The assumption that a heat perturbation mixes as a passive tracer may break down as the climatic warming increases. In the ocean model of Bryan *et al.* (*15*), a warm anomaly of 0.5°C penetrates significantly (~25 percent) less than a similar cold anomaly. Furthermore, global warming will be accompanied by changes in evaporation, precipitation, and wind stress over the ocean surface, and possibly by the addition of fresh water from melting ice sheets—all of which may affect the rate of ocean mixing. There is evidence that some mechanisms of ocean overturning are capable of sudden changes (*16*), and the paleoclimate record reveals cases of large warming within periods of no more than several decades (*16, 17*). Thus we cannot exclude the possibility that the climate may at some point undergo a rapid transition to the equilibrium climate for current atmospheric composition.

The existence of unrealized warming complicates the CO_2 and trace gas issue and limits the near-term effectiveness of reductions in greenhouse gas emissions. The strong dependence of this unrealized warming on the equilibrium climate sensitivity emphasizes the importance of narrowing uncertainties about the strength of climate feedback processes. This will require better understanding of many components of the climate system including clouds, the cryosphere, biogeochemical cycles, ocean mixing, vegetation, and the land surface.

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Acid Deposition, Smelter Emissions, and the Linearity Issue in the Western United States

Abstract. *The variation in sulfur dioxide emissions from nonferrous metal smelters in the western United States over a 4-year period is compared with the variation in sulfate concentrations in precipitation in the Rocky Mountain states. The data support a linear relation between emissions and sulfate concentration. The geographic separation of emissions sources and precipitation monitors indicates a sulfur transport scale exceeding 1000 kilometers.*

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The relation between SO_2 emissions at particular sources and acid deposition at distant receptors has been the subject of several investigations (*1, 2*). Because of the sparsity of historical deposition data, the lack of large excursions in emissions in recent years, and the high source density with low gradients, empirical studies of SO_2 emissions and deposition in eastern North America have not permitted the determination of definitive spatial or temporal relations between emissions at sources and deposition at distant receptors (*2*).

The intermountain region of the western United States (from the Sierra crest to the continental divide) is an especially suitable region for studying long-range transport and source-receptor relations because it is characterized by a few large

Table 1. Annual VWM sulfate concentrations at NADP recording stations (Fig. 1). All precipitation-monitoring stations in the intermountain region downwind (*9*) of the smelters that had data for at least 30 weeks during 10 months in 1981 (when a large emissions increase occurred) and 1982, including three stations just east of the continental divide, are listed. The error due to imprecision in sampling and chemical analysis was less than 10 percent (*18*). Quality control of sampling and analysis procedures by monitoring stations and the central analytic laboratory has been described (*19*). VWM sulfate concentration was averaged over all stations for each year to yield a CVWM; the difference between CVWM concentrations for 1981 and 1982 was statistically significant ($P < 0.01$, *t*-test) and greater than 0.47 mg per liter ($P = 0.05$, *t*-test). Values in parentheses for 1982 represent the standard deviation in monthly mean sulfate concentration, which is a measure of site-specific within-year variation. Data for the Hubbard Brook and Hopland sites, provided for comparison, are not included in the CVWM.

Site (number)	Annual mean sulfate concentration (milligrams per liter)			
	1980	1981	1982	1983
Alamosa, Colorado (1)		1.81	1.48 (0.75)	1.39
Sand Spring, Colorado (2)	1.05	1.60	0.96 (0.27)	1.05
Manitou, Colorado (3)		1.62	0.98 (0.42)	0.91
Pawnee, Colorado (4)	1.50	2.17	0.83 (0.49)	1.14
Rocky Mount, Colorado (5)		1.57	0.91 (0.35)	0.83
Yellowstone, Wyoming (6)		1.56	0.79 (0.27)	0.53
Craters of the Moon, Idaho (7)		0.91	0.61 (0.29)	0.65
Organ Pipe, Arizona (8)		2.14	0.87 (0.30)	0.64
CVWM (*5*)	1.28	1.60	0.86	0.85
Standard error (*6*)	0.22	0.14	0.06	0.08
Hubbard Brook, New Hampshire	2.45	2.25	2.13	1.65
Hopland, California	0.50	0.33	0.34	0.33

