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Duration of and decoupling between carbon isotope excursions during the end-Triassic mass extinction and Central Atlantic Magmatic Province emplacement

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ABSTRACT

Changes in $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ from marine strata occur globally in association with the end-Triassic mass extinction and the emplacement of the Central Atlantic Magmatic Province (CAMP) during the break up of Pangea. As is typical in deep time, the timing and duration of these isotopic excursions has remained elusive, hampering attempts to link carbon cycle perturbations to specific processes. Here, we report $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ from Late Triassic and Early Jurassic strata near Levanto, Peru, where intercalated dated ash beds permit temporal calibration of the carbon isotope record. Both $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ exhibit a broad positive excursion through the latest Triassic into the earliest Jurassic. The first order positive excursion in $\delta^{13}C_{org}$ is interrupted by a negative shift noted in many sections around the world coincident with the extinction horizon. Our data indicate that the negative excursion lasts 85 ± 25 kyrs, longer than inferred by previous studies based on cyclostratigraphy. A 260 ± 80 kyr positive $\delta^{13}C_{org}$ shift follows, during which the first Jurassic ammonites appear. The overall excursion culminates in a return to pre-perturbation carbon isotopic values over the next 1090 ± 70 kyrs. Via chronologic, isotopic, and biostratigraphic correlation to other successions, we find that $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ return to pre-perturbation values as CAMP volcanism ceases and in association with the recovery of pelagic and benthic biota. However, the initiation of the carbon isotope excursion at Levanto predates the well-dated CAMP sills from North America, indicating that CAMP may have started earlier than thought based on these exposures, or that the onset of carbon cycle perturbations was not related to CAMP.

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1. Introduction

The present-day rate of anthropogenic CO_2 emissions and the contemporaneous sixth mass extinction in Earth's history (e.g., Ceballos et al., 2015) motivate studies of similar past global change and associated loss of biodiversity. The end-Triassic mass extinction is one such analogue, when the breakup of Pangea was associated with the rapid emplacement of the Central Atlantic Magmatic Province (CAMP). CAMP emissions of CO_2 and other volatiles are implicated in putative changes including ocean acidification (see Greene et al., 2012 for a review) and climate change, which together are hypothesized to have resulted in the mass extinction (e.g., Guex et al., 2004, 2016; Palfy and Kocsis, 2014) during the Triassic–Jurassic transition.

Changes in the isotopic composition of sedimentary organic carbon during the extinction interval suggest major perturbation to the global carbon cycle. However, the timing and duration of C isotope excursions and their potential relationship to CAMP remain unclear. An initial negative $\delta^{13}C_{org}$ excursion (ICIE, Hesselbo et al., 2002) is coincident with the onset of extinction and is followed by a positive excursion observed in many stratigraphic sections (e.g., Bachan et al., 2012; Guex et al., 2004; Hesselbo et al., 2002; Williford et al., 2007). Interpretations of the mechanism(s) responsible for the carbon isotope shifts vary and include input of mantle or sedimentary-rock derived CO_2 (e.g., Bachan and Payne, 2016; Beerling and Berner, 2002; Paris et al., 2016), release of methane from gas hydrates destabilized by climate warming (Bachan and Payne, 2016; Beerling and Berner, 2002; Palfy et al., 2001), and changes in marine ecosystems responsible for organic matter cycling and export (e.g., van de Schootbrugge et al., 2013). Carbon cycle models exploring the causes of excursions during this interval have remained inconclusive (e.g., Bachan and Payne, 2016;

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Beerling and Berner, 2002; Paris et al., 2016), in part because model results depend on the poorly known temporal duration of isotope excursions. Moreover, few studies have reported coupled records of C isotopes from both organic and carbonate C for the end-Triassic, further limiting the range of information available for interpreting C cycle changes. Multiple high-resolution records of both organic and inorganic carbon isotopes (Kump and Arthur, 1999) offer the potential to greatly improve understanding of carbon cycle changes during this interval.

U–Pb dating of volcanic ashes from the Triassic–Jurassic succession near Levanto, in northern Peru, provides a framework to assess carbon isotope changes with temporal resolution not possible from other sections (Guex et al., 2012; Schaltegger et al., 2008; Schoene et al., 2010; Wotzlaw et al., 2014). In this study, we report organic and carbonate carbon isotope records through the Triassic–Jurassic interval from the Levanto section, use the results to offer new insight into the timing of carbon cycle perturbations, and compare the Levanto record to other datasets to assess the global significance of the observed signals spanning the Late Triassic and Early Jurassic.

2. Levanto section

A continuous section of the Aramachay Formation spanning the majority of the Rhaetian (latest Triassic) and Hettangian (earliest Jurassic) was sampled at a half-meter scale over 105 meters at a road-cut site near the town of Levanto (locality 6°18′29.13″S, 77°53′17.55″W). The Aramachay Formation, present throughout much of Peru, was deposited in extensional basins during the Triassic–Jurassic transition (Rosas et al., 2007). The strata at Levanto consist of thinly to thickly bedded organic and carbonate-rich mudstones devoid of traction and current-related sedimentary structures, suggesting deposition well below storm wave base. Surficial weathering enhances lamination and bedding differentially across the outcrop, but in polished slabs and thin sections the lithology is relatively uniform.

