Publisher: GSA
Journal: GEOL: Geology
DOI:10.1130/G49065.1

[1]Supplemental Material: **[[Please provide a Supplemental Material caption.]]** Please visit https://doi.org/10.1130/XXXXX to access the supplemental material, and contact editing@geosociety.org with any questions.

Pulsed volcanism and rapid oceanic deoxygenation during Oceanic Anoxic Event 1a

Kohen W. Bauer[1], Cinzia Bottini[2], Robert Frei[3], Dan Asael[4], Noah Planavsky[4], Roger Francois[5], N. Ryan McKenzie[1], Elisabetta Erba[3], and Sean A. Crowe[1,5*]

[1]*Department of Earth Science, University of Hong Kong, Pokfulam Rd, Hong Kong SAR*

[2]*Department of Earth Sciences, University of Milan, Via Mangiagalli 34, 20133 Milan, Italy*

[3]*Department of Geosciences and Natural Resource Management, University of Copenhagen, Rolighedsvej 231958, Frederiksberg C, Denmark*

[4]*Department of Earth & Planetary Sciences, Yale University, 210 Whitney Ave, New Haven, CT, 06511, USA*

[5]*Departments EOAS and M&I UBC, University of British Columbia, 2020-2207 Main Mall, Vancouver, BC, V6T 1Z4, Canada*

*Email: sean.crowe@ubc.ca

ABSTRACT

Widespread oceanic anoxia, biological crises, and volcanic activity are associated with the onset of Early Aptian (ca. 120 Ma) Oceanic Anoxic Event 1a (OAE1a). Reconstructions of oceanic deoxygenation and its links to broadly contemporaneous volcanism, however, remain poorly resolved. Here we use ~~novel~~ geochemical data, including δ^{53}Cr ratios and rare Earth element abundances, to ~~parse~~ the timing and tempo of submarine volcanism and global oceanic

Publisher: GSA
Journal: GEOL: Geology
DOI:10.1130/G49065.1

deoxygenation across this event. Pacific Ocean sediments deposited in the run up to OAE1a record multiple phases of marine volcanism associated with the emplacement of Ontong Java Plateau lavas. Rapid oceanic deoxygenation followed the initial phases of volcanism and a biocalcification crisis. Large swaths of the oceans likely became anoxic from the Tethys to the Pacific Oceans in <30 k.y. Oceanic anoxia persisted for almost a million years after this and was likely sustained through intensified continental and submarine weathering. These results paint a new picture of OAE1a in which volcanism, biological crisis, and oceanic deoxygenation are separated in time and linked through Earth system responses that operate on timescales of tens of thousands of years.

INTRODUCTION

Oceanic Anoxic Events (OAEs) occurred intermittently throughout the Phanerozoic Eon and are linked to major climatic anomalies, large igneous province (LIP) volcanism, and biological crises (Erba, 2004; Erba et al., 2010; Jenkyns, 2010). For instance, submarine volcanism and the emplacement of the Ontong Java Plateau (OJP) in the Pacific Ocean correlates with Early Aptian OAE1a (Bottini et al., 2012; Bottini et al., 2015; Larson, 1991; Mehay et al., 2009; Mills et al., 2017; Percival et al., 2021), which is globally demarcated by sedimentary C-isotope anomalies that subdivide the event into segments (C2–C7) (Menegatti et al., 1998) (Fig. 1). Most radiometric ages for OJP lavas fall between 124 Ma and 120 Ma (Timm et al., 2011), and thus OJP volcanism is often implicated as the driver for biogeochemical upheaval across OAE1a. Os-isotope and Hg-concentration records suggest that the onset of volcanism was coeval with the beginning of OAE1a (C3, ca. 120.76 Ma) and that the main eruptive phase occurred between 120.70 Ma and 119.90 Ma (C3–C6) (Bottini et al., 2012; Percival et al., 2021; Tejada et al., 2009) according to the timescale of Malinverno et al. (2010) (Fig. 1).

