from Mars in one event about 2.8 million years ago (*14*), they must come from one location and might represent related flows derived from a common source, containing increasing portions of cumulus pyroxenes and increasing concentrations of elements with large ionic radii like K or La, inversely correlated with their Al content.

Finally, in comparing the composition of rocks and soils, it is apparent that the martian soil cannot be made from Barnacle Bill–type rocks directly, even if weathering and the addition of SO_2 and HCl from volcanic gases are taken into account. Addition of material richer in Mg and Fe as observed in martian meteorites might be the most straightforward way to explain the soil composition (Fig. 5). This might also be accomplished if ferromagnesian minerals in the local rocks are preferentially weathered and concentrated in the soil. However, the Al contents of Pathfinder soils mimic those of the nearby rocks, perhaps suggesting an admixture of locally derived soil with components of weathered mafic rocks that were globally distributed by the wind (*15*).

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The $^{18}O/^{16}O$ and $^{17}O/^{16}O$ Ratios in Atmospheric Nitrous Oxide: A Mass-Independent Anomaly

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Measurements of the oxygen isotope ratios ($^{18}O/^{16}O$ and $^{17}O/^{16}O$) in atmospheric nitrous oxide (N_2O) from La Jolla, Pasadena, and the White Mountain Research Station (elevation, 3801 meters) in California and the White Sands Missile Range in New Mexico show that N_2O has a mass-independent composition. These data suggest the presence of a previously undefined atmospheric process. The La Jolla samples can be explained by a mixing between an atmospherically derived source of mass-independent N_2O and biologically derived mass-dependent N_2O. Possible origins of the mass-independent anomaly in N_2O are discussed.

Nitrous oxide is a greenhouse gas and is involved in stratospheric ozone (O_3) depletion. On a per molecule basis, N_2O has more than 200 times the greenhouse forcing of carbon dioxide (CO_2). In the atmosphere, N_2O is lost through photolysis (90%) and photooxidation in the stratosphere by

$$N_2O + O(^1D) \rightarrow NO + NO\ (6\%) \qquad (1)$$

$$N_2O + O(^1D) \rightarrow N_2 + O_2\ (4\%) \qquad (2)$$

Reaction 1 accounts for the major source of nitric oxide (NO), which is known to catalytically destroy O_3, to the stratosphere (*1, 2*).

The global budget of atmospheric N_2O remains ambiguous, with an imbalance of about 30% between sources and sinks (*3*). Stable isotope analysis has proven useful in budgetary analysis of many atmospheric species (*4*). Previous isotopic studies have focused on $^{18}O/^{16}O$ and $^{15}N/^{14}N$ ratios in N_2O (*5–9*). Here, we present simultaneous measurements of all three stable oxygen isotopes in atmospheric N_2O.

Most reactions and physical processes involving isotope fractionation ultimately depend on mass and are termed mass-dependent. In a small but growing number of reactions, fractionations arise that do not follow this dependence. These latter processes are termed mass-independent. The quantum-level mechanism responsible for mass-independent fractionation has yet to be determined, but it is known to be related to molecular symmetry (*10, 11*). Observations of mass-independent isotope fractionations demonstrate that these processes generally occur in the gas phase in nonthermodynamic equilibrium. When found in nature, mass-independent compositions contribute specific information about source, sink, and transformation mechanisms of the species. For example, measurement of all three oxygen isotopes in stratospheric CO_2 has revealed a substantial photochemical coupling to O_3. The CO_2-O_3 interaction is only detectable with measurement of all three oxygen isotopes (*12*).

We analyzed atmospheric N_2O samples from four sites (*13*): (i) La Jolla, California (32.7°N, 117.2°W), situated about 1 km from the ocean and 16 km from downtown San Diego; (ii) the campus of the California Institute of Technology (CIT) in Pasadena (34.2°N, 118.2°W); (iii) the White Mountain Research Station (WMRS) at Mount Barcroft (37.5°N, 118.2°W) at an elevation of 3.8 km, east of Bishop, California; and (iv) the White Sands Missile Range (WSMR) (32.4°N, 106.3°W), at Las Cruces and Alamagordo, New Mexico, at an elevation of 1.2 km, about 70 km northeast of El Paso, Texas.

