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ORGANIC MATTER IN THE SEDIMENTS OF GUAYMAS BASIN, A STUDY BY ROCK-EVAL 7S®

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Abstract: The organic matter and sulfur present in the sediments of Guaymas Basin from three sites cored during IODP expedition 385 were characterized using Rock-Eval 7S® in order to study organic matter diagenesis. At the reference site, the downward evolution of total organic carbon (TOC) and total sulfur (TS) contents is comparable to that observed in many marine sediments, i.e. decrease of TOC and opposite increase of TS. This trend is modified at the hydrothermal site, in relation to the migration of fluids. No clear trends are observed at the site containing methane hydrates, probably because of poor sampling resolution.

Keywords: Guaymas Basin, Rock-Eval 7S®, organic matter, pyrite, anaerobic oxidation of methane

1 INTRODUCTION

Guaymas Basin (Mexico) is a young oceanic basin where organic-rich sediments accumulate rapidly. Sulfide generated by sulfate reduction is present in the sediment, and organic matter sulfurization should be favored because the delivery of detrital iron, that outcompetes organic matter for reaction with sulfide, is relatively low. In parallel, the basin is characterized by a high geothermal gradient and methane of both biogenic and thermogenic origin is present in abundance in the sediments. We aim to understand to which extent organic matter sulfurization influences the generation of biogenic methane. We here present the first step of this project, that corresponds to a characterization of the organic matter present in the sediments.

2 MATERIALS AND METHODS

The studied samples were collected during IODP expedition 385 (Teske et al., 2021). Three sites are investigated: Site U1545 where no perturbation is present, Site U1547 which is affected by a thick shallow magmatic intrusion and Site U1552, where the sediment hosts methane hydrates. The studied sediments were collected under a water depth of more than 1500 m. It is considered that the depositional context remained relatively constant during the deposition of the studied intervals, so that changes in organic matter characteristics and sulfur content are considered to result from post-depositional processes.

Sediment samples were immediately placed in an inert atmosphere and frozen after core recovery. Before analysis, the samples were rinsed with deionised water, dried in an oven and finely ground.

Rock-Eval 7S® analysis was applied using a temperature program adapted to recent organic matter and detection of the different sulfur forms (Espitalié et al., 2024). In addition to the usual Rock-Eval parameters describing the organic matter content, the different sulfur forms were quantified using the software Geoworks®.

