

16:53:02

OCA PAD AMENDMENT - PROJECT HEADER INFORMATION

11/09/94

Active

Project #: G-35-663                      Cost share #:                      Rev #: 5  
Center # : 10/24-6-R7545-0A0      Center shr #:                      OCA file #:  
Contract#: NAGW-3117                      Mod #: SUPPLEMENT 2              Work type : RES  
Prime # :                                      Document : GRANT  
Contract entity: GTRC  
Subprojects ? : Y                              CFDA: 43.002  
Main project #:                                PE #: N/A

Project unit:                      E & A SCI                      Unit code: 02.010.140  
Project director(s):  
CANFIELD D E                      E & A SCI                      (404)894-3890

Sponsor/division names: NASA                      / HEADQUARTERS/WASHINGTON, DC  
Sponsor/division codes: 105                      / 002

Award period:      920601      to      950531      (performance)      950531      (reports)

Sponsor amount	New this change	Total to date
Contract value	0.00	247,996.00
Funded	80,882.00	237,807.00
Cost sharing amount		0.00

Does subcontracting plan apply ? : N

Title: ANCIENT SULFUR BIOGEOCHEMISTRY

PROJECT ADMINISTRATION DATA

OCA contact: Anita D. Rowland                      894-4820

Sponsor technical contact                      Sponsor issuing office

MICHAEL MEYER, TECHNICAL OFFICER                      CALVIN D. MITCHELL  
(202)358-0292                      (202)358-0412

NASA HEADQUARTERS                      NASA HEADQUARTERS  
CODE: SLC                      GRANTS OFFICE  
WASHINGTON, DC                      WASHINGTON, DC

Security class (U,C,S,TS) : U                      ONR resident rep. is ACO (Y/N): Y  
Defense priority rating : N/A                      N/A supplemental sheet  
Equipment title vests with: Sponsor                      GIT X  
NONE PROPOSED.

Administrative comments -

SUPP. 2 FUNDS YR 3; FULLY FUNDED. BUDGETED INTO SUB G-35-X17. ONR ASSIGNED  
PROPERTY AND CLOSEOUT ADMINISTRATION

16:53:04

SUBPROJECTS OF MAIN PROJECT G-35-663

11/09/94

Project number

Spon/Div

Project Director

Project Unit

Total Contract

Total Funded

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G-35-X17

105/002

CANFIELD D E

E & A SCI

162,409.00

162,409.00

SR370

GEORGIA INSTITUTE OF TECHNOLOGY  
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 06/23/95

Project No. G-35-663\_\_\_\_\_ Center No. 10/24-6-R7545-0A0\_\_\_\_\_

Project Director CANFIELD D E\_\_\_\_\_ School/Lab E & A SCI\_\_\_\_\_

Sponsor NASA/HEADQUARTERS/WASHINGTON, DC\_\_\_\_\_

Contract/Grant No. NAGW-3117\_\_\_\_\_ Contract Entity GTRC

Prime Contract No. \_\_\_\_\_

Title ANCIENT SULFUR BIOGEOCHEMISTRY\_\_\_\_\_

Effective Completion Date 950531 (Performance) 950531 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	Y	_____
Final Report of Inventions and/or Subcontracts	Y	_____
Government Property Inventory & Related Certificate	N	_____
Classified Material Certificate	N	_____
Release and Assignment	N	_____
Other _____	N	_____

Comments \_\_\_\_\_

Subproject Under Main Project No. \_\_\_\_\_

Continues Project No. \_\_\_\_\_

Distribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Management	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other _____	N
_____	N

NOTE: Final Patent Questionnaire sent to PDPI.

GEORGIA INSTITUTE OF TECHNOLOGY  
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT (SUBPROJECTS)

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Closeout Notice Date 06/23/95

Project No. G-35-663

Center No. 10/24-6-R7545-0A0\_

Project Director CANFIELD D E \_\_\_\_\_

School/Lab E & A SCI \_\_\_\_\_

Sponsor NASA/HEADQUARTERS/WASHINGTON, DC \_\_\_\_\_

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Project # G-35-X17	PD CANFIELD D E	Unit 02.010.140	T
GRANT # NAGW-3117	MOD#	SUPPLEMENT 2	E & A SCI *
Ctr # 10/24-6-R7545-0A1	Main proj # G-35-663	OCA CO	ADR
Sponsor-NASA	/HEADQUARTERS/WASHING	105/002	
ANCIENT SULFUR BIOGE			
Start 920601	End 950531	Funded	162,409.00
		Contract	162,409.00

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LEGEND

1. \* indicates the project is a subproject.
  2. I indicates the project is active and being updated.
  3. A indicates the project is currently active.
  4. T indicates the project has been terminated.
  5. R indicates a terminated project that is being modified.
-

## Annual Progress Report for NASA Grant NAGW-3117

Title: Ancient Sulfur Biogeochemistry

Grantee:

Donald E. Canfield

School of Earth and Atmospheric Sciences

Georgia Institute of Technology

Atlanta, Ga 30332-0340

PH: (404) 894-3890

FAX: (404) 853-0232

Date: April 12, 1993

### Progress Report:

This report will be divided into 4 categories to document progress that has been made in 1) modern sediment studies, 2) stable isotope studies, 3) ancient sediment studies, and 4) a brief description of future plans.

