further oxidation of NO to NO_2 and the rate of ozone formation. This behavior can be explained by a chain reaction consisting of reactions 1, 2, 9, and 10:

$$\mathrm{HO_2 + NO_2 \rightarrow HNO_2 + O_2} \qquad (9)$$

$$\mathrm{HNO_2} + h\nu \rightarrow \mathrm{OH + NO} \qquad (10)$$

This chain reaction converts NO_2 to NO and will compete with reactions 1 through 3 under conditions of large $[NO_2]/[NO]$.

The carbon monoxide had 0.15 percent $Fe(CO)_5$ as its principal impurity (the hydrocarbon impurities were negligible, being less than 5 ppm). When iron carbonyl was not removed from the CO, the rate of oxidation of NO to NO_2 was accelerated even more than is shown in Fig. 1. In the presence of unpurified CO, only 60 minutes elapsed before all the NO was converted to NO_2 (defined as when $[NO] = [O_3]$). By comparison, with purified CO, 100 minutes elapsed (see Fig. 1); without CO, 130 minutes elapsed. Since the concentration of $Fe(CO)_5$ is an order of magnitude smaller than that of the NO, its pronounced effect can be explained only by a chain reaction. Because the carbonyl undergoes decomposition in sunlight (*6*) and is probably vulnerable to attack by oxygen atoms, a possible chain mechanism for its effect might include the following reactions:

$$\mathrm{Fe(CO)_5 + O \rightarrow Fe(CO)_4 + CO_2} \qquad (11)$$

$$\mathrm{Fe(CO)_5} + \xrightarrow{h\nu} \mathrm{Fe(CO)}_x + (5-x)\mathrm{CO}, \quad x < 5 \qquad (12)$$

$$\mathrm{Fe(CO)}_x + \mathrm{O_2} \rightarrow \mathrm{Fe(CO)}_x\mathrm{O_2} \qquad (13)$$

$$\mathrm{Fe(CO)}_x\mathrm{O_2} + (\mathrm{NO\ or\ CO}) \rightarrow \mathrm{Fe(CO)}_x\mathrm{O} + (\mathrm{NO_2, CO_2}) \qquad (14)$$

$$\mathrm{Fe(CO)}_x\mathrm{O} + (\mathrm{CO\ or\ NO}) \rightarrow \mathrm{Fe(CO)}_x + (\mathrm{CO_2, NO_2}) \qquad (15)$$

Other reaction mechanisms may be equally possible, but reactions 11 through 15 do show that the observed effects of $Fe(CO)_5$ can be accounted for in a plausible manner. Iron carbonyl is highly reactive in other free-radical systems: trace amounts of $Fe(CO)_5$ either quench hydrocarbon-air flames or reduce their flame velocities substantially (*7*); this compound formerly was used as an antiknock agent in gasoline (*6*).

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Sulfur Isotopes in Swaziland System Barites and the Evolution of the Earth's Atmosphere

Abstract. *Sedimentary barites from the Swaziland System of South Africa (more than 3000 million years old) have sulfur-34 ratios that are enriched by only 2.5 per mil with respect to contemporary sulfides. To explain this small fractionation, it is proposed that oxygen pressure in the earth's atmosphere was very low and that local oxidation occurred in a photosynthetic layer of the ocean.*

In this report we interpret the significance of sulfur isotope data from an isolated occurrence of sulfate separated in time by 2000 million years from any well-understood deposits. We hope to show that the deposit is sedimentary, that its sulfate may reasonably represent contemporary oceanic sulfate, and that its sulfur isotope composition may indicate roughly the oxygen content of the early atmosphere.

Beds of barite alternating with green chert, shale, and pebble conglomerate occur in a 20-m-thick zone of the Fig Tree or Upper Onverwacht Group, Swaziland Sequence, in the Barberton Mountain Land, South Africa. These occurrences are mentioned by Visser (*1*), and several of them are shown on the 1 : 50,000 map of the Barberton area published by the South African Geological Survey in 1955; they appear as an 8-km-long band, 11 km southeast of Barberton. The barite is recrystallized, but we consider it to be sedimentary for the following reasons: (i) it occurs in conformable layers, and cross-cutting veins have not been observed; (ii) the zone of barite beds is persistent within the same horizon for several kilometers along strike; (iii) no accompanying sulfide mineralization has been observed; and (iv) the barite-chert association found here is common in sedimentary barite deposits.

Strontium isotopic data provide strong evidence that these deposits were formed prior to the main metamorphic event of 3000 million years ago that affected the Barberton Mountain Land. Whereas the $^{87}Sr/^{86}Sr$ ratio established in graywackes and shales by this metamorphic event was 0.712 (*2*), the $^{87}Sr/^{86}Sr$ ratio in eight Barberton barites ranges from 0.70088 to 0.70172 (*3*). This lower $^{87}Sr/^{86}Sr$ ratio precludes derivation of the cations from a source with a high Rb/Sr ratio and suggests that they were derived from the upper mantle during volcanism associated with sedimentation (*4*).

Table 1 lists $\delta^{34}S$ values (*5*) for barites and for sulfides from approxi-

Table 1. Values of $\delta^{34}S$ for barites and sulfides of the Swaziland System.

