The Norian “chaotic carbon interval”: New clues from the $\delta^{13}$C$_{org}$ record of the Lagonegro Basin (southern Italy)

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ABSTRACT

A global carbon-isotope curve for the Late Triassic has the potential for global correlations and new insights on the complex and extreme environmental changes that took place in this time interval. We reconstruct the global $\delta^{13}$C$_{org}$ profile for the late Norian, improving on sparse published data from North American successions that depict a “chaotic carbon-isotope interval” with rapid oscillations. In this context, we studied three sections outcropping in the Lagonegro Basin (southern Italy), originally located in the western Tethys. The carbon-isotope profiles show four negative excursions correlatable within the Lagonegro Basin. In particular, a negative shift close to the Norian/Rhaetian boundary (NRB) appears to correlate with that observed in the North American $\delta^{13}$C$_{org}$ record, documenting the widespread occurrence of this carbon cycle perturbation. The $\delta^{13}$C$_{org}$ and $\delta^{18}$O$_{org}$ profiles suggest that this negative shift was possibly caused by emplacement of a large igneous province (LIP). The release of greenhouse gases (CO$_2$) to the atmosphere-ocean system is supported by the $^{34}$S enrichment observed, as well as by the increase of atmospheric pCO$_2$ inferred by different models for the Norian/Rhaetian interval. The trigger of this strongly perturbed interval could thus be enhanced magmatic activity that could be ascribed to the Angayucham province (Alaska, North America), a large oceanic plateau active ca. 214 ± 7 Ma, which has an estimated volume comparable to the Wrangellia and the Central Atlantic Magmatic Province (CAMP) LIPs. In fact, these three Late Triassic igneous provinces may have caused extreme environmental and climate changes during the Late Triassic.

INTRODUCTION

The Triassic is a key period in Earth’s history, characterized by breakup of the supercontinent Pangaea, episodes of biotic crises, and climate fluctuations (e.g., Ogg, 2012). This period is constrained by: (1) the end-Permian mass extinction—the most extensive biotic decimation of the Phanerzoic (e.g., Lucas, 1999; Benton and Twitchett, 2003; Lucas and Orchard, 2004; Erwin, 2006); and (2) the end-Triassic mass extinction (e.g., Hallam, 2002; Tanner et al., 2004; Richoz et al., 2007). The Triassic is also characterized by a dynamic climate regime (e.g., Preto et al., 2010; Rigo et al., 2012b; Trotter et al., 2015) and widespread geological and paleontological events, including humid and warm episodes (e.g., Carnian Pluvial Event, Upper Triassic, Simms and Ruffell, 1989, 1990; Simms et al., 1995; Ruffell et al., 2015), volcanism, and changes in the biosphere (e.g., Raup and Sepkoski, 1982; McElwain et al., 1999; Hallam, 2002; Marzoli et al., 2004; McRoberts et al., 2008; Lucas, 2010; Rigo and Joachimski, 2010; Rigo et al., 2012b; Dal Corso et al., 2012, 2014; Trotter et al., 2015). Stable isotopes play a critical role in biogeochemical cycles and therefore can provide important clues of ocean-water chemistry, oxygenation, and productivity of marine environments during the Triassic. Among these tools, one of the most widely applied is $\delta^{13}$C$_{org}$. This isotopic system varies in time as a function of productivity, organic carbon burial, and C assimilation pathways (C3 or C4). Therefore, $\delta^{13}$C$_{org}$ can provide essential clues on the evolution of ocean-water chemistry, oxygenation, and productivity of past marine environments (e.g., Hayes et al., 1999; Veizer et al., 1999; Payne et al., 2004; Korte et al., 2005; Lucas, 2010; Preto et al., 2012). In particular, excursions in marine $\delta^{13}$C$_{org}$ records that can be correlated globally are often thought to be related to global changes in the carbon cycle, such as those induced by marine and terrestrial extinction episodes (Berner, 2002; Galli et al., 2005; Payne and Kump, 2007; Korte and Kozur, 2010), which are often marked by negative $\delta^{13}$C$_{org}$ anomalies.

The carbon-isotope record of the Triassic has been studied in some detail, but its interpretation is complex because of the multiple ecological and geochemical controls on this proxy (e.g., Hayes et al., 1999; Veizer et al., 1999; Muttoni et al., 2004, 2010, 2014; Payne et al., 2004; Galli et al., 2005, 2007; Korte et al., 2005; Lucas, 2010; Maizza et al., 2010; Preto et al., 2012). A pronounced negative excursion is recorded at the Permian/Triassic boundary with oscillations in the lowermost Triassic, which is characterized by strong isotopic instability (e.g., Payne et al., 2004; Lucas, 2010). This is followed by a more stable period in the Middle Triassic (Payne et al., 2004; Tanner, 2010) and early Late Triassic...
composite potential for global correlation and would provide new insights on the environ-
ment of biotic crises (e.g., Rampino and Stothers, 1988; Jones and Jenkyns, 2001; Diakow et al., 2011, 2012; Maron et al., 2015) of North America seem to indicate
rapid oscillations of d13Corg that culminate in a positive d13Corg excursion at the Norian/Rhaetian boundary (e.g., Wignall, 2001; Richoz et al., 2007; Lucas, 2010). These processes evidently perturbed the global carbon cycle and caused episodes of
faunal turnovers. In particular, data from the Norian (ca. 227.0–205.7 Ma; Maron et al., 2015) of North America seem to indicate rapid oscillations of d13Corg that culminate in a positive d13Corg excursion that corresponds to the extinction of the bivalve Monotis, at the Norian/Rhaetian boundary (Ward et al., 2004; Wignall et al., 2007; Whiteside and Ward, 2011). This positive excursion is interpreted to have resulted from increased stagna-
tion in ocean circulation (Sephton et al., 2002; Ward et al., 2004). Tethyan sec-
tions have been investigated for d13Corg at the Norian/Rhaetian boundary (e.g., Atudorei, 1999; Gawlick and Bohm, 2000; Hauser et al., 2001; Muttoni et al., 2004, 2010; Hornung and Brandner, 2005; Korte et al., 2005; Preto et al., 2013; Bertinelli et al., 2016; Rigo et al., 2016), but the Norian organic carbon-isotope profile remains incomplete.

