Formation of iron sulphides and deep sulphate enrichment constrained by sulphur isotopes

Mark Zindorf[1], Christian März[1], Thomas Wagner[1], Harald Strauss[2]

[1] School of Civil Engineering and Geosciences, Newcastle University

[2] Institut für Geologie und Paläontologie, Westfälische Wilhelms-Universität Münster

Introduction

The PhD project "Reconstructing carbon and nutrient cycling in the Northeast Pacific Ocean over the past 15 million years" uses sediment samples from sites U1417, U1418 and U1419 recovered during IODP Expedition 341 to the Gulf of Alaska (Figure 1). The following objectives are targeted:

1.) Reconstruct nutrient cycling and redox development in the Gulf of Alaska
2.) Investigate post-depositional changes in the sediment column (early diagenesis)
3.) Link sedimentation and paleoproductivity to global climate patterns, for example the Pliocene-Pleistocene transition (~2.75 Ma BP) or the Miocene Climate Optimum (~15 Ma BP).

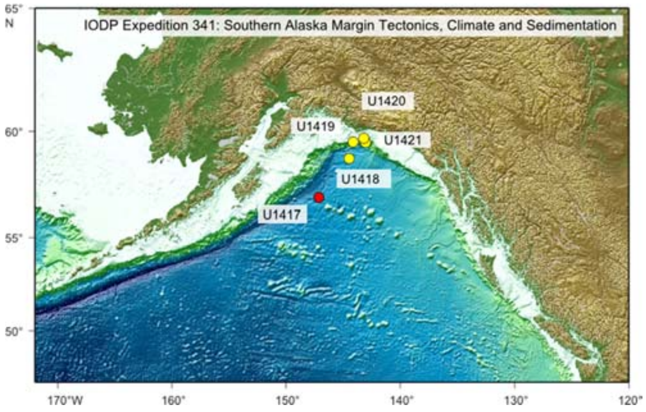

Figure 1: Operational area and drill sites of IODP Expedition 341. The red dot indicates the studied site U1417. Yellow dots indicate other sites drilled during Exp. 341 (*modified from Jaeger et al., 2014).*

In order to address the second objective, sediments from Site U1417 were analysed geochemically for major and minor element contents using X-ray fluorescence (XRF). Results were compared to shipboard pore water and gas data. We found that the diagenetic pattern at this site was significantly influenced by a deep influx of sulphate-rich water, leading to significant sedimentary sulphur enrichments in a deep, fully functioning sulphate-methane transition zone (SMTZ) where authigenic barite and pyrite precipitate (Reeburgh 1980; Niewoehner et al 1997; Boetius et al., 2000).

Such deep sulphate-rich fluid sources are not unknown in marine sediments. Discrete aquifers situated at the sediment-crust interface have been found in tectonically active environments like oceanic spreading centres (Elderfield et al., 1999; Engelen et al., 2008) and accretionary wedges (D'Hondt et al., 2004; Torres et al., 2015). However, they have never been reported for a hemipelagic, tectonically inactive intraplate site like U1417. Since bacterial sulphate reduction is an important energy source for microorganisms which are living deep in the sediments, understanding the mechanisms of sulphate delivery into the sediments has direct implications for the quantitative estimation and distribution of deep biosphere biomass (DeLong, 2004). In addition, as precipitation sites for various authigenic minerals, SMTZs are important sinks in the marine sulphur and carbon cycle, and understanding the causes for deep SMTZs fed by deep aquifers might have significant implications on global marine element budgets.

As an important step to understand the origin and biogeochemical conditioning of the deep aquifer water at Site U1417, a sulphur isotope study was carried out at the University of Münster.