#### 1) Modern sediment studies

My emphasis on modern sediment studies has been to understand the circumstances leading to organic carbon preservation, and the importance of Fe and Mn oxide reduction in sedimentary organic carbon oxidation. Since the preservation of organic carbon in sediments allows for the input of O<sub>2</sub> to the atmosphere, to understand the evolution of atmospheric O<sub>2</sub>, it is paramount to understand under what circumstances organic carbon is preserved. I have compiled a data set quantifying organic carbon preservation in a variety of different sedimentary environments (Fig. 1). Part of my research has been directed at modeling this data to understand how various factors including the availability of oxidants, sedimentation rate, and the presence of bioturbation, controls preservation. This model contains new elements with respect to how organic carbon oxidation is controlled, and was presented at the annual GSA meeting

last fall. It will soon be submitted to Marine Chemistry for inclusion in a special volume on organic carbon preservation.

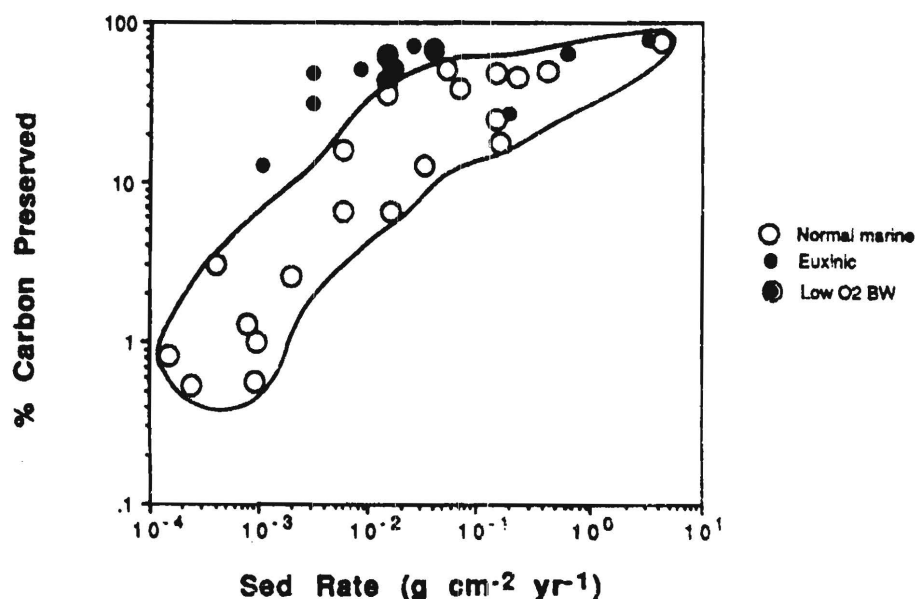


Fig. 1 % organic carbon preservation as a function of sediment deposition rate. Included are normal marine sediments, euxinic sediments, and low O<sub>2</sub> sediments from the California borderland basins.

In an early Proterozoic ocean, before sulfate reduction was a major process (we assume), organic matter oxidation by metal oxide reduction may have been quite significant, mainly because these oxides should have been abundant at this time (as evidence by massive Banded Iron Formation deposition). Adding weight to this possibility is our discovery that metal oxide reduction is very important in modern sediments (Fig. 2), even with competition by sulfate reducing organisms. A mathematical model is being developed to explore how much carbon may be oxidized by metal oxide reduction in Proterozoic-like conditions; namely, in the absence of oxic respiration, sulfate reduction, and bioturbation. This work has resulted in two papers which are now in press.

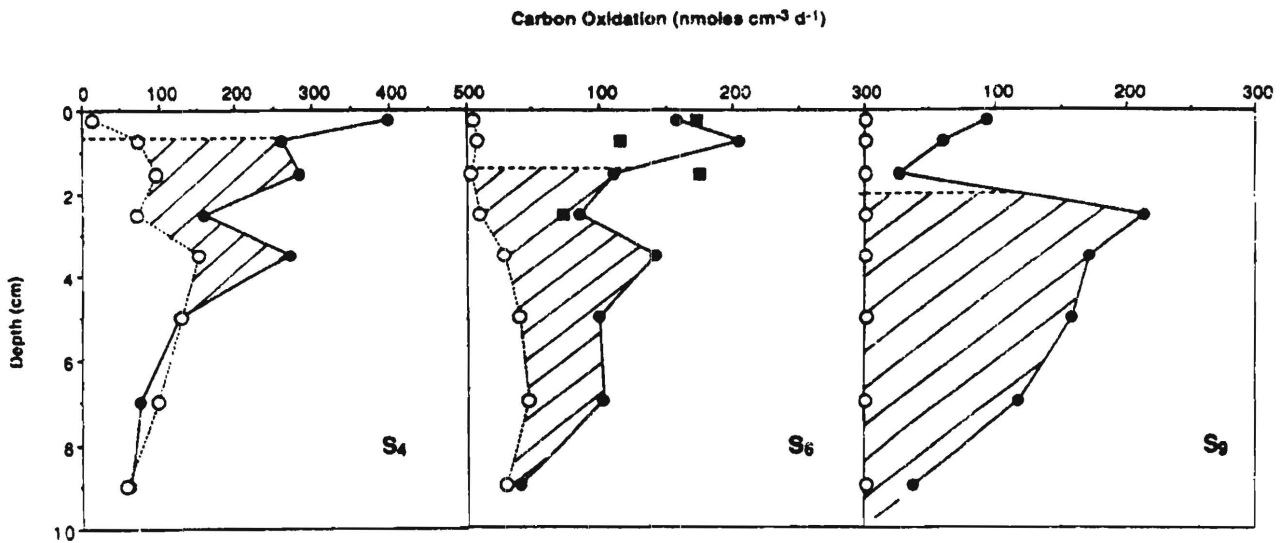


Fig. 2. Rates of carbon oxidation by various pathways in 3 sediments from coastal Denmark. The area above the dashed line represents the sum of carbon oxidation by O<sub>2</sub> respiration and denitrification. Hatched area represents carbon oxidation by metal oxide reduction (Fe reduction and Mn reduction).

