corresponding P-methyl phosphorus ylide 3 in near-quantitative yield (an ylide is a compound in which a positively charged atom from group 15 or 16 is connected to a carbon atom carrying a negative charge) (Fig. 2). Further investigation of 2* through analysis of the Laplacian of the electron density (20) and the electron localization function (21) reveals a strong “banana” P–P bond with large p character (the bond ellipticity is 0.45) in the plane of the ring and partial double-bond character (Wiberg bond indices = 1.2) for the P–C bonds (Fig. 5).

The calculations found that the open planar form (C₁₈-symmetry) of type 1a, analogous to that of amidinium salts, is not a minimum on the potential energy surface. This illustrates the striking difference between phosphorus and nitrogen chemistry (Fig. 6). However, pyramidalization at one of the phosphorus atoms leads to an alicyclic form 2*. The experimental observation of 2 can be explained by the presence of bulky disopropylamino groups because the steric demand in the linear form is larger than in the cyclic system.

Derivative 2 can be considered as resulting from a “cascade stabilization” of the electron-deficient carbocation center. As in the case of monophosphinocarbenium ions such as A, the first phosphorus atom gives electrons to the carboxation center and becomes positively charged and, therefore, highly electrophilic (22). The second phosphorus atom then acts as a Lewis base toward the first (Fig. 7).

This type of transformation of a cationic center into an anionic center is unlikely to be unique and should be of important synthetic utility. For example, preliminary calculations predict that the corresponding diphosphinomethylenephosphonium ions should exist in the cyclic form, with a negatively charged nitrogen atom. The synthesis of 2, combined with the recent preparation of a tricyclic tetraphosphabenzenecarboxylation isomer (23) (calculated in the carbon series to be 933 kJ/mol less stable than benzene), also suggests that the unique electronic properties of heavier main-group elements will allow the separation of a tricyclic tetraphosphabenzene without difficulty (Fig. 5).

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between different isotopes of sulfur and oxygen. As a result, observed isotope variation can be related by $\delta^{33}S = 0.515 \times \delta^{18}O$, $\delta^{34}S = 1.90 \times \delta^{18}S$, and $\delta^{17}O = 0.52 \times \delta^{18}O$ (10). The quantities $\Delta^{33}S$, $\Delta^{34}S$, and $\Delta^{17}O$ (11) reflect the deviation of measured isotope compositions ($\delta^{33}S$, $\delta^{34}S$, and $\delta^{17}O$) from mass fractionation arrays with origins at $\delta^{33}S_{\text{CDT}} = 0$, $\delta^{34}S_{\text{CDT}} = 0$, and $\delta^{17}O_{\text{CDT}} = 0$ for sulfur, and at $\delta^{17}O_{\text{SMOW}} = 0$ and $\delta^{18}O_{\text{SMOW}} = 0$ for oxygen (CDT, Canyon Diablo Troilite; SMOW, standard mean ocean water).

In addition, several isotopic fractionation processes are also known to produce mass-independent compositions ($\Delta^{33}S \neq 0$, $\Delta^{34}S \neq 0$, or $\Delta^{17}O \neq 0$) (12–14). These include fractionations that result from hyperfine interactions in solid and liquid phases and an increasing number of gas-phase reactions (13). The hyperfine effect derives from spin-orbit coupling in isotopes with odd-mass nuclei and is therefore limited to isotopomers that contain these nuclei (such as $^{33}S$ and $^{17}O$). Gas-phase mass-independent fractionations have been documented for a number of sulfur phases in laboratory experiments (SO$_2$, H$_2$S, CS$_2$, and SF$_6$) (12, 15, 16), but the physical chemical origin of the effect is still uncertain. The role of gas-phase mass-independent chemistry in determining the oxygen isotopic compositions of many atmospheric species is unequivocal (13), and these types of reactions may also play an important role in determining the sulfur isotope compositions of atmospheric species (15).

To examine sulfur isotope variability in early Earth, we extracted sulfur from sulfide and sulfate minerals in a variety of Precambrian samples. Sulfur isotopic analyses fall into two groups defined on the basis of $\Delta^{33}S$ values and geological age (Fig. 1; also see Web table 1 at www.sciencemag.org/content/1052160). Samples younger than 2090 Ma display a range of $\Delta^{33}S$ values from −0.11 per mil (‰) to 0.02‰ and are considered to be consistent with fractionation by mass-dependent processes. Sulfide and sulfate samples older than 2090 Ma exhibit a range of $\Delta^{33}S$ varying between 0.02 and 0.34‰, and samples older than 2450 Ma exhibit a much larger range of $\Delta^{33}S$, varying between −1.29 and 2.04‰.

