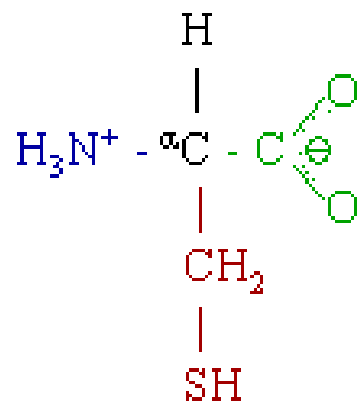


Global Sulfur Cycle

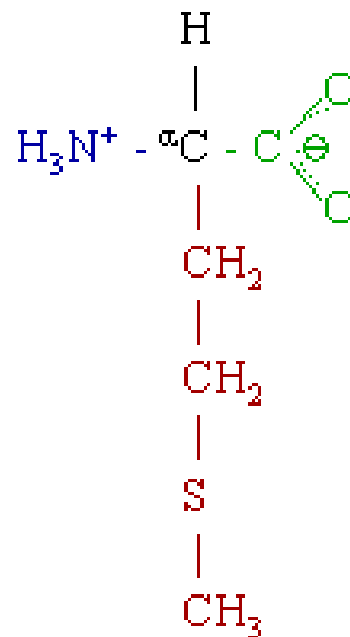
Sulfur's Role in the Living World:

Sulfur is an essential component of proteins (primarily two amino acids: **cysteine** and **methionine**), therefore essential for life.

An “average” cell may have approximately 1% S by dry weight.



Cysteine
(Cys / C)



Methionine
(Met / M)

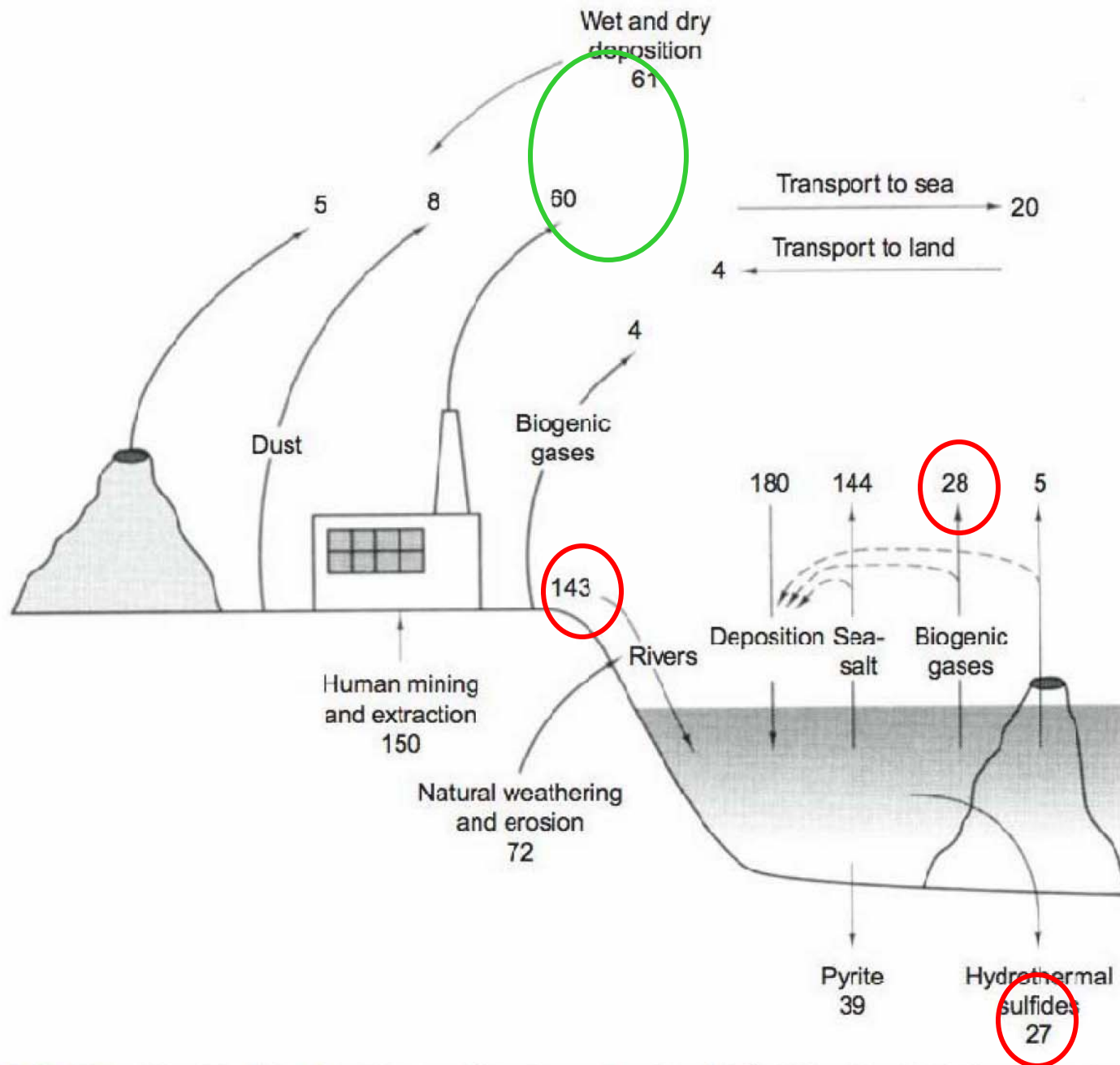


FIGURE 13.1 The global S cycle with annual flux shown in units of 10^{12} g S/yr. The derivation of most values is described in the text, with the marine values taken from Figure 9.22. The net flux from land to sea is extrapolated from Whelpdale and Galloway (1994).

Table 13-3 Major sulfur reservoirs (Tg S)

Reservoir	Major form(s)	Burden
Continental atmosphere ^a	OCS, SO ₄ ²⁻ , SO ₂ , DMS	1.6
Marine atmosphere ^a	OCS, SO ₄ ²⁻ , SO ₂ , DMS	3.2
Soils and land biota ^a	Reduced	3 × 10 ⁵
Lakes and rivers ^b	SO ₄ ²⁻	300
Marine biota ^c	Reduced	30
Seawater ^{a,d}	SO ₄ ²⁻	1.3 × 10 ⁹
Ocean sediments ^{a,e}	Gypsum (CaSO ₄) Pyrite (FeS ₂)	3 × 10 ⁸
Rest of lithosphere ^{a,e}	Pyrite (FeS ₂) Gypsum (CaSO ₄)	2.4 × 10 ¹⁰

^a Freney *et al.* (1983).

^b Calculated from mass of surface freshwater (1.3×10^{20} g H₂O) and average sulfate concentration (2.5×10^{-6} g S/g H₂O).

^c Calculated from carbon in ocean biota (3000 Tg) and approximate mass ratio for sulfur to carbon of 1:100.

^d Volkov and Rozanov (1983).

^e Migdisov *et al.* (1983).

From: Jacobson, Charlson, Rodhe & Orians 2000

TABLE 13.1 Active Reservoirs of Sulfur near the Surface of the Earth

Reservoir	10¹⁸ g S
Atmosphere	0.0000028
Seawater	1280
Sedimentary rocks	
Evaporites	2470
Shales	4970
Land plants	0.0085
Soil organic matter	0.0155
Total	8720

Sources: From Holser et al. (1989) and Dobrovolsky (1994).

Atmospheric sulfur budget (10^{12} g/yr):

Input--

Natural emissions on land (volcanic Eruptions, dust, biogenic)=17

Human mining etc. = 60

Sea salt = 144

Sea biogenic = 28

Sea volcanic eruptions = 5

Total input = 254

Human contribution = $60/254 \times 100 = 24\%$

Output--

Deposition on land = 60

Ocean deposition = 180

Total output = 240.