## 2) Stable isotope studies

I have just completed my sulfur extraction line and anticipate that I will obtain isotopic values within the next month. This will not be too soon as there are several projects which have been completed except for isotopic analysis. One project is a study of sulfate reduction and sulfur isotopic fractionation in stromatolites from Walker Lake, Nevada. I have determined that sulfate reduction is active within the stromatolite and is retained as pyrite. If the sulfur bound in pyrite is isotopically fractionated, then stromatolites may prove to be an important environment by which to trace the evolution of sulfate reduction. In another study I have collected both sulfate and sulfide from an newly discovered elemental sulfur disproportionating organism. If isotopic fractionation is observed during the disproportionation, this may go far in explaining the large sulfur

isotopic fractionation found in modern sediments. Samples have also been collected to explore isotopic fractionation in microbial mats.

### 3) Ancient Sediments

I have, with my student Richard Jakiel, traveled to the 2.5 bybp Mt McRae shale in Newman Western Australia. We were able to collect core material of the shale, which has very pyritiferous sections. Together with Doug Crowe at University of Georgia, we will explore fine-scale sulfur isotopic composition with a laser/mass spec. This will allow us to see if different generations of pyrite have obviously different isotopic compositions. We hope to distinguish possible sulfate reduction sulfur from other sources including assimilatory sulfur. This work is in progress and publishable results are anticipated within the next year.

### 4) Upcoming projects

In addition to work in progress as discussed above, in the next year we will make an additional trip to the McArther Basin in Northern Australia. The sediment was deposited here about 1.7 bybp and will allow to "step forward in time" in our look for the evolution of sulfate reduction, and the effects of this evolution on ocean chemistry. In another project I will explore the isotopic fractionation of sulfate in thermophilic sulfate reducing bacteria. This should prove informative as many believe the Archean and early Proterozoic oceans to have been much warmer than today.

## Bibliography

Canfield, D.E., and Des Marais, D.J. (in press) The cycling of carbon, sulfur and free oxygen in a microbial mat. **Geochimica et Cosmochimica Acta**.

Canfield, D. E., Thamdrup, B. and Hansen, J. W. (in press) The anaerobic degradation of organic matter in Danish coastal sediments: Fe reduction, Mn reduction and sulfate reduction. **Geochimica et Cosmochimica Acta**.

Van Cappellen, P., and Canfield, D.E. (in press) Comment on "Lack of evidence for enhanced preservation of sedimentary organic matter in the oxygen minimum of the Gulf of California" **Geology**.

Canfield, D.E., Jørgensen, B.B., Fossing, H., Glud, R., Gundersen, J., Ramsing, N.B., Thamdrup, B., Hansen, J.W., and Nielsen, L.P. and Hall, P.O.J. (in press) Pathways of organic carbon oxidation in three continental margin sediments. **Marine Geology**.

Raiswell, R., Canfield, D.E. and Berner, R.A. (in press) A comparison of iron extraction methods for the determination of degree of pyritization and the recognition of iron-limited pyrite formation. **Chemical Geology**.

### IN PREPARATION

Canfield, D.E., Raiswell, R. DOP as paleoenvironmental indicator: revisited

Canfield, D.E. Organic carbon preservation in marine sediments.

Budget for 5/1/93-4/30/94

<u>Budget Category</u>	<u>Request</u>
1. Salaries and Wages	
1.1 Dr. D. Canfield (P.I.) <sup>1</sup>	12,000
3 months @ \$4000/mo	
1.2 Graduate Student	13,000
50% GRA	
Total Salaries and wages	<u>24,500</u>
2. Fringe Benefits	<u>3,264</u>
27.2% of 1.1	
3. Travel	
3.1 Australia	5,000
3.2 Meetings	1,500
3.3 Acton Lake, Ohio	1,000
Total travel	<u>7,500</u>
4. Services and Supplies	
4.1 Machine and glass shop	4,000
4.2 Chemical supplies and glassware	7,000
4.3 SEM/TEM	3,500
4.4 Sulfur isotope analysis	5,000
4.5 Publication	1,000
Total services and supplies	<u>20,500</u>
5. Total Direct Costs	<u>55,764</u>
6. Indirect costs @ 44.9% of MTDC	<u>25,263</u>
7. Total costs requested from NASA	<u>81,527</u>

G-35-663  
2

Annual Progress Report for NASA Grant NAGW-3117

Title: Ancient Sulfur Biogeochemistry

Grantee:

Donald E. Canfield

School of Earth and Atmospheric Sciences

Georgia Institute of Technology

Atlanta, Ga 30332-0340

PH: (404) 894-3890

FAX: (404) 853-0232

Date: May 10, 1994

Progress Report:

This report will be divided into 4 categories to document progress that has been made in 1) modern sediment studies, 2) stable isotope studies, 3) ancient sediment studies, and 4) a brief description of future plans.

