Article:

Hesselbo, SP, Little, CTS orcid.org/0000-0002-1917-4460, Ruhl, M et al. (2 more authors) (2020) Comments on “Paleosalinity determination in ancient epicontinental seas: A case study of the T-OAE in the Cleveland Basin (UK)” by Remirez, M. N. and Algeo, T. J. Earth-Science Reviews, 208. 103290. ISSN 0012-8252

https://doi.org/10.1016/j.earscirev.2020.103290

Stephen P. Hesselbo (Exeter)

Crispin T. S. Little (Leeds)

Micha Ruhl (Trinity College, Dublin)

Nicolas Thibault (Copenhagen)

Clemens V Ullmann (Exeter)

Remirez and Algeo (2020), referenced as R&A20 below, present new analyses of proposed elemental proxies for palaeo-salinity, as applied to the Toarcian Oceanic Anoxic Event (T-OAE) in the Cleveland Basin, UK. The manuscript discusses B/Ga, Sr/Ba, and S/TOC ratios, and is further structured as a test of the hypothesis of local basinal restriction during sea-level lowstand, versus regional/global anoxia during sea-level rise/highstand. The results are interpreted, controversially, to indicate brackish or even freshwater conditions on the seafloor during the T-OAE and, by implication, even greater degrees of freshening in the surface waters. While the results form a useful basis for further discussion, an omission from the study is an overall sedimentological, mineralogical, and palaeontological context.

Palaeontology

According to the B/Ga ratio palaeo-salinity proxy as interpreted by R&A20, waters were either brackish or fresh in the Cleveland Basin during deposition of nearly the entire studied section covering part of the Pliensbachian and Toarcian. However, this inference is not supported by the body fossil or trace fossil content of these strata. The authors acknowledge that the presence of ammonites is a problem for their palaeo-salinity interpretations, particularly during the T-OAE interval. Ammonites occur throughout the studied section and at times are abundant (e.g. Harries and Little 1999, Howarth 2002 and references therein). The authors invoke drifting as one of three possible explanations for the presence of ammonites in the Exaratum Subzone (T-OAE interval). However, there is no particular evidence to support this assertion (e.g. a preponderance of post-mortem encrusted shells) and their occurrence is no different in this part of the succession than any other part of the sequence, or indeed other marine rocks of Jurassic age. Applying Occam's Razor rule here would suggest that ammonites lived in the Cleveland Basin waters throughout the Pliensbachian and Toarcian time intervals rather being transported there. Infrequent inferences that some ammonites might have inhabited reduced-salinity water masses, cited by R&A20, are based on application of oxygen-isotope and clumped isotope techniques, with their own inherent caveats about thermal alteration, diagenesis, and $\delta^{18}O$-to-temperature calibrations. Nevertheless, even in the cited cases, salinity reduction is inferred not to have passed below 20 psu.

The authors discuss the presence of the pseudoplanktonic crinoids *Pentacrinites dichotomus* and *Seirocrinus subangularis* in the Cleveland Basin section, and suggest that these could also be parautochthonous, being brought in from elsewhere on driftwood. While the pseudoplanktonic nature of these crinoids is generally accepted, the most obvious place for driftwood to come from is the vegetated margins of the Cleveland Basin itself, rather than a hypothetical 'other' place. Thus, Occam's Razor again suggests that the presence of the pseudoplanktonic crinoids is indicative of marine conditions in the Basin. Throughout the Mesozoic, these species are exclusively present in fully marine environments, and become absent where there is any evidence of a deviation from fully marine (stenohaline) conditions in the water column.

Belemnites are also present throughout the Pliensbachian and Toarcian time intervals, but are not mentioned in the paper, besides their attempted use, through geochemistry of the rostrum, for reconstructing salinity changes over the T-OAE. Belemnites were marine animals and almost certainly were subject to little post-mortem drifting, having a heavy calcitic rostrum that would sink rapidly onto the seafloor. It is possible that belemnites were not restricted to shallow waters (Hoffmann and Stevens, 2019), and that nektobenthic forms could have lived under a somewhat freshened watermass lid, but freshening of the bottom waters must be ruled out by the belemnite occurrences.