On a three-isotope plot with $\delta^{17}O$ on the ordinate and $\delta^{18}O$ on the abscissa (Fig. 1 and Fig. 2), a mass-dependent enrichment is indicated by $\delta^{17}O \approx (0.5)\delta^{18}O$ and a mass-independent one by $\delta^{17}O \neq (0.5)\delta^{18}O$. Mass-dependent N_2O samples include N_2O from nylon production (*14*), NH_4NO_3 decomposition, aqueous NO disproportionation, and tank N_2O standards (Matheson Gas, Montgomeryville, Pennsylvania). The error associated with purification and analysis of $\delta^{18}O$ and $\delta^{17}O$ in N_2O is ±0.1 per mil (*15*). The deviation from a purely mass-dependent fractionation is defined by the value $^{17}\Delta$, where $^{17}\Delta = \delta^{17}O - [0.515(\delta^{18}O)]$. The mass-dependent coefficient (0.515) was determined from replicate analysis of a range of commercial N_2O gases (Fig. 1). The data represented in Fig. 1 have $^{17}\Delta \leq 0.1$ per mil. Any isotopic fractionation associated with the extraction, purification, and analysis of N_2O produces a purely mass-dependent fractionation ($^{17}\Delta = 0$).

All samples of atmospheric N_2O are mass independently fractionated ($^{17}\Delta \neq 0$)

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(Fig. 2). The mass independence does not represent a sampling, extraction, or purification artifact because all of these processes were measured to be strictly mass-dependent. It is unlikely that the scatter in Fig. 2 was derived from extraction of atmospheric N_2O, because nearly all of the N_2O was collected as determined from the measurement of air volume (*16*). The variation in $\delta^{18}O$ in tropospheric N_2O is consistent with the variation seen by other researchers (*5*). Furthermore, there is no isotopic exchange between H_2O and N_2O (*5*, *17*). An average $^{17}\Delta$ value of about 1 per mil was calculated for all atmospheric N_2O. Data from La Jolla taken routinely from January 1993 through February 1997 show that no seasonal trend exists in the $\delta^{18}O$.

The CIT data are isotopically light in comparison with the rest of the data. These samples are likely to be dominated by primary sources, including both natural and anthropogenic N_2O. The data from WSMR indicate an enrichment in both $\delta^{18}O$ and $\delta^{17}O$ compared with the samples from CIT. Air at WSMR was dominated by industrial pollution transported from El Paso and Ciudad Juarez, Mexico, and free tropospheric air as determined by meteorological and trace species concentration data (*18*). Samples from WMRS show the greatest enrichment in heavy oxygen isotopes of all tropospheric N_2O samples. The WMRS samples have higher $\delta^{18}O$ and $\delta^{17}O$ values than nearly all the La Jolla data. Air masses at WMRS were dominated by free tropospheric air and some air from the Central Valley of California and possibly the stratosphere. The WSMR and WMRS data suggest that mass-independent compositions increase with altitude or distance from primary N_2O sources.

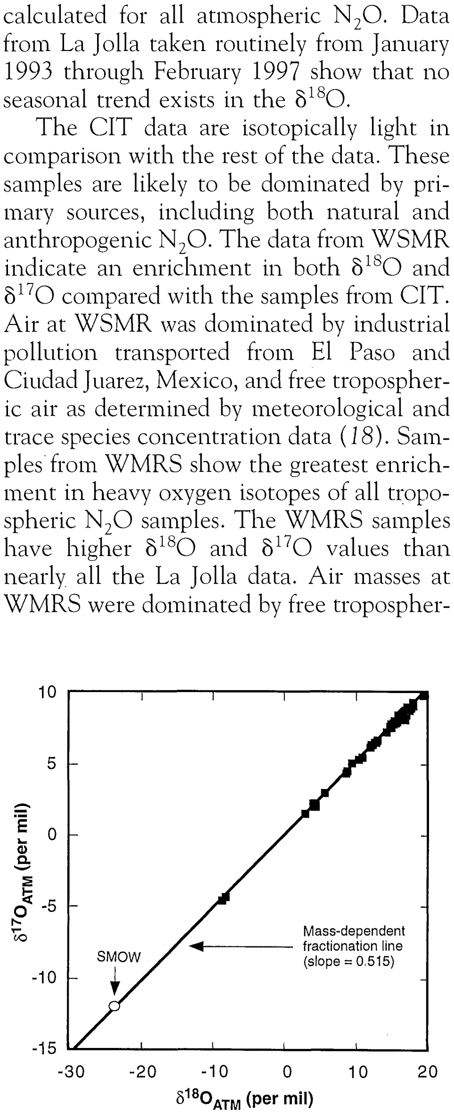

Fig. 1. Mass-dependent nitrous oxide isotope data. A three-isotope plot showing mass-dependent N_2O from a number of laboratory and industrially produced N_2O. The units are per mil relative to air O_2 ($\delta^{18}O_{ATM}$). The mass-dependent fractionation line is defined by these data and has a slope of 0.515. Mass-dependent fractionations in N_2O will have a $\delta^{17}O/\delta^{18}O$ ratio of 0.515. Uncertainty in each sample is indicated by the size of the data point. Data that do not plot on the mass-dependent fractionation line are termed mass independent. SMOW is plotted for reference (open circle).

