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Die Berichte können bei:

Frau Gisela Boelen
Sonderforschungsbereich 261
Universität Bremen
Postfach 330 440
D 28334 BREMEN
Telefon: (49) 421 218-4124
Fax: (49) 421 218-3116
e-mail: eggerich@uni-bremen.de

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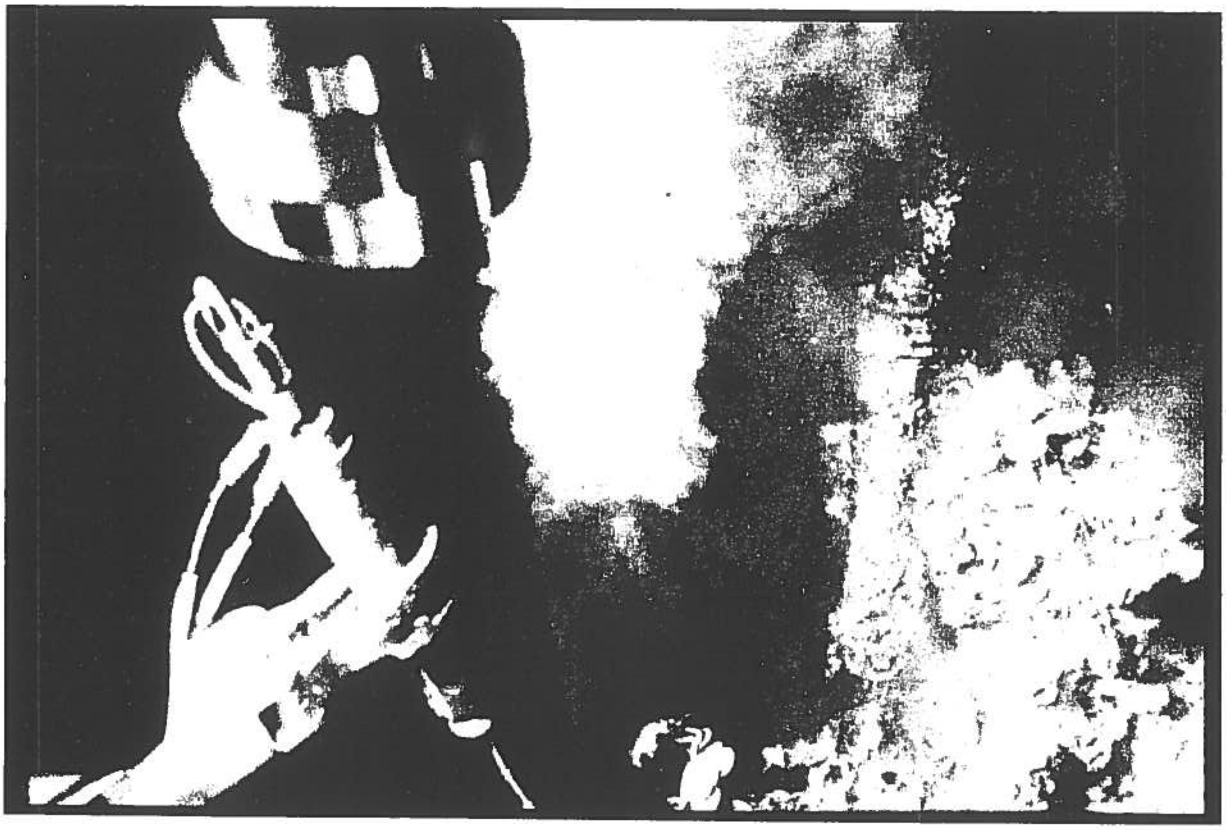

Andreas Weber

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1. Gutachter: Prof. Dr. Bo Barker Jørgensen
2. Gutachter: Prof. Dr. H.D. Schulz

Prüfer:

Prof. Dr. M. Olesch
Prof. Dr. R.X. Fischer

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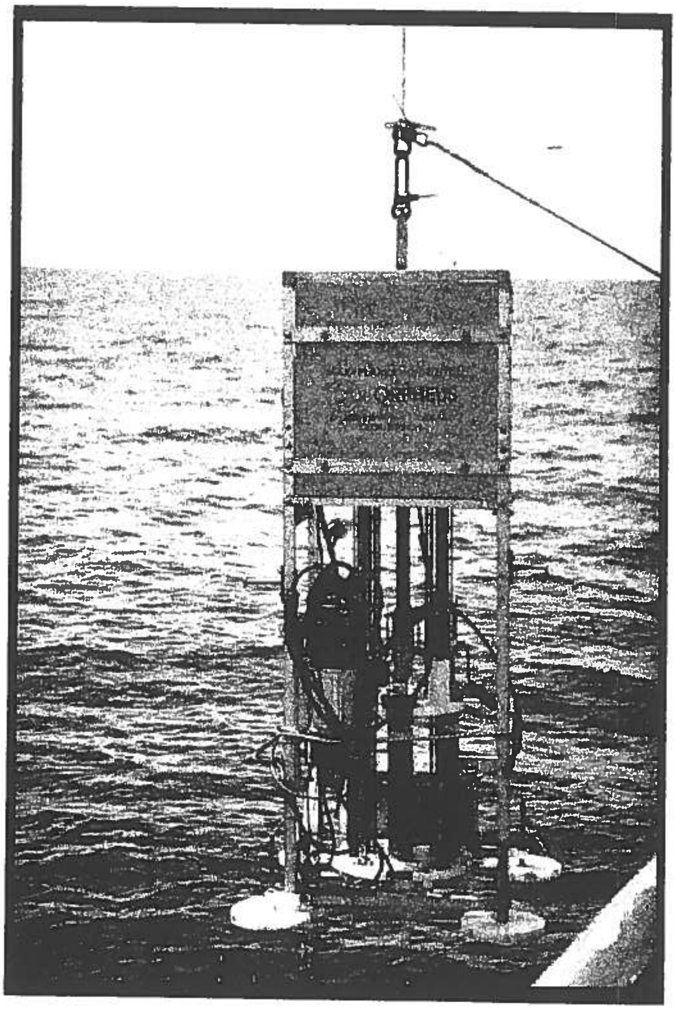

Das neue Inkubationsgerät ORPHEUS für Radiotracer-Untersuchungen

INHALTSVERZEICHNIS

1. Vorwort und Danksagung

Diese Dissertation schließt sich an die Promotionsschrift: „Entwicklung und Erprobung eines benthischen Landersystems zur *in situ* Bestimmung von Sulfatreduktionsraten mariner Sedimente" meines Kollegen Dr. Oliver Greeff an. Das von ihm entwickelte freifallende Landersystem LUISE wurde von mir durch einen Temperatursensor für Sedimentmesungen ergänzt und gezielt an verschiedenen marinen Standorten mit unterschiedlichen Sedimentverhältnissen eingesetzt. Diese Arbeit stellte unter anderem auch eine technische Herausforderung dar, insofern, daß für die Beprobung hydrothermaler Sedimente mit extrem heißen und korrosiven Umgebungsbedingungen ein neues Inkubationsgerät: der ORPHEUS entwickelt wurde.

Ziel dieser Arbeit war es, die Bedeutung der bakteriellen Sulfatreduktion in verschiedenen marinen Sedimenten (Schwarzes Meer, Ägäis und Urania Becken sowie Golf von Kalifornien) durch *in situ* Messungen zu quantifizieren. Ein weiterer Schwerpunkt war es, Unterschiede in den Sulfatreduktionsraten zwischen *in situ* inkubierten Sedimentkernen und im Labor inkubierten Kernen zu untersuchen.

Die in den einzelnen Arbeiten vorgestellten Ergebnisse basieren auf Daten, die ich während drei Forschungsfahrten zwischen 1997 und 1998 erheben konnte. Im einzelnen waren dies die RV PETR KOTTSOV Expedition in das nordwestliche Schwarze Meer im September 1997, die RV METEOR Expedition M40/2 in die Ägäis im Dezember 1997 und die RV ATLANTIS Expedition in den Golf von Kalifornien im April 1998.

Während der Forschungsreise in das Schwarze Meer wurden *in situ* Messungen gleichzeitig mit drei Landergeräten: dem Sulfatreduktionslander LUISE sowie einem profilierenden Lander und einem Kammerlander meiner Kollegen Frank Wenzhöfer und Wolfgang Riess durchgeführt, um ein möglichst zusammenhängendes Bild vom Abbaugeschehen organischen Kohlenstoffs von der oxischen in die anoxische, sulfidische Zone zu erhalten.

Hydrothermale Stoffflüsse in der südlichen Ägäis sowie Stoffflüsse im anoxischen Urania Becken wurden während der Meteor Expedition M40/2 untersucht. Dabei wurde der Lander LUISE zur *in situ* Messung von Sulfatreduktionsraten in hydrothermal beeinflussten Sedimenten vor der Insel Milos und in der Caldera der Insel Santorin sowie im hochsalinen, fast 4000 m tiefen Urania Becken westlich vor Kreta eingesetzt.

Ein genaues Positionieren des freifallenden Landers LUISE zur gezielten Untersuchung eines „Hot Vent Systems" wäre stark vom Zufall abhängig, da keine Steuerung möglich ist. Deshalb wurde in Anlehnung an diesen Landertyp im Rahmen dieser Dissertation ein neues Inkubationsgerät: der ORPHEUS zur Beprobung von hydrothermalen Tiefseesedimenten entwickelt, der mit einem Forschungstauchboot oder einem remote operating vehicle (ROV) eingesetzt werden kann.

Der für *in situ* Inkubationen konzipierte ORPHEUS wurde im Rahmen dieser Arbeit zum ersten Mal erfolgreich in hydrothermalen Tiefseesedimenten des Guaymas Beckens im Golf von Kalifornien mit dem Forschungstauchboot ALVIN eingesetzt. Neben den *in situ* Messungen wurden auch Versuche zur Temperaturabhängigkeit der bakteriellen Sulfatreduktion unter Laborbedingungen durchgeführt.

Die hier vorliegende Dissertationsschrift ist im wesentlichen in drei Teile gegliedert. In der Einleitung werden die grundsätzlichen Fragestellungen der eingereichten Manuskripte erläutert. Alle im zweiten Teil vorgestellten Manuskripte sind in englischer Sprache abgefaßt und bei internationalen Fachzeitschriften zur Veröffentlichung eingereicht worden, oder werden in Kürze eingereicht:

„Sulfate reduction in Black Sea sediments; *in situ* and laboratory radiotracer measurements from the shelf to 2000 m depth" von **A. Weber**, W. Riess, F. Wenzhöfer und B.B. Jørgensen

Die dieser Arbeit zugrundeliegende Forschungsreise wurde von mir organisiert und koordiniert. Die Fahrtleitung übernahm Herr Prof. Dr. Jørgensen. Das Manuskript dieser Arbeit wurde von mir verfaßt. Von Wolfgang Riess und Frank Wenzhöfer wurden Meßergebnisse des „diffusive oxygen uptake" (DOU), des „total oxygen uptake" (TOU) sowie „dissolved inorganic carbon" (DIC) für diese Arbeit zur Verfügung gestellt. Das Manuskript wurde bei Deep Sea Research eingereicht.

„Bacterial sulfate reduction in hydrothermal sediments of the Guaymas Basin, Gulf of California, Mexico: *in situ* and laboratory radiotracer measurements", von **A. Weber** und B.B. Jørgensen

Das Manuskript dieser Arbeit wurde von mir verfaßt. Das Inkubationsgerät ORPHEUS wurde von mir konzipiert und mit Hilfe der technischen Werkstatt des Max-Planck-Institutes realisiert. Während einer Tauchfahrt mit ALVIN, an der ich teilnehmen konnte, wurde das Gerät zur Beprobung hydrothermaler Sedimente erfolgreich eingesetzt.

Die Fahrtleitung hatte Prof. Dr. Holger Jannasch. Dieses Manuskript wird bei Deep Sea Research eingereicht.

„Deep-water secondary productivity and intense sulphate reduction in a hypersulphidic basin in the Mediterranean Sea: Implications for the sulphur isotope record", von W. Ziebis, M.E. Böttcher, **A. Weber**, J.C. Miquel, S.M. Sievert, P. Linke.

Das Manuskript dieser Arbeit wurde von Wiebke Ziebis verfaßt. Zu dieser Arbeit habe ich mit *in situ*- und Labormessungen von Sulfatreduktionsraten in Sedimenten des Urania Beckens sowie in der Wassersäule beigetragen. Sämtliche Laborarbeiten und Berechungen der Raten wurden von mir durchgeführt. Die Fahrtleitung hatte Dr. Peter Linke. Dieses Manuskript wurde bei Nature eingereicht.

„Geochemistry and sulfate reduction rates in hydrothermally influenced sediments in the Aegean Sea", von W. Ziebis, und **A. Weber**

Diese Arbeit beinhaltet meine Ergebnisse der Forschungsreise M40/2 in die Ägäis. Mein Anteil an dieser Arbeit war die Bestimmung von Sulfatreduktionsraten (*in situ*- und Laborinkubationen) in hydrothermalen und nicht hydrothermalen Sedimenten vor der Insel Milos und in der Caldera der Insel Santorin mit dem Lander LUISE. Dieses Manuskript wird bei Continental Shelf Research eingereicht.

Im dritten Teil werden die wichtigsten Ergebnisse zusammengefaßt und ein Ausblick auf die Landertechnologie gegeben.

Die hier vorliegenden Artikel entsprechen dem Inhalt nach den eingereichten Manuskripten. Zum Zeitpunkt der Einreichung dieser Arbeit sind noch alle Manuskripte dem Review-Prozeß unterworfen, das kann zu nachträglichen Änderungen führen.

Danksagung

Die vorliegende Arbeit entstand am Max-Planck-Institut für marine Mikrobiologie in Bremen unter der Leitung von Herrn Prof. Dr. Bo Barker Jørgensen, dem ich für das stete Interesse mit zahlreichen Anregungen, die angenehme Arbeitsatmosphäre und die großzügige Benutzung von Gerätschaften und Materialien am Institut herzlichst danke. Herr Prof. Dr.

Horst D. Schulz hat sich freundlicherweise bereit erklärt, das Zweitgutachten zu übernehmen; herzlichen Dank dafür.

Finanziell unterstützt wurde diese Arbeit über einen Zeitraum von drei Jahren durch Fördermittel der Max-Planck-Gesellschaft.

Desweiteren gilt mein besonderer Dank Herrn Dr. Oliver Greeff. Von ihm konnte ich ein einsatzfähiges Seeforschungsgerät: die LUISE übernehmen. Herrn Dr. Henrik Fossing danke ich für die fundierte Einführung in die Thematik der Sulfatreduktion, die für mich, als Mineralogen zunächst sehr abstrakt erschien, sowie Herrn Dr. Tim Ferdelmann und Herrn Dr. Volker Brüchert für die wichtigen Anregungen bei der Interpretation der Ergebnisse. Dies trug erheblich zum Gelingen der Arbeit bei. An dieser Stelle danke ich auch Frau Dr. Susan Boehme für die kritische Durchsicht der englischsprachigen Manuskripte.

Ganz herzlichen Dank möchte ich vor allem den technischen Angestellten des Max-Planck-Institutes aussprechen, die oft „im Verborgenen“ die wissenschaftliche Arbeit unterstützten. Dabei möchte ich vor allem Kirsten Neumann erwähnen, ihre Unterstützung an Bord und im Labor hat wesentlich zur raschen Bearbeitung des Probenmaterials beigetragen. Ein ganz herzliches Dankeschön auch an die Techniker der Landergruppe: Axel Krack, Stephan Meyer, sowie Volker Meyer, die mit ihrem technischen und elektronischen Rat zu einem guten Gelingen der Landereinsätze beigetragen haben. Mein besonderer Dank gilt auch den weiteren Mitgliedern des Technikerteams: Georg Herz, Olaf Eckhoff und Gerd Kothe, die sich immer wieder bereit erklärt haben kurzfristig einige große und kleine Ersatzteile zu fertigen. Vielen Dank auch an Frederike Hoffmann und Jan Kaiser, die mir im Labor während der knappen Zeit zwischen den Forschungsfahrten bei der Probenaufbereitung tatkräftig zur Seite standen.

Allen nicht namentlich genannten Kollegen des Max-Planck-Institutes und Freunden danke ich für ihre Geduld und Verständnis an nicht immer reibungslosen Tagen.

Nicht zuletzt danke ich besonders herzlich meinen „*in situ*“- Kollegen der Landergruppe Wolfgang Riess und Frank Wenzhöfer für die gute und fruchtbare Zusammenarbeit zu Wasser und zu Lande.

Den Sulfatreduzierern mariner Sedimente danke ich für ihren aktiven Einsatz am Entstehen kleiner und großer Raten.

2. Einleitung

2.1 Abbauwege organischer Substanz am Meeresboden

In den oberen 10 bis 100 Metern des Meerwassers sind mikroskopische einzellige Algen für den größten Teil der globalen Pflanzenproduktion verantwortlich. Die hier produzierte Biomasse wird in der photischen Zone aber nicht vollständig umgesetzt und sinkt als organischer Detritus durch die Wassersäule zum Meeresboden. Dieser vertikale Flux von partikulärem Kohlenstoff wird auch als „mariner Schnee" (mit Partikelgrößen > 200 µm) bezeichnet und ist abhängig von der Primärproduktion im Oberflächenwasser (Suess, 1980). Aber nur 25-50% der vom Plankton in der Wassersäule synthetisierten Kohlenstoff-, Stickstoff- und Phosphorverbindungen verlassen die photische Zone und erreichen den Meeresboden (Wollast, 1991). Am Meeresboden wird ein Großteil des abgesunkenen organischen Materials wieder mineralisiert, jedoch werden nur etwa 10 % davon langsam im Meeresboden begraben und sind für einen C_{org}-Gehalt von 1-3 % (Trockengewicht) in Schelf-Sedimenten verantwortlich (Berner, 1982).

Sedimente haben eine hohe Aufnahmefähigkeit für organisches Material und haben deshalb eine Pufferfunktion für küstennahe Ökosysteme. Eine Vielfalt von Mikroorganismen, die ein breites Spektrum von Elektronenakzeptoren nutzen, sind verantwortlich für den Abbau organischen Materials in marinen Sedimenten. Abhängig von der bakteriellen Aktivität im Sediment und dem Sauerstoffgehalt im Bodenwasser, können anoxische Bedingungen auftreten, was zu einer Verschiebung der Grenzschicht zwischen oxischen und anoxischen Verhältnissen führt und dramatische Veränderungen im Sediment und der benthischen Lebensgemeinschaft hervorrufen kann. So können sich z.B. geochemische Gradienten im Sediment, der Nährstofffluß in das darüberliegende Bodenwasser oder die Abbauwege mikrobieller Prozesse ändern (Jørgensen, 1996).

Es läßt sich eine vertikale Zonierung der Abbauvorgänge in der Sedimentsäule nach abnehmendem Redoxpotential und Energiegewinn feststellen: a) aerobe Respiration, b) Denitrifikation, c) Mangan (Mn(IV))- und Eisenreduktion (Fe(III)), d) Sulfatreduktion, e) Methanogenese (Jørgensen, 1996).

Die Oxidation organischen Materials zu Kohlendioxid (CO_2) und Wasser (H_2O), erfolgt hauptsächlich durch Mikroorganismen und kann je nach Sedimenttiefe über einen oder mehrere der oben dargelegten Wege ablaufen. Das sedimentierte organische Material wird in erster Linie durch aerobe Mikroorganismen und Tiere auf dem Meeresboden mineralisiert.

In küstennahen Sedimenten beschränkt sich dieser Abbauvorgang auf eine sauerstoffhaltige, nur wenige Millimeter dicke Schicht an der Sedimentoberfläche und auf die Gangsysteme des Benthos (Revsbech et al., 1980, Jørgensen und Revsbech, 1985). Unter der Zone der Sauerstoffeindringtiefe tritt eine schmale Zone der Denitrifikation auf (Sørensen, 1978, Nielsen et al., 1992). Das beim Abbau von organischer Substanz freigesetzte Nitrat dient hier als Elektronenakzeptor und wird zu molekularem Stickstoff (N_2) oder in geringem Umfang auch zu Ammonium (NH_4^+) reduziert. Bis auf wenige Ausnahmen, z.B. bei hoher Nitratkonzentration im Sediment, hat dieser Prozeß jedoch eine weitaus geringere Bedeutung für die C_{org}-Oxidation (Sørensen et al., 1979).

Bis noch vor wenigen Jahren wurde angenommen, daß der Abbau organischen Materials in Sedimenten größtenteils durch aerobe Respiration sowie durch Sulfatreduktion erfolgt (Jørgensen, 1978, Fossing und Jørgensen, 1990). Heute weiß man, daß auch noch andere Elektronenakzeptoren für die Mineralisation organischen Kohlenstoffs verantwortlich sind, inbesondere oxidierte Mangan- und Eisenspezies. Die Mangan- und Eisenreduktion findet in der braunen, oxidierten, oberflächennahen Sedimentschicht unter der Zone der aeroben Respiration und Denitrifikation statt und erstreckt sich bis zu einer Tiefe von etwa 10 cm. Die Sulfatreduktion als dominierender anaerober Prozeß tritt unmittelbar darunter und bis in mehrere Meter Tiefe auf. Die hohe Verfügbarkeit von Sulfat zusammen mit der effektiven bakteriellen Aktivität, organischen Kohlenstoff zu oxidieren (ein Mol Sulfat kann zwei Mol Kohlenstoff der Oxidationsstufe 0 oxidieren) verleiht diesem Stoffwechselprozeß große Bedeutung. Die anaeroben Mineralisationsprozesse der Mangan- und Eisenreduktion sowie der Sulfatreduktion dominieren neben der auf die obersten Millimeter des Sediments beschränkten O_2-Respiration die anaerobe Oxidation organischen Kohlenstoffs (Canfield et al., 1993, Thamdrup und Canfield, 1996). Dabei entstehen weitere reduzierte Komponenten wie H_2S bei der Sulfatreduktion und Mn^{2+} und Fe^{2+} bei der bakteriellen Mangan- und Eisenreduktion. Die Mangan- bzw. Eisenreduktion ist indirekt, bzw. direkt mit dem Schwefelkreislauf verbunden (Abb. 1), wobei der Schwefelkreislauf aufgrund seiner unterschiedlichen Oxidationsstufen weitere metabolische Reaktionen ermöglicht (Oxidation, Reduktion und Disproportionierung).

Schließlich folgt als energieärmster Prozeß unter der Sulfatreduktionszone noch die Methanogenese, bei der organisches Material zu CO_2 und Methan (CH_4) umgesetzt wird (Crill und Martens, 1986; Kuivila et al., 1990).

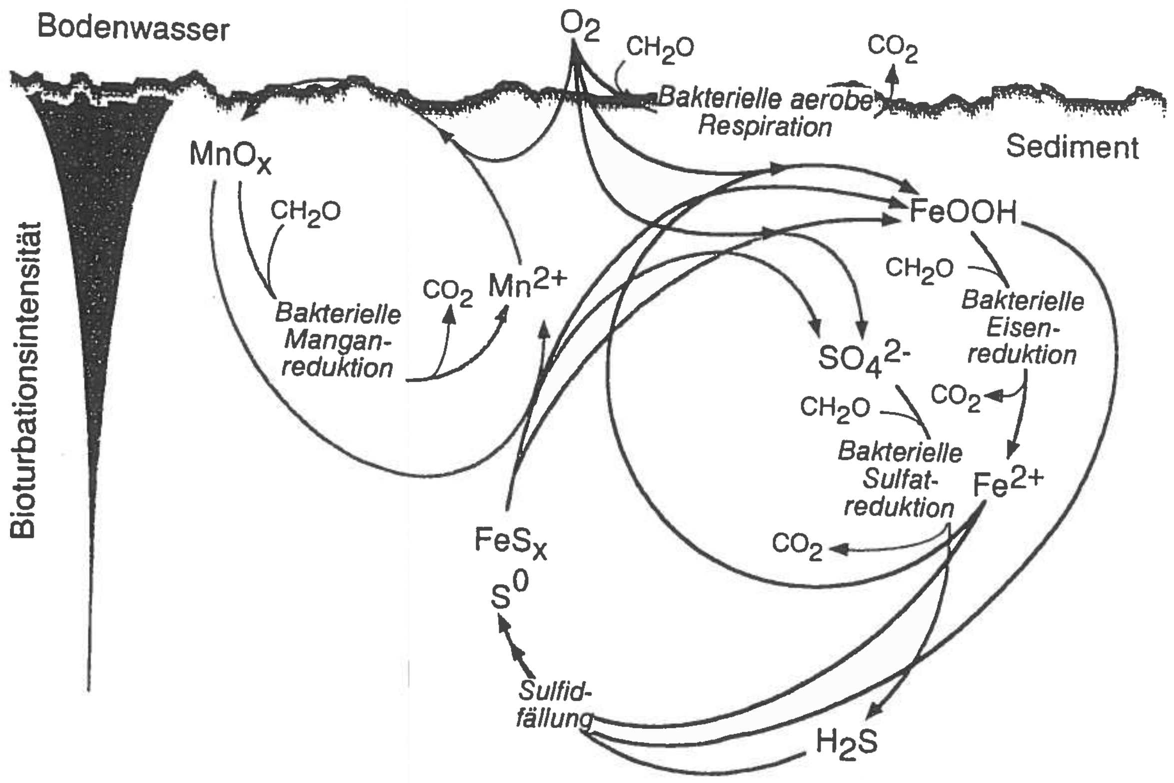

Abb. 1: Vereinfachte Darstellung der Kopplung zwischen Sauerstoff-, Mangan-, Eisen-, und Schwefelkreisläufen in marinen Sedimenten (aus Jahrbuch der Max-Planck-Gesellschaft zur Föderung der Wissenschaften e.V., 1995, Sonderdruck des Max-Planck-Institutes Bremen, 231-238).

2.2 Abbau organischen Kohlenstoffs durch Sulfatatmung

Weltweit gesehen, ist die Oxidation organischen Kohlenstoffs in marinen Sedimenten durch die aerobe Respiration bestimmt. An zweiter Stelle folgt der Abbauweg der Sulfatreduktion (Jørgensen, 1983; Henrichs und Reeburgh, 1987). Allerdings wechselt die relative Bedeutung der beiden Mineralisationsprozesse in Abhängigkeit vom Sediment. In euxinischen Sedimenten mißt man weitaus höhere Sulfatreduktionsraten als in normalen marinen Sedimenten, weil im euxinischen Milieu hauptsächlich sulfatreduzierende Bakterien organisches Material abbauen. In küstennahen Sedimenten ist die Sulfatreduktion etwa gleichbedeutend mit der aeroben Mineralisation, dagegen dominiert in vielen Tiefseesedimenten die aereobe Respiration. (Jørgensen, 1983; Canfield, 1989). Chemisch gesehen ist die Sulfatreduktion eine Redoxreaktion (1).

(1) Sulfatreduktion:

$$H^+ + CH_2O + \frac{1}{2} SO_4^{2-} \rightarrow CO_2 + \frac{1}{2} H_2S + H_2O$$

Ausschließlich strikt anaerobe sulfatreduzierende Bakterien sind für die Reduktion von Sulfat zu Sulfid verantwortlich und deren ökologische Bedeutung ist erkennbar an grau bis schwarz gefärbten Sedimenten (durch FeS und FeS_2) mit intensiven H_2S-Geruch. Es wird geschätzt, daß etwa 50 bis 90% der weltweiten Sulfatreduktion in küstennahen Sedimenten, auf dem Schelf und am Kontinentalhang auftritt (z.B. Ivanov, 1978, Jørgensen, 1983, Volkov und Rozanov, 1983).

In vielen küstennahen Sedimenten sind sulfatreduzierende Bakterien hauptsächlich in den oberen Zentimetern des Meeresbodens aktiv. Ein hoher Anteil an organischem Material im Sediment führt zu einem hohen bakteriellem Umsatz, einer Abnahme von Sauerstoff und einem Absinken des Redoxpotentials (Eh). Zusammen mit Sulfat, verfügbarem organischen Substraten und einem geeigneten pH-Wert kann eine optimale Umgebung für sulfatreduzierende Bakterien geschaffen werden (Skyring, 1987).

Es wurden verschiedene Arten mariner sulfatreduzierender Bakterien, wie *Desulfotomaculum*, *Desulfovibrio* oder *Desulfovibiro aestaurii* beschrieben (Zobell und Rittenberg, 1948), die z.B. einfache organische Verbindungen wie Lactat, Pyruvat, Fumarat oder Formiat oxidieren können. Erst sehr viel später gelang es einen weiteren Sulfatreduzierer: *Desulfobacter postgatei* zu isolieren, der auch Fettsäuren, wie z.B. Acetat oder Propionat als Substrat oxidieren kann (Widdel und Pfennig, 1981, 1982). Mit diesen Arbeiten wurde die Bedeutung der Sulfatreduktion im globalen Kohlenstoffkreislauf immer deutlicher.

2.3 Messung biologischer Sulfatreduktion in marinen Sedimenten

Nur ein geringer Anteil des bei der Sulfatreduktion freigesetzten Schwefelwasserstoffs wird an die überstehende Wassersäule abgegeben. Statt dessen wird freies Sulfid im Porenwasser akkumuliert oder als Pyrit (FeS_2) permanent im Sediment festgelegt. Der größte Teil (90%) des Schwefelwasserstoffs im Porenwasser wird im oxidativen Schwefelkreislauf zu Sulfat reoxidiert. Aufgrund der rasch ablaufenden Kreislaufreaktionen von Sulfat zu Sulfid und zurück zu Sulfat (2), ist es nicht möglich die tatsächlichen Mineralisationsraten des organischen Materials über die Untersuchung der Sulfat- und Schwefelwasserstoff-Konzentrationen zu beobachten.

(2) Reoxidation der reduzierten Verbindung:

$$O_2 + \tfrac{1}{2} H_2S \rightarrow \tfrac{1}{2} SO_4^{2-} + H^+$$

Erst mit Hilfe des Einsatzes von sog. Radiotracern gelang es Sulfatreduktionsraten direkt zu messen. Die ersten Messungen dieser Art wurden von Sorokin (1962) durchgeführt, der radioaktives Sulfat ($^{35}SO_4^{2-}$) in homogenisiertes Sediment mischte.

Durch Zugabe von $^{35}SO_4^{2-}$ beobachtet man im Laufe der Zeit eine Anhäufung von radioaktiv markiertem $H_2{}^{35}S$ während $^{35}SO_4^{2-}$ reduziert wird. Um Sulfatreduktionsraten in Abhängigkeit von der Sedimenttiefe zu untersuchen, injiziert man $^{35}SO_4^{2-}$ horizontal, in regelmäßigen Abständen in ungestörte Sedimentkerne und läßt den Sedimentkern einige Zeit bei *in situ* Temperaturen inkubieren. Anschließend wird der Kern segmentiert und die Sedimentscheiben in Zinkacetat konserviert (Jørgensen, 1978; Zhabina und Volkov, 1978; Fossing und Jørgensen, 1989). Bei einer Destillation mit Cr^{2+}-Salzen unter salzsauren Bedingungen wird radioaktives $H_2{}^{35}S$ aus den im Sediment fixierten radioaktiven Schwefelverbindungen wieder freigesetzt. Aus dem Verhältnis der Radioaktivität im Schwefelwasserstoff zu der im nicht umgesetzten Sulfat, läßt sich eine Umsatzrate berechnen:

$$\text{Rate} = \frac{[SO_4^{2-}] \bullet (^{35}S\text{-}H_2S) \bullet \alpha}{(^{35}S\text{-}SO_4^{2-}) \bullet t} \text{nmol } SO_4^{2-} \text{ cm}^{-3} \text{ d}^{-1}$$

$[SO_4^{2-}]$ = Sulfatkonzentration, ($^{35}S\text{-}SO_4^{2-}$) und ($^{35}S\text{-}H_2S$) = absolute Sulfat- und Sulfidradioaktivitäten, t = Inkubationszeit, gemessen in Tagen, α = Isotopen-Fraktionierungsfaktor der bakteriellen Sulfatreduktion (Jørgensen, 1978).

Die Untersuchung dieser biogeochemischen Stoffkreisläufe wirft aber Probleme auf, da die dafür erforderliche Probenahme von Sedimentkernen durch verschiedene Faktoren beeinflußt wird. Die Probenahme wird mit Geräten, wie z.B. dem Box-Corer oder dem Multi-Corer durchgeführt. Das Sediment wird mit diesen Geräten an Bord des Forschungsschiffes gebracht, um daran Beobachtungen und Experimente im Labor durchzuführen. Das Sediment wird dabei aber vor der Untersuchung seiner natürlichen Umgebung entrissen. In der Zeit zwischen Entnahme der Probe unter dem Einfluß des kalten Bodenwassers sowie unter dem hohen Druck der überlagernden Wassersäule und der Konservierung der

Sedimentprobe an Bord des Schiffes, erwärmt sich der Sedimentkern beim Aufstieg durch die Wassersäule und wird je nach Wassertiefe einer Dekompression ausgesetzt. Es ist zu klären, ob, und in welchem Umfang dabei die biologischen und chemischen Parameter der Probe vor der eigentlichen Untersuchung verändert werden und spätere Meßergebnisse verfälschen. Besonders offensichtlich wird diese Fragestellung auch bei der Beprobung hydrothermal beeinflußter Sedimente, die oft hohe Gaskonzentrationen (Methan) im heißen Sediment aufweisen und bei Atmosphärendruck an Bord des Schiffes heftig entgasen können. Eine massive Störung der Stratifizierung des Sedimentkerns sowie der Porenwassergradienten wäre das Resultat. Folglich sollten biogeochemische Experimente sofern möglich, ohne Druckentlastung der Probe in natürlicher Umgebung erfolgen.

Eine Möglichkeit diese Problematik zu umgehen, ist die Untersuchung biogeochemischer Stoffkreisläufe unter *in situ* Bedingungen auf dem Meeresboden. Abgesehen von der optimalen Möglichkeit, Probenahmen und Experimente mit Forschungstauchbooten oder sogenannten ROV´s (remote operated vehicle) durchzuführen, wurden je nach Anwendung neue technologische Ansätze entwickelt, um unter *in situ* Bedingungen zu arbeiten. Man konzipierte freisinkende, autonome Instrumente, die bis ca. 6000 m Wassertiefe einsetzbar sind, sogenannte Lander (Tengberg et al., 1995), wie z.B. Kammer-Lander für *in situ* Inkubationen abgeschlossener Sedimentvolumina (Jahnke und Christiansen, 1989) oder profilierende Landergeräte zur *in situ* Messung von Mikroprofilen, wie z.B. von O_2 über die Sediment-Wasser Grenzschicht (Reimers, 1987). Der Vorteil dabei ist, daß das eigentliche Inkubationsexperiment oder die Messung bereits auf dem Meeresboden abgeschlossen sind und die Proben an Bord des Schiffes nur noch fixiert, bzw. die Meßdaten ausgelesen werden müssen.

Die ersten Ergebnisse dieser Untersuchungen zeigten, daß durchaus Unterschiede zwischen Laborexperimenten und Messungen unter *in situ* Bedingungen festzustellen waren (z.B. Glud et al., 1994). Es wird vermutet, daß diese Unterschiede auf Dekompression und Erwärmung der Proben während des Aufstiegs durch die Wassersäule zurückzuführen sind. Nicht immer zeigen diese Vergleiche signifikante Abweichungen voneinander. So z.B. ließen *in situ* und Labormessungen von Sulfatreduktionsraten in unterschiedlichen Wassertiefen keine systematischen Unterschiede erkennen (Martens et al., 1998).

Vorausgegangene Landerarbeiten waren schließlich Grundlage für die technische Realisierung des Landergerätes LUISE zur *in situ* Messung von Sulfatreduktionsraten (Greeff et al., 1998). Mit diesem Inkubationslander wurden im Rahmen dieser Arbeit 17 Probenahmen mit *in situ* Inkubationen durchgeführt, mit dem Ziel, *in situ*

Sulfatreduktionsraten von verschiedenen marinen Sedimenten zu erhalten, deren Bedeutung im Vergleich zu anderen Mineralisationsprozessen festzustellen und eventuell auftretende Unterschiede zu Labormessungen zu erklären.

Im Rahmen dieser Dissertation wurde in Anlehnung an den Lander LUISE ein neues Inkubationsinstrument, der ORPHEUS, für Radiotracer Experimente auf dem Meeresboden entwickelt. Dies wurde notwendig, weil die gezielte Beprobung von hydrothermalen „Vent"-Sedimenten mittels herkömmlicher freifallender Landergeräte nicht mehr möglich war. Neben der zielgenauen Beprobung mußte gewährleistet sein, daß die Funktionstüchtigkeit von ORPHEUS auch bei extremen Temperaturen sowie korrosiven Umgebungsbedingungen erhalten bleibt. Hinzu kam die Anforderung, daß dieses Inkubationssystem mit dem Forschungstauchboot ALVIN abgesetzt werden sollte, so daß hohe technische Anforderungen in Bezug auf Dimension, Gewicht und Handling gestellt wurden.

Aufgrund der Bauweise dieses Gerätes besteht auch die Möglichkeit, ORPHEUS als Modul in ein größeres Landersystem zu integrieren und am gleichen Probenahmeort gleichzeitig zu Messungen geochemischer Gradienten, ergänzende Radiotracer Inkubationen durchzuführen.

Abgesehen vom Inkubationsinstrument ORPHEUS, das gezielt am Meeresboden abgesetzt werden kann, tritt bei freifallenden Landergeräten generell das Problem der Störung der Sedimentoberfläche auf. Dies kann bereits der Fall sein, bevor das Gerät den Boden berührt, durch eine dem Lander vorauslaufende Druckwelle, spätestens aber in dem Moment, in dem der Lander den Meeresboden berührt. Diese Erfahrungen wurden auch mit dem Lànder LUISE bei verschiedenen Einsätzen während der Forschungsreise in das Schwarze Meer gemacht. Hier kann nur vor jedem Einsatz eine genaue Studie der Sedimentverhältnisse durch Box-Corer oder Multi-Corer Kerne helfen, die Sinkgeschwindigkeit des Landers so zu beeinflussen, daß eine Störung des „Fluffy Layer" so gering wie möglich gehalten wird.

