The Chemical Composition of Martian Soil and Rocks Returned by the Mobile Alpha Proton X-ray Spectrometer: Preliminary Results from the X-ray Mode

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The alpha proton x-ray spectrometer (APXS) on board the rover of the Mars Pathfinder mission measured the chemical composition of six soils and five rocks at the Ares Vallis landing site. The soil analyses show similarity to those determined by the Viking missions. The analyzed rocks were partially covered by dust but otherwise compositionally similar to each other. They are unexpectedly high in silica and potassium, but low in magnesium compared to martian soils and martian meteorites. The analyzed rocks are similar in composition to terrestrial andesites and close to the mean composition of Earth's crust. Addition of a mafic component and reaction products of volcanic gases to the local rock material is necessary to explain the soil composition.

Before Pathfinder there were two major sources of information on the chemistry of the martian surface: First, the XRF-analyses of the two Viking landers (*1*) and, second, the analytical data of martian meteorites (*2*), assuming that they are rocks from the martian surface ejected into space by large impacts. Although the two landing sites of Viking 1 and Viking 2 were about 6500 km apart from each other, the composition of the soils analyzed at both sites was rather similar and was interpreted to represent the weathering products of mafic igneous rocks (*3*). In particular, it was suggested that sulfur and chlorine were introduced by the interaction of volcanic gases with the mafic surface material, forming sulfates and chlorides (*4*, *5*). The question of a possible presence of other salts like carbonates and nitrates in addition to sulfates and chlorides remained unresolved. The martian meteorites are more variable than the Viking analyses, but generally also of mafic to ultramafic composition.

The APXS was designed to obtain the chemical composition of martian rocks as well as soils. The technique of the APXS is based on three kinds of interactions of alpha particles from a radioactive source with matter: Rutherford backscattering (alpha mode), (α,p) nuclear reactions of alpha particles with some light elements (proton mode), and generation of characteristic x-rays in the sample through ionization by alpha particles (x-ray mode). As a result of these interactions three different energy spectra are obtained, each one recorded in 256 channels.

Data from these three modes are partly complementary and partly redundant: In the alpha-mode the APXS measures all elements heavier than helium. Sensitivity and resolution is excellent for the light elements C, N, and O. However, resolution becomes poor for elements heavier than Si. In the x-ray mode, the APXS measures all elements heavier than Na, with increasing resolution capabilities for heavier elements. In the proton-mode complementary data are obtained for the elements in the transition regions, that is for Na, Mg, Al, and Si.

With the combination of alpha, proton, and x-ray modes, it is possible, in principle, to measure the abundances of all elements in the sample except H and He, at detection limits of typically several tenths of a weight percent. The depth of analysis depends on the sample, and is typically of the order of a few to some tens of micrometers. Analysis is performed on samples of 50-mm diameter. The technique is relatively insensitive to surface roughness of the sample analyzed (*6*, *7*), and the measurement geometry does not have to be known precisely. All relevant elements were measured and the sum of their concentrations was normalized to 100%. The APXS has been described in detail elsewhere (*8*). The rover provided mobility to the APXS and enabled it to analyze a variety of samples selected from images taken by the Imager for Mars Pathfinder (IMP) on the lander.

As of sol 58 (31 August 1997), the APXS has analyzed a total of six soil sites and five rocks (Table 1). Two circumstances have prevented full exploitation of the data returned for analysis: Atmospheric CO_2 significantly influenced the measured spectra in the alpha mode, while the data obtained in the x-ray mode during the martian day time are noisy. Corrections for the interference of CO_2 in the alpha mode requires careful recalibration of the instrument at the same conditions (CO_2 pressure and temperature) encountered on Mars during sample measurements. This recalibration may take up to several months. Proton spectra are not affected by CO_2, but they can only be used together with the alpha data. X-ray spectra are also not affected by the CO_2 atmosphere and measurements during the martian nighttime yielded low noise data with good energy resolution. Therefore, we analyzed x-ray data predominantly collected at night. The x-ray spectrum of rock A-3, Barnacle Bill, obtained on 6 July 1997 (sol 3)—the first rock ever analyzed on the surface of Mars—and the x-ray spectrum of a typical martian soil—