Therefore, the aim of this study is to verify the occurrence and to under-
stand the causes of the Norian organic carbon-isotope perturbations in the Tethyan realm, in particular in the Lagonegro Basin (southern Italy), as a con-
tribution to the construction of a more complete global Corg isotope curve for the Late Triassic. For this purpose, we investigated three geological sections, representing intermediate to distal basinal pelagic successions, for the concentra-
tion of total organic carbon (TOC) and organic carbon isotopes (d13Corg).
2010). Instead, the distal facies, which are characterized by the transition from the carbonate sedimentation of the Calcari con Selce to the siliceous deposition of Scisti Silicei, occurred with different patterns between the uppermost Triassic and the lowermost Jurassic (Scandone, 1967; Rigo et al., 2005, 2012a; Giordano et al., 2010).

The Lagonegro Basin has been investigated at three localities, where the Norian/Rhaetian interval is well documented: the Pignola-Abriola, Mount Volturino, and Madonna del Sirino sections (Fig. 1). These successions belong to the Calcari con Selce and Scisti Silicei and generally display good exposure and continuity in the field.

Pignola-Abriola Section

The Pignola-Abriola section crops out along the road between the villages of Pignola and Abriola (Potenza province, southern Italy) on the moutainside of Mount Crocetta (geographic coordinate system, datum WGS 84: 40°33′N, 15°47′1.71′′E). This section spans from the upper part of the Calcari con Selce, where the Norian/Rhaetian transition is documented (Amodeo, 1999; Bazzucchi et al., 2005; Rigo et al., 2005, 2016; Tanner et al., 2006; Giordano et al., 2010), to the lowermost part of the Scisti Silicei. The Pignola-Abriola section lacks the red shales level of the “transitional interval” that conventionally marks the uppermost portion of Calcari con Selce. The basal part (from 0 to 13 m) of the Pignola-Abriola section consists of thin-bedded cherty limestones, sometimes dolomitized, shales, and rare thin layers of calcarenites with platform-derived bioclasts. The overlying 37 m consist of alternations of dark-gray shales, thin beds of limestones, and black cherty layers. This part of the section is characterized by a progressive decrease in the relative abundance of carbonates in favor of the cherty and siliceous components (Amodeo, 1999; Bazzucchi et al., 2005; Rigo et al., 2005, 2016; Tanner et al., 2006; Giordano et al., 2010). Repeated thin and well-laminated interbeds of black shales with the shaly interval across and above the NRB suggest a transient period between suboxic and/or anoxic to more oxic conditions (Casacci et al., 2016). The observed sedimentation pattern suggests that the Pignola-Abriola section belongs to the intermediate facies association (Scandone, 1967; Rigo et al., 2005; Giordano et al., 2010; Casacci et al., 2016).

The Pignola-Abriola section yields rich assemblages of conodonts and pyritized radiolarians (Bazzucchi et al., 2005; Rigo et al., 2005, 2016; Bertinelli et al., 2016), which were used to construct a biostratigraphic framework for the section (Fig. 2), following the conodont and radiolarian biozonations proposed respectively by Kozur and Mock (1991) and Carter (1993) and summarized in Rigo et al. (2016) and Bertinelli et al. (2016). The conodont alteration index (CAI) of the Pignola-Abriola specimens is ≤1.5 (Giordano et al., 2010). Mockina zappei and Mockina slovakensia are present from the base of the section (Giordano et al., 2010). Mockina bidentata is recovered from ~7 m, defining the base of the M. bidentata Zone (Kozur and Mock, 1991; Giordano et al., 2010). The lowest occurrence (LO) of the conodont Misikella hermsteinii marks the base of the M. hermsteinii–P. andrusovi Zone (Kozur and Mock, 1991), at meter 21.4 (Giordano et al., 2010). Misikella hermsteinii occurs with Norigondolella steinbergensis and Parvigondolella andrusovi. At ~32 m, the first occurrence of M. hermsteinii/Misikella posthernsteinii transitional form is observed. At 44.9 m, Misikella koes-senensis and M. posthernsteinii appear. The first appearance datum (FAD) of M. posthernsteinii delineates the base of the Rhaetian stage and defines the base of the eponymous conodont biozone (Kozur and Mock, 1991; Giordano et al., 2010). Misikella ultima appears at ~54.2 m with Misikella kovaci.

The radiolarians are generally pyritized and not well preserved but are still useful in allowing the recognition of two assemblage zone boundaries: the base of the Betraccium deweveri Assemblage Zone (Carter, 1993) at ~22 m (late Norian in age), and the base of the Proparvicingula moniliformis Assemblage Zone at 41 m.

Mount Volturino Section

The Mount Volturino section is located along the southern slope of Mount Volturino (geographical coordinate system, datum WGS 84: 40°24′13.46″N; 15°49′2.25″E). This succession can be ascribed to the Calcari con Selce and the Scisti Silicei. The basal part of the section is characterized by red shales ascribed to the “transitional interval” (Giordano et al., 2010, 2011). The overlying 56 m consists of cherty limestones with red shale intercalations, red cherts, radiolarites, black siliceous shales, and silicified calcarenites rich in organic matter (Giordano et al., 2010, 2011; Rigo et al., 2016). This section belongs to the intermediate facies association (Scandone, 1967; Giordano et al., 2010, 2011).