Publisher: GSA
Journal: GEOL: Geology
DOI:10.1130/G49065.1

OJP volcanism likely triggered biotic turnover, climatic perturbations, and widespread oceanic deoxygenation. For example, OJP volcanism injected large masses of CO_2 into the ocean-atmosphere system (Mehay et al., 2009), which contributed to a warm greenhouse climate, accelerated hydrologic cycle, and increased weathering and nutrient delivery to the oceans (Bottini et al., 2015). Nutrient delivery, in turn, can drive eutrophication with increased primary productivity and water-column oxygen demand (Westermann et al., 2013). Indeed, the onset of OAE1a (C3, ca. 120.76 Ma) is delineated by the deposition of organic matter (OM)-rich black shales~~, which continued across~~ a million year interval (C3–C6, 120.76–119.66 Ma), which implies OM accumulation in oxygen-poor waters (Jenkyns, 2010) (Fig. 1). OAE1a is also associated with global Os- and Sr-isotope excursions that are thought to represent volcanic activity and basalt-seawater interaction with corresponding changes in ^{188}Os and ^{86}Sr delivery to the oceans (Bottini et al., 2012; Mills et al., 2017). However, the response times of the Os- and Sr-isotope perturbations across OAE1a are vastly different, >50 k.y. and >1 m.y., respectively, and this is generally attributed to their differing residence times in the ocean (Os is ~40 k.y., Sr is ~5 m.y.). Similar (~1 m.y.) dynamics in the Li- and Ca-isotope systems—both with >1 m.y. residence times—have been attributed to enhanced continental weathering resulting from volcanic CO_2-induced warming (Blattler et al., 2011; Lechler et al., 2015). These observations imply that volcanism may have triggered OAE1a and associated feedbacks, but current records of both ocean redox state and volcanism generally lack the resolution required to evaluate the timing and tempo of OJP eruptions and their relationship to the hallmark biogeochemical perturbations of OAE1a. This limitation makes the cause-and-effect relationships of LIP eruptions, oceanic deoxygenation, and biotic turnover during OAE1a difficult to establish.

Publisher: GSA
Journal: GEOL: Geology
DOI:10.1130/G49065.1

To reconstruct the eruption history of the OJP and associated oceanic deoxygenation, we established multiple geochemical records (Fe speciation, manganese enrichments (Mn_{EF}), rare Earth element (REE) abundances, and $\delta^{53}Cr$ ratios) in sediments that record OAE1a (Table 1). These proxies have relatively short residence times in the ocean (<10 k.y.) and thus respond to environmental changes on similar timescales. The Fe-speciation proxy quantifies sediment ratios of highly reactive Fe (Fe_{HR}) to total Fe (Fe_{Tot}) (Fe_{HR}/Fe_{Tot}), and values >0.38 are diagnostic of sediment deposition under anoxic conditions (Raiswell et al., 2018). Cerium (Ce/Ce*) and Europium (Eu/Eu*) anomalies (i.e., the deviation of Ce and Eu concentrations relative to neighboring REEs) are widely used to trace oceanographic processes (Nozaki, 2001). Ce is redox active and Ce anomalies (Ce/Ce*) reflect ~~the~~ seawater oxygenation state, whereas ~~the~~ anomalies (Eu/Eu*) of europium, which is also redox active, trace seawater mixing with hydrothermal fluids (Olivarez and Owen, 1991). Chromium isotopes ($\delta^{53}Cr$) are an additional paleoredox proxy (Frei et al., 2009) and are useful in fingerprinting both depositional redox state and hydrothermalism (Bauer et al., 2019; Bauer et al., 2021). Together, these data resolve distinct intervals of volcanism, followed by oceanic deoxygenation, which is, in turn, followed by shifts in oceanic chemistry related to continental and submarine weathering.

METHODS

We analyzed sedimentary rocks deposited on the southeastern margin of the Tethys Ocean (Cismon core) and in the Pacific Ocean (Deep Sea Drilling Project [DSDP] Site 463) (see Supplemental Material[1]). Lithologically, the sites are dominated by chemical precipitates whose compositions may directly reflect their seawater provenance (carbonates and OM-rich shales; Erba and Larson, 1998). All samples are stratigraphically constrained and can thus be temporally correlated between sites. We conducted total digests and selective leaches to speciate metals

Publisher: GSA
Journal: GEOL: Geology
DOI:10.1130/G49065.1

buried in detrital (lithogenic) and authigenic materials (non-lithogenic), respectively. Elemental concentrations and Cr isotopic compositions were measured in both digests and leaches (0.5 N HCl) and screened for detrital sediment contribution (Figs. DR2–DR4[1]). Detailed methods and tabulated data can be found in Table DR1[1].

