Temporal and spatial dynamics of paleo-redox conditions across the Triassic-Jurassic boundary

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Abstract

The end-Triassic mass extinction was among the most severe biotic crises of the Phanerozoic. It has been linked with the global expansion of marine anoxia, and the prolongation of these conditions within epeiric seas has been proposed as a cause for the suppression of biodiversity during the Hettangian. Testing this interpretation is complicated by spatially heterogenous patterns of local marine redox conditions within the western Tethys European Epicontinental Shelf. In this study we assess the redox state within this region by focusing on two carbonate successions in Italy. Based on I/Ca ratios, these locations record distinct local background redox conditions, with Val Adrara showing notably lower pre-extinction oxygen saturation state compared to Mount Sparagio. To better explain these differences, $\delta 44Ca$ and trace element analyses were used to identify the roles of mineralogical and diagenetic effects on the preservation of primary redox signals. A framework of multiple elemental (Sr, Mg, Mn, I) and isotopic ($\delta 13C$, $\delta 18O$, $\delta 44Ca$, $\delta 238U$ and $\delta 34SCAS$) ratios was developed to identify factors that could influence carbonate geochemistry. Both sites probably retain some primary variation in $\delta 238U$, $\delta 34SCAS$ and I/Ca, but they are likely also shaped by changing mineralogy and early diagenetic conditions which complicates interpretations of the seawater composition. Where the redox signals are largely preserved, we interpret differences in pre-extinction I/Ca between the two sites to reflect distinct local oxygenation states. Model simulations show that ocean circulation and hydrological regime could have been important drivers of spatial heterogeneity in paleo-redox conditions across the European Epicontinental Shelf.

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1	Temporal a	and	spatial	dynamics	of	paleo-redox	conditions	across	the	Triassic-Jurassic
2	boundary									

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14 Key Points

15	•	Calcium isotope ratios were measured for two carbonate successions in Italy spanning the
16		Triassic-Jurassic boundary interval
17	•	Paired proxy data indicate the sites underwent different modes of diagenetic alteration but
18		retain some primary redox signals
19	•	Ocean circulation strength and depth of vertical mixing may explain the difference in
20		local redox conditions

21 Abstract

22 The end-Triassic mass extinction was among the most severe biotic crises of the 23 Phanerozoic. It has been linked with the global expansion of marine anoxia, and the prolongation 24 of these conditions within epeiric seas has been proposed as a cause for the suppression of 25 biodiversity during the Hettangian. Testing this interpretation is complicated by spatially 26 heterogenous patterns of local marine redox conditions within the western Tethys European 27 Epicontinental Shelf. In this study we assess the redox state within this region by focusing on two 28 carbonate successions in Italy. Based on I/Ca ratios, these locations record distinct local 29 background redox conditions, with Val Adrara showing notably lower pre-extinction oxygen saturation state compared to Mount Sparagio. To better explain these differences, δ^{44} Ca and trace 30 31 element analyses were used to identify the roles of mineralogical and diagenetic effects on the 32 preservation of primary redox signals. A framework of multiple elemental (Sr, Mg, Mn, I) and isotopic (δ^{13} C, δ^{18} O, δ^{44} Ca, δ^{238} U and δ^{34} S_{CAS}) ratios was developed to identify factors that could 33 influence carbonate geochemistry. Both sites probably retain some primary variation in δ^{238} U, 34 35 δ^{34} S_{CAS} and I/Ca, but they are likely also shaped by changing mineralogy and early diagenetic 36 conditions which complicates interpretations of the seawater composition. Where the redox signals 37 are largely preserved, we interpret differences in pre-extinction I/Ca between the two sites to 38 reflect distinct local oxygenation states. Model simulations show that ocean circulation and 39 hydrological regime could have been important drivers of spatial heterogeneity in paleo-redox 40 conditions across the European Epicontinental Shelf.

41

43 Plain Language Summary

44 The end-Triassic mass extinction, 200 million years ago, may have been caused by rapid injection 45 of large quantities of carbon from volcanoes analogous to modern-day fossil fuel consumption. 46 The main killing mechanism may have been anoxia, or low dissolved oxygen content, in the 47 shallow ocean. Understanding the distribution of dissolved oxygen in the shallow ocean where 48 many organisms live is imperative for predicting future ecosystem sustainability. Carbonate 49 sediments record the chemical composition of seawater upon deposition, preserving information 50 about ancient ocean conditions Several carbonate-based geochemical proxies can be used to infer 51 the oxygen saturation state in the ocean, but their values can be altered by post-depositional 52 processes. During the Triassic, Europe was inundated with a shallow sea where carbonate 53 limestone deposition occurred, but the local seawater composition differs between two sites in 54 Italy. We use the carbonate calcium isotope ratios, which are sensitive to post-depositional 55 alteration, to investigate the effect of alteration on the proxy signals. While alteration influences 56 the absolute values of the seawater composition preserved at the two sites, the overall trends in 57 oxygen saturation are distinct and mostly unaltered. Earth system modeling suggests that the 58 difference between sites may be due to ocean circulation and hydrological patterns.

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65 **1. Introduction**

The end-Triassic mass extinction (~200 Ma) was among the most important biotic crises of the 66 67 Phanerozoic, resulting in the loss of nearly 20% of marine animal families (Bambach, 2006; 68 Kiessling et al., 2007). Losses were severe amongst many groups, especially scleractinian corals, 69 which lost up to 96% of their genera (Hautmann, 2006). The disappearance of characteristic 70 Triassic fauna closely coincides with an abrupt negative carbon-isotope ($\delta^{13}C_{org}$) excursion in 71 organic matter of up to -5 ‰ (Hesselbo et al., 2002; van de Schootbrugge et al., 2008; Bachan et al., 2016; Wignall and Atkinson 2020). The negative $\delta^{13}C_{org}$ excursion is contemporaneous with 72 73 the emplacement of the Central Atlantic Magmatic Province (CAMP) (Schoene et al., 2010; 74 Blackburn et al., 2013) suggesting a scenario of rapid injection (< 20 ka) of highly depleted carbon 75 (up to -70 ‰) followed by the enhanced burial of organic carbon leading to a prolonged positive 76 excursion (Hesselbo et al, 2002; Bachan et al., 2016). Recovery of marine communities was 77 spatially variable, being notably rapid in nearshore communities in NW Europe (Atkinson and 78 Wignall 2019) but skeletal abundance remains suppressed until the Sinemurian in Tethyan 79 carbonates (Singh et al., 2023).

Enrichment of redox-sensitive elements and the restructuring of microbial communities support widespread marine anoxia as a kill mechanism (van de Schootbrugge et al., 2008; Wignall and Atkinson 2020; He et al., 2020a; Beith et al., 2021; Onoue et al., 2022). Understanding the extent and degree of deoxygenation in the shallow ocean (<100 m), where most organisms live, is essential to assessing the ecological impacts of the event. Carbonate-based water-column redox proxies show heterogeneous spatial patterns of deoxygenation within the European Epicontinental Shelf (EES) along the western margin of the Tethys Ocean (Fig. 1) (e.g., Luo et al., 2018; He et al., 2022a; Singh et al., 2023), raising questions about whether some have been diagenetically
altered or if they record original spatial variation.

89 In this study, we focus on two locations: Mount Sparagio in Sicily and Val Adrara in the 90 Lombardy Basin of the southern Italian Alps (Fig. 1). The peritidal carbonate succession at Mount 91 Sparagio, in the southeastern region of the EES, records an abrupt positive shift in carbonateassociate sulfur isotope ($\delta^{34}S_{CAS}$) ratios coincident with the extinction interval, indicating a rapid 92 93 and intense onset of global anoxia commencing near the Triassic-Jurassic boundary (Fig. 2; He et 94 al. 2020). This signature correlates with a negative excursion in carbonate-phase δ^{238} U, another 95 indicator of global anoxia, recorded in the shallow carbonate ramp deposits at the Val Adrara (Fig. 96 3; Jost et al., 2017).

97 Carbonate-hosted, redox-sensitive elemental and isotopic ratios can track seawater composition (Kampschulte and Strauss, 1996; Zhang et al., 2020). The variations in seawater δ^{34} S 98 and δ^{238} U compositions are controlled by the burial fluxes under reducing conditions and the size 99 100 of the seawater reservoir (Bottrell and Newton, 2006; Chen et al., 2021). Microbial sulfate 101 reduction occurring under anoxic conditions imparts a large negative fractionation in the available sulfate by preferential incorporation of the lighter ³²S isotope into sulfide minerals, thus leaving 102 the seawater sulfate pool enriched in ³⁴S (Kampschulte and Strauss, 2004; Sim. et al., 2011). The 103 reduced form of uranium (U^{4+}) is less soluble than the oxidized form (U^{6+}) . The preferential 104 removal of ²³⁸U in anoxic settings leads to its depletion in the seawater pool (Zhang et al., 2020). 105 Consequently, the isotopic signatures of both δ^{238} U and δ^{34} S_{CAS} recorded in carbonate respectively 106 107 decrease and increase in response to expanding seafloor anoxia. The magnitudes of their isotopic 108 offsets from seawater values are often considered to reflect the global extent of anoxia (Fike et al., 109 2015; Zhang et al., 2020; Chen et al., 2021). Iodate (IO_3^{-}), the oxidized form of iodine, can be

incorporated into the calcite lattice whereas the reduced form iodide (I⁻) is excluded (Lu et al.,
2020). Iodate is rapidly reduced under low-oxygen conditions, so that low I/Ca likely reflects
carbonate accumulation beneath dysoxic-anoxic water masses (Lu et al., 2020).

113 While both Val Adrara and Mount Sparagio record signals of enhanced global extent of anoxic 114 settings during the positive δ^{13} C excursion, the local seawater conditions, as indicated by I/Ca (or 115 I/(Ca+Mg)), are distinct (He et al., 2022a; Singh et al., 2023). Background I/Ca values prior to the 116 positive excursion at Mount Sparagio are elevated relative to Val Adrara (Figs. 2 and 3). During 117 the excursion, I/Ca values decrease to near zero at Val Adrara. At Mount Sparagio, the highly 118 variable background I/Ca values only reduce to between 1-2 µmol/mol, higher still than the pre-119 excursion values at Val Adrara. We explore whether the discrepancy in local expressions of the 120 I/Ca signal along the northern and southern EES margins reflects diagenetic overprinting, 121 differences in original mineralogy, or contrasting primary redox conditions.

Calcium isotope ratios (${}^{44}Ca/{}^{40}Ca$, commonly reported as $\delta^{44}Ca$) are a versatile tool for 122 123 constraining post-depositional processes, such as dolomitization or recrystallization (Fantle et al., 124 2020), and for fingerprinting the effects of different primary carbonate minerals (Higgins et al., 125 2018). At low-temperature conditions, kinetic isotope effects are believed to dominate, with 126 important rate-dependent fractionation of Ca isotopes into different calcium-bearing mineral 127 phases (Tang et al., 2008). Under slow precipitation rates, such as may occur during authigenic or 128 diagenetic carbonate precipitation, no appreciable fractionation may be observed (Fantle and 129 DePaolo, 2007; Jacobson and Holmden, 2008). Thus, δ^{44} Ca can be used to track the diagenetic 130 history of carbonates. In addition, calcite and aragonite exhibit different fractionations (Gussone et al., 2003), which makes δ^{44} Ca a potentially useful indicator of primary carbonate mineralogy. 131 Here, δ^{44} Ca measurements are employed to examine the role of local mineralogical and diagenetic 132

effects on the preservation state of carbonate-based redox proxies (δ^{238} U, δ^{34} S_{CAS}, I/Ca). We first investigate the presence of co-variability of δ^{44} Ca with other elemental components (Sr/Ca, Mg/Ca, Mn/Sr) considered diagnostic of different diagenetic and source-mixing regimes. These analyses allow us to test the robustness of the redox gradient in the EES. Then, we discuss potential drivers of the spatial redox pattern in the EES based on simulations conducted with the Community Earth System model.

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141 Figure 1: Paleo-geographical context of EES during the Late Triassic Rhaetian stage (~205 Ma). 142 (A) Paleogeographic reconstruction of Pangaea, highlighting the location of the EES (box) and approximate location of modern-day Italy. (B) Site locations on map of modern Italy modified 143 144 from Bachan et al. (2012). (C) Map of the northwestern Tethys epeiric sea. Arrows indicate 145 proposed circulation pathways accounting for speculative bathymetry and emerged landmasses, and arrow color distinguishes between cool water (blue) and warm water (red). The thickness of 146 147 the arrow indicates the current strength. Dotted lines are proposed flow paths modified from Ruvalcaba Baroni et al. (2018) with considerations based on CESM 1.2.2 simulations for the 148 149 Triassic-Jurassic and Rhaetian configurations (Scotese, 2014). Modern-day geographic 150 coordinates were rotated to paleo-coordinates using the R package Chronosphere and the Scotese PALEOMAP reconstruction (Kocsis and Raja, 2023; Scotese and Wright, 2018). IB: Iberian 151

Mountains, AM: Amorican, BM: Bohemian Massif, CSH: Corsican-Sardinian High. 1: Mount
Sparagio, Italy (Todaro et al., 2018), 2. Val Adrara, Italy (van de Schootbrugge et al., 2008), 3.
Kuhjoch, Austria (Li et al., 2022b), 4. Rosswinkel, Luxembourg (Richoz et al., 2012), 5.
Mingolshiem, Germany (Luo et al., 2018), 6. Mariental, Germany (Richoz et al., 2012). 7. Filikirk,
United Kingdom (Beith et al., 2021), 8. St. Audrie's, United Kingdom (Li et al., 2022b), 9.
Doniford Bay, UK (Paris et al., 2010). See Table S3, supplementary materials for literature
summary of redox conditions at these sites.