1) Modern sediment studies

My emphasis on modern sediment studies has been to understand the circumstances leading to organic carbon preservation, and the importance of Fe and Mn oxide reduction in sedimentary organic carbon oxidation. Since the preservation of organic carbon in sediments allows for the input of  $O_2$  to the atmosphere, to understand the evolution of atmospheric  $O_2$ , it is paramount to understand under what circumstances organic carbon is preserved. This subject has also been the topic of considerable debate. I have recently completed a thorough literature review and modelling study which quantifies the preservation of carbon under various circumstances of sediment deposition (Canfield, Marine Geology, in press). Of special interest is the observation that bottom water anoxia does not in all cases lead to the enhanced preservation of carbon, as has often been thought. It is only in slowly depositing sediments that the less efficient anaerobic decomposition of carbon leads to

enhanced preservation. This situation is explored in a new model for carbon preservation. This model is further unique in that cometabolism of "refractory" organics by active microbial populations has been considered. Cometabolism may dramatically influence the preservation of the refractory organics, and has never before been considered as an influence on sedimentary carbon preservation.

In an early Proterozoic ocean, before sulfate reduction was a major process (we assume), organic matter oxidation by metal oxide reduction may have been quite significant, mainly because these oxides should have been abundant at this time (as evidence by massive Banded Iron Formation deposition). Adding weight to this possibility is our discovery that metal oxide reduction is very important in modern sediments, even with competition by sulfate reducing organisms. This work has resulted in two papers (Canfield et al. 1993 a,b). As a continuation of this project sediments from Costa Rica and the coast of Chile have been sampled this winter. These sediments are interesting because they span a wide range of bottom water  $O_2$  values; in some ways analogous to the changing ocean chemistry through the Proterozoic. Also, a mathematical model is being developed to explore the significance of various carbon oxidation pathways under Proterozoic-like conditions; namely, with progressively increasing amounts of sulfate reduction,  $O_2$  respiration and finally, bioturbation.

## 2) Stable isotope studies

Major progress has been made in this area over the past year. The isotope extraction line is up and running, with several significant results. First, in cooperation with Bo Thamdrup at the Max-Planck Institute for Marine Microbiology in Bremen, Germany, we have isolated and identified a marine sedimentary bacteria which disproportionates  $S^0$  to sulfate and sulfide. The organism also fractionates sulfur during the process such that sulfate is 20‰ heavier than the initial  $S^0$ , and sulfide is 10‰ lighter. This is extremely significant because 90% of all sulfide formed in sediments

by sulfate reduction is oxidized to  $S^0$ , and subsequently disproportionated. This process explains the large 60‰ fractionations between sulfate and sulfide commonly observed in marine sediments, as sulfate reducing bacteria alone can only account for about 20-25‰ of the fractionation. The important implications are: 1) we can now explain the isotopic composition of sulfides in modern sediments, and importantly: 2) disproportionation requires an oxidative sulfur cycle, which requires  $O_2$ . Hence, the oxygenation of surface ocean waters to near present-day levels should be obvious in the emergence of light, modern day-like sulfur isotopic values. The disproportionation work is currently being written for submission to Science magazine. Further laboratory work on isotopic discrimination during other sulfur oxidation pathways (thiosulfate and sulfite disproportionation, for example) is underway. A full accounting of the isotopic composition of sulfides in modern microbial mats and stromatolites, as homologs to ancient sedimentary systems, is also underway.

### 3) Ancient Sediments

We have collected samples from the 2.5 bybp Mt McRae shale in Newman, Western Australia. We were able to collect core material of the shale, which has very pyritiferous sections. Careful petrographic observation shows that much post depositional fluid flow has occurred in the core, as is true for many (if not most) early Proterozoic sediments. We are characterizing the nature of the fluid flow together with sulfur isotopic implication of the flow. However, we can be certain that the only source for sulfur within the shale was either sulfate reduction or the liberation during thermal maturation of organic sulfur compounds. We should, with the help of element analysis of the shale, be able to distinguish between these two possibilities, and to offer a reasonable estimate of sulfate reduction rates during the deposition of the shale. This will be an important constraint on the timing of the emergence of significant sulfate reduction during the Proterozoic. This work is in progress and publishable results are anticipated within the next year.

#### 4) Upcoming projects

In addition to the work discussed above, in the next year we will make an additional trip to the McArthur Basin in Northern Australia. The sediment was deposited about 1.7 bybp and will allow us to "step forward in time" in our look for the evolution of sulfate reduction, and the effects of this evolution on ocean chemistry. I have also been in contact with Andy Knoll at Harvard, who has made available to me his excellent collection of the Mesoproterozoic Amadeus basin, also in Australia. I am also beginning a systemic literature and sample collecting program to look for the beginnings of "modern" sedimentary sulfide values, and the emergence of the oxidative sulfur cycle as outlined above. In another project I will explore the isotopic fractionation of sulfate in thermophilic sulfate reducing bacteria. This should prove informative as many believe the Archean and early Proterozoic oceans to have been much warmer than today.

#### Bibliography

The following manuscripts have received either total or partial support from NASA's exobiology program:

- Canfield, D. E. (1993) Organic matter oxidation in marine sediments, in: R. Wollast, L. Chou, and F. Mackenzie "**Interactions of C,N,P and S Biogeochemical cycles**", NATO-ARW. pp. 333-363.
- Boudreau, B.P. and Canfield, D.E. (1993) A comparison of closed and open system models for porewater pH and calcite saturation state. **Geochimica et Cosmochimica Acta** 57, 317-334.
- Canfield, D.E., and Des Marais, D.J. (1993) The cycling of carbon, sulfur and free oxygen in a microbial mat. **Geochimica et Cosmochimica Acta**, v. 57, 3967-3883.
- Canfield, D. E., Thamdrup, B. and Hansen, J. W. (1993a) The anaerobic degradation of organic matter in Danish coastal sediments: Fe reduction,

Mn reduction and sulfate reduction. **Geochimica et Cosmochimica Acta**, v. 57. 3971-3984.