During bacterial sulphate reduction, sulphur undergoes an isotope fractionation (Canfield, 2001), and the reaction product H_2S becomes enriched in the lighter ^{32}S isotope compared to the initial value of seawater sulphate (+21 ‰; Boettcher et al., 2007). This mechanism holds true as long as fresh sulphate supply is maintained (open system). If the bacterial consumption of the sulphate pool is faster than the diffusional re-supply, the heavier ^{34}S isotope becomes gradually enriched in the (pore water) sulphate and, as a consequence of isotope fractionation during bacterial sulphate reduction, also in the H_2S which can then become even heavier than the initial seawater value (closed system). The H_2S formed during bacterial sulphate reduction is incorporated into authigenic pyrite, which serves as sedimentary archive of the prevailing diagenetic system. Therefore, sulphur isotopes in pyrite can be used to distinguish between open- or closed-system conditions, and can help solving the question if the sulphate pool is constantly recharged (resulting in constantly negative $\delta^{34}S$ values in pyrite), or if the sulphate pool is progressively exhausted (resulting in positive $\delta^{34}S$ values for pyrite) (Canfield, 2001). Here we use this isotopic approach to identify whether the sulphate-rich aquifer at the bottom of Site U1417 is currently connected to the overlying seawater sulphate pool, or represents a pool of old buried seawater or remnants of an old, now inactive aquifer.

Multiple sulphur isotopes have only recently gained more attention (Farquhar et al., 2000; 2003; Ono, 2007; Strauss et al., 2012 and others). Here, not only the abundant isotopes ^{32}S and ^{34}S are analysed, but also the minor sulphur isotopes ^{33}S and ^{36}S. Originally it was believed that in case of mass dependent fractionation (including bacterial sulphate reduction), no additional information can be obtained from the analysis of these isotopes regarding biogeochemical sulphur cycling. Recently, it was found that the deviation in fractionation of ^{33}S from that expected by mass dependent fractionation can be used to distinguish between dissimilatory sulphate reduction and disproportionation reactions forming the sulphide (Farquhar et al., 2003; Johnston et al., 2005). This deviation is expressed as $\Delta^{33}S$. The role of $\Delta^{36}S$ is not yet understood, but since this information is a by-product of the analysis for ^{33}S, it is usually recorded to create a data base for further proxy development.

Methods

Pyrite abundance in freeze-dried and homogenized sediment samples has been determined by the chromium reduction method (Canfield et al., 1986). Around 500 mg of sediment were boiled with 50 ml of 50% (v/v) HCl for 45 min to dissolve iron monosulphides (e.g., amorphous Fe-S, mackinawite and greigite), and subsequently with an acidic solution of $CrCl_2$ for another 45 min to reduce iron disulphides (e.g., pyrite). For both steps, the released H_2S was captured in an $AgNO_3$ solution and precipitated as Ag_2S. From the Ag_2S yield, iron sulphide-bound sulphur was calculated. In addition, the content of iron in mono- and disulphides in the sediments could be stochiometrically calculated. The Ag_2S precipitate was subsequently used for the sulphur isotope measurements. In total, 40 samples were selected, depending on the diagenetically interesting intervals and the general abundance of iron disulphides (iron monosulphides were below detection limit in all samples). Sample distribution can be seen in Figure 2.

Two different methods of sulphur isotope analysis were applied: Conventional ^{32}S and ^{34}S analysis was carried out on all 40 selected samples. For this, 200 µg Ag_2S and 300 – 600 µg V_2O_5 were weighed into tin capsules and analysed in duplicate using a Finnigan MAT DeltaPlus mass spectrometer interfaced to an Elementar analyser (EA-irMS).

The results are presented in the standard delta notation ($\delta^{34}S$) as permil deviation from the Vienna Canyon Diablo Troilite standard (VCDT).

On 19 selected samples, multiple S isotopes were measured. For this, 2 mg of sample were fluorinated to SF_6 (e.g., Ono et al., 2006) and analysed with a ThermoScientific MAT 253. Results are presented as permil deviation of the isotope ratio between ^{33}S (^{36}S) and ^{32}S of the sample and the calculated ratio which would be expected from unbiased mass dependent fractionation ($\Delta^{33}S = \delta^{33}S - 1000 \times ((1 + \delta^{34}S/1000)^{0.515}) - 1$; cf. Hulston and Thode, 1965; Farquhar et al., 2000).