Trotz einer Reihe bereits durchgeführter Studien - einschließlich dieser Arbeit - sind viele Fragen bezüglich der Unterschiede Labor- und *in situ* Inkubation noch nicht geklärt. Nur durch weitere Landereinsätze, möglichst in Tiefseesedimenten (> 2000 m) mit signifikanten Druck- und Temperaturunterschieden zur Wasseroberfläche, kann die Auswirkung dieser physikalischen Parameter auf Sulfatreduktionsraten bei Labor- und *in situ* Inkubationen verifiziert werden.

3. Ergebnisse und Diskussion

3.1

Sulfate reduction in Black Sea sediments; *in situ* and laboratory radiotracer measurements from the shelf to 2000 m depth

A. Weber, W. Riess, F. Wenzhöfer, B.B. Jørgensen

Max Planck Institute for Marine Microbiology, Celsiusstr. 1, 28359 Bremen, Germany

3.1.1 Abstract

Sulfate reduction rate (SRR) measurements were carried out *in situ* with the benthic lander LUISE and in parallel by shipboard incubations, in shelf, slope and deep sea sediments along a transect off the Romanian coast to the deep anoxic basin of the Black Sea. *In situ* SRR at the Romanian shelf were significant lower (58-80%) than laboratory incubated sediments. Below the chemocline the differences were in a range of 4 to 32%. The highest rates measured on a depth integrated basis were 1.97 mmol m^{-2} d^{-1} (Stn. 0, shelf) and 1.54 mmol m^{-2} d^{-1} (Stn. 5, lower transition zone). At shelf stations 2 and 3 *in situ* measured SRR underestimated the actual rates because the surface sediment was lost when the lander touched the sea floor. A lower sinking rate of 0.7 m s^{-1} was found to be suitable for undisturbed coring. At all stations SRR decreased to values ~ 3 nmol cm^{-3} d^{-1} or less below 15 cm sediment depth.

Furthermore, the relative significance of the main oxidants was investigated. The predominant mineralization process on the shelf is oxygen respiration. The importance of sulfate reduction in comparison to total remineralization increased from 5.6 to 46.5 % (Stn. 1-3). In the lower transition zone (Stn. 5, 181 m water depth) SRR increased to levels of shallow water rates. This data suggest sulfate reduction is the predominant pathway of carbon remineralization in this zone. Below the transition zone SRR (laboratory and *in situ*) were in a range of 0.22 mmol m^{-2} d^{-1} to 0.68 mmol m^{-2} d^{-1}. Preliminary calculations indicate that Mn and Fe reduction together could be of roughly similar importance to carbon oxidation as sulfate reduction at Stn. 1-3 and probably less than half of the contribution from sulfate reduction at Stn. 4. The two depositional environments of the Black Sea (oxic shelf and anoxic basin) were well characterized by significant differences in CNS depth profiles together with C_{org}:S ratios. Increasing atomic ratios of C_{org}:N suggests that sulfate reduction was limited by the quality of organic matter reaching the sea floor.

3.1.2 Introduction

The Black Sea is a land-locked deep basin which contains the largest permanently anoxic water body in the world with a volume of 423,000 km^3 (Deuser, 1974). This is a result of its separation from the Mediterranean and only limited exchange through the narrow and shallow sill (34 m) of the Bosphorus, which connects the Black Sea with the Sea of Marmara (Ünlüata et al., 1989). The Black Sea was a freshwater lake during the Pleistocene (Izdar and Ergün, 1991). With the rise of the sea level saline Mediterranean water flows through the Bosphorus into the Black Sea (Gunnerson and Özturgut, 1974), a freshwater input come from the major rivers Danube, Dnieper and Dniester (Tolmazin, 1985a).

Between the two water masses a cold intermediate layer with a temperature of 7° C established between 50 and 100 m (Murray et al., 1991a). A permanent halocline separates an upper low salinity layer (S = 18.1 ‰) from a 2000 m deep anoxic water body with a salinity of 22.3 ‰ (Tolmazin, 1985a; Murray et al., 1989 and 1991b). The anoxic conditions of the Black Sea began 5000-7000 years ago (Ross and Degens, 1974; Deuser, 1974; Degens et al., 1978; Calvert et al., 1987) and since then the chemocline has risen to its present depth at 160-180 m along the periphery and 95-100 m in the central Black Sea (Fashchuk, 1995; Bezborodov and Eremeev, 1991 and 1992). Hydrogen sulfide reaches 400 µM in the huge anoxic water mass below the brackish surface layer (Brewer and Spencer, 1974; Millero, 1991). Current hydrographic conditions are described in detail by Gunnerson and Özturgut (1974); Sorokin (1983); Ünlüata, et al. (1989); Vinogradov (1991); Codispoti et al. (1991); Latif et al. (1991) and Buesseler et al. (1994).

Because of its stratification caused by temperature and salinity gradients, the Black Sea is an ideal natural laboratory for studies of oxidant changes through the transition from oxic shelf sediments to sulfidic deep sea sediments. An important question is how the relative significance of the main oxidants changes across the shelf break and upper slope where the oxic/anoxic interface intercepts the sea floor. This interface is characterized by very low oxygen and by relatively high nitrate concentrations. It is a zone which has many similarities to continental margin sediments underlying waters with strong upwelling, extensive oxygen depletion and high nitrate concentration. In the Black Sea, however, the stratification is more stable and independent of season.

The dynamics of the oxic/anoxic interface and its influence on mineralization processes in sediments are still unknown. Mineralization processes in Black Sea sediments such as sulfate reduction were investigated so far only under laboratory conditions.

Radiotracer sediment investigations of sulfate reduction were carried out the first time by Sorokin (1962), followed by Vaynshteyn et al. (1985), Lein et al. (1986 and 1990), Lein and Ivanov (1990) and Albert et al. (1995). In this marine environment with low bottom water temperature (7°-9° C) and warm surface water (19.6° C during this study) temperature increase in the water column influences biological and chemical processes in sediment cores during recovery and may not reflect the original mineralization processes occurring in the sediment column.

Furthermore, we expected increasing effects of decompression (52 to 2045 m water depth) on SRR measured in sediment cores under laboratory conditions. Thus it was necessary to study these processes under real *in situ* conditions. Longterm incubations at the sea floor by use of a benthic lander for radiotracer studies, a chamber lander and a profiling lander can avoid temperature and pressure influences during the experiments and should reflect the actual biological or chemical activity in the sediment (Glud et al., 1994). Except *in situ* measurements of benthic fluxes on the north western Black Sea shelf (Friedl et al., 1998), no investigations were reported of SRR measurements in sediments under *in situ* conditions. *In situ* measurements of sulfate reduction in the Black Sea water column were reported by Albert et al. (1995).

This was the first time *in situ* measurements of mineralization processes in sediments were realized within a short lateral distance by the deployment of three different types of benthic landers to study oxidant changes in Black Sea sediments along a transect through the transition zone. Direct measurements of oxygen uptake, reduction of manganese and iron oxides, sulfate reduction, carbon dioxide and ammonium release were performed. We report here SRR along a transect through the interface and the differences between *in situ* and laboratory incubations. We present carbon, sulfur and nitrogen relationships. We also discuss the relative significance of sulfate reduction in comparison to aerobic mineralization and Mn and Fe reduction in oxic shelf sediments.

3.1.3 Methods

3.1.3.1 Field sites

Samples were obtained from ten stations (Table 1) in the western Black Sea during the Black Sea cruise onboard the Russian RV Petr Kottsov in September 1997. The sampling stations were situated along a transect (except Stn. 0 near oil drilling platform, Gloria), which extended over a length of ~ 225 km off the Romanian coast from 62 m to 2046 m water depth (Fig. 1). Thus, the transition from fully oxic to sulfidic conditions was studied. The *in situ* sediment temperatures, measured by a temperature sensor on the benthic lander, LUISE, and bottom water oxygen concentrations (Riess et al., unpublished manuscript) are shown in Table 1. Stations 1-4 are located on the shelf; 5 and 6 on the upper slope, 7 on the lower slope and Stn. 8 in the deep basin.

Table 1. Station locations, water depth, sediment temperature (LUISE sensor) and bottom water oxygen concentrations (n.d. = no data).

Stn.- No.	**Position**	**Water depth (m)**	**Sediment temp. (°C)**	**O_2-bottom water (µmol l^{-1})**
0	43°27'68 N, 29°33'26 E	52	n.d.	n.d.
1	44°15'07 N, 29°45'04 E	62	6.6	211
2	43°53'84 N, 29°58'57 E	77	7.2	213
3	43°51'05 N, 30°10'45 E	100	7.6	75
4	43°43'08 N, 30°05'90 E	130	n.d.	< 5
5	43°42'63 N, 30°06'12 E	181	8.6	0
6	43°40'47 N, 30°07'54 E	396	8.9	0
7	43°31'61 N, 30°13'33 E	1176	9.1	0
8	42°53'67N, 30°40'23 E	2045	n.d.	0
H	43°41'79 N, 30°06'67 E	300	n.d.	0

Sediment properties changed significantly with the transition from oxic to sulfidic conditions. On the shelf and at the shelf break the sea floor was covered by mussels, *Mytilus galloprovinciales* and *Modiolus phaseolinus* overlying a light gray mud. Just beyond the shelf break (Stn. 5), partly laminated and partly mixed sediments occurred. This sediment was apparently influenced by changes in the chemocline depth and by sediment transport from the shelf to the deep basin. Sediment from Stn. 6 to 8 was a finely laminated coccolith ooze. This typical Black Sea sediment consists principally of the coccolithophore species, *Emiliania huxley*, (Ross and Degens, 1974; Calvert et al., 1987; Lyons, 1991 and Hay et al., 1991).

Except for Stn. 7 (gelatinous layer), a fluffy layer (Stn. 5, 6 and 8) or fluffy particles between the shells (Stn. 1 to 4) were observed at the sediment/water interface in all of the multiple cores and most of the benthic lander cores along the transect. Station H (300 m water depth) was situated at the upper slope and only the water column was studied for hydrographic parameters.

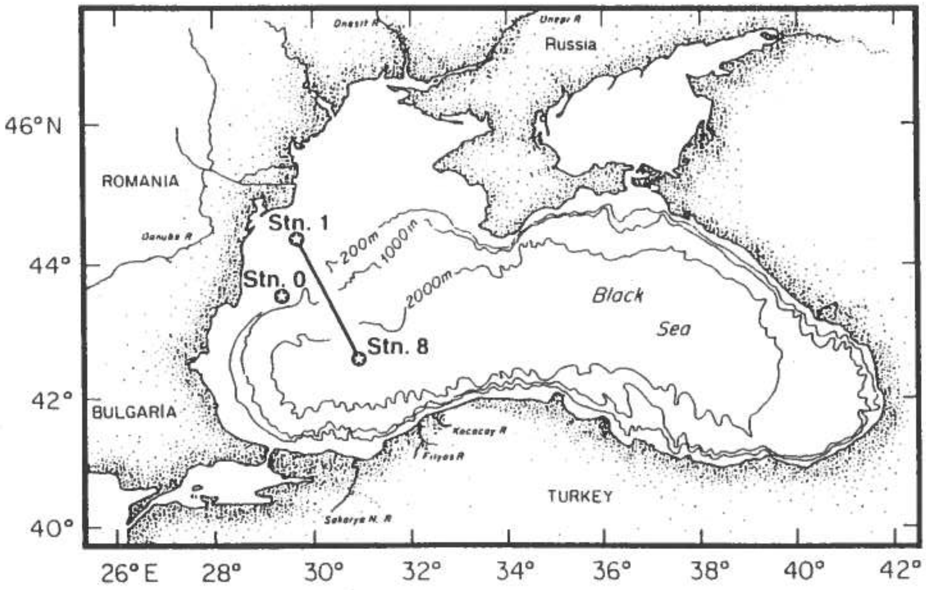

Fig. 1: Map of the Black Sea showing the transect from Stn. 1 to Stn. 8 and Stn. 0.

3.1.3.2 *In situ measurements of oxygen microprofiles obtained by a benthic profiling lander*

An autonomous benthic profiling lander was used to measure *in situ* microprofiles of oxygen with a depth resolution of 100 µm (Reimers, 1987; Glud et al., 1994). During this cruise the profiling lander was equipped with 2-4 oxygen microelectrodes of the Clark-type with a guard cathode and an internal reference (Revsbech, 1989). The tip diameter of the microelectrodes was 10-30 µm, the 90% response time was < 1 sec, and the stirring sensitivity was < 1 %. A two point calibration using the constant sensor signal in the bottom water, compared to Winkler titration concentration, and the zero signal recorded onboard was performed. The diffusive oxygen uptake (DOU) was calculated from the oxygen gradients in the diffusive boundary layer (Rasmussen and Jørgensen, 1992) applying Fick´s first law of diffusion: DOU = $D_0(dC/dz)$, where, C is the O_2-concentration, z is depth, and D_0 is the diffusion coefficient in water at *in situ* temperature and salinity (calculated from Li and Gregory, 1974) and Broecker and Peng, 1974)).

3.1.3.3 *In situ measurements of nutrient fluxes and total oxygen uptake with a benthic chamber lander*

A free falling autonomous chamber lander (Janke and Christiansen, 1989; Glud et al., 1994) was used to measure fluxes at the sediment water interface and the respiration rates of the sediment and the dense bivalve fauna. Two chamber lander deployments were carried out at Stations 1 through 4 whereas only one deployment was performed at the deeper Stations 5 to 8. The preprogrammed lander incubated 900 cm^2 of the sea floor with 10 to 20 cm of the overlying water.

Two Clark-type mini electrodes (stirring effect < 1 %, 90 % response time < 1 sec) recorded the decrease (< 25%) of oxygen in the chamber over time. Ten water samples were taken from the chamber during incubation for later analysis of ΣCO_2, NO_3^-, NH_4^+ and other dissolved components. The chamber was closed by a shovel at the end of the deployment and the sediment and overlying water were retrieved. Subsamples were taken from the chamber for meiofaunal counts and identification and also for sediment analysis. The remaining sediment was then sieved for macrofaunal identification and quantification.

Immediately after recovery of the lander the water samples were divided and frozen (for analysis of NO_3^-, NH_4^+) or fixed with $HgCl_2$ (for ΣCO_2) in gastight containers (exetainer, LABCO) for later analysis. The NO_3^- measurements were done with a NO-NO_2-NO_x Analyzer (Thermo Environmental Instruments, 42C (see Braman and Hendrix, 1989). NH_4^+ was measured by the flow injection method of Hall and Aller (1992). ΣCO_2 was measured with a coulometer (UIC, ASTM D-513 Method G, "Carbon Dioxide Evolution, Coulometric Titration Method"). Fluxes of the different solutes were calculated by linear regression of the time series of concentrations.

No tube-dwelling macrofauna was found. The vast majority of the fauna consisted of mussels that had their water inlet and –outlet directed to the open water. Thus, bioirrigation and biopumping within the sediment was negligible. Therefore the difference between the total oxygen uptake (TOU) in the chamber minus the diffusive oxygen uptake (DOU) of the sediment was adressed to the respiration of the fauna (Glud et al., 1994).

3.1.3.4 In situ radiotracer measurements with the benthic lander LUISE

In situ radiotracer measurements of sulfate reduction in the sediment were carried out with the autonomous benthic lander LUISE (Greeff et al., 1998). The lander lowers six polycarbonate coreliners with a length of 60 cm and 36 mm I.D. into the sediment. One of the coreliners was replaced by a sensor to determine the sediment temperature to a depth of 60 cm. After a preprogrammed time allowing the lander reach the sea floor, three cores were injected vertically with 0.5 ml radiolabelled sulfate diluted in bottom water (~ 150 kBq $^{35}SO_4^{2-}$ per cm core). The dilution allows an even distribution of tracer in the sediment core. The incubation times were 10 to 48 h, longest at the deepest stations because we expected decreasing SRR with increasing water depth.

During ascent and recovery of the lander, additional sulfate reduction may occur. The error due to transient warming and decompression was calculated by injecting the two (when working with temperature sensor) or three remaining cores shortly before ascent of the lander. The incubation time ranged between 2 and 4 h. The data from these short-term incubations reflect the temperature and pressure influence on sediment cores on the background of a short *in situ* incubation. The short-term data were subtracted from the results of the long-term *in situ* incubations. Thus, effects of temperature increase and decompression on the long-term incubated sediment cores during ascent and recovery were corrected (Greeff et al., 1998).

Immediately after recovery of the lander the cores were sectioned and the incubation was stopped. The upper 0-5 cm were sectioned into 1 cm segments, the following 5-15 cm into 2 cm segments, and the remaining core into 5 cm segments. The metabolic activity was terminated by fixing the sediment slices in 20 ml of 20% zinc acetate. The fixed sediment samples were kept at 4° C before processing in laboratory.

3.1.3.5 Laboratory measurements

In order to evaluate potential differences between *in situ* and laboratory rates, sulfate reduction was also determined in the lab using a whole-core $^{35}SO_4^{2-}$ incubation method (Jørgensen, 1978). Three undisturbed subcores (same diameter as the *in situ* cores) were sampled from freshly collected sediment cores obtained by a multiple corer deployed at the same locations as the lander. Immediately after subsampling, the cores were injected horizontally with 10 µl tracer solution (~ 150 kBq $^{35}SO_4^{2-}$ per injection through silicone filled ports at 1 cm intervals). The subcores were incubated for the same time as the *in situ* sediment cores in the dark at *in situ* temperatures. At the end of incubation the cores were sliced and sulfate reduction was stopped in the same way as the cores from the benthic lander LUISE. At all stations *in situ* and laboratory SRR were calculated from two or three replicates (except Stn. 7 and 8 where we only obtained one laboratory and one *in situ* core). Additional cores were taken for sulfate and porosity determination.

All laboratory and *in situ* SRR were determined using a single step acid Cr- II distillation method to volatilize and trap the total reduced sulfur species (Fossing and Jørgensen, 1989). To avoid foaming due to the amount of calcium carbonate (*Mytilus*- and *Modiolus* shells), 6 N HCL was added to the reaction flask instead of 12 N HCL typically used for this reaction. The H_2S evolved from the total reduced inorganic sulfur (TRIS) was precipitated in 5% ZnAc. After distillation, the ZnS suspension was mixed with scintillation fluid (Ultima Gold XR, Packard) and counted in a liquid scintillation counter. Sulfate reduction rates were calculated according to Jørgensen (1978).

3.1.3.6 Sulfate and total reduced inorganic sulfur (TRIS)

Porewater for geochemical investigations was squeezed out of the sediment with a porewater press. Sulfate was measured in zinc-preserved porewaters by non-suppressed ion chromatography (Waters, 100 µl injection volume). The flow rate was 1,0 ml min^{-1} and the eluent was 1mM isophthalate buffer in 10% methanol, adjusted to pH 4,7 with saturated Na-borohydrate solution.

3.1.3.7 Analyses of CNS

Total carbon, nitrogen and sulfur were measured in a CNS-analyser (Fisions NA 1500, Series 2) by flash combustion (e.g. Verado et al., 1990). For determination of organic carbon the samples were weighed into a silver container and pretreated with 6 N HCL to dissolve inorganic carbonate ($C_{total} - C_{organic} = C_{carbonate}$). After drying, the samples were measured the same way as the samples for total CNS determination. Sulphanilamide was used as an analytical CNS-standard.

3.1.3.8 Water column data

Water samples were collected by a rosette water sampler and hydrographic parameters (temperature, salinity and pressure) were simultaneously measured by a CTD (Sea-Bird SBE 19) at Station 1 to 3, 5, 7, 8 along the transect and Stn. H (hydrography station). Oxygen, nitrate, sulfide and methane were measured onboard. Immediately after recovery, the O_2 concentration in the water samples was determined by Winkler titration (Strickland and Parson, 1972). Sulfide was determined photometrically from Zn-preserved samples using the methylene blue method (Cline, 1969). Nitrate was measured after reduction to nitrite with spongy cadmium in samples buffered at pH 8.5 and nitrite was analyzed colorimetrically (Jones, 1984).

3.1.4 Results

3.1.4.1 Sediment description/Shelf stations

The shelf sediments (Stn. 1-4) were typically a light gray, occasionally greenish, soft mud with a superficial fluffy layer or fluffy aggregates (0-2.5 cm) of yellow-brownish color. There were found numerous shells of dominantly *Mytilus galloprovinciales* at Stn. 1 and dominantly *Modiolus phaseolinus* at Stn. 2 and 3 (see Kiseleva, 1981 and Riess et al., unpublished manuscript). Living species were only found in the top 2 cm of sediment. The underlying sediment down to 25 cm depth consisted of gray-brown clayey mud with abundant mussel shells. At Stn. 4, the sediment surface was a gray, soft mud at the sediment surface with a thin oxidized layer (yellow-brownish color) and empty shells of *Modiolus phaseolinus*. At this water depth (130 m) meiofauna was predominant. Below 25 cm depth at Station 1-4 the sediment was a gray, sometimes greenish clay with broken shells of *Mytilus* and *Modiolus*. In the gray subsurface sediment of Stn. 4 between 25 and 30 cm depth broken shells of fresh water molluscs (*Dreissena* spp.) were observed. Riess et al. (unpublished manuscript) found a significant decrease of macrofaunal biomass from 2000 g m^{-2} at Stn. 1 to 150 g m^{-2} at Stn. 3.

The sediment of station 0 near the oil drilling platform Gloria differed from that of the transect stations. A brownish, oxidized fluffy layer covered a soft black mud which reached a depth of 10 cm. Below this depth the sediment was more consolidated and consisted of clayey mud of different shades of black and gray mud with abundant shells of *Mytilus* spp. The benthos was not identified at this station.

3.1.4.2 Slope and deep sea stations

Laminated sediments were observed on the slope at Stn. 5 (181 m water depth) and at deeper stations. Brownish-gray or black fluff (0-3 cm) overlay a black soft mud (1-5 cm), which became more greenish towards 10 cm depth. The sediment structure and color was different between lander and multiple corer sediment cores. Below 10 cm sediment depth, the cores became more heterogeneous consisting of soft laminated sediment with thin layers of a gray clay penetrated with shells at 26 and 34 cm below the sediment surface. Porosity decreased significantly below 20 cm (end of the varved sediment) from 0.86 to 0.68 at 45 cm depth.

At Stn. 6, 7 and 8 we observed finely laminated coccolith ooze (Ross and Degens, 1974; Hay, 1988 and Lyons, 1991) covered by a thin (0-1.5 cm) dark-gray fluffy layer, except Stn. 7 which had a 2-3 cm thick whitish, gelatinous surface layer. The whole cores had a sulfidic smell. At Stn. 6 and 7, the light and dark laminated sediment was very soft but cohesive and persisted over the whole core length of 55 cm. The sediment cores from Stn. 8 also consisted of light and dark laminae, but showed a sharp boundary at 30 cm sediment depth. Below this depth, a non-laminated dark-brown layer of organic-rich mud (water content between 80 and 83%) with an organic carbon content up to 13% (dw) occurred.

3.1.4.3 Hydrographic conditions

CTD data from Stn. 5 (Fig. 2), depict the stratified water column. Temperature was constant (19.6° C) to 22 m water depth, then dropped steeply to reach a minimum of 7.1° C at 70 m (see also Tolmazin, 1985a). Salinity increased from 18.3 ‰ in the surface water to 20.6 ‰ at 150 m water depth. Maximum concentrations of oxygen (328.9 µmol l^{-1}) appeared at 26 m water depth, then decreased to the detection limit at 140 m water depth. Nitrate had a broad maximum of 10.4 µmol l^{-1} at 90-100 m water depth and dropped to zero at 140-150 m water depth.

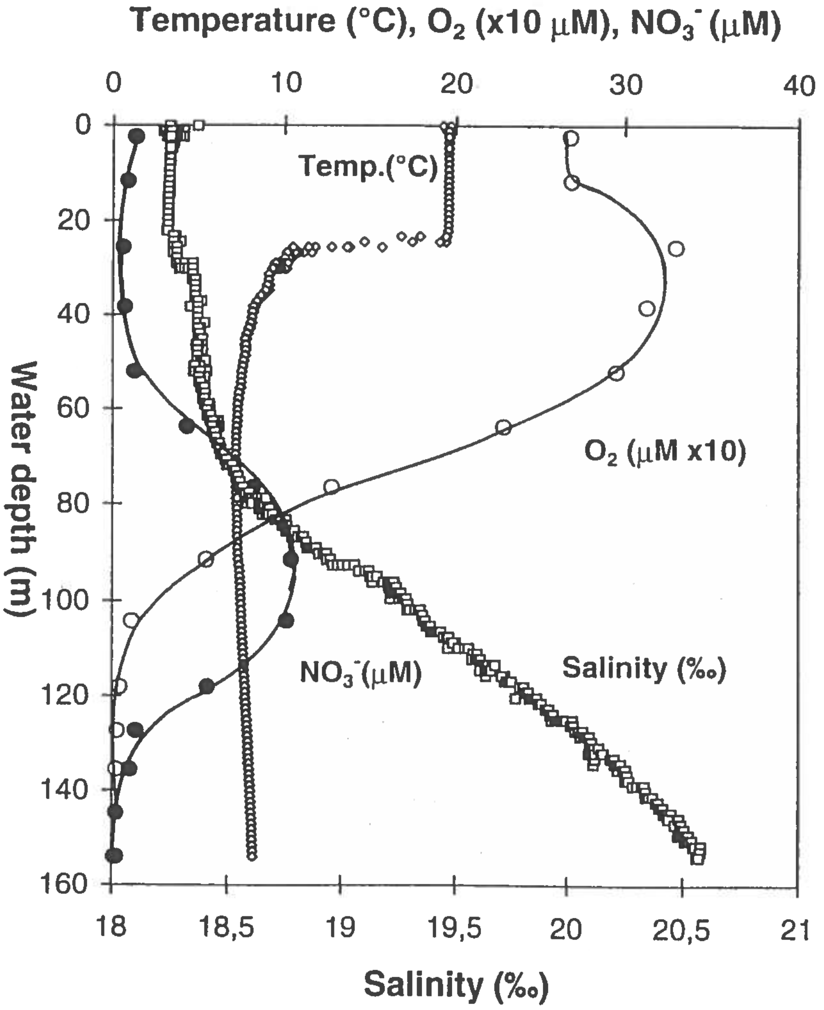

Fig. 2: Hydrographic profiles at Stn. 5 (181 m) where the sea floor was below the oxic zone.

3.1.4.4 Oxygen uptake (TOU and DOU) in shelf sediments

Because of the dense pavement of mussels on the shelf, only a few, incomplete *in situ* microprofiles of oxygen were obtained in sediments of Stations 1 to 4. Oxygen in the near-bottom water was detectable only at Stations 1 to 4 (62 to 130 m) whereas at Stn. 5 (181 m) no traces of oxygen were detectable. Electrode readings from the profiling and the chamber lander (data not shown) indicated that at Stn. 4 oxygen content was extremely low at a few µmol l^{-1} or zero indicating that the transition zone between oxic and anoxic conditions in the near-bottom water was little below 130 m but above 181 m water depth (Table 1 and Fig. 2). Diffusive (DOU) and total (TOU) oxygen uptake rates were calculated. The DOU decreased from 11.9 (Stn. 1) to 2.3 mmol m^{-2} d^{-1} (Stn. 3). DIC-fluxes were similar to the total oxygen fluxes at Station 1 and 2. The total oxygen uptake rates were 2-3 fold higher than the diffusive oxygen uptake rates. Both total and diffusive oxygen uptake rates decreased with increasing water depth (Table 2).

Table 2. Total (TOU) and diffusive (DOU) oxygen uptake and dissolved inorganic carbon (DIC) fluxes at shelf and slope stations along the transect (n.d. = no data).

Station/ water depth (m)		**TOU ($mmol\ m^{-2}\ d^{-1}$)**	**DOU ($mmol\ m^{-2}\ d^{-1}$)**	**DIC-flux ($mmol\ m^{-2}\ d^{-1}$)**
1	62	39.8	11.9	37.7
2	77	11.1	5.8	10.4
3	100	4.3	2.3	n.d.
4	130	n.d.	n.d.	n.d.
5	181	0	0	n.d.

3.1.4.5 Sediment sulfate reduction rates

Sulfate reduction was measured in both shipboard and *in situ* incubations to evaluate potential differences caused by transient warming, decompression, and other factors associated with sediment handling during laboratory incubations. Sulfate reduction rates are presented in Fig. 3, 4 and 5. The fluffy surface layer of sediment from Stn. 1 obtained by the benthic lander LUISE was slightly disturbed, at Stn. 2 and 3 the surface layer was lost, whereas subcores from the multiple corer were largely undisturbed.

The profiles show several main characteristics: (a) SRR in shelf sediments are significantly higher than in deep basin sediments. (b) In shelf and upper slope sediments the peak rates were found below the sediment surface, whereas the sulfate reduction maximum in deep basin sediments was found at the sediment surface. (c) SRR rates decreased with sediment depth and with water depth. (d) Except Stn. 5 and 6 and 7 *in situ* SRR were significantly lower than shipboard measured SRR.

Laboratory and *in situ* incubated sediment cores from the shelf had maximum sulfate reduction at 1-3 cm below the sediment surface (Fig. 3 and 4). Laboratory maxima ranged from 14 (Stn. 3) to 41 nmol $cm^{-3}\ d^{-1}$ (Stn. 0, Fig. 3). *In situ* rates showed average values of 5 (Stn. 3) and 14 nmol $cm^{-3}\ d^{-1}$ (Stn. 4). A clear difference was found between laboratory and *in* *situ* incubations at Stn. 1, 2 and 3. Sulfate reduction rates differed up to 4-fold (Fig. 4). Station 5 revealed much higher SRR than the neighbouring stations 4 and 6 with *in situ* rates of 43 nmol cm^{-3} d^{-1} and laboratory measured rates of 23 nmol cm^{-3} d^{-1}. Below the chemocline (Stn. 6-8), *in situ* SRR at the sediment water interface showed mean values of 4-10 nmol cm^{-3} d^{-1}, whereas laboratory rates ranged from 9-20 nmol cm^{-3} d^{-1} (Fig. 5).

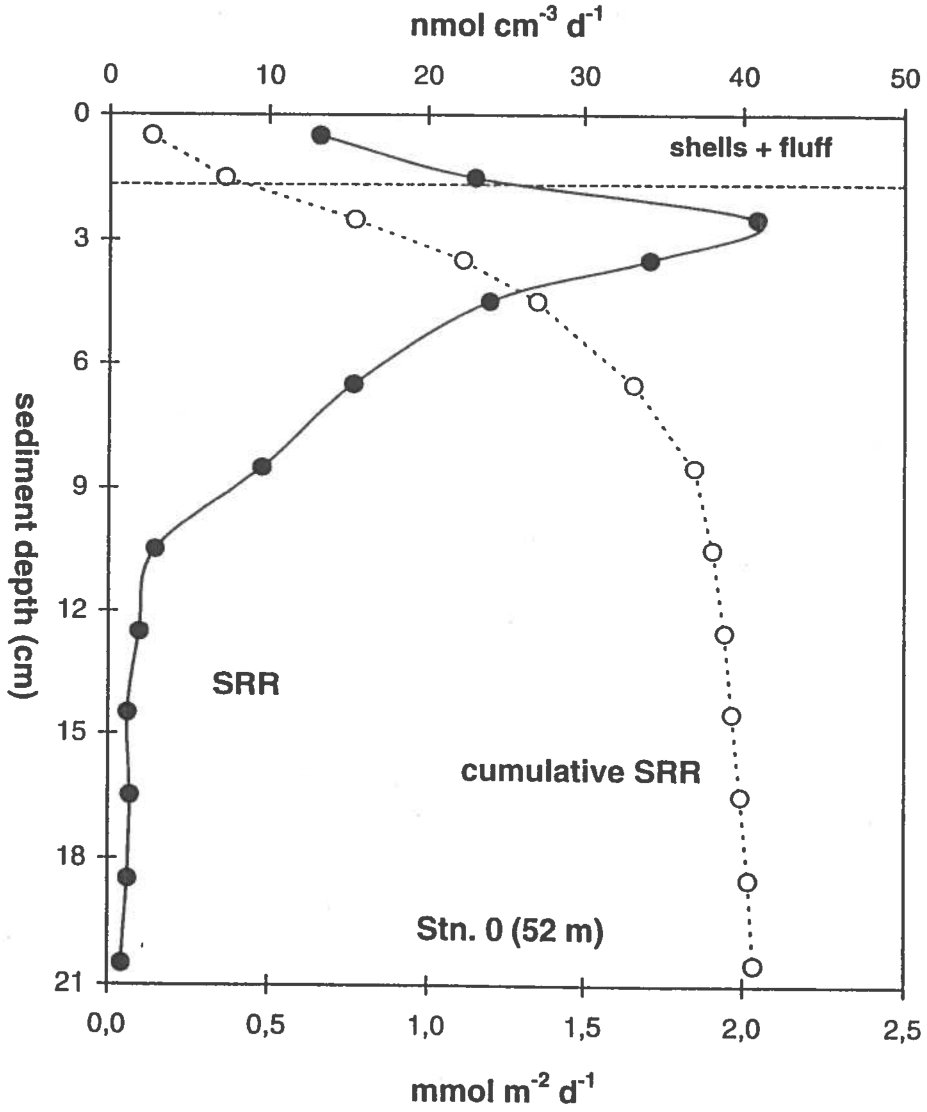

Fig. 3: Sulfate reduction rate and cumulative SRR vs. sediment depth at Stn. 0 on the Romanian shelf near the oil drilling platform Gloria.

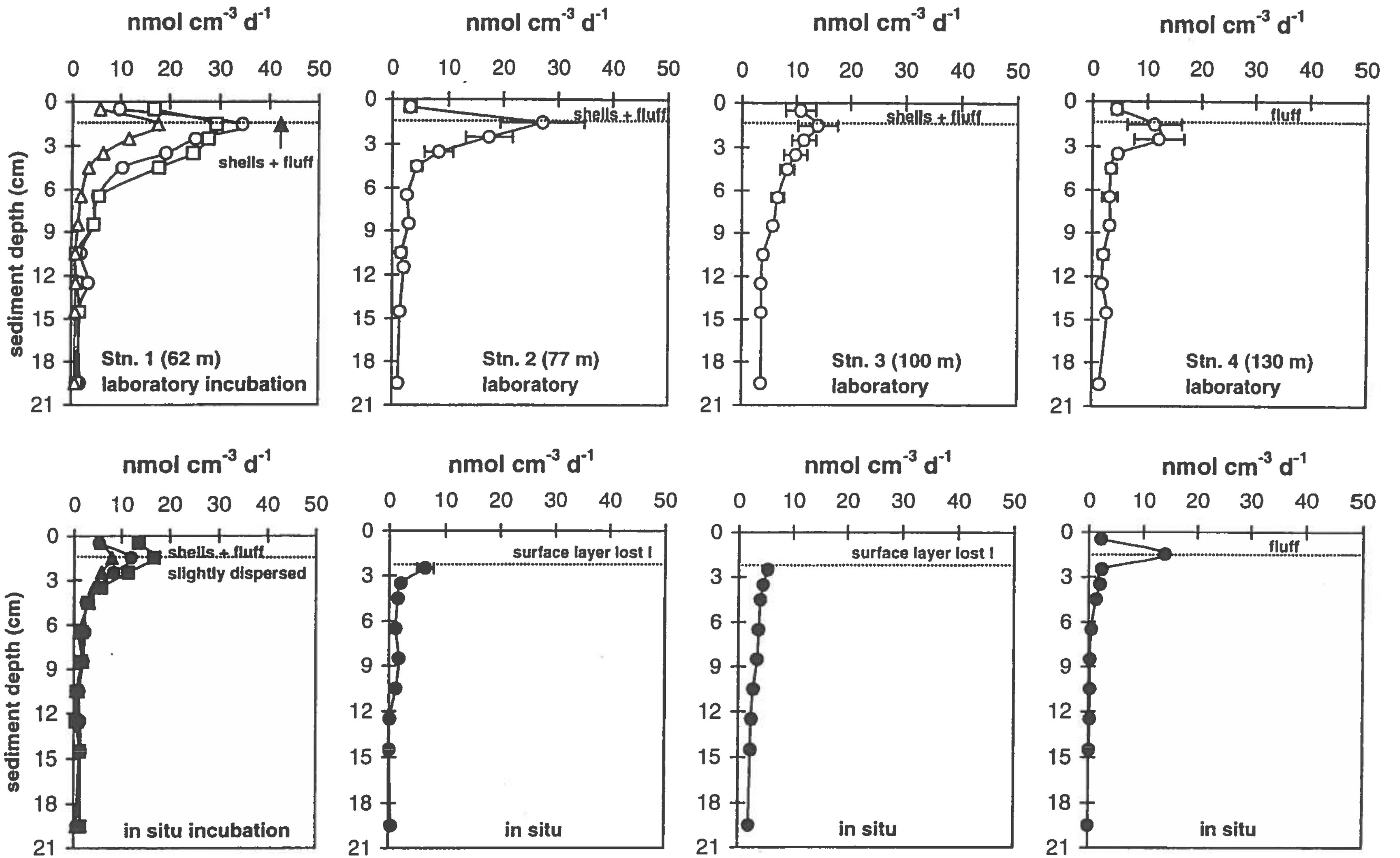

Fig. 4: Sulfate reduction rates vs. sediment depth from Stn. 1-4. At Stn. 1 data from all three sediment cores are shown. *In situ* and laboratory profiles at Stn. 2 and 3 and laboratory profile at Stn. 4 were obtained in triplicate. Error bars show standard deviations of the mean (n=3). At Stn. 4 (*in situ* incubation) a mean value of two sediment cores is presented.