The “transitional interval” is characterized by a rich assemblage of conodonts and several pyritized radiolarians, unlike the Scisti Silicei, which provides a good assemblage of radiolarians but few conodonts (Fig. 2). The CAI of the Mount Volturino specimens is 3 (Giordano et al., 2010, 2011). Parvigondolella lata, M. bidentata, and P. andrusovi first occur at ~12 m. The first occurrence (FO) of M. hermsteinii, which defines the base of the M. hermsteinii–P. andrusovi Zone (Kozur and Mock, 1991; Giordano et al., 2010, 2011), occurs at ~18 m along with Parvigondolella vielyencki. At ~39 m, M. hermsteinii/M. posthernsteinii transitional form (Giordano et al., 2010, 2011) first occurs. Unfortunately, radiolarians from the “transitional interval” are very poorly preserved (Giordano et al., 2010). The base of the B. deweveri Assemblage Zone (Carter, 1993) occurs at 41 m. The base of the P. moniliformis Zone occurs at 45 m, while the base of the Globolaxtorum tozeri Zone is at 51 m (Giordano et al., 2010, 2011). The Rhaetian/Hettangian boundary is approximately located in the upper portion of the section, within the Nevers Member of the Scisti Silicei (Fig. 2; Bertinelli, 2003).

Madonna del Sirino Section

The section of Madonna del Sirino is located on the western flank of Mount Sirino, along the trail connecting the Madonna del Busco Sanctuary to the Madonna del Sirino Sanctuary (geographic coordinate system, datum WGS 84: 40°07′N; 15°48′E). The upper part of the Calcari con Selce and the Scisti
Figure 1. Paleogeography and structural map showing the tectonic units of the Lagonegro Basin. Black solid stars indicate outcrops of studied sections. Paleogeography (A) modified from Cosentino et al. (2010); structural map (B) modified from Bertinelli et al. (2005b).
Figure 2. Lithostratigraphy, conodont, and radiolarian biozonation, total organic carbon (TOC), and δ13Corg of Lagonegro sections. Biostratigraphy is based on, and integrated from, Giordano et al. (2010). Three δ13Corg decreases (S1, S2, and S3, gray bars) are correlated using biostratigraphy. These δ13Corg events show similar magnitude (3‰–5‰). Their durations have been established using the age model of Pignola-Abriola section provided by Maron et al. (2015): S1 = ~0.7 m.y., S2 = ~1 m.y., S3 = ~1.3 m.y. In particular, the S3 decrease culminated at the Norian/Rhaetian boundary. TOC roughly doubles within S3 at Pignola-Abriola and begins to increase by the Norian/Rhaetian boundary at the other two sections.
Siliciclastics are exposed in this section. The Calcaro con Selce consists of well-bedded micritic limestones, commonly with cherty nodules. The red horizon distinctive of the “transitional interval” lies in the upper part of Calcaro con Selce exposed at this section (Reggiani et al., 2005; Tanner et al., 2007). This interval consists of siliceous shales and scattered radiolitaries (Passeri et al., 2005). The overlying sediments belonging to Scisti Silicini are made up of red and green radiolarian-bearing siliceous shales and cherts with minor calcarenites (Reggiani et al., 2005; Tanner et al., 2007). The Madonna del Sirino section is characterized by small amount of platform-derived carbonates and slumps and by a reduced thickness of Scisti Silicini, thus it belongs to the distal facies association (Scandone, 1967; Miconnet, 1982; Rigo et al., 2005).

Conodont occurrences are scattered (Fig. 2), with a CAI of 3 (Reggiani et al., 2005). In contrast, radiolarians are abundant. *M. bidentata* first occurs at the base of the section, while *P. andrusovi* and *M. hersteinii* appear at ~12 m. The FO of *M. hersteinii* marks the base of the *M. hersteinii–P. andrusovi* Zone (Kozur and Mock, 1991). At ~25 m, the rich radiolarian assemblages permit the identification of the base of the *P. moniliformis* Zone (Carter, 1993). The base of the *G. tozeri* Zone occurs at ~33 m. The Rhaetian-Hettangian boundary is approximately located in the upper portion of the section, within the Nevera Member (Fig. 2), between the last occurrence of Rhaetian radiolarians and the first occurrence of Jurassic radiolarians (Reggiani et al., 2005).

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METHODS

The Lagonegro Basin has been investigated for total organic carbon (TOC) content and organic carbon isotopes (δ¹³Corg). For the TOC analyses, we analyzed 101 rock samples from the Pignola-Abriola section, 80 samples from the Mount Volturino section, and 47 samples from the Madonna del Sirino section. For the δ¹³Corg analyses, we analyzed 96 samples from the Pignola-Abriola section, 50 samples from the Mount Volturino section, and 31 samples from the Madonna del Sirino section (see Supplemental Material). All samples were washed in high-purity water and selected to avoid sampling unrepresentative portions (e.g., fracture-filling mineralization, bioturbation, and diagenetic alteration). A few grams of each sample were reduced to a fine powder using a Retsch RM00 grinder and dried overnight at 40 °C.

The TOC investigations were conducted at the University of Padova. The powders were treated with a 10% HCl solution in silver capsules to remove inorganic carbon (i.e., carbonate component). Successively, they were dried on a hot plate at 50 °C and analyzed using a Vario Macro CNS Elemental Analyzer. Results were calibrated against Sulfanilamide standard (N = 16.25%; C = 41.81%; S = 18.62%; H = 4.65%). The analytical uncertainty of the instrument, expressed as relative standard deviation, is σ = 0.5%.