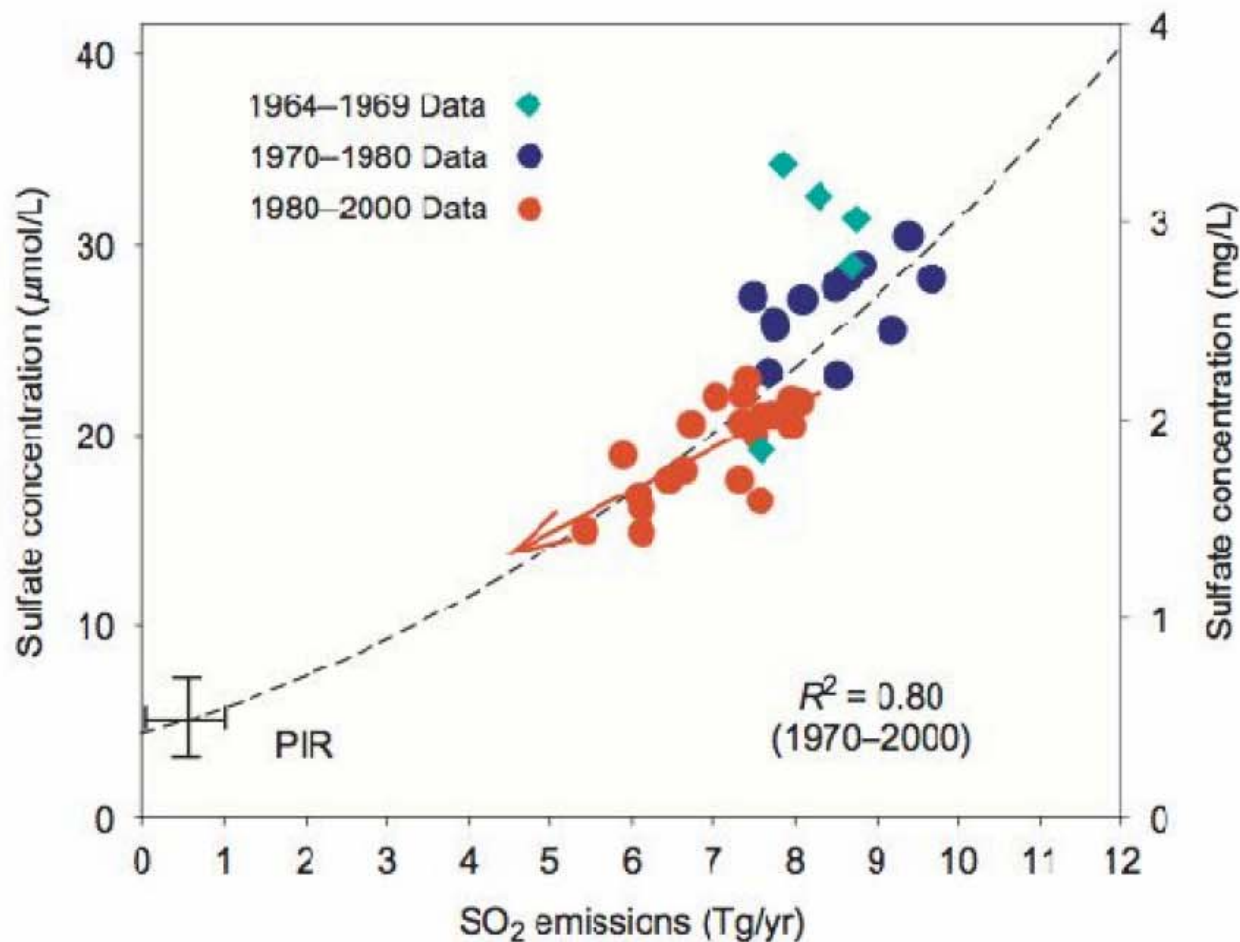


FIGURE 13.2 Sulfate concentration in wetfall precipitation at New Hampshire's Hubbard Brook Experimental Forest, as a function of SO₂ emissions in the estimated 24-hr source area. This shows the decline in both parameters as a result of the implementation of the Clean Air Act. (PRI shows the levels of the pre-industrial revolution.) *Source: From Likens et al. 2005. Used with permission of RSC Publishing, copyright Royal Society of Chemistry.*

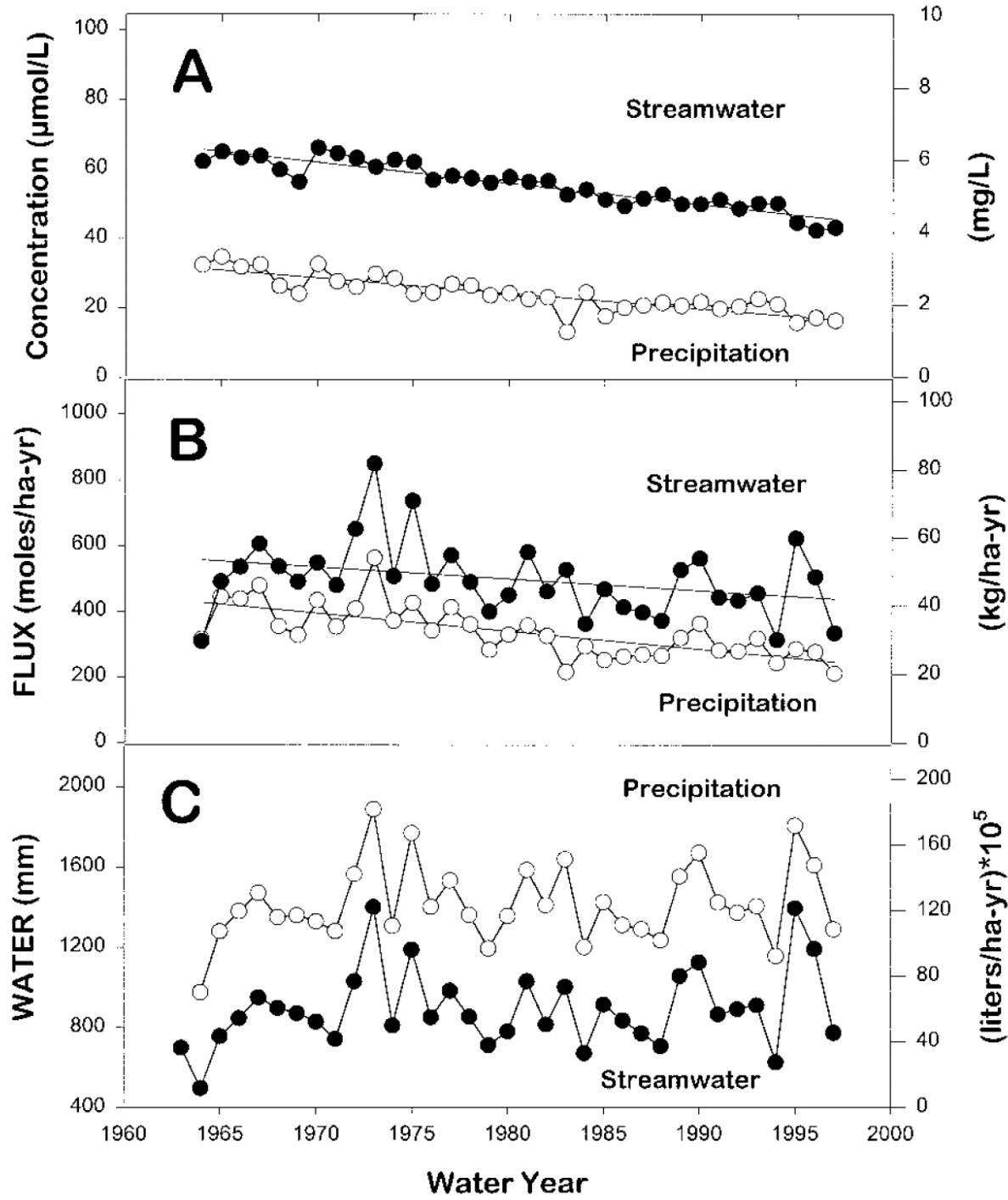
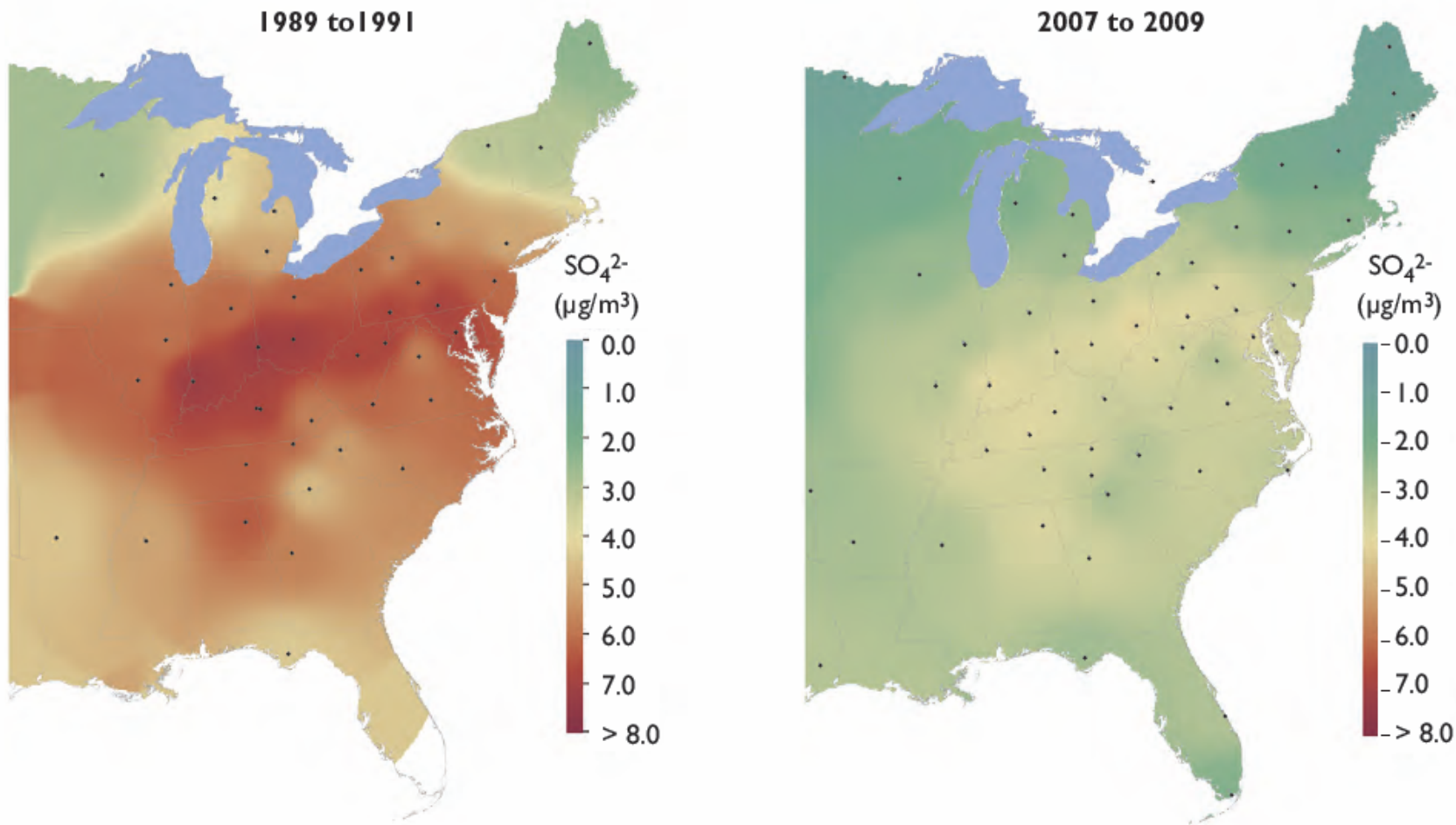