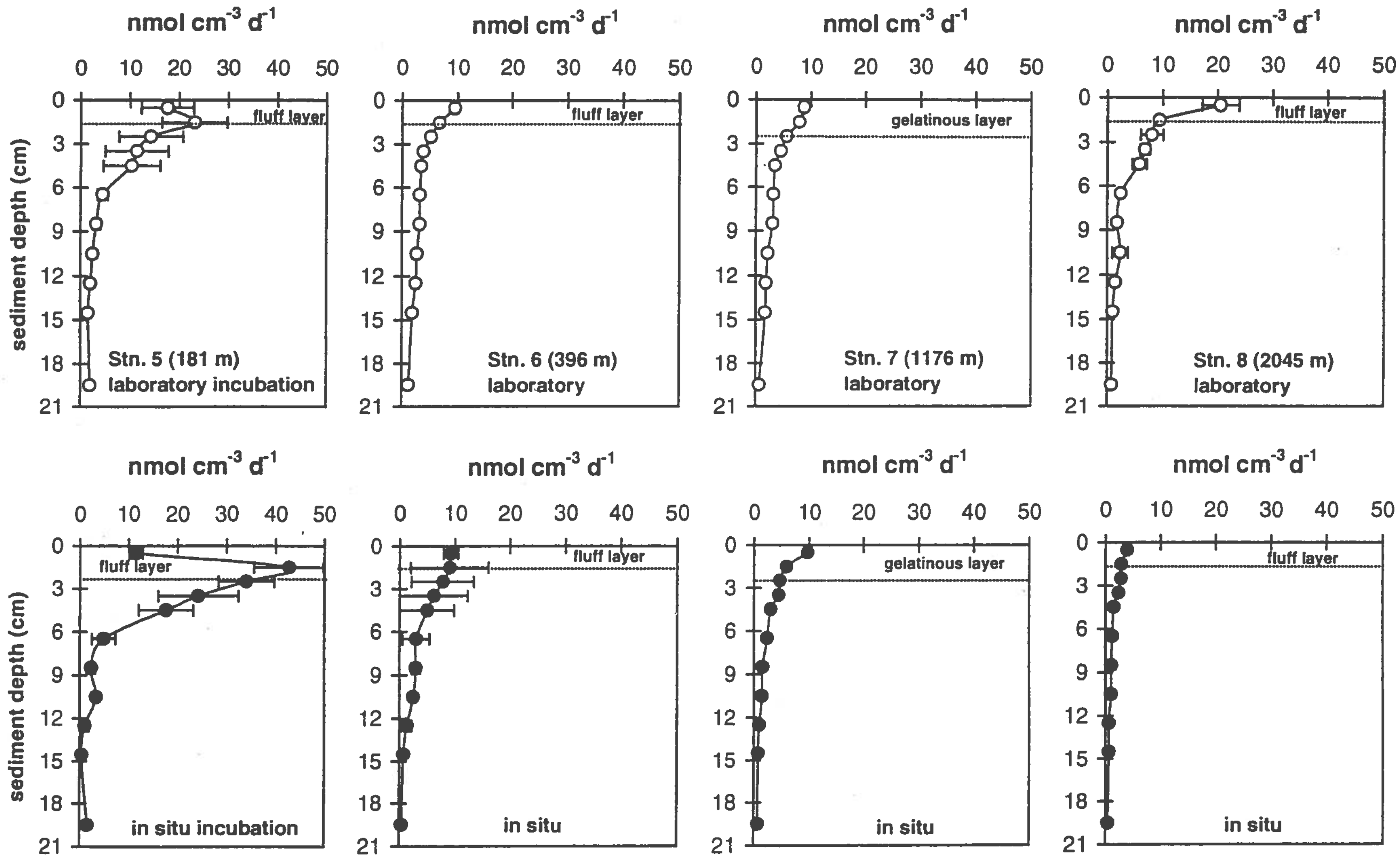

Fig. 5: Sulfate reduction rates vs. sediment depth from Stn. 5-8. Profiles of Stn. 5 (*in situ* and laboratory), *in situ* incubated cores of Stn. 6 and laboratory cores of Stn. 8 were obtained in triplicate. Error bars show standard deviations of the mean (n=3). Laboratory incubations of Stn. 6 and *in situ* incubations of Stn. 7 were determined of a mean value of two sediment cores. Laboratory incubation of Stn. 7 and *in situ* incubation of Stn. 8 are represented by one core.

Depth integrated rates of SRR between 0 and 15 cm (Fig. 6) measured shipboard showed a significant decrease from 1.97 mmol m^{-2} d^{-1} at 52 m depth (Stn. 0 oil drilling platform Gloria) to 0.61 mmol m^{-2} d^{-1} (Stn. 4, shelf edge) at 130 m depth on the shelf break, *in situ* rates decreased from 0.49 (Stn. 1) to 0.24 mmol m^{-2} d^{-1} (Stn. 4). The areal rates at the oxic-anoxic transition (Stn. 5) were significantly higher 1.04 mmol m^{-2} d^{-1} (laboratory incubation) and 1.54 mmol m^{-2} d^{-1} (*in situ* incubation). Areal rates of sulfate reduction in the sulfidic zone at Stn. 6 and 7 were almost identical (0.42-0.56 mmol m^{-2} d^{-1}) except the areal rates of *in situ* and laboratory incubations at Stn. 8 (0.22-0.68 mmol m^{-2} d^{-1}). Below 12-15 cm sediment depth, SRR decreased to 3 nmol cm^{-3} d^{-1} or less in all sediment cores from Stn. 0 to Stn. 8. Sulfate reduction was not limited by sulfate in the top 15 cm, because there was only little decrease in sulfate concentrations (data not shown).

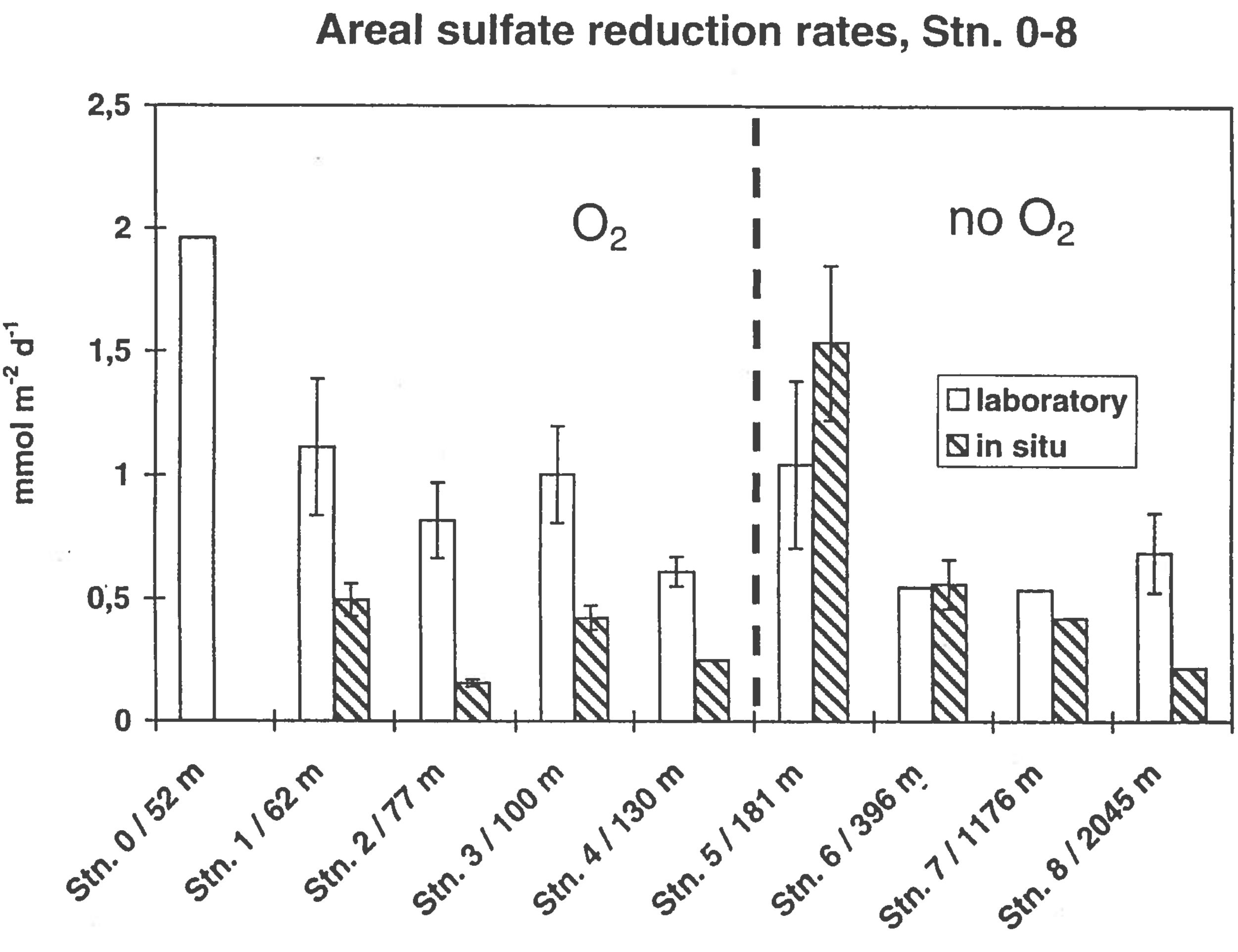

Fig. 6: Depth integrated rates of sulfate reduction between 0 and 15 cm from transect stations 0-8. Error bars show standard deviations of the mean (n=3). Areal rates without error bars were calculated from mean values of two cores (Stn. 0, 4, 6 and 7) or from only one core (laboratory Stn. 7 and *in situ* Stn. 8).

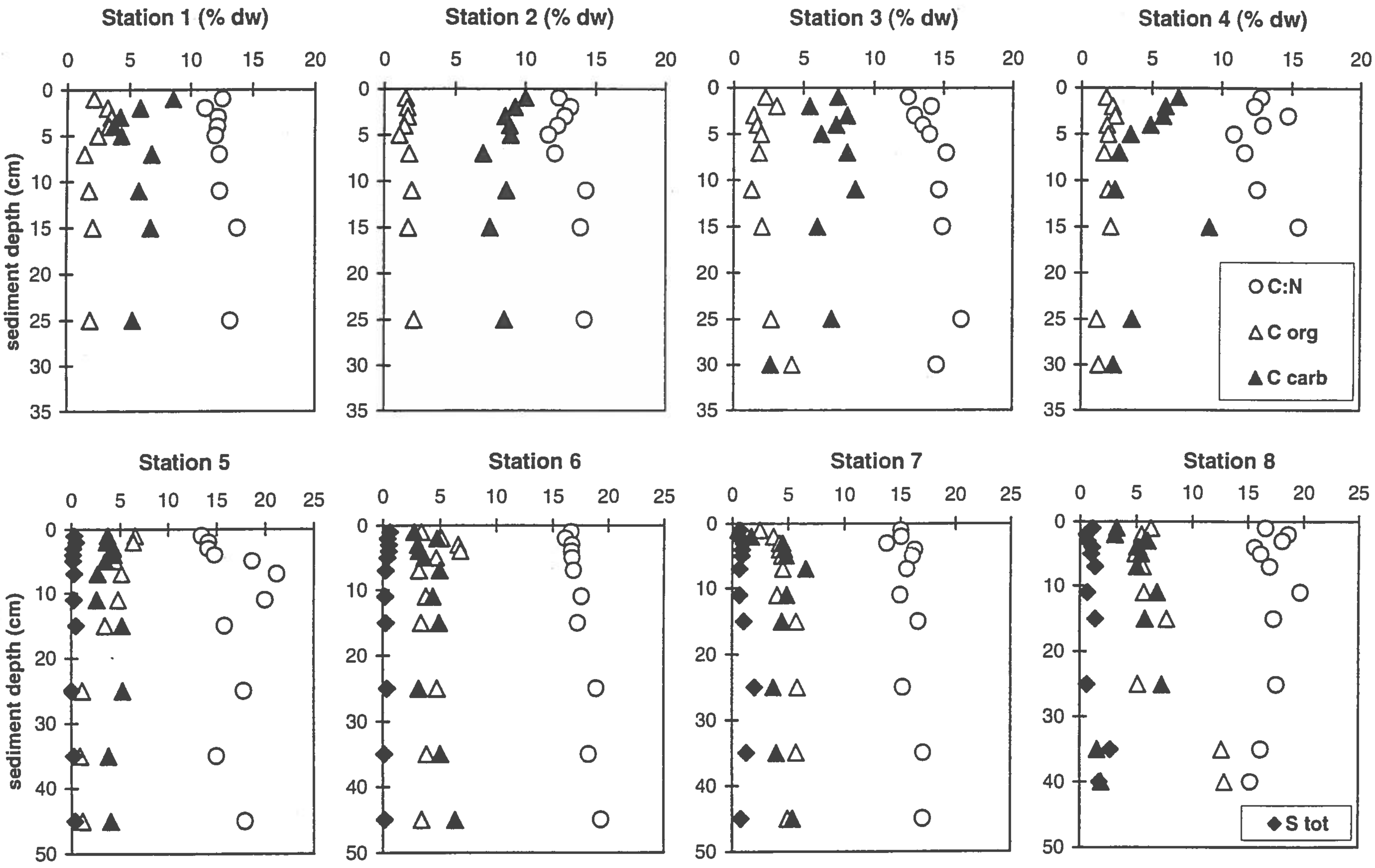

Fig. 7: Concentrations of C_{org}, $C_{carbonate}$, S_{total} and atomic C_{org}:N ratios vs. sediment depth of Stn. 1 to 8. The data are shown in % dry weight.

3.1.4.6 Carbon, sulfur and nitrogen

Depth profiles of organic carbon, carbonate carbon, total sulfur and atomic ratios of C_{org}:N are presented for Stn. 1-8 (Fig. 7). At the shelf stations 1-4 a significant amount of carbonate carbon was measured (up to 10% dw at Stn. 2) due to abundant *Mytilus* spp. and *Modiolus* spp. shells at the sediment surface. Carbonate carbon decreased significantly in surface sediments at Stations 1 and 4. Organic carbon concentrations varied from 1 to 3% (dw). In contrast to the shelf stations, the C_{org} concentrations were significantly higher in the sediment of Stn. 5-8 and achieved peak values of ~ 13% dw at a depth of 35-40 cm at Stn. 8.

In comparison to Stn. 1-4, where total sulfur concentrations were below 0.3 % (dw) or at the detection limit, significant sulfur concentrations were measured at Stn. 5 to 8. The average sulfur concentrations measured over the whole sediment cores of Stn. 5 to Stn. 8 varied between (0.2 and 1.2 % dw). Highest sulfur concentrations (2.7% dw) were found at Stn. 8 at 35-40 cm depth. Depth profiles of nitrogen concentrations showed average values of 0.14% dw to 0.3% dw (data not shown). Atomic ratios of C_{org}:N were constant with sediment depth except at Stn. 5, where the ratio increased at 5 cm depth from 15 to 20 (Fig. 7).

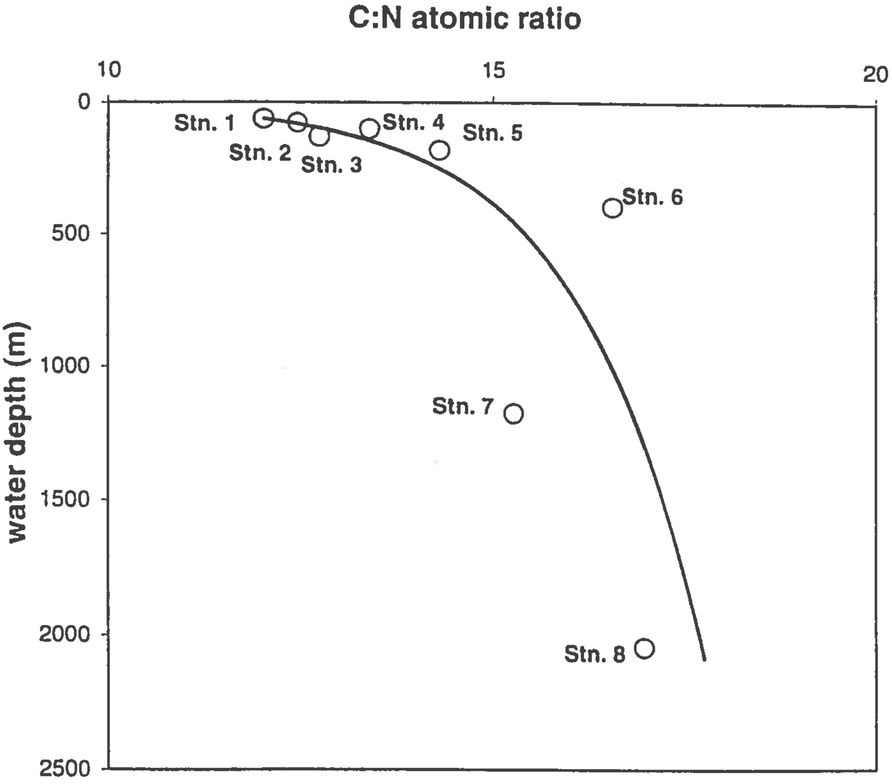

Fig. 8: Atomic C_{org}:N ratios (mean for 0 to 5 cm sediment depth) of Stn. 1-8 vs. water depth. The curve shows an exponential fit through the data. The ratios were calculated from C_{org} and N values obtained by CNS analysis.

A plot of average atomic C_{org}:N ratios of Stn. 1 to Stn. 8 versus water depth revealed an increase from 12 to 17 (Fig. 8). In Figure 9, C_{org} and total sulfur data (obtained by CNS analysis) were plotted for stations above and below the chemocline. The two data sets differ by a substantially lower sulfur to carbon ratio in the oxic shelf sediments in comparison to the deeper anoxic stations.

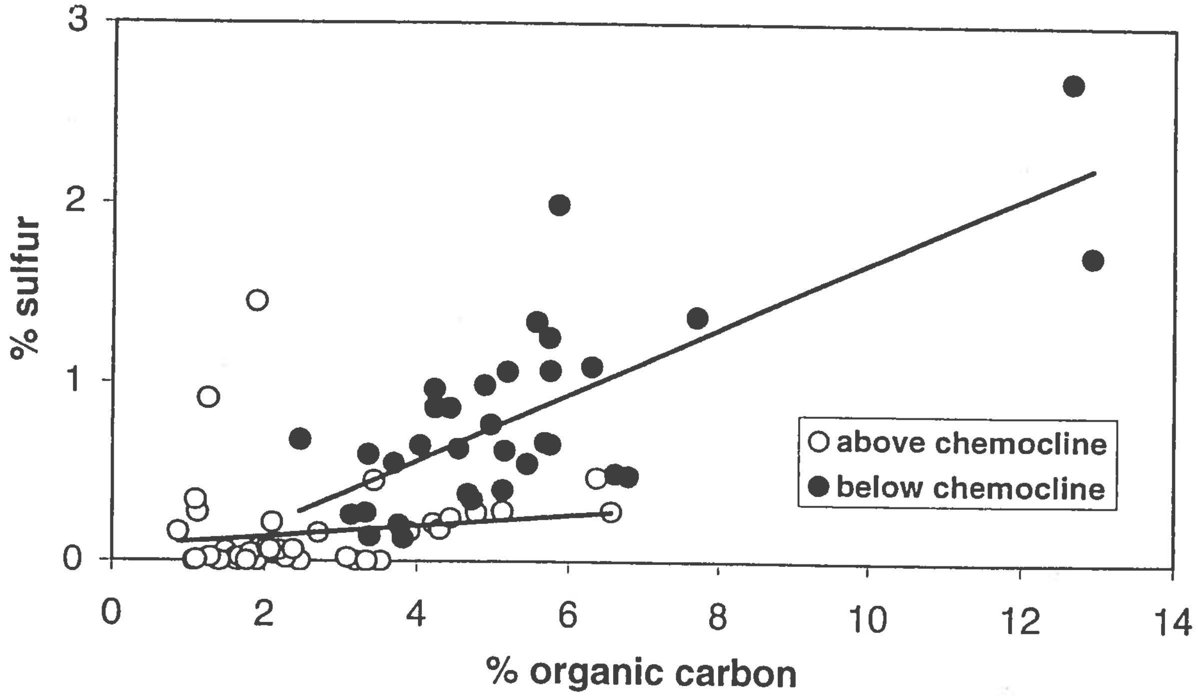

Fig. 9: Organic carbon and total sulfur concentrations of Black Sea sediments above and below the chemocline (data from Stn. 1-8). The solid lines show linear regressions through the two data sets. The data were obtained by CNS analysis.

3.1.5 Discussion

3.1.5.1 In situ and laboratory measurements of sulfate reduction

During this cruise it was the first time *in situ* SRR were obtained from Black Sea sediments. A comparison of laboratory measured SRR with rates of *in situ*-incubated sediment cores, showed significant differences. Areal *in situ* SRR were generally lower than laboratory measured SRR, except areal rates at Stn. 5 and 6. The differences are most significant at the shelf stations where *in situ* incubations were 58-80% lower than the laboratory shipboard incubations (Fig. 5) which is may be due to temperature effects on laboratory cores during recovery, and other factors associated with sediment handling during laboratory incubations, or the disturbance of the loose texture of the sediment surface at Stn. 2 and 3 by the benthic lander. Differences between *in situ* and laboratory incubations at Stations 6-8 below the chemocline are in a range from 4 to 32%. A long incubation time and a relatively analogous quality of organic matter below the chemocline is may be responsible for lesser variance between laboratory and *in situ* cores. Except Stn. 2 and 3 where the surface layer was obviously disturbed it can be assumed that the differences between *in situ* and laboratory incubations at the other transect stations were not caused by sampling of the benthic lander but most likely by recovery and handling artefacts of laboratory cores.

The explanation for differences between *in situ* and shipboard measured rates of sulfate reduction are still not clear (Jannasch and Wirsen, 1982; Jannasch and Taylor, 1984; Parkes et al., 1995). Recent work on pressure dependence of sulfate reduction on the continental slope off North Carolina (Martens et al., 1998) or Angola (Ferdelman et al., in press) at water depths of 750 and 3500 m respectively, showed no systematic differences between *in situ* and shipboard incubations. In comparison, the sampling stations on the Romanian shelf had water depths of P 130 m only, and pressure effects are, therefore, not likely, whereas it is quite possible that differences at Stn 7 and 8 (1176 and 2045 m water depth) could be caused by decompression and temperature increase during recovery.

Temperature, is the second factor which may enhance sulfate reduction in subcores for shipboard incubations. The exposure time to surface water and atmospheric temperature of subcores for shipboard incubations was 1-2 h during retrival of the multiple corer and subsampling. These subcores were subsequently preincubated for temperature adjustment in the dark at *in situ* temperature. In comparison to the doubling time (11-25 h) of mesophilic sulfate reducers (Widdel and Pfennig, 1981; Brysch et al., 1987 and Lien et al., 1998), exposure time is probably too short to increase bacterial population significantly by temperature increase.

Another reason for widely differing *in situ* and laboratory SRR at shelf Stations 2 and 3 is the loose texture of the sediment which is particularly susceptible for disturbance during a sampling procedure by a benthic lander, like LUISE. The most likely explanation is, that the surface layer of the sediment at Stn. 2 and 3 was suspended by the bow wave of the lander as it touched the sea floor. In comparison to the multiple corer sediment cores about 1 to 2.5 cm surface sediment was slightly dispersed (Stn. 1) or lost (Stn. 2 and 3). The *in situ* sulfate reduction rates at Stn. 2 and 3 showed no subsurface maximum at 1-3 cm sediment depth (Fig. 4).

The sinking rate of ~ 1.0 m s^{-1} with 12 glass spheres of the lander LUISE (Greeff et al., 1998) was most likely too fast and the impact on the sea floor caused a serious disturbance of the surface sediment with its loose texture. To reduce this effect as far as possible, the benthic lander was equipped with three further glass spheres to increase the bouyancy and to obtain a lower sinking rate of 0.7 m s^{-1}. This seems to be a more suitable sinking rate because the sediment surface of Stn. 1 was only slightly dispersed and no differences in stratification of the surface layers between subcores from the multiple corer (we assume undisturbed coring) and sediment cores obtained by the lander LUISE at Stn. 4 were observed. Comparing the sediment cores from Stn. 5 to 8 there were no differences in stratification between multiple corer and lander cores may be due to the cohesiveness of the laminated sediments.

Station 5 does not fit with the overall trend of lower *in situ* than laboratory rates (Fig. 6). The differences between *in situ* and laboratory rates could be explained by lateral heterogeneity, as indicated by the different structures of the upper 10 cm of sediment obtained by the multiple corer and the lander. The lander cores had a black fluffy layer of up to 3 cm thickness (Fig. 5) and a clayey, greenish underlying mud with laminated sediment below a sediment depth of 10 cm, whereas the sediment from the multiple corer had a gray-brownish 1-2 cm thick fluffy layer with laminated sediment immediately below. Because of sediment heterogeneity there are probably also differences in organic matter composition between sampling site of the lander and the multiple corer which may cause a significant difference in SRR.

Sediment from Stn. 6-8 was very homogeneous, the surface layers were not disturbed by either sampling procedure, and we observed only little difference between *in situ* and laboratory SRR. At Stn. 8 only one *in situ* core was obtained by the benthic lander, with an areal rate which was 3-fold lower than the laboratory rate of 0.69 mmol m^{-2} d^{-1}. We assume the difference is due to effects of increasing temperature and decompression on sediment cores during recovery. It is also known that sediment is very similar at different sites in the anoxic basin (Lyons, 1991) but apparently the quality of substrate availability at the sea floor may differ between stations at the same depth.

3.1.5.2 Comparison of sulfate reduction rates

Sulfate reduction rates in Black Sea sediments measured in this and during earlier studies are compared in Table 3. The stations were selected according to comparable water depth and from the western part of the Black Sea. Sulfate reduction was measured by Sorokin (1962) who mixed $^{35}SO_4^{2-}$ into the sediment. His results obtained from deep basin sediments were in the range of 0.04 to 0.68 mmol m^{-2} d^{-1}. These SRR of three locations with comparable water depth in the north western part of the Black Sea were similar to our results obtained at Stn. 5, 6 and 8 (Table 3).

Later measurements from locations in the western part of the Black Sea were presented by Vaynshteyn et al. (1985) and Lein et al. (1986 and 1990). Their measured rates in surface sediments were partly higher than our data obtained from laboratory and *in situ* incubations in the northern part of the Romanian shelf (Stn. 0-4). In sediments below the chemocline they obtained peak rates of < 2 nmol cm^{-3} d^{-1} at the sediment surface. By comparison with our results from deep water stations their rates were up to 4-fold lower. Lein et al. (1986) investigated sediment on the Bulgarian shelf with areal rates in a range of 0.02 to 10 mmol m^{-2} d^{-1}. Albert et al. (1995) measured sulfate reduction in sediments from two stations in the central part of the Black Sea and found a maximum of about 20 nmol cm^{-3} d^{-1} in the fluffy layer. These rates are consistent with our rates in the fluffy layer of three cores in a range from 19 to 27 nmol cm^{-3} d^{-1} at Stn. 8 (2045 m water depth). The mean areal rate of Albert et al. (1995) of 1.37 mmol m^{-2} d^{-1} (0-20 cm) is 2-fold higher than our laboratory areal rate (0-15 cm) of 0.68 mmol m^{-2} d^{-1} and about 6-fold higher than our *in situ* depth integrated rate (0-15 cm) of 0.22 mmol m^{-2} d^{-1} at Stn. 8 (Table 3).

Table 3. Comparison of areal sulfate reduction rates (0-15 cm) obtained in this study (all data are laboratory rates) with previously published rates. Means are shown.

Water depth (m)	*This study* Stn.-No.	mmol m^{-2} d^{-1}	*Sorokin (1962)* Stn.-No.	mmol m^{-2} d^{-1}	*Vaynshteyn et al.,(1985)* Stn.-No.	mmol m^{-2} d^{-1}	*Lein et al., (1986)* Stn.-No.	mmol m^{-2} d^{-1}	*Lein et al., (1990)* Stn.-No.	mmol m^{-2} d^{-1}	*Albert et al., (1995)* Stn.-No.	mmol m^{-2} d^{-1}
16							5	0.02-10				
52	0	1.96										
54					598	1.15						
60					590	4.05						
62	1	1.11										
77	2	0.82										
86					568	0.81						
100	3	1.00										
130	4	0.61										
180	5	1.04	4772	2.12								
250			4773	1.42								
396	6	0.54										
1176	7	0.53										
1400									842	0.22		
1450									852	0.23		
2000			4750-4753	0.04-0.68								
2045	8	0.68										
2100					584	0.02					BS 2 - 2	1.37
2141									806	0.18		

3.1.5.3 The importance of sulfate reduction as an anaerobic mineralization pathway in Black Sea sediments

The total oxygen uptake (TOU) measured *in situ* by a benthic chamber lander was used for the quantification of mineralization in the oxic shelf sediments. We make the assumption that TOU represents the total C_{org} consumption in sediments is approximately equivalent to the total organic carbon oxidation to ΣCO_2 (Canfield et al., 1993, Glud et al., 1994, Ferdelman et al., in press) in high bottom water O_2 concentrations.

In addition to the direct consumption of oxygen by organotrophic respiration, TOU also represents oxidation of reduced compounds from anaerobic processes (Jørgensen 1982; Canfield et al., 1993). Assuming that the burial of reduced sulfur compounds, and the benthic flux of H_2S are negligible, the depth integrated SRR can be compared with TOU-fluxes and the importance of sulfate reduction in total carbon oxidation can be calculated (Table 4). The role of denitrification in sediments within the nitrate maximum zone between 90 and 100 m water depth (Fig. 2) is not known. However, we assume that the pathway of denitrification is negligible at the Romanian shelf because nitrate concentrations are very low as in many other coastal environments (Sørensen et al., 1979).

Aerobic mineralization was dominating over sulfate reduction on the Romanian shelf where the water column was oxic to a depth of 130 m. At Stations 1 and 2 the degradation of organic material via sulfate reduction contributed little to total carbon mineralization (Table 4) although these stations had the highest sulfate reduction rates. With increasing water depth sulfate reduction became relatively more important although the rates decreased. The availability and quality of organic matter which reaches the sea floor for bacterial sulfate reduction became worse because of its progressing decomposition in the water column (Suess, 1980, Jørgensen, 1996). The proportion of sulfate reduction in comparison to total carbon mineralization increased from 5.6 (Stn. 1) to 46.5% at Stn. 3 (Table 4). Because of decreasing oxygen concentrations sulfate reduction is increasing and organic matter is more and more mineralized by anaerobic bacterial processes. At Stn. 4 the importance of sulfate reduction in total carbon oxidation can only be estimated because oxygen was present in very low concentrations (≤ 5 µmol l^{-1}) no DOU and TOU fluxes could be calculated. Instead of macrofauna, a high density of nematodes were present in the sediment (Riess et al., unpublished manuscript) which also contributed to total carbon oxidation. Station 4 had still no sulfide-flux out of the sediment, which means that reduced sulfur compounds were reoxidized by oxygen, iron-, and manganese oxides.

Table 4. Changes of total oxygen uptake (TOU) and sulfate reduction rates (SRR) within the transect from Stn. 1 to 8. The importance of sulfate reduction (SRR % of total remineralization) was estimated for Stn. 4-8, n.d. = not determined).

Stn.- No.	**TOU (mmol m^{-2} d^{-1})**	**SRR (mmol m^{-2} d^{-1}) (*in situ* / laboratory)**	**SRR (% of total remineralization)**
0	n.d.	1.97 (laboratory)	n.d.
1	39.8	0.49 – 1.11	5.6
2	11.1	0.16 – 0.82	14.7
3	4.3	0.42 – 1.00	46.5
4	n.d.	0.25 – 0.61	~ 60 – 80
5	n.d.	1.54 – 1.04	~ 90 – 100
6	n.d.	0.56 – 0.54	~ 100
7	n.d.	0.42 – 0.54	~ 100
8	n.d.	0.22 – 0.68	~ 100

The difference between TOU and carbon oxidation coupled to sulfate reduction corresponds to carbon oxidation by oxygen respiration, Mn reduction and Fe reduction. For stations 1-4, sediment incubations were performed during the cruise to estimate the contributions of Mn and Fe reduction using the approach of Canfield et al. (1993) and Thamdrup and Canfield (1996). These incubations showed that sulfate reduction was the only significant carbon oxidizing process below 1 cm depth in the sediments (B. Thamdrup, pers. comm.) Above this depth, both Mn and Fe oxids were available in high concentrations, and could serve as terminal electron acceptors. The exact quantification of these respiration in the surface sediment is hampered by the spatial resolution of the assay, and by carbonate precipitation which precluds the determination of total carbon oxidation rates from the accumulation of dissolved inorganic carbon. Preliminary calculations indicate that Mn and Fe reduction together could be of roughly similar importance to carbon oxidation as sulfate reduction at Stn. 1-3 and half of the contribution from sulfate reduction at Stn. 4 (B. Thamdrup, pers. comm.). Thus, oxygen appears to be the most important electron acceptor at Stn. 1 and 2. The presence of H_2S in the pore water at deeper stations indicates that Mn oxides and poorly crystalline Fe oxides are absent and Mn and Fe reduction are therefore not likely to be of significance in carbon oxidation there.

Station 5 does not fit to the trend of decreasing SRR due to increasing water depth and revealed SRR just as high as the rates measured at the shelf. In this water depth (181 m) we found anoxic conditions. In contrast to the shelf stations where oxygen respiration is the main process for organic matter oxidation, sulfate reduction at Stn. 5 was not suppressed any more by O_2 and SRR rose up significantly. At this station a sulfide-flux out of the sediment of 0.23 mmol m^{-2} $d^{-1}$was modeled which is significantly lower than the sulfate reduction rate of 1.54 mmol m^{-2} d^{-1}. Consequently, a major part of H_2S produced by sulfate reduction must have been precipitated by Fe or Mn (mainly FeS and FeS_2).

In comparison to Stn. 5, SRR decreased to a third at Stn. 6 (396 m water depth), may be caused by lower quality and smaller amount of available organic matter (Suess, 1980; Jørgensen, 1996). A maximum in water column SRR occurred within 200 and 300 m water depth at station BS 2 –2 (Albert et al., 1995) and contributes to a decreasing quality of organic carbon which reaches the sea floor below the chemocline. Additionally increasing atomic C_{org}:N ratios below the periphery from 12 to 17 (Fig. 8) confirms this theory.

Below the chemocline (< 200 m) sulfate reduction is the dominant mineralization process (Jørgensen et al., 1991; Jannasch, 1991 and Lein and Ivanov, 1991). Laboratory SRR at Stn. 6, 7 and 8 were comparable. The environment seems to be more stable than on the shelf and quality and amount of organic material probably does not change very much between 400 and 2000 m. At these stations a permanently H_2S-flux out of the sediment was modeled, which fits very well to the SRR at Stn. 7 (sulfide efflux: 0.49 mmol m^{-2} d^{-1}) but is lower at Stn. 6 (sulfide efflux: 0.27 mmol m^{-2} d^{-1}) and a sulfide efflux of 0.17 mmol m^{-2} d^{-1} at Stn. 8 (J. Zopfi, pers. comm.). At Stn. 8 the sulfide efflux is comparable to the *in situ* SRR of 0.22 mmol m^{-2} d^{-1}.

3.1.5.4 Carbon, sulfur, nitrogen relationships

Atomic ratios of C_{org}:N increased from 12 in oxic shelf sediments to 17 in anoxic deep water sediments (Fig. 8). In comparison to the deep basin, C_{org} and N concentrations at the shelf were 2-3-fold lower that is indicative of the ability of organic matter reaching the sediment (Fig. 7). A part of the organic detritus was mineralized in the water column (Albert et al., 1995) which results in a rapid increase of the atomic C_{org}:N ratio within the transition zone. The main increase occurred between Stn. 5 and 6 (Fig. 8). High concentrations of C_{org} and N in the anoxic sediments are an evidence for burial of organic carbon and leads to the conclusion: organic matter that reaches the sea floor below the chemocline, is only in a small amount available for nutrient regeneration by sulfate reduction.

The burial ratio of organic carbon to reduced sulfur in anoxic sediments varies significantly in different marine environments (Berner and Raiswell, 1983). In the Black Sea carbon and sulfur conditions plotted for Stn. 1-8 define two different environments of deposition depending upon water depth (Fig. 9). In oxic shelf sediments very low sulfur concentrations (sometimes near the detection limit) were measured which implies that all the reduced sulfide is oxidized and not buried in the sediment as pyrite. In comparison to this observation high sulfur concentrations up to 2.7 % were measured in the deep basin sediments which was not surprisingly and is due to the fact of a sulfidic anoxic basin. In contrast to the shelf stations sulfur was buried in the sediment controlled by the availability of Fe.

According to Leventhal (1983) the linear regression of a plot of S_{tot} versus C_{org} should give a positive intercept on the S axis for an euxinic environment. In this study we found a negative intercept may be due to the high amount of residual carbon. The two data points plotted on the right end of the regression line for anoxic sediments are typical for a sapropel layer which was observed at Stn. 8 below 30 cm depth. The linear regression for the shelf stations gives an intercept of a few tenth of a percent sulfur which was in the range of oxic marine data (Leventhal, 1983).

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3.2

Bacterial sulfate reduction in hydrothermal sediments of the Guaymas Basin, Gulf of California, Mexico: *in situ* and laboratory radiotracer measurements

A. Weber, B.B. Jørgensen

Max Planck Institute for Marine Microbiology, Celsiusstr. 1, 28359 Bremen, Germany

3.2.1 Abstract

Depth distribution and temperature dependence of bacterial sulfate reduction were studied in hydrothermal surface sediments of the southern trough of the Guaymas Basin at 2000 m water depth. Ship-board measurements were compared to *in situ* incubations employing a new benthic instrument, ORPHEUS, from the submersible ALVIN. *In situ* temperatures ranged from 2.8° C at the sediment surface to > 130° C at 30 cm depth in the proximity of active vent chimneys. Sediment cores recovered from geothermally heated mud were incubated in the laboratory at 3°, 12°, 25°, 35°, 60°, 70°, 80° and 90° C. The peak rates of bacterial sulfate reduction (2550 nmol cm^{-3} d^{-1}) were found in surface sediments (0-5 cm) covered with *Beggiatoa* mats. In the subsurface sediment below 15 cm sediment depth a new substrate pool was apparently available and the thermophilic activity rose to a subsurface maximum of 3350 nmol cm^{-3} d^{-1}. *In situ* incubations with ORPHEUS also showed highest sulfate reduction rates in surface sediments covered with *Beggiatoa* mats (*in situ* temperature 11°C). Hydrothermal sediments incubated in a temperature gradient block at 0-120° C revealed optimum temperatures for mesophilic to thermophilic sulfate reducers between 40°-60° C. In sediment from 15-20 cm depth with *in situ* temperatures of 71°-93° C thermophilic to hyperthermophilic sulfate reduction was found in the temperature range 70°-90° C and above.