For the δ¹³Corg measurements, all the pulverized rock samples were acid-washed with 10% HCl for at least three hours, usually overnight. Successively, the samples were neutralized in deionized water, dried at 40 °C overnight, and wrapped in tin capsules. Forty-one samples from the Pignola-Abriola section were analyzed using a GVI Isoprime continuous-flow–isotope ratio mass spectrometer (CF-IRMS) at Rutgers University: multiple blank capsules and certified isotope standards (International Atomic Energy Agency [IAEA] N-1 = 0.43‰, IAEA N-3 = 4.72‰, National Bureau of Standards [NBS] 22 = -30.03‰, Coplen et al., 2006) and an in-house sediment standard were added for every batch of isotopic analysis. The standard deviation of the in-house standards during the period of analyses was better than 0.2‰. The other 60 samples from the Pignola-Abriola section and the samples from all the other sections were analyzed using a Delta V Advantage mass spectrometer connected to a Flash HT elemental analyzer at the University of Padova. For every set of analysis, multiple blank capsules and isotope standards (IAEA CH-6 = -10.45‰, IAEA CH-7 = -32.15‰, Coplen et al., 2006) were included. The standard deviation of the in-house standard during the period of analyses was better than 0.3‰.

Duration of isotopic excursions has been calculated by applying the age model proposed by Maron et al. (2015) on the Pignola-Abriola section (see Supplemental Material [see footnote 1]). This model is based on the magnetostratigraphic correlation with the Newark APTS (Maron et al., 2015).

**RESULTS**

We construct late Norian global δ¹³Corg records for three sections outcropping in the Lagonegro Basin (southern Italy). Several lines of evidence indicate that our δ¹³Corg data record a likely primary signal. First, the conodont alteration index (CAI) of specimens recovered in the Lagonegro Basin ranges between ≤1.5 (Pignola-Abriola; Giordano et al., 2010) and 3 (Mount Volturino and Madonna del Sirino; Bazzucchi et al., 2005; Reggiani et al., 2005; Rigo et al., 2005, 2012a), suggesting that the burial temperatures never exceeded 100 °C (Epstein et al., 1977; Di Leo et al., 2002) and 200 °C (Epstein et al., 1977; Bazzucchi et al., 2005; Reggiani et al., 2005; Rigo et al., 2005, 2012a), respectively. The effect of these temperatures is negligible on the δ¹³Corg signal, because temperatures approaching those of oil generation are required to significantly alter the δ¹³Corg primary signal (Cramer and Saltzman, 2007). Second, the Pignola-Abriola δ¹³Corg trend is consistent with (and adds significant detail to) the δ¹³Corg profile illustrated in Preto et al. (2013) for the Norian/Rhaetian interval (S3 in Fig. 3). The Pignola-Abriola δ¹³Corg profile shows greater detail than the Mount Volturino and Madonna del Sirino profiles. This different resolution is mainly related to the greater abundance of organic matter in the samples (see the TOC content in Fig. 2) of the Pignola-Abriola section, which allows us greater density of δ¹³Corg analyses. The samples also contain a higher siliciclastic component (i.e., dark shales and marls), and this lithological feature is likely related to the more proximal position of the Pignola-Abriola section within the Lagonegro Basin (Scandone, 1967; Amodeo, 1999; Bertinelli et al., 2005b; Rigo et al., 2005, 2016; Giordano et al., 2010, 2011).

The Pignola-Abriola δ¹³Corg profile depicts three decreases (S1, S2, and S3) followed by a recovery phase toward background values (Fig. 2). Using the
The Norian carbon and strontium decreases are compatible with the late Rhaetian–early Hettangian warming interval (sensu Trotter et al., 2015). Figure 3 shows the correlation of the Lagonegro δ13Corg profiles with published records: (1) Kennecott Point section, Queen Charlotte Islands, British Columbia, Canada (Hesselbo et al., 2002; then Whiteside et al., 2010; (2) δ13Corg and δ13Ccarb of Pignola-Abriola section, Lagonegro Basin, Italy (this work, chronology by Maron et al., 2015; δ13Ccarb record modified from Preto et al., 2013); (3) composite δ13Ccarb record from Muttoni et al. (2014); Pizzo Mondello (southern Italy, from ca. 215 to ca. 209 Ma) and Brumano (northern Italy, from ca. 206 to ca. 202 Ma) and Italcementi Quarry (northern Italy, dashed line); (4) composite δ13Ccarb record from Korte et al. (2005); (5) Mount Volturino section, Lagonegro Basin, Italy (this work); (6) Madonna del Sirino section, Lagonegro Basin, Italy (this work); (7) composite profile for Queen Charlotte Islands: Kennecott Point (from 0 to 120 m) and Frederick Islands (from –215 m to –135 m) (Whiteside and Ward, 2011); (8) Lake Williston, British Columbia, Canada (Wignall et al., 2007); and (9) 87Sr/86Sr profile from Callegaro et al. (2012): data from conodonts (Callegaro et al. [2012] original data and Korte et al. [2003]). The 87Sr/86Sr profile has been locally weighted smoothing curve (10%).

In particular, S3 appears to occur also in other Tethyan and North American successions (chemostratigraphic correlation highlighted by the orange bar). This correlation is well constrained by conodont, ammonoid, radiolarian, and bivalve biostratigraphy. Biostratigraphic correlations between ammonoid and conodont biozones are based on Rigo et al. (2016). The carbon-isotope stratigraphy of the Pignola-Abriola section depicts three decreases of similar magnitude (3%–5%) and duration (≈1 m.y.) throughout the late Norian (S1, S2—highlighted by gray bars; and S3—highlighted by the orange bar). In particular, S3 appears to occur also in other Tethyan and North American successions (chemostratigraphic correlation highlighted by the orange bar). This correlation is well constrained by conodont, ammonoid, radiolarian, and bivalve biostratigraphy. S3, along with S1 and S2, correlates with the decreasing trends in the 87Sr/86Sr record (Callegaro et al., 2012). All these oscillations occur within the W3 warming interval (sensu Trotter et al., 2015; blue and red bars). Fire scars (red bar) left on petrified trunks, indicating wildfires, show similar age (Norian) (Byers et al., 2010). The Carboniferous large igneous province (LIP) is 214 ± 7 Ma (Ernst and Buchan, 2001; Prokoph et al., 2013), compatible with the Norian carbon and strontium decreases. The late Rhaetian–early Hettangian δ13Corg signature of the Central Atlantic Magmatic Province (CAMP) is highlighted by R1 gray bar: its original areal extent (Marzoli et al., 1999) is shown on the map as a gray dotted area. All the discussed sections are shown on the map: (1) British Columbia Islands (Canada); (2) Lake Williston (Canada); and (3) Lagonegro Basin (Italy).
Correlations with Published Records

