).
19. In Fig. 4, it is assumed that C(2) is the conformer responsible for the 747 cm⁻¹ upper bound in the C→B spectrum on the basis of the relative energies of other barriers shown.
20. Density functional theory calculations at the Becke3LYP/6-31+G(d) level of theory predict barriers for the A-B and A-F isomerizations that are several hundred wavenumbers higher than experiment. However, the computed barriers for A→C(1), A→D, and A→E are close to those measured. This suggests that the pathway for A-B and A-F isomerizations may proceed by some pathway other than the direct one computed.
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Supporting Online Material

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Figs. S1 and S2

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Formation of Secondary Organic Aerosols Through Photooxidation of Isoprene

Magda Claeys,^{1*} Bim Graham,^{2,3} Gyorgy Vas,¹ Wu Wang,¹
Reinhilde Vermeylen,¹ Vlada Pashynska,¹ Jan Cafmeyer,⁴
Pascal Guyon,² Meinrat O. Andreae,² Paulo Artaxo,⁵
Willy Maenhaut⁴

Detailed organic analysis of natural aerosols from the Amazonian rain forest showed considerable quantities of previously unobserved polar organic compounds, which were identified as a mixture of two diastereoisomeric 2-methyltetrols: 2-methylthreitol and 2-methylerythritol. These polyols, which have the isoprene skeleton, can be explained by OH radical-initiated photooxidation of isoprene. They have low vapor pressure, allowing them to condense onto preexisting particles. It is estimated that photooxidation of isoprene results in an annual global production of about 2 teragrams of the polyols, a substantial fraction of the Intergovernmental Panel on Climate Change estimate of between 8 and 40 teragrams per year of secondary organic aerosol from biogenic sources.

Aerosols are of climatic interest because they act as cloud condensation nuclei (1) and scatter and absorb solar radiation (2). It has been well established that photooxidation products of monoterpenes (e.g., α - and β -pinene) (3, 4), which are

biogenic volatile organic compounds (VOCs) emitted mainly by terrestrial vegetation, contribute to the aerosol budget (5, 6). However, it has been assumed that the much larger emissions of isoprene (7) do not result in secondary organic aerosol (SOA) formation in the atmosphere (8). Knowledge of the degradation mechanisms of isoprene, which represents almost 50% of all biogenic non-methane hydrocarbons on the global scale (7), is of considerable interest for air quality modeling (9). It has recently been proposed that the heterogeneous reaction of isoprene on acidic particles could be an important source of humic-like substances, which contribute 20 to 50% of the water-soluble organic aerosol at urban and rural sites in Europe (10). Here, we report evidence that photooxidation of isoprene is a substantial source of SOA, contrary to previous assumptions.

As part of the Cooperative Large-Scale Biosphere-Atmosphere Experiment in Amazonia Airborne Regional Experiment (LBA-CLAIRE) 1998 and 2001 experiments, atmospheric aerosols were collected at Balbina (1°55'S, 59°24'W), 125 km north of Manaus, Brazil, during the wet season (11). Backward air mass trajectories indicated that this site was not affected by anthropogenic sources, given that surface air masses originated from the northeast to east and had traveled 1000 km over the most remote regions of the Amazonian rain forest for almost a week before being sampled. The organic compounds present in the aerosol samples are, therefore, believed to be characteristic of local and regional atmospheric chemical phenomena rather than of long-range transport. The Amazon basin contains the world's largest humid forest ecosystem, which is known to emit large quantities of VOCs (7, 12). Because solar radiation and the production of OH radicals are at a maximum in the tropics, the formation of photooxidation products from natural VOCs is expected to be important.

Selected aerosol samples were subjected to analysis by gas chromatography-mass spectrometry (GC-MS) for detailed characterization of organic compounds (11). Figure 1 presents a GC-MS total ion current chromatogram of the trimethylsilylated (TMS) extract of the fine size fraction [particulate matter with diameter <2.5 μ m (PM_{2.5})] of a typical aerosol sample collected during the CLAIRE 2001 campaign with a high-volume (Hi-Vol) air sampler. Compounds 1 and 2 correspond to the newly found compounds, which were identified as diastereoisomeric forms (threo and erythro) of a polyol, specifically 2-methylthreitol and 2-methylerythritol. The structures of these compounds were elucidated with a combination of electron ionization (EI) and methane chemical ionization GC-MS, and then confirmed by a comparison of the GC-MS data with data from synthesized reference compounds (11).