3.2.2 Introduction

The Guaymas Basin spreading center is situated in the Gulf of California, as part of the plate-tectonic system along the East Pacific Rise (Curray et al., 1979). In contrast to other deep-sea vent sites, the transform fault area is covered by sediment with an average thickness of 100 m (Curray et al., 1982) resulting from pelagic and terrigenous material sedimenting at a rate of >1 mm yr^{-1} (Curray et al., 1979). Magmatic intrusions below the thick sediment cover drive an upward hydrothermal flux which penetrates the overlying porous sediment and maintains a recharging seawater circulation (Gieskes et al., 1982; Lonsdale and Becker, 1985; Fisher and Becker, 1991).

The hydrothermal fluids emanate either diffusive through the seafloor with temperatures generally below 200° C (Von Damm et al., 1985) or from mounds and chimneys rising over the seafloor. Where the fluids contain enough metal sulfides, black smokers can be observed with emission temperatures of up to 350° C. During the upward flux of the hydrothermal fluids the organic-rich (2-4% C_{org}) diatomaceous sediment (Simoneit et al., 1979) is exposed to temperatures of 200°-250° C (Einsele et al., 1980). This results in diagenetic conversions in the sediment due to chemical interactions between hydrothermal fluids and sediment, such as metal sulfide precipitation and high-temperature pyrolysis of the deeper organic-rich sediments (Kawka and Simoneit, 1987). Thermal alteration of the organic matter generates petroleum-like products composed of aliphatic and aromatic hydrocarbons (Simoneit and Lonsdale, 1982; Bazylinsky et al., 1988), which are partly carried to the sediment surface by the upward hydrothermal flux. This transport makes a variety of substrates (e.g. formate, acetate, propionate and lactate) available for microbial degradation within a temperature range of 3° to > 100° C (e.g. Simoneit and Lonsdale, 1982; Simoneit, 1985).

The hydrothermal sediments covering the basin floor present ideal conditions for sulfate reduction by mesophilic and thermophilic and even hyperthermophilic microorganisms (Jørgensen et al., 1990 and 1992; Elsgaard et al., 1994). The sediments are anoxic to the surface and rich in H_2S (Jørgensen et al. 1990). The overlying sea water is depleted in oxygen to a concentration of 28 µM (Gundersen et al., 1992). The microbial sulfate reduction in the anoxic surface sediments of the Guaymas Basin is controlled by steep temperature gradients in the range of 3° to > 100°C and by the availability of substrates such as volatile fatty acids or aliphatic and aromatic hydrocarbons brought to the surface sediments by the circulation of hydrothermal fluid.

High methane concentrations in the hot sediment complicate process studies in retrieved samples because of extensive methane ebullition at atmospheric pressure. Consequently, experiments should optimally be done without pressure release. We measured sulfate reduction under *in situ* conditions with a new benthic instrument, ORPHEUS. In parallel, we carried out laboratory measurements of the depth zonation of sulfate reduction in a temperature range from 3° to 90° C using radiolabeled $^{35}SO_4^{2-}$. A further goal was to study the temperature-dependent activity of sulfate-reducing bacteria in hydrothermal sediments from different temperature zones, using a temperature gradient block and time series experiments with added organic substrates (mixture of formate, acetate, propionate, butyrate and lactate). It was the objective of these investigations to determine the magnitude of organic mineralization in hydrothermal sediments and to search for the upper temperature limit of bacterial sulfate reduction.

3.2.3 Methods

3.2.3.1 Site Description

The Guaymas Basin (Fig. 1) comprises two rift valleys, the northern and the southern trough separated by a transform fault. Sediment samples from the southern trough were taken in April-May 1998 during a R/V ATLANTIS expedition, voyage 3, leg 18 (Table 1), employing the research submersible DSR/ALVIN (dive series 3203 to 3208).

In fields of a few hundred square meter on the seafloor, hot hydrothermal fluids (< 200° C) emanate diffusive from the sediment, visible by a shimmering of the cold (2.8° C) overlying sea water, and black metal sulfide precipitates or crusts are formed in the otherwise light-brown colored sediment. Additionally, mounds and chimneys continuously discharge hot vent fluid with temperatures of up to 350° C.

Surrounding the chimneys and the diffuse sites of hot pore fluid outflow, thick whitish or yellow-orange mats of filamentous sulfur bacteria, *Beggiatoa* spp., grew on the sea floor. The *Beggiatoas* obviously do not tolerate hot sediment surfaces. With the exception of one sediment sample taken outside the area of hydrothermal influence (Stn. 6), all cores were recovered from sites in which diffusive hot pore fluids were discharged, forming vertical gradients from 2.8° C to > 130 °C over a depth of 0-30 cm. Additionally, sediment covered by bacterial mats with moderate temperatures at the sediment surface were sampled. Around the sampling sites on cliffs, mounds and numerous chimneys, dense *Beggiatoa* mats occurred in association with colonies of *Riftia* tube worms.

Table 1. Dive locations and samples for sulfate reduction measurements obtained by ALVIN and ORPHEUS

Station/Dive	Name of site	Position	Site characteristics and kind of measurement
1 / (3203)	Everest	27N00.762 / 111W24.656	dense *Beggiatoa* mats, Temp.: 117°C at 35 cm, sediment for whole-core incubations
2 / (3204)	MFOG	27N00.764 / 111W24.558	sediment partly covered with *Beggiatoa* mats (~ $100 m^2$), Temp.: 91°C at 35 cm, ORPHEUS deployment (*in situ* incubation)
3 / (3205)	MFOG	27N00.888 / 111W24.734	no *Beggiatoa* mats in push cores, Temp.: 105°C at 25 cm, sediment for temperature gradient block and times series experiments
4 / (3206)	Rebecca´s Roost	27N00.471 / 111W24.541	no *Beggiatoa* mats in push cores, Temp.: 104°C at 25 cm, sediment for whole core incubations taken 0.5 m left and right of the ORPHEUS deployment from dive 3204
5 / (3207)	Rebecca`s Roost	27N00.435 / 111W24.612	push cores with *Beggiatoa* mats, Temp.: 133°C at 35 cm, sediment for temperature gradient block experiments
6 / (3208)	Rebecca´s Roost	27N00.762 / 111W24.656	outside the hydrothermal vent area, cold sediment for whole-core incubations

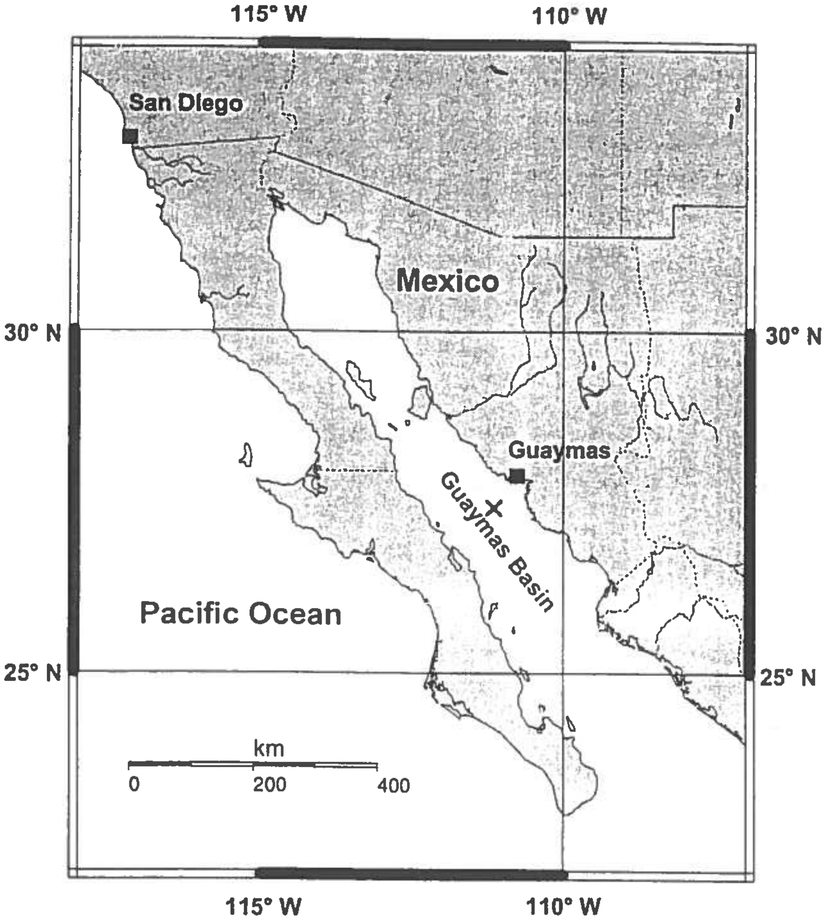


Fig. 1: Map of the Gulf of California showing the Guaymas Basin dive area (X)

3.2.3.2 Sediment sampling

In situ incubations with the benthic incubation instrument „ORPHEUS"

In situ radiotracer measurements of sulfate reduction were carried out with a new benthic incubation system, ORPHEUS, designed for radiotracer experiments in the sea-bed (Fig. 2). The lander may be deployed to incubate sediments *in situ* in shallow water or down to a depth of 6000 m. In contrast to classical free-falling lander systems (Reimers, 1987; Janke and Christiansen, 1989; Tengberg et al., 1995; Greeff et al., 1998) for deep sea research, the instrument was positioned directly on the site by a submersible (an ROV could also be used).

ORPHEUS is supported by an aluminum frame measuring 60 cm x 60 cm and has an overall height of 200 cm. Without buoyancy, the instrument weighs 70 kg in water. The mechanical principle of the incubation instrument is similar to the benthic lander LUISE (Greeff et al., 1998). The frame carries a central unit with the injection system. A drive motor (80 W) situated within the aluminum frame simultaneously lowers three core tubes fixed to a moveable POM plate into the sediment (max. 40 cm). The three polycarbonate core tubes of

62 mm (I.D.) and 50 cm long are sealed by a piston at the top and are resistant to heat up to 138° C. In even hotter and corrosive sediments, such as in the Guaymas Basin, the polycarbonate tubes can be replaced with titanium. After the cores reach their end position controlled by reed-type switches which interrupt the power supply for the drive motor, canulas for tracer injection are driven each by small injection motors into the core tube. The motion of the injection motor is coupled to a piston moving the plunger of a syringe containing the radiotracer. Thus the tracer is injected continuously into the sediment through the descending canula. (Greeff et al., 1998). During the pre-programmed incubation, cores and canulas remain in the sediment which is thereby kept at the *in situ* temperature gradient.

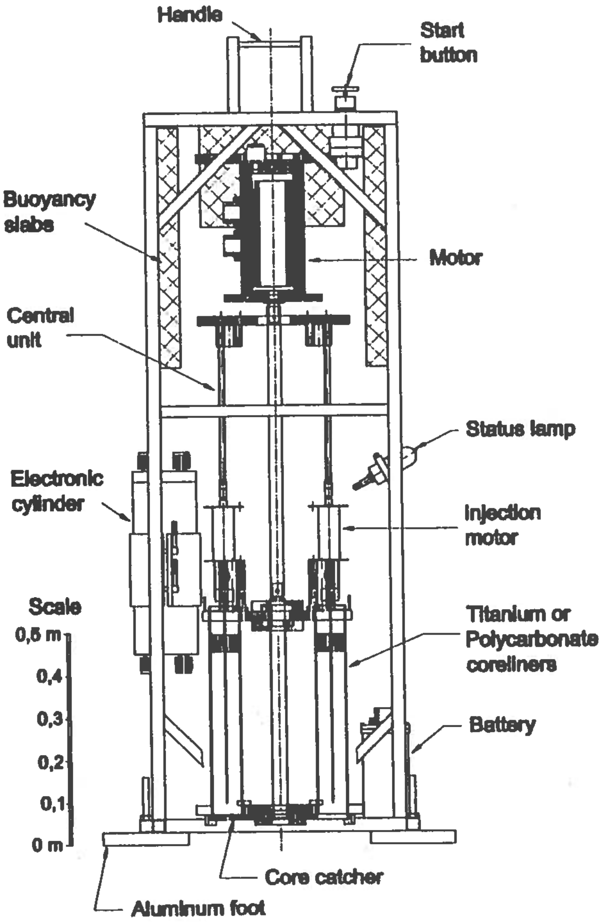


Fig. 2: The new benthic incubation instrument ORPHEUS for *in situ* radiotracer measurements, which was deployed by ALVIN.

Subsequent to coring and incubation of the three sediment cores, these are retracted up into the frame and tightly sealed by a core catcher at the bottom. ORPHEUS is also equipped with a sensor to measure the *in situ* temperature gradient in sediments at 10 mm resolution. The sensor may be replaced by a fourth core tube. A weight limit of 45 kg under water should not be exceeded when the instrument is operated by the submersible, due to the limited load-bearing capacity of the ALVIN manipulator. For this reason, ORPHEUS was equipped with four buoyancy slabs. Two 17 - Ah batteries, kept in a Perspex box with pressure compensation, supply the electronic parts (24 V) and the motors (12 V) with power for approximately 30 hours.

The programming of the instrument by computer operates with a multi-step sequential routine, i.e. after a pre-set time interval the core tubes are driven into the sediment, then the tracer is injected, and the filled core-liners are retracted into the frame and sealed after the incubation time is over. An event control mechanism was introduced by which interventions can be made at any time in this programmed schedule by pressing a "start button" (Fig. 2) with the manipulator arm of the submersible ALVIN. It is thus possible to jump program steps if required, e.g. to reduce the time before injection. A status lamp, a red light-emitting diode, goes on for 10 seconds prior to each new program step and indicates whether the procedure has started. This makes it possible to follow the sequence of events by watching the program performance from the submersible.

In the dive expedition to the Guaymas Basin, ORPHEUS was not transported to the seafloor by ALVIN, but was launched one hour prior to the ALVIN dive as a free-falling lander equipped with ballast, buoyancy and pinger. On the seafloor, ORPHEUS was then picked up by ALVIN, positioned on an appropriate sediment site and set in operation. On the next day's dive, the ALVIN manipulator released its ballast whereafter ORPHEUS rose back to the sea surface and was retrieved. The incubation time lasted 19 hours. The advantage of this procedure was that ALVIN's transport "basket" was available for other equipment.

Immediately after recovery of the lander, the cores were cooled and sectioned into 1 cm segments. The time between recovery and sectioning was about 30 min. Metabolic activity was terminated by fixing the sediment slices in 20 ml of 20% ZnAc-solution. The fixed sediment samples were kept at 4° C until distillation.

Push core samples

During all dives in the Guaymas Basin, ALVIN recovered push-core samples, 30 cm long and 50 mm I.D. or 50 cm long and 150 mm I.D. from the sediment. These cores were used for pore water analysis, preparation of sediment slurries for temperature gradient block and time series experiments, as well as for incubation of whole cores. Prior to each sample recovery, a vertical temperature gradient was recorded at 5 cm depth resolution with the ALVIN temperature sensor.

After sampling, the coring tubes were stored in quivers, in order to prevent loss of sediment in the course of rising to the surface. Subcores of 20-35 cm length were taken from the large push-cores. Although the sediment was occasionally disturbed along the coring tube wall, the sediment surface and the center of the large push-cores remained mostly intact. Upon preparing the subcores an intensive smell of H_2S and petroleum was noticeable. The small push-cores were mostly used for pore water or porosity measurements or for sulfate reduction experiments.

3.2.3.3 Laboratory measurements of sulfate reduction

Experiments with sediment slurries

The temperature dependence of bacterial sulfate reduction was studied in sediment slurries made from samples of different sediment depths and *in situ* temperatures.

A large sediment core without *Beggiatoa* mat was taken at Stn. 3, in the immediate vicinity of the ORPHEUS deployment site, and subdivided into five depth intervals: 0-6, 6-12, 12-18, 18-24 and 24-30 cm. Additional hydrothermal sediment samples covered with *Beggiatoa* mats were recovered at Stn. 5 and subdivided into two depth intervals: 10-17 and 17-25 cm (data not shown).

In order to study the temperature dependence of bacterial sulfate reduction in different depth ranges under surplus of substrate, a substrate solution (pH 7.2) composed of formate, acetate, propionate, butyrate and lactate, each at a final concentration of 1 mM was added to the suspensions. Slurries were prepared in 2 l aspirator bottles under N_2 from sediment diluted 1:2 with N_2-purged local seawater. During continuous stirring, aliquots of 10 ml slurry were transferred under N_2 to 15-ml Hungate test tubes (Hungate, 1969). The tubes were sealed with thick black butyl rubber stoppers, screw-capped and pre-incubated for 30 min. to reach temperature equilibration.

A stable temperature gradient was established in an insulated aluminum block of 2 m length, heated 120° C at one end and cooled to 0° C at the other. The block had 4 slots for each of 31 equidistant incubation temperatures. After temperature equilibration, 100 µL

$^{35}SO_4^{2-}$ ~ 500 kBq (Amersham) was injected into each tube through the butyl stopper. The tubes were shaken and incubated for 43 hours. The temperatures in the gradient block were checked at regular intervals and remained constant within ± 0.6° C.

For time series experiments, the pre-incubated tubes containing slurry from the five sediment depths were incubated at seven constant temperatures: 12°, 25°, 35°, 60°, 70°, 80° and 90° C. The series was incubated for 31, 69 and 97 h to observe changes in activity over time due to growth of the sulfate reducers. All incubations were stopped by adding 20 ml 20% ZnAc-solution and storing in the cold at 4° C.

Whole-core incubations

Sulfate reduction rates (SRR) were also determined by a whole-core $^{35}SO_4^{2-}$ incubation method (Jørgensen, 1978). Subcores of 26 mm I.D. from hydrothermal sediment were incubated for 20 h at 12°, 23°, 35°, 60°, 70°, 80° and 90° C. After equilibration at the incubation temperature, each core was injected horizontally with 5 µl $^{35}SO_4^{2-}$ tracer solution (~ 500 kBq per injection) through silicone filled ports at 1 cm depth intervals. To end incubation, the uppermost 0-5 cm were sliced into 1 cm sections and the rest into 2 cm sections. Metabolic activity was terminated by transferring the sediment slices directly into 20 ml of 20% ZnAc-solution. The sediment samples were carefully mixed and kept cold until further treatment.

Sulfate reduction was determined using a single-step acid Cr- II distillation method to trap the total reduced sulfur species (Fossing and Jørgensen, 1989). The H_2S evolved from the total reduced inorganic sulfur (TRIS) was precipitated in 5% ZnAc. The resulting ZnS-suspension was mixed with scintillation fluid (Ultima Gold XR, Packard) and counted in a liquid scintillation counter. Sulfate reduction rates were calculated according to Jørgensen (1978).

3.2.3.4 Sediment and pore water analysis

Additional subcores were sliced into 1 cm (0-5 cm depth) and 2 cm sections (> 5 cm depth) to determine the porosity and total C, N and S contents in the hydrothermal sediments. Pore water from 1 cm sections of the sediment cores was pressed under N_2 through 0.45 µm filters and preserved in 1% $ZnCl_2$-solution. Sulfate was measured by non-suppressed ion chromatography (Waters) and H_2S (precipitated as ZnS) was analyzed spectrophotometrically using the methylene blue method (Cline, 1969).

3.2.4 Results

3.2.4.1 Sediment description

The hydrothermal sediments in the Guaymas Basin occur as scattered sites with strong temperature changes within short lateral distances, depending on the hydrothermal flow through the sediment column. The uppermost 14 cm had a black color due to the precipitation of metal sulfides (mostly FeS). This layer consisted of a soft mud with a sharp transition to a more solid, green-gray, clayey sediment, which became more and more consolidated with depth. A dark-brown fluffy layer covered a large area of hydrothermally influenced sediments, e.g. at the ORPHEUS landing site (Stn. 2) near active chimneys. The sediment of deeper layers consisted of a fine-grained, dark gray clay. At other sites, the upper layer was olive-gray, with a loose texture, was more clayey and silty, and partly had a granular texture below the surface. During processing of the sediments a penetrating smell of petroleum and H_2S was released. The occurrence of whitish, sometimes yellow-orange *Beggiatoa* mats (thickness > 1 cm) on the sediment surface (Fig. 3) was a sign of lower temperatures at the sediment surface and of emanating sulfide-rich pore fluid. After the cores were brought on deck, methane, H_2S and other volatiles originating from high-temperature pyrolysis were gassing out of the cores. This sometimes causes a disturbance in the stratification of sediment cores.

Sediment outside the area of hydrothermal influence differed in color and consistency from the thermally altered sediments and were brown turning into more gray-brown with increasing depth.

Fig. 3: Whitish and yellow-orange *Beggiatoa* mats covering the sediment surface at Stn.1.

3.2.4.2 Profiles of temperature, sulfate and H_2S

During the *in situ* incubation at Stn. 2, a temperature profile was measured with the ORPHEUS sensor (Fig. 4A). The temperature increased almost linearly from 2.8° C at the sediment surface to 64° C at 16 cm depth with a gradient of 3.4-5.2° C cm^{-1}. In the more consolidated clayey sediment below 16 cm, the temperature gradient was 1.8-2.5° C cm^{-1} and the highest temperature measured was 97° C at 31 cm depth. Temperature gradients varied considerably within short distances. Within 15-20 cm distance from the temperature sensor the temperature at 31 cm depth must have exceeded 138° C, because the polycarbonate coring tube had begun to melt.

Sulfate and H_2S were measured in the pore water which had been recovered in the immediate vicinity of the ORPHEUS landing site. The average concentration of sulfate in the upper 6 cm was at 23 mM and decreased to 16 mM at the transition (6-7 cm) to more solid and clayey sediments (Fig. 4C). The concentrations of H_2S varied between 0.45 and 4 mM. (Fig. 4B). Outside the hydrothermal vent area, sulfate decreased almost linearly from 28 mM at the surface to 26 mM at 25 cm depth (Fig. 4D).

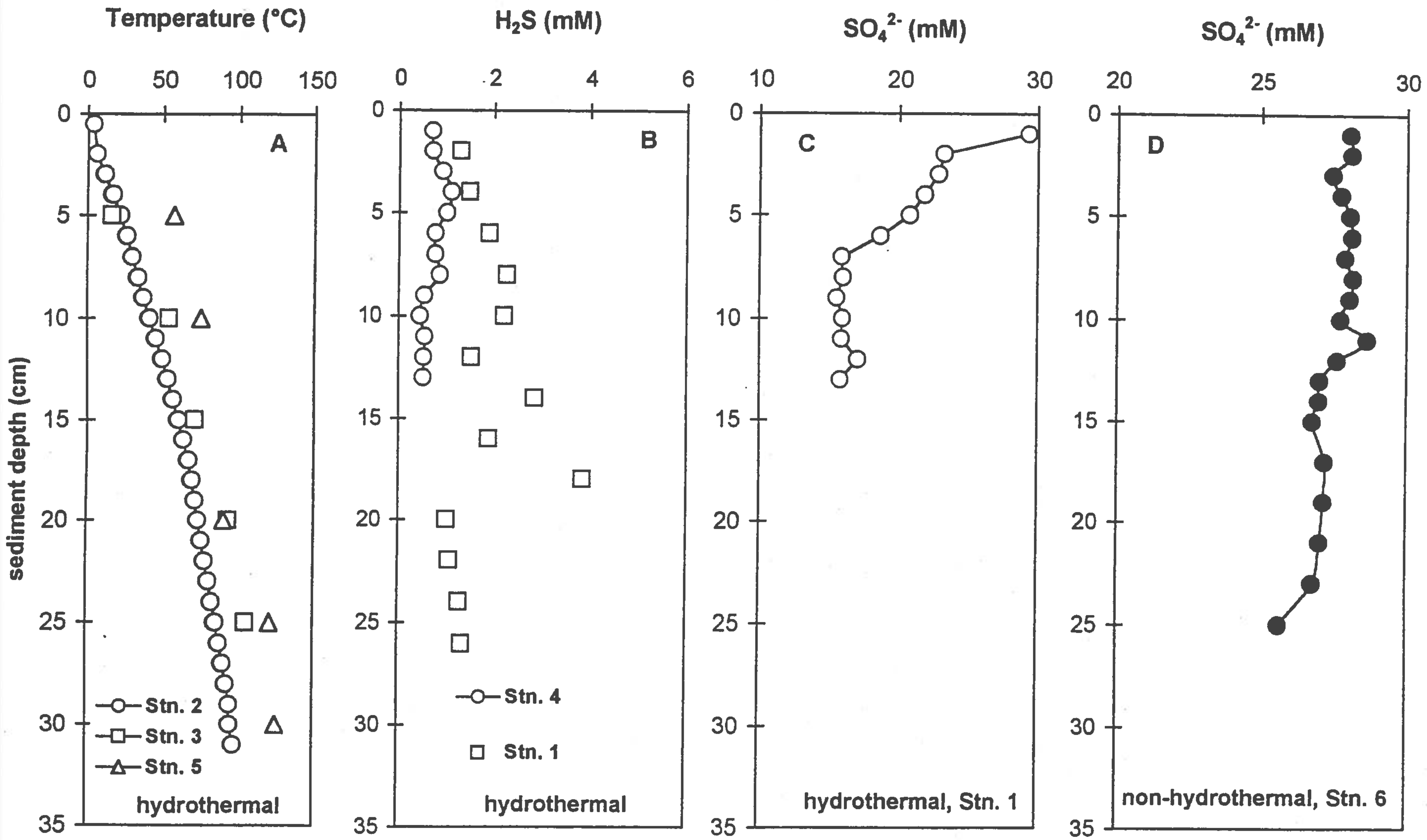


Fig. 4: Temperature, H_2S and SO_4^{2-} vs. sediment depth in the same hydrothermal sampling field and in a non-hydrothermal sediment. H_2S in the non-hydrothermal sediment was below our detection limit (< 1µM).

3.2.4.3 Sulfate reduction in sediment cores

Laboratory incubations

Sulfate reduction in hydrothermal sediment cores recovered from Stn. 4 displayed different depth distributions as a function of incubation temperature (Fig. 5). At 25° C highest rates of of sulfate reduction, 600-819 nmol cm^{-3} d^{-1}, were found in the top 0-7 cm and rates decreased with depth. On an areal and depth integrated basis, 93% of the measured sulfate reduction took place in the upper 15 cm. At 60°, 70°, 80° and 90° C highest activities were found below 15 cm (comprising 62-96% of the measured sulfate reduction), whereas the upper 10 cm revealed only minor activity (up to 46 nmol cm^{-3} d^{-1}, 70° C). At 60° C, a maximum SRR was reached at 25 cm sediment depth. The highest rates were measured at 70° C with 3350 nmol cm^{-3} d^{-1} at 23 cm depth. The maximum SRR at 80° and 90° C was found at 27 cm (1300 nmol cm^{-3} d^{-1}), and 19 cm (165 nmol cm^{-3} d^{-1}), respectively.

Depth profiles of sulfate reduction were also studied in the laboratory in hydrothermal sediment from Stn. 1 and in non-hydrothermal sediment from Stn. 6 were studied in the laboratory (Fig. 6). At 60°, 70° and 90° C only one core each was used, whereas all other profiles represent mean values from two incubated cores. At most temperatures (12°, 23°, 35°, 70°, 80° and 90° C) highest rates were measured in the upper 5 cm of the hydrothermal sediments. More than 90% of the measured sulfate reduction took place in the upper 15 cm. In the 60° C core half of the measured reduction took place below 15 cm. The highest rates in this sediment were 1970 and 2550 nmol cm^{-3} d^{-1} at 35° and 70° C, respectively.

Maximum subsurface rates were found at 60° (390 nmol cm^{-3} d^{-1}) and 70° C (2440 nmol cm^{-3} d^{-1}) in 21 and 7 cm sediment depth, respectively. The cores incubated at 80° and 90° C had significantly lower SRR as compared to the other incubation temperatures. Sulfate reduction rates outside the hydrothermal area (2.8° C) were much lower than rates in the hydrothermal sediments and had a maximum of 5.3 nmol cm^{-3} d^{-1} at 19 cm sediment depth. In all cores SRR decreased below 15 cm depth to < 10 nmol cm^{-3} d^{-1}.

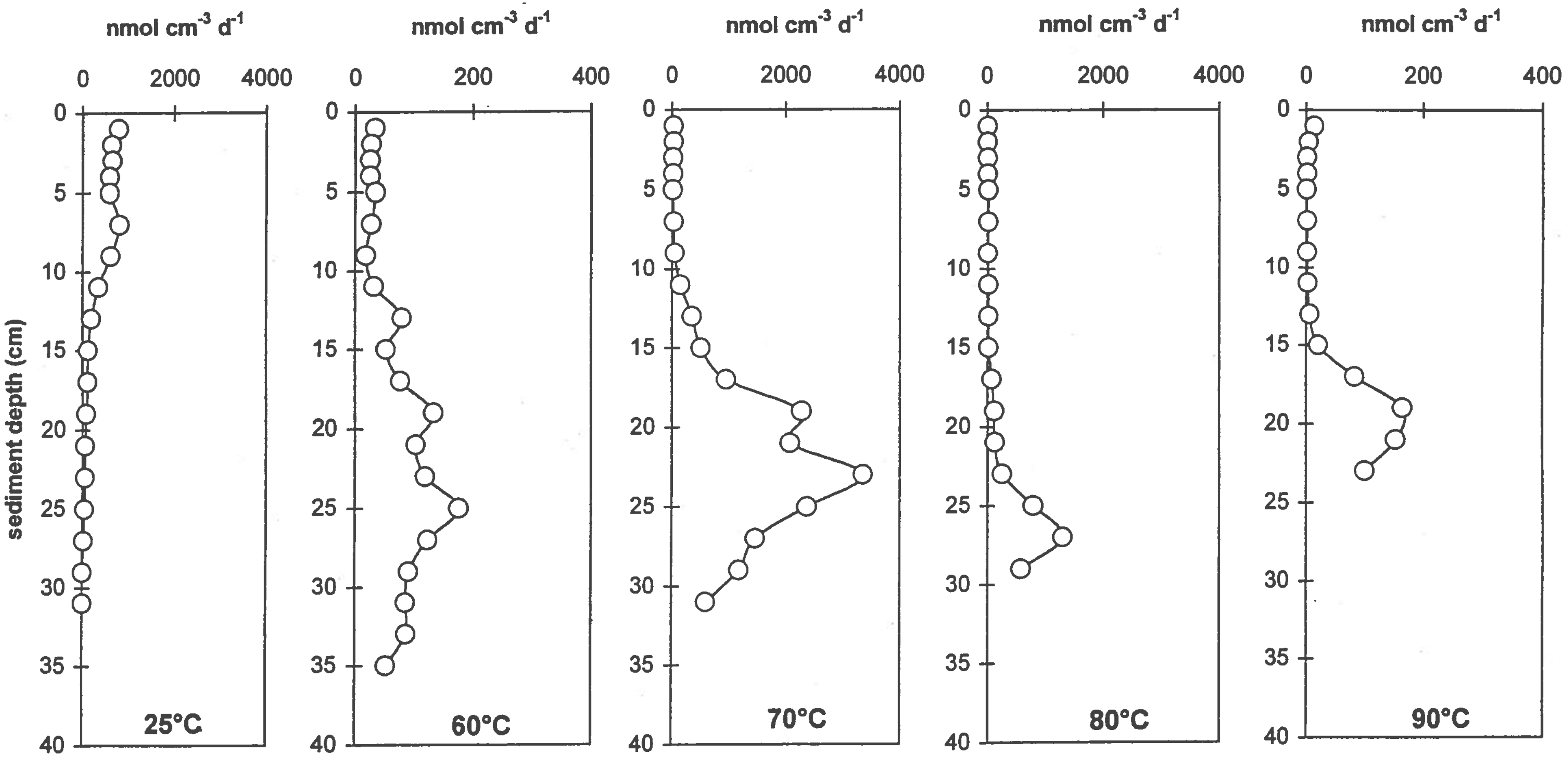


Fig. 5: Sulfate reduction rates in hydrothermal sediments (Stn. 4, no bacterial mats) incubated at different temperatures. Note the different scales for the rates.

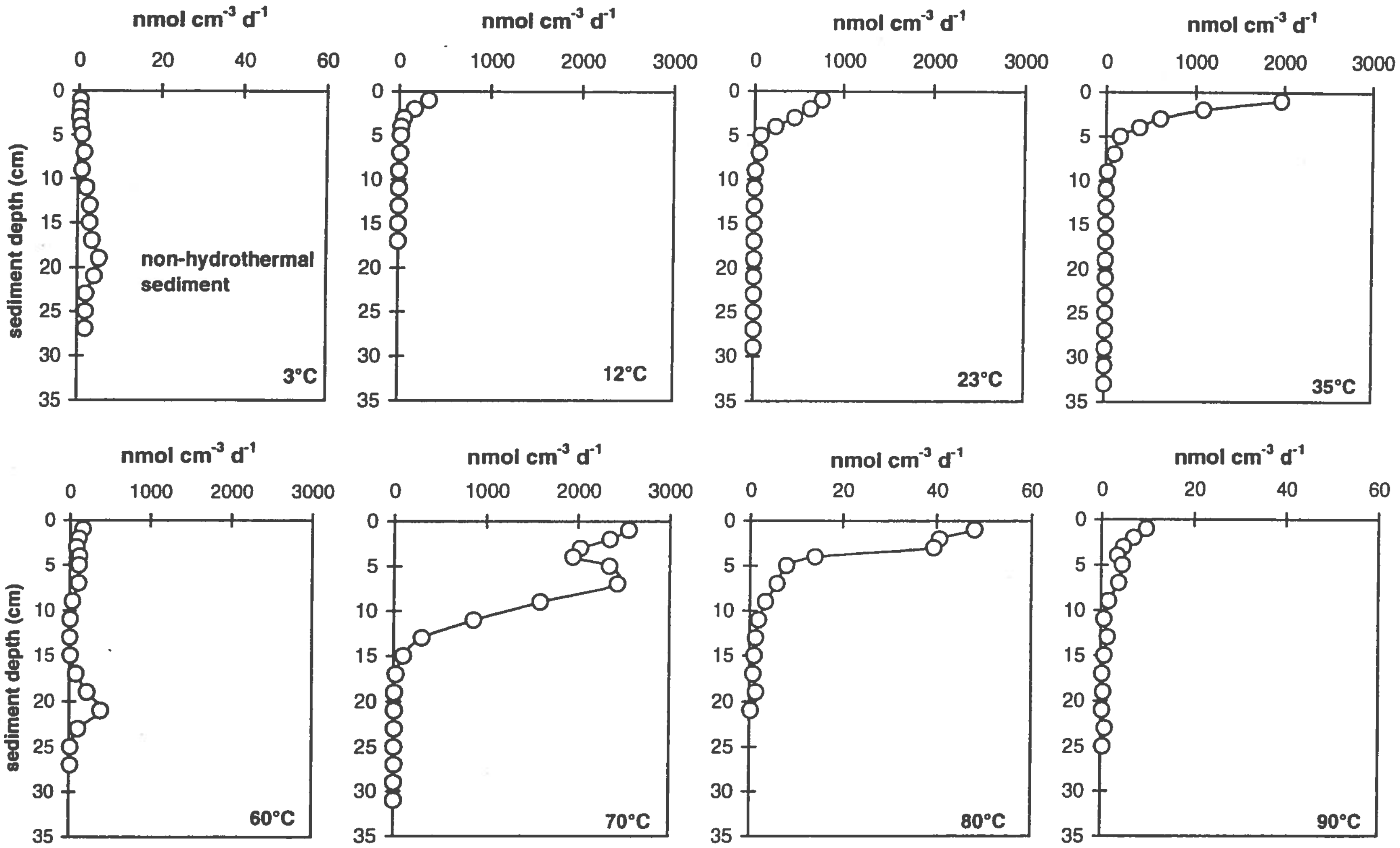


Fig. 6: Sulfate reduction rates in hydrothermal sediment covered with bacterial mats (Stn. 1) and non-hydrothermal sediment (Stn. 6) incubated at different temperatures. Note the different scale for the 3°, 80° and 90° C data.

In situ incubation with the benthic instrument ORPHEUS

The benthic instrument ORPHEUS was successfully deployed at Stn. 2 (dive 3204, 2011 m water depth) in a flat area sloping up towards a row of low chimneys. The 100 m^2 sampling field was partially covered with a thin *Beggiatoa* mat and was hydrothermally active with shimmering water, scattered low chimneys (partially active) and venting cracks.

This was the first time sulfate reduction was measured *in situ* with a benthic incubation instrument in hydrothermal deep sea sediments. Highest relative rates were found in the upper 10 cm of the sediment (Fig. 7). The distribution of sulfate reduction with depth was measured together with the temperature gradient and showed a maximum rate at a depth of 3 cm and at an *in situ* temperature of 11° C. Sulfate reductions rates decreased significantly with depth and became very low below 10 cm depth.

