CHROMANS AS SIGNALS OF FRESHWATER INCURSIONS PROMOTING SALINITY STRATIFICATION IN THE LOWER PERMIAN IRATI FORMATION, PARANÁ BASIN

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Introduction

The Irati Formation in the Paraná Basin (Brazil) is presumably the second largest oil shale deposit in the world, containing up to 26 wt.% TOC. The sediments are natural archives for depositional environment, biodiversity and palaeoclimate change of southwestern Gondwana during the Lower Permian. Especially the organic fraction in the black shales is considered result of the freshwater influxes in the Irati Sea, which influenced the primary production and salinity stratification. The preservation of the organic matter (OM) is thus cause of a positive water balance and resulting anoxic bottom conditions which may have prevailed throughout deposition of these black shales (Goldberg and Humayun, 2016; Reis et al., 2018).

To unravel the depositional palaeoenvironment regarding freshwater incursion and salinity, the distribution of methyltrimethyltridecylchromans (MTTCs) could be useful based on empirical studies, and is applied in form of the chroman ratio (5,7,8-triMe-MTTC/total MTTCs; Sinninghe Damsté et al., 1993). MTTCs are oxygen-containing compounds present in aromatic fractions, but of still unclear specific origin and formation pathways (Tulipani et al., 2015). In this context, the MTTCs distribution was used herein to assess water salinity and freshwater incursions into the Irati Sea, being correlated to other palaeosalinity indexes. To accomplish this, GC-FID and GC-MS of the saturated and aromatic fractions from extracted soluble OM were performed on 17 outcrop samples of the Irati Fm. (black shales). These samples were collected at two sites in the Paraná Basin, Amaral Machado Quarry (Saltinho City, São Paulo State) and São Mateus do Sul City (Paraná State), being sampled from the base to the top of the Lower (SM 2.1, 2.2, 2.3, 2.4, 2.6) and Upper (SM 3.1, 3.2, 3.5, 3.6, 3.7) units of São Mateus and an unit of Amaral Machado (AMa 1, 5, 7, 11, 17, 23, 24).

Results

The 8-Me-MTTC, 5,8- and 7,8-diMe-MTTC, and 5,7,8-triMe-MTTC chromans were identified in the aromatic fractions of Irati black shales, in which their spectra are characterized by molecular peaks at m/z 386, 400 and 414 and relatively high abundance peak ions at m/z 121, 135 and 149, respectively (*cf.* Sinninghe Damsté et al, 1987). The calculated chroman ratios markedly increase from the base to the top of the units (Fig. 1), which suggests a progressively decreasing salinity of the surface water due to influx of freshwater. This surface water may have been enriched in OM from the land together with nutrients stimulating primary productivity, and raised the organic flux to the sea floor (Goldberg and Humayun, 2016). This potential scenario is supported by the increasing TOC contents towards the top of the units (*cf.* Reis et al., 2018).

Basal samples 1, 5, and 7 from Amaral Machado Quarry with chroman ratios of 0.28, 0.18 and 0.44 respectively, and also samples 2.1, 2.2 and 2.3 from the lower São Mateus section

with chroman ratios of 0.36, 0.46 and 0.49 were possibly deposited in a mesosaline to hypersaline environment, while samples from the top and all samples from the upper São Mateus do Sul were deposited under normal marine conditions (chroman ratio > 0.6) if the chroman ratio is plotted against the Pr/Ph ratio (Fig. 1a; acc. Schwark et al., 1998). Samples AMa 1 and 5 present Pr/Ph ratios < 1, which corroborate a hypersaline environment.

Figure 1 Co-variation of chroman ratio with Pr/Ph ratio (a), gammacerane index (b) and β -carotane index (c).

Gammacerane and β -carotane indexes, alternative proxies for palaeosalinity, were also correlated to the chroman ratio (Figs. 1b and 1c), presenting an inverse correlation. These results corroborate with decreasing salinity of the surface water due to fresh water incursions, as the samples from the top of all units present lower values of the palaeosalinity indexes.

Moreover, high gammacerane concentrations point to water column stratification in the depositional environment. In addition, also tetrahydrophenanthrene (THP) was identified in the aromatic fractions of all samples in high concentration, in which its spectrum is characterized by a molecular ion at m/z 238, a base peak at m/z 223, and fragment ions at m/z 179, 193 and 208. Its detection corroborates the stable water stratification, since it possibly originates from tetrahymanol (similar to gammacerane), that is synthesized by bacterivorous ciliates living at the interface of stratified water layers (Sinninghe Damsté et al., 1999).

Conclusions

Water column stratification was presumably a major control in the formation of black shales in the Irati Sea, and is supported herein by the detection of tetrahydrophenanthrene at high concentrations, in addition to the known occurrence of gammacerane. The build-up of stratification was driven and intensified by freshwater incursions, which is reflected by the increasing chroman ratio towards the top of the units along with the general decrease of palaeosalinity parameters, such as the gammacerane and β -carotane indexes.

References

- Goldberg, K., Humayun, M., 2016. Brazilian Journal of Geology 46, 377-393.
- Reis, D.E.S., Rodrigues, R., Moldowan, J.M., Jones, C.M., Brito, M., Cavalcante, D.C., Portela, H.A., 2018. Marine and Petroleum Geology 95, 110-138.
- Schwark, L., Vliex, M., Schaeffer, P., 1998. Organic Geochemistry 29, 1921-1952.
- Sinninghe Damsté, J.S., Köster, J., Baas, M., Ossebaar, J., Dekker, M., Pool, W., Geenevasen, A.J., 1999. Tetrahedron Letters 40, 3949-3952.
- Sinninghe Damsté, J.S., Keely, B.J., Betts, S.E., Baas, M., Maxwell, J.R., de Leeuw, J.W., 1993. Organic Geochemistry 20, 1201-1215.
- Sinninghe Damsté, J.S., Kock-Van Dalen, A.C., de Leeuw, J.W., Schenck, P.A., Guoying, S., Brassel, S.C., 1987. Geochimica et Cosmochimica Acta 51, 2393-2400.
- Tulipani, S., Grice, K., Greenwood, P., Schwark, L., Böttcher, M.E., Summons, R.E., Foster, C.B., 2015. Chemical Geology 409, 61-68.