Other macrofossils that are present in the Cleveland Basin during the T-OAE interval include the bivalves *Pseudomytiloides dubius* and species belonging to the genus *Bositra*. These occur in great numbers, commonly forming shell pavements (e.g. Harries and Little 1999, Caswell et al. 2009). Neither of these taxa belong to groups that have any known brackish or freshwater fossil representatives. Whilst *Pseudomytiloides dubius* is thought to have been facultatively pseudoplanktonic, there are far too many other fully marine macrofossil specimens, and far too little wood in the Falciferum Zone to support the drift hypothesis of R&A20 as a likely explanation for their abundant occurrence in the Cleveland Basin.

Away from the T-OAE interval, the B/Ga ratio palaeo-salinity proxy in Figure 3 indicates that reduced salinity conditions prevailed during the Pliensbachian to the Toarcian Tenuicostatum Zone, and the Falciferum Subzone and Bifrons Zone. Given the long time intervals represented by these strata, one would expect that if brackish water conditions had been present, this would be reflected in the benthic macrofossil and trace fossil assemblages. However, this is not the case, and the faunas from the Pliensbachian and Tenuicostatum Zone are characterized by a high diversity of bivalves, gastropods, and importantly, brachiopods and benthic crinoids, the latter two groups being stenohaline. The diversity of benthic faunas in the Falciferum Subzone is reduced, but increases again in the Bifrons Zone, once more including stenohaline benthic crinoids and brachiopods (e.g. Harries and Little 1999; Caswell et al. 2009). Trace fossils in the Pliensbachian and Toarcian Tenuicostatum Zone are also what would be expected in marine sequences (e.g. *Chondrites* and *Rhizocorallium*).

In contrast to the observations summarised above, if conditions were mostly of reduced salinity, one should expect the preservation of a range of fossil remains, both macrofossil and microfossil, from species thriving under reduced salinity conditions. However, fossils that indicate low salinities (e.g., brackish or freshwater ostracods) have not been described from the studied strata, raising further questions as to why the fossil fauna of Cleveland Basin sections only contains specimens characteristic of fully marine conditions. This further weakens another line of argument employed by R&A20, that the beds containing typically marine fossils are unrepresentative of the overall depositional environment.

Published reconstructions of sea level and salinity change

Reference to published work does not fully represent the views of previous authors. A good example is in relation to the sea-level history inferred by Thibault et al. (2018). Those authors discuss in detail the short-term 'backstepping' nature of the coarsening-up cycles in the Grey Shale to Mulgrave Shale succession, in the context of an overall fining (deepening) upwards trend (see e.g. fig. 2 of that paper and discussion on p.384). The overall fining upward trend that starts at the top of the Pliensbachian and culminates in the middle Toarcian. As acknowledged by R&A20, increased silt content in the middle of the Jet Rock may also be related to climate-related increased sediment supply (e.g. Xu et al. 2018) which further complicates the interpretation of sea-level change, but the backstepping pattern over the whole interval renders the idea of a significant regional sea-level fall through the OAE interval unlikely. Moreover, although R&A20 frame their discussion in terms of eustatic sea-level rise versus increased climatic humidity and freshwater runoff, many previous authors have argued that these major changes acted in concert, not in opposition (e.g. Jenkyns 1988; Hesselbo et al., 2007).

Neither of the two spatially resolved palaeoceanographic models cited by R&A20 (Bjerrum et al., 2001; Dera and Donnadieu, 2012) results in calculated reductions in salinity to brackish levels in the Cleveland Basin. Dera and Donnadieu suggest a maximum of 5 psu reduction in the Laurasian Seaway, whereas about 4 psu can be read from the model presented by Bjerrum et al. (2001). Similarly, cited work on fossil calcite-based salinity reconstruction, Saelen et al. (1996) argue for about 5 psu and Bailey et al. (2003) for less than 3 psu. More recently, a model study on Toarcian palaeoceanographic processes across European epicontinental shelf basins (Ruvalcaba Baroni et al., 2018) suggests that regionally, fully marine conditions occur throughout this time-interval, with surface water salinity values remaining close to mean ocean values of 33–36 PSU, depending on latitude and geographical position. Belemnite data presented in Ullmann et al. (2014) rather suggest that belemnites may have occupied shallow water habitats during the T-OAE, making a fresh-water lid even less likely. While some of the above studies accommodate some degree of freshening, this freshening is consistently argued to have been much less than shifting even the upper water column into R&A20's brackish field of 10-25 psu.