Results and preliminary discussion

The record of pyrite $\delta^{34}S$ exhibits an unusually wide range of values at Site U1417 with values ranging from -46 ‰ to +60 ‰ (Figure 2). Throughout the whole core, negative values $\delta^{34}S$ can be found, indicating open system conditions. For the interval between 700 m and 750 m depth CCSF-A, this also means that a deep aquifer is constantly delivering fresh sulphate to the deep SMTZ, and the system is not fed from an old buried pool of seawater. The isotope ratios also indicate that the process of deep sulphate delivery is still active. However, isotope ratios measured at pore water sulphate exhibit highly positive values between +40 ‰ and +57 ‰, indicating advanced sulphate limitation here (Strauss et al., unpublished data). Possibly sulphate reduction already happened during the way of the deep aquifer and this signal is not only produced by pyrite formation at the site. Taken together it can be concluded that the sulphate pool at the bottom of the sediment column at Site U1417 exists in limited, but not closed-system conditions.

The only exceptions to the negative sulphur isotope values at U1417 are found in two zones: around 350 m depth (CCSF-A), and between 600 and 700 m depth (CCSF-A). Here the $\delta^{34}S$ of pyrite shows distinctly positive excursions, but these excursions are intercalated between negative $\delta^{34}S$ values. Therefore, they most likely indicate single events rather than long-lasting changes in paleo-environmental and/or diagenetic conditions. As preliminary interpretation, these intervals have been linked to increases in sedimentation rate at Site U1417. This process might lead to episodic closed-system conditions by cutting off a pore-water sulphate pool from the overlying sea water supply. This hypothesis can only be confirmed once a better age model is available, and hence a better constraint on the variability of sedimentation rates.

Multiple sulphur isotopes are still pending for interpretation.

