REASSESSING THE SYNGENEITY OF BIOMARKERS FROM SOUTH CHINA: LATE NEOPROTEROZOIC OR NOT?

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Earth experienced major changes during the Late Neoproterozoic (Cryogenian and Ediacaran) to early Cambrian transition. Notably, these include multiple occurrences of extreme glacial conditions as well as major perturbations in the chemical composition of the atmosphere-ocean system, which may have led to the radiation of multicellular life on earth (Lenton et al., 2014). The transition from dominant bacterial to eukaryotic marine primary productivity was one of the most profound ecological revolutions in the Earth's history.

As ancient phytoplankton rarely leave a fossil record, hydrocarbon biomarkers which are molecular fossils of membrane lipids can provide complementary information on placing key points of early life evolution (Brocks et al., 2017; Love et al., 2009). The well-developed Late Neoproterozoic successions, especially black shales, in South China offer a potential opportunity to help fill the biomarker gap during this important transition time.

Abundant biomarkers have been previously reported from high maturity Late Neoproterozoic sedimentary rocks in South China, including the Cryogenian Datangpo and Ediacaran Doushantuo formations (Wang et al., 2008; Zengye et al., 2017). These biomarkers include pristane, phytane, various steranes, hopanes, neohopanes, and tricyclic terpanes and were suggested to be organic molecular evidence of the survival of photosynthetic eukaryotes in palaeo-oceanic environments during the Snowball Earth era. However, contamination of geological samples with anthropogenic petroleum products during drilling, storage and sampling can be particularly problematic when studying organic-lean Precambrian samples, because these contaminants may over-print the original indigenous biomarker profile, potentially resulting in misleading interpretations (French et al., 2015).

To re-evaluate the provenance and validity of the biomarkers, fresh drill core was collected from black shales of the Datangpo and Doushantuo formations in South China. In order to ensure the indigeneity of the solvent extracted hydrocarbons, their composition was determined by conducting experiments under strict laboratory procedures, including with slice experiments on a precision saw that removed external surfaces. The surfaces of interior sub-samples were further solvent sonicated with the DCM:MeOH (9:1 v:v) mixture to check for any possible introduced contamination during the cutting process. In addition to checking and excluding potential contaminations in all consumables and instruments, combusted quartz sands were tested as system blanks at the beginning of each sample preparation round to monitor the level of contamination (<1 ng/g rock).

No steranes were detected in the interior of any of the samples (Figure 1a), and only trace amounts of hopanes in just one sample from the Doushantuo Formation (xs-199). On the contrary, solvent extraction of millimetre-thick slices cut from the external surfaces of the black shales reveals strikingly high level of contamination from organic residues on the sample surfaces. These contaminants include n-alkanes (C_{10}~C_{33}), isoprenoids, monomethylalkanes,

aromatic hydrocarbons (naphthalene, phenanthrene and their alkyl isomers) and abundant biomarkers such as tricyclic terpanes, hopanes and steranes (Figure 1b). The concentrations of hopanes measured in sample xs-199 are too low to be quantified accurately, yet concentrations of hopanes and steranes in the exterior sub-samples exceed blank concentrations by more than 3 order of magnitude due to the surficial contamination.

By noticing significant discrepancies in the hydrocarbon compositions between the exterior and interior sub-samples in this study, previously published biomarker data (Wang et al., 2008; Zengye et al., 2017) are likely to be incorrect. These results demonstrate that previously studied Late Neoproterozoic samples from South China probably host mixtures of indigenous over-mature hydrocarbons as well as numerous biomarker contaminants from core surfaces. Consequently, previous reports of biomarkers can no longer provide valid evidence for interpreting the sedimentary environment or evaluating the contribution of eukaryotic photosynthesis to marine primary productivity during the Snowball Earth period in South China.

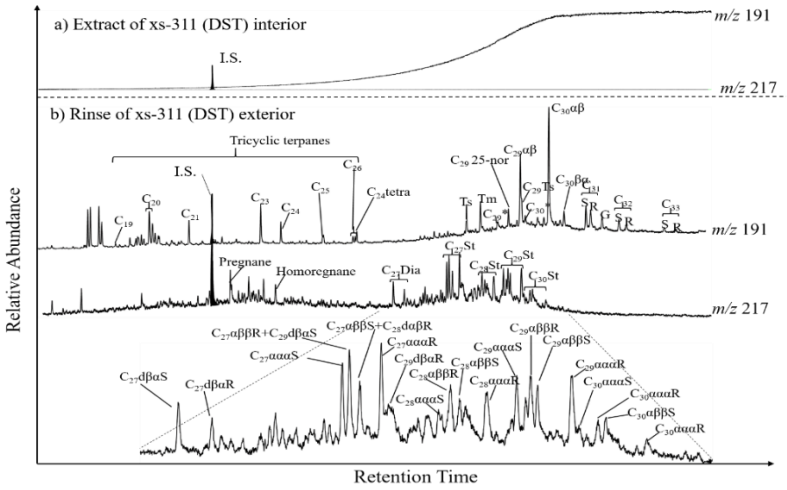

Figure 1 *a) Solvent extract of the interior of sample xs-311 (Doushantuo Formation), showing no biomarkers detected. b) Biomarker contaminants from organic residues on the exterior surfaces of sample xs-311. Hopanes-m/z 191. Steranes-m/z217. Internal standard: p-Terphenyl (160 ng).*

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