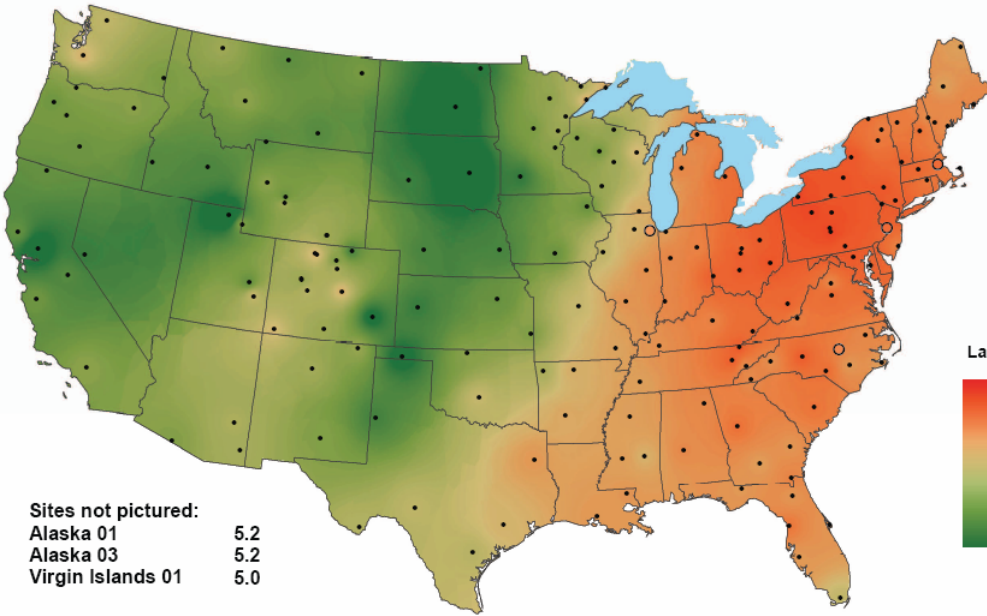
Figure 3. A. Annual, volume-weighted concentrations of SO_4^{2-} in bulk deposition and streamwater for W6 of the HBEF during 1964–1997. The probability for a larger F-ratio for both regression lines is $p < 0.001$; the r^2 for bulk precipitation is 0.72, and for streamwater is 0.87. B. Annual inputs of SO_4^{2-} in bulk deposition and outputs in stream water for W6 during 1964–1997. The probability of a larger F-ratio for the regression line for stream water is $p = 0.067$, $r^2 = 0.10$; and for bulk deposition is $p < 0.001$, $r^2 = 0.48$. C. Annual amount of precipitation and streamflow for W6 of HBEF during 1964–1998. (From: G.E. Likens et al. 2002. Biogeochemistry **60**: 235–316)



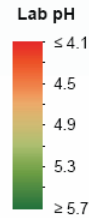
Note: For maps depicting CASTNET data for the conterminous United States, visit <http://www.epa.gov/castnet>. Dots on all maps represent monitoring sites. Lack of shading for southern Florida on the map on the left indicates lack of monitoring coverage in the 1989 to 1991 time period.

Figure 2-7. Annual mean ambient sulfate concentrations in the eastern United States for the 1989–1991 and 2007–2009 observation periods (U.S. EPA. 2010c).

Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2000



From: NADP--The National Atmospheric Deposition Program
<http://nadp.sws.uiuc.edu/>



Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2010

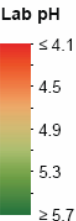
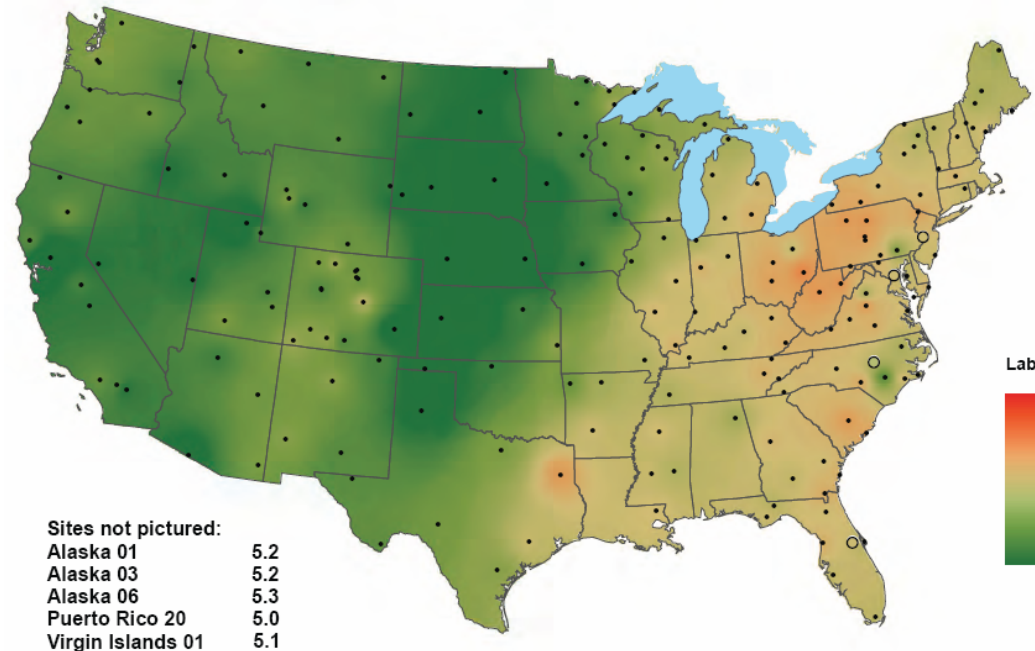