159

160 **2. Methods**

161 2.1. Study Site and Geological Setting

162 Approximately centered at 30°N paleolatitude, the EES was a warm, semi-restricted 163 collection of silled basins and carbonate platforms during the early Mesozoic. Fragmentation of 164 Pangaea permitted limited water exchange between the Boreal, Tethys, and the Panthalassa Ocean 165 to the west (Fig. 1), although the precise timing of connection and amount of exchange in the Late 166 Triassic are poorly constrained (Dore, 1991; Sha, 2002, Korte et al. 2015). Italy was mostly submerged in the southeastern region of the EES during the Triassic-Jurassic boundary interval, 167 168 but intermittent subaerial exposure is evident in both Sicilian and Tuscan sections (Fig. 1) 169 (Santantonio and Carminati, 2011; Bernardi et al., 2018).

170 2.1.2. Stratigraphy of Mount Sparagio

The Rhaetian to lower Hettangian succession at Mount Sparagio was deposited in a peritidal setting with intermittent subaerial exposure (Fig. 2) (Todaro et al., 2018). The studied section at Mount Sparagio is subdivided into three units: A, B, and C (Todaro et al., 2018). Units A (below the studied section) and B are assigned to Rhaetian age based on the occurrence of megalodontids and the benthic foraminiferan *Triasina hantkeni*. These lower units are characterized by the stacking of shallowing-upward cycles capped by red paleosols. Unit C lacks the large megalodontid bivalves (Todaro et al., 2018). There is an approximately 20 m-thick barren
interval capping unit B, concurrent with the onset of anoxia in the basin (He et al., 2022; He et al.,
2020). Unit C is dated to the early Hettangian due to the absence of *T. hantkeni* and the occurrence
of *Thaumatoporella parvovesiculifera* (Todaro et al., 2018). Unit C sediments were deposited in
slightly deeper waters than the lower units and lacks paleosols.



Figure 2: Chemo-stratigraphy and redox trends at Mount Sparagio (modern coordinates: 38°3'
 44.18" N, 12°43'9.19" E). The grey bar indicates the extinction interval. Solid lines trending with
 carbon and oxygen isotope ratios are loess smoothing regressions.

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187 2.1.3. Stratigraphy of Val Adrara

188 The Val Adrara site is in the Lombardy Basin of the Southern Italian Alps (Jadoul and 189 Galli, 2008; Bachan et al., 2012). Sedimentary sequences at Val Adrara record deposition on a 190 passive-margin carbonate ramp (Santantonio and Carminati, 2011) and are assigned Rhaetian

191 through Hettangian ages based on palynological associations and carbon-isotope stratigraphy (Fig. 192 3; van de Schootbrugge et al., 2008). The lowermost Rhaetian-age Zu Formation is a fossiliferous 193 packstone consisting of an unrestricted marine assemblage. It is abruptly overlain by the Malanotte 194 Formation, which is devoid of fossils and is interpreted as the extinction interval (Fig. 3; Jadoul 195 and Galli, 2008; Bachan et al., 2012). The lower Malanotte consists of thinly bedded micritic 196 limestone (marl), which grades into carbonate-rich mud and wackestones (Jadoul and Galli, 2008). 197 The negative excursion in $\delta^{13}C_{carb}$, with a magnitude of -5.0 ‰, coincides with the extinction 198 interval and occurs entirely within lower silty-marl portion of the Malanotte Formation (van de 199 Schootbrugge et al., 2008; Bachan et al., 2012). The silty marl layer of the lower Malanotte 200 Formation is most likely correlative with the marly layer at Sparagio (Todaro et al. 2022). 201 However, neither site has been absolutely dated, so the timing and duration of this interval is poorly 202 constrained (Bachan et al. 2012; Todaro et al. 2018). Therefore, in both stratigraphic columns this 203 interval is not assigned to either the Rhaetian or Hettangian and is broadly referred to as the 204 Triassic-Jurassic boundary interval (Fig. 2 and 3). The negative excursion is followed by a small 205 positive excursion terminating at the top of the Malanotte Formation. The overlying Albenza 206 Formation is composed of 100 m of cross-bedded onlitic and peloidal grainstones interbedded with 207 cm-scale layers of dolomicrite (Bachan et al., 2012). Another pulse of volcanism is inferred from 208 a second -4.0 ‰ negative carbon isotope excursion at the base of the Albenza Formation and the 209 protracted positive carbon-isotope excursion that follows terminates at the top of the Albenza 210 Formation (Bachan et al., 2012; Bachan and Payne, 2016). Evidence of expanded global anoxia 211 commences during this positive excursion and may have suppressed faunal recovery in this region 212 (Singh et al. 2023). The Albenza Formation is sparsely fossiliferous with skeletal grains only 213 become abundant again at the Albenza-Sedrina contact (Singh et al. 2023). The lower Sedrina 214 consists of packstone and grades into a thinly bedded cherty limestone with abundant sponge 215 spicules (van de Schootbrugge et al., 2008; Singh et al., 2023). The upper Sedrina is interpreted to 216 have been deposited below storm wave base following rapid subsidence due to the onset of 217 extensional activity in the Hettangian (Santantonio and Carminati, 2011).



Figure 3: Chemostratigraphic trends at Val Adrara (modern coordinates: $45^{\circ}43'29.33''N$ 9°57'32.29''E). Error bars for $\delta^{238}U$ and $\delta^{44}Ca$ are 2σ . See Fig. 2 for lithologic key.

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221 2.2. Sample Preparation and Analysis

Published geochemical data were compiled to compare redox trends at the sites (Figs. 2 and 3). These data include carbon- and oxygen-isotope profiles for the Val Adrara section (van de Schootbrugge et al., 2008), estimates of global anoxia from $\delta^{34}S_{CAS}$ at Mount Sparagio (He et al., 2020), and from $\delta^{238}U$ at Val Adrara (Jost et al., 2017), and I/Ca at Val Adrara and I/(Ca+Mg) from Mount Sparagio as indicators of local redox conditions (He et al., 2022a; Singh et al., 2023). 227 Calcium-isotope data on different powered samples from the upper Zu limestone and Malanotte 228 Formation were previously reported in Jost et al. (2016). These data bracket the negative carbon 229 isotope excursion, but only include the rising limb of the subsequent positive excursion (Fig. 3). 230 Here we report bulk carbonate δ^{44} Ca and trace elemental (Sr, Mn, Mg) concentrations data that 231 span the full stratigraphic range for both sites (Fig. S2 and S3, supplementary materials). We also 232 measure carbon- and oxygen-isotope compositions for new samples from Mount Sparagio (n = 233 52).

234 2.2.1. Carbon and oxygen isotope measurements

For samples from the Mount Sparagio section, about 10 mg of carbonate powder were drilled from the cleaned rock slab using a hand drill. Powder was reacted with 100% H₃PO₄ at 70 °C to extract CO₂ for ¹³C/¹²C and ¹⁸O/¹⁶O measurements. We used the Chinese national standard, an Ordovician carbonate from a site near Beijing (reference number GBW04405, $\delta^{13}C =$ 0.57 ± 0.03 ‰ VPDB; $\delta^{18}O = -8.49 \pm 0.13$ ‰ VPDB) to monitor the accuracy. These measurements were performed using a Finnigan MAT 253 mass spectrometer in the Nanjing Institute of Geology and Palaeontology.

242 2.2.2. Calcium isotope ratios and trace elemental analysis

Measurement of carbonate δ^{44} Ca values at the University of Chicago closely followed the method of Razionale et al. (2022). Briefly, carbonate samples were dissolved in buffered acetic acid at a ratio of ~1 mg/mL and Ca²⁺ was chromatographically isolated using a Dionex ICS-6000 with variable strength MSA eluent. Samples were matrix matched at 1 ppm Ca²⁺ in 2% nitric acid for sample-standard bracketing and each post-chromatography eluent was measured twice by Neptune XT as 90 integration cycles monitoring masses 42, 43, 43.5, and 44. Outlier cycles

exceeding $\pm 3\sigma$ for the ⁴⁴Ca/⁴²Ca, ⁴⁴Ca/⁴³Ca, or ⁴³Ca/⁴²Ca intensity ratios were removed, as were 249 entire sets of cycles when the ⁴⁴Ca/⁴²Ca ratio of successive bracketing standards changed 250 251 by >0.2‰. Following a correction for strontium interference and a run-specific concentration effect, values of $\delta^{44/42}$ Ca were corrected to NIST 915b and scaled to $\delta^{44/40}$ Ca ratios using a kinetic 252 253 mass law (Young et al., 2002) and assuming no radiogenic ⁴⁰Ca-excess. Samples are reported relative to seawater by setting the $\delta^{44/40}$ Ca value of 915b equal to -1.15‰. Measurements were 254 only considered successful if the two final $\delta^{44/40}$ Ca determinations on the same post-column 255 256 solution were within 0.2‰. Accuracy and precision were confirmed through measurement of $\delta^{44/40}$ Ca values in Princeton University Aragonite (PUA), measured as -1.42 ± 0.17‰ (2 σ , n = 30), 257 258 and of San Salvador Sand (SSS), measured as $-1.31 \pm 0.15\%$ (2σ , n = 28). The precision of 915b 259 measurements ($\pm 0.16\%$, 2σ , n = 40) agreed with these reference materials; furthermore, for 260 samples chromatographically isolated at least twice (36/49), two times the mean standard deviation in replicate $\delta^{44/40}$ Ca values was 0.15%. Precision for each sample is reported as the largest of either 261 262 replicate measurements or the mean reproducibility of 915b, PUA, and SSS ($\pm 0.16\%$, 2σ).

263 2.2.3. Trace metal concentrations

264 A suite of major- and trace-element abundances were measured using a Thermo Scientific 265 iCAP RQ inductively-coupled plasma mass spectrometer (ICP-MS) at the University of Chicago, 266 following a standard geochemical protocol as described in Bryant et al. (2022). In brief, small 267 aliquots of the dissolved samples were subsampled, adjusted to approximately 10 ppm Ca in 2% 268 HNO₃ prior to analysis to mitigate matrix effects, and spiked with an internal standard solution 269 containing Sc, Y, and In. At the beginning of each run, a calibration curve was generated for each 270 element to calculate elemental concentrations. Calibration standards, calibration blanks, and 271 duplicate samples were analyzed intermittently throughout each run for quality control. V, Cr, Mn,

and Fe ratios are reported from analytical runs in Kinetic Energy Discrimination (KED) mode, while Sr, U, and Mg ratios are reported from analytical runs in Standard (STD) mode. Data are reported as molar ratios to Ca + Mg. In addition, Mg/(Mg+Ca) ratios were independently measured via ion chromatography during chromatographic separation of calcium, as outlined above.

276 **3. Results**

277 At Val Adrara prior to the onset of the positive carbon-isotope excursion, δ^{44} Ca composition steadily decreases from -1.0% in the upper Zu limestone to a minimum of -1.65% in the 278 279 Malanotte Formation in our new dataset (Fig. 3, Table S1). Calcium isotope ratios were measured 280 for two samples at the same stratigraphic heights at Val Adrara as Jost et al. (2016) with one at 20 281 m in the Zu limestone and the other at 67.2 m in the Malanotte Formations. Both have a systematic offset of about 0.14 ‰ with these new data being more positive. A shift toward lower δ^{44} Ca is 282 observed in the Malanotte in both datasets (Fig. 3). During the positive $\delta^{13}C$ excursion in the 283 Albenza Formation, δ^{44} Ca values are highly variable between -1.72 ‰ and -1.20 ‰. A gradual 284 trend toward more positive δ^{44} Ca values, ranging from -1.12 ‰ to -0.98 ‰, occurs at the 285 286 lithological change from oolitic grainstone to fossiliferous packstone in the upper Albenza 287 Formation.