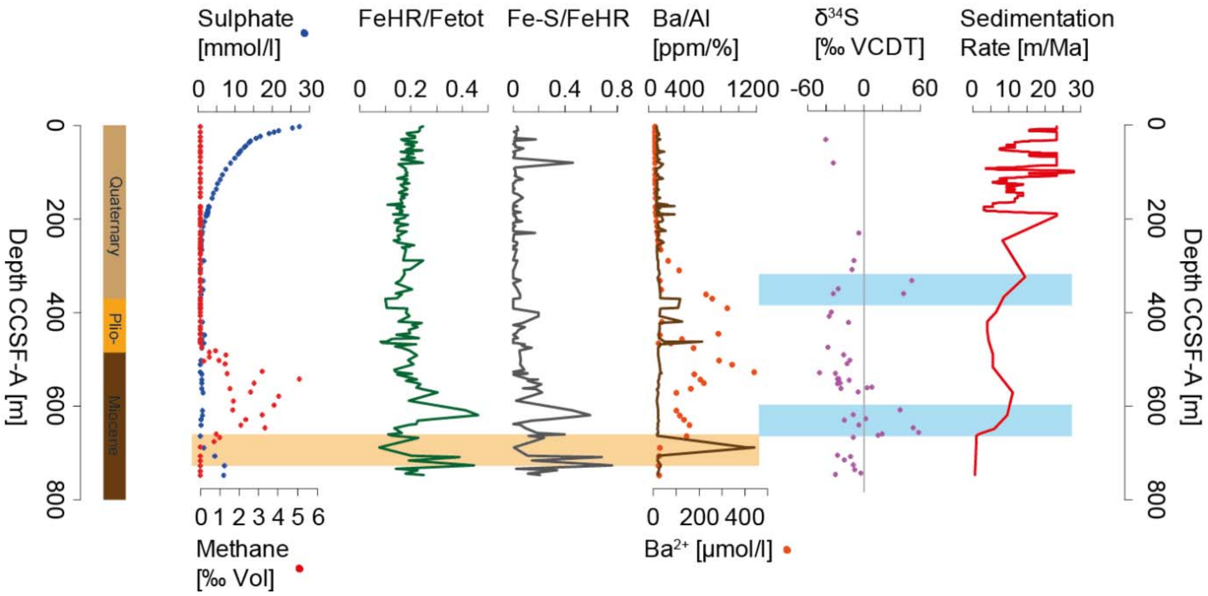

Figure 2: Profiles of diagenetically relevant sediment and pore water components. Sulphate and methane profiles indicate a fully functioning SMTZ deeper in the sediment with sulphate concentrations increasing downcore (brown bar). Here, barite (brown) and pyrite (green, grey) formation occurs. FeHR/Fetot ratios indicate how much of the total available iron can react or has already reacted with sulphur. Fe-S/FeHR indicates how much of the highly reactive iron has already reacted with sulphur. Ba/Al ratios (brown) and pore water Ba^{2+} (orange dots) indicate barite formation from pore water barium and sulphate in the deep SMTZ. Sulphur isotopes (purple) are negative except for two intervals where sedimentation rates increased (red, blue bars).

Fe-S = iron-bound sulphur, FeHR = highly reactive sulphur, Fetot = total sulphur.

Outlook and future work

During the course of the PhD project, I will attempt to reveal further details about the evolution of diagenetic processes at Site U1417. First efforts will focus on determining how long the deep aquifer has been active in order to constrain how long certain diagenetic fluxes (e.g., sulphate, dissolved barium) must have been stable allowing formation of the observed authigenic mineral enrichments in the deep SMTZ (e.g., barite , pyrite). This result will then be compared to the timing of different tectonic events, including the onset of sedimentation at U1417 (i.e., crustal age), the eruption of several adjacent seamounts, and crustal bending at the location of Site U1417 due to imminent subduction at the Aleutian Trench. This is expected to give an indication about the relevance of these processes towards the deep aquifer formation. Later, these data, together with other previously obtained geochemical data, will be used to model the evolution of the complete diagenetic pattern at Site U1417 applying a reaction-transport model (e.g. Aguilera et al., 2005, Arndt et al., 2009).

Acknowledgments

I am very grateful to ECORD for making this project possible with this research grant. Also, I want to thank the Group for Historische und Regionale Geologie in Münster for their support. Particularly I thank Artur Fugmann and Andreas Lutter for their support in the lab.

Literature:

Aguilera, D. R., Jourabchi, P., Spiteri, C., Regnier, P., 2005. A knowledge-based reactive transport approach for the simulation of biogeochemical dynamics in Earth systems. Geochemistry Geophysics Geosystems, 6 (7).

Arndt, S., Hetzel, A., Brumsack, H.-J., 2009. Evolution of organic matter degradation in Cretaceous black shales inferred from authigenic barite: A reaction-transport model. Geochimica et Cosmochimica Acta, 73, 2000-2022.

Boetius, A., Ravenschlag, K., Schubert, C. J., Rickert, D., Widdel, F., Gleseke, A., Amann, R., Joergensen, B. B., Witte, U., Pfannkuche, O., 2000. A marine microbial consortium apparently mediating anaerobic oxidation of methane. Letters to Nature, 407 (5) 623-626.

Böttcher, M. E., Brumsack, H.-J., Dürselen, C.-D., 2007. The isotopic composition of modern seawater sulfate: I. Coastal waters with special regard to the North Sea. Journal of Marine Systems, 67, 73-82.

Canfield, D.E., 2001. Biogeochemistry of sulfur isotopes. In Valley, J.W., and Cole, D.R. (eds.), Stable isotope geochemistry. Reviews in Mineralogy and Geochemistry, 43, 607–636.