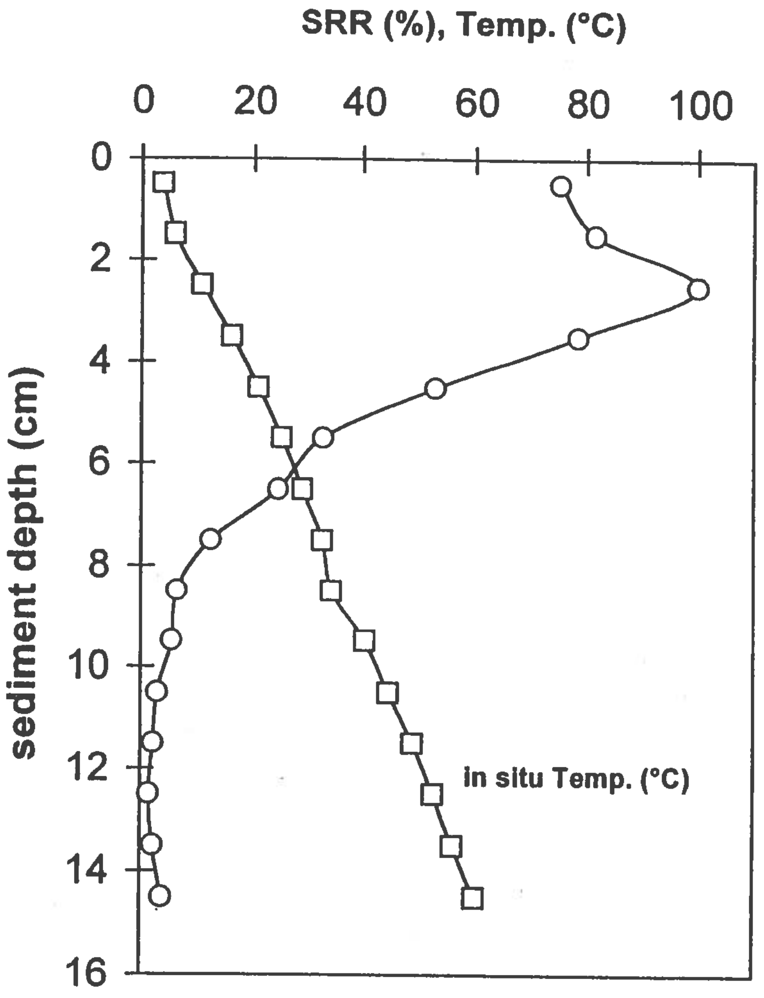


Fig. 7: Distribution of sulfate reduction and temperature with sediment depth from an *in situ* incubation with the benthic instrument ORPHEUS in a hydrothermal sediment partly covered with bacterial mats.

Sulfate reduction in sediment slurries

The influence of temperature on microbial sulfate reduction was studied in substrate-amended suspensions of hydrothermal sediment from Stn. 3 (Fig. 8). The temperature gradient block experiments showed rather comparable temperature optima of sulfate reduction at depths between 0 and 24 cm with decreasing peak rates at increasing depth.

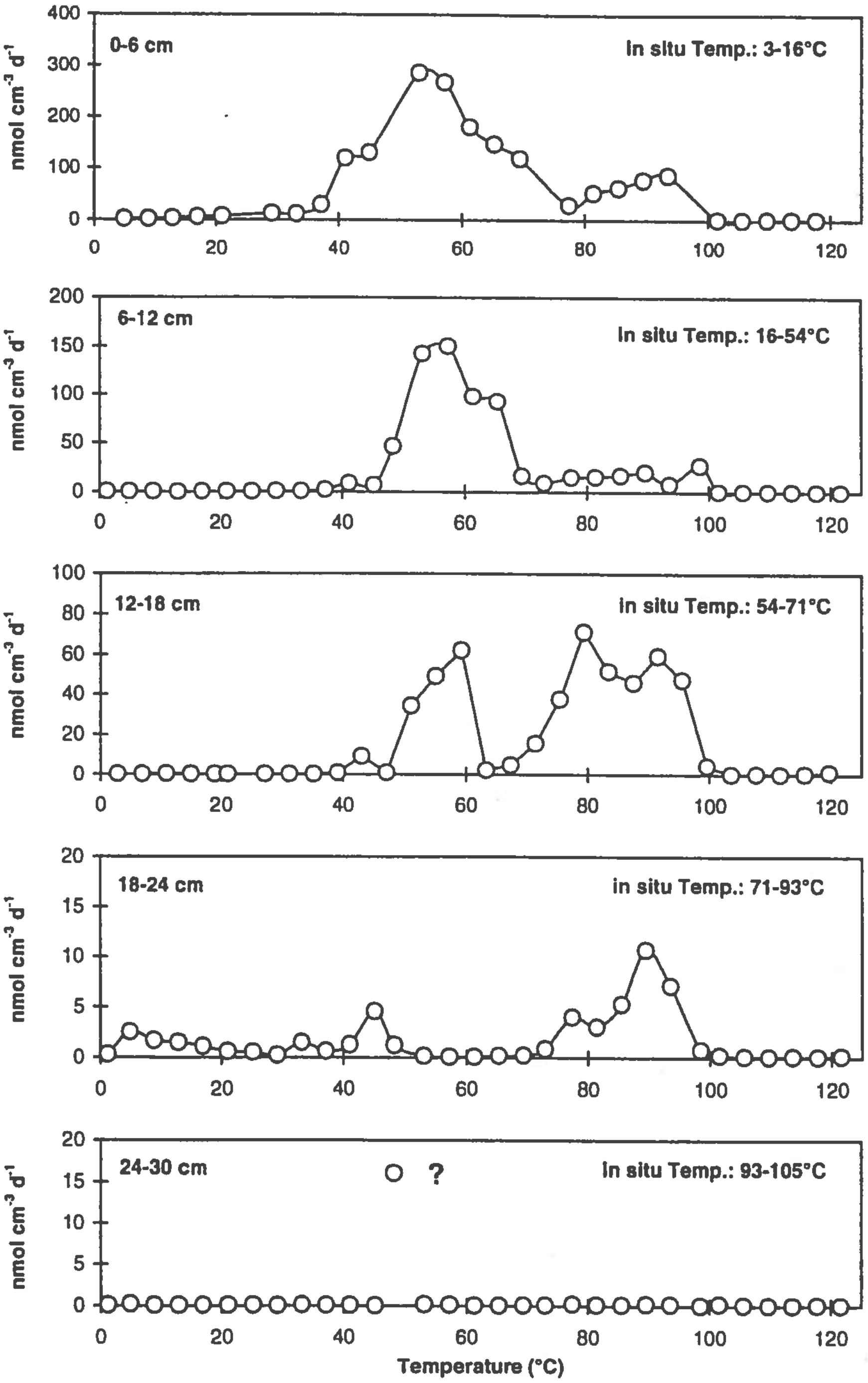


Fig. 8: Temperature dependence of sulfate reduction rates in slurried hydrothermal sediment (Stn. 3) from 0-6, 6-12, 12-18, 18-24 and 24-30 cm sediment depth. A substrate mixture of short-chain fatty acids was added to all slurries. The *in situ* temperature ranged from 16° C at 5 cm to 105° C at 25 cm depth.

In the upper 0-6 cm two maxima of SRR were formed: 286 nmol cm^{-3} d^{-1} at 53° C and 86 nmol cm^{-3} d^{-1} at 93° C. At 6-12 cm, maximum rates of 150 and 27 nmol cm^{-3} d^{-1} were found at 57° and 90°-98° C respectively. At 12-18 cm, mesophilic activity was absent and a thermophilic optimum was observed at 59° C (62 nmol cm^{-3} d^{-1}). Another thermophilic range between 79° and 91° C had sulfate reduction rates from 71 to 59 nmol cm^{-3} d^{-1}. At 18-24 cm, SRR was very low, but still had peaks at 45° and 90° C (4 and 11 nmol cm^{-3} d^{-1}). At 24-30 cm, sulfate reduction was not detectable (except for one stray data point at 48° C). An incubation with hydrothermal sediment from a different site (Stn. 5, Fig. 9) showed a different temperature dependence. At 10-17 cm depth, a maximum rate occurred between 60° and 70° C, (128 nmol cm^{-3} d^{-1}) with a shoulder up to 98° C. Sulfate reduction was not measurable above 100° C at any depth.

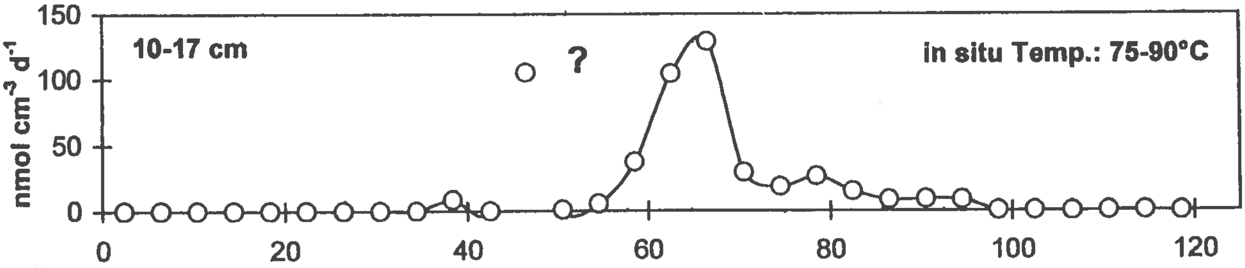


Fig. 9: Temperature dependence of sulfate reduction rates in a slurried hydrothermal sediment from 10-17 (Stn. 5). A substrate mixture of short-chain fatty acids was added to all slurries. The *in situ* temperature ranged from 75°-90° C.

In addition to the temperature gradient block experiments, time series incubations of SRR were done with the same sediment slurries as used in Fig. 7 at fixed temperatures of 12°, 25°, 35°, 60°, 70°, 80° and 90° C (Fig. 10). Generally, the highest SRR occurred in the surface sediment (0-6 cm) where the SRR clearly increased with incubation time at 35°-80° C.

The highest rate (231 nmol cm^{-3} d^{-1}) in the surface sediment was measured at 60° C after 91 hours. Below 35° C, sulfate reduction was only detectable down to 12 cm depth. Sulfate reduction was also significant in deeper sediment layers at higher temperatures of 60°-90° C, but data are rather noisy.

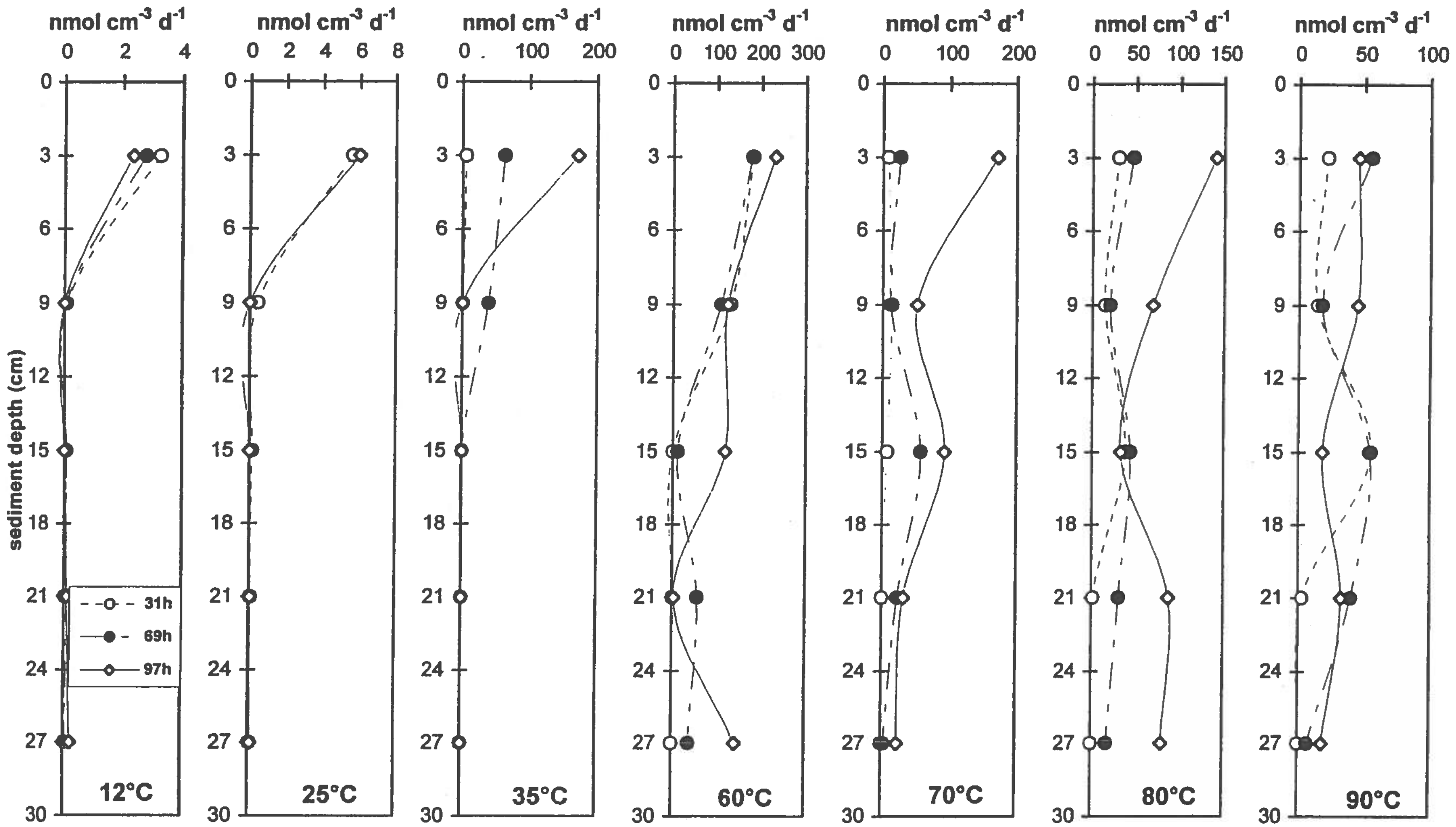
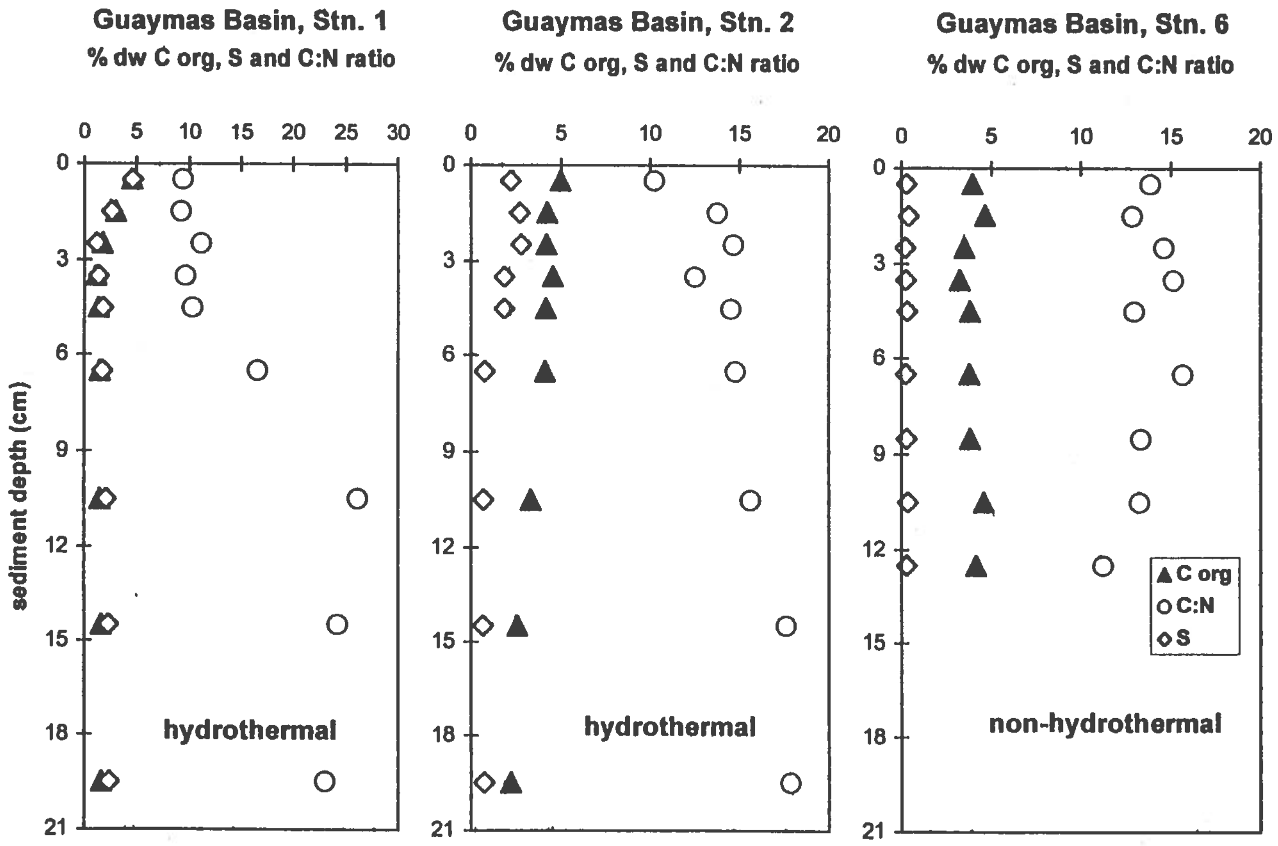


Fig. 10: Temperature dependence of sulfate reduction rates in slurried hydrothermal sediments (Stn. 3) from five different depth intervals and three different incubation times (31, 69 and 97 h). A substrate mix of short-chain fatty acids was added to all slurries. The *in situ* temperature ranged from 16° C at 5 cm to 105° C at 25 cm depth.

3.2.4.4 CNS data

Depth profiles of carbon, nitrogen and sulfur were measured in two hydrothermal sediments (Stn. 1 and 2) and a non-hydrothermal sediment (Stn. 6). Additionally, atomic ratios of organic C and N were calculated (Fig. 11). There was a steep increase of the molar C_{org}:N-ratios from 10 to 22.5 at 5-10 cm depth in the hydrothermal sediment of Stn. 1. Another remarkable feature was the elevated sulfur content (2.7 to 4.6%) in the upper 3 cm of the two hydrothermal sediments. Organic carbon decreased in hydrothermal sediments with depth from 5% at the surface to 1.5-2% at 20 cm depth. The non-hydrothermal site of Stn. 6 exhibited an average sulfur content of 0.3% over the entire depth profile. In this sediment organic carbon remained constant (~ 4%) in the upper 0-13 cm as did nitrogen (~ 0.4%). Nitrogen decreased strongly (data not shown) with depth in the hydrothermal sediments, from 0.8 to 0.1% at Stn. 1 and from 0.5 to 0.1 % at Stn. 2.



Guaymas Basin, Stn. 1
% dw C org, S and C:N ratio

Guaymas Basin, Stn. 2
% dw C org, S and C:N ratio

Guaymas Basin, Stn. 6
% dw C org, S and C:N ratio

Fig. 11: Concentrations of C_{org}, S_{total} (in % dry weight) and atomic C:N ratios vs. sediment depth at the hydrothermal sampling sites of Stn. 1 and 2 and in non-hydrothermal sediments of Stn. 6.

C_{org}:S weight ratios in hydrothermal sediments were 0.7-5.4 (Fig. 12). Sediment from Stn. 2 showed a distinct increase of C:S weight ratios from 2.5 to 5.4 below 5 cm. The C:S weight ratio was significantly higher outside the hydrothermal vent area with a mean of 13.7.

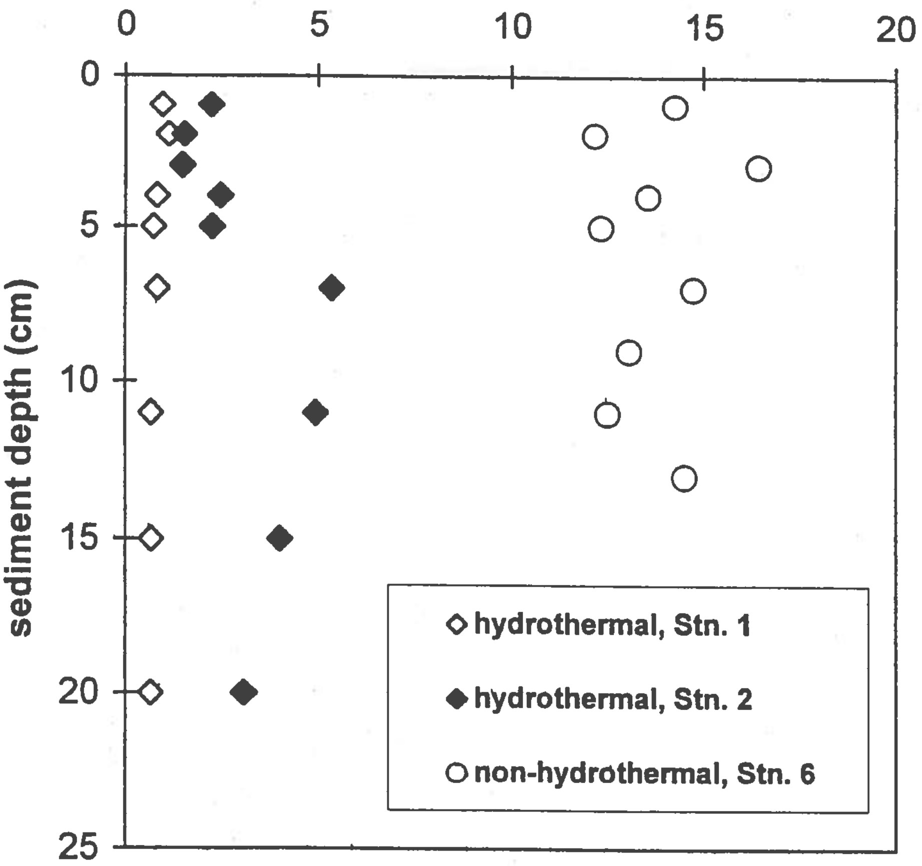


Fig. 12: Weight ratios of C:S in hydrothermal (Stn. 1 and 2) and non-hydrothermal sediments (Stn. 6).

3.2.5 Discussion

3.2.5.1 Sampling site characteristics

The upward flow of hydrothermal solutions containing dissolved substances, such as alkali elements, alkaline earth metals, metals, and anions (SO_4^{2-}, HCO_3^-) induces chemical alterations in the sediment: Precipitation of metal sulfides and crust formation of metal sulfides or carbonates which occur irregularly in the otherwise fine-grained clayey sediment. The result is a high degree of heterogeneity in the sediment structure, permeability, temperature gradients and geochemistry of the pore water.

The alteration of organic matter by hydrothermal solutions, which provides a variety of aliphatic acid ions as potential substrates for sulfate reduction, is a further reason for the variability of SRR. Within an area of several 100 m^2, completely different sediment conditions occur (Table 1). The very hot zones of the sea floor are characterized by diffusive emissions of hydrothermal fluids which are visible from the submersible ALVIN. These are distinct from the cooler sediment surfaces on which the thick *Beggiatoa* mats frequently grow.

In situ and laboratory measured SRR varied from low to extremely high rates and peak rates occurred at different depth depending on temperature and availability of substrates. Extreme SSR occurred below 20 cm at Stn. 4 ("Rebecca´s Roost" site) where the *in situ* temperature was up to 100° C and where substrates were obviously coming from deeper sediment strata provided by thermocatalysis of organic matter (Fig. 5). In the same sampling field at Stn. 1 ("Everest" site), sediment covered with dense *Beggiatoa* mats occurred where high H_2S fluxes provided an ideal habitat for these giant chemoautotrophic sulfide oxidizing bacteria (Jørgensen, 1990). In contrast to the subsurface maxima caused by hyperthermophilic sulfate reducers, peak rates of mesophilic sulfate reduction were found at the sediment surface (Fig. 6).

3.2.5.2 Sediment geochemistry

Depending on the prevalent hydrothermal influence, strongly diverging geochemical gradients were measured in the diatomaceous sediments of the Guaymas Basin (Fig. 4, see also Jørgensen et al., 1992, Elsgaard et al., 1994). The influence of hydrothermal fluids on chemical gradients depends on the permeability of the sediment. The changes observed in these gradients correlate with the transition from the unconsolidated, muddy surface sediment, where microbial processes are influenced by both, the circulation of seawater and hydrothermal fluids. In 7-15 cm depth the sediment become clayey and more solid, depending on the sampling site and temperature controls most of the microbial activity.

Geochemical gradients in the sediment outside the hydrothermal vent area differ strongly, as no free sulfide could be determined, sulfate concentrations remained relatively constant over the entire depth profile (28-26 mM), and temperature did not increase with depth.

Sulfide released from thermochemical and biological sulfate reduction can reach very high concentrations in surface sediments (Jørgensen et al., 1992). The sulfide flux supports the growth of chemoautotrophic bacteria, e.g. *Beggiatoa* mats, which consume the emerging sulfide (Gundersen et al., 1992). The overlying seawater has a temperature of 2.8° C and contains 28 mM oxygen (Gundersen et al., 1992). Anaerobic conditions, therefore, are prevalent from just a few millimeters below the surface of a bacterial mat or sediment. Total sulfur concentrations of up to 4.6% (dry weight) in hydrothermal sediments (Fig. 11), resulted from high pyrite concentrations (200 µmol S cm^{-3}, Jørgensen et al., 1992), or from the accumulation of elemental sulfur in the bacterial mats.

It is difficult to distinguish between hydrothermal and non-hydrothermal sediments on the basis of organic carbon contents. Hydrothermal sediment from Stn. 2 (partly covered with *Beggiatoa* mats) and non hydrothermal sediment from Stn. 6 revealed similar C_{org} contents, however, in hydrothermal sediments, there may be marked fluctuations in C_{org}. The atomic C_{org}:N ratios also show high variability within the area of hydrothermal influence (Fig. 11), because of the variable chemical composition of the upward percolating pyrolysates. If these hydrocarbons contain very low amounts of nitrogen, this could lead the observed shift in the C_{org}:N ratio at the transition from the unconsolidated muddy sediment to the clayey and more compacted sediment.

There was a distinct difference in carbon-sulfur relationships between hydrothermal and non-hydrothermal sediments (Fig. 12). This is due to the metal sulfide enrichment in hydrothermal sediments leading to a high, but variable sulfur content.

3.2.5.3 Sulfate reduction and substrates

Previous investigations demonstrated that sulfate reduction in hydrothermal sediments is substrate-limited (e.g. Elsgaard et al., 1994). For this reason, all slurry experiments were performed with added substrate, to stimulate sulfate-reducing bacteria and to study the effect of temperature on sulfate reduction alone.

Extremely high SRR were observed under hydrothermal influence in carbon-rich sediments (up to 5% C_{org}, Fig. 11) of the Guaymas Basin. Similar rates of several 100 to up to 1000 nmol cm^{-3} d^{-1} occur in organic-rich coastal sediments (Fossing and Jørgensen, 1989) or in Spartina salt marshes (Skyring et al., 1979), but are extreme for deep-sea or deep-basin sediments. In hydrothermally influenced sediments, high SRR may occur (up to 3350 nmol cm^{-3} d^{-1}, Fig. 5) because there is a continuous supply of substrates (hydrocarbons) or crude oil from deeper sediment strata available by thermochemical degradation of organic matter coming to surface sediments with hot pore fluids. In the relatively cooler surface sediments the dissolved substrates may be precipitated and enriched in the sediment.

Short-chain aliphatic acid anions (e.g. acetate and propionate) originating from the thermocatalytic decomposition of deposited organic material, occur at depth of 20 cm or more where temperatures are > 100° C and reach very high concentrations of > 1100 µm (Martens, 1990). Aliphatic and aromatic hydrocarbons are transported to the surface sediment by upward percolating hydrothermal fluids and can serve as substrates for the sulfate reducing bacteria (Simoneit, 1985; Kawka and Simoneit, 1987). Rueter et al. (1994) demonstrated that, under mesophilic conditions, sulfate-reducing bacteria are able to utilize aliphatic and aromatic hydrocarbons as electron donors. The potential of sulfate reducing bacteria to oxidize numerous straight-chain aliphatic hydrocarbons (Aeckersberg et al., 1991, 1998), and even to utilize toluene under anoxic conditions (Rabus et al., 1993) adds to the broad spectrum of substrates.

At the interface between opposed gradients of oxygen in the water column and H_2S in the sediment, a second substrate pool is provided by fermentation of chemosynthetically produced *Beggiatoa* biomass at the sediment surface.

3.2.5.4 Sulfate reduction and bacterial mats

The special hydrothermal environment of the Guaymas Basin supports dense populations of the giant nitrate accumulating sulfur bacteria *Beggiatoa* spp.. The classical *Beggiatoa* habitat is the interface between opposed gradients of oxygen in the water column and H_2S in the sediment (Jørgensen and Revsbech, 1983). Laboratory and *in situ* measured SRR of up to 2250 nmol cm^{-3} d^{-1} in hydrothermal sediments with overlying *Beggiatoa* mats (Fig. 6) are the highest rates yet measured in hydrothermal deep sea sediments. These rates are considerably higher than the maximum rate of 140 nmol cm^{-3} d^{-1} determined from another hot vent mat system in the Guaymas Basin (Jørgensen et al., 1990) and exceed the SRR in the surface layer of hydrothermal sediments without bacterial mats (Fig. 5). The rates are similar to those measured in continental shelf sediments in areas of strong upwelling, e.g. along the coast of Chile, Peru and Namibia (Ferdelman et al., 1997, Fossing, 1990, Ferdelman et al., in press). All these sediments are populated by related, nitrate-accumulating sulfur bacteria, *Thioploca* and *Thiomargarita* (Jørgensen and Gallardo, 1999; Schulz et al., 1999). A depth-integrated rate (0-15 cm) of 218 mmol m^{-2} d^{-1} can be calculated on the basis of this rate value but is related to "hot spot" areas which focus the organic flux and could not occur over a large area. In these small scale areas where H_2S rich pore fluid emanates from the sediment *Beggiatoa* mats occur and provides a variety of substrates from fermentation of chemoautotrophically synthesized biomass.

In situ measurements of sulfate reduction with the benthic incubation instrument ORPHEUS in a hydrothermal sediment with a dark fluffy layer and partly covered with *Beggiatoa* mats confirm the laboratory results and demonstrate mesophilic sulfate reduction with an *in situ* temperature of 11° C at 3 cm depth where the peak rate occurred (Fig. 7).

3.2.5.5 Sulfate reduction and temperature

Laboratory and *in situ* measurements showed peak rates at the sediment surface in a temperature range of 3°-45° C (Fig. 6 and 7). The occurrence of these remarkably high rates is associated with the presence of sulfide-oxidizing *Beggiatoa* mats. Maximum rates were also observed at hyperthermophilic incubation temperatures between 70° and 90° C. This implies that thermophilic or hyperthermophilic sulfate reducers must be present at the sediment-water interface and become active as soon as appropriate temperatures prevail (Fig. 6). Due to the thermal alteration of organic matter, substrate is available at high concentrations (> 1100 µm, Martens, 1990) in the subsurface sediment at 20-35 cm depth at *in situ* temperatures from 90° to 104° C, and is, as soon as the temperature allows, decomposed by hyperthermophilic sulfate reducing bacteria. Conversely, the core incubated at 25° C did not display any maximum values at all in the deeper layers of sediment, suggesting that mesophilic sulfate reducers were absent at this sediment depth and thermophiles were activated only at higher temperatures.

Sediment slurries incubated between 0°-120° C generally displayed a mesophilic range below 40° C and two thermo- hyperthermophilc ranges to which sulfate-reducing bacteria were well adjusted: 40°-60° C and 70°-90° C (Fig. 8 and 9). Comparable temperature ranges were also found by Jørgensen (1990, 1992) and Elsgaard et al. (1994). The upper temperature limit for sulfate reduction found in the present study, ≤ 100°C, was somewhat higher than the temperature growth limit of the hyperthermophilic archaea *Archaeglobus* spp. (Stetter, 1988; Stetter et al., 1993). This species, *Archaeglobus profundus*, was isolated from hydrothermal sediments of the Guaymas Basin, and is capable of growing at a temperature of up to 90° C (Burggraf et al., 1990).

There was no indication for sulfate reduction at *in situ* temperatures above 100° C (Fig. 8 and 9). A different temperature dependence was observed in hydrothermal sediment at Stn. 6. Thermophilic sulfate reduction was found between 40° and 50° C as well as between 60° and 70° C in 10-17 cm depth. Jørgensen et al. (1992) observed extremely thermophilic sulfate reduction in the temperature range between 100° C and 110° C and concluded from this observation, that sulfate reducers were still capable to reduce sulfate above 100° C. Elsgaard et al. (1994) demonstrated sulfate reduction in slurry experiments up to a temperature of 102° C. May be sulfate reducers are not able to grow at this temperature but they could still be able to reduce sulfate. This observation could not be confirmed in the present study.

Time course experiments (Fig. 10) revealed that there is a difference in the development of different groups of temperature-specific sulfate reducers. Despite a long incubation time, of up to 4 days (Fig. 10) there is no development of sulfate reducers below 10 cm depth at low temperatures between 12° and 35° C. There is thermophilic and hyperthermophilic sulfate reduction at high temperatures ≥ 60° C. Despite the noisy data, it is evident that there has been some growth of hyperthermophilic sulfate reducers between 60° C and 90° C.

The temperature range for microbial sulfate reduction still lies clearly below the temperatures of ~ 200° C at which thermochemical sulfate reduction can be assumed (Goldhaber and Orr, 1995). Ultimately, the distinction and the significance of biological or thermochemical sulfate reduction can only be determined at indicated *in situ* temperatures by means of isotope fractionation. (Machel, 1995; Canfield and Teske, 1996).

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3.3

Deep-water secondary productivity and intense sulfate reduction in a hypersulfidic basin in the Mediterranean Sea: Implications for the sulfur isotope record

W. Ziebis[1], M. E. Böttcher[1], A. Weber[1], J. C. Miquel [2], S. M. Sievert[1], P. Linke[3]

[1]Max- Planck Institute for Marine Microbiology, Celsiusstr.1, D-28359 Bremen, Germany

[2]IAEA International Atomic Energy Agency, Marine Environment Laboratory, B. P. 800, MC-98012, Monaco

[3]GEOMAR - Research Center for Marine Geosciences, Dept. Environmental Geology, Wischhofstr. 1-3, D-24148 Kiel, Germany

3.3.1 Introduction

Three deep basins filled with brine were discovered in the Mediterranean Ridge, south-west of Crete in late 1993 and early 1994 (MEDRIFF consortium, 1995). The basins were named after the three oceanographic vessels: L'Atalante, Discovery and Urania. The brine originates from dissolution of Messinian evaporites that lie beneath the seafloor (MEDRIFF consortium, 1995, Wallmann et al., 1997). The Urania Basin, has an overall water depth of 3570 m. A sharp pycnocline at 3490 m is separating the 80 m deep brine with a salinity of 162 ‰ from the sea water above. Due to the density difference of the two water bodies, organic material sinking through the water column accumulates at the brine - sea water interface. Within a 20 m thick chemocline above the hypersaline deep water bacterial numbers and microbial activity strongly increase. Bacterial sulfate reduction rates determined in this intermediate layer (14 nmol SO_4^{2-} cm^{-3} d^{-1}) are the highest measured in a marine water column so far. The 80 m deep homogenous brine contains 10 mM hydrogen sulfide and is the most sulfidic body of water reported for the marine environment. The high biomass concentration and secondary productivity in the intermediate layer further increases the concentration of particulate organic carbon, which is 15-fold enriched in the brine compared to the sea-water above. The hypersaline and hypersulfidic conditions in the deep basin do not inhibit organic matter remineralisation by sulfate-reducing bacteria, organic carbon undergoes further decomposition on its way through the brine and is therefore not accumulated in the sediment. Sulfate reduction rates in the sediment have been measured for the first time based on *in situ* incubations with an autonomous lander at the depth of 3570 m and show only minor variations to parallel on-board ship incubations.

The sulfur isotopic composition is constant throughout the deep basin with a depletion of ^{34}S by 40 ‰ in hydrogen sulfide compared to sulfate at corresponding depths. This confirms bacterial sulfate reduction and suggests that growth of bacteria which are able to disproportionate intermediate sulfur species is hindered by the extremely high sulfide concentrations.

The subduction of the African plate below Europe has resulted in the formation of active volcanic arcs in the Tyrrhenian and Aegean Seas and the Mediterranean Ridge. In the tectonic province of the Ridge a number of deep anoxic basins have been discovered in recent years (De Lange and Haven, 1983; Scientific Staff of Cruise Bannock 1984-12, 1985; MEDRIFF consortium, 1995). The L´Atalante, Discovery and Urania Basins were identified in 1993 and 1994 south-west of Crete in a plateau that lies between the crest of the Mediterranean Ridge and the Matapan Trench. The Urania Basin (35°14´ E, 21°28´ N) has been first investigated as part of the MEDRIFF programme in 1993 (MEDRIFF consortium, 1995). The depression in the deep-sea floor is horse-shoe shaped with a diameter of app. 6 km. We report here biogeochemical investigations that were carried out during Meteor cruise M40/2 in December 1997 in the north-western branch of the 3570 m-deep basin.

3.3.2 Results and Discussion

The concentration of dissolved oxygen and the redox potential decrease rapidly within a 20-m thick chemocline above the sea water-brine interface at 3490 m water depth (Fig. 1a, b). The homogenous brine has a salinity of 162 ‰ and its major ion composition is similar to those of the Tyro and the Bannock Basin (De Lange and Haven, 1983; De Lange et al., 1990). The deep stagnant water contains high concentrations of 90 mM sulfate (Fig. 1a) and a constant sulfide concentration of 10-11 mM has been determined throughout the 80 m deep basin (Fig. 1b). It contains thus 5 times and 3.5 times more H_2S than it has been reported for the euxinic Tyro Basin (2.2 mM) and Bannock Basin (3 mM), respectively (De Lange et al., 1990; Luther III et al., 1990). The concentration of sulfide in the Urania Basin is even 2-3 mM higher than the bottom water of the hypersulfidic Framvaren fjord (8 mM) (Andersen et al., 1988) and exceeds all values reported for anoxic basins in the marine environment. In the 20 m thick intermediate layer above the brine profiles of dissolved oxygen and counter-diffusing sulfide show very steep concentration gradients, indicating rapid cycling of sulfur compounds. The profiles suggest that sulfide oxidation takes place predominantly at the lower border of the chemocline.