This variation is consistent with large mass-independent compositions. The relation between $\Delta^{33}S$ and $\Delta^{34}S$ (Fig. 2) and between $\delta^{18}S$ and $\delta^{17}O$ (Fig. 3) rules out the possibility that hyperfine interactions account for the observations. The most likely explanation of observed $\Delta^{33}S$ and $\Delta^{34}S$ values for early Proterozoic and Archean sulfide and sulfate is, therefore, the presence of one or more gas-phase, mass-independent chemical reactions in the sulfur cycle.

Photochemical reactions are thought to be important in the early Proterozoic and Archean atmosphere and may be relevant to the sulfur cycle before 2090 Ma. Photochemical reactions have been suggested as the source of nonzero $\Delta^{33}S$ values in martian samples (martian meteorites) (15). Our data indicate that a profound change occurred in the sulfur cycle between 2090 and 2450 Ma. This change might represent the onset of a process capable of homogenizing mass-independent sulfur reservoirs or the suppression of one or more atmospheric reactions that had occurred before this interval.

Two basic models have been suggested for Earth’s early sulfur cycle. The first is that the Archean sulfur cycle did not differ significantly from the preanthropogenic sulfur cycle (7–9) and that the dominant source of oceanic sulfate was oxidative weathering of continental sulfides and weathering of continental sulfates. The second is that oxidative weathering did not play a significant role in the Archean sulfur cycle and that the principal source of oceanic sulfate was photochemical oxidation of volcanogenic sulfur species in the Archean atmosphere (6). Our mass-independent sulfur isotope data strongly support a pre–2090-Ma sulfur cycle that was influenced by atmospheric chemical reactions. All of our data for samples of barite and of barite plus chert that are older than 2090 Ma have negative $\Delta^{33}S$ values. One analysis of Archean barite from the Sargur Group of Karnataka, India (17), also yields a negative $\Delta^{33}S$ value. Most of our data for samples of pelitic and psammitic rocks older than 2090 Ma have positive $\Delta^{33}S$ values. These observations are consistent with the existence of two reservoirs: a water-soluble (oceanic?) sulfate reservoir with negative $\Delta^{33}S$ values and an insoluble reservoir of reduced sulfur with positive $\Delta^{33}S$ values. Oxidative weathering would have mixed these reservoirs by transferring sulfur from reduced to oxidized reservoirs, producing sulfate with a positive (or juvenile) $\Delta^{33}S$ signature that would dilute (or even eliminate) the negative $\Delta^{33}S$ signature of its global oceanic counterpart. We infer that the transition to a sulfur cycle more like the modern preanthropogenic sulfur cycle occurred after 2090 Ma, when higher levels of atmospheric oxygen overwhelmed the atmospheric sources of oceanic sulfate through oxidative and microbial weathering of continental sulfides. Further insight into the nature of this transition will be obtained once the atmospheric reaction (or reactions) responsible for producing the effect are identified.

It is also possible that the atmospheric chemistry responsible for producing the observed mass-independent sulfur isotopic compositions before 2090 Ma may have stopped operating as a result of a change in atmospheric composition or actinic flux. Some have suggested that changes in the solar spectrum [ul-

Fig. 1. Plot of $\Delta^{33}S$ values versus sample age. Variable $\Delta^{33}S$ values for samples with geological ages greater than the transition interval at 2090 to 2450 Ma are interpreted as an indication of atmospheric influence of the sulfur cycle. Homogeneous $\Delta^{34}S$ values for samples with geological ages less than 2090 Ma are interpreted as an indication of a sulfur cycle dominated by oxidative weathering of continental sulfide and sulfate. The dark gray band at $\Delta^{34}S = 0$ represents the mean and 1 SD of data collected to date from younger sulfide and sulfate from 73 samples that include mantle xenoliths, marine barite, desert gypsum, evaporite, massive pyrite, channel deposits, ash deposits, and building surface deposits. Age data for these samples are compiled in (30).