RESULTS

Manganese concentrations in sediments from both sites display strong temporal variability. In the ~100 k.y. before OAE1a (C2), aluminum-normalized Mn (Mn_{EF}) concentrations (PAAS normalized, Mn_{EF} ~1.0 [McLennan, 2001]) at DSDP Site 463 are strongly enriched (Mn_{EF} = 19), whereas pre-OAE1a Mn_{EF} values at the Cismon site are typical of deep-sea sediments (Mn_{EF} = ~7) (Fig. 2). At the onset of OAE1a (C3), a second large Mn enrichment is observed at DSDP Site 463 (Mn_{EF} = 21), which is followed by a decrease to Mn_{EF} <1 in less than 30 k.y. (Fig. 2). Mn in Cismon sediments also drops to Mn_{EF} <1 during the first 30 k.y. of C3 (Fig. 2). Mn_{EF} values at both sites remain mostly at <1.0 for the rest of OAE1a (C3–C6) (Fig. 2).

The isotopic composition of Cr differs greatly in Tethys Ocean and Pacific Ocean sediments. Pre-OAE1a (C2) $\delta^{53}Cr$ values at both sites fall within the crustal range (igneous silicate Earth (ISE) = –0.121 ± 0.10; Schoenberg et al., 2008). However, at the onset of OAE1a (C3), $\delta^{53}Cr$ values diverge at the two sites. At Cismon, $\delta^{53}Cr$ values rise to isotopically heavier values, whereas at DSDP Site 463, $\delta^{53}Cr$ values drop to light values (–0.84‰) (Fig. 2). Cismon sediments have $\delta^{53}Cr_{HCl}$ (range = +0.29‰ to +1.34‰, mean = +0.86‰) and $\delta^{53}Cr_{Bulk}$ (range = –0.2‰ to +0.34‰, mean = +0.13‰) values that are mostly heavy relative to the ISE for the rest of OAE1a (C3–C6) and return to ISE compositions following the event (C6, Fig. 2). In contrast, sediments deposited at DSDP Site 463 during OAE1a have $\delta^{53}Cr_{HCl}$ (range = –0.23‰ to

Publisher: GSA
Journal: GEOL: Geology
DOI:10.1130/G49065.1

+0.11‰, mean = –0.07‰) and $\delta^{53}Cr_{Bulk}$ (range = –0.18‰ to +0.47‰, mean = +0.02‰) that mostly fall in the ISE range (Fig. 2).

REE concentrations in OAE1a sediments are dynamic and coherent. REE signals in OAE1a sediments are primary and free of appreciable siliciclastic contamination (Figs. DR2–DR4). At both sites, pre-OAE1a (C2) Ce/Ce* values are typical of sediments deposited ~~by~~ oxygenated seawater at ~0.4 (Nozaki, 2001) (Fig. 2). ~~However, d~~during C2, ~100 k.y. before OAE1a, Eu/Eu_{HCl}* values at DSDP Site 463 show a positive ~~spike~~ (+1.37) that is coeval with strong Mn-enrichment (phase I, Fig. 2). Within the first ~30 k.y. of OAE1a (C3), both the Cismon and DSDP sites record a shift in Ce/Ce* to more positive values, which reach >0.80 (Fig. 2). At the onset of C3, Eu/Eu_{HCl}* values at DSDP Site 463 display a second large positive excursion (+1.44) that is also mirrored by Mn-enrichment and a large negative $\delta^{53}Cr$ excursion (phase II, Fig. 2). During OAE1a (C3–C6), both sites have Ce/Ce* values consistently above 0.4 ($Cismon_{mean}$ = 0.63, DSDP Site 463_{mean} = 0.82) and return to pre-excursion values following C6 (Fig. 2). During C4, DSDP Site 463 sediments record a third positive Eu/Eu* anomaly in both bulk and 0.5 N HCl extractable pools (phase III, Fig. 2). This excursion is less apparent in the other proxies but evident in Hg-concentrations at DSDP Site 463 (Fig. 1).