Mass-dependent processes seem to be consistent with low $\delta^{18}O$ values. The $\delta^{18}O$ values of soil N_2O are variable and uniformly low with respect to tropospheric N_2O (*5*, *9*). It is expected that isotopic values of soil N_2O will show mass-dependent character, as all biological reactions measured are mass dependent. A linear trend in a three-isotope plot (Fig. 2) requires a mixing of two components. In our data, it is likely that these two components are air from soil or biologically derived N_2O and an atmospheric source of mass-independent N_2O. Deviation from a straight line is presumably due to other minor mass-dependent sources. All known mass-independent reactions are in the gas phase; thus, an atmospheric process involving N_2O is required to explain the observations. The observed altitudinal trend is consistent with this explanation. Reactions 1 and 2 are thought to produce a mass-dependent fractionation (*19*); thus, a new atmospheric process—a source, sink, or exchange reaction—must exist for atmospheric N_2O.

The $\delta^{18}O$ value of stratospheric N_2O is high (*9*, *20*). The isotopic fractionation for N_2O is $\varepsilon = \pm 0.3$ per mil for photolysis and $\varepsilon = 6$ per mil ($\alpha = 0.994$) for reaction with $O(^1D)$ (*19*, *21*). The N_2O photooxidation reaction accounts for only 10% of the N_2O sink. This analysis implies that $\alpha = 0.9994$ or about 1/20 of the measured fractionation in the stratosphere (*20*, *22*). Although unlikely, it is possible that there is a wavelength dependency in isotopic fractionation in N_2O photolysis (*23*). However, on the basis of the stratospheric samples (*9*, *20*) and measurements (*19*), a process other than photolysis or photooxidation involving N_2O must occur in the stratosphere.

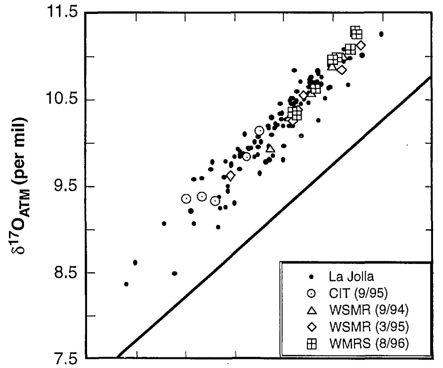

Fig. 2. Atmospheric nitrous oxide oxygen isotope data. An enlargement of Fig. 1 in the 14 to 21 per mil ($\delta^{18}O_{ATM}$) region with tropospheric N_2O data plotted. The mass-dependent fractionation line is as defined in Fig. 1. La Jolla data were taken between January 1993 and February 1997; other data were taken as indicated in the plot.

Recently, a number of novel reaction mechanisms that may produce or destroy N_2O in the atmosphere have been suggested (*24–26*). Four decades of research (*27*, *28*) have focused on the production and destruction of N_2O in reaction chambers with N_2, O_2, O_3, and ultraviolet (UV) light. The availability of UV light and high O_3 concentrations in these studies require that reactions involving O_3 occur in the stratosphere, although the possibility of a tropospheric process is not ruled out. Isotopically, O_3 as a source molecule is ideal. In laboratory experiments, O_3 production is accompanied by a large mass-independent fractionation with $\delta^{17}O \approx \delta^{18}O \approx 85$ per mil (*29*). Both stratospheric O_3 (*10*) and tropospheric O_3 (*30*) are known to have a mass-independent enrichment of $\delta^{18}O \approx 100$ per mil. An anomalous isotopic signature may result without a substantial change in concentration of atmospheric N_2O. For instance, an N_2O process with a 100 per mil mass-independent fractionation derived from atmospheric O_3 would account for only 1% of the N_2O budget, on the basis of the average $^{17}\Delta$ value of 1 per mil in Fig. 2. Reactions that produce even greater fractionations in atmospheric N_2O could affect the budget less. In ion-molecule reactions of the type described by Griffith and Gellene (*31*), fractionations of greater than 10,000 per mil have been observed. Although the mechanism responsible for production of the mass-independent component in atmospheric N_2O is yet unknown, its isotopic signature is defined by Fig. 2. The possibility of both new sources and sinks (*25*) makes $\delta^{17}O$ and $\delta^{18}O$ the definitive measurements of atmospheric N_2O.