¹Department of Pharmaceutical Sciences, University of Antwerp, Universiteitsplein 1, B-2610 Antwerp, Belgium. ²Biogeochemistry Department, Max Planck Institute for Chemistry, Post Office Box 3060, D-55020 Mainz, Germany. ³Atmospheric Research, Commonwealth Scientific and Industrial Research Organisation, PMB 1, Aspendale, Victoria 3195, Australia. ⁴Department of Analytical Chemistry, Institute for Nuclear Sciences, Ghent University, Proeftuinstraat 86, B-9000 Gent, Belgium. ⁵Institute of Physics, University of São Paulo, Rua do Matão, Travessa R, 187, CEP 05508-900 São Paulo, Brazil.

*To whom correspondence should be addressed. E-mail: magda.claeys@ua.ac.be

Mass spectra of the TMS derivatives of compounds **1** and **2** are shown in figs. S1 and S2, and those of the synthesized reference compounds are given in fig. S3.

Taking into account that 2-methylthreitol and 2-methylerythritol have the C₅ isoprene skeleton, it is logical to propose that isoprene is the precursor for their formation in the atmosphere. To date, the photooxidation of isoprene in the atmosphere has been believed to result only in volatile products—particularly formaldehyde, methacrolein, and methyl vinyl ketone—and not in condensable products that can be found in the aerosol phase. A primary plant origin of the 2-methyltetrols could be ruled out because they are not known to be present in plant leaves (13), they were not found in a composite sample of leaves from Amazonian tree species (11), and they occur as a mixture of diastereoisomers, consistent with a non-enzymatic formation process. Because the 2-methyltetrols are not of primary biogenic origin, they have to be considered as SOA components. The 2-methyltetrols have, to our knowledge, not been reported before, either in chamber experiments with isoprene or from ambient aerosols. A possible reason that they have not been detected in earlier aerosol composition studies is that the methods generally used are targeted to the determination of dicarboxylic acids. These methods are based on methylation of carboxylic groups and GC-MS, or on direct liquid chromatography-MS with electrospray ionization in the negative ion mode, and are not well suited to the analysis of neutral polyols.

Chamber experiments with isoprene under simulated atmospheric conditions have generally been performed in the presence of relatively high levels of ozone and NO_x (8), conditions that are different from natural tropical atmospheric conditions, which, except in the burning season, are characterized by low NO_x concentrations [(NO) < 100 parts per thousand (ppt)] (14). It is known that the photooxidation of isoprene is dominated by its reaction with OH radicals, because its reaction with ozone is relatively slow (15). When the OH radical-initiated photooxidation of isoprene has been investigated in the absence of NO_x, aerosol formation has been noted (8), and furthermore, the formation of 1,2-diol derivatives (i.e., 2- and 3-methyl-3-butene-1,2-diol) has been demonstrated (16). For the formation of the 1,2-diols, a reaction mechanism involving a reaction with HO/O₂ followed by self- and cross-reactions of peroxyradicals (RO₂) has been proposed (16). The formation of the 2-methyltetrols from isoprene in the present study under tropical atmospheric conditions can be explained by two cycles of these reactions (Fig. 2) [further discussion of potential formation mechanisms is available in the supporting online material (SOM) text]. The yield of the 2-methyltetrols from isoprene oxidation of 0.2% (0.4% in mass terms) is consistent with the low aerosol carbon yields in chamber experiments (8). The vapor pressures of the 2-methyltetrols are expected to be very low (<1.6 × 10⁻⁵ Torr, the

value calculated for 2,3,4-pentanetriol at 27°C), so that these products are expected to be predominantly in the condensed phase (17). A gas-to-particle transfer mechanism, most likely condensation onto preexisting particles, operates in aerosol formation from 2-methyltetrols.