DISCUSSION

Ontong Java Plateau Volcanism

Manganese abundances and Eu/Eu* patterns in Aptian sediments resolve several distinct and previously unrecognized volcanic phases associated with the emplacement of the OJP in the Pacific Ocean (Fig. 2). Elevated Mn_{EF} and Eu/Eu* in sediments deposited at DSDP Site 463 occur in three distinct intervals: ~100 k.y. before OAE1a (phase I, C2), at its onset (phase II, C3), and during OAE1a (phase III, C3–C4). These intervals of elevated Mn_{EF} and Eu/Eu* likely

reflect sediment deposition from seawater mixed with hydrothermal fluids and signal multiple discrete pulses of volcanism in the Pacific Ocean. These volcanic phases are likely resolved at DSDP Site 463 owing to its proximity to the OJP (Erba et al., 2015), whereas the distal Cismon sediments display little evidence for such volcanism, which implies that the Tethys Ocean was mostly isolated from direct hydrothermal influence at this time. This is supported by Hg-concentration trends (Fig. 1), which reveal appreciable Hg-cycle perturbations only in Pacific Ocean sediments proximal to the OJP source (Percival et al., 2021).

OJP emplacement gave rise to both short- and long-term changes in seawater chemistry that developed earlier than previously thought and persisted across hundreds of thousands of years. ~~The short oceanic residence time of Mn and Eu of ~<1 k.y. led to responses on similar timescales and thus resolves marine hydrothermalism in proximal sediments.~~ This phenomenon is observed through abrupt (~10 k.y.) coeval excursions in Mn_{EF} and Eu/Eu_{HCl}* at DSDP Site 463 during volcanic phases I, II, and III. In contrast, the much more gradual decline in $^{187/188}Os$ over ~75 k.y. from ca. 120.73 Ma to ca. 120.65 Ma (C4) is globally synchronous, postdates volcanic phases I and II, and likely results from protracted submarine alteration of large volumes of fresh OJP basalt (Fig. 2). This basaltic material was likely emplaced episodically in the preceding 200 k.y. during volcanic phases I and II (Fig. 2). Non-radiogenic Os-isotope compositions are maintained throughout OAE1a at both sites, which implies a sustained shift in the mass balance of Os fluxes to the oceans and continued basalt alteration as a long-term source of ^{188}Os. Local records in the Pacific Ocean therefore reveal a more complex and episodic volcanic history than that resolved by the global Os- and Sr-isotope responses that are thought to signal sustained volcanic input to the oceans over >100 k.y.

Timing Oceanic Deoxygenation

Publisher: GSA
Journal: GEOL: Geology
DOI:10.1130/G49065.1

Volcanic fluids associated with phases I and II were injected into oxygenated seawater in the Pacific Ocean. The most pronounced Mn_{EF} at DSDP site 463 coincides with the largest positive Eu/Eu* anomalies and a large negative excursion in $\delta^{53}Cr$ to –0.84‰ (phase II, Fig. 2). In the modern oxygenated oceans, sediments deposited in close proximity to active hydrothermal vents show similarly negative $\delta^{53}Cr$ values (–1.20‰) that are imparted through both partial reduction of seawater Cr(VI) by hydrothermal Fe(II) and diagenetic Cr(III) oxidation by sedimentary Mn-oxides (Bauer et al., 2019). Collectively, Cr-isotope compositions and Eu/Eu* anomalies in DSDP Site 463 sediments all signal hydrothermal fluid mixing with oxygenated seawater. Volcanic phases I and II thus occurred when the Pacific Ocean was well oxygenated at least at the location of DSDP Site 463 sediment deposition.

Oceanic anoxia likely expanded to global scales in the aftermath of volcanic phase II, which occurred <30 k.y. after the start of the OAE1a at both sites (Fig. 2). Fe speciation at both sites displays a transition to Fe_{HR}/Fe_{Tot} values >0.38, which occurred in <30 k.y. between ca. 120.76 Ma and 120.73 Ma (Fig. 2) and reveals rapid oceanic deoxygenation during C3. Synchronous shifts in Mn_{EF} and Ce/Ce* in sediments from both sites also imply changes that are best explained through rapid basin-scale deoxygenation. For instance, the strongly elevated Ce/Ce* values at both sites imply large-scale reductive dissolution of sediment Mn minerals (German and Elderfield, 1990; German et al., 1991) and signal likely expansion of oceanic anoxia into the deeper oceans where Mn nodules tend to accumulate. The Fe_{HR}/Fe_{Tot} and Ce/Ce* values that first record anoxic conditions, moreover, are immediately preceded by declining Mn_{EF} to values of <1 at both sites (C3, Fig. 2), which likely reflects local Mn loss from sediments due to reductive Mn-oxide dissolution under anoxic conditions. This process is often observed in modern anoxic marine sediments (Brumsack, 1989). Similar Ce/Ce* excursions to

values >0.8 in other Tethyan sediments further support widespread anoxia during OAE1a (Bodin et al., 2013).