At Mount Sparagio, pre-excursion δ^{44} Ca values have relatively small variability, ranging from -0.57 ‰ to -0.91 ‰ (Table S1) and are enriched relative to Val Adrara. The δ^{44} Ca values begin to fluctuate rapidly with a spread from -1.10 ‰ to -0.40 ‰ at the same time as the increase in δ^{34} S_{CAS} and decrease in I/(Ca+Mg). The carbon isotopic composition of unit B at Mount Sparagio is highly variable, with δ^{13} C values ranging from -3.15 ‰ to 2.46 ‰ (Table S1). A positive trend emerges approximately 50 m below the inferred extinction window at the top of unit B and 294 continues through the end of the record, peaking at a value of 3.04 ‰ (Table S2). A corresponding 295 positive trend is also observed in the δ^{18} O record.

296 Minor- and trace-element concentrations at Mount Sparagio are relatively uniform 297 throughout with the exception of the Triassic-Jurassic boundary interval where Mg, Sr, Mn, U, 298 and V concentrations, all normalized to (Ca+Mg), increase by almost an order of magnitude then 299 decrease to pre-excursion values (Fig. S1). There is a step decrease in Cr/(Ca+Mg) from an average 300 of ~5.5 µmol/mol to 2.5 µmol/mol at the boundary. At Val Adrara, Mg/(Ca+Mg) ratios remain 301 lower than 0.1 mol/mol throughout with only one value at ~175 m in the Albenza Formation that 302 is elevated in both Mg/(Ca+Mg) (~0.4 mol/mol) and Mn/(Ca+Mg) (~0.3 mmol/mol). Redox 303 sensitive trace elements Mn, V, and Cr decrease at the boundary interval in the Malanotte 304 Formation. V and Cr/(Ca+Mg) remain low for the lower 100 m of the Albenza Formation and then 305 begin trending toward pre-excursion values. Mn/(Ca+Mg) remains low until the Sedrina 306 Formation. Sr/(Ca+Mg) are overall higher than at Mount Sparagio (~1 mmol/mol) with some 307 elevated values (~3 mmol/mol) during the Malanotte Formation.

308 **4. Discussion**

Here we integrate published geochemical datasets with newly measured δ^{44} Ca values to 309 310 constrain the impact of sedimentary processes, mineralogy, and diagenesis on these three redox 311 proxy signals. By building a framework of geochemical tracers with differential responses and 312 sensitivities to diagenetic regimes (Table 1), potential influences of lithification processes on 313 primary redox signals can be teased apart. In terms of I/Ca, we aim to investigate (1) whether the 314 deoxygenation trend observed at both sites is the result of diagenetic loss of carbonate-associated 315 iodate; and (2) whether the overall low I/Ca at Val Adrara could be the result of more severe 316 diagenesis compared to Mount Sparagio.

317 4.1. Review of diagenetic redox proxies

318 Table 1 summarizes the predicted directional changes in isotopic and elemental 319 compositions of a primary carbonate initially formed under normal-marine conditions undergoing 320 one of two modes of diagenesis (sediment- and fluid-buffered) and one of four fluid compositions 321 (meteoric, seawater, evaporitic brine, and reducing pore fluid). The table is structured in this 322 manner to highlight contrasting susceptibilities to alteration under different diagenetic 323 environments of non-stoichiometric redox-sensitive elements compared to that of major 324 constituents. Covariation between two (or three) paleo-proxies can elucidate the complex post-325 depositional history of the sediment and fidelity of the original signal (Fantle et al., 2020).

Table 1: Summary of expected response of tracers under different conditions. Symbol key: Up 326 327 arrow (\uparrow) indicates isotopically heavier or more positive. Down arrow (\downarrow) indicates isotopic 328 lighter or more negative. The number of arrows indicates the sensitivity of the proxy to that process/mode of diagenesis. A dash (-) indicates that the proxy is largely unaffected by the 329 330 process. Sources: δ^{13} C and δ^{18} O (Oehlert and Swart, 2014; Ahm et al., 2018; Swart and Oehlert, 331 2018; Reis et al., 2019), δ^{44} Ca (Fantle and Higgins, 2014; Kimmig and Holmden, 2017; 332 Higgins et al., 2018); Mg/Ca (Higgins and Schrag, 2006; Stewart et al., 2015); Sr/Ca (Stewart 333 et al., 2015; Ahm et al., 2018; Higgins et al., 2018); δ^{238} U (Romaniello et al., 2013; Chen et al., 2018; Lau and Hardisty, 2022) $\delta^{34}S_{CAS}$ (Gill et al., 2008); I/Ca (Hardisty et al., 2014; Lau 334 and Hardisty, 2022); Mn/Sr (Lohmann, 1988; Jacobsen and Kaufman, 1999; Ahm et al., 2018) 335

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Process / E	Major Element			Major Element		Trace Element		Trace		
	Isotope					Isotope		element		
		Non-I	Redox S	Sensitive	e		Redox Sensitive			
Style	Environment	δ ¹³ C	δ ¹⁸ Ο	δ ⁴⁴ Ca	Mg/Ca	Sr/Ca	δ^{238} U	$\delta^{34}S_{CAS}$	I/Ca	Mn/Sr
Fluid buffered	Meteoric (oxygenated)	↓	$\downarrow\downarrow$	$- \text{ or } \downarrow$	$\downarrow\downarrow$	↓	—	_	– or	1
(open system)	Seawater (oxygenated)	_	_	1	_	↓	_	_	?	1
	Reducing pore fluids	↓	_	_	_	_	↑ ↑	↑	Ļ	$\uparrow\uparrow\uparrow$
	Dolomitization (evaporitic brine)	_	Î	↑ ↑↑	↑ ↑↑	ŢŢ	Ļ		_	Î
Sediment Buffered	Closed System	_	Ļ			\downarrow				1

The establishment of geochemical disequilibrium allowing for directional exchange between the solid phase and sediment pore fluid can occur under either open or closed conditions (Table 1). Open systems or fluid-buffered modes of diagenesis in which a high degree of exchange occurs tend to be more chemically evolved than closed or sediment-buffered systems where pore fluids are isolated (Higgins et al., 2018). Fluid-buffered diagenesis refers to the processes under which high advective fluid flow through sediment pore space alters the precursor carbonate compositions in the direction of the fluid composition (Higgins et al., 2018; Fantle et al. 2020).

Meteoric fluid-buffered diagenesis occurs when CO₂-rich freshwater derived from either precipitation or runoff percolates through unsaturated pore space (Lohmann, 1988; Flugel, 2010). Disequilibrium resulting from the mixing of different fluid compositions in the carbonate pore 356 space leads to dissolution and recrystallization of metastable polymorphs of calcite. Degassing of 357 dissolved CO₂ results in the inorganic precipitation of carbonate, typically causing δ^{13} C of the bulk carbonate to decrease. Covariation between δ^{18} O and δ^{13} C is a conventional method of identifying 358 359 early meteoric diagenesis, but it is not a definitive indicator in every setting (Swart and Oehlert, 360 2018, Fantle et al. 2020). Under meteoric fluid-buffered conditions secondary precipitates derive 361 most of their calcium from the precursor material, so little calcium isotope fractionation occurs 362 (Kimming and Holmden, 2017). Recrystallization with oxygenated fluids can also result in 363 leaching of more soluble minor elements (e.g., Sr and Mg) (Stewart et al., 2015) while redox-364 sensitive trace-elements that are only soluble under reducing conditions may be retained (Lau and 365 Hardisty, 2022). A reduction in I/Ca is predicted to occur under oxygenated fluid diagenesis only 366 under very high fluid/rock ratios (Lau and Hardisty, 2022). Due to the low concentrations of U 367 and SO₄²⁻ in fresh water, meteoric diagenesis is expected to lower carbonate-associated U and S concentrations but should not appreciably alter the $\delta^{34}S_{CAS}$ and $\delta^{238}U$ composition, as their 368 369 dissolution does not impart fractionation (Gill et al., 2008; Zhang, et a 2020; Chen et al., 2021).

For both δ^{238} U and δ^{34} S_{CAS}, the redox state of the pore water plays a more significant role 370 in the degree of alteration. In downcore studies on the variation of δ^{238} U in modern carbonates 371 undergoing active diagenesis, δ^{238} U values heavier than seawater have been attributed to the 372 preferential incorporation of less soluble ²³⁸U under sulfidic pore-water conditions (Romaniello et 373 374 al., 2013; Chen et al., 2018). There are currently no post-depositional processes known to increase 375 I/Ca values, but studies on recent and ancient carbonates report potential decreases under 376 dolomitization (Hardisty et al., 2014; Hardisty et al., 2017; He et al., 2022b) and modeling demonstrates that I/Ca is highly sensitive to reducing fluids, more so than δ^{238} U and δ^{34} S_{CAS} (Lau 377 378 and Hardisty, 2022). The Mn/Sr ratio can be used to qualitatively trace suboxic conditions due to

the differences in redox potential and solubility of Sr^{2+} and Mn^{2+} (Lohmann, 1988). An accepted threshold value that can indicate diagenetic alteration under some types of mildly reducing conditions is Mn/Sr greater than 0.2 mol/mol.

382 Dolomitization, where the fluid is a high-Mg brine, causes both Mg/Ca and δ^{44} Ca values 383 to increase whereas Sr is lost due to exclusion from the dolomite lattice. Dolomitization may 384 elevate Mn/Sr ratios via loss of Sr (Ahm et al., 2018) and decrease δ^{238} U due to leaching of 235 U 385 (Romaniello et al., 2013). Brine composition is not expected to substantially alter δ^{34} S_{CAS}, even if 386 derived from sulfate evaporites, unless conditions are sulfidic (Shurr et al., 2021).

387 Under sediment-buffered conditions with little advective fluid flow, the dissolved Ca pool 388 approaches the isotopic composition of the sediment (Fantle et al., 2010; Lau and Hardisty, 2022). 389 Limited exchange between fluid and sediment undergoing dolomitization or aragonite-to-calcite 390 neomorphism may alter the elemental composition, but the isotopic composition of the precursor 391 is preserved due to the lack of any substantial material exchange (Ahm et al., 2018; Higgins et al., 392 2018). Sr concentrations may be lowered by sediment-buffered diagenesis if undergoing aragonite-393 to-calcite neomorphism (~1-4 mmol/mol) but not to the same extent as under fluid-buffered 394 conditions (<1 mmol/mol) (Banner and Hanson, 1990; Ahm et al., 2018). An increase in Mn/Sr 395 results from the loss of Sr. Increasing temperature with burial depth is largely responsible for decreasing δ^{18} O under sediment-buffered conditions (Murray and Swart, 2017). 396





Figure 4: Cross plots of δ^{44} Ca against carbonate-based redox proxies. The top row (panels a-d) is 398 color-coded by Mg/Ca ratio, indicative of dolomitization, where a value of 1.0 mol/mol is 399 400 stoichiometric dolomite and the bottom row (panels e-h) is colored by Mn/Sr ratio, indicative of 401 reducing pore fluids. The dotted boxes encompass the range of values during the positive carbon excursion. The solid grey boxes encompass most of the range of background (pre- and post-402 403 excursion) values. The small insert within each panel illustrates the expected trends of primary 404 carbonate geochemical evolution due to dolomitization (brown dotted arrow), shifts in local or global anoxic conditions (red dotted line), reducing pore fluids (blue dotted arrow) and 405 recrystallization from primary carbonate under fluid-buffered conditions (black solid arrow). 406

At Mount Sparagio, there is little covariation between δ^{44} Ca and δ^{34} S_{CAS} or I/Ca (Fig. 4a-408 409 c). The δ^{44} Ca values at Mount Sparagio are relatively high and a few points are elevated with respect to Mg/Ca (>0.5 mol/mol) or Mn/Sr (> 2.0 mol/mol), especially during the excursion, but 410 411 there are no systematic correlations to indicate that dolomitization or reducing fluids significantly impacted the redox signals. Two out of five samples during the $\delta^{34}S_{CAS}$ excursion interval (Fig. 412 4e) show elevated Mn/Sr and Mg/Ca, and slightly higher δ^{44} Ca. These two δ^{34} S_{CAS} values may 413 414 have been post-depositionally elevated by reducing pore fluids, whereas other samples from the δ^{34} S_{CAS} excursion appear to be better preserved. At Val Adrara, the low δ^{238} U values during the 415

416 excursion, indicative of expanded global anoxia, have low Mg/Ca, Mn/Sr and δ^{44} Ca (Fig. 4b and 417 4f). Neither the new dataset nor that of Jost et al. (2016) reveals any covariation between δ^{238} U 418 and δ^{44} Ca, suggesting minimal diagenetic alteration of the δ^{238} U signal.