TABLE 13.2 Sources of Acidity in Acid Rainfall Collected in Ithaca, New York, on July 11, 1975 (ambient pH 3.84)

Component	Concentration in precipitation (mg/liter)	Contribution to	
		Free acidity at pH 3.84 ($\mu\text{eq/liter}$)	Total acidity in a titration to pH 9.0 ($\mu\text{eq/liter}$)
H ₂ CO ₃	0.62	0	20
Clay	5	0	5
NH ₄ ⁺	0.53	0	29
Dissolved Al	0.050	0	5
Dissolved Fe	0.040	0	2
Dissolved Mn	0.005	0	0.1
Total organic acids	0.43	2	5.7
HNO ₃	2.80	40	40
H ₂ SO ₄	5.60	102	103
Total		144	210

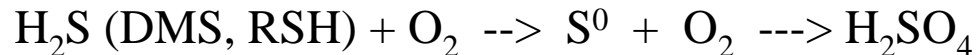
Source: From: Galloway et al. (1976). Copyright 1976 by the American Association for the Advancement of Science. Used with permission.

Sulfur Transformations

Desulfuration (analogous to ammonification):



Oxidative transformations:

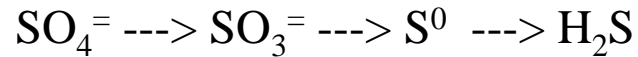


Oxidizing sulfur is the primary energy source for the microbial communities of the deep-sea hydrothermal vent ecosystem. Sulfur oxidation produce acid, so *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* are used in mining.

Fossil fuel sulfur: $\text{SO}_2 + \text{H}_2\text{O} \text{ ----> H}_2\text{SO}_3$ (sulfurous acid)
or $\text{SO}_3 + \text{H}_2\text{O} \text{ ----> H}_2\text{SO}_4$ (sulfuric acid)

Sulfur Transformations-continue

Reductive sulfur transformations:



Sulfate reduction occurs at wide range of pH values, pressure, temperature and salinity.

Sulfate reduction is inhibited by oxygen, nitrate, ferric ions. H₂S is very toxic to aerobes and plant roots. Assimilatory sulfate reduction happen in many organisms.

The changes of valence and the different forms of sulfur transformations are analogous to nitrogen transformation.

Naturally occurring sulfur compounds and their oxidation state

Oxidation state	Gas	Aerosol	Aqueous	Soil	Mineral	Biological
-II	H ₂ S, RSH DMS		H ₂ S, HS ⁻ S ⁼ , RS ⁻	S ⁼ , HS ⁻	S ⁼	Methionine Cysteine
-I					FeS ₂	
0				S ₈	S ⁰	
+II			S ₂ O ₃ ⁼			
+IV	SO ₂	HSO ₃ ⁻	HSO ₃ ⁻ , SO ₃ ⁼	SO ₃ ⁼		
+VI	SO ₃	HSO ₄ ⁻ , SO ₄ ⁼	HSO ₄ ⁻ , SO ₄ ⁼	CaSO ₄	CaSO ₄ , CaSO ₄	

Natural emission of volatile sulfur compounds to the atmosphere
(10^{12} g S per year)

Source	SO₂	H₂S	DMS	CS₂	Total
Oceanic	0-15	38-40	0.3	0.4	38-57
Salt marsh		0.8	0.6	0.1	1.7-1.8
Inland swamps		11.7	0.8	2.8	17
Soil and plants		3-41	0.3	0.6-1.5	5-48
Burning of biomass	7	0-1			7.1-9.1
Volcanoes	8	1			9
Total	15	16-71	40-45	3.8-4.7	79-143

The CLAW (Charlson, Lovelock, Andreae, & Warren. 1987)

Negative feedback Hypothesis:

warmer seawater --> more DMS --> more aerosols --> more albedo --> cooling

However, no clear evidence so far indicates that this negative feedback has played a significant role in the global temperature regulation.

Table 1. Surface Seawater Concentration and Ocean-to-Atmosphere Transference of DMS^a

Latitude Band	Mean Concentration, nM	Mean Annual Flux, $\mu\text{mol m}^{-2} \text{d}^{-1}$		Annual Emission, Tg S yr ⁻¹		
		N00	W99	LM86	N00	W99
80°–90°N	0.9	0.9	4.1	0.00	0.00	0.01
70°–80°N	4.5	8.9	13.6	0.13	0.18	0.29
60°–70°N	4.0	5.8	8.3	0.10	0.13	0.21
50°–60°N	3.8	5.9	10.7	0.34	0.41	0.75
40°–50°N	2.7	5.8	9.7	0.57	0.75	1.18
30°–40°N	2.4	6.6	9.6	0.94	1.26	1.69
20°–30°N	2.4	6.5	8.9	1.16	1.56	1.97
10°–20°N	2.7	9.3	14.7	1.96	2.68	3.94
0°–10°N	2.9	10.6	14.8	2.45	3.38	4.33
0°–10°S	2.7	8.2	11.3	2.05	2.81	3.59
10°–20°S	2.1	7.8	11.3	1.85	2.51	3.42
20°–30°S	2.1	6.7	9.1	1.63	2.22	2.86
30°–40°S	1.9	5.9	8.5	1.51	2.05	2.82
40°–50°S	1.4	5.6	9.4	1.36	1.88	2.86
50°–60°S	1.0	3.8	6.7	0.72	1.04	1.58
60°–70°S	1.4	3.2	5.0	0.26	0.38	0.48
70°–80°S	1.5	1.9	2.3	0.01	0.02	0.02
80°–90°S	0.0	0.0	0.0	0.00	0.00	0.00
Global mean flux	5.7	8.8				
Global emission				17.0	23.3	34.6

(From: R. Simó & J. Dachs, 2002. GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 16, NO. 4, 1078-1088) Surface seawater concentration and ocean-to-atmosphere transference of DMS within 10-latitude bands: annual mean of the concentration and flux, and annual integration of total emission. N00 and W99 refer, respectively, to the use of parameterizations of the air-sea exchange constant rate as given by Nightingale et al. [2000] and Wanninkhof and McGillis [1999]. The annual emission estimated with the classical Liss and Merlivat [1986] parameterization (LM86) is also shown for the sake of comparison with previous works.

(From: R. Simó & J. Dachs, 2002. GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 16, NO. 4, 1078-1088)