Canfield, D. E., Raiswell, R., Westrich, J. T., Reaves, C. M., Berner, R. A., 1986. The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. Chemical Geology, 54, 194-155.

DeLong, E. F., 2004. Microbial life breathes deep. Science, 306 2198-2200.

D'Hondt, S., Jørgensen, B. B., Miller, D. J., Batzke, A., Blake, R., Cragg, B. A., et al., 2004. Distributions of microbial activities in deep subseafloor sediments. Science, 306, 2216–2221.

Elderfield, H., Gieskes, J. M., 1982. Sr isotopes in interstitial waters from marine sediments from Deep Sea Drilling Project cores. Nature, 300, 493-497.

Engelen, B., Ziegelmüller, K., Wolf, L., Köpke, B., Gittel, A., Cypionka, H., Treude, T., Nakagawa, S., Inagaki, F., Lewer, M. A., Steinsbu, B. O., 2008. Fluids from the oceanic crust support microbial activities within the Deep Biosphere. Geomicrobiology, 25, 56-66.

Farquhar, J., Bao, H. M., Thiemens, M., 2000. Atmospheric influence of Earth's earliest sulfur cycle. Science, 289 (5480), 756–758.

Farquhar, J., Johnston, D. T., Wing, B. A., Habicht, K. S., Canfield, D. E., Airieau, S., Thiemens, M. H., 2003. Multiple sulphur isotopic interpretations of biosynthetic pathways: implications for biological signatures in the sulphur isotope record. Geobiology 1 (1), 27–36.

Hulston, J.R., Thode, H.G., 1965. Variations in the S^{33}, S^{34}, S^{36} contents in meteorites and their relation to chemical and nuclear effects. Journal of Geophysical Research 70, 3475–3484.

Jaeger, J.M., Gulick, S.P.S., LeVay, L.J., and the Expedition 341 Scientists, 2014. Proceedings of the Integrated Ocean Drilling Program, Volume 341.

Johnston, D. T., Farquhar, J., Wing, B. A., Kaufman, A., Canfield, D.E., Habicht, K.S., 2005. Multiple sulfur isotope fractionations in biological systems: a case study with sulfate reducers and sulfur disproportionators. American Journal of Science 305 (6–8), 645–660.

Niewoehner, C., Hensen, C., Kasten, S., Zabel, M., Schulz, H. D., 1997. Deep sulfate reduction completely mediated by anaerobic methane oxidation in sediments of the upwelling area off Namibia. Geochimica et Cosmochimica Acta, 62 (3) 455-464.

Ono, S., 2007. Multiple-sulphur isotope biosignatures. Space Science Reviews, 135 (1–4), 203–220.

Ono, S., Wing, B.A., Johnston, D., Farquhar, J., Rumble, D., 2006. Mass-dependent fractionation of quadruple stable sulfur isotope system as a new tracer of sulfur biogeochemical cycles. Geochimica et Cosmochimica Acta 70, 2238–2252.

Reeburgh, W. S., 1980. Anaerobic methane oxidation: Rate depth distributions in Skan Bay sediments. Earth and Planetary Science Letters, 47, 345-352.

Strauss, H., Bast, R., Cording, A., Diekrup, D., Fugmann, A., Garbe-Schönberg, D., Lutter, A., Oeser, M., Rabe, K., Reinke, D., Teichert, B., Westernströer, U., 2012. Sulphur diagenesis in the sediments of the Kiel Bight, SW Baltic Sea, as reflected by multiple stable sulphur isotopes. Isotopes in Environmental and Health Studies, 48, 166-179.

Torres, M. E., Cox., T., Hong, W.-L., McManus, J., Sample, J. C., Destrigneville, C., Gan, H. M., Gan, H. Y., Moreau, J. W., 2015. Crustal fluid and ash alteration impacts on the biosphere of Shikoku Basin sediments, Nankai Trough, Japan. Geobiology, 13 (6) 562-580.