Strata are typically thickly bedded in the lower part of the section (0–60 m) where ash beds are less abundant, but appear thinly bedded where strata are punctuated by greater ash bed frequency (Fig. 1A, ashes denoted by white stars). In the Supplement (Fig. S1), marker beds (e.g., Fig. 1B) are reported next to a stratigraphic column reflecting bedding. Ashes can reach up to 4 cm (Fig. 1C). From 60 to 65 m, meter-scale packages of thin (∼1 cm) beds alternate with meter-scale individual thick beds, followed by 30 cm scale packages of thin beds alternating with 30 cm thick beds between 65 and 75 m. The remaining section includes similar alternations in thin and thick beds, which transition into laterally discontinuous concretionary beds, with some ovate concretions measuring over 1 m in diameter within the typical mudstone host rock (e.g., Fig. 1D). Evidence of bioturbation is absent throughout the section, suggesting bottom water oxygenation remains low through the entire measured interval. Laminae are typically visible in polished hand samples (Fig. 1E), and examination of 217 thin sections representing the entire outcrop revealed consistent laminated mudstone lithology, indicating no major change in depositional environment throughout the section. The consistent lithology through the Levanto section and absence of major environmental or depositional changes seen in outcrop, hand sample, or thin section (see Fig. 2) leads us to conclude that the geochemical data presented here are not predominantly controlled by changes in depositional environment.

3. Methods

Samples for geochemical and petrographic analyses were collected every half-meter (225 total samples); surficial weathering was avoided. As noted in section 2, 217 of 225 samples were thin sectioned and evaluated for lithology and degree of alteration. We measured organic and inorganic carbon isotopes ($\delta^{13}C_{carb}$, $\delta^{13}C_{org}$), weight percent carbonate (%CARB), and weight percent organic carbon (%TOC) using an Elemental Analyzer (Costech) and Automate auto-sampler coupled to a Picarro Cavity Ring Down spectrometer (e.g., Subhas et al., 2015). Complete carbonate removal is critical for yielding accurate $\delta^{13}C_{org}$ measurements, given the risk for recalcitrant carbonate phases to remain after decarbonation in marine sedimentary rocks; thus, we utilized heated (70 °C) 1M HCl during decarbonation (e.g., the 'rinse method' from Brodie et al., 2011). Isotope data are reported with stratigraphy in Fig. 3.

Using ash bed dates and ammonite occurrences from Guex et al. (2012) and Wotzlaw et al. (2014), we assigned ages to samples by interpolating constant sedimentation rate between ash beds (age model in Fig. 3). To estimate the duration of isotope excursions, we related ash bed ages to the stratigraphic height encompassed by each excursion, using a Monte Carlo approach to estimate uncertainties. Specifically, we randomly sampled 100,000 sets of ages from the normal distribution characterized by the mean $\pm 1\sigma$ age range defined by the U–Pb date of each ash bed. For each set of randomly sampled ages, we calculated an age model (as in Fig. 3). For each age model, we determined the duration of each isotope excursion based on the ages inferred for the stratigraphic height of the excursion start and end points. The resulting distributions of 100,000 determinations of excursion duration were found to be approximately normal; we report the median and 68% range (effectively equivalent to the propagated 1σ uncertainty) of each distribution.

Isotopic data and isotope excursion durations with 1σ ranges are shown in Fig. 4, using the last occurrence of *Choristoceras crickmayi* to denote the onset of the end-Triassic extinction (ETE; just before 201.51 ± 0.15 Ma; Wotzlaw et al., 2014) and the first occurrence of *Psiloceras spelae* to denote the Triassic–Jurassic boundary (TJB; 201.36 ± 0.17 Ma; Wotzlaw et al., 2014). The complete dataset is reported in Table S1. More detail, including a discussion of the relationship between our measured section and the ash beds reported in Guex et al. (2012) and Wotzlaw et al. (2014), detailed geochemical methods, and error estimation is provided in the Supplement.

4. Results

4.1. $\delta^{13}C_{org}$: *isotope excursions and their durations*

Rhaetian $\delta^{13}C_{org}$ values oscillate around −30‰ until the onset of a positive excursion. These oscillations are approximately 0.5‰ and occur with ∼400 kyr duration during the Rhaetian, suggesting possible Milankovitch cyclicity. Three points deviate to more positive values ∼202.15 Ma, followed by an increase at 201.85 Ma that marks the start of a sustained positive excursion. The broad positive excursion (black bar in Figs. 3 and 4) lasts 1720±90 kyrs, ending ∼200.1 Ma, approximately 700 kyrs prior to the Hettangian-Sinemurian boundary. The duration would be longer by ∼300 kyrs if the start of the excursion was at 202.15 Ma (dashed black bar in Fig. 4), but these differences do not affect our interpretations. Several notable second-order features punctuate the broad positive excursion, denoted by colored bars on Figs. 3 and 4, including:

1. A positive shift of ∼2‰ begins ∼201.85 Ma, persists for 285 ± 90 kyrs, and reaches a maximum at the extinction horizon (light green bar, Figs. 3 and 4).
2. A negative shift of ∼1.5‰ begins at the extinction horizon, as noted in many other sections around the world (the afore-

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