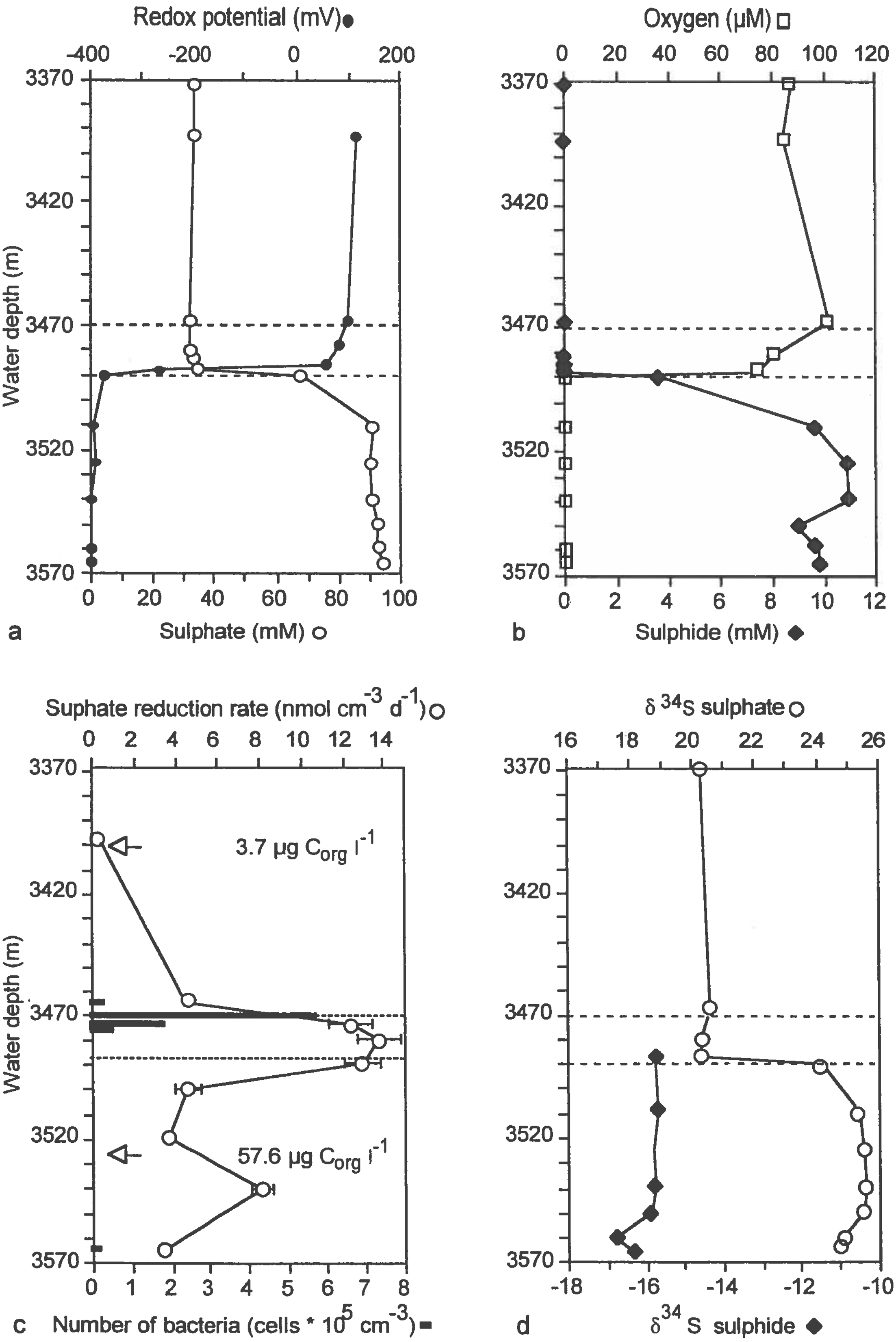

Fig. 1: Investigations in the water column. a) Redox potential and sulfate concentration b) Oxygen and sulfide concentrations c) Sulfate reduction rates and bacterial cell numbers, the arrows indicate the depth of the deployment of the *in situ* pumps and the according numbers give the concentration of organic carbon at these depths d) Sulfur isotopic ratios of sulfate and sulfide. The dashed lines indicate the position of the chemocline.

At the depth between sea water and brine, video inspection revealed a layer of dense particle accumulation (Fig. 2). Export of organic material to deep ocean floors occurs mainly in the form of sinking particulate matter. The transit of organic particles to the sea floor is hindered at the interface in the deep basins because of the density difference between seawater and brine and leads to the formation of an organic rich layer similar to the fluff layer covering the sediment surface in areas of anoxic basins like the Black Sea.

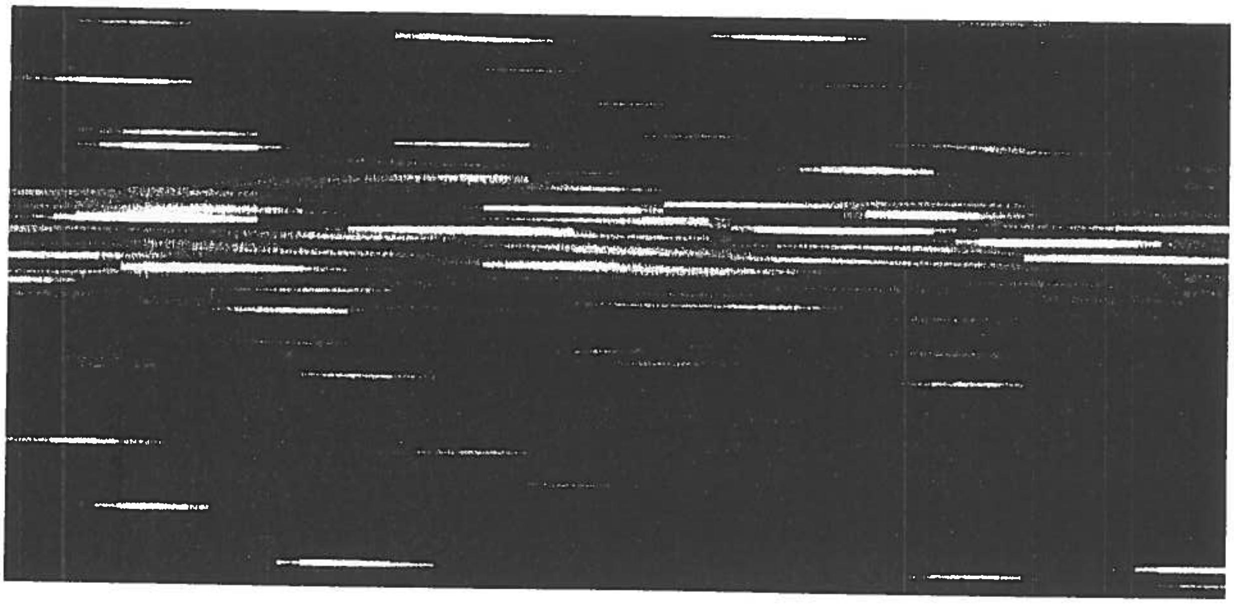

Fig. 2: Photograph of particle accumulation at the brine – sea water interface at 3490 m water depth.

At the interface between sea water and brine secondary bacterial production is stimulated by the high input of organic carbon and the availability of nutrients diffusing up from the brine. The concentrations of bacterial cells increased in this zone significantly, by more than order of magnitude. Highest values of $5.5 \bullet 10^5$ cells ml^{-1} were found at the upper boundary of the chemocline (Fig. 1c). Sulfate reduction measured in incubated water samples showed highest rates of 13-14 nmol cm^{-3} d^{-1} within the 20 m thick intermediate layer (Fig. 1c). These are the highest rates measured in a marine water column. For comparison, in the Black Sea, the largest known basin in which sulfate reduction is observed within the water column, rates of 0.036 nmol cm^{-3} d^{-1} have been determined at the 100 m deep oxic/anoxic interface (Jørgensen et al., 1991; Albert et al., 1995). Here, the deep anoxic water contains approx. 400 µM sulphide. Comparable rates of 20 nmol SO_4^{2-} cm^{-3} d^{-1} were determined in a 1-2 cm thick flocculent layer covering the Black Sea sediment surface (Albert et al., 1995). Based on the isotopic composition of sulfate, sulfate reduction was also suggested to occur at the brine - sea water interface of the Tyro and Bannock Basin (Luther

III et al., 1990). Sulfate reducing bacteria fractionate the sulfur atoms producing sulfide which is enriched in ^{32}S. Consequently, the sulfate that remains will be more enriched in ^{34}S. The concentration and sulfur isotopic composition of sulfate above the chemocline of the Urania Basin are typical for Mediterranean sea water indicating that no sulfate reduction took place in the water column. The extremely high sulfate and sulfide concentrations below the chemocline show a constant sulfur isotopic composition (Fig. 1d). Hydrogen sulfide is consistently depleted in ^{34}S by ~ 40 ‰ compared to sulfate at corresponding depths, indicating that microbial dissimilatory sulfate reduction is taking place. The isotopic fractionation results in a $\delta\ ^{34}S$ value for the remaining sulfate which is considerably higher than the mean value for ocean water which is close to +20 ‰. The isotopic fractionation is within the range observed in experiments with pure cultures of sulfate reducing bacteria (Habicht and Canfield, 1996). When compared to isotopic fractionation in the Tyro and Bannock Basin (Henneke et al., 1997) it is suggested that the extremely high sulfide concentration hinders the growth of bacteria which are able to disproportionate intermediate sulfur species that can be formed upon re-oxidation of hydrogen sulfide (Canfield and Thamdrup, 1994) at the interface. A similar fractionation of ~ 40 ‰ is also observed in the hypersulfidic (8 mM) Framvaren Fjord (Andersen et al., 1988). A combined mass and isotope balance of the anoxic water column demonstrates that sulfate with an isotopic composition of Messinian evaporites (about +22 ‰) was the original sulfate source of the brine.

The chemoautotrophic activity in the chemocline leads to the synthesis of new cells which is the major source of particulate organic carbon (POC). For the determination of particulate material *in situ* pumps were deployed in the water column 60 m above the chemocline and in the brine 30 m below the interface. Compared to the low content of 3.7 µg POC per litre in the sea water above the interface there was a 15-fold increase of POC in the deep brine to 58 µg POC l^{-1}. This phenomenon is very similar to the investigations in the Tyro and Bannock Basin (Henneke and De Lange, 1990) where values of approx. 50 µg POC were measured in the brine compared to very low values in the sea water above (~ 5 µg l^{-1}). Directly in the chemocline of these basins, the POC content increased even to values of ~150 µg l^{-1}. For the Urania Basin a similar value can be expected. A sulfate reduction rate of 14 nmol SO_4^{2-} cm^{-3} d^{-1} means an assimilation rate of about twice as much carbon (28 nmol C cm^{-3} d^{-1} or 336 ng C cm^{-3} d^{-1}). Assuming that half of the assimilated carbon is used for the production of cell mass this would yield 168 µg carbon per liter and day. Thus, the high concentration of POC in the brine is due to an accumulation of organic particles at the interface and a subsequent secondary bacterial productivity. A productivity attributed only to sulfate reducing bacteria can be estimated to account for approx. 60 g C l^{-1} y^{-1}. The average primary productivity in the open eastern Mediterranean Sea is 26 g C m^{-2} y^{-1} (Bethoux, 1989)

Dissolved organic carbon (DOC) was not measured during this investigation but for the Tyro and Bannock Basin 4 mg DOC were measured close to the interface and in the brine compared to 1-2 mg l^{-1} in sea water above (Henneke and De Lange, 1990). The DOC is utilized by free-living sulfate-reducing bacteria and transformed to POC. A similar mid-water increase of bacterial biomass was also observed at the brine - sea water interface of the Tyro and Bannock Basins (Erba, 1991).

Below the chemocline of the Urania Basin sulfate reduction is on-going with rates between 2 and 4 nmol SO_4^{2-} cm^{-3} d^{-1} (Fig. 1c). The hypersaline and hypersulphidic conditions in the deep basin do not appear to inhibit organic matter utilisation and decomposition by sulfate reducing bacteria.

In the surface sediments, profiles of sulfate and ammonium concentrations continue with constant high values from the brine into the sediment (Fig. 3a). Organic carbon content (Fig. 3a) was determined to be extremely low (2-5 mg per g sediment) compared to the high POC concentrations in the brine, suggesting that despite the accumulation of organic particles at the brine - sea water interface and the secondary productivity, organic carbon is not accumulated and preserved in the sediment but is remineralised in the deep basin by sulfate reducing bacteria. In contrast, the upper 14 cm of sediment contain between 600 and 700 mg sulfur per g sediment (dry weight) (Fig. 3b). The main fraction is elemental sulfur. In the brine a concentration of 93 mg elemental sulfur l^{-1} has been determined which is formed by the oxidation of sulfide at the interface and is sedimenting through the water column to the sea floor. The thickness of the sulfur-rich layer in the sediment could give an indication of the time scale of the formation of this extreme sulfidic environment. Sulfate reduction rates in the sediment were measured by *in situ* incubations with an autonomous lander for the first time at this abyssal depth and in parallel on-board ship incubations. The determined rates (Fig. 3c) are comparable with the measurements in the water column and peak in 3-5 cm sediment depth.

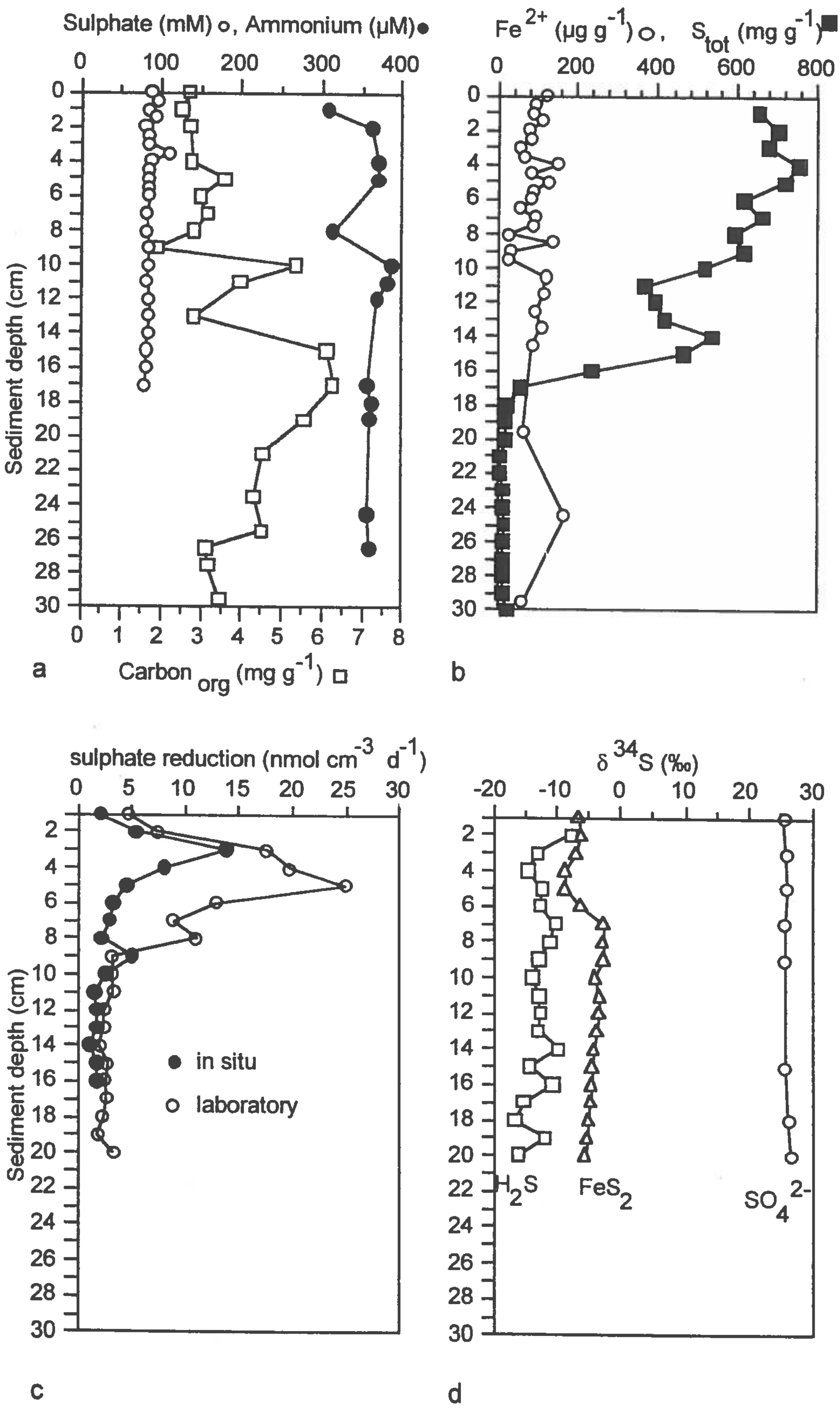

Fig. 3: Investigations in the sediment. a) Sulfate and ammonium concentrations in sediment pore water, organic carbon content in mg per g dry weight of sediment b) Iron and total sulfur concentrations c) Sulfate reduction rates measured *in situ* and in whole-core incubations in the laboratory d) Sulfur isotopic ratios of sulfur species.

The profiles of the *in situ* and laboratory incubations show a very similar curvature, down to 3 cm depth the profiles are almost identical, deeper in the sediment the laboratory incubations show slightly higher rates. This implies that the pressure effect on sulfate reduction rates is minor and that the measurements in the deep water column are reliable. Sulfur isotope partioning during microbial sulfate reduction is similar to the water column (Fig. 3d). The isotopic composition of the S^0 (+ pyrite) fraction in the chemocline is similar to that of surface sediments. Heavy isotope enrichment in the pyrite (+S^0) fraction compared to co-existing hydrogen sulfide is probably related to polysulfides and / or sulfur species derived from organic matter.

At the brine - sea water interface of the deep Urania Basin, the accumulation of organic matter stimulates microbial activity which leads to a high secondary productivity in the deep extreme environment. The chemoautotrophic activity sustains the two layer system, characterised by a sharp chemocline, and has a strong impact on the biogeochemical evolution of the brine and the geological record in the sediment. Extremely high bacterial sulfate reduction rates in the intermediate layer between sea water and brine result in the highest sulfide concentrations reported for a marine basin and determine the sulfur isotopic fractionation. The organic carbon is not preserved in the sediment due to the proceeding activity of sulfate reducing bacteria in the hypersulfidic basin.

We conclude that these investigations are of great importance for the understanding of the sulfur cycling in extreme environments and the geological record of marine processes.

3.3.3 Methods

Water samples were taken with Niskin bottles, images were obtained with a digital camera mounted on a CTD rosette system (SBE911plus). Two parallel profiles were sampled at the same day. Dissolved oxygen was measured in triplicate samples by standard Winkler titration. Salinity was measured refractrometrically. Redox potential was determined in water samples using a platinum electrode (Ingold) and a pH / mV - meter (WTW).

Water samples for the analyses of dissolved hydrogen sulfide and sulfate were immediately transferred to 20 % zinc acetate (w/v) and later converted into Ag_2S and $BaSO_4$ respectively, the sulfur isotopic ratio was determined by combustion-isotope-ratio mass spectrometry (C-irmMS). Results are given in the δ-notation with respect to the V-CDT standard with an overall precision of +/- 0.2 ‰.

The total number of bacterial cells was determined in water samples preserved in formaldehyde-seawater solution (2 % final concentration) by the AODC (Acridyne Orange Direct Count) method using an epifluorescense microscope. Sulfate reduction rates were measured in triplicate water samples that were filled from Niskin bottles carefully into 10 ml serum vials. The vials were filled from the bottom and allowed to overflow for 15 s before being sealed with butyl stoppers. Within 30 min the vials were injected with 200 kBq (50 µl) of carrier free ^{35}S sulfate, thoroughly mixed and incubated in the dark at *in situ* temperature for 10 hours. Bacterial activity was stopped by transferring the samples into an equal volume of 20 % zinc acetate (w/v).

At two depth (60 m above and 30 m below the seawater - brine interface) two parallel *in situ* pumps were deployed (Challenger Oceanic Mark II) to collect particulate material on two kinds of filters (Nuclepore 1.0 µm and GFF) with a diameter of 293 mm. Carbon was analysed on 25 mm ø subsamples of the GFF filters by high temperature oxidation using a CHN-O-Rapid HERAEUS element analyser. The organic carbon fraction was measured in samples pre-treated with 1 M phosphoric acid solution to remove carbonates. Two replicates of each sample were run to reduce variability due to potential sample heterogeneity. Elemental sulfur was determined in the filtrate of the nuclepore filter by HPLC.

Sediment samples were obtained with a box corer (50 cm x 50 cm). The sediment was stratified with a light grey colour down to approx. 14 cm sediment depth, below this depth the sediment was homogeneously black. Subcores (56 mm ø) were taken from the boxcore and sliced in a glove bag under nitrogen atmosphere. Pore water was extracted with a pore water press from 1 cm sections and preserved in zinc acetate (20 %) or zinc chloride (2 %) for determination of sulfhide or sulfate respectively or deep-frozen for the analyses of ammonium by the flow injection method for small samples (Hall and Aller, 1992). Sulfate was measured by ion chromatography. The carbon and sulfur content were determined on dried 1 cm sediment samples by high temperature oxidation using a Fisons 1500 NCS element analyser. Samples for the determination of organic carbon were decarbonated by washing with 1 M HCl. Wet sediment samples of 2 mm intervals were immediately transferred to 0.5 N or 0.25 M hydroxylamine hydrochloride in 0.25 M HCl for the extraction of total iron Fe(II) + Fe (III) and Fe (II) respectively and subsequent colourimetrical measurement (Lovely and Philips, 1987).

Determination of sulfate reduction in the sediment was carried out using the autonomous lander LUISE (lander for underwater *in situ* experiments) (Greeff et al., 1998). This free-falling instrument allows *in situ* injection of radio-labelled sulfate into six enclosed sediment cores to determine sulfate reduction rates in the sediment down to 60 cm sediment depth. After landing on the sea floor and an initial wait cycle carrier free ^{35}S sulfate was injected into the cores which were then incubated directly at the sea floor for a period of 10-12 hours. Immediately after recovery on deck the cores were sliced in 1 cm intervals into 20% zinc acetate solution to stop the reaction. Parallel to the *in situ* incubations subcores (36 mm ø) taken from a box core were injected and incubated in the laboratory. In all samples ^{35}S incorporation into total reducible inorganic sulfur (TRIS) was determined using the single-step chromium reduction method (Fossing and Jørgensen, 1989). Sulfur species and sulfur isotopic composition were determined in 1 cm sediment sections that were sliced under nitrogen atmosphere into 20 % zinc acetate and deep-frozen.

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3.4

Geochemistry and sulfate reduction rates in hydrothermally influenced sediments in the Aegean Sea

Wiebke Ziebis, Andreas Weber

Max Planck Institute for Marine Microbiology, Celsiusstr. 1, 28359 Bremen, Germany

3.4.1 Abstract

During Meteor cruise M40/2 to the Aegean Sea (Greece) in December 1997 new hydrothermal areas at water depths of 100-130 m, off the south to south-east coast of the volcanic island Milos, which is located in the central part of the Hellenic Volcanic Arc, were discovered. In a very active gas venting area sediment cores were retrieved that were characterized by extensive outgassing that continued even 24 hours after retrieval. By exact positioning of the research vessel along estimated fracture zones a hot vent area was sampled successfully and sediment cores were brought on board ship with temperature of 103° C. During the cruise investigations were also carried out in the central caldera of the volcanic island Santorini. To investigate and compare different hydrothermal areas, the physical and geochemical conditions at three sampling stations (reference station, gas vent, hot vent) off Milos and at one station in the northern part of the central caldera of Santorini were studied in detail. The autonomous lander LUISE was deployed successfully at these sites to carry out *in situ* incubations for the assessment of sulfate reduction rates in the different hydrothermally influenced sediments.

3.4.2 Introduction

The increasing discoveries of submarine hydrothermal systems along all continental active margins have raised the attention of different fields of research to investigate their importance in the marine environment. Shallow water hydrothermal systems offer the opportunity to carry out detailed investigations in order to study their influence on the surrounding sedimentary environment and water column processes.

One of the seismically most active area on earth is the Aegean Sea. A major geomorphological feature is the active Hellenic Volcanic Arc which was formed by the subduction of the African plate below Europe. The concave shaped arc stretches out from the main land of Greece to the coast of Turkey and geothermal areas have been described for a number of islands (Fytikas et al., 1989; Varnavas and Cronan, 1991) which are connected by submarine ridges. There have been relatively few studies on submarine venting activity in coastal and shelf areas. Extensive venting has been reported recently for the coastal water off the island of Milos which is situated in the central part of the arc (Fig. 1). Milos is one of the best studied hydrothermal areas in the Aegean (Fytikas, 1989; Botz et al., 1996; Cronan and Varnavas, 1993; Fitzsimmons et al., 1997). An area of 35 km^2 geothermally active seabed (Dando et al., 1995a) has been calculated to occur around the island mainly off the south to the south-east coast from the shore line to 300 m water depth.

Because of the shallow water depth venting is of the gasohydrothermal type with gas and hot fluid (< 150° C) emerging through the sandy sea floor. Gases mainly consist of CO_2 (up to 90 %) with H_2, H_2S and CH_4 also present at concentrations of 3, 8 and 10% respectively (Dando et al., 1995a; Fitzsimmons et al., 1997). During recent investigations in Palaeochori Bay (Ziebis et al., submitted) it was shown that venting activity occurred along fracture zones and is most intense where fault lines intercept. In some areas extensive streams of gas bubbles emerged from the sea floor, releasing large volumes of gases to the water column. In other areas the sediment is covered by white and yellow precipitates and it was shown that in these zones hot acidic vent fluid emerged through the permeable sea bed (Ziebis et al., submitted). A number of studies has been carried out to investigate venting activity in the coastal area down to 80 m water depth as part of Mast-2 and Mast-3 projects (Dando et al., 1995a; Dando et al., 1995b; Fitzsimmons 1997; Southward et al., 1997; Thiermann et al., 1994, 1997) but beyond 100 m water depth only some sites of active venting have been discovered and not yet investigated. The biogeochemistry of hydrothermally influenced surface sediments in coastal and shelf areas has been very little investigated so far. In Santorini three volcanic islands are bordering a central caldera and two central islands, Palaea Kameni and Nea Kameni, where the centre of hydrothermal discharge is located (Smith and Cronan, 1983; Cronan et al., 1995). During Meteor cruise M40/2 it was our aim to find other areas of hydrothermal activity in deeper water off the island of Milos and in the central caldera of Santorini. Objectives were to investigate and compare the geochemistry and biogeochemical processes (sulfate reduction rates) at different hydrothermally influenced sites.

3.4.3 Materials and Methods

3.4.3.1 Study area and sampling

During a cruise with RV Meteor to the Aegean Sea in December 1997, three stations south-east off the island Milos and one station in the northern part of the central caldera of Santorini island were investigated. Sediment sampling was carried out with a box corer (50 x 50 cm) and a multiple corer. Inspection of the sea floor prior to sampling was done using an ROV. Off the south coast of Milos, at Stn. 618, no hydrothermal activity was obvious and it was chosen as „reference station". In order to find active areas, we projected the geological fault zones, known from a geological map of the island Milos, off shore. It was known from previous investigations that the vents off the coast of Milos in Palaeochori Bay appeared along these fracture zones and active venting was most intense at the interception of fault lines (Ziebis et al., submitted). To the south-east of the island, at a crossing of prolongued fault lines, intense gas bubbling could be seen by echo sounding. Sampling was only possible with the box corer and we retrieved sediment cores that were vigorously outgassing. Gas bubbles even continued to emerge from the sediment cores 24 hours after retrieval. This station is named „Milos gas vent" in the following. During further inspection of the area, at Stn. 786, we discovered by ROV inspection, areas that were covered by white and yellow precipitates, indicating hydrothermal activity. We succeeded to sample exactly in an active area and the sediment core brought on deck had a temperature of 103° C. This station was called „Milos hot vent" (see Fig. 2 for positions and Table 1). During the course of the cruise along the Helenic Volcanic Arc, we tried to find active areas also in the central caldera of Santorini. Although ROV inspection and echosounding gave no indication of hydrothermal activity, we chose a station in the northern part of the caldera (Stn. 714), where venting activity is believed to occur. This station was named „Santorini caldera" (Fig. 3). The exact positions and the water depths are listed in Table 1. At the same sites the autonomous lander LUISE was successfully deployed for *in situ* incubations to assess sulfate reduction rates in the different areas.

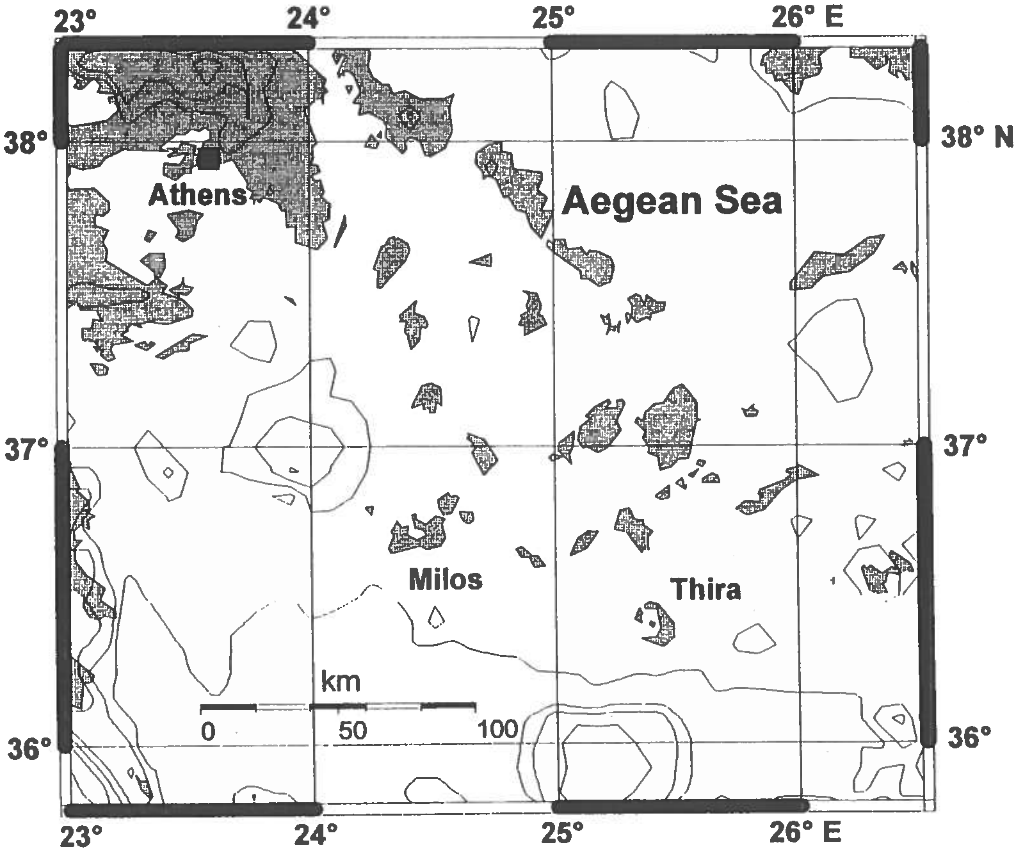


Fig. 1: Map of the Aegean Sea indicating the location of the volcanic islands Milos and Santorini (Thira) situated on the Hellenic Volvanic Arc.

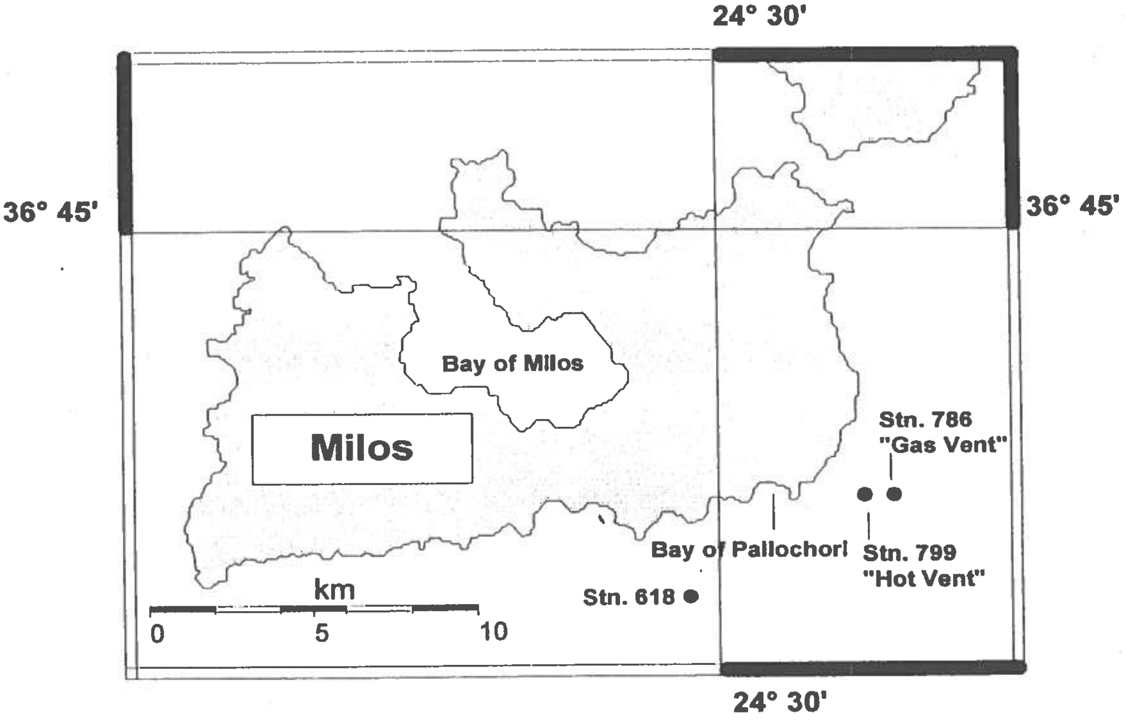


Fig. 2: Locations of the three sampling stations off the island Milos.

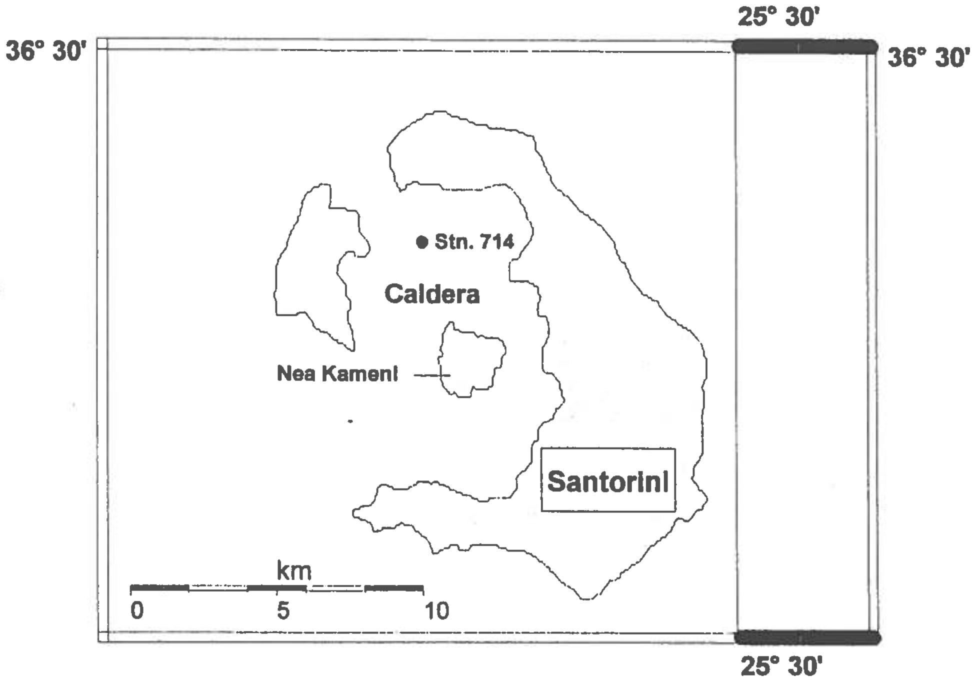


Fig. 3: The island Santorini with the sampling station indicated.

Table 1. Sampling stations

Stn. No.	Name	Position	Water depth
618	Milos reference station	36°38,86`N, 24°30,11E	103
786	Milos gas vent	36°40,05`N, 24°33,37E	132
799	Milos hot vent	36°40,09`N, 24°32,96E	112
714	Santorini caldera	36°26,61`N, 25°23,00E	381

3.4.3.2 Sediment profiles

Sediment cores were brought immediately after retrieval to the laboratory for measuring profiles of temperature along with pH, redox potential and oxygen; pH was determined in 1 cm depth intervals using a combination pH electrode together with a temperature probe connected to a WTW pH/mV meter, thus the pH values were temperature compensated. Redox potential was measured with an Ingold electrode using the same meter. Dissolved oxygen was measured using clark-type micro-electrode mounted on a micromanipulator, profiles were measured in depth increments of 250 μm.

3.4.3.3 Chemical analyses

Sediment cores were sliced under nitrogen atmosphere in a glove bag. For the analyses of iron concentrations sediments were sectioned in 0.2 cm intervals for the top 1 cm sediment, in 0.5 cm section to a depth of 10 cm and in 1 cm section below this depth. Poorly crystalline Fe (III) and HCl extractable Fe (II) concentrations were extracted from sediments and analyzed according to a method described by Lovley and Phillips (1987) and modifications by Kostka and Luther III (1994). 200 mg of subsample (wet sediment) of each sediment section was added to 10 ml 0.5 M HCl in a pre-weighed plastic vial. After shaking for 1 hour the sample centrifuged (5 min., 4000 rpm). 100 µl of the supernatant were added to 5 ml of Ferrozine (1 g l^{-1}) in 50 mM Hepes buffer at pH 7. Fe (II) was subsequently determined spectophotometrically at 562 nm. For the determination of total HCl extractable iron a second subsample (100 µl) was added to a reducing Ferrozine solution (Ferrozine with 1% hydroxylamine hydrochloride) and measured after 3 h reaction time. Fe (III) was calculated as the difference between total Fe and Fe (II) concentrations.