The detailed comparison of the studied sections indicates that the carbon-isotope records are correlatable within the Lagonegro Basin, especially for S3, suggesting that these recurrent decreases in δ13Corg are likely a common feature within the Basin. The correlation among the studied sections cannot be considered an artifact of the lithostratigraphy, because the base of the Scisti Silicei has been shown to be diachronous within the Basin (Giordano et al., 2010, 2011). Moreover, based on chemostratigraphy integrated with biostratigraphy, the isotopic trend appears unrelated to the lithological facies; in fact, coeval shifts are observed in different lithotrophic units (Fig. 2).

Only a few other Norian sections have been investigated for the organic carbon-isotope record. Wignall et al. (2007) observed a ~3‰ negative δ13Corg shift at the Norian/Rhaetian boundary in the composite Lake Williston record (British Columbia, Canada), likely correlatable with our S3 event (Fig. 3), based on biostratigraphic constraints. Specifically, the extinction of the large forms of bivalve Monotis, the FAD of the conodont Proparvicingula moniliformis, and the base of the radiolarian Proaraneasterina moniliiformis Zone are considered virtually coeval biohorizons (Rigo et al., 2016) and have been suggested in fact to be used to approximate the base of the Rhaetian stage (Ogg in Gradstein et al., 2012; Rigo et al., 2016; Bertinelli et al., 2016). Notably, S3 in Lake Williston is not characterized by a highly noisy record as in Pignola-Abriola (Fig. 3), where the high-frequency fluctuations are probably due, as discussed above, either to the higher sampling resolution or to mixed carbon sources.

In the Kennecott Point section (Queen Charlotte Islands, British Columbia, Canada), Ward et al. (2004) recognized a positive δ13Corg excursion corresponding with the extinction of the bivalve Monotis, at the Norian/Rhaetian boundary, which is interpreted as resulting from enhanced stagnation due to subdued ocean circulation (Sephton et al., 2002; Ward et al., 2004). This result conflicts with the negative δ13Corg shift recorded at the Norian/Rhaetian boundary in the Lagonegro Basin (Maron et al., 2015; Rigo et al., 2016; this work). In fact, Ward et al. (2004) and subsequently Whiteside and Ward (2011) establish the base of the Rhaetian stage at the last occurrence of the bivalve Monotis. In their work, Ward et al. (2004) noticed a reduction in maximum Monotis shell size approaching the final extinction. The presence of dwarfed forms has been observed also by McRoberts et al. (2008) and explained as a peculiar feature of Monotis around the Norian/Rhaetian boundary in response to stressed environments and/or during recovery phases following mass extinction events. Therefore, the δ13Corg negative peak (δ13Corg = −30.5‰) occurring ~10 m below the positive δ13Corg excursion recorded in Kennecott Point section...
and coinciding with the last occurrence of the large-sized Monotis (i.e., ~8 cm, Ward et al., 2004) could be correlated with the minimum δ13Corg value reached in S3 in the Lagonegro Basin (Fig. 3). Whiteside and Ward (2011) implemented the Kennecott Point δ13Corg record with new data from Frederick Islands (Queen Charlotte Islands, British Columbia, Canada), offering an almost complete Norian organic carbon-isotope stratigraphy for the Queen Charlotte Islands. The North American Norian δ13Corg record is characterized by rapid oscillations associated with relatively low faunal generic diversity (Whiteside and Ward, 2011). These carbon-cycle perturbations are referred to as a “chaotic carbon interval,” which is in contrast to stable carbon-isotope intervals characterized by high-richness faunas (Whiteside and Ward, 2011). Using the biostratigraphic constraints proposed by Rigo et al. (2016), the conodont and radiolarian biozones recognized in the Lagonegro Basin can be correlated to the ammonoid biozones of the North America realm. Specifically, the ammonoid Gromohalorites cordilleranus Zone coincides with the conodont Mockina bidentata Zone and Parvigondolella andrusavoi–Misikella hernsteini Zone, while the Paracoclocleras amoenum Zone corresponds to the conodont M. posthernsteini Zone and radiolarian Propravicingula moniliformis Zone (Orchard, 1991; Carter, 1993; Daygs and Daygs, 1994; McRoberts et al., 2008). Therefore, we tentatively correlated S1 and S2 with the two Norian decreases recorded at Queen Charlotte Islands as shown in Figure 3. In agreement with the biostratigraphic correlations summarized in Rigo et al. (2016), S1 and S2 should occur within the base of the ammonoid G. cordilleranus Zone, while S3 should reach its minimum close both to the base of the ammonoid P. amoenum Zone and the disappearance of large forms of bivalve Monotis. As already discussed, a significant negative peak occurred in correspondence to the extinction of the Norian Monotis forms, which we correlated to the S3 minimum. According to this correlation, the observed δ13C perturbations can be traced over wide areas (i.e., North America and Tethys domains): in fact, the Lagonegro Basin was located on the eastern side of the supercontinent Pangea, while the Queen Charlotte Islands were positioned on the other side of the Panthalassa Ocean during the Norian (Fig. 3). These results consequently suggest a global significance of the δ13C perturbations and, in turn, of the mechanisms affecting the organic carbon record during the late Norian.

