

***Interactive comment on* “Central Tethyan platform-top hypoxia during Oceanic Anoxic Event 1a” by Alexander Hueter et al.**

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This study examines geochemical proxies, mainly for watermass redox conditions, in Upper Cretaceous platform carbonates in Croatia that were deposited during OAE1a (Early Aptian). These deposits accumulated on the Adriatic Carbonate Platform, which covered an immense area (>500,000 km²) in the central Tethys during the Early Cretaceous.

The authors' main theses are that (1) redox conditions became at least somewhat reducing, possibly in multiple pulses rather than a single event, on the platform top during OAE1a, and (2) reduced oxygen levels played a role in stressing shallow-marine biotas during this event.

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My opinion is that, while the presented data do not conflict with the main interpretations of this study, some of the data are open to alternative interpretations.

Detailed comments:

1) A couple of aspects of the Adriatic Carbonate Platform are not sufficiently addressed. First, what were the water depths on the platform top? Was it on the order of a few meters, like on the modern Great Bahama Bank? Presumably, the platform top was shallow if algae and corals were growing profusely on it, but this point needs to be discussed explicitly.

If the Adriatic Carbonate Platform was quite shallow, then this characteristic as well as its open margins would make the Great Bahama Bank a much more appropriate analog than the Late Pennsylvanian Midcontinent Sea of North America, which was flooded to depths of 100 m during glacio-eustatic highstands and which was nearly landlocked in its geography. The climatic boundary conditions were also quite different—in the Pennsylvanian, Gondwanan glaciation was driving large eustatic fluctuations, whereas in the Cretaceous, continental ice mass was limited, and sea-level fluctuations were small. For this reason, the Adriatic Carbonate Platform would probably have built up to close to sea level. (I thank the authors for making use of my work on the LPMS, but it is probably not the best choice of analog.)

Second, the study site is shown at a paleolatitude of 22 degrees N. This is squarely in the dry subtropics, so there was probably strong evaporation over the top of a large platform like this. If platform-top water depths were quite shallow, then evaporation may have been strong enough to make these waters significantly more saline than normal seawater. This might have set up off-platform flow of a hypersaline watermass, which would have had consequences relevant to the interpretations of the present study (e.g., a mechanism to drive lateral advection or upwelling of open-ocean waters onto the platform top) as well as to topics that are not considered here (e.g., formation of warm saline deep waters in the Tethys).

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2) The interpretations of redox proxies in this study are not incorrect, but they are incomplete. Additional considerations that need to be discussed in the manuscript include the following:

First, several redox-sensitive trace elements (As, V, and Mo) were used to evaluate redox variations. The elemental data were generated with LA-ICP-MS, and presumably the authors targeted carbonate samples and steered away from shaly samples. If the samples are 100

If the study samples are not pure carbonate, then raw trace element concentrations are not particularly meaningful unless an Al concentration curve is plotted next to them, or the trace element concentration profiles are Al-normalized. At various points in the manuscript, increases in trace element concentrations are attributed to more reducing conditions (e.g., Page 7, Line 22), but what if they just reflect an increase in the clay content of samples? The data needed to test this possibility have not been supplied.

Because redox-sensitive trace elements are local redox proxies, they will reflect platform-top conditions (i.e., at the site of deposition), not conditions in adjacent basinal areas, so the statement that “Redox sensitive elements still display low concentrations, pointing to ongoing oxygen depletion in the basin” (Page 11, line 37) seems suspect.

Second, cerium anomalies (Ce/Ce^*) have been widely used as a paleoredox proxy, but too many studies have failed to demonstrate that the measured REEs represent a hydrogenous source (i.e., seawater-derived) and not just a detrital source. If the REEs in a sample are mainly detrital in origin, then they cannot comment on depositional redox conditions. The sources of REEs can be readily tested using two approaches: (1) Y/Ho ratios, and (2) LREE/HREE ratios. Y/Ho ratios are 25-30 for REEs in clay minerals, but typically >60 for REEs in seawater. The relative amounts of REEs drawn from lithogenous versus hydrogenous sources can be estimated from how closely Y/Ho ratios in the study samples approach these endmember values. Furthermore, REE distributions are roughly flat in clay-rich samples (i.e., LREE/HREE close to 1.0; although

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there may be strong MREE enrichment if phosphate is present), but they will show LREE depletion (usually with a flattish MREE-HREE distribution) in samples containing hydrogenous REEs. The theory for these applications was discussed in Chen et al., 2015 [Chen, J., Algeo, T.J., Zhao, L., Chen, Z.Q., Cao, L., Zhang, L. and Li, Y., 2015. Diagenetic uptake of rare earth elements by bioapatite, with an example from Lower Triassic conodonts of South China. *Earth-Science Reviews*, v. 149, pp. 181-202]. Before Ce/Ce^* can be meaningfully used as a paleoredox proxy, it is necessary to first demonstrate that the REEs in a sample are mainly of hydrogenous origin based on these two tests. I suspect that the REEs in the present study samples are of hydrogenous origin, but this needs to be demonstrated rather than surmised.