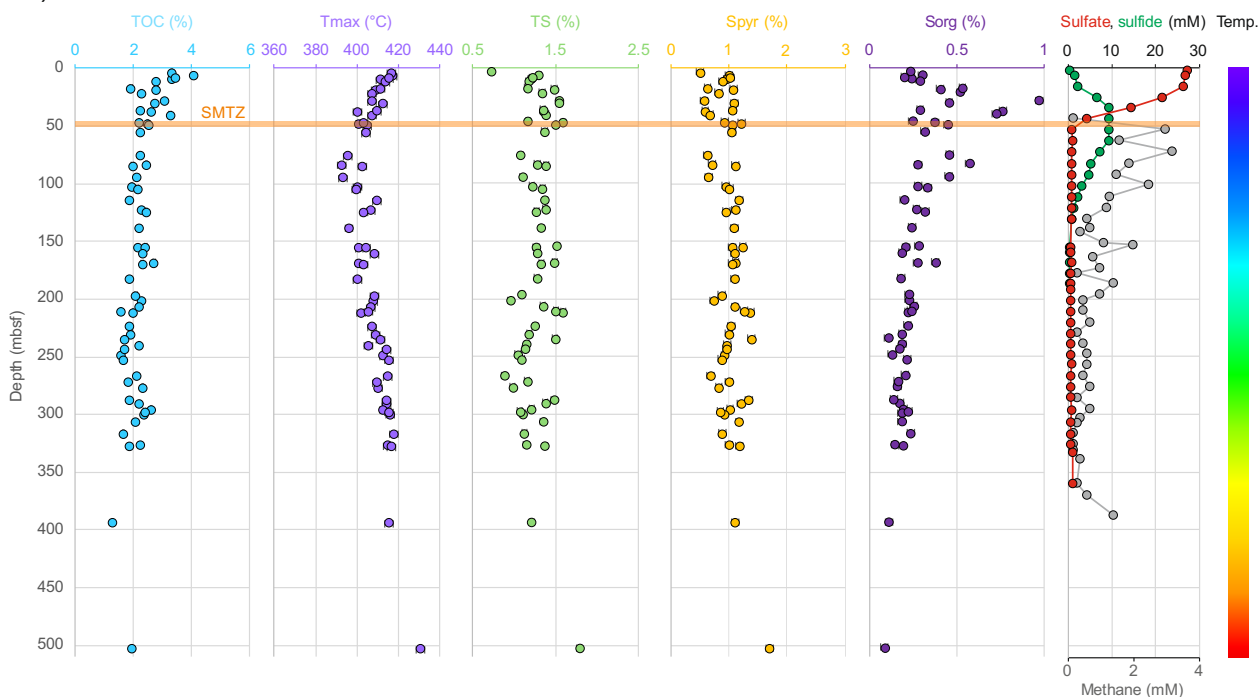
3 RESULTS AND DISCUSSION

3.1 Organic carbon and total sulfur

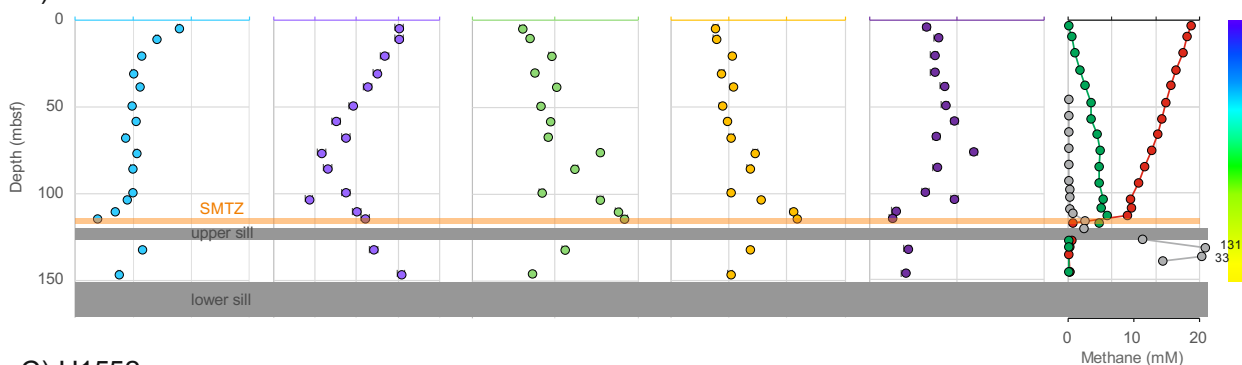
The total organic carbon (TOC) and total sulfur (TS) contents of the sediment show identical trends and values in the upper 70 m at sites U1545 and U1547 (Fig. 1A, B). Maximum TOC values close to 4 wt% are observed in the shallowest samples followed by a rapid decrease to 2 wt% in the upper 50 m and relatively constant values below. In parallel, TS increases rapidly from 0.6 - 1% in the shallowest samples to 1.5 % at ~50 mbsf. Though the involved depth scales can be markedly different between sites, such downwards evolution of TOC and TS contents has long been observed in many marginal and marine sediments (e.g. Goldhaber and Kaplan, 1974; Berner, 1984), and can be related to organic matter degradation by organoclastic sulfate reducing bacteria. High sulfate reduction rates were measured in surface sediments at

site U1545 and at site U1548, located very close to site U1547 (Nagakura et al., 2022), which supports this interpretation.