Causes of Carbon-Cycle Perturbations

The multiple δ13Corg events documented in the Norian were likely caused by retention of 13C or the release of isotopically light carbon into the atmosphere-ocean system. This relative increase in 13C can originate from different mechanisms, such as the isolation of an epeiric sea, a decrease in primary productivity, or input of 13C from a comet impact, methane hydrate dissociation, peatland thermal decomposition, and/or enhanced magmatic activity (e.g., Kent et al., 2003; Hesselbo et al., 2004; Higgins and Schrag, 2006; Jenkins, 2010; Tanner, 2010; Meyers, 2014; Schaller et al., 2016). S1 and S2 are recognizable at least at a basinal level, while S3 seems to have a more convincing global occurrence (Rigo et al., 2016). Therefore, since S1–S2 and S3, are likely different in nature, different causative mechanisms should be invoked to explain these perturbations in the δ13Corg curve.

S1 and S2 require some local mechanism(s) affecting the Lagonegro Basin during the late Norian. These two decreases might be explained as the result of changes in relative contributions of δ13Corg components. Organic matter present in sediments can include a number of different components, such as bacteria, phytoplankton, zooplankton, pollen, and/or other terrestrial biomass. Each of these components is characterized by a specific value of δ13Corg. This means that changes in relative contributions of these components could affect the bulk δ13Corg record, without necessarily requiring changes in the global isotope composition of the ocean and/or the atmosphere (van de Schootbruggae et al., 2008; Fio et al., 2010; Bartolini et al., 2012), which instead would be reflected as global δ13C variations.

The interpretation of S3 requires a more comprehensive discussion. Because this δ13Corg decrease has been clearly recognized on both sides of the supercontinent Pangea, we should consider only those mechanisms able to affect the global carbon cycle. Therefore, we can exclude some of the above-listed hypotheses. First, it is well established that the Lagonegro Basin was a branch of the western Tethys, not an epeiric sea (Şengör et al., 1984; Catalano et al., 2001; Stampfli et al., 1991; Stampfli and Marchant, 1995; Ciarcapica and Passeri, 1998, 2002; Stampfli et al., 1998; Stampfli et al., 2003; Speranza et al., 2012). Second, the decrease in primary productivity, as explanation for δ13Corg decrease, should result in a TOC decrease; instead, TOC maintains almost constant values throughout the Lagonegro Basin record and even increases in the Pignola-Abriola S3, where it roughly doubles (Fig. 2). Third, a comet impact can release ~106 to 107 Gt of light carbon (δ13C = −45%) depending on its size (Greenberg, 1998), producing a rapid (less than 1 k.y.) negative shift in the δ13C values of ~0.2‰–1.6‰ (Kent et al., 2003; Kahiho et al., 2009). A comet impact is thus able to cause sudden and short-lived decreases in the δ13C record, which contrasts with the gradual and relatively slow decreases over S3 of the studied δ13Corg profiles. Moreover, the only impact structure crater documented in the upper Norian is the Manicougan crater, which has a radiometric age of ca. 214.5 (214.5 ± 0.5 Ma with 40Ar/39Ar and 214.56 ± 0.05 Ma with U/Pb dating, Ramezani et al., 2005), ~3 m.y. before S1.

Among the remaining hypotheses, the most plausible mechanism able to introduce isotopically light carbon into the atmosphere-ocean system throughout the latest Norian could be the injection of volcanicogenic greenhouse gases. The Rhaetian δ13Corg decrease (R1) might instead be correlated with the negative organic carbon-isotope excursion recognized worldwide just before the Triassic/Jurassic boundary, the so-called initial negative carbon-isotope excursion (CIE) (McElwain et al., 1999; Pálfy et al., 2001, 2007; Hesselbo et al., 2002; Dal Corso et al., 2014). The initial CIE is proposed as a prelude phase of the main CAMP activity (e.g., Hesselbo et al., 2002; Guex et al., 2004; Whiteside et al., 2010; Ruhl and Kurschner, 2011; Dal Corso et al., 2014). If this is true, the Norian organic carbon-isotope perturbations recorded in the Lagonegro Basin could be interpreted as pre-CAMP volcanic
activity, and S3 might have been caused by a separate input of volcanogenic CO₂ to the atmosphere-ocean system. We cannot exclude a priori that S1 and S2 also might be the result of inputs of volcanogenic CO₂. In fact, the recurrent δ¹³C_carb decreases (S1, S2, and S3) during the Norian could be interpreted as representing the typical pulsing behavior of magmatic activity (e.g., Tolan et al., 1989; Saunders et al., 1997; Courtillot and Renne, 2003; Jerram and Widdowson, 2005; Ernst et al., 2008; Greene et al., 2012). We cannot exclude that S1 and S2 might occur at global scale, but we were not able to recognize them in the North American Lake Williston section because this succession covers a limited interval across only the Norian/Rhaetian boundary δ¹³C_carb. Moreover, the correlation with the composite British Columbia Islands succession is not straightforward because of a gap immediately below the Norian/Rhaetian boundary. Nevertheless, in order to take into consideration on one hand results and on the other hand the reliability of proposed correlations, the following interpretations can be considered more pertinent for S3 and hypothetical for S1 and S2.

These volcanic emissions would have enhanced chemical weathering via acceleration of the hydrological cycle and increased nutrient discharge (e.g., nitrates and phosphates) to the ocean, driving increased biological productivity (e.g., Jones and Jenkyns, 2001; Jenkyns, 2010; Pogge von Strandmann et al., 2013) and resulting in high TOC content, which is observed in the case of the Pignola-Abriola S3 event.