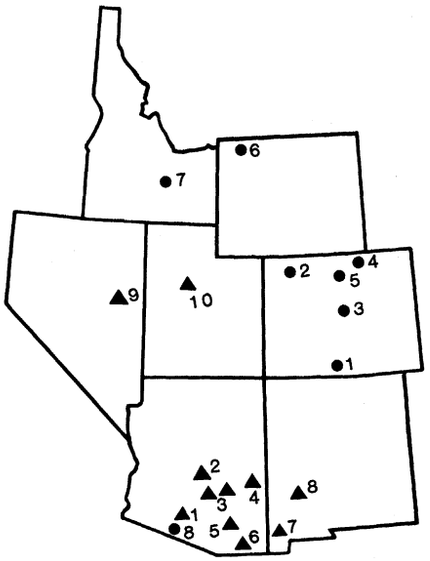

Fig. 1. Locations of nonferrous metal smelters (▲) and NADP monitoring stations (●) included in the study. Key to smelters: (1) Ajo, Arizona; (2) Miami, Arizona; (3) Hayden, Arizona (two sources); (4) Morenci, Arizona; (5) San Manuel, Arizona; (6) Douglas, Arizona; (7) Hidalgo, New Mexico; (8) Hurley, New Mexico; (9) McGill, Nevada; and (10) Garfield, Utah. Key to NADP stations is given in Table 1.

point sources with fluctuating emissions—nonferrous metal smelters—which are responsible for most of the region's SO_2 emissions. In this report, we compare the time series of smelter emissions with that of annual average wet sulfate concentration using data from National Atmospheric Deposition Program (NADP) stations in Colorado, Wyoming, and Idaho, which are remote from major sources, as well as from one station in Arizona near the smelters (*3*). The large variation in both emissions and concentration over the period of our study allowed us to identify unambiguously the smelter emission signal in the concentration data. Such large variations can be thought of as representing an unintentional experiment on the atmosphere that could not be performed readily in the eastern United States. A previous study (*4*) covering a restricted area identified the smelter emission signal in airborne sulfate particle data.

Concentrations of sulfate and other species in precipitation have been measured weekly by the NADP network since 1978. At locations in the intermountain region and other nearby receptors, only a few monitors operated for an entire year before 1980. Annual volume-weighted mean (VWM) concentrations of sulfate in precipitation for each station examined (Fig. 1) are listed in Table 1, along with the annual combined volume-weighted means (CVWM) (*5*). As an indication of intra-annual concentration variability, we determined for 1982 the standard deviations (*6*) in monthly mean (*5*) sulfate concentrations at each station (Table 1) and found them to be an average of 42 percent of the respective annual means.

The nonferrous metal smelters (Fig. 1) are a probable major source of the sulfate detected in precipitation because in 1980 and 1981 they emitted 63 and 74 percent, respectively, of the SO_2 in the intermountain region (*7, 8*). In addition,

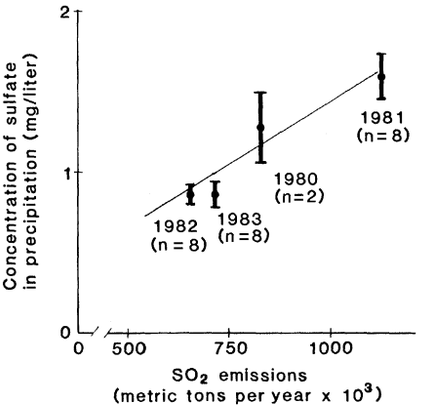

Fig. 3. CVWM sulfate concentrations (Table 1) plotted against SO_2 emissions (Table 2); *n* is the number of monitoring stations included in the mean. The least-squares regression line is drawn only for the region of the *x*-axis where the 90 percent confidence interval in the estimate of concentration is less than ±1.0 mg per liter. The slope of the line is 1.63 ± 0.32 mg per liter per 10^6 metric tons of SO_2.

surface winds over the region indicate a general southwest to northeast airflow that is persistent from month to month for the entire year (*9*). A long-range transport modeling study that used upper-level winds also indicated that smelters are a significant source of sulfate in precipitation at stations in the Rocky Mountains (*10*). Data for SO_2 emissions from all nonferrous metal smelters in the intermountain region (grouped by state) that operated during the period 1980 to 1983 are compiled in Table 2. The smelters at Hurley and Hidalgo, New Mexico, which are immediately east of the continental divide, are also included. As an indication of the intra-annual emissions variability, we determined the standard deviation in monthly aggregate emissions and found them to be an average of 30 percent of the average monthly emissions during the period 1980–1982.