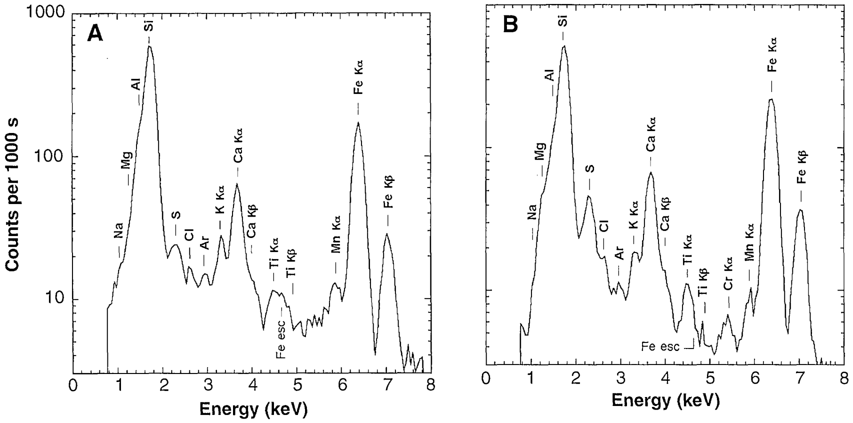

Fig. 1. (**A**) X-ray spectrum of rock A-3, Barnacle Bill, measured on sol 3 for a period of 13,780 s at night time. A normalized count rate per 1000 s is shown as function of x-ray energy. The Ar peak in the spectrum is from 1.6% Ar in the martian atmosphere and is more pronounced in the cases when the APXS sensor was not in immediate contact with the sample. The energy resolution of the x-ray detecting system was 254 eV (full width at half maximum) at 6.4 keV Fe line. (**B**) X-ray spectrum from A-15, the dark soil at the Mermaid Dune site. It was acquired at nighttime on sol 28 for a period of 10,510 s.

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Table 1. Composition of the target sites, expressed as oxides in weight percent, normalized to a sum of 98%. Org. sum is the original sum of the oxides before normalization.

Name		Na_2O	MgO	Al_2O_3	SiO_2	SO_3	Cl	K_2O	CaO	TiO_2	FeO	Org. sum
Soils												
A-2	After deploy	2.3±0.9	7.9±1.2	7.4±0.7	51.0±2.5	4.0±0.8	0.5±0.1	0.2±0.1	6.9±1.0	1.2±0.2	16.6±1.7	68.6
A-4	Next to Yogi	3.8±1.5	8.3±1.2	9.1±0.9	48.0±2.4	6.5±1.3	0.6±0.2	0.2±0.1	5.6±0.8	1.4±0.2	14.4±1.4	78.2
A-5	Dark next to Yogi	2.8±1.1	7.5±1.1	8.7±0.9	47.9±2.4	5.6±1.1	0.6±0.2	0.3±0.1	6.5±1.0	0.9±0.1	17.3±1.7	89.1
A-8	Scooby Doo	2.0±0.8	7.1±1.1	9.1±0.9	51.6±2.6	5.3±1.1	0.7±0.2	0.5±0.1	7.3±1.1	1.1±0.2	13.4±1.3	99.2
A-10	Next to Lamb	1.5±0.6	7.9±1.2	8.3±0.8	48.2±2.4	6.2±1.2	0.7±0.2	0.2±0.1	6.4±1.0	1.1±0.2	17.4±1.7	92.9
A-15	Mermaid Dune	1.3±0.7	7.3±1.1	8.4±0.8	50.2±2.5	5.2±1.0	0.6±0.2	0.5±0.1	6.0±0.9	1.3±0.2	17.1±1.7	98.9
Rocks												
A-3	Barnacle Bill	3.2±1.3	3.0±0.5	10.8±1.1	58.6±2.9	2.2±0.4	0.5±0.1	0.7±0.1	5.3±0.8	0.8±0.2	12.9±1.3	92.7
A-7	Yogi	1.7±0.7	5.9±0.9	9.1±0.9	55.5±2.8	3.9±0.8	0.6±0.2	0.5±0.1	6.6±1.0	0.9±0.1	13.1±1.3	85.9
A-16	Wedge	3.1±1.2	4.9±0.7	10.0±1.0	52.2±2.6	2.8±0.6	0.5±0.2	0.7±0.1	7.4±1.1	1.0±0.1	15.4±1.5	97.1
A-17	Shark	2.0±0.8	3.0±0.5	9.9±1.0	61.2±3.1	0.7±0.3	0.3±0.2	0.5±0.1	7.8±1.2	0.7±0.1	11.9±1.2	78.3
A-18	Half Dome	2.4±1.0	4.9±0.7	10.6±1.1	55.3±2.8	2.6±0.5	0.6±0.2	0.8±0.1	6.0±0.9	0.9±0.1	13.9±1.4	92.6
Calculated "soil-free rock"		2.6±1.5	2.0±0.7	10.6±0.7	62.0±2.7	0	0.2±0.2	0.7±0.2	7.3±1.1	0.7±0.1	12.0±1.3	