Sample	$\delta^{34}S$	Remarks
		Barites
A185	+3.5	Coarse green barite associated with chert, central zone
9B2	+3.1	
B11	+3.1	
B20	+3.8	
B14	+3.5	Barite and conglomerate, west workings
B15	+3.4	Elongated barite crystals, east workings
B17	+3.7	Barite in conglomerate, easternmost part of district
Approximately	*contemporaneous sulfides*	
A177	+1.1	Disseminated pyrite in graywacke, Fig Tree Group
R5	−0.1	Pyrite in Fig Tree iron formation
R6	+1.6	Pyrite from dolomite bed underlying barite
	−0.9	Galena in quartz vein, Rosetta mine (*19*)

mately equivalent stratigraphic horizons of the Swaziland Sequence. Sulfur isotope variations are small within each group, and, unlike more recent sulfate-sulfide pairs, there is only a 2.6 per mil separation between barite and pyrite. Before presenting an analysis of these data, we shall briefly review the present sulfur cycle.

In the present ocean $\delta^{34}S$ of sulfate is +20.4 per mil, and the ocean is a reservoir for 1.3×10^{15} metric tons of SO_4^{2-} (*6*). Sulfides precipitated from the ocean vary considerably in their isotopic composition, but averages of a large number of determinations show stratified sulfide deposits associated with volcanics to be 17.5 per mil lower in $\delta^{34}S$ and other sedimentary sulfide deposits to be 11.7 per mil lower in $\delta^{34}S$ than contemporary sulfates (*7*). The average $\delta^{34}S$ for sulfide in basic magmas is probably about +1 per mil (*8*). The accepted mechanism for enrichment of ocean sulfate in ^{34}S is the organic reduction of sulfate to sulfide accompanied by a depletion of the sulfide in ^{34}S by 15 per mil or more (*6*). Since this is the only quantitatively important reaction in the sulfur cycle that produces a large isotope fractionation, the cumulative effect is an increase in $\delta^{34}S$ of the sulfate reservoir (*6, 9*). There is little fractionation between crystalline sulfate and dissolved sulfate; and measurements of Phanerozoic evaporites have given a detailed record of past $\delta^{34}S$ variation in the ocean, ranging from +11 per mil in the Permian to about +30 per mil in the Cambrian (*6*). Far fewer data exist for barite than for evaporite minerals, but most syngenetic and oceanic barites have sulfur isotope compositions similar to the sulfate composition of the contemporary ocean (*7, 10, 11*). In some environments sedimentary barite can have $\delta^{34}S$ values considerably higher than the $\delta^{34}S$ of the ocean (*11*).

Sulfates are formed by other processes, such as low-temperature volcanic reactions. These reactions generally are characterized by sulfate-sulfide isotope fractionation similar in magnitude to fractionation between sedimentary pairs (*12*). Only supergene sulfate and sulfate from carbonaceous chondrites consistently have low $\delta^{34}S$ values comparable to the Barberton barites; and, in carbonaceous chondrites, sulfate sulfur is generally slightly depleted in ^{34}S with respect to sulfide sulfur (*13*).

We consider the data in Table 1 to be strong evidence that the geochemical cycle of sulfur during deposition of the Swaziland Sequence was grossly different from the present sulfur cycle. A possible starting point in evaluating these data is Holland's model for the evolution of the earth's atmosphere (*14*). He proposed that at roughly the time of deposition of the Swaziland System, 3200 million years ago, H_2S was replaced or supplemented in the atmosphere by SO_2.

We propose a model for deposition of the Swaziland Sequence in which the present large oceanic sulfate reservoir did not exist. Cations for the Barberton barites were provided by volcanic and volcanogenic sources; oxidation occurred in an oxidizing photosynthetic zone near the ocean surface in which, as Cloud has suggested (*15*), primitive organisms may have used electron donor reactions such as $Fe(OH)_2 + OH^- \rightarrow Fe(OH)_3 + e^-$ instead of reactions involving free oxygen. Under these conditions, green or purple sulfur bacteria could oxidize H_2S or S^{2-} to SO_4^{2-} in the photosynthetic layer. In the presence of anomalous concentrations of Ba^{2+}, precipitation of $BaSO_4$ would follow. Kaplan and Rittenberg (*16*) have shown that oxidation of sulfide to SO_4^{2-} by *Chromatium* sp. produces little isotopic fractionation. Thus this model is consistent with the very small difference in $\delta^{34}S$ between barite and sulfides from the Swaziland Sequence. Furthermore, Harrison and Thode (*17*) have demonstrated that, in the concentration range of 6×10^{-4} to 1×10^{-5} mole/liter of SO_4^{2-}, biological sulfate reduction results in fractionation factors of 1.003 to 0.997 (that is, a 3 per mil depletion of $\delta^{34}S$ in the sulfide at 6×10^{-4} mole/liter and a 3 per mil *enrichment* at 1×10^{-5} mole/liter of SO_4^{2-}), so that it is unlikely that large fractionation could occur as long as the concentration of SO_4^{2-} in the ocean was controlled by cations like Ba^{2+} and Sr^{2+}.

Recently Chukhrov *et al.* (*18*) have presented evidence for ^{34}S enrichment in sulfate minerals of rocks metamorphosed at about 2500 million years ago. Their data presumably are obtained from low percentages of sulfur-bearing minerals such as lazurite in veins and pegmatites in highly metamorphosed rocks that sometimes contain H_2S and native sulfur. We suggest that great care should be taken to distinguish depositional and postdepositional processes in these rocks.

Although the Barberton Mountain Land data perhaps can be explained in other ways, we believe they imply that the sulfur cycle was different and that the atmosphere was less oxidizing in the Early Precambrian than at present.

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4. For a more detailed discussion of strontium data, see V. R. Murthy and E. C. Perry, Jr., in preparation.
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