These recurrent inputs of isotopically light carbon are recorded also in the Norian/Rhaetian composite δ¹³C_carb profile constructed by Muttoni et al. (2014) (Fig. 3). This composite δ¹³C_carb curve depicts three negative peaks at ca. 212, 206, and 202 Ma, correlatable with the dating of the minimum δ¹³C_carb values of S1, S3, and R1 respectively (ca. 211.5, 206, and 201 Ma; Fig. 3). Unfortunately, this δ¹³C_carb curve (Muttoni et al., 2014) has a gap exactly in the interval between 209 and 207 Ma, when S2 may have occurred. To further support the global significance of S3, we also compare our data with the δ¹³C_carb profile of Korte et al. (2005), which displays a minimum value of the δ¹³C_carb at ca. 206 Ma, correlatable with the S3 negative δ¹³C_carb peak at Pignola-Abriola (Fig. 3). This line of evidence further highlights the global meaning of the Norian/Rhaetian boundary carbon-cycle perturbation (i.e., S3).

The occurrence of Norian volcanic activity is also supported by an increase of surface water temperature of the Tethyan subtropics of ~6 °C (~1.5‰), re-
corded in the δ¹⁸Ophos curve from biogenic apatite (labeled “W3” in Trotter et al., 2015). The W3 warming phase is documented in the Norian and is correlatable with S1, S2, and S3 (Fig. 3). A late Norian warming is further supported by paleoecological and pedogenic evidence, which estimate an increase of atmospheric CO₂ from 600 to 2100–2400 ppm and 2000–3000 ppm, corresponding to a warming of ~3–4 °C and ~7–10 °C, respectively (McElwain et al., 1999; Cleveland et al., 2008). The proposed scenario is hence in agreement with estimates based on numerical coupled ocean-atmospheric climate models performed for the Upper Triassic (Huynh and Poulsen, 2005).

An additional piece of evidence supporting the hypothesis of a magmatic activity as the source of isotopically light carbon in the system is the δ⁸⁷Sr/δ⁸⁶Sr record (Callegaro et al., 2012). Because the residence time of strontium is longer (~2.4 m.y.; Jones and Jenkyns, 2001) than the mixing time of the ocean (~1–2 k.y.; e.g., Broecker and Li, 1970; Gordon, 1973; Hodell et al., 1990; Garrett and St. Laurent, 2002), the δ⁸⁷Sr/δ⁸⁶Sr curve is representative of the global seawater composition (Veizer et al., 1997; Korte et al., 2003). The δ⁸⁷Sr/δ⁸⁶Sr composi-
tion of seawater is controlled by two major fluxes: the riverine flux, whose δ⁸⁷Sr/δ⁸⁶Sr depends on the balance between the weathering of highly radiogenic old sialic crust and less radiogenic young basalts (average δ⁸⁷Sr/δ⁸⁶Sr = ~0.710) and the hydrothermal flux, sourced from the mantle δ⁸⁷Sr (average δ⁸⁷Sr/δ⁸⁶Sr = ~0.703; e.g., Faure, 1986; Palmer and Edmond, 1989; Veizer et al., 1997; Taylor and Lasaga, 1999). Therefore, increases of seawater δ⁸⁷Sr/δ⁸⁶Sr are commonly interpreted as increased continental weathering of highly radiogenic old sialic crust and/or denudation rates, which in turn could be driven by humid climate and/or tectonics (Palmer and Elderfield, 1985; Raymo et al., 1988; Hodell et al., 1989), whereas negative shifts are usually linked to weathering of young basalts (which implies the emplacement of some kind of volcanic activity) and/or increased rate of seabed spreading (Berner and Rye, 1992; Jones and Jenkyns, 2001). The δ⁸⁷Sr/δ⁸⁶Sr profile (Callegaro et al., 2012) depicts three negative excursions correlatable with the δ¹³C_carb decreases recognized throughout the late Norian in the Lagonegro Basin, Queen Charlotte Islands and Lake Williston sections (Fig. 3). However, at the base of the Rhaetian stage, the δ⁸⁷Sr/δ⁸⁶Sr curve shows an opposite trend compared to the δ¹³C_carb record. In fact, while the δ¹³C_carb returns to background values, the δ⁸⁷Sr/δ⁸⁶Sr profile keeps decreasing, suggesting two possible scenarios: (1) a lag in response time of the δ⁸⁷Sr/δ⁸⁶Sr system due to its longer seawater residence time; or (2) persistent magmatic activity and/or weathering of volcanic rocks, coupled with increase of primary productivity and/or inhibition of the organic matter oxidation processes (increasing δ¹³C_carb). The decrease in efficiency of organic matter recycling mechanisms may be related to oxygen-depleted conditions, which is supported by the high TOC content (Fig. 2, see TOC content after S3 in Pignola-Abriola). Moreover, the Rhaetian δ¹³C_carb profile is mimicked by the δ¹⁸O/δ⁶⁸O curve recorded in Japan (Kuroda et al., 2010) and in the United Kingdom (Cohen and Coe, 2007), suggesting that an abrupt and intense large-scale event affected multiple isotopic systems during the Late Triassic, causing large perturbations in the δ¹³C_carb, δ¹⁸O_carb, δ⁸⁷Sr/δ⁸⁶Sr, and ¹⁸⁷ Os/¹⁸⁸ Os records. Seawater ¹⁸⁷ Os/¹⁸⁸ Os, like δ⁸⁷Sr/δ⁸⁶Sr, is controlled by two major fluxes: (1) weathering of continental crust (average ¹⁸⁷ Os/¹⁸⁸ Os = ~1.3) and (2) mantle and/or extraterrestrial inputs (average ¹⁸⁷ Os/¹⁸⁸ Os = ~0.13) (e.g., Shirley and Walker, 1998; Peucker-Ehrenbrink and Ravizza, 2000; Cohen and Coe, 2007; Kuroda et al., 2010). In particular, young mantle-derived basalts could release large amounts of unradiogenic Os; hence, based on this rationale, Os isotopes are used to identify the initiation of major basalt volcanism (e.g., Cohen and Coe, 2007; Ravizza and Peucker-Ehrenbrink, 2003; Turgeon and Creaser, 2008; Tejada et al., 2009; Kuroda et al., 2010).