The 2-methyltetrols, 2-methylthreitol and 2-methylerythritol, are expected to be hygroscopic and to have a water solubility comparable to those reported for racemic D,L-threitol (i.e., 8.8 g ml⁻¹ water) and meso-erythritol (i.e., 0.64 g ml⁻¹ water), respectively (18). The hygroscopic growth of submicrometer aerosol particles has been studied with tandem differential mobility analysis at the same remote rain forest site in central Amazonia during the LBA-CLAIRE 1998 campaign (19). In that study, hygroscopic particles could be identified that were typical of the pristine rain forest atmosphere and were believed to contain oxidation products of biogenic compounds. In addition, it has been demonstrated that most aerosol particles contain enough water-soluble material to be able to act efficiently as cloud condensation nuclei (20).

In addition to the 2-methyltetrols, the extract of the fine size fraction of the wet season aerosols contained other oxygenated organic compounds, i.e., mono- and dihydroxydicarboxylic acids and polysaccharidic compounds (Fig. 1). The mono- and dihydroxydicarboxylic acids and saccharidic compounds were identified by comparing their EI mass spectra and GC behaviors with those of

authentic standards. The mono- and dihydroxydicarboxylic acids included malic acid, α-hydroxyglutaric acid, tartaric acid, and previously unobserved minor compounds, which occurred as a mixture of diastereoisomers (threo and erythro) and were tentatively identified as 2,3-dihydroxyglutaric acids (Fig. 1, compounds **4** and **6**) (11). The major identified saccharidic compounds were levoglucosan, arabinol, mannitol, and glucose. Of the mono- and dihydroxydicarboxylic acids, malic, tartaric, and α-hydroxyglutaric acid have been previously reported in Amazonian aerosols at appreciable atmospheric concentrations (>10 ng m⁻³) (21). As for the atmospheric origin of these compounds, malic acid has been proposed to be a late product in the photochemistry of unsaturated fatty acids (22), but other biogenic sources, such as *n*-alkanes emitted by the forest vegetation, could also be considered. The other mono- and dihydroxydicarboxylic acids, tartaric acid, α-hydroxyglutaric acid, and the 2,3-dihydroxyglutaric acids likely have the same atmospheric origin as malic acid. Levoglucosan (1,6-anhydro-β-D-glucopyranose) is a molecular marker for biomass burning (23), which has proven useful for monitoring biomass burning in Amazonian aerosols (21, 24). The sugar alcohols, arabinol and mannitol, are attributed to natural background and are believed to originate from fungal spores, whereas the monosaccharide, glucose (a common plant sugar), is likely due to pollen (25).