Electric power plants account for two-thirds or more of the remaining SO_2 emissions in the region (*8*). Their emissions from 1980 to 1982 varied by less than 4 percent of the total emissions from smelters plus power plants (*11*), which together account for about 90 percent of regional emissions. By comparison, the variation in smelter emissions was an order of magnitude larger than that in power plant emissions during the period.

Annual sulfate concentrations for all recording stations are plotted against time for the period 1980–1983 in Fig. 2. The figure illustrates a generally synchronous variation of the concentrations at all intermountain and nearby stations with smelter emissions values. This vari-

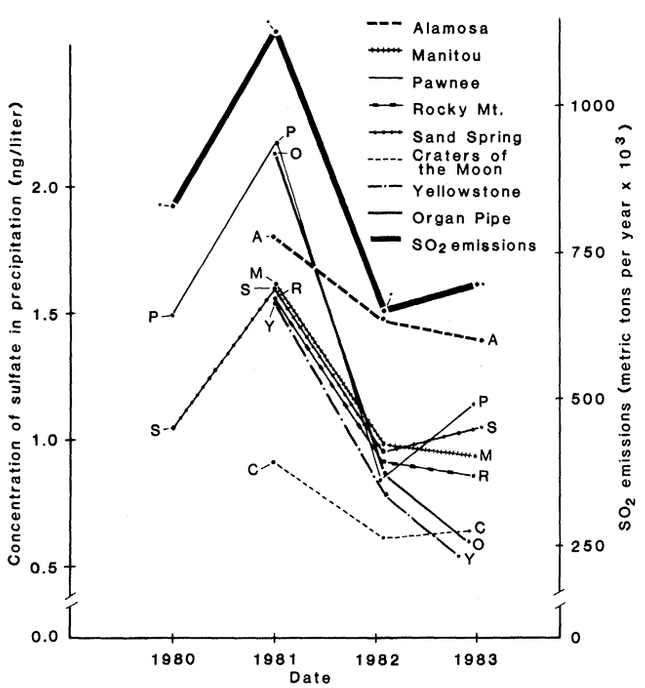

Fig. 2. Emissions of SO_2 from nonferrous metal smelters in Arizona, Utah, Nevada, and New Mexico (heavy line) and sulfate concentrations recorded at NADP stations in Colorado, Wyoming, Idaho, and Arizona (other lines). The curve for SO_2 emissions represents the time series for total emissions from smelters as given in Table 2.

with smelter emissions values. This variation was not observed for groups of stations in other states (*3*). For comparison, concentrations measured at the stations in Hopland, California (far west of the Sierra crest), and Hubbard Brook, New Hampshire, are listed in Table 2. Figure 2 indicates that nonferrous metal smelters contribute significantly to sulfate concentrations at these stations and that a large fraction of precipitation sulfate originates at distant smelter sources. We know of no other explanation for the observed pattern of similar and simultaneous changes in sulfate concentration at stations more than 1000 km from the sources and separated from one another by a comparable distance. Furthermore, an initial analysis of 1979 data indicates that concentrations (at sites 2 and 3, the only sites from which sufficient data were available) and emissions both declined from 1979 to 1980. Our interpretation is consistent with the importance of long-range transport suggested for these smelters and other sources in previous studies (*4, 9, 12*). Other studies (*4, 13*) indicate a relation between aerosol sulfate concentrations and smelter emissions over a more restricted area during 1979–1980.

A plot of the CVWM sulfate concentration against smelter emissions for each year (Fig. 3) shows that emissions from nonferrous metal smelters are linearly related to concentrations of sulfate in precipitation at stations remote from these sources. Variation in emissions from smelters may account for nearly all the variation in annual average sulfate concentrations at this group of stations.

This analysis is based on annual average data because on a shorter time scale changes in concentrations arising from emission changes are obscured by variations in photochemical behavior due to the seasonal cycle in the incident solar flux, atmospheric temperatures, and related parameters. In addition, the number of precipitation events included in monthly or weekly average concentrations is so small that fluctuations due to local meteorology diminish the significance of concentration differences. The persistence of the surface wind vectors (*9*) over the year suggests that the comparison of annual emissions and concentration data reflects the causal relation between smelter emissions and sulfate concentrations on a shorter time scale.

We have excluded changes in airborne, soil-based material as an important source of sulfate concentration variations. Although base cation concentrations also tend to vary (*3*) with sulfate concentrations, studies of fine particles (*4, 14*) and bulk precipitation (*15*) indicate that airborne base cations are largely of nonsulfate (presumably carbonate) origin in this region. The relation between sulfate and base cations may arise from increased metal-carbonate solubility with increasing acidity of atmospheric droplets.