The Cr-isotope compositions at both sites, though different, could reasonably be interpreted as reflecting anoxia in both the Tethys and Pacific Oceans during OAE1a (C3–C6). For example, the heavy $\delta^{53}Cr$ excursions ($\delta^{53}Cr_{Bulk}$ +0.34‰, $\delta^{53}Cr_{HCl}$ +1.34‰) at the Cismon site document partial to near-complete reduction of seawater Cr(VI) under anoxic conditions, which preserves the heavy $\delta^{53}Cr$ of seawater Cr(VI) (Reinhard et al., 2014). In contrast, at DSDP Site 463, the $\delta^{53}Cr$ values fall mostly within the ISE range during OAE1a and instead reflect sustained hydrothermal input into the Pacific Ocean. Hydrothermal release of mantle Cr ($\delta^{53}Cr$ = ISE) into anoxic waters would not have supported Cr redox reactions or appreciable Cr-isotope fractionation. Notably, $\delta^{53}Cr$ records in sediments deposited during OAE2 (ca. 92 Ma) display excursions to isotopically lighter values (Holmden et al., 2016; Wang et al., 2016). This signal similarly has been ~~interpreted to reflect~~ an increased flux of hydrothermal Cr large enough to mask an excursion to isotopically heavier values expected under expanded oceanic anoxia. Patterns in $\delta^{53}Cr$ records across different OAEs thus appear to have some common drivers.

CONCLUSIONS AND IMPLICATIONS

Our data resolve the relative timing of volcanism and oceanic deoxygenation during OAE1a and provide new insight into the relationships between these characteristic features of the event. For example, a global decline in calcareous nannoplankton in the fossil record (Erba et al., 2010) occurs at the onset of volcanic phase II and predates oceanic deoxygenation by ~100 k.y. (Fig. 2), which makes anoxia an unlikely driver of the nannoconid crisis. Instead, this timing implies that acidification of the ocean (Wang et al., 2020) resulting from the early phases of OJP volcanism may have played a more important role. We also now pinpoint oceanic deoxygenation

to a <30 k.y. interval at the onset of C3 well before intensified weathering is reflected in oceanic chemistry some 150–300 k.y. later (Lechler et al., 2015). Oceanic deoxygenation has often been attributed to eutrophication that arises from enhanced weathering-driven nutrient fluxes to the oceans. Our new timing, however, now suggests that initial deoxygenation was an even more immediate response to volcanic phases I and II. Such responses could include changes to oceanic circulation and declining oxygen solubility in seawater as the result of warming of the ocean or eutrophication driven directly by the hydrothermal supply of bio-limiting metals (Bottini et al., 2015). Higher-resolution analyses of the rock record and Earth system modeling could help test these hypotheses over the relevant timescales.

REFERENCES CITED

Bauer, K.W., Cole, D.B., Asael, D., Francois, R., Calvert, S.E., Poulton, S.W., Planavsky, N.J., and Crowe, S.A., 2019, Chromium isotopes in marine hydrothermal sediments: Chemical Geology, v. 529, no. 119286, https://doi.org/10.1016/j.chemgeo.2019.119286.

Bauer, K.W., Planavsky, N.J., Reinhard, C.T., and Cole, D.B., 2021, The Chromium Isotope System as a Tracer of Ocean and Atmosphere Redox: Cambridge, UK, Cambridge University Press, **[[Pages?]]** https://doi.org/10.1017/9781108870443.

Blattler, C.L., Jenkyns, H.C., Reynard, L.M., and Henderson, G.M., 2011, Significant increases in global weathering during Oceanic Anoxic Events 1a and 2 indicated by calcium isotopes: Earth and Planetary Science Letters, v. 309, no. 1–2, p. 77–88, https://doi.org/10.1016/j.epsl.2011.06.029.

Bodin, S., Godet, A., Westermann, S., and Follmi, K.B., 2013, Secular change in northwestern Tethyan water-mass oxygenation during the late Hauterivian-early Aptian: Earth and Planetary Science Letters, v. 374, p. 121–131, https://doi.org/10.1016/j.epsl.2013.05.030.