419 The decreases in I/Ca from background level into the excursion interval at both sites are 420 not associated with any systematic increase in Mg/Ca, Mn/Sr, or δ^{44} Ca (Fig. 4c-d, g-h). Only one 421 value at each site during the excursion interval is considerably elevated in either Mn/Sr or Mg/Ca 422 to suggest potential alteration under reducing pore fluids. Therefore, the local deoxygenation trends recorded by I/Ca at both sites appears robust. At both sites, δ^{44} Ca becomes more variable 423 424 during the excursion but does not trend more positive. Mount Sparagio shows higher Mn/Sr (up to 425 0.4 mol/mol) and δ^{44} Ca compared to Val Adrara, especially before the excursion interval, but there 426 is no apparent trend. Because there is no process currently known to elevate I/Ca, these values at 427 Mount Sparagio either reflect original redox conditions or possibly early oxygenated fluidbuffered diagenesis resulting in higher δ^{44} Ca. 428

429 4.3. Carbonate Mineralogy

430 **Table 2:** Approximate end-member mineralogical element and isotopic compositions of carbonate 431 precipitated from normal marine conditions. Sources: Sr/Ca and Mg/Ca (Morse and Mackenzie, 432 1990; Cicero and Lohmann 2001; Holcomb et al., 2009; Gussone et al., 2015), average δ^{44} Ca for 433 modern carbonate platform aragonite sediment and high-Mg calcite from Higgins et al. (2018), 434 low-Mg calcite from Marriott et al., (2004) and Blättler et al. (2012), calcite cement from Erhardt 435 et al. (2020), and dolomite from Ahm et al. (2018).

	Aragonite	High-Mg Calcite	Low-Mg Calcite	Dolomite	Calcite Cement
Sr/Ca	7-10	1.5-4	1-1.5	<1.0	<1.0
(mmol/mol)					
Mg/Ca	2-6	6-50	2-4	100-1000	0.5-15
(mmol/mol)					
Modern δ ⁴⁴ Ca	-1.38	-1.13	-0.8	-0.68	-0.42
(SW, ‰)					



437 Figure 5: (a) Sr/Ca and Mg/Ca for Val Adrara (closed) and Mount Sparagio (open) colored by 438 lithology. End-member carbonate mineralogy (e.g. dolomite, aragonite) labels placed in the 439 approximate ranges of their compositions. LMC = low-magnesium calcite and HMC = highmagnesium calcite. (b) Cross plot of Sr content and δ^{44} Ca with a linear mixing model (red solid 440 line) (Farkaš et al., 2017) between aragonite and calcite endmembers in Table 2 relative to Triassic 441 seawater composition of -0.4 ‰ (Farkas et al. 2007;). In the model, aragonite has a Sr 442 443 concentration of 8000 ppm and δ^{44} Ca of -1.8 %. Primary calcite has a Sr concentration of 500 444 ppm and δ^{44} Ca of -1.5 ‰. Dotted blue is line possible trajectory for fluid-buffered neomorphism 445 of 100% aragonite with marine water of Triassic composition based a model by Lau et al. (2017). 446

447 We can further disentangle the diagenetic history and identify original carbonate source materials of these sites by plotting δ^{44} Ca against other isotopic and elemental ratios. Sr 448 concentrations and Sr/Ca and Mg/Ca ratios together with δ^{44} Ca can be used to identify mineralogy 449 450 and sources of carbonate (Fig. 5). Approximate end-member ratios for different carbonate 451 mineralogies are given in Table 2. Samples from Val Adrara largely fall within the Sr/Ca vs Mg/Ca 452 space for aragonite and high-magnesium calcite (HMC) (Fig. 5a) whereas samples from Mount Sparagio have very low Sr/Ca (<1mmol/mol) and high δ^{44} Ca throughout regardless of lithology 453 (Gussone et al. 2020), indicative of recrystallization under fluid-buffered conditions. At Val 454 455 Adrara, the marl limestone of the Malanotte Formation is elevated in Sr/Ca ratios relative to other 456 lithologies. The two samples with Sr/Ca greater than 1 mmol/mol at Mount Sparagio also belong 457 to the marl layer within the TJ boundary interval (heights 203 and 209 m) (Fig. 2). Jost et al. (2016) 458 recognized a large shift in Sr concentration within the Malanotte Formation, coincident with the 459 negative excursion in δ^{44} Ca (Fig. 3). Increases in Sr/Ca ratios are observed at both sites in the new 460 datasets (Fig. S1 and S2).

461 Here we evaluate the covariation in Sr content and δ^{44} Ca using a simple linear mixing model 462 between aragonite and calcite endmembers, and plausible recrystallization pathways with different 463 starting proportions of aragonite (Fig. 5b). Using a mass-balance approach, Jost et al. (2016) 464 concluded that up to 80% in the negative δ^{44} Ca shift at Val Adrara in the Malanotte Formation 465 could be attributed to an increase in aragonite in the original mineralogy. A greater contribution of 466 aragonite to the original sediment could result from (1) migration of carbonate facies and mixing 467 between deeper-water calcite and shallow-water aragonite sediments and/or (2) a shift in primary 468 production favoring those that precipitate aragonitic skeletons (Farkas et al. 2016). At both Val 469 Adrara and Mount Sparagio, the thin marl layer at the Triassic-Jurassic boundary interval occurs 470 just before an inferred eustatic deepening indicated by a transition to carbonate mud-dominated 471 lithology, therefore eustatic changes are unlikely to increase the proportion of aragonite. Pelagic 472 calcifiers did not become abundant enough to be major sediment producers until the Middle 473 Jurassic (Suzuki and Oba, 2015) and are therefore not a likely contributor to the change in 474 aragonite observed Val Adrara. Benthic organisms with aragonite skeletons may be, on average, 475 more susceptible to ocean acidification and rising carbonate compensation depth than their calcite-476 producing counterparts (Hautmann et al., 2008); however, only a modest relationship between 477 skeletal mineralogy and extinction risk has been observed at the TJ boundary (Kiessling et al. 478 2007). Abundant megalodontid bivalves at Mount Sparagio (Todaro et al. 2018) could have

479 contributed to the slightly higher Sr/Ca values before their extinction (Fig. S1). Petrographic 480 analysis on thin sections at Val Adrara revealed an increase in abundance of aragonitic calcareous 481 algae within the Malanotte Formation (Singh et al., 2023). A shift in environmental conditions 482 favoring growth of calcareous algae that disaggregated in fine-grained aragonitic needles could 483 explain both the proportional increase in aragonite at Val Adrara and the texture of the sediment, 484 but a closer inspection at Mount Sparagio would be needed to explain the regional extent of this 485 marl layer.

486 The mixing of sediments from different carbonate sources (platform, pelagic, and meteoric cement) can be recognized by a linear covariation between δ^{13} C and δ^{44} Ca (Ahm et al., 2018; 487 488 Higgins et al., 2018). At Val Adrara, there is a moderate covariation (Pearson's r = -0.70, p-value = 0.005) between δ^{13} C and δ^{44} Ca that suggests some mixing between sources, if not a reflection 489 490 of open-system neomorphism, but the values stay in the region of marine deposition (Fig. 6). In 491 contrast, there is no correlation in δ^{13} C and δ^{44} Ca values for samples from Mount Sparagio 492 (Pearson's r = 0.08, p-value = 0.56) and most points fall near the zone of Triassic seawater value 493 (Farkas et al., 2007). There is an apparent non-linear covariation of Sr and δ^{44} Ca at Val Adrara 494 (Fig. 5b). Neomorphism of aragonite in fluid-buffered settings results in loss of Sr that is more rapid than diagenetic resetting of δ^{44} Ca. None of the values at Val Adrara fall on the mixing curve 495 496 but the marlstones with higher Sr content generally track the trajectory of recrystallization from 497 an original sediment with high aragonite content. In contrast, the carbonates at Mount Sparagio are inferred to have been originally calcite, influenced by marine fluids. High δ^{44} Ca and low Sr 498 499 content is also often found in marine cements (Cicero and Lohmann 2001; Gussone et al. 2020), 500 and these cements may still capture primary seawater trace metal composition (Erhardt et al., 501 2020).

502 Carbonate mineralogy itself does not impart a considerable effect on incorporation of iodate 503 into the carbonate (Feng and Redfern, 2018), but because iodine may be reduced but not 504 completely excluded upon recrystallization (Hardisty et al. 2017), the overall I/Ca trends may 505 reflect the conditions under which aragonite neomorphism occurred. It is impossible to separate 506 fully the potential impacts of aragonite neomorphism at Val Adrara, fluid-buffered calcite 507 diagenesis at Mount Sparagio, and primary redox variations, but we consider it likely that 508 diagenetic effects did not completely eradicate the redox signals and there was a true difference in 509 local conditions between the sections.

510



Figure 6: Covariation between bulk $\delta^{13}C_{carb}$ and $\delta^{44}Ca$ at Val Adrara (solid square) and Sparagio (open circles) colored by $\delta^{18}O$ value (Higgins et al., 2018). Dotted boxes are the approximate ranges isotopic composition of Triassic carbonate sources based on the estimated deviation from modern seawater value (grey bar) (Farkas et al. 2007). Regression lines (solid line) are given for data from Val Adrara (black) and Mt. Sparagio (red).

517 4.4 Potential Drivers of contrasting local redox conditions on the Tethys margin

518 I/Ca data for Val Adrara and Mount Sparagio suggest the existence of a redox gradient in 519 the EES at the Triassic-Jurassic boundary, with dissolved oxygen decreasing northwards. A 520 literature compilation for the redox conditions before and after extinction for several sites on the 521 EES confirms that this gradient was of regional significance (Fig. 1c). To investigate the 522 mechanisms leading to this N-S redox gradient in ocean anoxia and organic carbon burial, we 523 analyzed the results of a 200 Ma simulation conducted with the Community Earth System Model 524 (CESM) version 1.2.2 (Li et al., 2022a). While this simulation does not provide dissolved oxygen 525 concentrations, the temperature, precipitation, and surface wind fields may shed light on regional 526 atmospheric and oceanic circulations and thus help explain the contrasting paleoceanographic 527 conditions in the northern vs southern EES.





531

532 There are notable differences in the hydroclimatic conditions between the two study sites 533 on the EES (Fig. 7). Annual temperatures are slightly warmer at Mount Sparagio (~27°C) 534 compared to Val Adrara (23-25°C), mainly resulting from differences in the paleolatitudes of the two sections. This difference in ocean temperatures does not help explain the differences in ocean oxygenation. Because the solubility of oxygen in seawater decreases with increasing temperatures (Garcia and Gordon, 1992) the difference in sea-surface temperatures would, if anything, lead to a gradient opposite to what is observed, with higher dissolved oxygen concentrations in the (colder) northern part of the EES. This finding implies that other mechanisms must have been at play.

541 The explanation may be found in precipitation. The northern and southern regions of EES 542 are simulated to have been in two different hydrological regimes, where Val Adrara was estimated 543 to have received significantly more precipitation (up to 120 mm yr⁻¹) compared to Mount Sparagio 544 $(60-70 \text{ yr}^{-1})$ (Fig. 7a). This result is consistent with conceptual models for the regional circulation 545 patterns throughout the Jurassic period which propose that increased atmospheric CO₂ enhanced 546 the hydrologic cycle at northern latitudes, leading to more freshwater runoff from Laurasia into 547 the restricted northern basins (van de Schootbrugge et al., 2020; Onoue et al., 2022). Density 548 stratification due to an overlying low-salinity water mass may have established shallow subsurface 549 dysoxia at Val Adrara. Val Adara is a shallow-water, high-energy location subject to frequent 550 agitation producing the ooids and pelsparites that dominate the section. Deep-water anoxia 551 spilling/upwelling into this shallow location may be an alternative scenario to be tested in future 552 modeling study.

Regional ocean circulation may have reinforced the redox gradient on the EES. Oceanatmosphere general circulation models simulating this Boreal-Tethys gradient during the Toarcian Ocean Anoxic Event (T-OAE, ~183 Ma) suggest that a limb from an equatorial gyre may have produced strong currents on the southern margin permitting vertical mixing (Ruvalcaba Baroni et al., 2018). These currents may have been weakened due to rough bathymetry and restriction within 558 the EES. Annual wind stress results from CESM for the Triassic-Jurassic boundary indicate that 559 Mount Sparagio was in the path of high oncoming easterly wind bands (Fig. 7b), whereas Val 560 Adrara was positioned in a zone of relatively low wind stress. Based on these patterns of wind 561 stress, regional geography, and anoxic development within the EES water circulation pathways 562 are proposed to explain the spatial pattern of oxygen depletion at the Triassic-Jurassic boundary 563 (Fig. 1). Future work with a high-resolution, biogeochemistry-enabled model will be necessary to 564 determine the precise mechanisms for this redox gradient, by quantifying the respective 565 contributions of climate, ocean circulation, nutrient input to the ocean and possibly ocean 566 gateways.