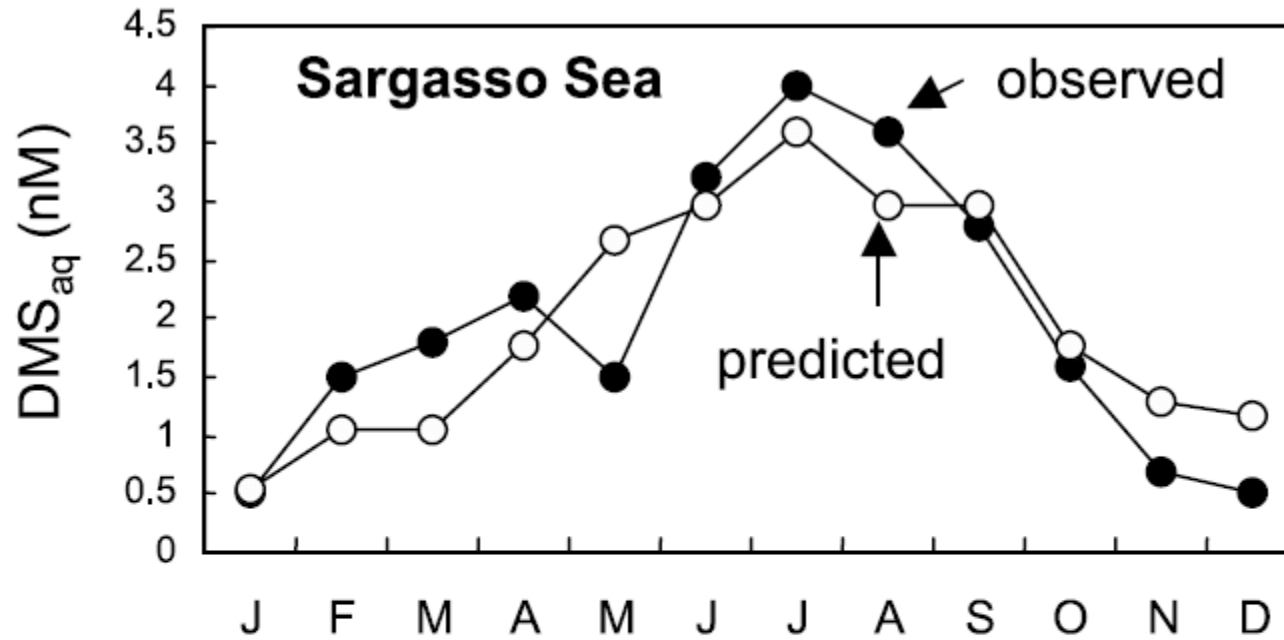


Figure 3. Prediction of local DMS seasonality. The surface DMS concentrations measured monthly in 1992 at the Bermuda time series station (BATS) [Siegel and Michaels, 1996; Dacey et al., 1998] are compared with the concentrations predicted by applying the algorithm to contemporaneous surface chlorophyll concentrations [Siegel and Michaels, 1996; Dacey et al., 1998] and MLDs [Doney, 1996].

(From: R. Simó & J. Dachs, 2002. GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 16, NO. 4, 1078-1088)

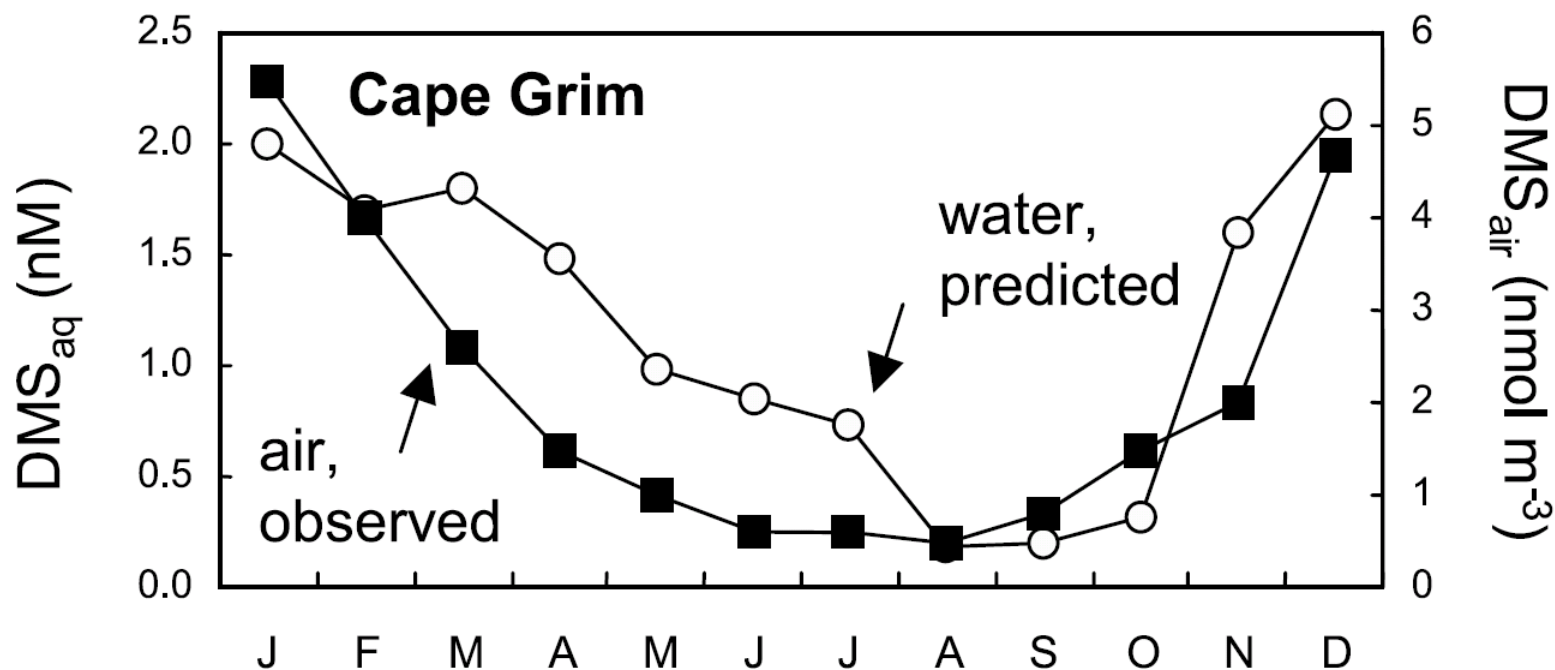


Figure 4. Seawater-predicted versus atmospheric-measured DMS concentrations. The atmospheric DMS concentrations measured at Cape Grim (monthly averages between 1993 and 1996 [Ayers and Gillet, 2000]) are compared with the oceanic DMS concentrations estimated from chlorophyll and MLD climatologies for a square area between 38°–50°S and 120°–143°E, upwind of Tasmania.

TABLE 13.3 Global Budget for Carbonyl Sulfide in the Atmosphere

Sources	COS (10^{12} g S/yr)
Oceans	0.04 ^a
Anoxic soils	0.03
Biomass burning	0.04 ^b
Fossil fuels	0.06
Volcanoes	0.02
Oxidation of CS ₂	0.25 ^c
Oxidation of DMS	0.16
Total sources	0.60
Sinks	
Vegetation uptake	0.24
Soil uptake (oxic)	0.13
Oxidation by OH	0.09
Stratospheric photolysis	0.02
Total sinks	0.48

^a Net.

^b Compare, 0.14 Tg S/yr; Andreae and Merlet (2001).

^c 44% from anthropogenic sources.

Sources: From Kettle et al. (2002), except volcanic flux (Chin and Davis 1993).

Oxygen Isotope Constraints on the Sulfur Cycle over the Past 10 Million Years

There are nine known isotopes of sulfur of which four are stable:

Isotope	Average crustal abundance (%)
^{32}S	95.0
^{33}S	0.76
^{34}S	4.22
^{36}S	0.014