Canfield, D.E., Jørgensen, B.B., Fossing, H., Glud, R., Gundersen, J., Ramsing, N.B., Thamdrup, B., Hansen, J.W., and Nielsen, L.P. and Hall, P.O.J. (1993b) Pathways of organic carbon oxidation in three continental margin sediments. **Marine Geology**, v. 113, 27-40.

Van Cappellen, P., and Canfield, D.E. (1993) Comment on "Lack of evidence for enhanced preservation of sedimentary organic matter in the oxygen minimum of the Gulf of California" **Geology**. v. 21, 570-571.

#### **In Press:**

Raiswell, R., Canfield, D.E. and Berner, R.A. (1994) A comparison of iron extraction methods for the determination of degree of pyritization and the recognition of iron-limited pyrite formation. **Chemical Geology**.

Canfield, D.E. (1994) Factors influencing organic carbon preservation in marine sediments. **Chemical Geology**, v. 115

Canfield, D.E. and Des Marais (1994) Cycling of carbon, sulfur, oxygen and nutrients in a microbial mat. In: L.J. Stal and P. Caumette, eds., "Structure, Development and Environmental Significance of Microbial Mats" NATA-ARW, Springer-Verlag.

Des Marais, D.J. and Canfield, D.E. (1994) The carbon isotope biogeochemistry of microbial mats. In: L.J. Stal and P. Caumette, eds., "Structure, Development and Environmental Significance of Microbial Mats" NATA-ARW, Springer-Verlag.

Bebout, B.M., Paerl, H.W., Bauer, J.E., Canfield, D.E. and Des Marais, D.J. (1994) Nitrogen cycling in microbial communities: the quantitative importance of N-fixation and other sources of N for primary production. In: L.J. Stal and P. Caumette, eds., "Structure, Development and Environmental Significance of Microbial Mats" NATA-ARW, Springer-Verlag.



MAX PLANCK INSTITUTE FOR MARINE MICROBIOLOGY  
DEPARTMENT FOR BIOGEOCHEMISTRY

MPI for marine Microbiology, Fahrenheitstr. 1, W-28359 Bremen

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**Discipline Scientist**  
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**Dr. Donald Canfield**  
**Fahrenheitstr. 1**  
**W-28359 Bremen, Germany**  
**email: don@postgate.mpi.uni-**  
**bremen.de**  
**PH: 49(0421)2208-175**  
**FAX: 49(0421)2208-130**

April 17, 1995

Dear Mike,

Please find enclosed my final report for NASA Grant NAGW-3117 "Ancient Sulfur Biogeochemistry". Again, it has been a pleasure to work in the Exobiology program, and I hope we can maintain close contact during my stay in Germany.

Sincerely,

Don Canfield

Final Report for NASA Grant NAGW-3117

Title: Ancient Sulfur Biogeochemistry

Grantee:

Donald E. Canfield  
School of Earth and Atmospheric Sciences  
Georgia Institute of Technology  
Atlanta, Ga 30332-0340  
PH: (404) 894-3890  
FAX: (404) 853-0232

Now at:

Max Planck Institute for Marine Microbiology  
Fahrenheitstr. 1  
28359, Bremen, Germany  
PH: (49) 421 2208 175  
FAX: (49) 421 2208 130

Date: April 18, 1995

Rational:

The sediment geochemical record is rich with indicators of environmental change over the course of Earth history. The challenge in understanding this record is first to collect information that has been minimally affected by post depositional processes, and second, to learn to faithfully interpret the information. This research has focused primarily on the interpretation of the ancient sulfur isotopic record as it pertains to the evolution of the sulfur cycle on Earth. The modern oceans are rich in dissolved sulfate, and sulfate reduction is a major process of sedimentary carbon oxidation. The accumulation of sulfate in ancient oceans was a major milestone in the evolution of the Earth surface environment. This is because sulfate is the largest reservoir of oxidized species on the Earth surface, and the significant accumulation of sulfate in seawater signalled the beginnings of modern-style carbon cycling.

The sulfide produced during sulfate reduction is depleted in the isotope  $^{34}\text{S}$ , compared to the starting sulfate. This phenomena creates the basis for interpreting the ancient sulfur record.

However, the range in possible fractionations during sulfate reduction, and environmental controls on the fractionation, is poorly known. Also, the complete suite of factors other than sulfate reduction by which modern sediments acquire their sulfur isotopic signature is not known. This is demonstrated by noting that pure cultures of sulfate reducing bacteria cannot produce the isotopic composition of sulfide in modern marine sediments (Fig. 1). Our goals have been: 1) to understand the controls on the isotopic composition of sulfide in modern marine sediments, and to apply this understanding to ancient sediments; 2) to better define the history of sedimentary sulfur, allowing us to better understand how this history speaks to environmental change; 3) to explore case-studies of sediment diagenesis in ancient sediments to compliment the isotopic record. We have made significant progress in all of these areas.

