Multiple-isotope Insights into the Earth's Earliest Sulfur Cycle

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How different was the Earth's earliest sulfur cycle from the present-day sulfur cycle? Arguments have been made both in favor of and against an early sulfur cycle dominated by oxidative weathering (Canfield, 1998; Holland, 1984; Kakegawa and Ohmoto, 1999; Ohmoto, 1996; Ohmoto and Felder, 1987; Ohmoto et al., 1993; Walker and Brimblecombe, 1985). Arguments have also been made for and against microbial sulfate reduction prior to 2750Ma (Cameron, 1982; Canfield et al., 2000; Kakegawa and Ohmoto, 1999; Ohmoto, 1996; Ohmoto and Felder, 1987; Ohmoto et al., 1993; Schidlowski, 1992). Research has also explored the implications of a primitive atmosphere and ocean on the sulfur cycle (Kasting et al., 1989; Walker and Brimblecombe, 1985). Here we demonstrate that important new insights into these issues may be obtained by including $\delta^{33}S$ and $\delta^{36}S$ with measurements of $\delta^{34}S$.

Thermodynamic, kinetic and biological fractionation processes are all thought to fractionate isotopes according rules determined by the relative mass differences of the isotopic species. These processes produce highly correlated arrays on plots of $\delta^{33}S$ vs. $\delta^{34}S$, and $\delta^{36}S$ vs. $\delta^{34}S$ and follow the approximate relationships, $\delta^{33}S \sim 0.515 \cdot \delta^{34}S$, and $\delta^{36}S \sim 1.91 \cdot \delta^{34}S$ (Hulston and Thode, 1965). The exact nature of these arrays depends on the chemical or physical fractionation process (Matsuhisa et al., 1978). Empirical observations indicate that marine barite and evaporites have evolved with $\delta^{33}S = 1000$ permil $((1 + \delta^{34}S/1000)^{0.518} - 1))$ (regression of over 150 measurements - data collected at UCSD). Measurements of hydrogen sulfide produced in a preliminary experiment to investigate dissimilatory sulfate reduction yielded $\delta^{33}S = 1000$ permil $((1 + \delta^{34}S/1000)^{0.509} - 1))$ which is thought to arise in part from the strong kinetic component of biological fractionations. The impetus to initiate this research was to explore the possibility of using small differences in mass-dependent fractionation relationships to test hypotheses about the operation of dissimilatory sulfate reduction before 2.75 Ga. The idea was to measure $\Delta^{33}S$ for a number of samples older than 3 Ga and to see if they followed a relationship with an exponent closer to 0.518 or 0.509. The difference for a 10 permil fractionation would be a $\Delta^{33}S$ of 0.09 permil which is resolvable within the analytical uncertainties of the measurements.

In addition to mass-dependent fractionation processes, there are also certain gas-phase reactions that do not obey mass-dependent fractionation laws. These effects can fractionate all isotopes and are collectively termed mass-independent because they do not obey classical mass-dependent theory. They are capable of producing compositions that lie significantly off the mass fractionation line. The physical-chemical origin of the mass-independent effect is still a subject of considerable research (e.g., (Gellene, 1996; Hathorn and Marcus, 1999; Janssen et al., 1999; Mauersberger et al., 1999; Zmolek et al., 1999), but the expression of these mass-independent fractionation processes in the Earth's atmosphere is widespread and unequivocal (Thiemens, 1999). It is enlightening to consider that almost all oxygen species in the air we breathe that have been measured to date (with the possible exception of water vapor) possess a mass-independent component that can be attributed either directly to gas-phase chemical reactions or to transfer reactions of anomalous oxygen from species formed by these chemical reactions.

Multiple-isotope sulfur data ($\delta^{33}S$, $\delta^{34}S$, and $\delta^{36}S$) for sulfide and sulfate minerals from a variety of Precambrian samples fall into two groups on the basis of $\Delta^{33}S$ and geological age (Figure 1). Samples younger than 2090 Ma display a range of $\Delta^{33}S$ from -0.11 permil to +0.02 permil and are considered to be consistent with fractionation by mass-dependent processes. Our sulfide and sulfate samples older than 2090 Ma, but younger than 2450 Ma, exhibit a range of $\Delta^{33}S$, varying between +0.02 and +0.34 permil, and samples older than 2450 Ma exhibit a much larger range of $\Delta^{33}S$, varying between -1.29 and +2.04 permil, and indicating large mass-independent compositions. The observed $\Delta^{33}S$ are too large to be produced by dissimilatory sulfate reduction. Our data do not follow the mass-dependent arrays that would be formed by microbial sulfate reduction (e.g., $\delta^{33}S \sim 0.509 \cdot \delta^{34}S$). Our data do not rule out the possibility of microbial sulfate reduction occurring before 2750 Ma, but the existence of a large $\Delta^{33}S$ indicates that $\delta^{34}S$ fractionations cannot be used without $\delta^{33}S$ data to argue for the presence or absence of microbial sulfate reduction when $\delta^{34}S$ fractionations are small.

What could have effected the observed change in the sulfur cycle at ~2090-2450 Ma? This change might represent the onset of a process capable of homogenizing mass-independently fractionated sulfur reservoirs that were produced by the cumulative effect of one or more atmospheric gas-phase reactions and/or the suppression of these atmospheric reactions that had occurred before ~2090-2450 Ma. Two basic models have been suggested for the Earth's early sulfur cycle. The first argues that the Archean sulfur cycle does not differ significantly from the pre-anthropogenic sulfur cycle (Kakegawa and Ohmoto, 1999; Ohmoto, 1996; Ohmoto and Felder, 1987; Ohmoto et al., 1993), and that the dominant source of oceanic sulfate is oxidative weathering of continental sulfides and weathering of continental sulfates. The second model argues 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 (Walker and Brimblecombe, 1985). Our mass-independent sulfur isotope data are consistent with a pre-2090-2450 Ma sulfur cycle that was influenced by atmospheric chemical reac-

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tions and that is significantly different from the present-day sulfur cycle. Our data also indicate that the evidence for the occurrence of microbial sulfate reduction before 2750 Ma needs to be reassessed.

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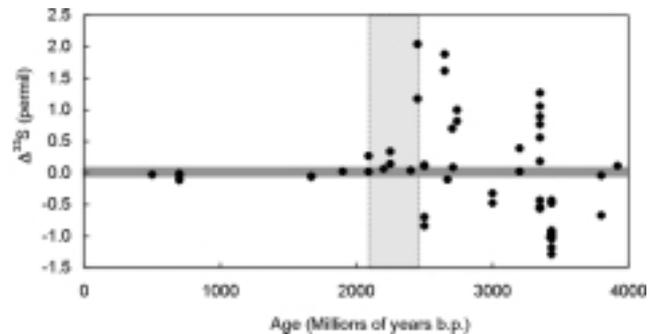
Figure 1. Plot of $\Delta^{33}S$ vs age for sulfide and sulfate of Precambrian age.