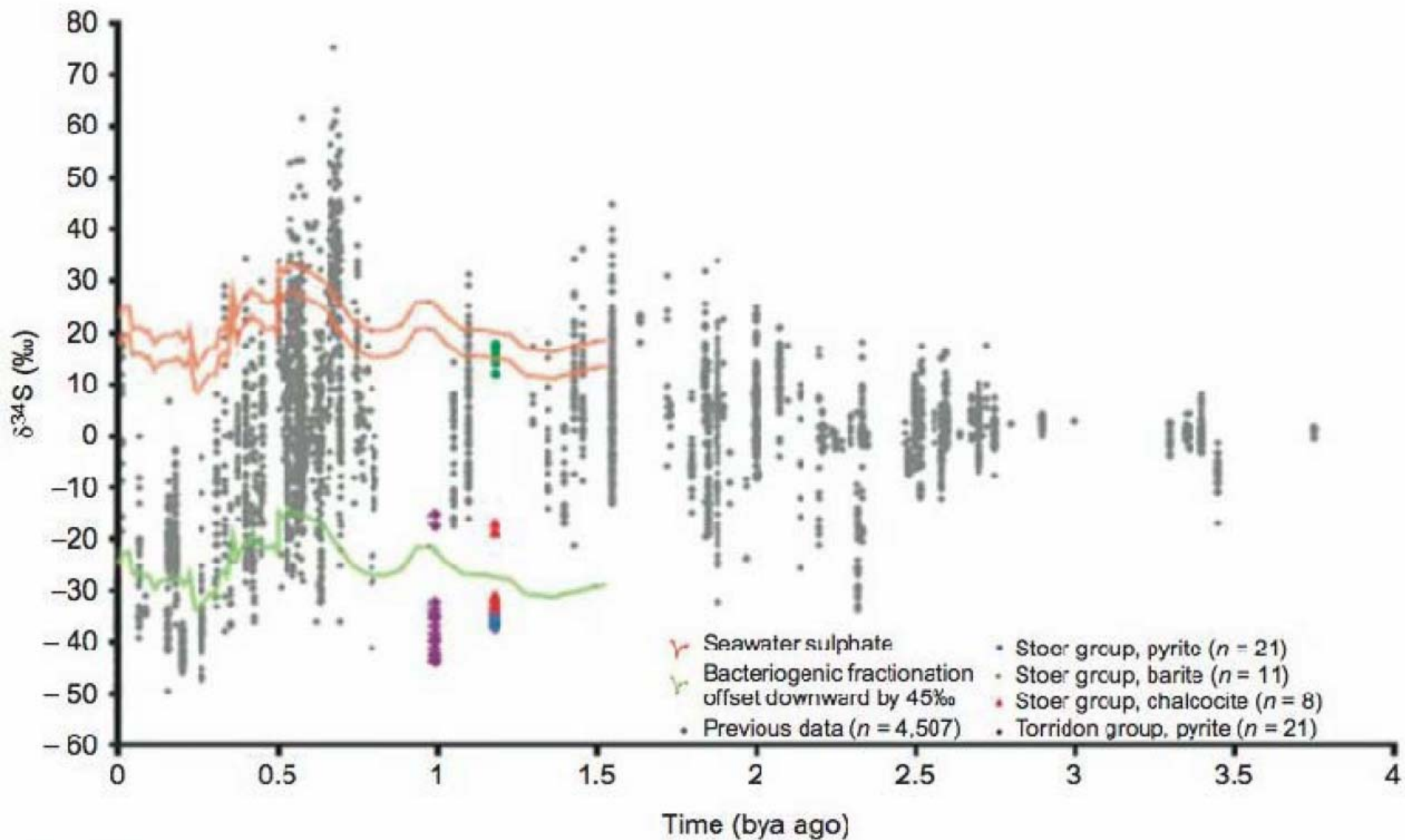


FIGURE 13.3 $\delta^{34}\text{S}$ in sedimentary pyrites through geologic time. *Source: Modified from Parnell et al. (2010).*

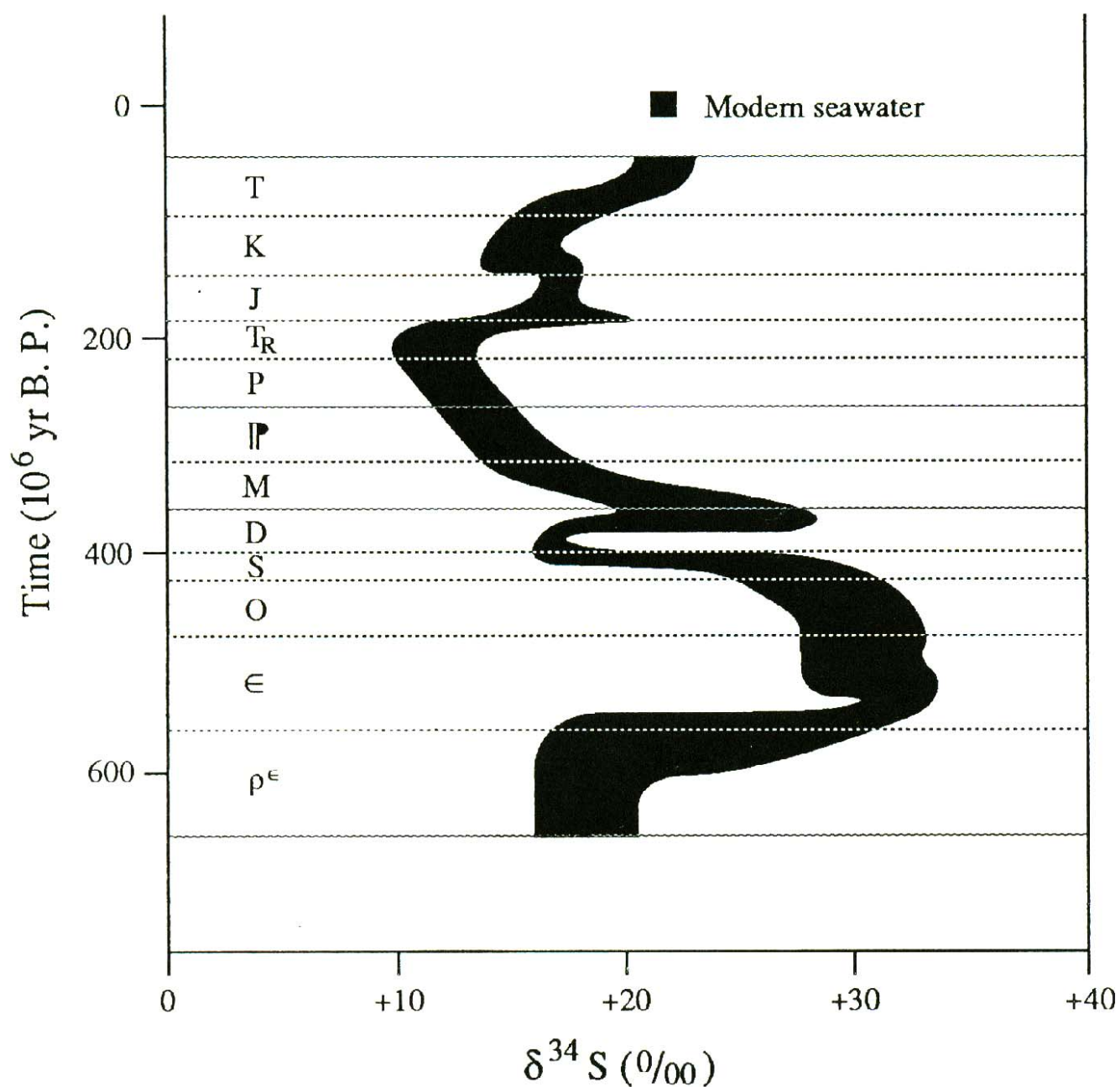


FIGURE 13.5 Variations in the isotopic composition of seawater SO_4 through geologic time. *Source: From Kaplan (1975). Used with permission from the Royal Society of London.*