Mermaid Dune, A-15—are shown in Fig. 1.

Because the results from the alpha and proton modes are not yet available, for the sake of simplicity in analyzing the x-ray data we assumed that there were no carbonates, nitrates, or hydrates in the martian samples, and that oxygen is assigned to the other rock-forming elements stoichiometrically (Fe as FeO, S as SO_3). The analyses (Table 1), expressed as oxides, have been normalized to 98% for the following reasons: First, mainly due to variations in the measurement geometry, the sums of the primary analyses added up to between 68.6 and 99.2%, with a mean value of 88.5%. Second, data for P, Cr, and Mn have large errors and were not included in our analysis. For the sum of P_2O_5, Cr_2O_3, and MnO a value of 2% has been assumed, leaving 98% for the remaining oxides. Data for Na_2O have large errors (about 40% relative), because the Na x-ray line is of low intensity and buried in the spectral lines of Mg and even Al. This low intensity is due to a low concentration of Na in the sample, but is also due to significant absorption of its low energy photons (1.04 keV) in the sample itself, the CO_2 atmosphere between sample and detector, and the Be entrance window of the x-ray detector. Uncertainties (Table 1) were derived from the range in differences found between certified and measured values for eight reference standards.

To demonstrate the accuracy achievable with APXS in the x-ray mode alone, we obtained chemical analyses of a slice of the martian meteorite Zagami and a powdered sample of the C2 chondrite Murchison subject to the same procedures as applied to the Pathfinder samples during our laboratory calibrations (Table 2). Five individual chips of about 0.5 g each of Zagami were analyzed with conventional techniques and the measured compositions were variable, indicating that the Zagami sample is chemically heterogeneous (9). For Murchison a powdered sample was analyzed.

The soils at the Pathfinder site have similar compositions to those measured at the Viking sites , but they also show some differences. For the purpose of comparison, all soils have been normalized to 44% by weight of silica (Fig. 2). Pathfinder soils are

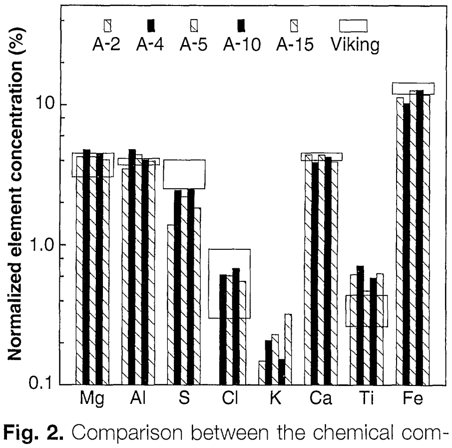

Fig. 2. Comparison between the chemical composition of five measured Pathfinder soils A-2, A-4, A-5, A-10, and A-15, normalized to an SiO_2 content of 44% by weight, and the Viking soil data. The box for the Viking data reflects the range of the individual element concentrations, which were normalized to an SiO_2 content of 44% after being recalculated to 100% by weight.