The late Norian volcanic activity seems to resemble the best known Meso-
zoic LIPs, such as the Wrangellia (estimated duration: late Ladinian–early Norian, U-Pb zircon dating from a gabbro sill: 232.2 ± 1.0 Ma, Mortensen and
cent estimates range between 225 and 450 × 10^3 km³ (Ernst and Buchan, 2001; et al., 2013). The total volume of the Angayucham oceanic plateau has been (late Rhaetian–early Hettangian, e.g., Marzoli et al., 2006a, 2006b; Blackburn et al., 2013), and the Karoo-Ferrar (Toarcian, 183.1 Ma, e.g., Bompfleur et al., 2014; Sell et al., 2014). The emplacement of all these LIPs coincides with episodes of significant biotic crises, suggesting that a causal relationship might exist between eruptions and climate change (e.g., Rampino and Stothers, 1988; Furin et al., 2006; Rigo et al., 2007, 2012a; Rigo and Joachimski, 2010). With respect to the tempo, the estimated duration of the Norian activity is very similar to those inferred for the CAMP and the Wrangellia. The main phase of CAMP volcanism lasted less than 1.6–2 m.y.; a comparable duration of 2 m.y. has been proposed for the Wrangellia phase (Green et al., 2010, 2012). These durations are consistent with those estimated in the Pignola-Abriola section, where the δ¹³Corg decreases last between 0.7 and 1.3 m.y. The total duration of the late Norian volcanic activity, from S1 to S3, is ~7 m.y., if the age model of Maron et al. (2015) is adopted; this is consistent with the total duration of the Karoo-Ferrar event (~8–10 m.y.; Jourdan et al., 2007; Hastie et al., 2014) and of each major pulse of the Karoo-Ferrar LIP, which lasts from ~0.8–3 to 4.5 m.y. (Jourdan et al., 2007). All these estimated durations are comparable to those observed in the Pignola-Abriola section during the late Norian (~1.3 m.y. for each decrease).

The sparse and rare outcrops of Norian successions limit the recognition of volcanic deposits associated with the emplacement of a LIP during the late Norian, which is identifiable so far only by its geochemical signatures. Volcanic deposits linked to this event could have undergone subduction, accretion as allochthonous terranes, or collision. Recent dating of the Late Triassic Angayucham large igneous province (Alaska, Pallister et al., 1989) gives an estimated age of 214 ± 7 Ma (Ernst and Buchan, 2001; Prokoph et al., 2013), which is consistent with both the Norian age of the CAMP and δ¹³Corg decreases (from ca. 214–206 Ma, Maron et al., 2015) and distinguishable from those of Wrangellia (late Ladinian–early Norian, Mortensen and Hulbert, 1991) and CAMP activities (late Rhaetian–early Hettangian, e.g., Marzoli et al., 2006a, 2006b; Blackburn et al., 2013). The total volume of the Angayucham oceanic plateau has been evaluated from the areal extent of outcropping ophiolites, and the most recent estimates range between 225 and 450 × 10^3 km³ (Ernst and Buchan, 2001; Prokoph et al., 2013). This volume is not dissimilar from that of the Wrangellia oceanic plateau (~500–1000 × 10^3 km³); Lassiter et al., 1995; Ernst and Buchan, 2001; Prokoph et al., 2013), although it is of a single peak (S3). It is also worth noting that the estimated durations for the secondary and short-lived δ¹³Corg peaks in the Pignola-Abriola section range between ~10 and 100 k.y. according to the age model of Maron et al. (2015), which essentially means that each single peak might represent an input of ¹³C-rich carbon in the ocean-atmosphere system due to a combination of possible sources, which include volcanic gases, methane release, and wildfires. Whereas wildfires and methane hydrate dissociation contributed to the magnitude of the Norian δ¹³Corg decreases, they should be considered as possible amplification factors of the magmatic activity, which we propose as the trigger mechanism of the Norian carbon-cycle perturbations.

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CONCLUSIONS

The organic carbon-isotope record of the Lagonegro Basin (western Tethys) shows the occurrence of a ~5‰ negative shift close to the Norian/Rhaetian transition, preceded by two additional δ13Corg decreases of similar magnitude (3‰–5‰), correlatable within the Lagonegro Basin. Moreover, the carbon-isotope perturbation close to the Norian/Rhaetian boundary is correlatable (using biostatigraphy) with that recognized in the North America realm, supporting the idea that the latest Norian carbon cycle was affected at a global scale. We propose that the trigger mechanism for the input of isotopically light carbon in the ocean-atmosphere system was the emplacement of a large igneous province, possibly amplified by consequent feedbacks. The δ13Corg profile, the 87Sr/86Sr curve, and increase in the pCO2 values strongly support this scenario.

This suggested late Norian volcanic activity was thought to be active between 214 and 206 Ma and is tentatively attributed to the Angayucham province, a complex ocean plateau originally located on the western margin of North America and today occurring in Alaska. The late Norian δ13Corg records presented here improve the Late Triassic organic-carbon-isotope record, which displays a series of decreases we link to the emplacement of different LIPs: the late Ladinian–early Norian Wrangellia, (possibly) the late Norian Angayucham, and the late Rhaetian–early Hettangian CAMP. These events may have had extreme environmental consequences, such as a decrease in primary productivity and/or a warming phase, which could have favored the establishment of humid conditions and episodes of seawater oxygen depletion, biotic crises, and extinctions, contributing to the complex history of this particular period of time.

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