For the extraction of pore water sediment cores were sectioned under nitrogen atmosphere in 1 cm sections that were squeezed in a pore water press under nitrogen pressure. Samples were deep frozen for the later analyses of ammonium, manganese, barium and lithium. Pore water for dissolved sulfide and sulfate were transferred to 20% (wt/vol) ZnAc and 2% (wt/vol) $ZnCl_2$ respectively. Ammonium was analyzed by using a flow injection system with gas exchange and conductivity detection (Hall and Aller, 1992). Bulk concentrations of manganese, lithium and barium in pore water samples were analysed by using ICP - MS. Sulfide was measured using the methylene blue method (Cline, 1969). Sulfate was determined by non-suppressed anion chromatography using a Waters 510 high performance liquid chromatography pump, a Waters WISP 712 autosampler (100 µl injection volume), a Waters IC-Pak anion exchange column (59 x 4.6 mm) and a Waters conductivity detector.

Subcores for the determination of total carbon, nitrogen and sulfur as well as for sediment porosity and density were sectioned in 1 cm intervals and frozen until further processing in the laboratory. Porosity was determined on subsamples that were dried at 60° C. C, N and S concentrations were analyzed using a Fisons 1500 NCS elemental analyzer. Organic carbon was measured in subsamples that were decarbonated by washing with 1 M HCl prior to analysis. Inorganic carbon (C_{in}) was calculated from the difference between total carbon and organic carbon (C_{org}).

3.4.3.4 Sulfate reduction rate measurements

In situ radiotracer measurements with the benthic lander LUISE

In situ radiotracer measurements of sulfate reduction were carried out with the autonomous benthic lander LUISE (Greeff et al., 1998) (Fig. 4). The free-falling system lowered six polycarbonate coreliners with a length of 60 cm (ø 36 mm) into the sediment. One core liner can be replaced by a temperature sensor for *in situ* measurement to a sediment depth of 60 cm. After a lag period (pre-programmed security time until the lander reached the sea floor), radio-labelled sulfate diluted in bottom water from the same station was injected into the cores. By means of a central spindlebar, driven by electrical motors, canulas were vertically inserted into each core injecting 500 µl tracer solution (200 kBq $^{35}SO_4^{2-}$, Amersham) in 1 cm depth increments. The cores were incubated at the sea floor for periods of 7 to 11 hours depending on the water depth. Longer incubation periods were planned for deeper areas because sulfate reduction rates were expected to be lower. Immediately after recovery of the lander, the cores were sliced into centrifuge tubes containing 10 ml ZnAc solution to stop further bacterial activity. The upper 0-5 cm were sectioned into 1 cm segments, the following 5-15 cm into 2 cm segments and the remaining core into 5 cm segments. The samples were kept refrigerated (4° C) until further processing.

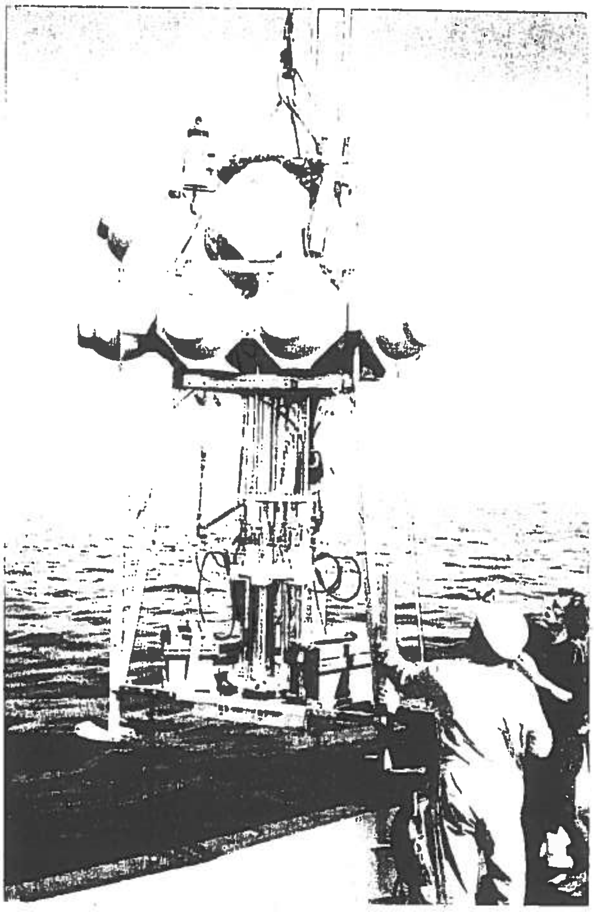


Fig. 4: The benthic lander LUISE (Lander for Underwater *in situ* Experiments)

3.4.3.5 Whole core laboratory experiments

In order to evaluate potential differences between *in situ* and laboratory studies, sulfate reduction rates were also determined in the laboratory using a whole-core $^{35}SO_4^{2-}$ incubation method (Jørgensen, 1978). Three or more undisturbed sediment cores (with the same diameter as the *in situ* cores) were subsampled from freshly collected sediment cores obtained by a multiple corer deployed at the same locations as the lander. Immediately after subsampling the cores were injected horizontally with 10 µl tracer solution (200 kBq $^{35}SO_4^{2-}$ per injection) through silicone filled ports at 1 cm intervals. The subcores were incubated in the dark at *in situ* temperatures. The incubation time was equal to the time period of the *in situ* incubations at the same locations. At the end of the incubation experiments bacterial activity was stopped by slicing 1 cm sections of the cores into 10 ml ZnAc solution. Samples were stored at 4° C until further processing. At all stations *in situ* and laboratory SRR were calculated from three replicate cores.

3.4.3.6 Incubation experiments in a temperature gradient block

The temperature gradient was regulated in an insulated block of aluminium (1.3 m long, 15 x 15 cm square size) by heating electrically at one end and cooling with a circulation thermostat at the other end. A constant temperature gradient between 8° C and 97 °C was established for the experiments. Sediment cores (ø 10 cm) retrieved by a multiple corer were subdivided into 2 or 3 depth ranges (0-7 cm, 8-15 cm and 15-21 cm). Subsamples of 10 cm^3 were transferred under nitrogen atmosphere to 15 ml Kimble vials, that were closed with butyl stoppers and screw capped. The vials were placed into the holes of the thermo block for a temperature equilibration time of 30 min. The block consisted of 3 rows with 14 holes, thus allowing incubations at 14 different temperatures in intervals of 5-6° C of three replicate samples. After 30 min. 10 µl tracer tracer solution (200 kBq $^{35}SO_4^{2-}$) was injected through the butyl stopper and the sample was mixed vigorously. The samples were incubated for 8-10 hours. Metabolic activity was terminated by fixing sediment samples in 20 ml of 20% ZnAc solution. The samples were kept cooled (4° C) until further processing in the laboratory.

All laboratory and *in situ* SRR were determined using a single step acid Cr^+-distillation method to volatilize and trap the total reduced sulfur species as AVS and CRS ($^{35}SO_4^{2-}$ incorporated into AVS acid volatile sulfide = dissolved sulfide + iron monosulfide) and CRS (Cr–reducible S = pyrite + elemental S) (Fossing and Jørgensen, 1989). The H_2S that evolved from the total reduced inorganic sulfur (TRIS) was precipitated in ZnAc traps. After the distillation, the ZnS suspension was mixed with scintillation fluid (Ultima Gold XR, Packard) and counted in a liquid scintillation counter. Sulfate reduction rates were calculated according to Jørgensen (1978).

3.4.4 Results

3.4.4.1 Sediment description

Off the coast of Milos the sediment at the reference station had a homogenous light brown color and consisted mainly of quartz sand of a median grain size of 200 µm. The cores retrieved from the gas vent station were composed of a slightly finer sand, median grain size 180 µm and the sediment had a gray color throughout the sediment depth. Intensive gas bubbling occurred in the cores (Fig. 5). The uppermost 0-10 cm of the sediment of the hot vent sample had a yellow-brownish color and were composed of sand (median grain size 180 µm). On the sediment surface yellow colored and white fluffy precipitates were found in some cores. In recent investigation at shallow submarine vents in the bay of Palaeochori, it was shown that the precipitate forms in areas where hot, sulfidic vent fluid is emerging from the sea floor (Ziebis et al., submitted). Below 10 cm depth the sediment was more consolidated and consisted of a dark gray silty sand. At 25 cm depth the sediment was very compacted and coring was limited to the upper sediment. From the gas vent and even more from the hot vent sample an intensive H_2S smell was obvious. Sulfide measurements showed values between 200 and 500 µM (data not shown) for the hot vent samples. During sampling procedure the H_2S emerged from the sediment, especially by the stripping of gas bubbles in the gas vent, thus the measurements are believed to have underestimated the sulfide contents of the samples and are not shown here. In previous investigations the H_2S concentrations in areas of hot fluid venting in Palaeochori Bay were in the range of 1-1.5 mM.

The sediment cores taken in the central Santorini caldera had a conspicuous reddish color. The upper 10 cm of the caldera sediment was a very soft, red-brownish mud (Fig. 7). Below this depth the sediment was consolidated and the color changed to green-brown. Below 15 cm depth the sediment was a compacted gray-greenish clay. At 23 cm depth a three cm thick pumice tuff layer occurred.

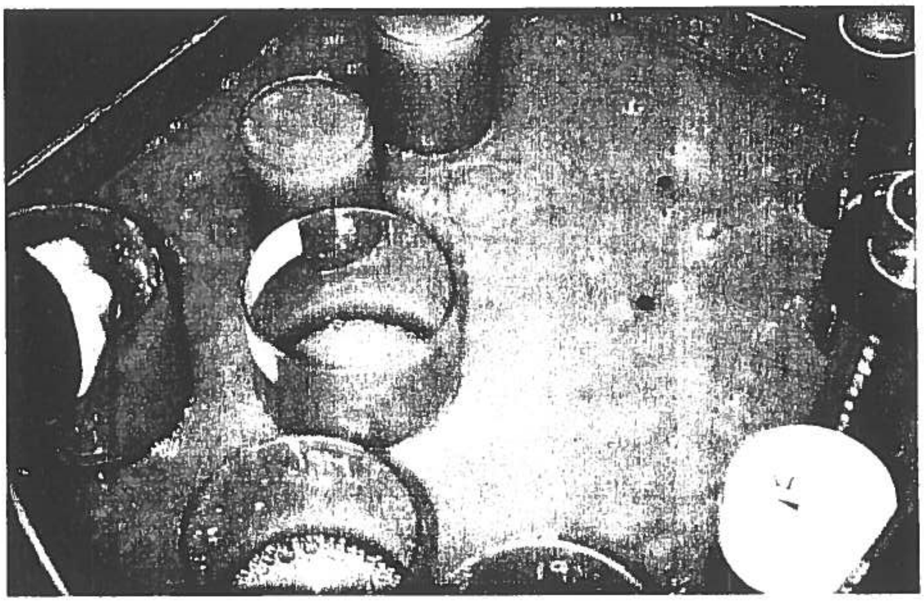


Fig. 5: Box - core sample of the gas vent showing the vigorous emerging of gas bubbles

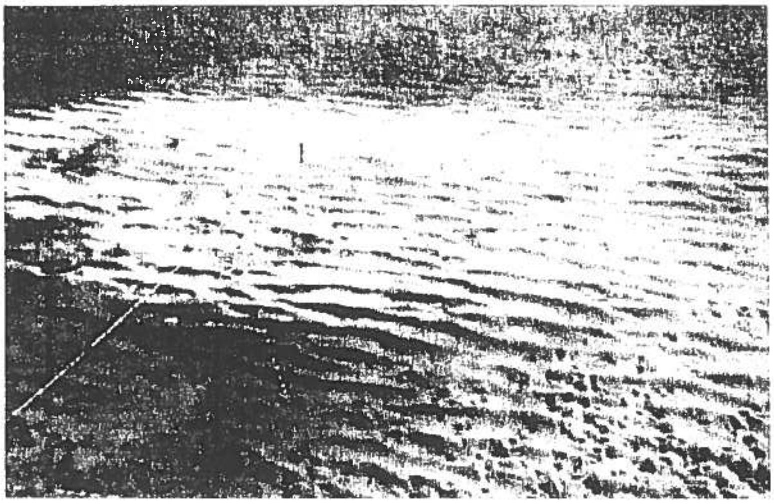
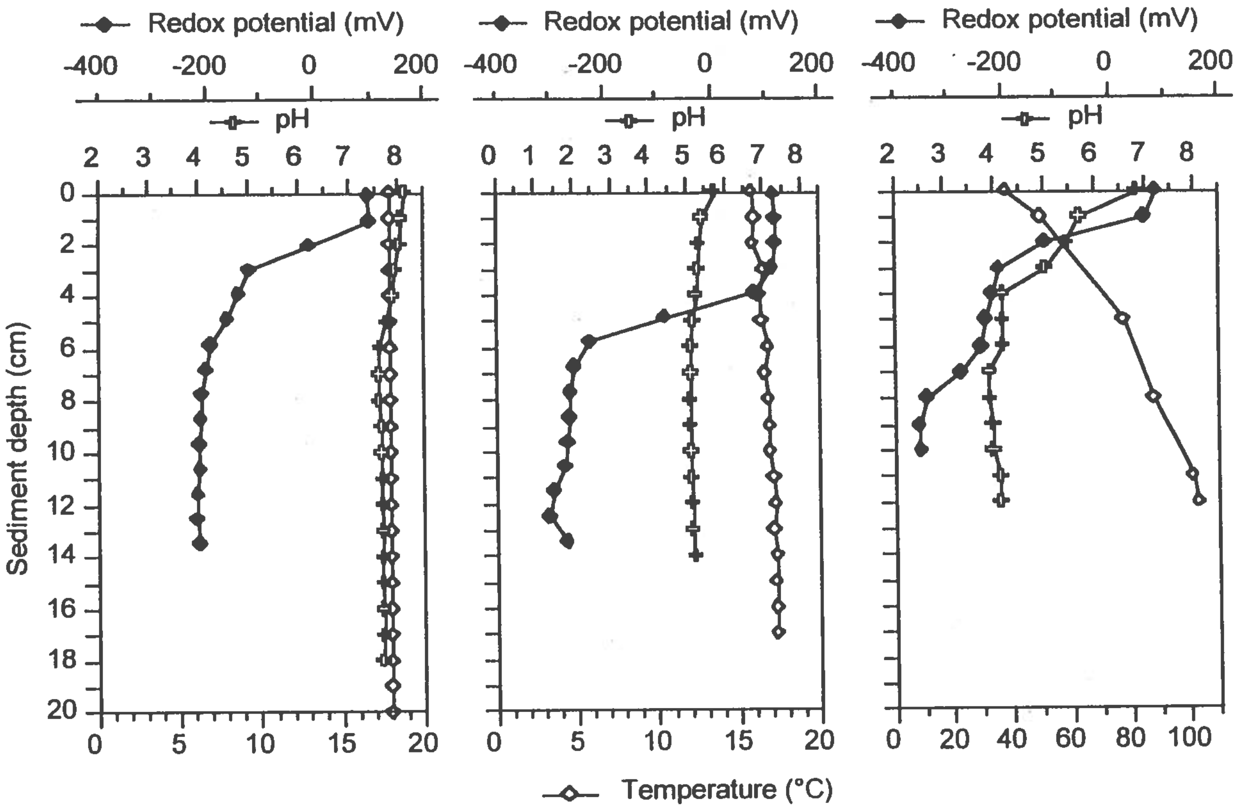


Fig. 6: Hot vent in shallow water depth(12 m) in Palaeochori Bay off the island Milos. White and yellow precipitates cover the sediment surface, where hot vent fluid is emerging from the sea floor.

Fig. 7: Box – core sample retrieved from the sea floor of the central Santorini caldera.

3.4.4.2 Profiles

The temperature, pH, redox potential and oxygen profiles measured in sediment cores taken at the three stations off Milos (reference station, gas vent, hot vent) showed significant differences between non-hydrothermal area and hydrothermal areas as well as between the two hydrothermal stations (Fig. 8).



Milos reference

a

Milos gas vent

b

Milos hot vent

c

Fig. 8: Profiles of temperature, pH and redox potential measured in sediment cores retrieved from the three Milos stations

The temperature in the sediment core taken in the gas vent area did not differ from the ambient sediment temperature although there was a slight increase of temperature with sediment depth. In contrast the pH was 3 units lower than the values measured at the reference station and stayed constant with depth. The redox potential exhibited a two times thicker oxidized surface layer (6 cm) than the core from the reference station (3 cm) (Fig. 8a, b). Oxygen penetrated down to 12 mm compared to 7-8 mm oxygen penetration depth (Fig. 9a, b) in the sandy sediment of the reference station. The oxygen profile also showed a penetration of surface water with high oxygen concentration down to a depth of 7 mm. Compared to the typical curvature of diffusive oxygen transport in the core of the reference station a different transport process was believed to be responsible. It is suggested that the vigorous upward flow of gas bubbles lead to a constant mixing within the upper layer, thus transporting oxygen into the sediment. This would also explain the profile of the redox potential. The core taken in the hot vent area had an elevated temperature of 33° C at the surface which increased with sediment depth to 103° C at 12 cm sediment depth. The pH value dropped more than 3 units from 7.4 at the sediment surface to 4 at 4 cm sediment depth. The sediment was reduced below 2 cm sediment with extremely negative redox potential values of -380 mV. Oxygen decreased at the sediment water interface to 50% air saturation and only little oxygen penetrated into the top 1 mm of the sediment (Fig. 9c). This core showed an obvious hydrothermal influence of hot, acidic, reduced vent fluid. The sediment core retrieved from the sea floor of the Santorini caldera showed similar temperature, pH and redox potential profiles as were measured at the Mills reference station (data not shown) and exhibited also typical oxygen profile with a penetration depth of 5 mm (Fig. 9d).

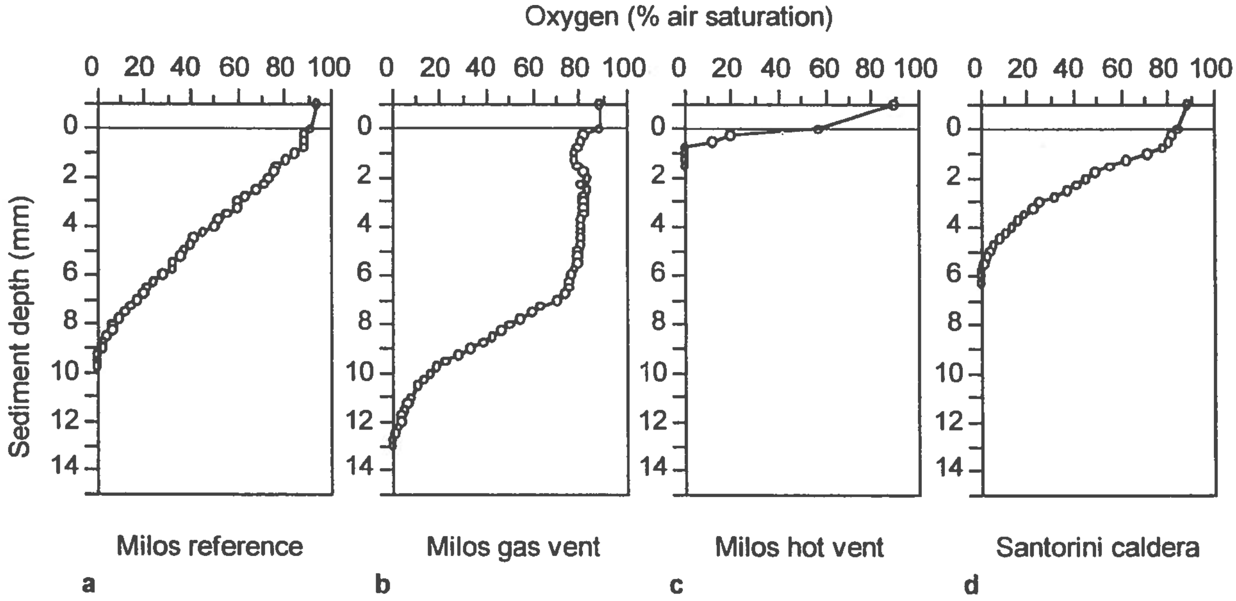
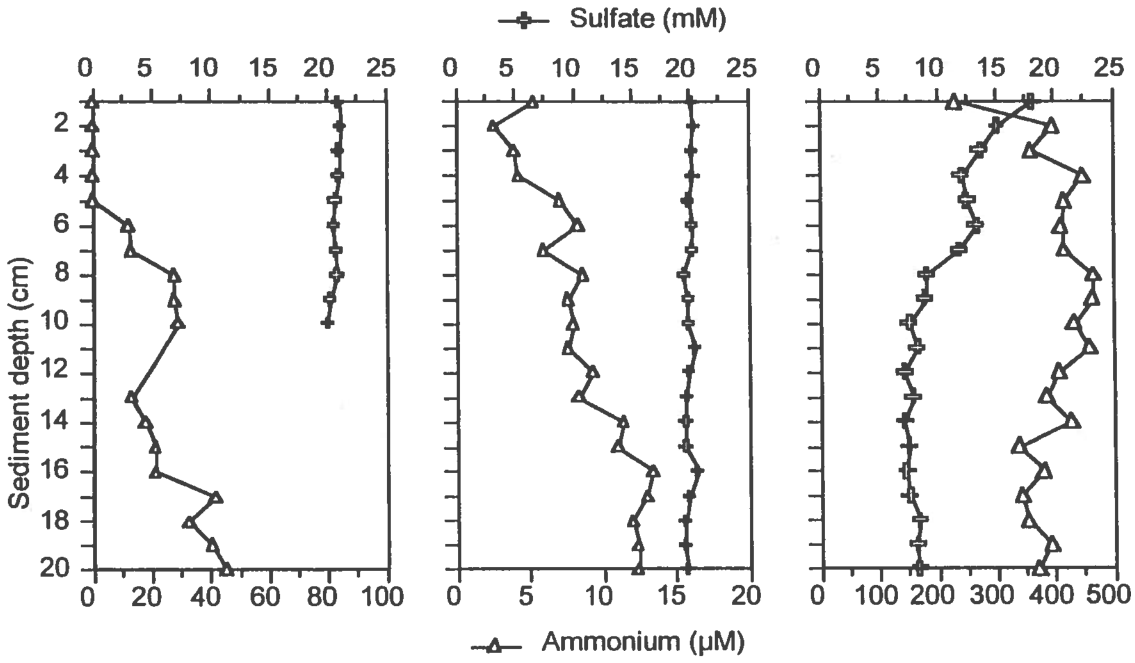


Fig. 9: Gradients of dissolved oxygen measured with clark-type microelectrodes in the sediment cores taken at the three Milos stations and at the Santorini caldera station. Profiles were measured in depth intervals of 250 μm.

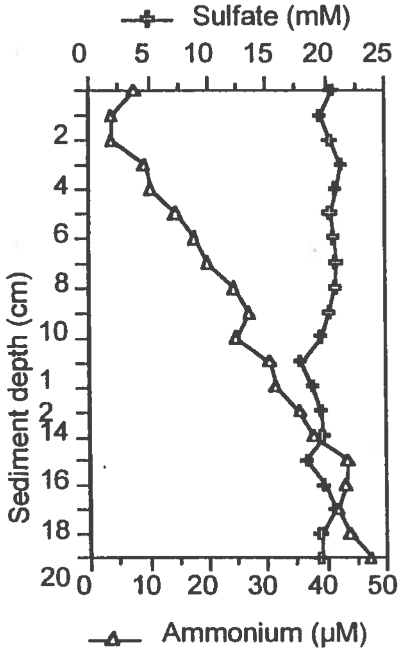
The depth distribution of pore water sulfate and ammonium concentrations showed significant differences in the four investigated areas.



Milos reference station
a

Milos gas vent
b

Milos hot vent
c



Santorini caldera
d

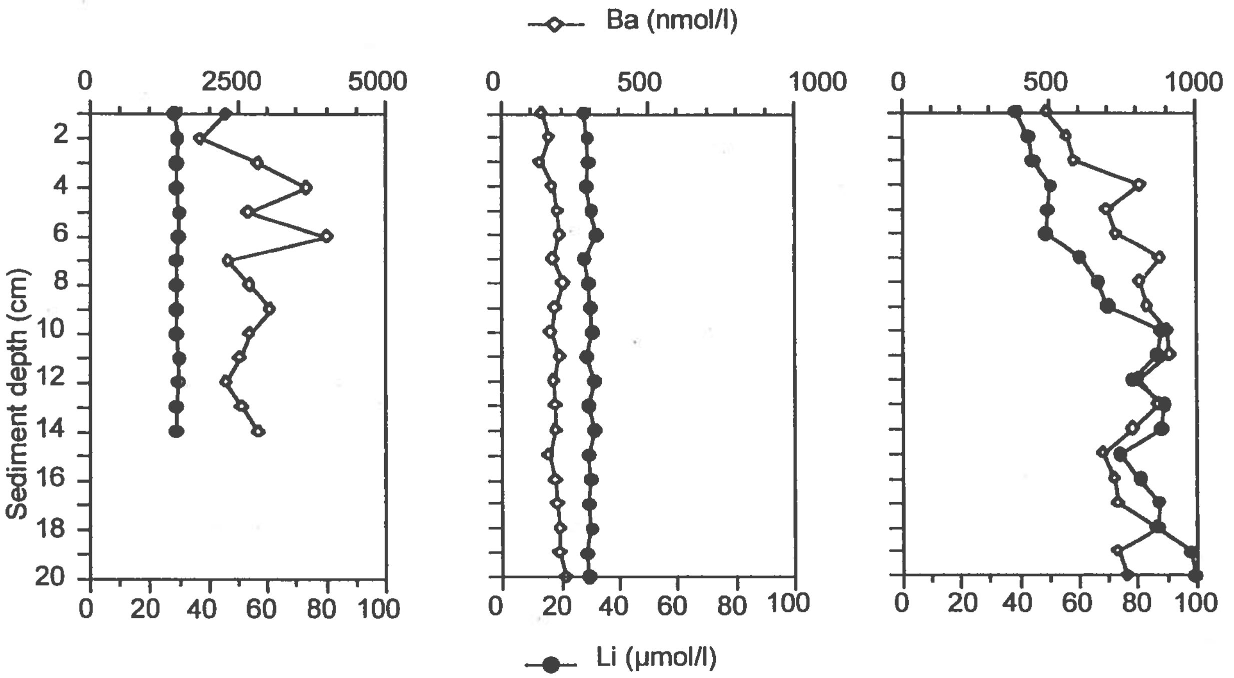
Fig. 10: Depth distribution of pore water ammonium and sulfate concentrations (Note the different scales for ammonium concentrations).

The sediment of the reference area had a typical constant sea water sulfate concentration of 22 mM. Ammonium was close to detection limit in the upper 5 cm, below this depth ammonium concentration increased with sediment depth to 40 µM (Fig. 10a). In the sediment of the gas vent the sulfate concentration had normal sea water values but ammonium was depleted to concentrations of 5-12 µM, showing only slight increase with depth (Fig. 10b). The homogenous distribution of ammonium throughout the sediment further constrained a mixing or stripping effect by the out-gassing. The sediment core taken at the hot vent sediment was extremely enriched in ammonium of up to 400 µM. The profile indicated a flux of ammonium from the sediment into the water column. In contrast sulfate concentrations were lower than in the ambient sea water and decreased with depth (Fig. 10c). This is in accordance with recent investigations of hydrothermal vents in the shallow area of Palaeochori Bay (Ziebis et al., submitted) that showed a depletion of sulfate in the hydrothermal fluid emerging through the upper permeable sea bed and an enrichment of ammonium of up to 900 µM.

In the sediment core of the Santorini caldera sulfate concentration showed no difference to ambient sea water concentrations and ammonium concentrations were comparable to the Milos reference station (Fig. 10d).

The concentration of barium and lithium in pore water of the 4 sites revealed a significant hydrothermal signal in the gas vent and in the hot vent area. The sediment core of the reference station showed high barium concentration around 2500 nM and lithium concentrations of 28 µM, which were constant with sediment depth (Fig. 11a). The sediment core taken at the gas vent again showed a very homogenous distribution throughout the core. Lithium occurred in similar concentrations as in the reference sediment but barium was drastically depleted to a concentration of 100 nM (Fig. 11b). The hot sediment core exhibited also an anomaly of very low barium concentrations and they increased with depth from 400 nM at the surface to 1000 nM at 20 cm sediment depth. The profile of lithium concentration showed an enrichment with depth from 50 to 100 µM (Fig. 11c). The pore water profiles in the hot vent sediment suggest a flux of barium and lithium from the sediment to the water column. The concentration profiles measured in the sediment core of the Santorini caldera were similar to the Milos reference station measurements and showed no obvious hydrothermal influence.

The concentrations of iron and manganese showed significant differences between the sediment cores sampled at the three Milos stations and the sediment core extracted from the sea floor in the Santorini caldera, which was extremely enriched in both elements.



Milos reference station

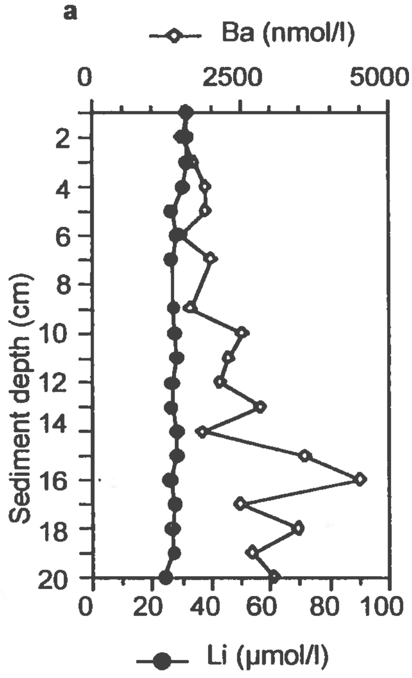
Milos gas vent

Milos Hot vent

a

b

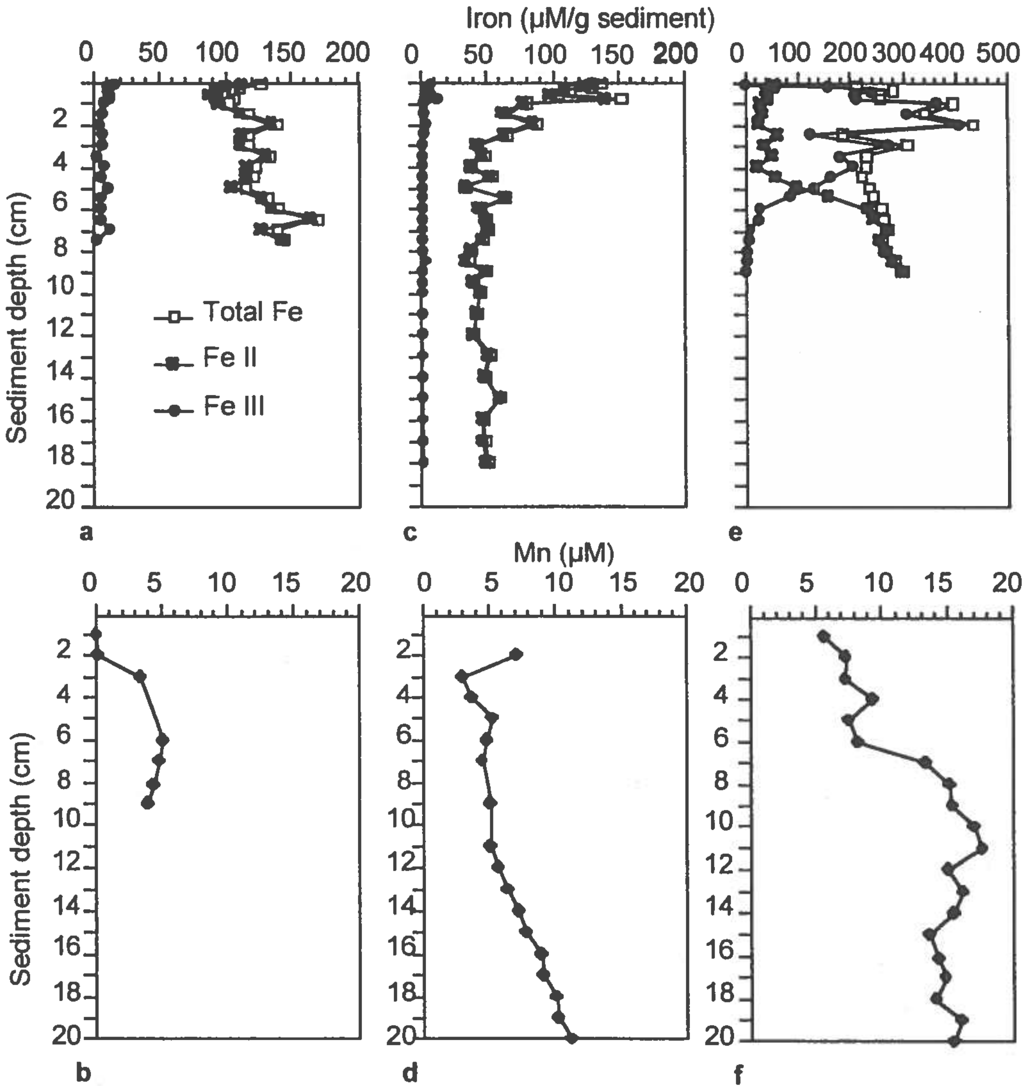
c



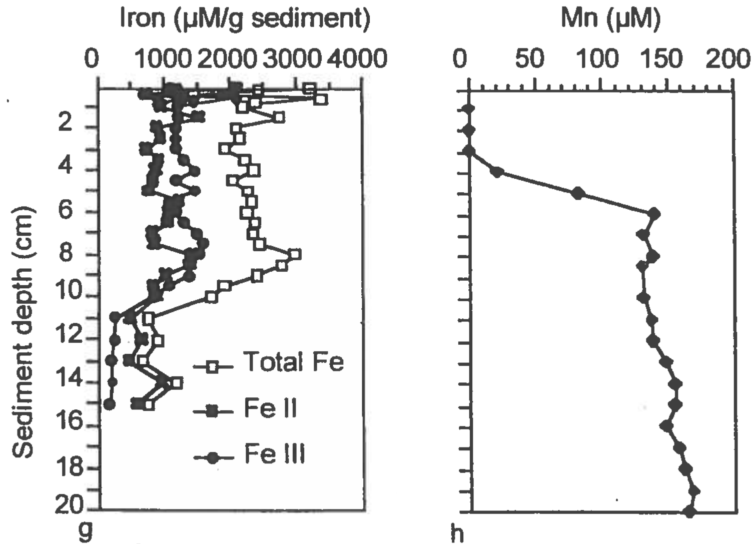
Santorini Caldera

d

Fig. 11: Depth distribution of pore water barium and lithium concentrations. (Note the different scales for the barium concentrations).



Milos reference station Milos gas vent Milos hot vent



Santorini caldera

Fig.12: Depth distribution of iron concentration (total Fe , Fe II and Fe III) extracted from wet sediment samples and distribution of manganese measured in pore water samples.

Concentrations of HCl extractable iron at the reference station and the gas vent station were in the same range (Fig. 12). Except for the upper mm, where low concentrations of ferric iron were measured, the total iron was mainly Fe (II). The main difference was an increase of iron concentration with depth in the gas vent core. In contrast, the sediment core from the hot vent exhibited 2-3 times higher total iron concentrations (Fig. 12e) and in the top 5 cm it consisted mainly of Fe (III). It is unlikely that the iron is oxidized by dissolved oxygen in this sediment thus, it is suggested that a thermally influenced oxidation is taking place. Manganese concentrations were also similar at the reference station and at the gas vent, while an enrichment was shown at the hot vent with increasing concentrations at deeper sediment depths. The sediment core from the Santorini caldera exhibited extremely high total iron concentrations of up to 3000 µM g^{-1} sediment wet weight, an increase by a factor of more than 100 compared to the other stations (Fig. 12g). The iron content was constantly high down to 8 cm sediment depth and was composed of almost equal portions of Fe (II) and Fe (III). Below this depth total iron concentrations decreased and consisted mainly of Fe (II). Below 5 cm sediment depth, manganese concentrations were also enriched 10 times in comparison to the Milos sediments. These measurements are in accordance with investigations by Cronan et al. (1995), who explained this enrichment by a hydrothermal input of iron and manganese to the upper sediment layer in this part of the caldera from presently active hydrothermal vents off the Kameni Islands. Other authors (Puchelt et al., 1973) believe that the metal enrichments occur in sediments overlying geological faults and the enrichments result from the leaching of underlying rocks by hot acidic solutions.

A comparison of the total nitrogen and sulfur contents as well as the concentrations of organic carbon in the different areas depicted a difference between hydrothermally influenced sediments and the surrounding sandy sediments.