Table 2. Compositional data in weight percent of martian meteorite Zagami and the C2 chondrite Murchison performed by APXS and (*9*).

	Zagami APXS counting time: 127,470 s	Zagami (*9*)	Murchison APXS counting time: 242,030 s	Murchison APXS counting time: 20,360 s	Murchison (*9*)
Na_2O	2.3	0.7 to 1.2	1.5	0.7	0.2
MgO	8.8	8.6 to 11.6	18.2	18.2	19.9
Al_2O_3	7.1	4.8 to 6.2	2.4	2.3	2.3
SiO_2	49.6	48.4 to 50.9	31.0	31.0	28.5
SO_3	0.3	0.15 to 0.29	7.8	7.8	7.9
K_2O	0.25	0.13 to 0.24	0.06	0.04	0.04
CaO	10.9	9.7 to 11.1	2.0	1.8	1.9
TiO_2	1.0	0.74 to 1.4	0.04		0.06
FeO	17.4	18.0 to 24.5	30.2	30.2	27.1

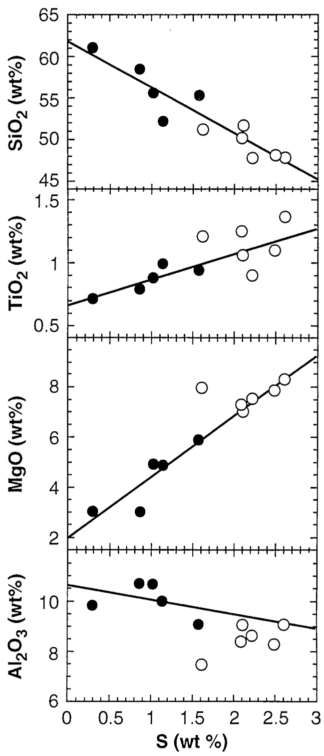

Fig. 3. Linear regression lines for Si, Ti, Mg, and Al versus S of Pathfinder rocks only (filled circles). The linear correlation coefficients for each element are as follows: Si, 0.76; Ti, 0.85; Mg, 0.88; and Al, 0.38. The extrapolated values at zero S give the calculated S-free rock composition. As soils (open circles) were not included in the regression, but plot on the regression line, the zero S values represent a "soil-free rock" composition too.

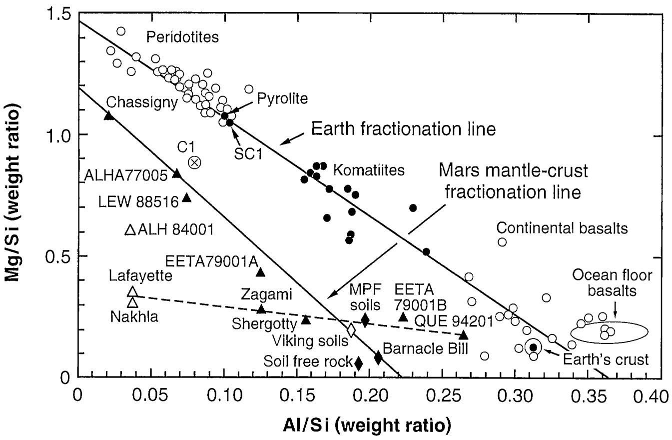

Fig. 4. Mg/Si versus Al/Si diagram of martian meteorites (filled triangles), mean values of Viking soils (open diamond), and Pathfinder soils (labeled as MPF soils), as well as Barnacle Bill and calculated "soil-free rock" composition (filled diamonds) in comparison with terrestrial samples.