Our study illustrates a response of precipitation chemistry to large changes in emissions at distant locations. The linear relation between changes in annual average sulfate concentrations and changes in emissions leads us to conclude that the overall atmospheric transformation process for SO_2 is effectively linear for the range of sulfate concentrations given in Table 1. Because these concentrations are at least half as great as those observed at many stations in the northeastern United States and are comparable to values recorded in the upper midwest and southeast (*16*), it appears that major nonlinearities are absent from the atmospheric chemistry of SO_2 over extended areas of the United States. Our data provide direct evidence from exclusively wet deposition monitors on the linearity question for North America. Previous comparisons between emissions and sulfate concentrations from bulk deposition monitors at Hubbard Brook (*2*) and indirect inferences drawn from mass budgets (*17*) and ion ratios (*2*) are consistent with our result. The magnitude of the standard errors (*6*) of the combined annual means (Fig. 3) is reasonably small (an average of 11 percent of the respective means), which suggests a geographic homogeneity of the intermountain airshed consistent with large-scale transport.

The question remains as to whether the emissions data permit a monthly or seasonal analysis of the relation between sulfate concentrations and smelter emissions. The unusual emissions change and atmospheric response reported here provide an ideal opportunity to improve long-range transport models.

Table 2. Sulfur dioxide emissions from nonferrous metal smelters. Monthly emission data were obtained from the smelter operators and from state air quality agencies, as indicated. For 80 percent of all emissions, data were derived by the materials-balance method, in which the weight of input and output materials is determined to within an uncertainty of less than ± 5.0 percent, and the sulfur content of all materials is determined to within an uncertainty of less than ±1.0 percent (*20*). Emissions are calculated as the difference between input and output sulfur, with uncertainties estimated at 5.0 percent. For the remaining 20 percent of emissions, data were derived directly from stack monitors, which may be less reliable.

State	SO_2 emissions (metric tons per year × 10^3)				Reference
	1980	1981	1982	1983	
Arizona	579.0	794.1	374.3	445.7	(*21*)
Utah	45.6	76.8	63.7	44.7	(*22*)
Nevada	78.9	114.9	87.7	28.3	(*22*)
New Mexico	121.9	144.9	128.9	181.2	(*23*)
Total	825.4	1130.4	654.6	699.9	
Monthly standard deviation	36.2	4.7	18.2	N.A.*	

* N.A., not available.

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24. We thank M. Kim for technical assistance.

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Stereostructure of the Archaebacterial C_{40} Diol

Abstract. *The stereostructure of the archaebacterial C_{40} diol has been established as (3R,7R,11R,15S,18S,22R,26R,30R)-3,7,11,15,18,22,26,30-octamethyldotriacontane-1,32-diol by stereorational total synthesis. This provides the final evidence necessary to establish the structure of an archaebacterial membrane substance that is a 72-membered-ring tetraether with 18 stereocenters.*

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The archaebacteria (*1*, *2*) [metabacteria (*3*)] include the methanogens, the extreme halophiles, extreme thermophiles, and some thermoacidophiles. It has been demonstrated that the archaebacteria are no more closely related to the eubacteria than to the eukaryotes, which suggests an evolutionary divergence for the archaebacteria. Several features set archaebacteria apart from the prokaryotes. For example, archaebacteria often do not have cell walls, and when they do the cell walls are not based on a muramic acid peptoglycan structure (*4*); and there are numerous differences in the structures of the *t*-RNA (*5*) and the ribosomal proteins of the two species (*6*). The only molecular feature that seems to be common to all of the archaebacterial species is the nature of their lipids (*7*), which are isopranyl glycerol ethers instead of the fatty acid glycerol esters found in all other species (*8–18*). These unusual lipids have interesting implications in lipid bilayer theory (*7*, *19*) and have been used as molecular fossils (*20*) in addition to being used to identify archaebacteria. The alkyl chains usually consist of phytane or biphytane [two phytanes linked together by a 4′–4 linkage (*21*)] units (*8–18*).