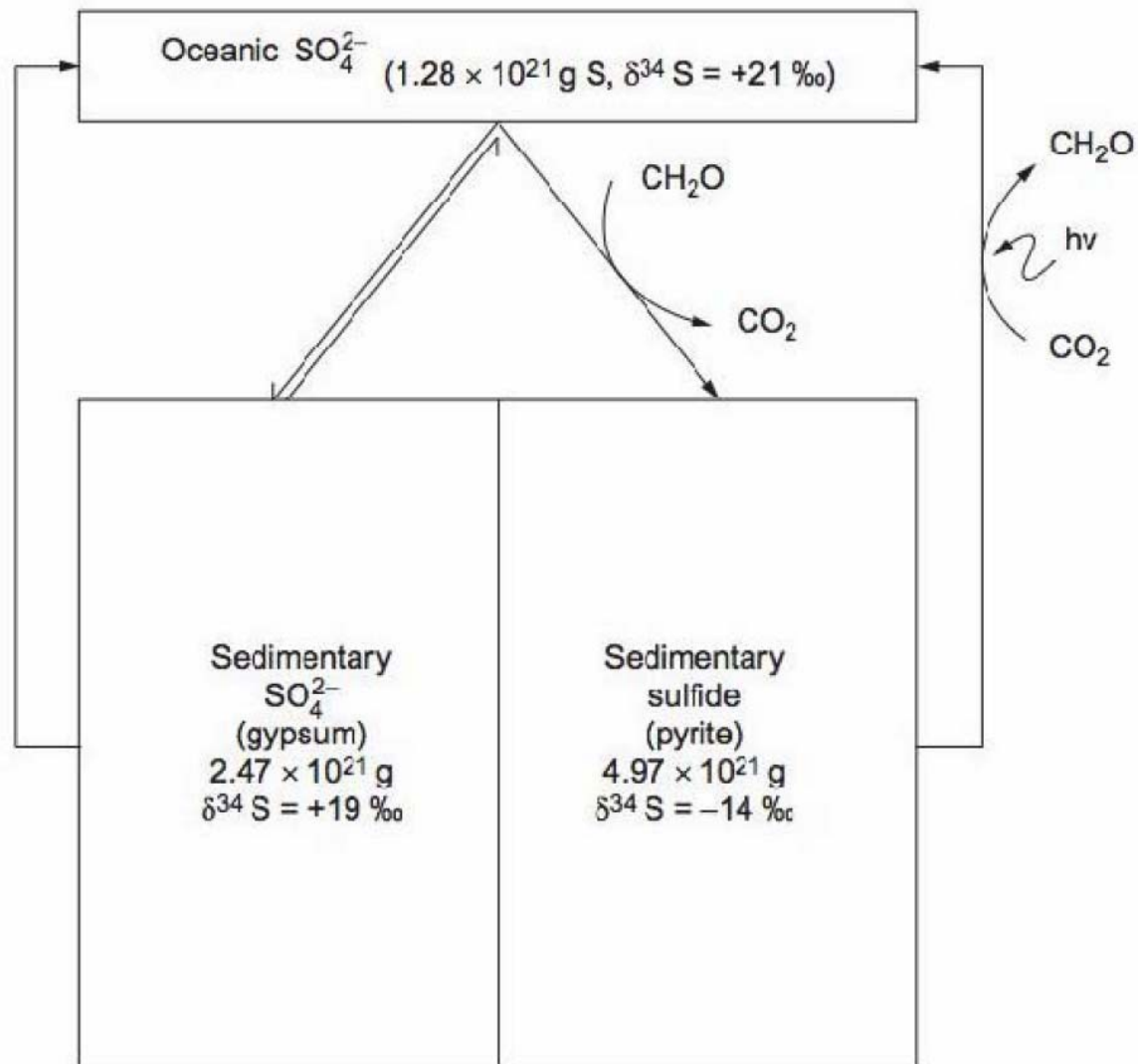


FIGURE 13.4 A model for the global sulfur cycle, showing the linkage and partitioning of S between oxidized and reduced pools near the surface of the Earth. Transfers of S from seawater to pyrite involve a major fractionation between ^{34}S and ^{32}S isotopes, whereas exchange between seawater SO_4 and sedimentary SO_4 (largely gypsum) involves only minor fractionation. The sum of all pools, nearly 10^{22} g S, represents the total outgassing of S from the mantle (compare to Table 2.3). About 15% now resides in the ocean. Estimates of the pool of S in sedimentary sulfides show a wide range of values; the value here, from Holser et al. (1989), is close to that estimated from the pool of sedimentary organic carbon (1.56×10^{22} g; Des Marais et al. 1992) divided by the mean C/S ratio in marine sediments (2.8; Raiswell and Berner 1986). Isotope ratios in seawater and gypsum are taken from Holser et al. (1989). The isotope ratio of S in sedimentary sulfides is derived by mass balance to yield $\delta^{34}\text{S}$ of +4.2 in the global inventory.

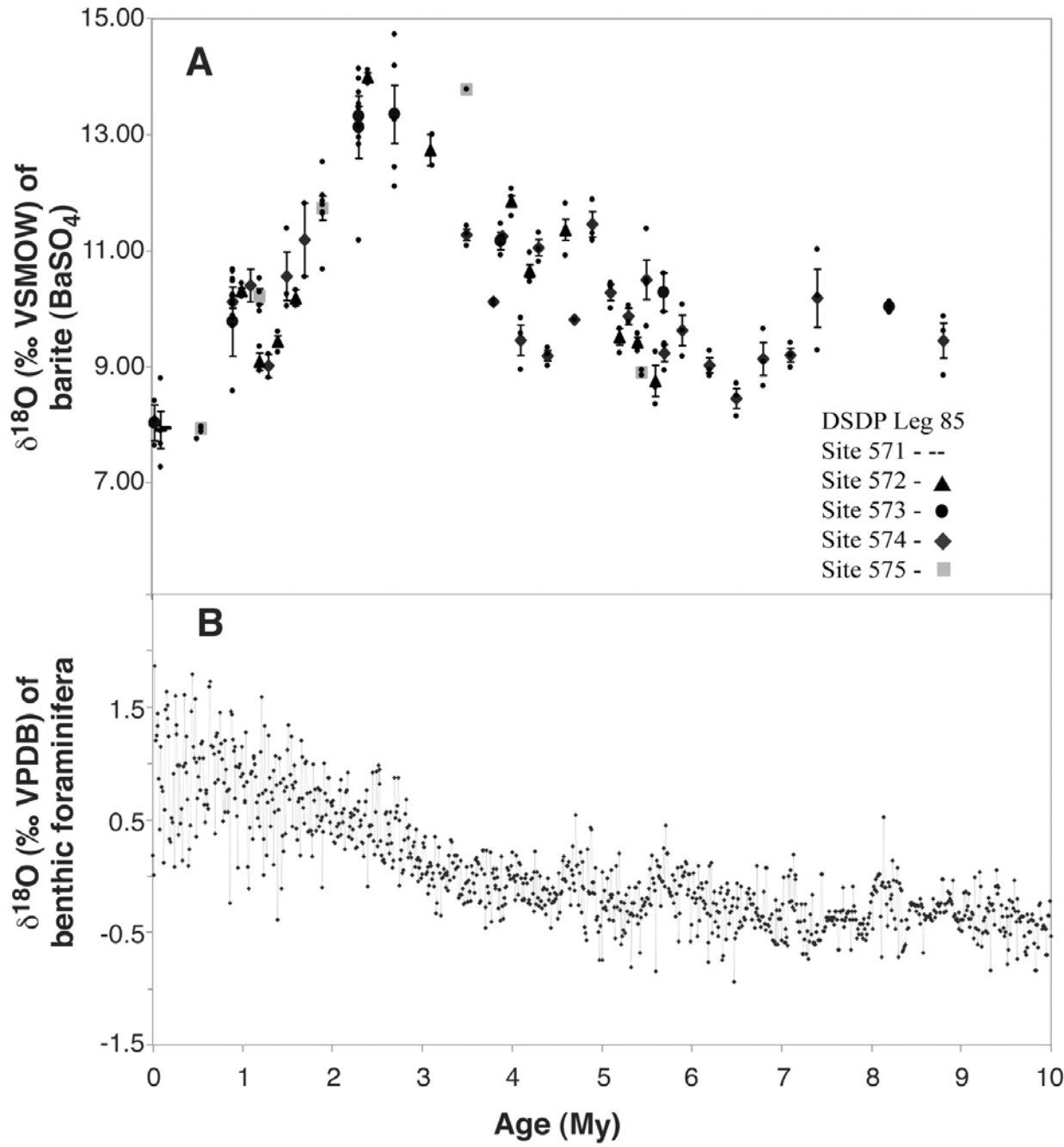


Fig. 1. (A) The $^{18}\text{O}_{\text{SO}_4}$ data for the past 10 My, measured in marine barite. Error bars are standard error, calculated from replicate measurements of each sample (small dots). (B) The ^{18}O benthic foraminifera from Zachos *et al.* (30). The increase in ^{18}O at 3 Ma coincides with the beginning of the decrease in the $^{18}\text{O}_{\text{SO}_4}$. VPDB, Vienna Pee Dee Belemnite.