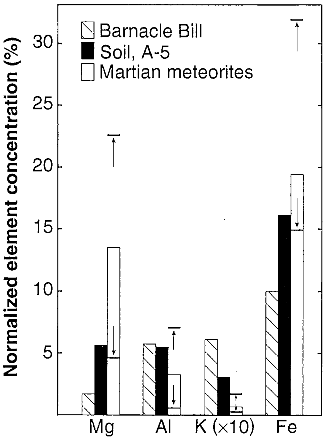

Fig. 5. Histogram of some element concentrations in Barnacle Bill (hatched bar), Pathfinder soil A-5 (filled bar), and martian meteorites (open bar). For Mg, K, and Fe the martian soil could be interpreted as a mixture of rocks and a more mafic component represented by the martian meteorites. The bars for the martian meteorites indicate the mean value of 11 martian meteorites, with the lowest and the highest value given by the arrows. All data are normalized to SiO_2 content of Barnacle Bill = 58.4% by weight.

generally lower in S and higher in Ti than the Viking soils. The Cl values, although still subject to considerable uncertainty for both sites, agree within their error bounds. As is evident from IMP images, but also from APXS sulfur data, the surfaces of the rocks are covered to varying degrees with adhering dust or a weathering rind similar in composition to the dust.

When plotted on two-component diagrams, the compositions of Pathfinder rocks form roughly linear arrays for most elements. Soil analyses lie at one end of these trends, indicating that the rock analyses probably represent mixtures of rock and adhering soil or a weathering rind. Because the rock analyses contain appreciably more S than is normally accommodated in magmas or igneous rocks, the approximate composition of the unaltered rock can be estimated by assuming that it contains no S. We have calculated linear regressions for plots of each element versus S, and extrapolated these data to zero S content (Fig. 3) (Table 1). The rocks that most closely match this composition are Shark and Barnacle Bill. High-resolution IMP images of these two rocks suggest minimal contamination by dust relative to other analyzed rocks, which exhibit higher red to blue reflectance ratios.

The compositions of the calculated "soil-free rock," Shark, and Barnacle Bill correspond to an andesite (*10*). Their CIPW norms are dominated by feldspars, orthopyroxenes, and quartz, with minor Fe-Ti oxides. However, we cannot be certain that these rocks are igneous. Some rocks appear to show vesicular textures, but the textures of other rocks are difficult to interpret and might be sedimentary or metamorphic. Alternatively, the high normative feldspar contents suggest that they could also be impact melts, although there is little evidence for depletion of volatile alkalis.

In the MgO-S plot (Fig. 3) the soil data points fall close to the regression line of the rocks if one neglects the one lowest in S (soil A-2). This could indicate that Mg was introduced in the form of magnesium sulfate. However, only about one-third of the measured MgO could be accounted for in this way.

We have listed A-8, Scooby Doo, as a soil sample in spite of its consolidated appearance because of its high SO_3 content. However, as is evident from Table 1, Scooby Doo—except for SO_3, Cl, and MgO—falls within the compositional range of the analyzed rock samples. This observation suggests that sedimentary rocks could form from soils at the Pathfinder landing site.

Geologic observations (*11*) suggest that the Pathfinder landing site may contain rocks carried by floods from the southern highlands, a heavily cratered terrain thought to represent the ancient martian crust. The compositions of the "soil-free rock," Shark, and Barnacle Bill may provide a more representative sampling of this crust than does the only ancient martian meteorite, the ALH84001 pyroxenite. With their high Al_2O_3, SiO_2, and alkali contents relative to martian meteorites, these andesite compositions are similar to the mean composition of Earth's crust. The primary difference is the high Fe contents of all the martian samples, which probably reflects a high FeO content of the martian mantle relative to Earth's mantle (*12*). The high Al content of the Pathfinder rocks may indicate derivation of their parent magmas from an early melt of the primitive martian mantle, with the parent magmas for shergottites and nakhlites (two subgroups of martian meteorites) derived later from already depleted sources (*13*).

Barnacle Bill's composition is taken as the Al-rich endpoint of the martian mantle-crust fractionation line, with the martian lherzolithes ALHA 77005 and LEW 88516 and the dunite Chassigny on the Al-poor side (Fig. 4). The basaltic shergottites (QUE 94201, Shergotty, and Zagami), which form a second fractionation line (Fig. 4), could be rocks derived from younger intrusions into the older martian crust. As they all are assumed to have been ejected 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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