Robustness of presented proxies

The paper invokes brackish conditions in the Cleveland Basin before and after the T-OAE to nearly freshwater conditions during the T-OAE interval, and the authors argue that this assessment is based on three palaeo-salinity proxies: the B/Ga ratio, the Sr/Ba ratio and the S/TOC ratio. However, it is not clear from the work presented whether the samples are representative of the general lithology. For example, pyrite in the Whitby Mudstone may be concentrated in nodules up to several centimetres across, which were presumably avoided in the original sampling campaign. Therefore, the samples are likely to under-estimate the S/TOC ratio in those intervals where pyrite nodules are common.

In the discussion of R&A20, Sr/Ba ratios are discounted (section 4.1.3) due to contamination relating to minor carbonate content of the section. Additionally, large, euhedral crystals of barite are known from the studied outcrops which would have been the result of prominent Ba fluxes through the sediment. A further issue with using Sr/Ba ratios is the well-known, potentially strong response of Ba in marine strata to changes in primary productivity of the overlying waters, and the Ba content of detrital material. Consequently, the palaeo-salinity analysis is actually based on two proxies (B/Ga and S/TOC; shown in Figure 3), not three.

Figure 3 of R&A20 shows the S/TOC ratio for sediments of the Margaritatus Zone to the Bifrons Zone, which varies from about 0.8 to 3. The largest values are in the Tenuicostatum Zone, whilst the smallest values occur in three parts of the section: Spinatum Zone, Exaratum Subzone and lower Bifrons Zone. The T-OAE interval values are not discernibly (and almost certainly not statistically) different to the values either above or below. Therefore, there is no obvious trend apparent in the parts of the section postulated to represent brackish, freshwater or marine conditions in the Basin. Apart from this, the S/TOC ratio is less an indicator of salinity (i.e., the total concentrations of dissolved salts/cations and anions in the water mass) and more an indicator of the sulphate concentration in the water mass. Different from the dominant ions in seawater (Na+, Cl-) which behave conservatively (i.e., no participation in biological/ diagenetic/ redox processes), sulphate is consumed by bacterial sulphate reduction, leading to the formation of sulphide minerals in the sediment. Sediments underlying a water mass of seawater salinity but with very low sulphate concentrations (e.g., ferruginous conditions) will display low S/TOC ratios. The authors acknowledge some of these reservations in section 4.1.1 stating that using S/TOC ratios for differentiation between marine and brackish conditions is problematic. Therefore, the argument about absolute salinity and salinity change rests nearly entirely upon the interpretation of whole rock B/Ga ratios.

Application of the B/Ga proxy

Given that the B/Ga proxy is based on assumptions that these elements are acquired and retained by the clay structures on the seafloor and not subsequently altered, it is important to understand the clay mineral assemblages and their geological evolution. The amount of B that can be taken up into clay minerals might depend on sedimentation and sediment burial rates as well, since the clay minerals need to be in unrestricted diffusive connection with the overlying seawater to effectively take up B. High sedimentation rates, quick burial and sediment lithification should hinder this B uptake. The outcrop sections referred to have been moderately deeply buried to the extent that, in terms of hydrocarbon maturation, the Toarcian succession is well within the oil window (e.g. French et al. 2014 and other references cited by R&A20) and the clay mineral assemblages show strong elements of diagenetic re-cystallization and authigenic precipitation (see e.g. Kemp et al. 2005 or Hesselbo et al. 2020). How do these clay mineral transformations affect B/Ga ratios of the whole rock? The authors argue that a systematic stratigraphic change in B/Ga ratios is evidence of a primary environmental signal, but if the elemental content is related to original detrital mineralogy combined with its subsequent diagenesis, stratigraphic trends would also have been the result (i.e. we should not expect diagenesis to be independent of stratigraphy). These perspectives require thorough investigation before the new proxy data can be applied to the question of palaeosalinity. The conflict with palaeontological data suggests that original mineralogic content and diagenetic processes are actually dominant in this case.