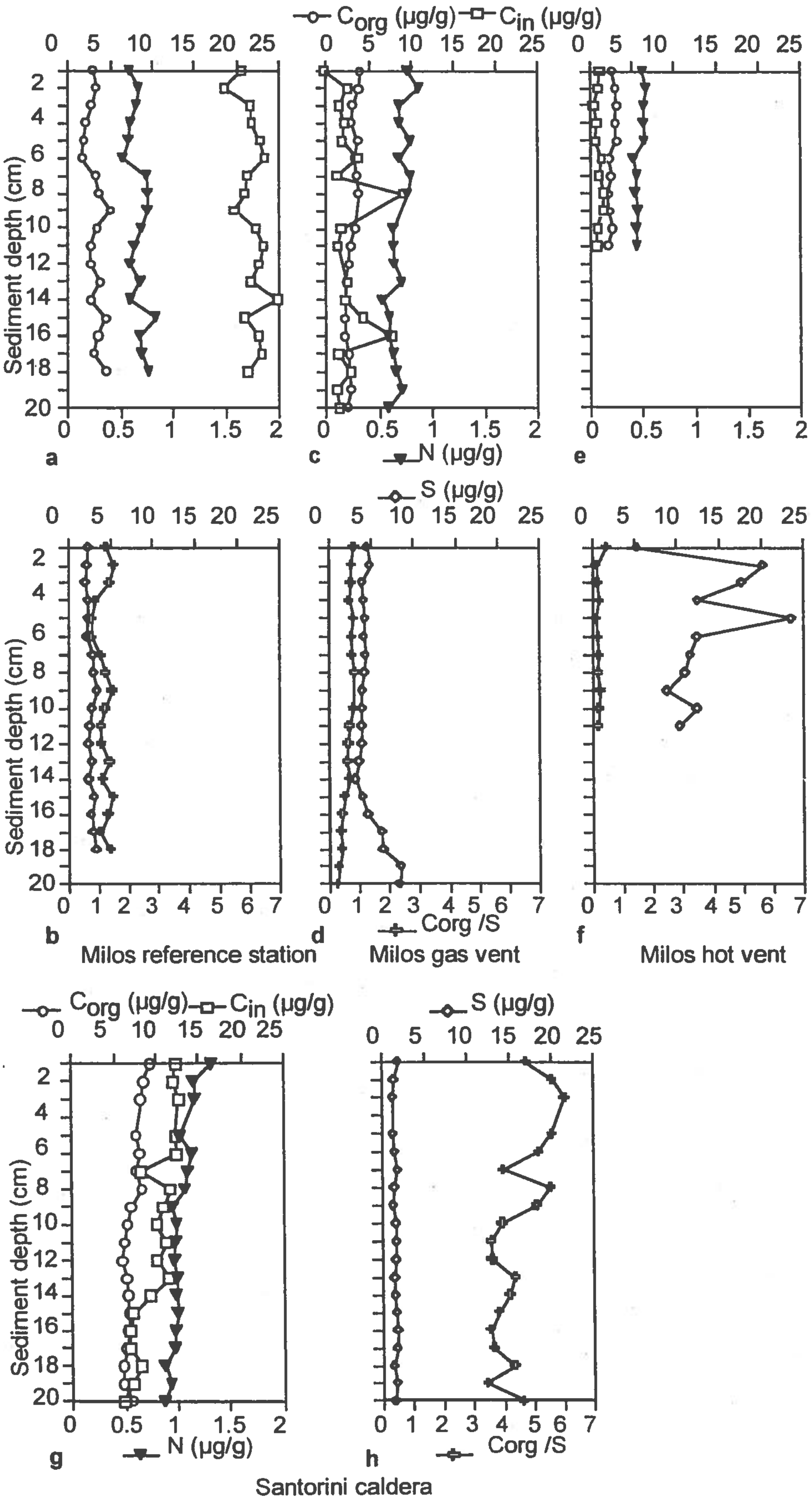


Fig. 13: Depth distribution of total nitrogen, organic and inorganic carbon as well as total sulfur contents and C_{org}/S weight ratios.

Whereas nitrogen occurred in similar low concentrations at the reference station and at the gas vent, it appeared in even lower concentrations in the hot sediment (Fig. 13a, c, e). Inorganic carbon was markedly decreased in the gas vent and the hot vent sample compared to the non-hydrothermal sediment by a factor of 5 to 10, respectively due to the conditions of low pH. Organic carbon concentrations were low in all three sediment cores (3-4 µg g^{-1} sediment dry weight) and showed only a minor difference between the stations. A major difference was shown in the total sulfur content of the hot vent sample with an enrichment of up to 24 µg g^{-1} sediment dry weight compared to 2 µg at the reference station and 5 µg at the gas vent station (Fig. 13b, d, f). At a sediment depth of 14 cm sulfur content is increasing in the gas vent sediment core. The organic carbon to sulfur ratio differed accordingly and showed very low values in the hot sediment. The Santorini sediment core had higher inorganic as well organic carbon contents (10 µg g^{-1} sediment dry weight) along with increased total nitrogen concentrations (15 µg g^{-1} sediment dry weight). The sulfur concentrations were low (2 µg g^{-1} sediment dry weight) and consequently the C_{org}/S ratios were much higher than measured in the Milos sediments (Fig. 13g, h).

3.4.4.3 Sediment sulfate reduction rates

Sulfate reduction rates in laboratory and *in situ* incubated sediment cores off Milos showed significant differences between vent sites and non hydrothermal sediments (Fig. 14, 15, 16).

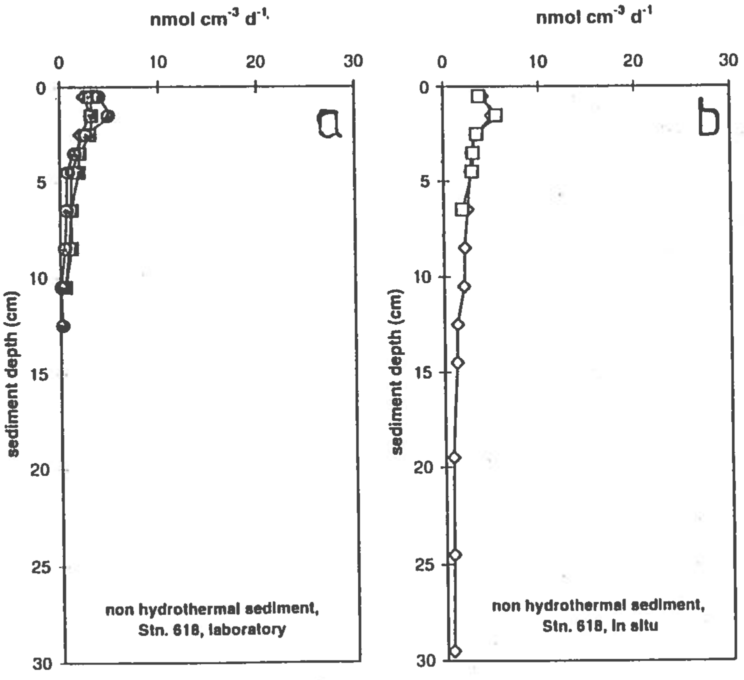


Fig. 14: Depth profiles of sulfate reduction rates at the reference station a) measured in laboratory whole core incubations b) measured in *in situ* incubations.

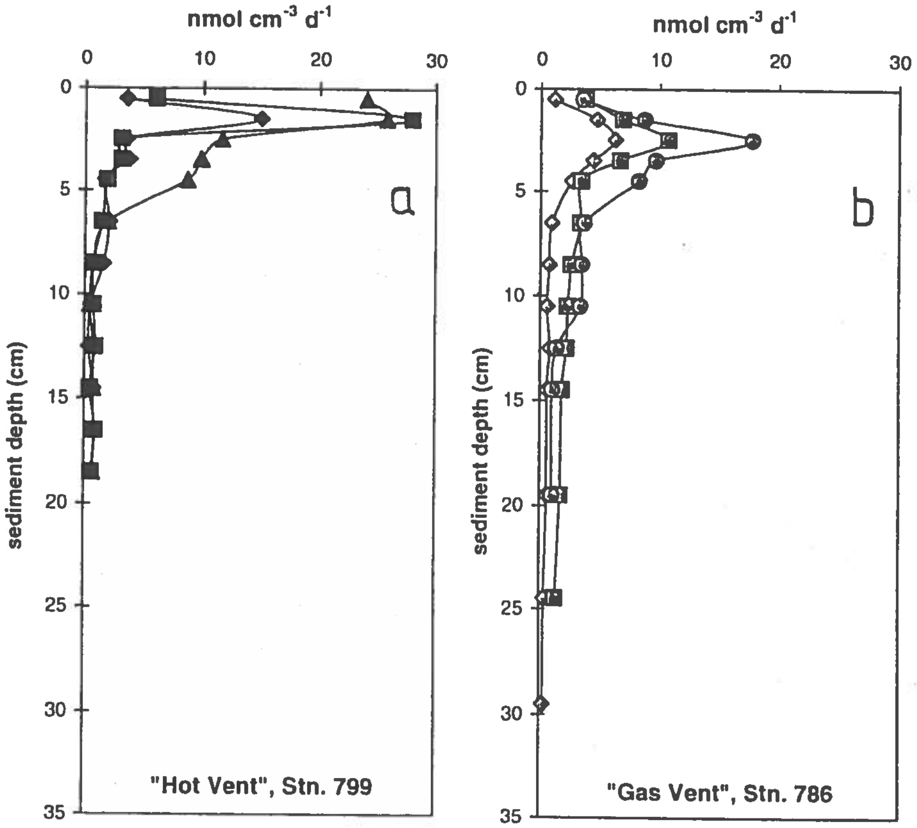


Fig. 15: Depth profiles of sulfate reduction rates a) measured at the hot vent station and b) at the gas vent station.

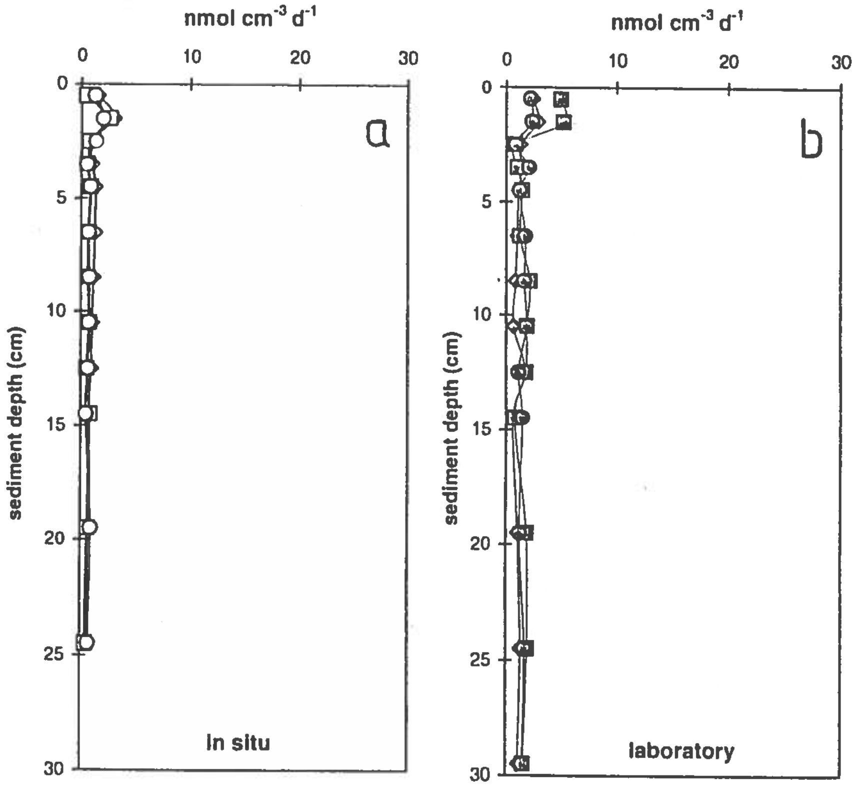


Fig. 16: Depth profiles of sulfate reduction rates measured at the Santorini caldera station. a) *in situ* incubations b) whole core laboratory incubations.

The highest sulfate reduction rates of 28 nmol cm^{-3} d^{-1} were measured in the hot vent sediment (Fig. 15 a). The gas vent had a maximum SRR of 18 nmol cm^{-3} d^{-1} (Fig. 15b). Highest rates occurred in both sediments just below the sediment surface between 2 and 3 cm sediment depth. Sulfate reduction rates in non-hydrothermal, sandy sediments were significant lower than at the vent site sediments (Fig. 14). They varied from 2.4 to 6 nmol cm^{-3} d^{-1} with a minor peak at 2 cm sediment depth. Sulfate reduction rates decreased to 1 nmol cm^{-3} d^{-1} or less below 15 cm sediment depth. At the reference station *in situ* rates were in the same order as shipboard measured sulfate reduction rates (Fig. 14).

SRR in the iron rich sediments of the caldera of Santorini were also very low (Fig. 16). Rates, obtained from laboratory and *in situ* incubations varied between 2 and 5 nmol cm^{-3} d^{-1} at 1-3 cm sediment depth. The *in situ* incubations showed lower rates than the laboratory incubation experiments. This effect might be explained by the deeper water depth of 381 m in the caldera compared to 100 to 130 m water depth at the Milos stations.

Sediment depth integrated rates (15 cm) of *in situ* obtained SRR in the Santorini caldera varied from 0.12 to 0.18 mmol m^{-2} d^{-1}, whereas laboratory incubated sediments revealed areal rates of 0.18 to 0.29 mmol m^{-2} d^{-1}. In comparison the areal rates of *in situ* incubations at the sandy reference station off Milos were higher (0.23 to 0.68 mmol m^{-2} d^{-1}), than laboratory measured SRR which varied between 0.14 to 0.42 mmol m^{-2} d^{-1}. At the vent sites slightly higher areal rates were calculated (0.26 to 0.89 mmol m^{-2} d^{-1}).

3.4.4.4 Temperature gradient block experiments

The incubation of sediment samples along a temperature gradient of 8° to 97° C showed a different effect of temperature variation on sulfate reduction rates in the different areas.

At the Milos reference station SRR reached in the upper 0-7 cm sediment layer values around 10 nmol cm^{-3} d^{-1} with a maximum found at a temperature around 30 °C (Fig. 17a). With increasing temperature the rates became lower. In the deeper sediment layer SRR exhibited two conspicuous peaks around 40° C and 90° C. Although the second peak was not so significant, the increased activity at these temperatures my indicate a mesophilic group of sulfate reducing bacteria having optimum conditions around 40° C as well as a thermophilic group that is stimulated by the high temperatures of 90° C, although the *in situ* temperature was around 18° C through out the sediment at this station.

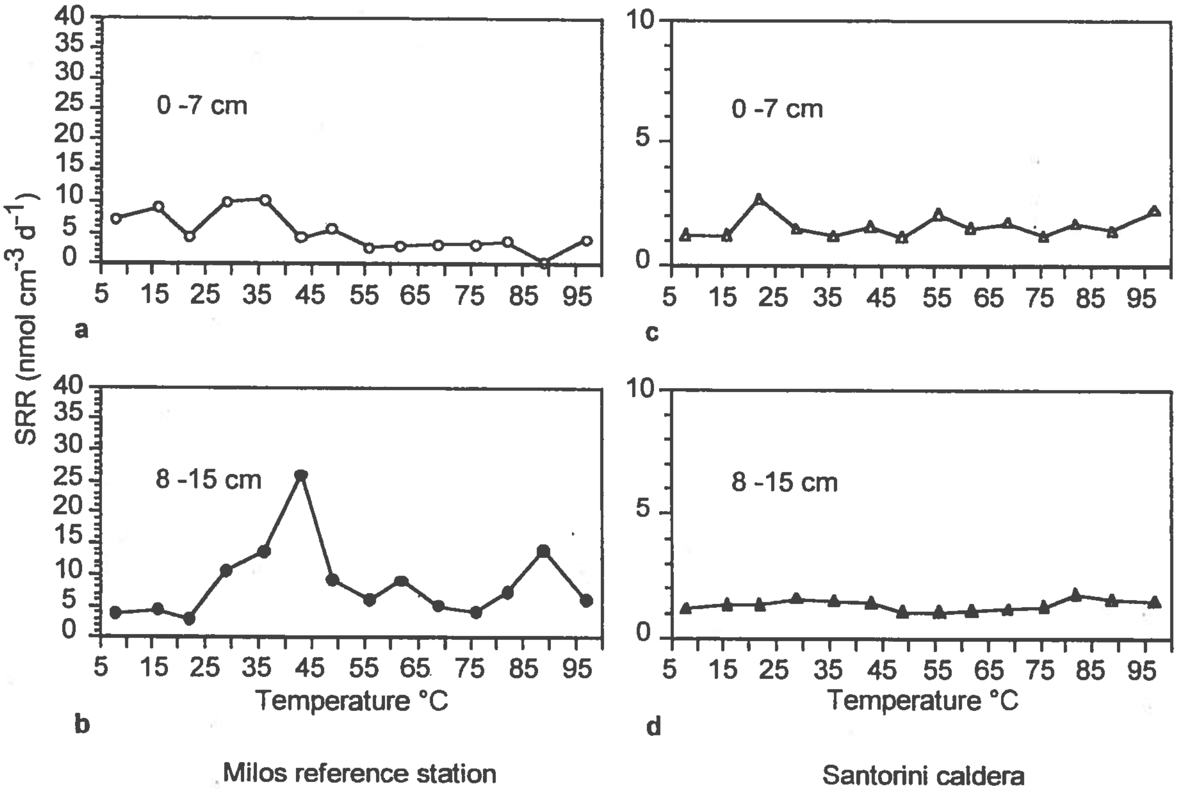


Fig. 17: Sulfate reduction rates obtained from temperature gradient incubations of sediment samples from the Milos reference station (a, b) and sediment samples from the Santorini caldera (c, d). Incubations were carried out with two different sediment sections (0-7 cm and 8-15 cm).

The SRR measured in Santorini samples were much lower and showed no significant peaks along the temperature gradient in both sediment layers (Fig. 17c, d).

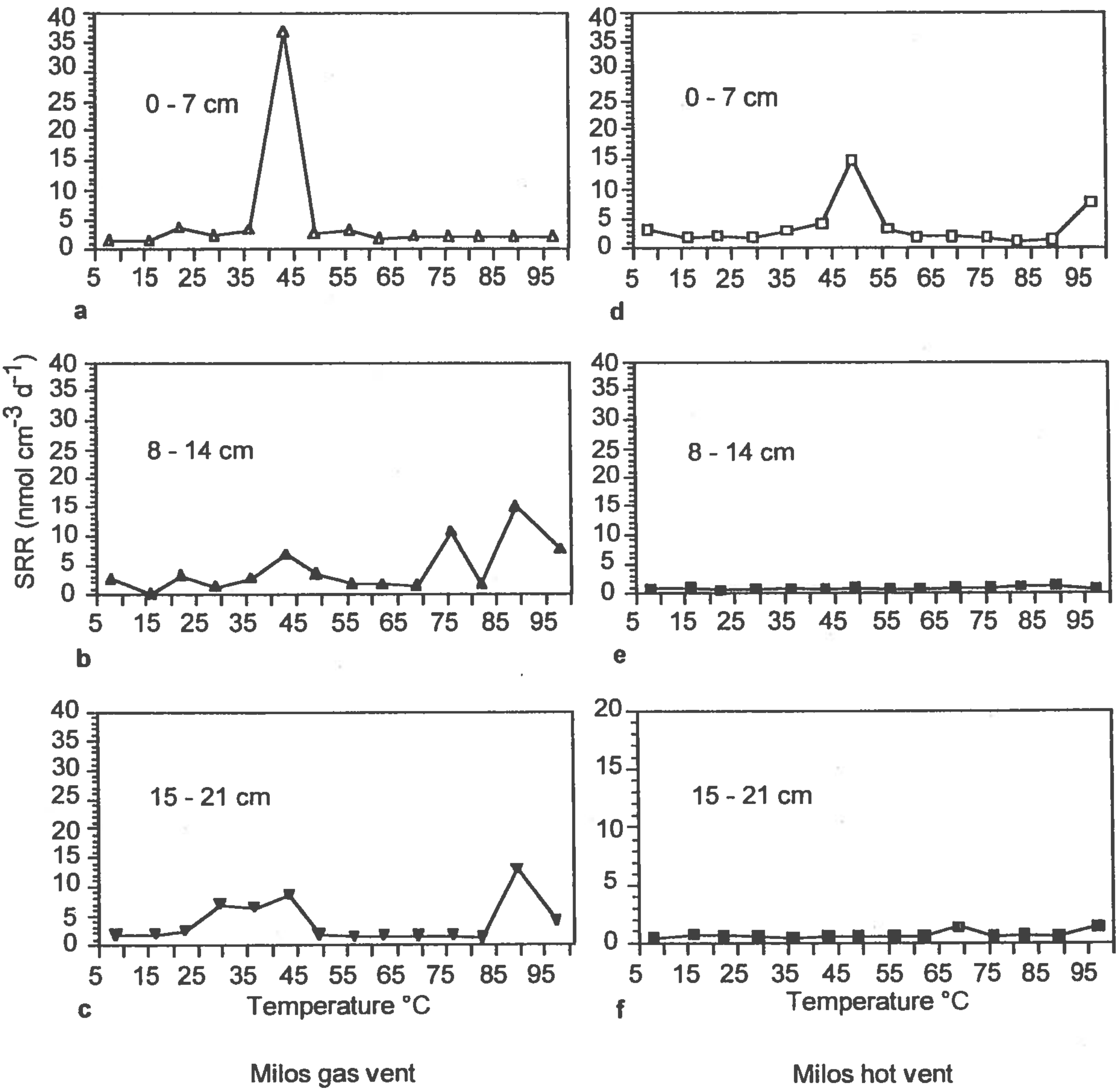


Fig. 18: Sulfate reduction rates obtained from temperature gradient incubations of sediment samples of the gas vent station (a,b,c) and the hot vent station (d, e, f). Experiments were carried out with sediment from three different depth intervals (0-7 cm, 8-14 cm, 15-21 cm).

In the surface layer SRR was comparable at both stations with a peak at 40° C and 50° C, although it is questioned if these peaks are significant (Fig. 18a, d). There seemed to be also a slight increase of SRR in the hot vent sample at a temperature of 95° C. In the lower layer (8-14 cm), the SRR in the hot vent sediment was low at all temperatures (Fig. 18e), whereas in the gas vent samples the SRR showed an increase compared to the upper sediment section and showed a minor increase around 30° C and also at higher temperatures of 75° C -90° C (Fig. 18b). In the third sediment section (15-21 cm) the SRR stayed low at all temperatures in hot vent sediment samples (Fig. 18f).The sediment samples of the gas vent showed two peaks along the temperature gradient, the first around 40° C and the second at 90° C, this is very similar to the results of the incubations of the reference station sediments. Although the highest temperature was measured in the hot vent sediment there seemed to be no sulfate reducing activity adapted to high temperature. The harsh conditions of low pH, high ammonium concentrations as well as the very low organic carbon concentrations in this sediment may prevent microbial sulfate reducing activity. In the ambient sediment of the reference station and at the gas vent station mesophilic bacteria favouring a temperature of 40° C and thermophilic bacteria preferring a temperature around 90° C seemed to be stimulated.

3.4.5 Conclusions

The three sampling stations off the island Milos showed significant differences in geochemical characteristics although they were located in close proximity to each other off the south-eastern coast at comparable depths. In the gas vent area a mixing of pore water constituents seemed to occur in the surface sediment due to the uplift effect of continuously emerging gas bubbles. The stream of gas bubbles carries massive volumes of gas to the water column but also induces a flux of solutes from the sediment to the water column. The temperature was not increased but the pH was very low. The sediment was depleted in barium but slightly enriched in manganese. The hot vent area was characterized by hot, acidic, reduced pore water that had also high ammonium and sulphide concentrations. The sediment was depleted in barium but slightly enriched in lithium and very enriched in iron compared to the surrounding sediment. From the hot vent area high fluxes from the sediment to the water column of trace elements, metals and nutrients that are transported in the upward flowing hydrothermal fluid are expected. Inorganic carbon was very low at both vent sites due to the low pH values. Organic carbon and total nitrogen were also low. Sulfate reduction was higher in the surface sediments of the vent sites compared to the non-hydrothermal site. The rates were comparable to other measurements in sandy sediments (Battersby et al., 1985). Incubation experiments along a temperature gradient showed no effect of increased temperature in the hot vent samples. SRR was restricted to the upper sediment layer, below this depth the extreme conditions of low pH, high ammonium and high sulfide concentrations, as well as the low organic content seem to prevent bacterial sulfate reduction. Sulfate reduction rate maxima were found at the reference station in the lower sediment horizon (8-14 cm), at temperature around 40° C and 90° C indicating a mesophilic and a thermophilic bacterial population of sulfate reducers responding to these temperature conditions. Similar effects were shown in the gas vent samples, where conditions are not as harsh as in the hot vents and SRR takes place also deeper in the sediment.

The main characteristic of the Santorini caldera sediment was the extreme enrichment in iron and manganese. Other signals of hydrothermal influence were not obvious. The sediments seem to receive hydrothermal input of iron and manganese enriched fluids from active vents off the Kameni islands (Cronan et al., 1995). Sulfate reduction rates were very low and not stimulated by increasing temperature. Iron reduction plays probably a more important role in these sediments.

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4. Zusammenfassung und Ausblick

Mehrere Forschungsreisen im Verlauf dieser Arbeit ermöglichten es, Sulfatreduktionsraten in marinen Sedimenten unter extremen Umgebungsbedingungen zu untersuchen. An den ausgewählten Probenahmestandorten wurden Sulfatreduktionsraten teilweise zum ersten Mal, sowohl unter *in situ* Bedingungen als auch durch Laborinkubationen an Bord eines Forschungsschiffes gemessen. Neben extrem anoxischen und sulfidischen Sedimenten im Schwarzen Meer und im Urania Becken wurden auch neu entdeckte hydrothermale Vent-Gebiete vor der griechischen Insel Milos, in der Caldera der Insel Santorin sowie extrem hydrothermal beeinflusste Sedimente des Guaymas Beckens im Golf von Kalifornien beprobt.

Schwarzes Meer

Aufgrund der ausgeprägten Schichtung dieses weitgehend anoxischen Beckens in eine dünne oxische Oberflächenwasserschicht und einer unterlagernden mächtigen, anoxischen und sulfidischen Wassermasse stellt das Schwarze Meer ein ideales, natürliches Labor für biogeochemische Untersuchungen im Bereich der Grenzschicht der beiden Wassermassen dar. Das Ziel dieser Forschungsreise war es, die Veränderung der Mineralisationsprozesse im Sediment entlang eines Tiefentransektes am Übergang von oxischen zu anoxischen Verhältnissen zu untersuchen.

Zur Quantifizierung der für die Remineralisierung verantwortlichen Prozesse im Sediment wurden zum ersten Mal drei verschiedene Landertypen gleichzeitig für *in situ* Messungen eingesetzt. Dabei konnte gezeigt werden, wie sich die Bedeutung der Oxidantien (terminaler Elektronenakzeptoren) entlang eines Transektes von oxischen zu anoxischen Bedingungen mit zunehmender Wassertiefe deutlich verändert. Sauerstoff spielt erwartungsgemäß als terminaler Elektronenakzeptor im Schelfbereich die größte Rolle. Mit zunehmender Wassertiefe nimmt der Sauerstoffgehalt im Bodenwasser ab und die Messungen ergaben eine kontinuierliche Zunahme des Anteils der Sulfatreduktion am Gesamtumsatz von 5,6 auf 46,5 % zwischen 60 und 100 m Wassertiefe. Die absoluten Sulfatreduktionsraten nahmen dagegen entlang des Transektes mit der Wassertiefe ständig ab und stiegen bei 181 m Tiefe im unteren Bereich der Übergangszone wieder deutlich an.
Aus diesen Beobachtungen schließen wir, daß die Verfügbarkeit organischen Materials für die Sulfatreduktion mit zunehmender Wassertiefe geringer wird, und solange noch Sauerstoff im Bodenwasser vorhanden ist, die Sulfatreduktion unterdrückt wird. In 181 m Wassertiefe ist kein Sauerstoff mehr im Bodenwasser vorhanden, anoxische Abbauprozesse treten in den Vordergrund und die Sulfatreduktion dominiert nun als Abbauprozeß für noch ausreichend

verfügbares organisches Material, so daß Sulfatreduktionsraten in der Größenordnung der Flachwasserraten liegen. Gleichzeitig zeigten erste Berechnungen, daß Mangan- und Eisenreduktion zusammen etwa die gleiche Bedeutung für den Kohlenstoffabbau im Schelfbereich haben, wie die Sulfatreduktion. Unter der Übergangszone nimmt der Sulfidgehalt in der Wassersäule stetig zu und die Sulfatreduktion ist nun der alleinige Abbauvorgang für organischen Kohlenstoff. Die Raten sind jedoch deutlich niedriger, als die auf dem Schelf gemessenen Raten, da die Qualität des organischen Materials mit zunehmender Wassertiefe immer schlechter wird, was sich durch die Zunahme der C_{org}:N-Verhältnisse von 12 auf 17 äußert.

Weiterhin konnte gezeigt werden, daß die unter *in situ* Bedingungen gemessenen Sulfatreduktionsraten an einigen Stationen niedriger sind, als die vergleichend ausgeführten Laborinkubationen. Im Schelfbereich ist dieser Unterschied deutlicher ausgeprägt (58-80 % geringere Raten), als im sulfidischen, anoxischen Becken (4-32 % geringere Raten). Teilweise sind diese Unterschiede auch auf eine Störung des Oberflächensedimentes oder auf Sedimentheterogenität zurückzuführen. Trotz dieser Unterschiede sind die gemessenen Sulfatreduktionsraten vergleichbar mit denen früherer Untersuchungen.

Guaymas Becken/Golf von Kalifornien

Die kohlenstoffreichen Tiefseesedimente des Guaymas Beckens bieten zusammen mit dem unbegrenzt zur Verfügung stehendem Sulfat ideale Voraussetzungen für eine intensive Reduktion von Sulfat durch mesophile, thermophile und hyperthermophile Mikroorganismen. Die Verteilung der Sulfatredukion in diesen hydrothermal beeinflussten Sedimenten ist in erster Line abhängig von den chemischen Gradienten, die aber innerhalb eines Probenahmestandorts völlig unterschiedlich geartet sein können.

Magmatische Intrusionen unter der Sedimentdecke sind für aufsteigende hydrothermale Porenwässer verantwortlich, die durch die Sedimentschicht diffundieren und diese Temperaturen von 200° bis 250° C aussetzen. Dabei wird der organische Kohlenstoff des Sediments einer thermischen Alteration unterzogen und es entstehen petroleumartige Produkte bestehend aus aliphatischen und aromatischen Kohlenwasserstoffverbindungen. Mit dem hydrothermalen Fluß gelangen diese Verbindungen in Oberflächensedimente und stehen als potentielle Substrate für die mikrobielle Sulfatreduktion im Temperaturbereich von 3° bis > 100° C zur Verfügung.

Eine zweite Substratquelle sind die nitratanreichernden Schwefelbakterien *Beggiatoa* spp., die in dichten Matten an der Sedimentoberfläche wachsen, dort wo schwefelwasserstoffreiche Porenwässer austreten. Mit der Fermentierung ihrer chemoautotroph synthetisierten Biomasse entsteht ebenfalls ein Pool von Nährstoffen für die Sulfatreduktion.

Die höchsten bisher in hydrothermalen Tiefseesedimenten gemessenen Sulfatreduktionsraten von 3350 nmol cm^{-3} d^{-1} wurden in konsolidierten Sedimenten unter 15 cm Tiefe gemessen. Bei *in situ* Temperaturen von 71°-93° C können nur thermo-hyperthermophile Sulfatreduzierer bei geeignetem Substratangebot für diese hohen Raten verantwortlich sein.

Bis zu 2550 nmol cm^{-3} d^{-1} wurden nahe der Sedimentoberfläche mit überlagernden *Beggiatoa* Matten gemessen. In diesem Bereich herrschen moderate Temperaturen vor und mesophile Sulfatreduzierer nutzen vorwiegend das Substratangebot der fermentierten Biomasse. *In situ* Messungen mit dem neu entwickelten Inkubationsinstrument ORPHEUS bestätigten extrem hohe Raten in Oberflächensedimenten mit Bakterienmatten bei *in situ* Temperaturen von 11° C.

Abhängig von der Inkubationstemperatur des hydrothermalen Sediments haben sich im wesentlichen zwei Temperaturbereiche herauskristallisiert an die sulfatreduzierende Bakterien gut angepaßt sind; das ist zum einen der mesophile-thermophile Bereich zwischen 40°-60° C sowie der hyperthermophile Bereich zwischen 70°-90°C.

Urania Becken

Das 3570 m tiefe Uraniabecken südwestlich von Kreta, ist eines von insgesamt drei tiefen Becken (L´Atalante und Discovery), auf deren Grund sich eine hochsaline Sole befindet und für biogeochemische Untersuchungen besonders interessant macht. In 3470 m Tiefe findet ein Übergang von normal salinem Seewasser zur Soleschicht statt. Aufgrund der Dichteunterschiede der beiden Wasserkörper reichert sich in einer etwa 20 m mächtigen Übergangszone organisches Material an und Bakterienzahl sowie Sulfatreduktion steigen stark an. In dieser Überganszone wurden die höchsten bisher in einer Wassersäule gemessenen Sufatreduktionsraten (14 nmol cm^{-3} d^{-1}) gefunden. Die 80 m mächtige Soleschicht setzt sich durch eine scharfe Pyknokline bei 3790 m von der Übergangszone deutlich ab. Sulfidgehalte von 10 mM und eine Salinität von 162 ‰ lassen eine biologische Aktivität unter dieses extremen Umgebungsbedingungen nahezu unmöglich erscheinen, trotzdem findet eine Remineralisierung organischen Kohlenstoffs durch Sulfatreduktion statt.

Zum ersten Mal wurden Sulfatreduktionsraten in Sedimenten des Beckens unter *in situ* Bedingungen mit dem Lander LUISE gemessen. Die *in situ* gemessene Rate (15 nmol cm^{-3} d^{-1}) ist niedriger, als die parallel dazu durchgeführten Inkubationen an Bord des Forschungsschiffes (25 nmol cm^{-3} d^{-1}) und ist wahrscheinlich auf Druck- und Temperaturänderungen bei der Bergung des Sedimentes für die Laborinkubationen zurückzuführen.

Milos und Santorin

In der südlichen Ägäis vor der Insel Milos und in der Caldera von Santorin wurden nach systematischer Suche während der Forschungsreise M40/2 neue Vent-Gebiete entdeckt. Die Sedimente dieses hydrothermal beeinflußten Gebietes waren Ziel für Messungen von Sulfatreduktionsraten sowohl unter *in situ* als auch unter Laborbedingungen. Die nur unwesentlichen Unterschiede zwischen Labor- und *in situ* Messungen sind wohl auf die geringen Druckdifferenzen und der nur geringfügig voneinander abweichenden Boden- und Oberflächenwassertemperaturen zurückzuführen. Aufgrund des limitierten C_{org}-Gehalts in den sandigen Sedimenten vor Milos wurde nur eine sehr geringe Sulfatreduktionsaktivität festgestellt (4-7 nmol cm^{-3} d^{-1}). Dagegen zeigten hydrothermal beeinflusste Sedimente deutlich höhere Raten.

Ähnlich, wie bereits in Sedimenten des Guaymas Beckens im Golf von Kalifornien konnten auch in Sedimenten vor Milos mesophile und thermo- hyperthermophile Temperaturbereiche sulfatreduzierender Bakterien gefunden werden. Auch detailierte geochemische Messungen zeigen deutliche Unterschiede vor allem bei Ammonium, Sulfid, aber auch Barium und Lithium zwischen nicht hydrothermal beeinflußten Sedimenten und zwischen heißen als auch kalten Vents. Besonders hervorzuheben sind die außergwöhnlich hohen Eisengehalte in Calderasedimenten von Santorin.

Im Gegensatz zu bereits durchgeführten *in situ* Beprobungen hydrothermaler Vents im Flachwasser konnten vom Schiff aus keine *in situ* Messungen hydrothermaler Sedimente durchgeführt werden. Es blieb dem Zufall überlassen, die punktartig auftretenden Ventsysteme mit einem freifallenden Lander oder einem Box- oder Multi-Corer zu treffen.

Eine Beprobung zweier Ventsysteme mittels Box-Corer war schließlich nur mit Hilfe eines eingesetzten ROV´s möglich. Unterschieden werden konnte dabei zwischen kalten „Vents“ (~ 20° C) und heißen „Vents“ (~ 103° C), die deutlich höhere Raten aufwiesen. Dabei ist zu berücksichtigen, daß chemische Gradienten, Temperatur und Sedimentverhältnisse und damit auch Sulfatreduktionsraten hydrothermaler Systeme bereits auf kleinem Raum stark voneinander abweichen können. Ein Vergleich verschiedener Vent-Systeme ist deshalb schwierig und ist nur mit genauer Kenntnis der geochemischen Gradienten möglich.

Technologie

Zukünftige Arbeiten über *in situ* Messungen von Sulfatreduktionsraten in marinen Sedimenten werden die Aufgabe haben, gezielt die Unterschiede zwischen *in situ* und Labormessungen heraus zu arbeiten. Ein Teilprojekt könnte dabei sein, die *in situ* Druckverhältnisse im Labor auf Sedimentkerne zu übertragen und den Einfluß einer Dekompression auf die Sulfatreduktionrate zu rekonstruieren. Die Lander-Technologie bietet trotz ausgefeilter Laborversuche immer noch die beste Möglichkeit biogeochemische Prozesse und Gradienten unter *in situ* Bedingungen ohne Druck- und Temperaturveränderungen des Sediments zu testen. Vor allem Untersuchungen an hydrothermalen Systemen sollten auf jeden Fall ohne Druckentlastung erfolgen, da bei Atmosphärendruck ein intensives Ausströmen gelöster Gase, vor allem Methan aus den beprobten Sedimentkernen erfolgt und die Meßergebnisse verfälschen kann.

Bei künftigen Einsätzen sollte über die Verbesserung des Sinkverhaltens insbesondere beim Aufsetzen des Gerätes auf dem Meeresboden nachgedacht werden. Man wird auch, um *in situ*- und Labormessungen besser vergleichen zu können, ein größeres Augenmerk auf die Probenahmestelle legen müssen. Ein gezieltes Absetzen der Landergeräte auf dem Meeresboden unter Videoüberwachung wird die Zukunft dieser Technologie sein.

Desweiteren wird man sich intensiver um eine modulare Bauweise von Seeforschungsgeräten bemühen müssen, um an einer Probenahmestelle mehrere unterschiedliche Messungen gleichzeitig vornehmen zu können. Die Neuentwicklung des Inkubationsgerätes ORPHEUS war ein erster Schritt in diese Richtung. Es ist ein kompaktes Gerät für Radiotracer Untersuchungen und wurde erfolgreich von dem Forschungstauchboot ALVIN abgesetzt und gestartet, um dann selbständig Messungen vorzunehmen; ein Absetzten mit einem ROV ist ebenfalls denkbar.

In künftigen Einsätzen wird es als modulares Bauteil in einem größeren Landersystem wichtige geochemische Messungen ergänzen.

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