To determine whether compounds were asso-

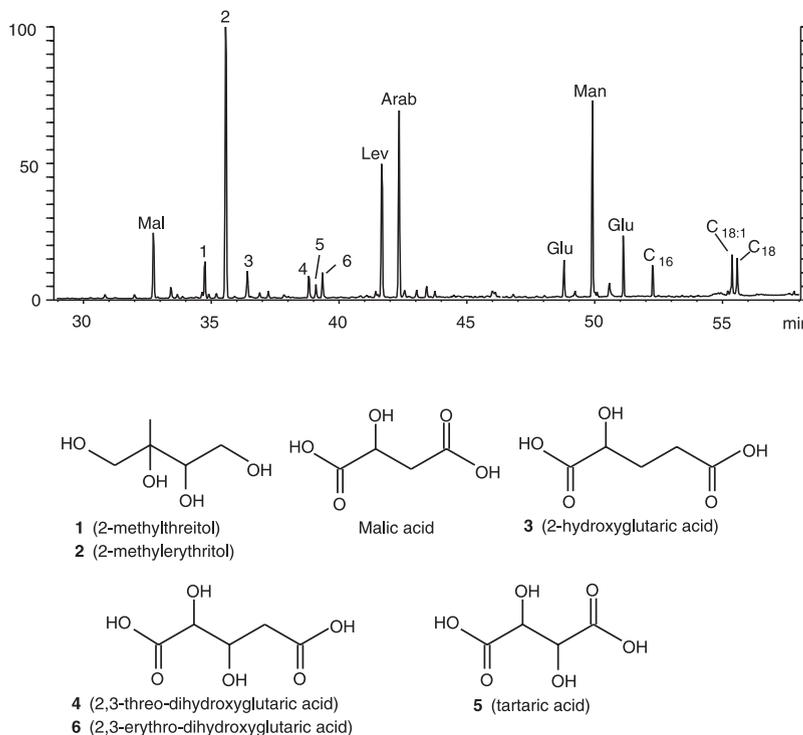


Fig. 1. GC-MS total ion current chromatogram obtained for a trimethylsilylated extract of the fine size fraction of a Hi-Vol sample collected during the LBA-CLAIRE 2001 campaign (25 to 27 July, day sampling only). Mal, malic acid; Lev, levoglucosan; Arab, arabinol; Glu, glucose (2 peaks); Man, mannitol; C₁₆, palmitic acid; C_{18:1}, oleic acid; C₁₈, stearic acid. Compounds **1** and **2** correspond to the previously unobserved 2-methyltetrols, i.e., 2-methylthreitol and 2-methylerythritol, respectively, arising from the photooxidation of isoprene.

ciated with fine- or coarse-mode particles, we analyzed a set of fine and coarse filter samples from daytime and nighttime collections during LBA-CLAIRE 2001. Quantitative determinations of the 2-methyltetrols, mono- and dihydroxydicarboxylic acids, and saccharidic compounds were performed by GC-flame ionization detection (Table 1) (11). The results obtained for the 2-methyltetrols show that they are enriched in the fine size fraction, suggesting that they are SOA components (i.e., formed by gas-to-particle conversion processes). The observation that 2-methyltetrols, formed by the daytime photooxidation of isoprene, are present at a considerable concentration in the nighttime sampling can be explained by the high chemical stability of the 2-methyltetrols and the lower nighttime temperatures, which favor condensation onto particles. Table 1 also shows that the 2-methyltetrols explain about 2% of the organic carbon (OC) in PM_{2.5} aerosols. Similarly, the mono- and dihydroxydicarboxylic acids—malic acid, α -hydroxyglutaric acid, the 2,3-dihydroxyglutaric acids, and tartaric acid—are enriched in the fine size fraction, as expected for SOA components. Levoglucosan, a primary organic aerosol component and a molecular marker for wood combustion (23), is associated with the fine size fraction, consistent with formation by a high-temperature combustion process. In contrast, the sugar alcohols, arabitol and mannitol, and the sugar, glucose, are enriched in the coarse size fraction, as could be expected for compounds typical of fungal spores and plant pollen (25). It is seen from Table 1 that the atmospheric concentration of the 2-methyltetrols is larger than that of malic acid, which was found to be the major hydroxydicarboxylic acid. The concentration of the 2-methyltetrols was comparable to that of oxalic acid, a dicarboxylic

acid which is typically the major water-soluble organic species identified in atmospheric aerosols (26). The concentration of oxalic acid during the LBA-CLAIRE 2001 campaign was on average 57 ng m⁻³ for the fine size fraction and 63 ng m⁻³ for the coarse fraction (25).

The atmospheric concentrations of the 2-methyltetrols, malic acid, levoglucosan, arabitol, mannitol, and glucose in 10 selected total filter samples from the LBA-CLAIRE 1998 wet season campaign are provided in table S1. During the 1998 campaign, the atmospheric concentration of levoglucosan was quite low (average, 0.46 ng m⁻³; range, 0 to 3.0 ng m⁻³), indicating clean air conditions that were not affected by biomass smoke. The combined atmospheric concentration of the two 2-methyltetrols and their percentage relative to the OC mass were 31 ng m⁻³ and 0.61 ± 0.39%, respectively, and, similar to the 2001 campaign, the concentration and percentage were higher than those of malic acid (7.2 ng m⁻³ and 0.10 ± 0.06%, respectively).