567 **5. Conclusions**

568 This study reports carbonate Ca isotope ratios from two Italian sequences, Mount Sparagio and 569 Val Adrara, that record the end-Triassic mass extinction. Geochemical data are used to assess the 570 role of diagenetic alteration and carbonate mineralogy on primary redox signals. The lack of covariation between diagenetic indicators (δ^{44} Ca, Mg/Ca, Mn/Sr) and redox proxies (I/Ca, δ^{34} S_{CAS} 571 572 and δ^{238} U) suggests that some of the primary signal is likely preserved and the inferred differences 573 in local redox between the two sites are legitimate, although diagenesis of inferred primary 574 aragonite and calcite phases also contributes to geochemical variation. Earth system model 575 reconstructions of the Triassic-Jurassic boundary suggest that the two sites were situated in 576 different hydrological regimes and circulatory patterns could have primed the northern site, Val 577 Adrara, for more reducing conditions. Looking forward, a coupled atmospheric-ocean model 578 integrating biogeochemical tracers and bathymetry may offer a better appraisal of the potential 579 drivers of the redox gradient. Paired with an assessment of pre- and post- extinction patterns at the

sites, we may gain an improved understanding of how physical environment interacted with marinelife during the end-Triassic mass extinction.

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592 **Open Research**

593 Newly generated δ^{44} Ca and trace element data is available in the Supplementary material and upon 594 request.

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1	Temporal a	and	spatial	dynamics	of	paleo-redox	conditions	across	the	Triassic-Jurassic
2	boundary									

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14 Key Points

15	•	Calcium isotope ratios were measured for two carbonate successions in Italy spanning the
16		Triassic-Jurassic boundary interval
17	•	Paired proxy data indicate the sites underwent different modes of diagenetic alteration but
18		retain some primary redox signals
19	•	Ocean circulation strength and depth of vertical mixing may explain the difference in
20		local redox conditions

21 Abstract

22 The end-Triassic mass extinction was among the most severe biotic crises of the 23 Phanerozoic. It has been linked with the global expansion of marine anoxia, and the prolongation 24 of these conditions within epeiric seas has been proposed as a cause for the suppression of 25 biodiversity during the Hettangian. Testing this interpretation is complicated by spatially 26 heterogenous patterns of local marine redox conditions within the western Tethys European 27 Epicontinental Shelf. In this study we assess the redox state within this region by focusing on two 28 carbonate successions in Italy. Based on I/Ca ratios, these locations record distinct local 29 background redox conditions, with Val Adrara showing notably lower pre-extinction oxygen saturation state compared to Mount Sparagio. To better explain these differences, δ^{44} Ca and trace 30 31 element analyses were used to identify the roles of mineralogical and diagenetic effects on the 32 preservation of primary redox signals. A framework of multiple elemental (Sr, Mg, Mn, I) and isotopic (δ^{13} C, δ^{18} O, δ^{44} Ca, δ^{238} U and δ^{34} S_{CAS}) ratios was developed to identify factors that could 33 influence carbonate geochemistry. Both sites probably retain some primary variation in δ^{238} U, 34 35 δ^{34} S_{CAS} and I/Ca, but they are likely also shaped by changing mineralogy and early diagenetic 36 conditions which complicates interpretations of the seawater composition. Where the redox signals 37 are largely preserved, we interpret differences in pre-extinction I/Ca between the two sites to 38 reflect distinct local oxygenation states. Model simulations show that ocean circulation and 39 hydrological regime could have been important drivers of spatial heterogeneity in paleo-redox 40 conditions across the European Epicontinental Shelf.

41

43 Plain Language Summary

44 The end-Triassic mass extinction, 200 million years ago, may have been caused by rapid injection 45 of large quantities of carbon from volcanoes analogous to modern-day fossil fuel consumption. 46 The main killing mechanism may have been anoxia, or low dissolved oxygen content, in the 47 shallow ocean. Understanding the distribution of dissolved oxygen in the shallow ocean where 48 many organisms live is imperative for predicting future ecosystem sustainability. Carbonate 49 sediments record the chemical composition of seawater upon deposition, preserving information 50 about ancient ocean conditions Several carbonate-based geochemical proxies can be used to infer 51 the oxygen saturation state in the ocean, but their values can be altered by post-depositional 52 processes. During the Triassic, Europe was inundated with a shallow sea where carbonate 53 limestone deposition occurred, but the local seawater composition differs between two sites in 54 Italy. We use the carbonate calcium isotope ratios, which are sensitive to post-depositional 55 alteration, to investigate the effect of alteration on the proxy signals. While alteration influences 56 the absolute values of the seawater composition preserved at the two sites, the overall trends in 57 oxygen saturation are distinct and mostly unaltered. Earth system modeling suggests that the 58 difference between sites may be due to ocean circulation and hydrological patterns.

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65 **1. Introduction**

The end-Triassic mass extinction (~200 Ma) was among the most important biotic crises of the 66 67 Phanerozoic, resulting in the loss of nearly 20% of marine animal families (Bambach, 2006; 68 Kiessling et al., 2007). Losses were severe amongst many groups, especially scleractinian corals, 69 which lost up to 96% of their genera (Hautmann, 2006). The disappearance of characteristic 70 Triassic fauna closely coincides with an abrupt negative carbon-isotope ($\delta^{13}C_{org}$) excursion in 71 organic matter of up to -5 ‰ (Hesselbo et al., 2002; van de Schootbrugge et al., 2008; Bachan et al., 2016; Wignall and Atkinson 2020). The negative $\delta^{13}C_{org}$ excursion is contemporaneous with 72 73 the emplacement of the Central Atlantic Magmatic Province (CAMP) (Schoene et al., 2010; 74 Blackburn et al., 2013) suggesting a scenario of rapid injection (< 20 ka) of highly depleted carbon 75 (up to -70 ‰) followed by the enhanced burial of organic carbon leading to a prolonged positive 76 excursion (Hesselbo et al, 2002; Bachan et al., 2016). Recovery of marine communities was 77 spatially variable, being notably rapid in nearshore communities in NW Europe (Atkinson and 78 Wignall 2019) but skeletal abundance remains suppressed until the Sinemurian in Tethyan 79 carbonates (Singh et al., 2023).

Enrichment of redox-sensitive elements and the restructuring of microbial communities support widespread marine anoxia as a kill mechanism (van de Schootbrugge et al., 2008; Wignall and Atkinson 2020; He et al., 2020a; Beith et al., 2021; Onoue et al., 2022). Understanding the extent and degree of deoxygenation in the shallow ocean (<100 m), where most organisms live, is essential to assessing the ecological impacts of the event. Carbonate-based water-column redox proxies show heterogeneous spatial patterns of deoxygenation within the European Epicontinental Shelf (EES) along the western margin of the Tethys Ocean (Fig. 1) (e.g., Luo et al., 2018; He et al., 2022a; Singh et al., 2023), raising questions about whether some have been diagenetically
altered or if they record original spatial variation.

89 In this study, we focus on two locations: Mount Sparagio in Sicily and Val Adrara in the 90 Lombardy Basin of the southern Italian Alps (Fig. 1). The peritidal carbonate succession at Mount 91 Sparagio, in the southeastern region of the EES, records an abrupt positive shift in carbonateassociate sulfur isotope ($\delta^{34}S_{CAS}$) ratios coincident with the extinction interval, indicating a rapid 92 93 and intense onset of global anoxia commencing near the Triassic-Jurassic boundary (Fig. 2; He et 94 al. 2020). This signature correlates with a negative excursion in carbonate-phase δ^{238} U, another 95 indicator of global anoxia, recorded in the shallow carbonate ramp deposits at the Val Adrara (Fig. 96 3; Jost et al., 2017).

97 Carbonate-hosted, redox-sensitive elemental and isotopic ratios can track seawater composition (Kampschulte and Strauss, 1996; Zhang et al., 2020). The variations in seawater δ^{34} S 98 and δ^{238} U compositions are controlled by the burial fluxes under reducing conditions and the size 99 100 of the seawater reservoir (Bottrell and Newton, 2006; Chen et al., 2021). Microbial sulfate 101 reduction occurring under anoxic conditions imparts a large negative fractionation in the available sulfate by preferential incorporation of the lighter ³²S isotope into sulfide minerals, thus leaving 102 the seawater sulfate pool enriched in ³⁴S (Kampschulte and Strauss, 2004; Sim. et al., 2011). The 103 reduced form of uranium (U^{4+}) is less soluble than the oxidized form (U^{6+}) . The preferential 104 removal of ²³⁸U in anoxic settings leads to its depletion in the seawater pool (Zhang et al., 2020). 105 Consequently, the isotopic signatures of both δ^{238} U and δ^{34} S_{CAS} recorded in carbonate respectively 106 107 decrease and increase in response to expanding seafloor anoxia. The magnitudes of their isotopic 108 offsets from seawater values are often considered to reflect the global extent of anoxia (Fike et al., 109 2015; Zhang et al., 2020; Chen et al., 2021). Iodate (IO_3^{-}), the oxidized form of iodine, can be

incorporated into the calcite lattice whereas the reduced form iodide (I⁻) is excluded (Lu et al.,
2020). Iodate is rapidly reduced under low-oxygen conditions, so that low I/Ca likely reflects
carbonate accumulation beneath dysoxic-anoxic water masses (Lu et al., 2020).

113 While both Val Adrara and Mount Sparagio record signals of enhanced global extent of anoxic 114 settings during the positive δ^{13} C excursion, the local seawater conditions, as indicated by I/Ca (or 115 I/(Ca+Mg)), are distinct (He et al., 2022a; Singh et al., 2023). Background I/Ca values prior to the 116 positive excursion at Mount Sparagio are elevated relative to Val Adrara (Figs. 2 and 3). During 117 the excursion, I/Ca values decrease to near zero at Val Adrara. At Mount Sparagio, the highly 118 variable background I/Ca values only reduce to between 1-2 µmol/mol, higher still than the pre-119 excursion values at Val Adrara. We explore whether the discrepancy in local expressions of the 120 I/Ca signal along the northern and southern EES margins reflects diagenetic overprinting, 121 differences in original mineralogy, or contrasting primary redox conditions.

Calcium isotope ratios (${}^{44}Ca/{}^{40}Ca$, commonly reported as $\delta^{44}Ca$) are a versatile tool for 122 123 constraining post-depositional processes, such as dolomitization or recrystallization (Fantle et al., 124 2020), and for fingerprinting the effects of different primary carbonate minerals (Higgins et al., 125 2018). At low-temperature conditions, kinetic isotope effects are believed to dominate, with 126 important rate-dependent fractionation of Ca isotopes into different calcium-bearing mineral 127 phases (Tang et al., 2008). Under slow precipitation rates, such as may occur during authigenic or 128 diagenetic carbonate precipitation, no appreciable fractionation may be observed (Fantle and 129 DePaolo, 2007; Jacobson and Holmden, 2008). Thus, δ^{44} Ca can be used to track the diagenetic 130 history of carbonates. In addition, calcite and aragonite exhibit different fractionations (Gussone et al., 2003), which makes δ^{44} Ca a potentially useful indicator of primary carbonate mineralogy. 131 Here, δ^{44} Ca measurements are employed to examine the role of local mineralogical and diagenetic 132

effects on the preservation state of carbonate-based redox proxies (δ^{238} U, δ^{34} S_{CAS}, I/Ca). We first investigate the presence of co-variability of δ^{44} Ca with other elemental components (Sr/Ca, Mg/Ca, Mn/Sr) considered diagnostic of different diagenetic and source-mixing regimes. These analyses allow us to test the robustness of the redox gradient in the EES. Then, we discuss potential drivers of the spatial redox pattern in the EES based on simulations conducted with the Community Earth System model.

139



141 Figure 1: Paleo-geographical context of EES during the Late Triassic Rhaetian stage (~205 Ma). 142 (A) Paleogeographic reconstruction of Pangaea, highlighting the location of the EES (box) and approximate location of modern-day Italy. (B) Site locations on map of modern Italy modified 143 144 from Bachan et al. (2012). (C) Map of the northwestern Tethys epeiric sea. Arrows indicate 145 proposed circulation pathways accounting for speculative bathymetry and emerged landmasses, and arrow color distinguishes between cool water (blue) and warm water (red). The thickness of 146 147 the arrow indicates the current strength. Dotted lines are proposed flow paths modified from Ruvalcaba Baroni et al. (2018) with considerations based on CESM 1.2.2 simulations for the 148 149 Triassic-Jurassic and Rhaetian configurations (Scotese, 2014). Modern-day geographic 150 coordinates were rotated to paleo-coordinates using the R package Chronosphere and the Scotese PALEOMAP reconstruction (Kocsis and Raja, 2023; Scotese and Wright, 2018). IB: Iberian 151

Mountains, AM: Amorican, BM: Bohemian Massif, CSH: Corsican-Sardinian High. 1: Mount
Sparagio, Italy (Todaro et al., 2018), 2. Val Adrara, Italy (van de Schootbrugge et al., 2008), 3.
Kuhjoch, Austria (Li et al., 2022b), 4. Rosswinkel, Luxembourg (Richoz et al., 2012), 5.
Mingolshiem, Germany (Luo et al., 2018), 6. Mariental, Germany (Richoz et al., 2012). 7. Filikirk,
United Kingdom (Beith et al., 2021), 8. St. Audrie's, United Kingdom (Li et al., 2022b), 9.
Doniford Bay, UK (Paris et al., 2010). See Table S3, supplementary materials for literature
summary of redox conditions at these sites.