Bottini, C., Cohen, A.S., Erba, E., Jenkyns, H.C., and Coe, A.L., 2012, Osmium-isotope evidence for volcanism, weathering, and ocean mixing during the early Aptian OAE 1a: Geology, v. 40, no. 7, p. 583–586, https://doi.org/10.1130/G33140.1.

Bottini, C., Erba, E., Tiraboschi, D., Jenkyns, H., Schouten, S., and Sinninghe Damsté, J., 2015, Climate variability and ocean fertility during the Aptian Stage: Climate of the Past, v. 11, no. 3, p. 383–402, https://doi.org/10.5194/cp-11-383-2015.

Brumsack, H.J., 1989, Geochemistry of recent TOC-rich sediments from the Gulf of California and the Black Sea: Geologische Rundschau, v. 78, p. 851–882, https://doi.org/10.1007/BF01829327.

Erba, E., 2004, Calcareous nannofossils and Mesozoic oceanic anoxic events: Marine Micropaleontology, v. 52, no. 1–4, p. 85–106, https://doi.org/10.1016/j.marmicro.2004.04.007.

Erba, E., and Larson, R.L., 1998, The Cismon APTICORE (Southern Alps, Italy): A “reference section” for the Lower Cretaceous at low latitudes: Rivista Italiana di Paleontologia e Stratigrafia, v. 104, no. 2, p. 181–191.

Erba, E., Bottini, C., Weissert, H.J., and Keller, C.E., 2010, Calcareous nannoplankton response to surface-water acidification around Oceanic Anoxic Event 1a: Science, v. 329, no. 5990, p. 428–432, https://doi.org/10.1126/science.1188886.

Erba, E., Duncan, R.A., Bottini, C., Tiraboschi, D., Weissert, H., Jenkyns, H.C., and Malinverno, A., 2015, Environmental consequences of Ontong Java Plateau and Kerguelen Plateau volcanism, *in* Neal, C.R., Sager, W.W., Sano. T., and Erba, E., The Origin, Evolution, and Environmental Impact of Oceanic Large Igneous Provinces: Geological Society of America Special Paper 511, p. 271–303, https://doi.org/10.1130/2015.2511(15).

Frei, R., Gaucher, C., Poulton, S.W., and Canfield, D.E., 2009, Fluctuations in Precambrian atmospheric oxygenation recorded by chromium isotopes: Nature, v. 461, p. 250–253, https://doi.org/10.1038/nature08266.

German, C.R., and Elderfield, H., 1990, Application of the Ce anomaly as a paleoredox indicator: The ground rules: Paleoceanography, v. 5, no. 5, p. 823–833, https://doi.org/10.1029/PA005i005p00823.

German, C.R., Holliday, B.P., and Elderfield, H., 1991, Redox cycling of rare earth elements in the suboxic zone of the Black Sea: Geochimica et Cosmochimica Acta, v. 55, no. 12, p. 3553–3558, https://doi.org/10.1016/0016-7037(91)90055-A.

Holmden, C., Jacobson, A.D., Sageman, B.B., and Hurtgen, M.T., 2016, Response of the Cr isotope proxy to Cretaceous Ocean Anoxic Event 2 in a pelagic carbonate succession from the Western Interior Seaway: Geochimica et Cosmochimica Acta, v. 186, p. 277–295, https://doi.org/10.1016/j.gca.2016.04.039.

Jenkyns, H.C., 2010, Geochemistry of oceanic anoxic events: Geochemistry, Geophysics, Geosystems, v. 11, no. 3, https://doi.org/10.1029/2009GC002788.

Larson, R.L., 1991, Latest pulse of Earth: Evidence for a mid-Cretaceous superplume: Geology, v. 19, no. 6, p. 547–550, https://doi.org/10.1130/0091-7613(1991)019<0547:LPOEEF>2.3.CO;2.

Lechler, M., von Strandmann, P., Jenkyns, H.C., Prosser, G., and Parente, M., 2015, Lithium-isotope evidence for enhanced silicate weathering during OAE 1a (Early Aptian Selli event): Earth and Planetary Science Letters, v. 432, p. 210–222, https://doi.org/10.1016/j.epsl.2015.09.052.

Malinverno, A., Erba, E., and Herbert, T.D., 2010, Orbital tuning as an inverse problem: Chronology of the early Aptian oceanic anoxic event 1a (Selli Level) in the Cismon APTICORE: Paleoceanography and Paleoclimatology, v. 25, no. 2, https://doi.org/10.1029/2009PA001769.