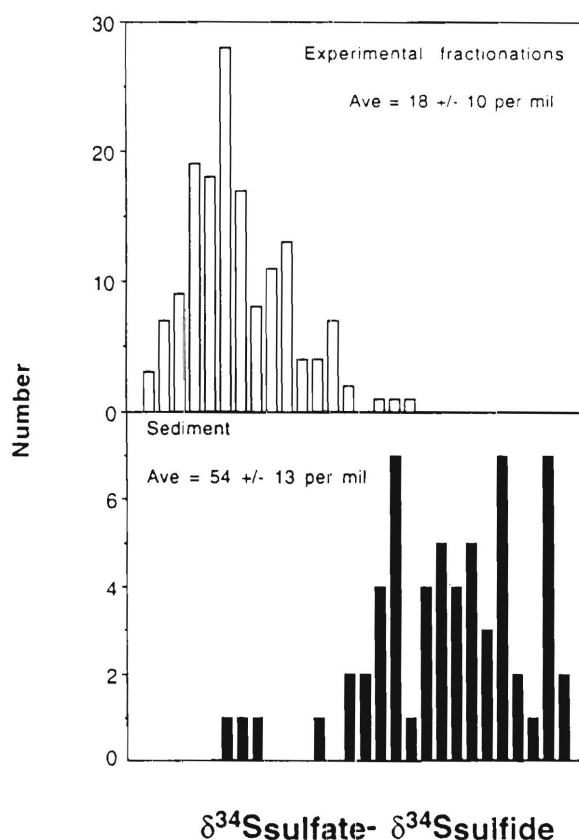


Fig 1. Isotopic fractionation during sulfate reduction for pure cultures of sulfate reducing bacteria (open bars), compared to isotopic composition of sulfide in marine sediments (Closed bars).

### Modern Sediment studies:

To explore the dilemma posed in Fig. 1, we have explored the isotopic consequences of the oxidative part of the sedimentary S-cycle. Our interest in this part of the S-cycle is spurred by the fact that most of the sulfide produced by sulfate reduction in sediments is reoxidized and lost from the sediment. We have first documented that elemental sulfur is an important intermediate in sulfide oxidation, and that the most likely fate of elemental sulfur is disproportionation (Eqn. 1; Canfield and Thamdrup, in press).



We have documented that elemental sulfur disproportionation is an autotrophic, bacterial process, conducted by a range of microorganisms. We are presently exploring the diversity of this bacterial population. Further, we have discovered that accompanying the disproportionation, there is an isotopic fractionation such that the sulfide is isotopically depleted in  $^{34}\text{S}$ , and the sulfate is isotopically enriched in  $^{34}\text{S}$  compared to the elemental sulfur (Fig. 2). Hence, with continued cycles of sulfide oxidation to elemental sulfur, and disproportionation, we can generate the isotopically light ( $^{34}\text{S}$ -depleted) sulfides in Fig. 1.

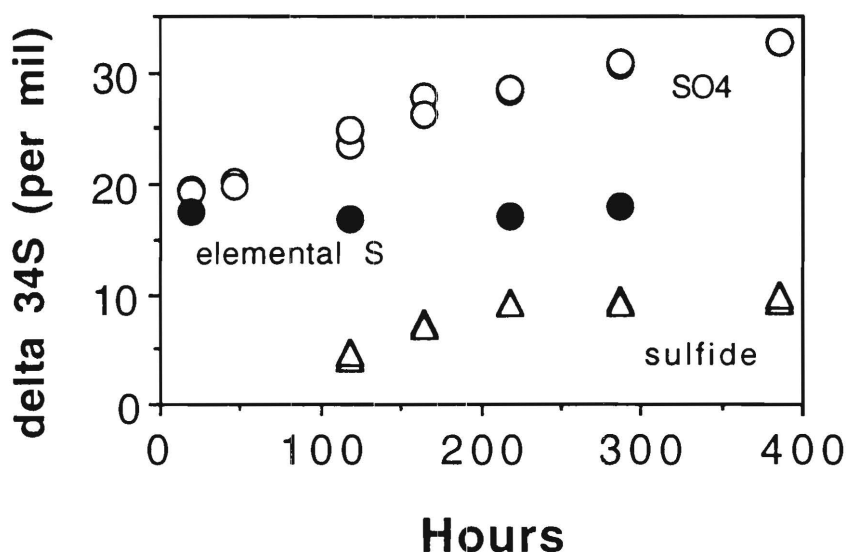


Fig. 2. The isotopic composition of sulfur species are shown in duplicate time course experiments on elemental sulfur-amended sediment undergoing active elemental sulfur disproportionation.

This is a major finding as it allows us for the first time to understand the isotopic composition of marine sedimentary sulfides, and provides an important basis for interpreting the sulfur isotope record through the Cambrian-Precambrian boundary (see below). These findings have been summarized in Canfield and Thamdrup (1994).

Previous workers have suggested that sulfate reduction has been an active process in marine sediments since 3.5 bybp. It is clear that little fractionation is observed in marine sedimentary sulfides from 3.5 bybp until about 2.2 bybp. However, these authors have argued sulfate reduction has taken place at very rapid rates in an ancient-warm ocean. The rationale is that at high rates of sulfate reduction, the demand for sulfate by an organism may be so high that no or little fractionation will occur, similar to the carbon fractionation during photosynthesis. We tested this model by exploring fractionation in microbial mats from Solar Lake, Sinai. Microbial mats support the highest rates of sulfate reduction on the modern Earth and provide an excellent environment to test the influence of rate on fractionation. Our results demonstrate that at different temperatures (to induce different rates, rate data not shown) and at different concentrations of sulfate (between seawater to 3 times seawater) relatively high fractionations of between 18 to 35 per mil were observed. (Fig. 3). Hence, rapid rates of sulfate reduction do support isotopic fractionation, and the ancient isotopic record between 2.2 and 3.5 bybp is consistent with limited rather than significant sulfate reduction in the ocean. Also note that sulfate reduction alone does not give enough fractionation to explain the isotopic composition of the sedimentary sulfides, consistent with discussion above. These results are presently being prepared for publication.