A common lipid constituent in the thermoacidophiles and methanogens is the diglyceryl tetraether **1** (Fig. 1), a natural product having a 72-membered ring with 18 stereocenters (*8–18*). The C_{40} diol **2** (Fig. 1), which is a structural component of **1**, has been detected in geologic sediment (*22*) and was recently isolated from a kerogen (*23*) and from a nonpolymerized sediment (*24*). The gross structure of **1** was determined correctly for a sample isolated from *Thermoplasma acidophilum* (*9*) after two earlier misassignments (*15*, *16*). The absolute stereochemistry at the glycerol stereocenters was also determined (*18*), but until now nothing was known about the stereochemistry at the 16 stereocenters bearing methyl groups. We have carried out a stereorational total synthesis of (3*R*,7*R*,11*R*,15*S*,18*S*,22*R*,26*R*,30*R*)-3,7,11,15,18,22,26,30-octamethyldotriacontane-1,32-diol and have shown it to be identical by high-resolution ^{13}C–nuclear magnetic resonance (NMR) spectroscopy, with a natural form of **2** obtained by degradation of **1** isolated from *Methanobacterium thermoautotrophicum*. The synthesis has provided the evidence necessary to completely define the structure of **1**.

The strategy we used in our synthesis is based on technology used for a synthesis of the vitamin E sidechain (*25*). Optically active β-hydroxy acid **3** (98.7 percent enantiomeric excess) is prepared by the Evans protocol (*26*) from valinol oxazolidone. Reduction of **3** with $LiAlH_4$ provides diol **4**, which is selectively protected to give the *t*-butyldimethylsilyl (*t*-$BuMe_2Si$) ether **5** (*27*). The corresponding propionate ester **6** is subjected to the Ireland variant of the Claisen rearrangement (*28*) to obtain **7**. Hydrogenation of **7** with Adams's catalyst gives the protected hydroxy acid **8**. It was determined that the Claisen rearrangement of **6** to **7** had given 95.5 percent (2*R*, 6*R*) and 4.5 percent (2*S*, 6*R*) by conversion of **8** with $LiAlH_4$ to alcohol **9**, which was assayed by Mosher's method (*29*). Treatment of *p*-toluenesulfonate (Ts) **10** with KCN in the presence of 18-crown-6 (*30*) affords nitrile **11**, which is reduced with diisobutylaluminum hydride to give the ten-carbon aldehyde **12**.

Reduction of aldehyde **12** with $LiAlH_4$ gives alcohol **13**, which is converted to the β-(methoxyethoxy)methyl (MEM) ether **14** (*32*). Removal of the *t*-$BuMe_2Si$ group with HF yields alcohol **15**, which is converted to methanesulfonate **16** by reaction with methanesulfonyl chloride. Reaction of **16** with lithium thiophenoxide gives **17**, which is oxidized with *m*-chloroperoxybenzoic acid to provide sulfone **18**.

Mesylate **19**, prepared from alcohol **13**, is treated with tetra-*n*-butylammonium iodide in tetrahydrofuran to obtain iodide **20**. Alkylation of the dianion of sulfone **18** with iodide **20** affords sulfone **21**, which is reduced by Danheiser's method (*32*) to obtain, after treatment of the crude product with HF in acetonitrile, alcohol **22**. Treatment of the corresponding methanesulfonate **23** with tetra-*n*-butyl-ammonium bromide in tetrahydrofuran gives bromide **24**, which is converted into the corresponding Grignard reagent; oxidation of the latter intermediate with silver nitrate gives the

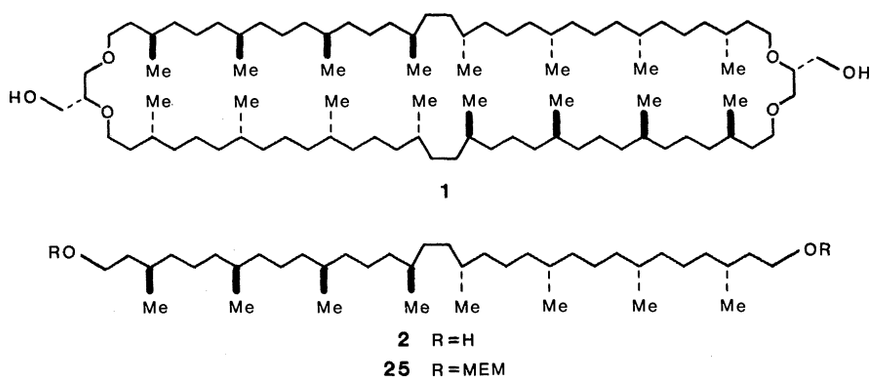

Fig. 1. Structures of a 72-membered-ring diglyceryl tetraether **1**, a C_{40} diol **2** that is its structural component, and the synthetic precursor to the diol **25**.