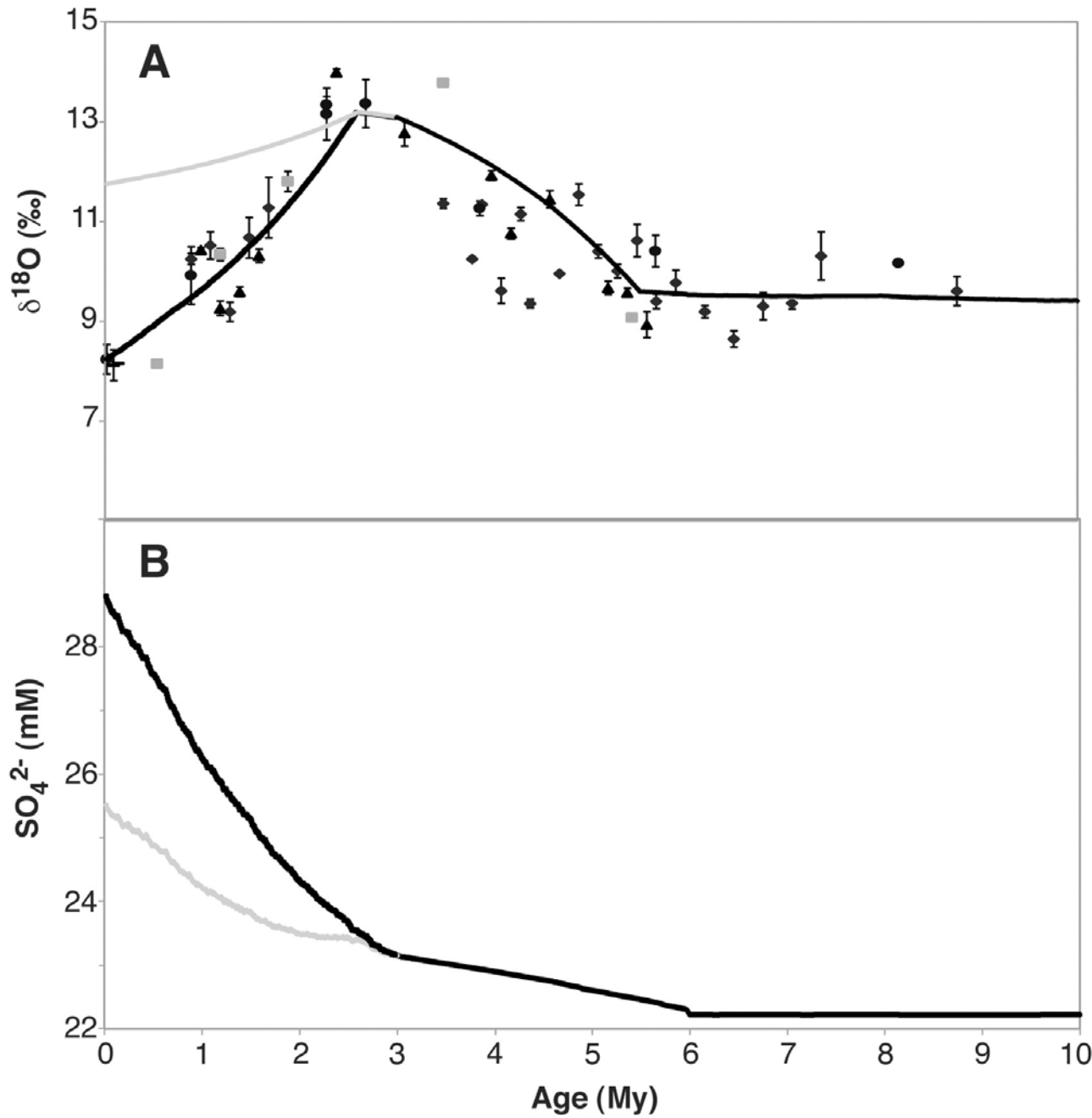
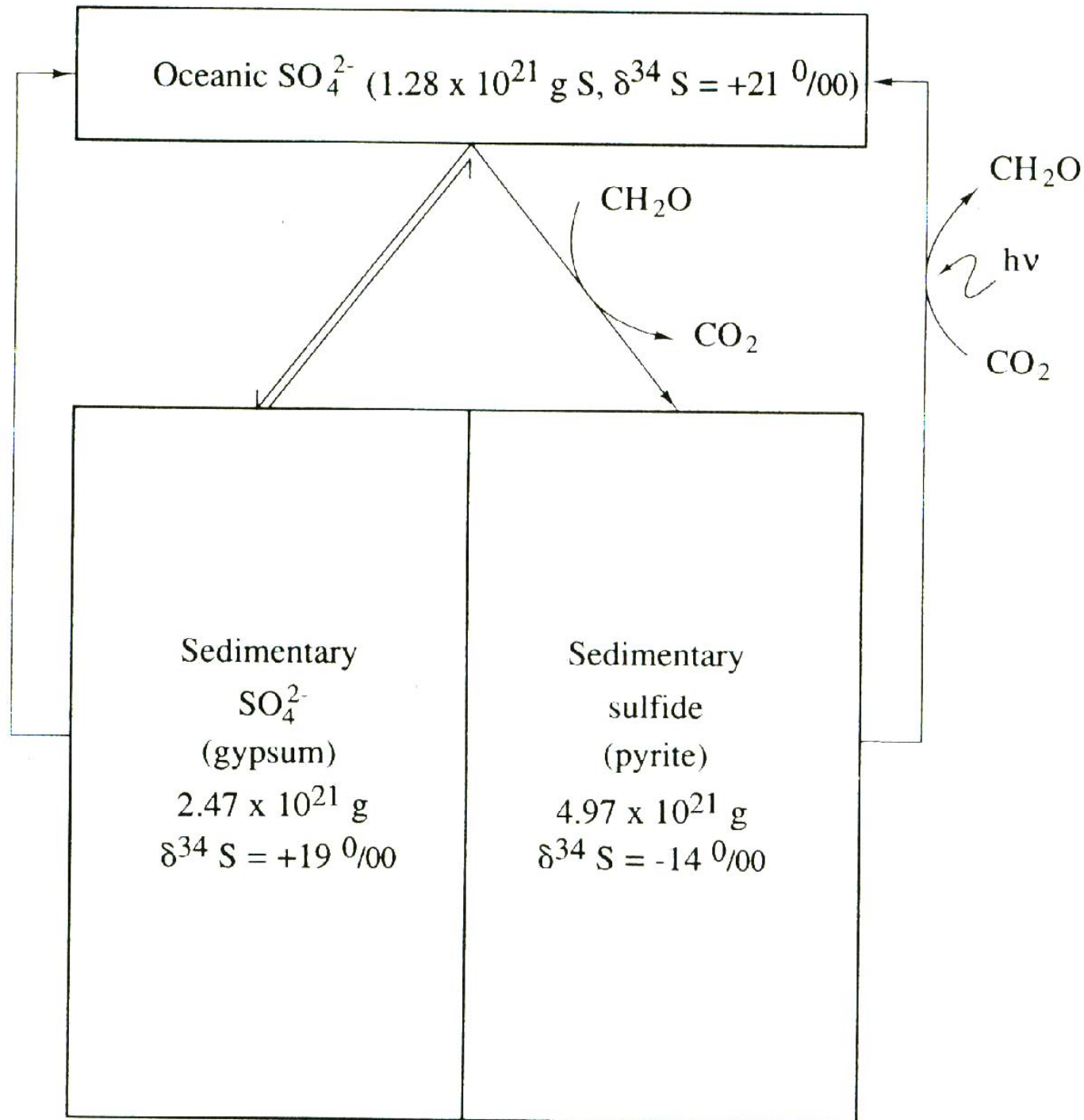


Fig. 2. (A) Model results for the $^{18}\text{O}_{\text{SO}_4}$ over the past 10 My compared with observed $^{18}\text{O}_{\text{SO}_4}$ data. The gray curve represents the modeled $^{18}\text{O}_{\text{SO}_4}$ if the decrease in $^{18}\text{O}_{\text{SO}_4}$ is due only to increased pyrite weathering on exposed continental shelves during glacial cycles. The black curve represents the modeled $^{18}\text{O}_{\text{SO}_4}$ when changes in sulfur cycling are induced between the Miocene and Plio-Pleistocene in addition to the pyrite weathering, including an increased percentage of sulfide reoxidized and decreased reoxidated fractionation. Data symbols are the same as in Fig. 1. (B) Model results for sulfate concentration for the two model scenarios. The small increase in sulfate concentration between 6 and 3 Ma is due to a small increase in reoxidation percentage.



Summary

1. Sulfur is an essential component of proteins, therefore essential for life.
2. The global sulfur cycle is discussed, and the atmospheric sulfur budget is highlighted.
3. The time-course of sulfur budget at the watershed (at Hubbard Brook) is shown and discussed.
4. Sulfur in the air is linked to acid deposition.
5. Sulfur exists in nature in many chemical forms. Three main types of sulfur transformations are illustrated.
6. Marine sulfur emissions and the CLAW hypothesis are deliberated in light of global climate change.