Additional studies on modern sediments have documented the significance of sulfate reduction on carbon oxidation in modern coastal sediments (Canfield et al., 1993a,b). Significantly, we have also for the first time documented the importance of Fe-oxides as an electron acceptor in carbon mineralization. The large importance of Fe-oxides in modern environments gives us an indication that Fe-reduction may have been a very significant process of carbon mineralization in ancient Fe-oxide-rich sediments deposited as Banded Iron Formations (BIF's). In a pair of papers (Van Cappellen and Canfield, 1993; Canfield, 1994) we have explored the relationship between the presence and absence of oxygen on the efficiency of

carbon preservation in sediments. Since the burial and preservation of carbon in sediments liberates oxygen to the atmosphere, an understanding of the factors influencing preservation is crucial to understanding the progressive oxidation of the Earth's surface environment. Also, we have explored the reaction kinetics of sulfide with Fe minerals, allowing us to use Fe mineralogy as an indicator of ancient depositional environments, and to explore if extensive periods of sulfidic waters persisted in the past (Canfield et al., 1992; Raiswell and Canfield, submitted). Finally, we have presented a model for the deposition of Fe in the modern euxinic Black Sea which shows that modern and ancient euxinic basins have a more similar Fe cycle than previously appreciated (Canfield et al, submitted).

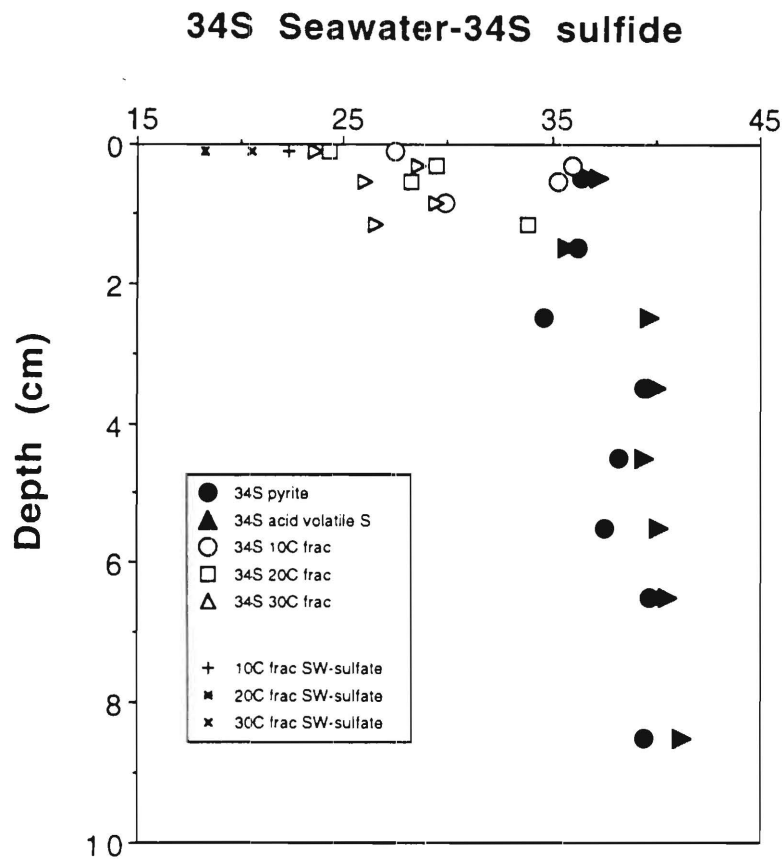


Fig. 3 The isotopic composition of reduced sulfur species in Solar Lake mats, compared to the fractionations measured during sulfate reduction by natural populations of sulfate reducing bacteria.

## Sulfur Isotopic Record:

We have conducted an extensive literature survey of sedimentary sulfur isotopic compositions from present through the Mesoproterozoic (1.6 bybp). In compiling the data, no sediment that has experienced any documented hydrothermal input has been used. Also, sediment with high degrees of metamorphism have also been excluded. The record (Fig. 4), shows the isotopic composition of sulfides, the isotopic composition of sulfate over time (open band), and the isotopic composition of sulfate displaced by 55 per mil. Key points include a consistent offset between seawater sulfate and most depleted sulfides from present to about 650 mybp. As discussed above (Fig. 2) an offset of this magnitude requires an initial fractionation by sulfate reduction (20-30 per mil), modified substantially by disproportionation during sulfide oxidation (variable from 0 to about 40 per mil). Before about 650 mybp, fractionations are reduced, and maximum displacements in seawater sulfate are 20 to 30 per mil, consistent with fractionation during sulfate reduction without modification by the oxidative S-cycle. We conclude that between about 750 to 650 mybp conditions became conducive to the operation of the oxidative S-cycle. The most likely way this could happen is if oxygen became more available. Thus, we believe that we see in the S-isotope record between, 750 and 650 my ago, the first direct indication of the rise in atmospheric O<sub>2</sub> that preceded the evolution of the Metazoans.