Third, the various redox proxies utilized in this study seem to be treated as equivalent to each other, but this is not at all the case—they have different temporal and spatial scales of significance owing to differences in seawater residence times. Carbonate U-isotopes represent a global-ocean redox proxy owing to the long residence time of U in seawater (450 kyr). At the other end of the spectrum, redox-sensitive trace metals are taken up locally across the sediment-water interface, and thus respond directly to local redox conditions (although also indirectly to basinal or global redox conditions through redox-related changes in their seawater inventory). Ce/Ce^* falls in between owing to a residence time in seawater of one to a few hundred years—which is long enough to record basinal effects but generally not long enough to record global effects owing to the 1000-2000 yr mixing time of the oceans. Thus, the redox proxies utilized in this study are providing different types/scales of redox information. The carbonate U-isotope and Ce anomaly proxies show similar secular patterns, suggesting that both are recording basin-scale shifts in redox conditions—they both appear to record a single large shift toward more reducing conditions during OAE1a. The trace-element proxies do not show significant covariation with the U and Ce proxies, and their largest peaks are below the OAE1a interval. However, their concentrations are so low (mostly a few ppm) that it is unclear whether they are recording redox variations at all (as opposed to clay content; see above). This is a critical issue for the interpretations of the

present study because the U and Ce proxies are likely to be recording a shift toward more reducing conditions in the larger Tethys Ocean basin, and not on the platform top per se—only the redox-sensitive trace elements provide information specifically about platform-top redox conditions, and if their concentrations are controlled by clay content, then there is no evidence for changes in redox conditions on the platform top during OAE1a. Indeed, this aspect of the interpretations of this study must be doubted, as it would be quite difficult to make a watermass that is only a few meters deep oxygen-depleted—such waters simply exchange gases too freely with the atmosphere.

3) Some terminology used in this study is non-standard, specifically the term "automicrite" (page 6). This term is not defined or described explicitly anywhere in the manuscript. Reading 'between the lines', I interpret it to mean "authigenic micrite", i.e., micrite precipitated in situ. If this is this case, however, then it is effectively a micritic cement, formed either on the seafloor or within sediment pore spaces—and it would be clearer to call it "micritic cement".

Two issues that must be addressed are: (1) what is the exact origin of "automicrite"?, and (2) what are the petrographic or field criteria used to distinguish this type of micrite from "detrital micrite"? In this regard, the authors appear to assume that the "automicrite" in their samples is a primary component, and not recrystallized material, but the images provided do not permit a definitive interpretation on this point. Basically all fine-grained carbonate recrystallizes in the burial environment, sometimes multiple times, and the recrystallization effects can be highly localized (e.g., see Algeo et al., 1992: [Algeo, T.J., Wilkinson, B.H. and Lohmann, K.C., 1992. Meteoric-burial diagenesis of Middle Pennsylvanian limestones in the Orogrande Basin, New Mexico; water/rock interactions and basin geothermics. *Journal of Sedimentary Research*, v. 62(4), pp. 652-670.] In the present study, Turpin et al. (2012) is cited as the source of "further criteria" for automicrite, but any relevant criteria need to be elaborated upon here.

4) The second goal of the study is to show the influence of reduced oxygen levels in stressing shallow-marine biotas during the OAE1a event. However, establishing

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the causation of biotic events is always quite difficult. Even assuming that there was unambiguous evidence of a shift toward reducing conditions on the platform top (which is not entirely clear; see above), how is it possible to show that changes in redox conditions and not in some covariant factor (such as water temperature) was the main biotic stressor?

Minor matters:

1) The manuscript contains many instances of past events being described in the present tense. Past events should be described using the past tense. 2) Page 2, line 31: what is an “out-of-balance reefal ecosystem”? The intended meaning is unclear here. 3) Page 6, line 18: what is the evidence for an "increased sedimentation rate"? 4) Some grammatical problems, e.g., page 11, line 32: "portions ... coincide" –need to have subject-verb agreement.

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