A) U1545



B) U1547



C) U1552

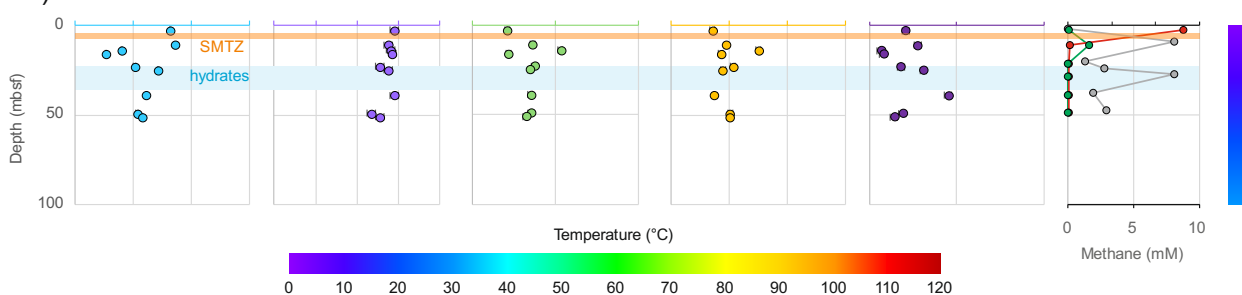


Figure 1. Vertical variation of Rock-Eval 7S® parameters in the sediment compared to porewater sulfate, sulfide and methane concentrations, and *in situ* temperature (Teske et al., 2021). A) Site U1545. B) Site U1547, C) Site U1552. For each parameter, the scale is the same from A) to C), except for methane concentration. SMTZ: sulfate-methane transition zone.

Below 70 mbsf, a progressive decrease of TOC values from ~2.2 to ~1.9 wt% and stable TS contents are observed at site U1545 (Fig. 1A). The presence of dissolved methane in the sediment between 50 and 250 mbsf indicates that methanogenesis is responsible for organic matter biodegradation in this depth interval, while the presence of ethane below 350 mbsf suggests that catagenesis might also contribute to the decrease of TOC values in the deepest parts of the core. This influence of catagenesis is supported by the progressive increase of Tmax values downwards at Site U1545. Despite its estimated age of ~400 ky, the deepest analyzed sample presents a Tmax value of 430°C, indicative of the early oil window (Espitalié et al.,

1985) which is consistent with the *in situ* temperature of ~115°C (Fig. 1A). The relative stability of TS content below 50 mbsf suggests that all reactive sulfur is rapidly fixed in the shallow sediments and not affected by deeper processes. At site U1547, a variability of TOC and TS values is observed below 70 mbsf, with several TOC values below 1.5 wt% and TS values higher than 2.0 wt%. Tmax values of the studied samples generally show a progressive increase downwards, indicating that the samples with low TOC and high TS values were not affected by metamorphism related to the upper or lower magmatic intrusions. Nevertheless, the high sulfur content suggests that these sediments were affected by sulfur-rich hydrothermal fluids generated during emplacement of the sills.

At site U1552 a general trend of TOC decrease and TS increase is observed on the studied interval. Nevertheless, values show a high variability in the uppermost 30 m of sediment (Fig. 1C), due to the presence of thick turbiditic deposits. At this site, the rapid TOC decrease and rapid TS increase associated with bacterial sulfate reduction are not observed, probably because of insufficient sampling resolution. Below 30 mbsf, TOC values decrease progressively and TS values are stable, which can be ascribed to methanogenesis as indicated by the presence of methane in the porosity. Methane hydrates were recovered at site U1552 between ~22 and ~32 mbsf (Teske et al., 2021). Fluid circulation associated with these hydrates might also explain the high variability of TOC and TS values in the uppermost 30 m of sediment.

3.2 Pyritic and organic sulfur

At site U1545, pyritic sulfur (Spyr) rapidly increases from 0.5 wt% at ~3 mbsf, to 1 wt% at ~6 mbsf. The Spyr content remains close to 1 wt% below, though with variability. This behavior is consistent with rapid formation of pyrite in the shallowest sediment, in relation to the high rate of organoclastic sulfate reduction (Nagakura et al., 2022). Organic sulfur (Sorg) increases from the shallowest sample (0.25 wt%) to a maximum of 1% at ~40 mbsf. Sorg content remains high in the sediments above 100 mbsf and a secondary maximum is observed at 85 mbsf. Below 100 mbsf, Sorg content progressively decreases downwards to reach a value of 0.1 wt% at ~500 mbsf. The increase in Sorg content in the upper 40 m of sediment is consistent with previous observations of diagenetic incorporation of sulfide resulting from bacterial sulfate reduction into the organic matter (Eglinton et al., 1994; Werne et al., 2003). Sulfurization is considered to be mostly associated with organoclastic sulfate reduction (Sinninghe Damsté and de Leeuw, 1990). Nevertheless, the Sorg increase is observed in a depth range where sulfate reduction rate is low (Nagakura et al., 2022), but is overall coincident with the peak of dissolved sulfide centered at the sulfate-methane transition zone (SMTZ; figure 1A). Organic matter sulfurization therefore appears to be mainly associated with anaerobic oxidation of methane and not to organoclastic sulfate reduction (Quijada et al., 2016). The decrease of organic sulfur content below 100 mbsf suggests that organic sulfur is lost during burial. Though the mechanisms involved in this de-sulfurization remain to be understood, one likely explanation is a rapid loss of organic sulfur because of thermal maturation, as indicated by the increase of Tmax values. Maturation experiments showed that the organic sulfur content of rocks significantly decreases during early maturation (Rosenberg et al., 2021).