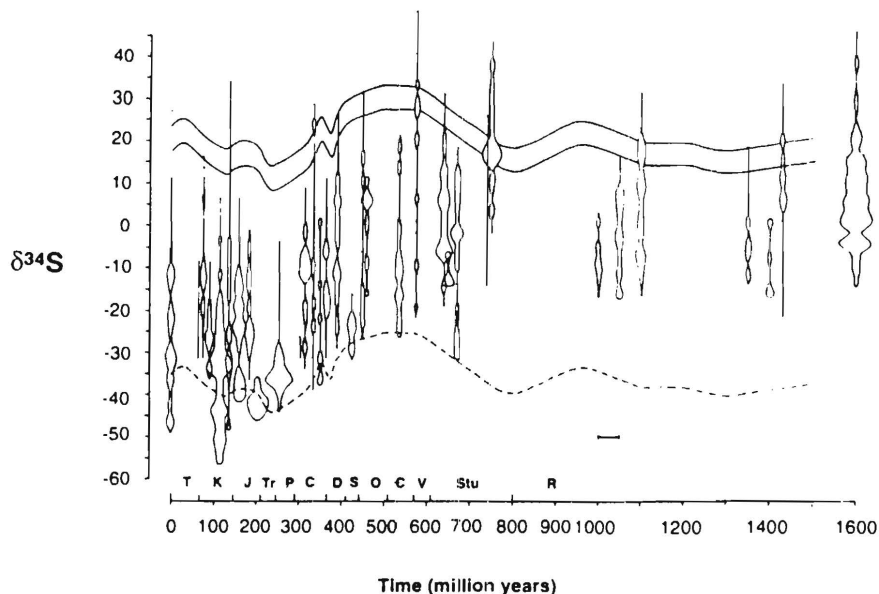


Fig. 4. Isotopic composition of sedimentary sulfide. See text for details.

We have further indications for the rise of atmospheric O<sub>2</sub> from the molecular phylogeny of sulfide oxidizing gradient bacteria that require O<sub>2</sub> for their metabolism. An internally calibrated molecular clock puts their evolution at about the same time. These results are currently being prepared for publication.

#### Site Studies:

We have travelled to the McRae shale in Western Australia. This shale was deposited about 2.5 bybp and we wish to explore the extent to which sulfate reduction dominated sediment diagenesis at this time. Our goal is to apply sediment analysis in addition to sulfur isotopic examination to evaluate the importance of sulfate reduction. Results are still preliminary, but sulfur isotopic compositions range from 0 to +15 per mil, indicative of, perhaps some sulfate reduction. Isotopic fractionations are, however, also consistent with modification by post-depositional S mobilization.

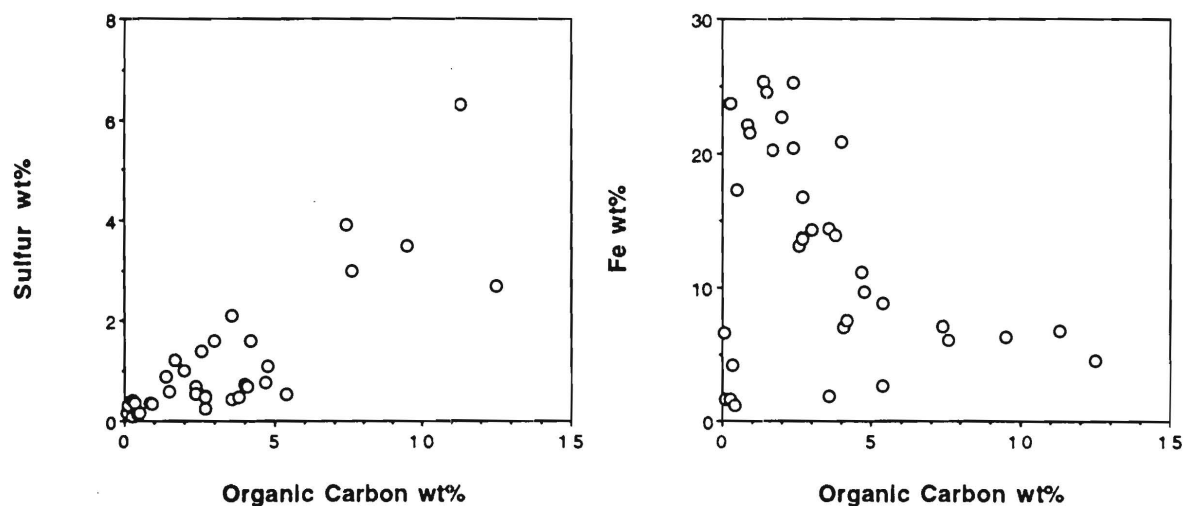


Fig. 5. Fe, sulfur, and organic carbon results from McRae shale sediments, Western Australia.

More informative is obtained from the sediment geochemical analysis. (Fig. 5). Here, we find that the concentration of organic carbon tracks that of sulfur. This means that sulfur is buried with carbon, as occurs in modern sediments supporting sulfate reduction. Hence, sulfate reduction is indicated. However, far more Fe oxides deposit in the sediment than are preserved as sulfide (Fig. 5; sulfur vs organic carbon would look like Fe vs organic carbon if all Fe was pyritized). In modern euxinic basins roughly 10 times more sulfide is produced than Fe deposits into the basin. Hence all Fe oxides are reacted with sulfide, and most of the sulfide is reoxidized back to sulfate at the chemocline. The predominance of Fe in McRae shale sediments, and during the time of BIF formation in general, requires that sulfate reduction must have been far less important than today. Otherwise all Fe oxides would have been reacted to form pyrite. Work on the McRae shale, and Fe mass balances for Precambrian oceans is still in progress.

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