McLennan, S.M., 2001, Relationships between the trace element composition of sedimentary rocks and upper continental crust: Geochemistry, Geophysics, Geosystems, v. 2, no. 4, https://doi.org/10.1029/2000GC000109.

Mehay, S., Keller, C.E., Bernasconi, S.M., Weissert, H., Erba, E., Bottini, C., and Hochuli, P.A., 2009, A volcanic CO_2 pulse triggered the Cretaceous Oceanic Anoxic Event 1a and a biocalcification crisis: Geology, v. 37, no. 9, p. 819–822, https://doi.org/10.1130/G30100A.1.

Menegatti, A.P., Weissert, H., Brown, R.S., Tyson, R.V., Farrimond, P., Strasser, A., and Caron, M., 1998, High-resolution δ^{13} stratigraphy through the early Aptian "Livello Selli" of the Alpine Tethys: Paleoceanography, v. 13, no. 5, p. 530–545, https://doi.org/10.1029/98PA01793.

Mills, J.V., Gomes, M.L., Kristall, B., Sageman, B.B., Jacobson, A.D., and Hurtgen, M.T., 2017, Massive volcanism, evaporite deposition, and the chemical evolution of the Early Cretaceous ocean: Geology, v. 45, no. 5, p. 475–478, https://doi.org/10.1130/G38667.1.

Nozaki, Y., 2001, Rare earth elements and their isotopes, *in* Thorpe, S.A., and Turekian, K.K., eds., Encyclopedia of Ocean Sciences, 1st ed.: Cambridge, Massachusetts, USA, Academic Press, p. 2354–2366.

Olivarez, A.M., and Owen, R.M., 1991, The europium anomaly of seawater: Implications for fluvial versus hydrothermal REE inputs to the oceans: Chemical Geology, v. 92, no. 4, p. 317–328, https://doi.org/10.1016/0009-2541(91)90076-4.

Percival, L., Tedeschi, L., Creaser, R., Bottini, C., Erba, E., Giraud, F., Svensen, H., Savian, J., Trindade, R., and Coccioni, R., 2021, Determining the style and provenance of magmatic activity during the Early Aptian Oceanic Anoxic Event (OAE 1a): Global and Planetary Change, v. 200, no. 103461, https://doi.org/10.1016/j.gloplacha.2021.103461.

Raiswell, R., Hardisty, D.S., Lyons, T.W., Canfield, D.E., Owens, J.D., Planavsky, N.J., Poulton, S.W., and Reinhard, C.T., 2018, The iron paleoredox proxies: A guide to the pitfalls, problems and proper practice: American Journal of Science, v. 318, no. 5, p. 491–526, https://doi.org/10.2475/05.2018.03.

Reinhard, C.T., Planavsky, N.J., Wang, X., Fischer, W.W., Johnson, T.M., and Lyons, T.W., 2014, The isotopic composition of authigenic chromium in anoxic marine sediments: A case study from the Cariaco Basin: Earth and Planetary Science Letters, v. 407, p. 9–18, https://doi.org/10.1016/j.epsl.2014.09.024.

Schoenberg, R., Zink, S., Staubwasser, M., and von Blanckenburg, F., 2008, The stable Cr isotope inventory of solid Earth reservoirs determined by double spike MC-ICP-MS: Chemical Geology, v. 249, no. 3–4, p. 294–306, https://doi.org/10.1016/j.chemgeo.2008.01.009.

Tejada, M.L.G., Suzuki, K., Kuroda, J., Coccioni, R., Mahoney, J.J., Ohkouchi, N., Sakamoto, T., and Tatsumi, Y., 2009, Ontong Java Plateau eruption as a trigger for the early Aptian oceanic anoxic event: Geology, v. 37, no. 9, p. 855–858, https://doi.org/10.1130/G25763A.1.

Timm, C., Hoernle, K., Werner, R., Hauff, F., van den Bogaard, P., Michael, P., Coffin, M.F., and Koppers, A., 2011, Age and geochemistry of the oceanic Manihiki Plateau, SW Pacific: New evidence for a plume origin: Earth and Planetary Science Letters, v. 304, no. 1–2, p. 135–146, https://doi.org/10.1016/j.epsl.2011.01.025.