At site U1547, both Spyr and Sorg increase in the upper 70 m of sediment (Fig. 1B). The increase is more progressive than at Site U1545, and can be mostly ascribed to organoclastic sulfate reduction, as the SMTZ is located deeper in the sediment. Below 70 mbsf, Spyr continues to increase downwards and reaches maximum values of 2.1% above the upper sill. Conversely, the Sorg content decreases and reaches minimum values of 0.15% above the upper sill. Though the Sorg content could have been affected by the thermal influence of the sill, the Tmax values of the sample do not support such conclusion. Therefore, as previously suggested, it appears more likely that the sulfur content and speciation of the samples located above the upper sill was influenced by hydrothermal fluid circulations. Neither sulfate nor sulfide are present in the porewater of sediments located between the upper and lower sills. The Spyr content in this interval is comparable to that observed at 70 mbsf, while the Sorg content is comparable to that of sediments of similar *in situ* temperature at Site U1545. The sediments between the two intrusions overall do not appear to be affected by the thermal influence, or hydrothermal fluids, associated with these intrusions.

At site U1552, an increase of the Spyr content is observed in the upper ~15 m of sediments, coincident with an increase of dissolved sulfide in the porosity. Below this depth, Spyr content fluctuates erratically around 1% while sulfide content in the porosity is negligible. The Sorg content remains below 0.5% in the studied section, showing erratic variations. It is inferred that the sharp geochemical gradients observed at this site, associated with the presence of gas hydrates, only allow efficient formation of pyrite in the shallow sediment but are not favorable to efficient organic matter sulfurization.

3.3 Tmax

Tmax is a well-known indicator of thermal maturity of the organic matter that also indirectly reflects its composition and environment of deposition (Espitalié et al., 1985). It is also modified by the presence of labile compounds or of organic sulfur, which shifts the Tmax towards low values (Rosenberg and Reznik,

2021). Tmax values of the shallowest samples are in the range observed for upwelling surface sediments (410-420°C; Wefer et al., 1998; D'Hondt et al. 2003) and decrease to ~380-390°C at intermediate depth (Figures 1A, B), before showing an expected increase with depth. At site U1545, the minimum Tmax values are observed around 80 mbsf, below the SMTZ, at a depth where *in situ* temperature is lower than 30°C and dissolved sulfide concentration in the porewater is low. At site U1547, the minimum Tmax values are also observed around 80 mbsf, above the SMTZ, at *in situ* temperature of ~50°C and high concentration of dissolved sulfide. Though the minimum of Tmax values is not observed at site U1552, a clear decreasing trend is also observed in the 50m of sediment analyzed here. This decrease of Tmax values could reflect the generation of labile microbial biomass in the sediment at intermediate depth. Nevertheless, the very different temperatures and geochemical composition of the sediment at the minimum of Tmax do not give support to this hypothesis. Alternatively, the decrease of Tmax values in the upper sediments could reflect the sulfurization of the organic matter in this interval (Rosenberg and Reznik, 2021).

4 CONCLUSION

At the reference site U1545, the downwards evolution of organic matter reflects the progressive influence of bacterial degradation followed by abiotic/thermal transformation. Sulfide released by organoclastic sulfate reduction and anaerobic oxidation of methane seems to mostly react with iron. Organic matter sulfurization is maximum at intermediate depth but decreases below, possibly due to early thermal cracking. This pattern is more or less also observed at the two other sites, though hydrothermal circulations possibly influenced the sulfur content at site U1547. The sediment at site U1552 is more heterogeneous, with the presence of thick clays deposits. Added to the presence of sharp geochemical gradients associated with gas hydrates, our sampling resolution does not allow to identify clear trends in organic matter and sulfur evolution.

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