In a study on VOCs performed at the same remote site in the Amazonian rain forest during the 1998 campaign (12), isoprene and its photooxidation products were measured, and it was concluded that isoprene chemistry can be regarded as a dominant process within this area. The isoprene mixing ratios were between 4 and 10 parts per billion (ppb), whereas those of the major photooxidation products of isoprene (methacrolein and methyl vinyl ketone) were always substantially below 1 ppb, pointing to a low oxidation capacity of the pristine atmosphere over the Amazonian rain forest; this is in agreement with ozone concentrations, which were always below 20

ppb. The median combined atmospheric concentration of the 2-methyltetrols found in the present work was 31 ng m⁻³, or 10 ppt, corresponding to about 0.2% of the isoprene mixing ratio (calculated for a mixing ratio of 5 ppb). It can thus be concluded that aerosol formation from isoprene has a low yield, but considering the large amounts of isoprene that are emitted by the rain forest vegetation, this source may be very important for SOA formation. The apparent yield of 0.2% (0.4% in mass terms) of the 2-methyltetrols can be used to estimate the global contribution of isoprene oxidation to SOA formation (SOM text). An annual global emission of isoprene of about 500 Tg (7) suggests a SOA source strength of about 2 Tg, which can be compared with the Intergovernmental Panel on Climate Change (27) estimate of between 8 and 40 Tg per year of SOA from biogenic sources.

Our results indicate that natural aerosols collected in Amazonia, Brazil, contain considerable amounts of the 2-methyltetrols, 2-methylthreitol and 2-methylerythritol, which can be explained by OH radical-initiated photooxidation of isoprene, as well

Fig. 2. Proposed formation of the 2-methyltetrols from isoprene by reaction with OH/O₂ followed by self- and cross-reactions of peroxyradicals. The intermediate 1,2-diols have been reported in chamber experiments with isoprene under low NO_x conditions (16).

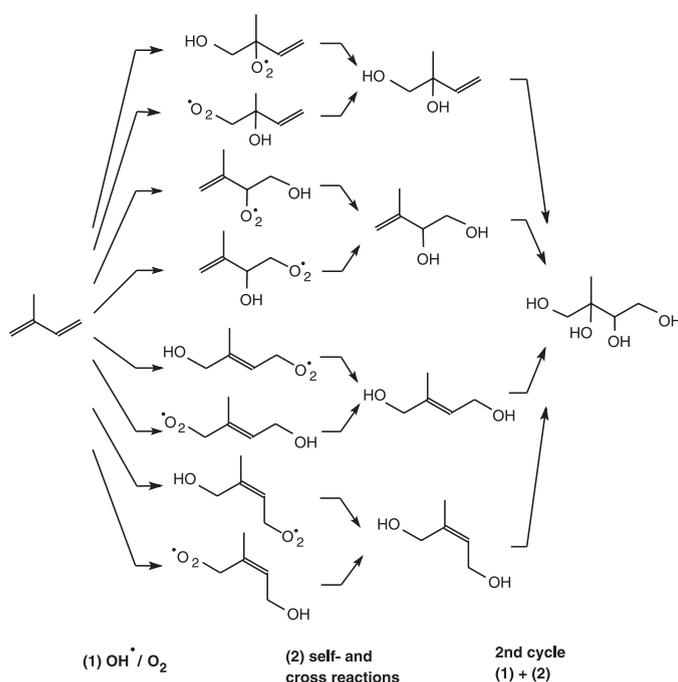


Table 1. Concentrations (ng m⁻³) of OC, elemental carbon (EC), polyhydroxylated compounds, and mono- and dihydroxydicarboxylic acids in fine and coarse filter samples from day and night collections with a Hi-Vol dichotomous sampler during the LBA-CLAIRE 2001 wet season campaign in Balbina, Brazil. The percentage carbon contributions to the OC are given in parentheses.

	Collection time 25 to 27 July 2001 day		Collection time 25 to 28 July 2001 night	
	Fine	Coarse	Fine	Coarse
OC	1550	2440	830	1610
EC	66	28	56	27
2-Methyltetrols (threo + erythro)	64.7 (1.84)	40.9 (0.74)	49.2 (2.62)	—*
Malic acid	32 (0.74)	10.9 (0.16)	11.6 (0.50)	—
α -Hydroxy glutaric acid	16.9 (0.44)	—	7.1 (0.35)	—
2,3-Dihydroxy glutaric acids (threo + erythro)	30 (0.71)	—	12.0 (0.53)	—
Tartaric acid	7.5 (0.15)	—	3.6 (0.14)	—
Levoglucosan	38 (1.10)	—	12.2 (0.66)	—
Arabitol	5.9 (0.17)	19.1 (0.34)	9.7 (0.51)	48 (1.31)
Mannitol	9.4 (0.24)	32 (0.52)	8.4 (0.40)	68 (1.68)
Glucose	15.6 (0.40)	134 (2.20)	0.6 (0.03)	2.7 (0.07)