Fig. 2. Plot of $\Delta^{33}S$ versus $\Delta^{34}S$ for samples older than 2090 Ma. The correlation between $\Delta^{33}S$ and $\Delta^{34}S$ is interpreted as evidence of mass-independent isotopic fractionations originating in gas-phase reactions rather than from hyperfine interactions, which would produce $\Delta^{33}S$ but not $\Delta^{34}S$. Mass-dependent processes plot at the origin of this plot. Error bars represent 1σ for analytical uncertainties of 0.05 and 0.3‰ for $\Delta^{33}S$ and $\Delta^{34}S$, respectively.
traviolet (UV) and visible wavelengths) resulting from main sequence brightening (18) could have affected atmospheric chemistry in Earth’s earliest atmosphere (19, 20). Although this change may account for our observations, changes in the abundance of absorbing species in the upper atmosphere exert a much stronger influence on lower atmospheric UV and on photochemistry (21). Higher surface UV resulting from a reduced ozone column depth in an atmosphere with low oxygen concentrations (22–24) may have played a role in determining atmospheric sulfur chemistry and in generating isotopically distinct sulfur reservoirs. Photolysis of SO₂, for instance, results in production of SO₃ (25) that converts to H₂SO₄ upon contact with water. This photochemical oxidation sequence has been shown to produce mass-independently fractionated sulfur (15). Whereas oxygen isotopic signatures of present-day products of atmospheric oxidation of reduced sulfur-bearing gases have been shown to possess mass-independent oxygen isotopic compositions that are thought to be the result of oxidation by isotopically anomalous ozone and hydrogen peroxide (26, 27), our oxygen isotope data for sulfate from barites from 3300 to 3400 Ma are mass-dependent (Δ¹⁷O = 0.01 ± 0.006‰). The lack of a similar mass-independent signature in our Archean barites may be a further indication that the sulfur oxidation pathways were different from that of the current atmosphere, possibly reflecting the exchange of sulfate (a product of SO₂ photooxidation) with water during the formation of sulfate. If this is the case, the buildup of atmospheric oxygen may have helped shut down the atmospheric chemical reactions that were responsible for generating isotopically anomalous sulfur-bearing reservoirs. An alternative explanation of the oxygen isotope data is that the original atmospheric oxygen isotopic signature has been lost because of exchange processes that occurred after sulfate formation.

If Δ³⁴S fractions reflect atmospheric fractionation processes, it is also possible that the same applies to Δ³⁵S fractions. Some workers have divided the sulfur isotope record into a period before 2750 Ma, when the range of Δ³⁴S was less than about 10‰, and a period after 2750 Ma, when the range of Δ³⁴S was greater than 10‰ (5, 28). These workers suggest that the change in magnitude for the range of observed Δ³⁴S fractions at 2750 Ma is evidence of the onset of microbial sulfate reduction. Other workers have suggested that the smaller range of Δ³⁴S before 2750 Ma also results from microbial sulfate reduction but at higher temperature conditions, possibly at lower oceanic sulfate concentrations or in closed systems (7–9). On three isotope plots (Fig. 3), our data do not follow the mass-dependent arrays that would be formed by microbial sulfate reduction (for example, Δ³⁴S ~ 0.515 × Δ³⁵S and Δ³⁶S = 1.90 × Δ³⁴S), and they allow that the Δ³⁴S record for samples older than 2750 Ma may be entirely atmospheric in origin. Although our data do not rule out the possibility of microbial sulfate reduction, they imply that Δ³⁴S values cannot be used alone to argue for the operation of (or examine the consequences of) metabolic processes that fractionated sulfur isotopes before 2750 Ma.

Similar sulfur isotope measurements can be used to resolve atmospheric inputs and to gain new insights into biogeochemical element cycles. The recent observation of mass-independently fractionated sulfur in this study and in martian meteorites (15) and of mass-independently fractionated oxygen in terrestrial and martian sulfates (27, 29) opens up possibilities for identifying additional components of the sulfur cycle on Earth and on other bodies in the solar system.

References and Notes
11. Those quantities are as follows: Δ¹⁷S = 1000[¹⁷S/(³⁴S + ³⁵S)], Δ¹⁸O = 1000[¹⁸O/(³⁴S + ³⁵S)], and Δ²⁸S = 1000[(¹³C/¹²C) + ³²S/³³S] – 1. Uncertainties for Δ¹⁷S, Δ¹⁸O, and Δ²⁸S are better than ±0.05, ±0.05‰, respectively.
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