159

160 **2. Methods**

161 2.1. Study Site and Geological Setting

162 Approximately centered at 30°N paleolatitude, the EES was a warm, semi-restricted 163 collection of silled basins and carbonate platforms during the early Mesozoic. Fragmentation of 164 Pangaea permitted limited water exchange between the Boreal, Tethys, and the Panthalassa Ocean 165 to the west (Fig. 1), although the precise timing of connection and amount of exchange in the Late 166 Triassic are poorly constrained (Dore, 1991; Sha, 2002, Korte et al. 2015). Italy was mostly submerged in the southeastern region of the EES during the Triassic-Jurassic boundary interval, 167 168 but intermittent subaerial exposure is evident in both Sicilian and Tuscan sections (Fig. 1) 169 (Santantonio and Carminati, 2011; Bernardi et al., 2018).

170 2.1.2. Stratigraphy of Mount Sparagio

The Rhaetian to lower Hettangian succession at Mount Sparagio was deposited in a peritidal setting with intermittent subaerial exposure (Fig. 2) (Todaro et al., 2018). The studied section at Mount Sparagio is subdivided into three units: A, B, and C (Todaro et al., 2018). Units A (below the studied section) and B are assigned to Rhaetian age based on the occurrence of megalodontids and the benthic foraminiferan *Triasina hantkeni*. These lower units are characterized by the stacking of shallowing-upward cycles capped by red paleosols. Unit C lacks the large megalodontid bivalves (Todaro et al., 2018). There is an approximately 20 m-thick barren
interval capping unit B, concurrent with the onset of anoxia in the basin (He et al., 2022; He et al.,
2020). Unit C is dated to the early Hettangian due to the absence of *T. hantkeni* and the occurrence
of *Thaumatoporella parvovesiculifera* (Todaro et al., 2018). Unit C sediments were deposited in
slightly deeper waters than the lower units and lacks paleosols.



Figure 2: Chemo-stratigraphy and redox trends at Mount Sparagio (modern coordinates: 38°3'
 44.18" N, 12°43'9.19" E). The grey bar indicates the extinction interval. Solid lines trending with
 carbon and oxygen isotope ratios are loess smoothing regressions.

186

187 2.1.3. Stratigraphy of Val Adrara

188 The Val Adrara site is in the Lombardy Basin of the Southern Italian Alps (Jadoul and 189 Galli, 2008; Bachan et al., 2012). Sedimentary sequences at Val Adrara record deposition on a 190 passive-margin carbonate ramp (Santantonio and Carminati, 2011) and are assigned Rhaetian

191 through Hettangian ages based on palynological associations and carbon-isotope stratigraphy (Fig. 192 3; van de Schootbrugge et al., 2008). The lowermost Rhaetian-age Zu Formation is a fossiliferous 193 packstone consisting of an unrestricted marine assemblage. It is abruptly overlain by the Malanotte 194 Formation, which is devoid of fossils and is interpreted as the extinction interval (Fig. 3; Jadoul 195 and Galli, 2008; Bachan et al., 2012). The lower Malanotte consists of thinly bedded micritic 196 limestone (marl), which grades into carbonate-rich mud and wackestones (Jadoul and Galli, 2008). 197 The negative excursion in $\delta^{13}C_{carb}$, with a magnitude of -5.0 ‰, coincides with the extinction 198 interval and occurs entirely within lower silty-marl portion of the Malanotte Formation (van de 199 Schootbrugge et al., 2008; Bachan et al., 2012). The silty marl layer of the lower Malanotte 200 Formation is most likely correlative with the marly layer at Sparagio (Todaro et al. 2022). 201 However, neither site has been absolutely dated, so the timing and duration of this interval is poorly 202 constrained (Bachan et al. 2012; Todaro et al. 2018). Therefore, in both stratigraphic columns this 203 interval is not assigned to either the Rhaetian or Hettangian and is broadly referred to as the 204 Triassic-Jurassic boundary interval (Fig. 2 and 3). The negative excursion is followed by a small 205 positive excursion terminating at the top of the Malanotte Formation. The overlying Albenza 206 Formation is composed of 100 m of cross-bedded onlitic and peloidal grainstones interbedded with 207 cm-scale layers of dolomicrite (Bachan et al., 2012). Another pulse of volcanism is inferred from 208 a second -4.0 ‰ negative carbon isotope excursion at the base of the Albenza Formation and the 209 protracted positive carbon-isotope excursion that follows terminates at the top of the Albenza 210 Formation (Bachan et al., 2012; Bachan and Payne, 2016). Evidence of expanded global anoxia 211 commences during this positive excursion and may have suppressed faunal recovery in this region 212 (Singh et al. 2023). The Albenza Formation is sparsely fossiliferous with skeletal grains only 213 become abundant again at the Albenza-Sedrina contact (Singh et al. 2023). The lower Sedrina 214 consists of packstone and grades into a thinly bedded cherty limestone with abundant sponge 215 spicules (van de Schootbrugge et al., 2008; Singh et al., 2023). The upper Sedrina is interpreted to 216 have been deposited below storm wave base following rapid subsidence due to the onset of 217 extensional activity in the Hettangian (Santantonio and Carminati, 2011).



Figure 3: Chemostratigraphic trends at Val Adrara (modern coordinates: $45^{\circ}43'29.33''N$ 9°57'32.29''E). Error bars for $\delta^{238}U$ and $\delta^{44}Ca$ are 2σ . See Fig. 2 for lithologic key.

220

221 2.2. Sample Preparation and Analysis

Published geochemical data were compiled to compare redox trends at the sites (Figs. 2 and 3). These data include carbon- and oxygen-isotope profiles for the Val Adrara section (van de Schootbrugge et al., 2008), estimates of global anoxia from $\delta^{34}S_{CAS}$ at Mount Sparagio (He et al., 2020), and from $\delta^{238}U$ at Val Adrara (Jost et al., 2017), and I/Ca at Val Adrara and I/(Ca+Mg) from Mount Sparagio as indicators of local redox conditions (He et al., 2022a; Singh et al., 2023). 227 Calcium-isotope data on different powered samples from the upper Zu limestone and Malanotte 228 Formation were previously reported in Jost et al. (2016). These data bracket the negative carbon 229 isotope excursion, but only include the rising limb of the subsequent positive excursion (Fig. 3). 230 Here we report bulk carbonate δ^{44} Ca and trace elemental (Sr, Mn, Mg) concentrations data that 231 span the full stratigraphic range for both sites (Fig. S2 and S3, supplementary materials). We also 232 measure carbon- and oxygen-isotope compositions for new samples from Mount Sparagio (n = 233 52).

234 2.2.1. Carbon and oxygen isotope measurements

For samples from the Mount Sparagio section, about 10 mg of carbonate powder were drilled from the cleaned rock slab using a hand drill. Powder was reacted with 100% H₃PO₄ at 70 °C to extract CO₂ for ¹³C/¹²C and ¹⁸O/¹⁶O measurements. We used the Chinese national standard, an Ordovician carbonate from a site near Beijing (reference number GBW04405, $\delta^{13}C =$ 0.57 ± 0.03 ‰ VPDB; $\delta^{18}O = -8.49 \pm 0.13$ ‰ VPDB) to monitor the accuracy. These measurements were performed using a Finnigan MAT 253 mass spectrometer in the Nanjing Institute of Geology and Palaeontology.

242 2.2.2. Calcium isotope ratios and trace elemental analysis

Measurement of carbonate δ^{44} Ca values at the University of Chicago closely followed the method of Razionale et al. (2022). Briefly, carbonate samples were dissolved in buffered acetic acid at a ratio of ~1 mg/mL and Ca²⁺ was chromatographically isolated using a Dionex ICS-6000 with variable strength MSA eluent. Samples were matrix matched at 1 ppm Ca²⁺ in 2% nitric acid for sample-standard bracketing and each post-chromatography eluent was measured twice by Neptune XT as 90 integration cycles monitoring masses 42, 43, 43.5, and 44. Outlier cycles

exceeding $\pm 3\sigma$ for the ⁴⁴Ca/⁴²Ca, ⁴⁴Ca/⁴³Ca, or ⁴³Ca/⁴²Ca intensity ratios were removed, as were 249 entire sets of cycles when the ⁴⁴Ca/⁴²Ca ratio of successive bracketing standards changed 250 251 by >0.2‰. Following a correction for strontium interference and a run-specific concentration effect, values of $\delta^{44/42}$ Ca were corrected to NIST 915b and scaled to $\delta^{44/40}$ Ca ratios using a kinetic 252 253 mass law (Young et al., 2002) and assuming no radiogenic ⁴⁰Ca-excess. Samples are reported relative to seawater by setting the $\delta^{44/40}$ Ca value of 915b equal to -1.15‰. Measurements were 254 only considered successful if the two final $\delta^{44/40}$ Ca determinations on the same post-column 255 256 solution were within 0.2‰. Accuracy and precision were confirmed through measurement of $\delta^{44/40}$ Ca values in Princeton University Aragonite (PUA), measured as -1.42 ± 0.17‰ (2 σ , n = 30), 257 258 and of San Salvador Sand (SSS), measured as $-1.31 \pm 0.15\%$ (2σ , n = 28). The precision of 915b 259 measurements ($\pm 0.16\%$, 2σ , n = 40) agreed with these reference materials; furthermore, for 260 samples chromatographically isolated at least twice (36/49), two times the mean standard deviation in replicate $\delta^{44/40}$ Ca values was 0.15%. Precision for each sample is reported as the largest of either 261 262 replicate measurements or the mean reproducibility of 915b, PUA, and SSS ($\pm 0.16\%$, 2σ).

263 2.2.3. Trace metal concentrations

264 A suite of major- and trace-element abundances were measured using a Thermo Scientific 265 iCAP RQ inductively-coupled plasma mass spectrometer (ICP-MS) at the University of Chicago, 266 following a standard geochemical protocol as described in Bryant et al. (2022). In brief, small 267 aliquots of the dissolved samples were subsampled, adjusted to approximately 10 ppm Ca in 2% 268 HNO_3 prior to analysis to mitigate matrix effects, and spiked with an internal standard solution 269 containing Sc, Y, and In. At the beginning of each run, a calibration curve was generated for each 270 element to calculate elemental concentrations. Calibration standards, calibration blanks, and 271 duplicate samples were analyzed intermittently throughout each run for quality control. V, Cr, Mn,

and Fe ratios are reported from analytical runs in Kinetic Energy Discrimination (KED) mode, while Sr, U, and Mg ratios are reported from analytical runs in Standard (STD) mode. Data are reported as molar ratios to Ca + Mg. In addition, Mg/(Mg+Ca) ratios were independently measured via ion chromatography during chromatographic separation of calcium, as outlined above.

276 **3. Results**

277 At Val Adrara prior to the onset of the positive carbon-isotope excursion, δ^{44} Ca composition steadily decreases from -1.0% in the upper Zu limestone to a minimum of -1.65% in the 278 279 Malanotte Formation in our new dataset (Fig. 3, Table S1). Calcium isotope ratios were measured 280 for two samples at the same stratigraphic heights at Val Adrara as Jost et al. (2016) with one at 20 281 m in the Zu limestone and the other at 67.2 m in the Malanotte Formations. Both have a systematic offset of about 0.14 ‰ with these new data being more positive. A shift toward lower δ^{44} Ca is 282 observed in the Malanotte in both datasets (Fig. 3). During the positive $\delta^{13}C$ excursion in the 283 Albenza Formation, δ^{44} Ca values are highly variable between -1.72 ‰ and -1.20 ‰. A gradual 284 trend toward more positive δ^{44} Ca values, ranging from -1.12 ‰ to -0.98 ‰, occurs at the 285 286 lithological change from oolitic grainstone to fossiliferous packstone in the upper Albenza 287 Formation.

At Mount Sparagio, pre-excursion δ^{44} Ca values have relatively small variability, ranging from -0.57 ‰ to -0.91 ‰ (Table S1) and are enriched relative to Val Adrara. The δ^{44} Ca values begin to fluctuate rapidly with a spread from -1.10 ‰ to -0.40 ‰ at the same time as the increase in δ^{34} S_{CAS} and decrease in I/(Ca+Mg). The carbon isotopic composition of unit B at Mount Sparagio is highly variable, with δ^{13} C values ranging from -3.15 ‰ to 2.46 ‰ (Table S1). A positive trend emerges approximately 50 m below the inferred extinction window at the top of unit B and 294 continues through the end of the record, peaking at a value of 3.04 ‰ (Table S2). A corresponding 295 positive trend is also observed in the δ^{18} O record.