*The dash denotes that the concentration was less than 10% of that in the fine size fraction; it is not given because of the large associated uncertainty. (The amount on the coarse filter has been corrected for the contribution from fine particles.)

as smaller amounts of mono- and dihydroxydicarboxylic acids. The 2-methyltetrols were identified as major oxygenated organic compounds in the fine size fraction, and it is estimated that they represent a SOA source strength of about 2 Tg per year. These compounds have low vapor pressure and are hygroscopic; they can therefore contribute to particle growth (28), enhance the ability of aerosols to act as cloud condensation nuclei, and result in the formation of haze (29) above forests. The 2-methyltetrols can be regarded as specific molecular markers for the photooxidation of isoprene in the ambient atmosphere and are, as such, of potential interest for source apportionment and air quality modeling studies. Contrary to widespread assumption, we suggest that photooxidation of isoprene emitted by forest vegetation results in substantial SOA formation.

References and Notes

1. T. Novakov, J. E. Penner, *Nature* **365**, 823 (1993).
2. M. O. Andreae, P. J. Crutzen, *Science* **276**, 1052 (1997).
3. T. Hoffmann *et al.*, *J. Atmos. Chem.* **26**, 189 (1997).
4. T. Hoffmann, R. Bandur, U. Marggraf, M. Linscheid, *J. Geophys. Res.* **103**, 25569 (1998).
5. I. G. Kavouras, N. Mihalopoulos, E. G. Stephanou, *Nature* **395**, 683 (1998).
6. I. G. Kavouras, E. G. Stephanou, *Environ. Sci. Technol.* **36**, 5083 (2002).
7. A. Guenther *et al.*, *J. Geophys. Res.* **100**, 8873 (1995).
8. S. N. Pandis, S. E. Paulson, J. H. Seinfeld, R. C. Flagan, *Atmos. Environ.* **25A**, 997 (1991).
9. H. Geiger, I. Barnes, I. Bejan, T. Benter, M. Spittler, *Atmos. Environ.* **37**, 1503 (2003).
10. A. Limbeck, M. Kulmala, H. Puxbaum, *Geophys. Res. Lett.* **30**, 1996 10.1029/2003GL017738 (2003).
11. Materials and methods are available as supporting material on Science Online.
12. J. Kesselmeier *et al.*, *Atmos. Environ.* **34**, 4063 (2000).
13. D. H. Lewis, D. C. Smith, *New Phytol.* **66**, 143 (1967).
14. A. L. Torres, H. Buchan, *J. Geophys. Res.* **93**, 1396 (1988).
15. R. Atkinson, W. P. L. Carter, *Chem. Rev.* **84**, 437 (1984).
16. L. Ruppert, K. H. Becker, *Atmos. Environ.* **34**, 1529 (2000).
17. J. H. Seinfeld, S. N. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change* (Wiley, New York, 1998), pp. 724–743.
18. S. Cohen, Y. Marcus, Y. Migron, S. Dikstein, A. Shafran, *J. Chem. Soc. Faraday Trans.* **89**, 3271 (1993).
19. J. Zhou, E. Swietlicki, H. C. Hansson, P. Artaxo, *J. Geophys. Res.* **107**, 8055 10.1029/2000JD00203 (2002).
20. G. C. Roberts, M. O. Andreae, J. Zhou, P. Artaxo, *Geophys. Res. Lett.* **28**, 2807 (2001).
21. B. Graham *et al.*, *J. Geophys. Res.* **107**, 8047 10.1029/2001JD003336 (2002).
22. K. Kawamura, R. Sempéré, Y. Imai, M. Hayashi, *J. Geophys. Res.* **101**, 18721 (1996).
23. B. R. T. Simoneit *et al.*, *Atmos. Environ.* **33**, 173 (1999).
24. Z. Zdráhal, J. Oliveira, R. Vermeylen, M. Claeys, W. Maenhaut, *Environ. Sci. Technol.* **36**, 747 (2002).
25. B. Graham *et al.*, *J. Geophys. Res.* **108**, 4766 10.1029/2003JD003990 (2003).
26. P. Saxena, L. M. Hildemann, *J. Atmos. Chem.* **24**, 57 (1996).
27. J. T. Houghton *et al.*, Eds. *Climate Change 2001: The Scientific Basis* (Cambridge Univ. Press, Cambridge, 2001).
28. W. R. Leitch *et al.*, *J. Geophys. Res.* **104**, 8095 (1999).
29. F. W. Went, *Nature* **187**, 641 (1960).
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Supporting Online Material

