CARBON ISOTOPIC COMPOSITION OF PRECAMBRIAN SEDIMENTS EXTRACTED BY STEPPED COMBUSTION; R. A. Socki, LESC, 2400 NASA Rd., Houston, TX 77058; C. S. Romanek, E. K. Gibson, SN2, NASA-JSC, Houston, TX 77058; and D. R. Stewart, Dept. of Chemistry, Vassar College, Poughkeepsie, NY 12601.

INTRODUCTION Previous studies have indicated that the current atmospheric composition was markedly different during the Archean (1). Earliest atmospheric constituents were probably stripped away during accretion; extensive outgassing created a secondary atmosphere that endured for the bulk of the Archean (2). The rise of extensive life on the planet (ca 2.0 Ga.) encouraged the eventual change from a reducing to an oxidizing atmosphere (3). Argon isotope dating (4) showed that volatiles trapped in selected sediments represents the atmosphere present at time of formation.

This work identifies sources of carbon released at different temperatures by examining their carbon isotopic composition during the stepped combustion of some Precambrian sediments. These experiments provide information about the oxidized or reduced character of carbon in the earth's earliest atmosphere and biosphere and on clues to the origin of life.

EXPERIMENTAL PROCEDURES Five Precambrian sediments ranging in age from 1.6 to 3.4 Ga. were ground, weighed, and heated in vacuo overnight at 150°C in quartz tubes. Samples were heated stepwise at 200°C intervals from 200°C to 100°C, and reacted with O₂ produced by heating CuO at 800°C in the presence of Pt heated to 1000°C. Evolved CO₂ was collected and separated cryogenically from water and non-condensible gases. CO₂ yields were measured with a capacitance manometer to ± 0.01 torr. Isotope analyses were made on a Finnigan MAT 251 gas source mass spectrometer and are reported in delta notation (6) relative to the PDB standard (5).

RESULTS AND DISCUSSION Data for carbon isotope composition produced from the stepped combustion of five Precambrian sediment samples are plotted as a function of release temperature and yield in Figure 1 (a-e). Fifty to ninety-eight percent of the carbon released from each sample combusts in the 400°-600°C temperature step, suggesting that carbonate phases contain most of the carbon in these rocks. Highly reactive carbonates and volatile organics such as kerogen combust in the 200°-400°C step and make up less than 2% of the total carbon (except for the Gorge Creek Group sample). Highly cross-linked organic species and non-reactive carbonates combust in the 600°-800°C step and comprise up to 30% of the total carbon. Carbon produced in the 800°-1000°C step is probably derived from refractory phases or from lower temperature components liberated during decrepitation of inclusions. They constitute less than 1% of the total carbon (except for the Gorge Creek Group and Ventersdorp Supergroup samples which are 5% and 7% total carbon, respectively).

Carbon isotope profiles support phase interpretations based on stepped combustion yields. The 400°-600°C step generally is most enriched in ¹³C, indicating a strong carbonate component while lower and higher temperature steps are generally depleted in ¹³C. The Earaheedy and McArthur Group profiles are the most enriched in ¹³C and show little change with temperature compared with the other samples while the Ventersdorp Supergroup and Gorge Creek Group profiles show strong depletions in ¹³C in the 600°-800°C and 800°-1000°C steps.

When temperature steps are plotted versus time for all samples two trends develop. The low temperature steps (200°-400°C and 400°-600°C) generally show a slight ¹³C depletion through time (5%) while the high temperature steps (600°-800°C and 800°-1000°C) generally track the lower temperature steps but are depleted by ~25%. The Earaheedy and McArthur Group profiles (1.6 to 1.7 Ga.) do not show this offset probably because of the lack of high
temperature phases and/or the presence of coarse-grained carbonate phases in these samples. The Ventersdorp Supergroup (2.64 Ga.) displays a larger offset (~35‰) with the high temperature steps having unusually low $\delta^{13}C$ values (~40‰). These data are similar to $\delta^{13}C$ values for kerogen from a previous study (6), which documented an anomalously depleted organic $^{13}C$ component in these rocks.

**CONCLUSIONS** Stepped combustion temperature profiles from Precambrian sediments reflect documented $\delta^{13}C$ values and trends from previous studies which separated and pre-treated carbon components before analysis. The data suggest that $\delta^{13}C$ values for carbonates and organics have remained constant or increased only slightly over the last 3.4 billion years.

**REFERENCES CITED**