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gold catalyst, and the N_2 and O_2 fractions were subsequently separated cryogenically. Pure O_2 was used for the mass spectrometric analysis. We collected air samples by in situ cryogenic trapping of N_2O and CO_2 from 1800 liters of air (*16*). All isotopic values are reported with the standard delta notation with respect to atmospheric O_2 (*32*).

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Stable Isotope Enrichment in Stratospheric Nitrous Oxide

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Nitrous oxide is a greenhouse gas that also plays a role in the cycling of stratospheric ozone. Air samples from the lower stratosphere exhibit $^{15}N/^{14}N$ and $^{18}O/^{16}O$ enrichment in nitrous oxide, which can be accounted for with a simple model describing an irreversible destruction process. The observed enrichments are quite large and incompatible with those determined for the main stratospheric nitrous oxide loss processes of photolysis and reaction with excited atomic oxygen. Thus, although no stratospheric source needs to be invoked, the data indicate that present understanding of stratospheric nitrous oxide chemistry is incomplete.

Nitrous oxide (N_2O) is an atmospheric trace gas that contributes to the greenhouse effect. It is also involved in the catalytic destruction of ozone in the stratosphere and is increasing in concentration by about 0.25% per year (*1*). The increase is believed to result from fertilizer use, emissions from internal combustion engines, biomass burning, and industrial processes (*2*). It is naturally produced by nitrification and denitrification in soils and in the oceans, and is destroyed in the stratosphere via photolysis (90%) and reaction with excited atomic oxygen [$O(^1D)$] (10%). Its atmospheric lifetime is between 100 and 150 years (*1*). Although the major sources and sinks of N_2O are known, they are poorly quantified and inadequately balanced, both in terms of mass exchange and in their N and O isotopic composition (*1–3*).

Stable isotopes have been used in the past to constrain sources and sinks of other atmospheric trace gases (*4*) but have yet to be successfully applied to N_2O. The isotopic approach to a global N_2O budget is hindered by the wide range of observed isotopic values for each of the major natural sources, making it difficult to assign a unique value to each of the source terms. Soil flux samples have been shown to be variable but consistently depleted in both ^{15}N and ^{18}O relative to atmospheric N_2O (*3*). Oceanic samples have exhibited a trend similar to typical nutrient profiles, with slightly depleted surface waters becoming progressively enriched along the nutricline and stabilizing with depth (*5*, *6*). Early analytical methods employed infrared absorption techniques (*7*) or required decomposition of N_2O with subsequent analyses of N_2 and CO_2 (*5*, *8*, *9*). The use of direct injection techniques was introduced in 1993 when Kim and Craig (*3*) reported heavy enrichment in both the N and O isotopes in two samples of stratospheric air. They proposed that a stratosphere to troposphere return flux of heavy N_2O could balance the observed isotopically light source terms, although a simple mass-balance model showed that this led to a considerable overcorrection. Direct injection of N_2O was subsequently shown to result in erroneous enrichment of $\delta^{15}N$ and $\delta^{18}O$ (*10*) when contaminated by trace amounts of CO_2 (*11*).

We present results for $\delta^{15}N$ and $\delta^{18}O$ of N_2O obtained from samples collected in the lower stratosphere (Table 1) (*12*). Five samples were collected at midnorthern latitudes on board NASA's WB-57 aircraft (*13*), and two samples were collected at high northern latitude during the 1988 Juelich balloon campaign (*14*). We also measured, for comparison, the isotopic composition of tropospheric N_2O sampled in La Jolla, California, under clean air conditions. Nitrous oxide mixing ratios decreased with height above the tropopause, whereas the heavy-isotope composition of the remnant N_2O was found to be increasingly enriched. If the process responsible for this enrichment is an irreversible sink and if the fractionation factor remains constant, the data should obey what is known as a Rayleigh distillation, in which the resulting isotopic enrichment is related to the fraction remaining by the equation

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