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Repeating Seismic Events in China

David P. Schaff^{1*} and Paul G. Richards^{1,2}

About 10% of seismic events in and near China from 1985 to 2000 were repeating events not more than about 1 kilometer from each other. We cross-correlated seismograms from ~14,000 earthquakes and explosions and measured relative arrival times to ~0.01 second, enabling lateral location precision of about 100 to 300 meters. Such precision is important for seismic hazard studies, earthquake physics, and nuclear test ban verification. Recognition and measurement of repeating signals in archived data and the resulting improvement in location specificity quantifies the inaccuracy of current procedures for picking onset times and locating events.

Each day, hundreds of seismic events are located by the traditional method of picking onset times of seismic waves recorded by seismometer networks and then interpreting these data with a travel time model to infer the epicenter (latitude/longitude), depth, and origin time of each event. Pick errors (i.e., errors in picking onset times) and errors in the models lead to uncertainties in event location amounting to a few percent of the station spacing. These errors frustrate efforts to understand the interactions between neighboring events and to obtain more precise models of Earth structure. Model error may be reduced by locating many earthquakes simultaneously, and pick error may be reduced by measuring relative arrival times by cross-correlation when possible (instead of onset times). Reduction in both types of error can lead to improvement in location precision of up to three orders of magnitude in specialized studies of small regions, typically using short windows (lengths of a few seconds) based on the *P*- and *S*-wave onsets (1–8). Here, we report improvements in epicentral locations over a broad area of diffuse seismicity, namely China and surrounding regions, using waveform cross-correlation on a large scale.

Repeating earthquakes or doublets arise when two events display nearly identical seismograms at a common station, implying that the events have similar focal mechanisms and similar locations. Doublets have primarily been observed in the creeping zones of major faults (9–12) and more recently in subduction zones (13–15). Clusters of repeating events are often called multiplets.

The cross-correlation coefficient *CC* quantifies waveform similarity, with values from 0 (no similarity) to 1 (a perfect match). We processed 12 GB of waveform data for about 14,000 events in and surrounding China as listed in the Annual Bulletin of Chinese Earthquakes (ABCE) from January 1985 to April 2000 (16, 17). The waveforms were acquired from several networks of stations that are archived by the IRIS Consortium (18).

We define a doublet to be an event pair having $CC \geq 0.8$ for time windows from 5 s before the *P*-wave to 40 s after the *Lg*-wave recorded at least at one station. An example of a pair of events in China (magnitude ~4.5) with similar waveforms, recorded at a station ~1100 km away, yields $CC = 0.8$ for a 220-s window bandpass-filtered from 0.5 to 5 Hz (Fig. 1). *Lg* is the largest amplitude phase and shows a high degree of correlation, even though it is a complex, scattered wave. The waveforms are similar even for unknown phases and coda as well as for the *P*- and *S*-waves.

An automated search isolated 1301 events that have $CC \geq 0.8$ with at least one other event (Fig. 2). These comprise 950 doublets, which can be grouped as 494 multiplets of various sizes (table S1). They are well distributed throughout seismic zones in and near China and represent more than 9% of the ABCE events from 1985 to 2000. Most events satisfy $CC \geq 0.8$ at only one station because of the sparse station coverage. As a general rule, high similarity of complex multiply scattered waves for an event pair requires the events to be no farther apart than about one-quarter of the dominant wavelength, which in our case is ~0.8 km (19, 20). If the signal-to-noise ratio is good enough to see different phases overlaid, it further supports the hypothesis that the

¹Lamont-Doherty Earth Observatory, ²Department of Earth and Environmental Sciences, Columbia University, Palisades, NY 10964, USA.

*To whom correspondence should be addressed. E-mail: dschaff@ldeo.columbia.edu