296 Minor- and trace-element concentrations at Mount Sparagio are relatively uniform 297 throughout with the exception of the Triassic-Jurassic boundary interval where Mg, Sr, Mn, U, 298 and V concentrations, all normalized to (Ca+Mg), increase by almost an order of magnitude then 299 decrease to pre-excursion values (Fig. S1). There is a step decrease in Cr/(Ca+Mg) from an average 300 of ~5.5 µmol/mol to 2.5 µmol/mol at the boundary. At Val Adrara, Mg/(Ca+Mg) ratios remain 301 lower than 0.1 mol/mol throughout with only one value at ~175 m in the Albenza Formation that 302 is elevated in both Mg/(Ca+Mg) (~0.4 mol/mol) and Mn/(Ca+Mg) (~0.3 mmol/mol). Redox 303 sensitive trace elements Mn, V, and Cr decrease at the boundary interval in the Malanotte 304 Formation. V and Cr/(Ca+Mg) remain low for the lower 100 m of the Albenza Formation and then 305 begin trending toward pre-excursion values. Mn/(Ca+Mg) remains low until the Sedrina 306 Formation. Sr/(Ca+Mg) are overall higher than at Mount Sparagio (~1 mmol/mol) with some 307 elevated values (~3 mmol/mol) during the Malanotte Formation.

308 **4. Discussion**

Here we integrate published geochemical datasets with newly measured δ^{44} Ca values to 309 310 constrain the impact of sedimentary processes, mineralogy, and diagenesis on these three redox 311 proxy signals. By building a framework of geochemical tracers with differential responses and 312 sensitivities to diagenetic regimes (Table 1), potential influences of lithification processes on 313 primary redox signals can be teased apart. In terms of I/Ca, we aim to investigate (1) whether the 314 deoxygenation trend observed at both sites is the result of diagenetic loss of carbonate-associated 315 iodate; and (2) whether the overall low I/Ca at Val Adrara could be the result of more severe 316 diagenesis compared to Mount Sparagio.

317 4.1. Review of diagenetic redox proxies

318 Table 1 summarizes the predicted directional changes in isotopic and elemental 319 compositions of a primary carbonate initially formed under normal-marine conditions undergoing 320 one of two modes of diagenesis (sediment- and fluid-buffered) and one of four fluid compositions 321 (meteoric, seawater, evaporitic brine, and reducing pore fluid). The table is structured in this 322 manner to highlight contrasting susceptibilities to alteration under different diagenetic 323 environments of non-stoichiometric redox-sensitive elements compared to that of major 324 constituents. Covariation between two (or three) paleo-proxies can elucidate the complex post-325 depositional history of the sediment and fidelity of the original signal (Fantle et al., 2020).

Table 1: Summary of expected response of tracers under different conditions. Symbol key: Up 326 327 arrow (\uparrow) indicates isotopically heavier or more positive. Down arrow (\downarrow) indicates isotopic 328 lighter or more negative. The number of arrows indicates the sensitivity of the proxy to that process/mode of diagenesis. A dash (-) indicates that the proxy is largely unaffected by the 329 330 process. Sources: δ^{13} C and δ^{18} O (Oehlert and Swart, 2014; Ahm et al., 2018; Swart and Oehlert, 331 2018; Reis et al., 2019), δ^{44} Ca (Fantle and Higgins, 2014; Kimmig and Holmden, 2017; 332 Higgins et al., 2018); Mg/Ca (Higgins and Schrag, 2006; Stewart et al., 2015); Sr/Ca (Stewart 333 et al., 2015; Ahm et al., 2018; Higgins et al., 2018); δ^{238} U (Romaniello et al., 2013; Chen et al., 2018; Lau and Hardisty, 2022) $\delta^{34}S_{CAS}$ (Gill et al., 2008); I/Ca (Hardisty et al., 2014; Lau 334 and Hardisty, 2022); Mn/Sr (Lohmann, 1988; Jacobsen and Kaufman, 1999; Ahm et al., 2018) 335

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Process / Elemental Ratios		Major Element			Major Element		Trace Element		Trace	
		Isotope					Isotope		element	
		Non-I	Redox S	Sensitive	<u> </u>		Redox Sensitive			
Style	Environment	δ ¹³ C	δ ¹⁸ Ο	δ ⁴⁴ Ca	Mg/Ca	Sr/Ca	δ^{238} U	$\delta^{34}S_{CAS}$	I/Ca	Mn/Sr
Fluid buffered	Meteoric (oxygenated)	↓	$\downarrow\downarrow$	$- \text{ or } \downarrow$	$\downarrow\downarrow$	↓	—	_	– or	1
(open system)	Seawater (oxygenated)	_	_	1	_	↓	_	_	?	1
	Reducing pore fluids	↓	_	_	_	_	↑ ↑	↑	Ļ	$\uparrow\uparrow\uparrow$
	Dolomitization (evaporitic brine)	_	Î	↑ ↑↑	↑ ↑↑	ŢŢ	Ļ		_	Î
Sediment Buffered	Closed System	_	Ļ			\downarrow				 ↑

The establishment of geochemical disequilibrium allowing for directional exchange between the solid phase and sediment pore fluid can occur under either open or closed conditions (Table 1). Open systems or fluid-buffered modes of diagenesis in which a high degree of exchange occurs tend to be more chemically evolved than closed or sediment-buffered systems where pore fluids are isolated (Higgins et al., 2018). Fluid-buffered diagenesis refers to the processes under which high advective fluid flow through sediment pore space alters the precursor carbonate compositions in the direction of the fluid composition (Higgins et al., 2018; Fantle et al. 2020).

Meteoric fluid-buffered diagenesis occurs when CO₂-rich freshwater derived from either precipitation or runoff percolates through unsaturated pore space (Lohmann, 1988; Flugel, 2010). Disequilibrium resulting from the mixing of different fluid compositions in the carbonate pore 356 space leads to dissolution and recrystallization of metastable polymorphs of calcite. Degassing of 357 dissolved CO₂ results in the inorganic precipitation of carbonate, typically causing δ^{13} C of the bulk carbonate to decrease. Covariation between δ^{18} O and δ^{13} C is a conventional method of identifying 358 359 early meteoric diagenesis, but it is not a definitive indicator in every setting (Swart and Oehlert, 360 2018, Fantle et al. 2020). Under meteoric fluid-buffered conditions secondary precipitates derive 361 most of their calcium from the precursor material, so little calcium isotope fractionation occurs 362 (Kimming and Holmden, 2017). Recrystallization with oxygenated fluids can also result in 363 leaching of more soluble minor elements (e.g., Sr and Mg) (Stewart et al., 2015) while redox-364 sensitive trace-elements that are only soluble under reducing conditions may be retained (Lau and 365 Hardisty, 2022). A reduction in I/Ca is predicted to occur under oxygenated fluid diagenesis only 366 under very high fluid/rock ratios (Lau and Hardisty, 2022). Due to the low concentrations of U 367 and SO₄²⁻ in fresh water, meteoric diagenesis is expected to lower carbonate-associated U and S concentrations but should not appreciably alter the $\delta^{34}S_{CAS}$ and $\delta^{238}U$ composition, as their 368 369 dissolution does not impart fractionation (Gill et al., 2008; Zhang, et a 2020; Chen et al., 2021).

For both δ^{238} U and δ^{34} S_{CAS}, the redox state of the pore water plays a more significant role 370 in the degree of alteration. In downcore studies on the variation of δ^{238} U in modern carbonates 371 undergoing active diagenesis, δ^{238} U values heavier than seawater have been attributed to the 372 preferential incorporation of less soluble ²³⁸U under sulfidic pore-water conditions (Romaniello et 373 374 al., 2013; Chen et al., 2018). There are currently no post-depositional processes known to increase 375 I/Ca values, but studies on recent and ancient carbonates report potential decreases under 376 dolomitization (Hardisty et al., 2014; Hardisty et al., 2017; He et al., 2022b) and modeling demonstrates that I/Ca is highly sensitive to reducing fluids, more so than δ^{238} U and δ^{34} S_{CAS} (Lau 377 378 and Hardisty, 2022). The Mn/Sr ratio can be used to qualitatively trace suboxic conditions due to

the differences in redox potential and solubility of Sr^{2+} and Mn^{2+} (Lohmann, 1988). An accepted threshold value that can indicate diagenetic alteration under some types of mildly reducing conditions is Mn/Sr greater than 0.2 mol/mol.

382 Dolomitization, where the fluid is a high-Mg brine, causes both Mg/Ca and δ^{44} Ca values 383 to increase whereas Sr is lost due to exclusion from the dolomite lattice. Dolomitization may 384 elevate Mn/Sr ratios via loss of Sr (Ahm et al., 2018) and decrease δ^{238} U due to leaching of 235 U 385 (Romaniello et al., 2013). Brine composition is not expected to substantially alter δ^{34} S_{CAS}, even if 386 derived from sulfate evaporites, unless conditions are sulfidic (Shurr et al., 2021).

387 Under sediment-buffered conditions with little advective fluid flow, the dissolved Ca pool 388 approaches the isotopic composition of the sediment (Fantle et al., 2010; Lau and Hardisty, 2022). 389 Limited exchange between fluid and sediment undergoing dolomitization or aragonite-to-calcite 390 neomorphism may alter the elemental composition, but the isotopic composition of the precursor 391 is preserved due to the lack of any substantial material exchange (Ahm et al., 2018; Higgins et al., 392 2018). Sr concentrations may be lowered by sediment-buffered diagenesis if undergoing aragonite-393 to-calcite neomorphism (~1-4 mmol/mol) but not to the same extent as under fluid-buffered 394 conditions (<1 mmol/mol) (Banner and Hanson, 1990; Ahm et al., 2018). An increase in Mn/Sr 395 results from the loss of Sr. Increasing temperature with burial depth is largely responsible for decreasing δ^{18} O under sediment-buffered conditions (Murray and Swart, 2017). 396





Figure 4: Cross plots of δ^{44} Ca against carbonate-based redox proxies. The top row (panels a-d) is 398 color-coded by Mg/Ca ratio, indicative of dolomitization, where a value of 1.0 mol/mol is 399 400 stoichiometric dolomite and the bottom row (panels e-h) is colored by Mn/Sr ratio, indicative of 401 reducing pore fluids. The dotted boxes encompass the range of values during the positive carbon excursion. The solid grey boxes encompass most of the range of background (pre- and post-402 403 excursion) values. The small insert within each panel illustrates the expected trends of primary 404 carbonate geochemical evolution due to dolomitization (brown dotted arrow), shifts in local or global anoxic conditions (red dotted line), reducing pore fluids (blue dotted arrow) and 405 recrystallization from primary carbonate under fluid-buffered conditions (black solid arrow). 406

At Mount Sparagio, there is little covariation between δ^{44} Ca and δ^{34} S_{CAS} or I/Ca (Fig. 4a-408 409 c). The δ^{44} Ca values at Mount Sparagio are relatively high and a few points are elevated with respect to Mg/Ca (>0.5 mol/mol) or Mn/Sr (> 2.0 mol/mol), especially during the excursion, but 410 411 there are no systematic correlations to indicate that dolomitization or reducing fluids significantly impacted the redox signals. Two out of five samples during the $\delta^{34}S_{CAS}$ excursion interval (Fig. 412 4e) show elevated Mn/Sr and Mg/Ca, and slightly higher δ^{44} Ca. These two δ^{34} S_{CAS} values may 413 414 have been post-depositionally elevated by reducing pore fluids, whereas other samples from the δ^{34} S_{CAS} excursion appear to be better preserved. At Val Adrara, the low δ^{238} U values during the 415

416 excursion, indicative of expanded global anoxia, have low Mg/Ca, Mn/Sr and δ^{44} Ca (Fig. 4b and 417 4f). Neither the new dataset nor that of Jost et al. (2016) reveals any covariation between δ^{238} U 418 and δ^{44} Ca, suggesting minimal diagenetic alteration of the δ^{238} U signal.

419 The decreases in I/Ca from background level into the excursion interval at both sites are 420 not associated with any systematic increase in Mg/Ca, Mn/Sr, or δ^{44} Ca (Fig. 4c-d, g-h). Only one 421 value at each site during the excursion interval is considerably elevated in either Mn/Sr or Mg/Ca 422 to suggest potential alteration under reducing pore fluids. Therefore, the local deoxygenation trends recorded by I/Ca at both sites appears robust. At both sites, δ^{44} Ca becomes more variable 423 424 during the excursion but does not trend more positive. Mount Sparagio shows higher Mn/Sr (up to 425 0.4 mol/mol) and δ^{44} Ca compared to Val Adrara, especially before the excursion interval, but there 426 is no apparent trend. Because there is no process currently known to elevate I/Ca, these values at 427 Mount Sparagio either reflect original redox conditions or possibly early oxygenated fluidbuffered diagenesis resulting in higher δ^{44} Ca. 428

429 4.3. Carbonate Mineralogy

430 **Table 2:** Approximate end-member mineralogical element and isotopic compositions of carbonate 431 precipitated from normal marine conditions. Sources: Sr/Ca and Mg/Ca (Morse and Mackenzie, 432 1990; Cicero and Lohmann 2001; Holcomb et al., 2009; Gussone et al., 2015), average δ^{44} Ca for 433 modern carbonate platform aragonite sediment and high-Mg calcite from Higgins et al. (2018), 434 low-Mg calcite from Marriott et al., (2004) and Blättler et al. (2012), calcite cement from Erhardt 435 et al. (2020), and dolomite from Ahm et al. (2018).