Reported B/Ga ratios vary from >1 to almost 7, with the smallest ratios during the T-OAE interval and there are considerable deflections at the top of this interval and also in the Tenuicostatum Zone. Although R&A20 argue that there is a co-variation of the B/Ga and S/TOC ratios, the covariation of B/Ga with S/TOC is not statistically significant ($r^2 = 0.005$; $p = 0.65$; $n = 48$), and would indicate a negative relationship rather than a positive one.

Reported B and Ga are very low and easily liable to detrital contamination. We assume that units should be in µg/g rather than ng/g as given in section 3.2, as upper crustal concentrations of B and Ga are three orders of magnitude higher (Rudnick and Gao, 2003). If these concentrations are indeed correct, they still fall into a concentration range where the proxy as developed by Wei and Algeo (2019) has nearly no predictive power. In the conclusion of Wei et. al. (2018), it is advised that B values of <75ppm, and Ga values of <25ppm should be avoided when evaluating B/Ga. Of the B/Ga values reported in the paper, 60% do not meet these criteria (>90% in unit III – attributed to maximum freshening).

Mo content

The implications for interpretation of Mo content of the T-OAE strata are discussed in the light of the freshwater hypothesis. To paraphrase, R&A20 favour only localised sequestration of Mo from seawater in hydrologically restricted basins within the regional seaway. The line of argument advanced is that if a decline in Mo/TOC values in the 'Jet Rock' in the Cleveland Basin were caused by expansion of anoxic black shale deposition during regional and/or eustatic sea-level rise during the OAE, then there should have been no reduction in salinity in the Cleveland Basin. Notwithstanding the palaeontological and mineralogical arguments outlined above, the data presented by R&A20 appear incompatible with their interpretation, because a significant increase in Mo_{ef} occurs at the top of their stratigraphic unit III (= 'Jet Rock') at the levels inferred to have had the most freshwater influence in the succession (cf. figs 3 and 6 of R&A20).

The Toarcian Mo-isotope evolution shows significant, ~0.6 ‰, variations through the Cleveland Basin T-OAE succession (Pearce et al., 2008), interpreted as due to intermittent changes in the rate of open ocean seawater exchange into the basin, with deviations to heavier $\delta^{98/95}$Mo values hypothetically resulting from a decreased rate of exchange and consequent greater proportional removal of Mo from local seawater into the underlying sediments (Dickson et al., 2017). The Mo-isotopic record from other basins across the European epicontinental seaway, including from the oxygenated and open-marine Belluno Basin of Italy, however, show constant $\delta^{98/95}$Mo compositions through the T-OAE negative carbon-isotope excursion (Exaratum Subzone), with values similar to the lightest values in the Cleveland Basin during this time (Dickson et al., 2017). This observation implies that in the Cleveland Basin, the rate of seawater exchange with the open ocean was periodically too rapid to enable substantial drawdown of aqueous Mo, despite the prevailing euxinia. Such an explanation is supported by the anti-phase relationship between $\delta^{98/95}$Mo and Mo concentrations in the Yorkshire succession, with enhanced drawdown and sedimentary Mo-fluxes from a refreshed basinal molybdenum inventory coinciding with isotopically lighter, open-ocean, $\delta^{98/95}$Mo values (Dickson et al., 2017). Although the Cleveland Basin was, in general, a sulphidic, restricted marine basin, the renewal rate of the basin waters thus is interpreted to be reflected in the $\delta^{98/95}$Mo fluctuations (Dickson et al., 2017).

If the hydrographic history of the Cleveland Basin were to have impacted on Toarcian salinity, especially to the extend advocated by R&A20, one would expect the suggested palaeo-salinity proxies to show a response in accord with the variations in $\delta^{98/95}$Mo values. This is, however, not observed in the presented B/Ga or S/TOC data. The available Mo-concentration and Mo/TOC data, as well as Mo-isotope data, show that the Cleveland Basin periodically returned to fully exchanging water masses with the open ocean, with global, and periodically basinal, Mo drawdown leading to the observed Mo concentration and isotope profiles. These findings do not match the model advocated by R&A20 in which complete restriction of the Cleveland Basin, without any meaningful open water mass exchange, would have led to persistent freshwater conditions throughout the T-OAE.