Wang, J., Jacobson, A.D., Sageman, B.B., and Hurtgen, M.T., 2020, Stable Ca and Sr isotopes support volcanically triggered biocalcification crisis during Oceanic Anoxic Event 1a: Geology **[[Volume and page numbers?]].**

Wang, X.L., Reinhard, C.T., Planavsky, N.J., Owens, J.D., Lyons, T.W., and Johnson, T.M., 2016, Sedimentary chromium isotopic compositions across the Cretaceous OAE2 at Demerara Rise Site 1258: Chemical Geology, v. 429, p. 85–92, https://doi.org/10.1016/j.chemgeo.2016.03.006.

Westermann, S., Stein, M., Matera, V., Fiet, N., Fleitmann, D., Adatte, T., and Foellmi, K.B., 2013, Rapid changes in the redox conditions of the western Tethys Ocean during the early Aptian oceanic anoxic event: Geochimica et Cosmochimica Acta, v. 121, p. 467–486, https://doi.org/10.1016/j.gca.2013.07.023.

Figure 1. Anatomy of Oceanic Anoxic Event (OAE) 1a is shown for the (A) Tethys Ocean and (B) Pacific Ocean. C-isotopes, carbonate C (gray lines), organic matter C (black lines), and stratigraphy are after Bottini et al. (2012) and Menegatti et al. (1998); Fe_{HR}/Fe_{Tot} (this study); $^{187/188}Os$ are after Bottini et al. (2012) and Tejada et al. (2009); nannoconid abundances are after Erba (2004); Hg concentrations are after Percival et al. (2021).

Figure 2. Oceanic Anoxic Event (OAE) 1a geochemistry is shown. Chronostratigraphy is after Malinverno et al. (2010). $^{40}Ar/^{39}Ar$ age distribution of Ontong Java Plateau lavas is after Timm et al. (2011). **(**A**)** C-isotopes are after Bottini et al. (2012) and Menegatti et al. (1998). (B)

Publisher: GSA
Journal: GEOL: Geology
DOI:10.1130/G49065.1

$^{187/188}$Os are after Bottini et al. (2012). (C) Mn_{EF}; pink shading is the PAAS Mn_{EF}. (D) Fe_{HR}/Fe_{Tot}; pink shading is <0.38. (E) δ^{53}Cr; pink shading indicates ISE range. (F) Ce/Ce*; pink shading shows modern composition of the upper ocean (<0.4). (G) Eu/Eu*; pink shading denotes modern composition of the upper ocean (<1.2). Note x-axis break between panels. DSDP—Deep Sea Drilling Project. **[[In the figure, Myrs should by m.y. Kyrs should be k.y.]]**

TABLE 1. GEOCHEMICAL PROXY DESCRIPTIONS

Proxy	Utility	Proxy Threshold	Threshold Calibration Reservoir	<Threshold	>Threshold	References
				Interpretation		
Manganese enrichment factor (Mn/Al)	paleoredox proxy, hydrothermal proxy	0–1	Modern oxygenated sediments	possibly anoxic sediments	hydrothermal Mn supply	(Böning, 2005; Brumsack, 1989)
Os-isotopes ($^{187/188}$Os)	weathering proxy	0.6	Modern oxygenated seawater	weathering of mafic lithology (^{188}Os-enriched)	weathering of felsic lithology (^{187}Os-enriched)	(Bottini et al., 2012)
Fe speciation (Fe_{HR}/Fe_{Tot})	paleoredox proxy	0–0.38	Modern oxygenated sediments	possibly oxic sediments	anoxic sediments	(Raiswell et al., 2018)
Cr-isotopes (δ^{53}Cr)	paleoredox proxy, hydrothermal proxy	–0.21–0.00 (‰)	Modern oxygenated sediments	possibly hydrothermal activity, possibly oxic sediments, possibly anoxic sediments	anoxic sediments	(Bauer et al., 2019, 2021)
Ce anomalies (Ce/Ce*)	paleoredox proxy	0–0.4	Modern oxygenated seawater	oxic sediments	anoxic sediments	(Bodin et al., 2013; Nozaki, 2001; Tostevin et al., 2016)
Eu anomalies (Eu/Eu*)	hydrothermal proxy	1.0–1.2	Modern oxygenated seawater	oxic sediments	hydrothermal Eu supply	(Olivarez and Owen, 1991)

[[Böning, 2005, and Tostevin et al., 2016 are not in the ref list. Please add the citations to the ref list or delete them from the table.]]