	Aragonite	High-Mg Calcite	Low-Mg Calcite	Dolomite	Calcite Cement
Sr/Ca	7-10	1.5-4	1-1.5	<1.0	<1.0
(mmol/mol)					
Mg/Ca	2-6	6-50	2-4	100-1000	0.5-15
(mmol/mol)					
Modern δ ⁴⁴ Ca	-1.38	-1.13	-0.8	-0.68	-0.42
(SW, ‰)					



437 Figure 5: (a) Sr/Ca and Mg/Ca for Val Adrara (closed) and Mount Sparagio (open) colored by 438 lithology. End-member carbonate mineralogy (e.g. dolomite, aragonite) labels placed in the 439 approximate ranges of their compositions. LMC = low-magnesium calcite and HMC = highmagnesium calcite. (b) Cross plot of Sr content and δ^{44} Ca with a linear mixing model (red solid 440 line) (Farkaš et al., 2017) between aragonite and calcite endmembers in Table 2 relative to Triassic 441 seawater composition of -0.4 ‰ (Farkas et al. 2007;). In the model, aragonite has a Sr 442 443 concentration of 8000 ppm and δ^{44} Ca of -1.8 %. Primary calcite has a Sr concentration of 500 444 ppm and δ^{44} Ca of -1.5 ‰. Dotted blue is line possible trajectory for fluid-buffered neomorphism 445 of 100% aragonite with marine water of Triassic composition based a model by Lau et al. (2017). 446

447 We can further disentangle the diagenetic history and identify original carbonate source materials of these sites by plotting δ^{44} Ca against other isotopic and elemental ratios. Sr 448 concentrations and Sr/Ca and Mg/Ca ratios together with δ^{44} Ca can be used to identify mineralogy 449 450 and sources of carbonate (Fig. 5). Approximate end-member ratios for different carbonate 451 mineralogies are given in Table 2. Samples from Val Adrara largely fall within the Sr/Ca vs Mg/Ca 452 space for aragonite and high-magnesium calcite (HMC) (Fig. 5a) whereas samples from Mount Sparagio have very low Sr/Ca (<1mmol/mol) and high δ^{44} Ca throughout regardless of lithology 453 (Gussone et al. 2020), indicative of recrystallization under fluid-buffered conditions. At Val 454 455 Adrara, the marl limestone of the Malanotte Formation is elevated in Sr/Ca ratios relative to other 456 lithologies. The two samples with Sr/Ca greater than 1 mmol/mol at Mount Sparagio also belong 457 to the marl layer within the TJ boundary interval (heights 203 and 209 m) (Fig. 2). Jost et al. (2016) 458 recognized a large shift in Sr concentration within the Malanotte Formation, coincident with the 459 negative excursion in δ^{44} Ca (Fig. 3). Increases in Sr/Ca ratios are observed at both sites in the new 460 datasets (Fig. S1 and S2).

461 Here we evaluate the covariation in Sr content and δ^{44} Ca using a simple linear mixing model 462 between aragonite and calcite endmembers, and plausible recrystallization pathways with different 463 starting proportions of aragonite (Fig. 5b). Using a mass-balance approach, Jost et al. (2016) 464 concluded that up to 80% in the negative δ^{44} Ca shift at Val Adrara in the Malanotte Formation 465 could be attributed to an increase in aragonite in the original mineralogy. A greater contribution of 466 aragonite to the original sediment could result from (1) migration of carbonate facies and mixing 467 between deeper-water calcite and shallow-water aragonite sediments and/or (2) a shift in primary 468 production favoring those that precipitate aragonitic skeletons (Farkas et al. 2016). At both Val 469 Adrara and Mount Sparagio, the thin marl layer at the Triassic-Jurassic boundary interval occurs 470 just before an inferred eustatic deepening indicated by a transition to carbonate mud-dominated 471 lithology, therefore eustatic changes are unlikely to increase the proportion of aragonite. Pelagic 472 calcifiers did not become abundant enough to be major sediment producers until the Middle 473 Jurassic (Suzuki and Oba, 2015) and are therefore not a likely contributor to the change in 474 aragonite observed Val Adrara. Benthic organisms with aragonite skeletons may be, on average, 475 more susceptible to ocean acidification and rising carbonate compensation depth than their calcite-476 producing counterparts (Hautmann et al., 2008); however, only a modest relationship between 477 skeletal mineralogy and extinction risk has been observed at the TJ boundary (Kiessling et al. 478 2007). Abundant megalodontid bivalves at Mount Sparagio (Todaro et al. 2018) could have

479 contributed to the slightly higher Sr/Ca values before their extinction (Fig. S1). Petrographic 480 analysis on thin sections at Val Adrara revealed an increase in abundance of aragonitic calcareous 481 algae within the Malanotte Formation (Singh et al., 2023). A shift in environmental conditions 482 favoring growth of calcareous algae that disaggregated in fine-grained aragonitic needles could 483 explain both the proportional increase in aragonite at Val Adrara and the texture of the sediment, 484 but a closer inspection at Mount Sparagio would be needed to explain the regional extent of this 485 marl layer.

486 The mixing of sediments from different carbonate sources (platform, pelagic, and meteoric cement) can be recognized by a linear covariation between $\delta^{13}C$ and $\delta^{44}Ca$ (Ahm et al., 2018; 487 488 Higgins et al., 2018). At Val Adrara, there is a moderate covariation (Pearson's r = -0.70, p-value = 0.005) between δ^{13} C and δ^{44} Ca that suggests some mixing between sources, if not a reflection 489 490 of open-system neomorphism, but the values stay in the region of marine deposition (Fig. 6). In 491 contrast, there is no correlation in δ^{13} C and δ^{44} Ca values for samples from Mount Sparagio 492 (Pearson's r = 0.08, p-value = 0.56) and most points fall near the zone of Triassic seawater value 493 (Farkas et al., 2007). There is an apparent non-linear covariation of Sr and δ^{44} Ca at Val Adrara 494 (Fig. 5b). Neomorphism of aragonite in fluid-buffered settings results in loss of Sr that is more rapid than diagenetic resetting of δ^{44} Ca. None of the values at Val Adrara fall on the mixing curve 495 496 but the marlstones with higher Sr content generally track the trajectory of recrystallization from 497 an original sediment with high aragonite content. In contrast, the carbonates at Mount Sparagio are inferred to have been originally calcite, influenced by marine fluids. High δ^{44} Ca and low Sr 498 499 content is also often found in marine cements (Cicero and Lohmann 2001; Gussone et al. 2020), 500 and these cements may still capture primary seawater trace metal composition (Erhardt et al., 501 2020).

502 Carbonate mineralogy itself does not impart a considerable effect on incorporation of iodate 503 into the carbonate (Feng and Redfern, 2018), but because iodine may be reduced but not 504 completely excluded upon recrystallization (Hardisty et al. 2017), the overall I/Ca trends may 505 reflect the conditions under which aragonite neomorphism occurred. It is impossible to separate 506 fully the potential impacts of aragonite neomorphism at Val Adrara, fluid-buffered calcite 507 diagenesis at Mount Sparagio, and primary redox variations, but we consider it likely that 508 diagenetic effects did not completely eradicate the redox signals and there was a true difference in 509 local conditions between the sections.

510



Figure 6: Covariation between bulk $\delta^{13}C_{carb}$ and $\delta^{44}Ca$ at Val Adrara (solid square) and Sparagio (open circles) colored by $\delta^{18}O$ value (Higgins et al., 2018). Dotted boxes are the approximate ranges isotopic composition of Triassic carbonate sources based on the estimated deviation from modern seawater value (grey bar) (Farkas et al. 2007). Regression lines (solid line) are given for data from Val Adrara (black) and Mt. Sparagio (red).

517 4.4 Potential Drivers of contrasting local redox conditions on the Tethys margin

518 I/Ca data for Val Adrara and Mount Sparagio suggest the existence of a redox gradient in 519 the EES at the Triassic-Jurassic boundary, with dissolved oxygen decreasing northwards. A 520 literature compilation for the redox conditions before and after extinction for several sites on the 521 EES confirms that this gradient was of regional significance (Fig. 1c). To investigate the 522 mechanisms leading to this N-S redox gradient in ocean anoxia and organic carbon burial, we 523 analyzed the results of a 200 Ma simulation conducted with the Community Earth System Model 524 (CESM) version 1.2.2 (Li et al., 2022a). While this simulation does not provide dissolved oxygen 525 concentrations, the temperature, precipitation, and surface wind fields may shed light on regional 526 atmospheric and oceanic circulations and thus help explain the contrasting paleoceanographic 527 conditions in the northern vs southern EES.





531

532 There are notable differences in the hydroclimatic conditions between the two study sites 533 on the EES (Fig. 7). Annual temperatures are slightly warmer at Mount Sparagio (~27°C) 534 compared to Val Adrara (23-25°C), mainly resulting from differences in the paleolatitudes of the two sections. This difference in ocean temperatures does not help explain the differences in ocean oxygenation. Because the solubility of oxygen in seawater decreases with increasing temperatures (Garcia and Gordon, 1992) the difference in sea-surface temperatures would, if anything, lead to a gradient opposite to what is observed, with higher dissolved oxygen concentrations in the (colder) northern part of the EES. This finding implies that other mechanisms must have been at play.

541 The explanation may be found in precipitation. The northern and southern regions of EES 542 are simulated to have been in two different hydrological regimes, where Val Adrara was estimated 543 to have received significantly more precipitation (up to 120 mm yr⁻¹) compared to Mount Sparagio 544 $(60-70 \text{ yr}^{-1})$ (Fig. 7a). This result is consistent with conceptual models for the regional circulation 545 patterns throughout the Jurassic period which propose that increased atmospheric CO₂ enhanced 546 the hydrologic cycle at northern latitudes, leading to more freshwater runoff from Laurasia into 547 the restricted northern basins (van de Schootbrugge et al., 2020; Onoue et al., 2022). Density 548 stratification due to an overlying low-salinity water mass may have established shallow subsurface 549 dysoxia at Val Adrara. Val Adara is a shallow-water, high-energy location subject to frequent 550 agitation producing the ooids and pelsparites that dominate the section. Deep-water anoxia 551 spilling/upwelling into this shallow location may be an alternative scenario to be tested in future 552 modeling study.

Regional ocean circulation may have reinforced the redox gradient on the EES. Oceanatmosphere general circulation models simulating this Boreal-Tethys gradient during the Toarcian Ocean Anoxic Event (T-OAE, ~183 Ma) suggest that a limb from an equatorial gyre may have produced strong currents on the southern margin permitting vertical mixing (Ruvalcaba Baroni et al., 2018). These currents may have been weakened due to rough bathymetry and restriction within
558 the EES. Annual wind stress results from CESM for the Triassic-Jurassic boundary indicate that 559 Mount Sparagio was in the path of high oncoming easterly wind bands (Fig. 7b), whereas Val 560 Adrara was positioned in a zone of relatively low wind stress. Based on these patterns of wind 561 stress, regional geography, and anoxic development within the EES water circulation pathways 562 are proposed to explain the spatial pattern of oxygen depletion at the Triassic-Jurassic boundary 563 (Fig. 1). Future work with a high-resolution, biogeochemistry-enabled model will be necessary to 564 determine the precise mechanisms for this redox gradient, by quantifying the respective 565 contributions of climate, ocean circulation, nutrient input to the ocean and possibly ocean 566 gateways.

567 **5. Conclusions**

568 This study reports carbonate Ca isotope ratios from two Italian sequences, Mount Sparagio and 569 Val Adrara, that record the end-Triassic mass extinction. Geochemical data are used to assess the 570 role of diagenetic alteration and carbonate mineralogy on primary redox signals. The lack of covariation between diagenetic indicators (δ^{44} Ca, Mg/Ca, Mn/Sr) and redox proxies (I/Ca, δ^{34} S_{CAS} 571 572 and δ^{238} U) suggests that some of the primary signal is likely preserved and the inferred differences 573 in local redox between the two sites are legitimate, although diagenesis of inferred primary 574 aragonite and calcite phases also contributes to geochemical variation. Earth system model 575 reconstructions of the Triassic-Jurassic boundary suggest that the two sites were situated in 576 different hydrological regimes and circulatory patterns could have primed the northern site, Val 577 Adrara, for more reducing conditions. Looking forward, a coupled atmospheric-ocean model 578 integrating biogeochemical tracers and bathymetry may offer a better appraisal of the potential 579 drivers of the redox gradient. Paired with an assessment of pre- and post- extinction patterns at the

sites, we may gain an improved understanding of how physical environment interacted with marinelife during the end-Triassic mass extinction.

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592 **Open Research**

593 Newly generated δ^{44} Ca and trace element data is available in the Supplementary material and upon 594 request.

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