To conclude, we have presented an array of sedimentological, palaeontological and geochemical arguments that go against the interpretation of R&A20 for the B/Ga ratio being a good proxy for palaeo-salinity changes in classic Pliensbachian/Toarcian sections of the Cleveland Basin.

References:

Caswell, B.A, Coe, A.L., Cohen, A.S., 2009. New range data for marine invertebrate species across the early Toarcian mass extinction. Journal of the Geological Society, London v. 166, p. 859–872.

Dickson, A.J., Gill, B. C., Ruhl, M., Jenkyns, H.C., Porcelli, D., Idiz, E., Lyons, T.W., van den Boorn, S.H.J.M., 2017. Molybdenum-isotope chemostratigraphy and paleoceanography of the Toarcian

Oceanic Anoxic Event (Early Jurassic). Paleoceanography v. 32, p. 813–829.

Harries, P.J., Little, C.T.S., 1999. The early Toarcian (Early Jurassic) and the Cenomanian–Turonian (Late Cretaceous) mass extinctions: similarities and contrasts. Palaeogeography, Palaeoclimatology, Palaeoecology v. 154, p. 39–66.

Hesselbo, S.P., Jenkyns, H.C., Duarte, L.V., Oliveira, L.C.V., 2007. Carbon-isotope record of the Early Jurassic (Toarcian) Oceanic Anoxic Event from fossil wood and marine carbonate (Lusitanian Basin, Portugal). Earth and Planetary Science Letters v. 253, p. 455–470.

Hesselbo, S.P., Hudson, A.J.L., Huggett, J.M., Leng, M.J., Riding, J.B., Ullmann, C.V., 2020. Palynological, geochemical, and mineralogical characteristics of the Early Jurassic Liasidium Event in the Cleveland Basin, Yorkshire, UK. Newsletters on Stratigraphy v. 53, p. 191–211.

Howarth, M. K., 2002. The Lower Lias of Robin Hood's Bay, Yorkshire, and the work of Leslie Bairstow. Bulletin of the Natural History Museum, London (Geology Series) v. 58(2), p. 81–152.

Jenkyns, H.C., 1988. The Early Toarcian (Jurassic) Anoxic Event: stratigraphic, sedimentary, and geochemical evidence. American Journal of Science v. 288, p. 101–151.

Kemp, S.J., Merriman, R.J., Bouch, J.E., 2005. Clay mineral reaction progress – the maturity and burial history of the Lias Group of England and Wales. Clay Minerals v. 40, p. 43–61.

Pearce, C.R., Cohen, A.S., Coe, A.L., Burton, K.W., 2008. Molybdenum isotope evidence for global ocean anoxia coupled with perturbations to the carbon cycle during the Early Jurassic. Geology v. 36, p. 231–234.

Ruvalcaba Baroni, I., Pohl, A., van Helmond, N.A.G.M., Papadomanolaki, N.M., Coe, A.L., van de Schootbrugge, B., Donnadieu, Y., Slomp, C.P., 2018. Ocean circulation in the Toarcian (Early Jurassic): a key control on deoxygenation and carbon burial on the European shelf. Paleoceanography and Paleoclimatology v. 33, p. 994–1012.

Thibault, N., Ruhl, M., Ullmann, C.V., Korte, C., Kemp, D.B., Gröcke, D.R., Hesselbo, S.P., 2018. The wider context of the Lower Jurassic Toarcian oceanic anoxic event in Yorkshire coastal outcrops, UK Proceedings of the Geologists' Association, v. 129, p. 372–391.

Wei, W., Algeo, T.J., Lu, Y., Lu, Y., Liu, H., Zhang, S., Peng, L., Zhang, J., Chen, L. (2018). Identifying marine incursions into the Palaeogene Bohai Bay Basin lake system in northeastern China. International Journal of Coal Geology, v. 200, p.1–17.

Wei, W., Algeo, T.J. 2019. Elemental proxies for paleosalinity analysis of ancient shales and mudrocks. Geochimica et Cosmochimica Acta, in press.