The dawn of CAMP volcanism and its bearing on the end-Triassic carbon cycle disruption

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Abstract: The cause-and-effect relationship between the c. 201 Ma eruption of the Central Atlantic magmatic province (CAMP) and the end-Triassic abrupt climate change and mass extinction is at present based on controversial temporal correlations. Upper Triassic sedimentary strata underlying CAMP basalts in Morocco illustrate a clear mineralogical and geochemical fingerprint of early CAMP basaltic eruptions, namely unusually high contents of MgO (10–32 wt%) and of mafic clay minerals (11–84%). In the same rocks a coincident negative carbon-isotope excursion (CIE) is present, equivalent to the so-called ‘initial negative CIE’ recorded worldwide shortly before the Triassic-Jurassic boundary. The new data show that the onset of CAMP activity preceded the end-Triassic carbon cycle disruption and that the initial negative CIE is unequivocally synchronous with CAMP volcanism. The results of this study strongly support the hypothesis that the culmination of pollution of atmosphere and seawater by CAMP-derived volcanic gases was the proximate cause of the end-Triassic mass extinction.

Supplementary material: The stratigraphic position of analysed samples, and the C-isotope, bulk-rock mineralogy, element analysis, Mg–Al–Si ternary diagram and trace-element analysis data are available at www.geolsoc.org.uk/SUP18707.

Mass extinction events that punctuate the evolution of life on Earth are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are often coincident with dramatic disturbances in the global carbon cycle that are registered in the geological record as negative carbon-isotope excursions (CIEs), suggesting sudden input into the ocean–atmosphere system of massive quantities of CH4 or CO2 (e.g. Hesselbo et al. 2001). Abrupt environmental and climatic disruption are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001). Abrupt environmental and biological changes are caused by paroxysmal environmental and climatic disruption (e.g. Wignall 2001).
As suggested by several researchers, one of the trigger mechanisms of the end-Triassic mass extinction and accompanying negative CIEs may have been the release of volcanic gases (mainly CO₂ and SO₂) from the Central Atlantic magmatic province (CAMP) into the ocean–atmosphere system (Hesselbo et al. 2002; Guex et al. 2004; Marzoli et al. 2004; Pálfy et al. 2007; Deenen et al. 2010; Whiteside et al. 2010; Ruhl et al. 2011; Schaller et al. 2011; Lindström et al. 2012; Mander et al. 2013). The relative timing of the magmatic event and of the negative CIEs, however, remains controversial. Radioisotopic dating (e.g. Schoene et al. 2010; Marzoli et al. 2011; Blackburn et al. 2013) suggests a synchrony between CAMP and mass extinction. A new zircon U–Pb radioisotopic age for a CAMP intrusion (Amelal sill), which possibly fed the second volcanic unit of the Argana Basin, Morocco, is indistinguishable in age (201.564 ± 0.23 Ma) from the calculated age of a palynological turnover; that is, the disappearance of *Patinasporites densus* and the ‘fern spike’, recorded in the Newark Basin and considered as recording the end-Triassic extinction (Blackburn et al. 2013). Radioisotopic dating of CAMP basalts does not resolve the relative timing of the onset of CAMP volcanism and of the carbon cycle perturbation and mass extinction. In fact, previous studies recording the initial negative CIE in continental sediments fixed it at a level below the first CAMP lava flows both in North America and Morocco (Deenen et al. 2010, 2011; Whiteside et al. 2010). Geochemical and mineralogical data from the marine section of Kendlbachgraben in the Northern Calcareous Alps (Austria) give evidence of distal deposition of mafic volcanic material, possibly deriving from early explosive CAMP activity that is coeval with or slightly precedes the initial CIE and the mass extinction level (Pálfy & Zajzon 2012). However, the extinction among various marine and terrestrial fauna and flora seems to have started before the initial CIE (e.g. Wignall & Bond 2008; Lindström et al. 2012; Mander et al. 2013). Hence, potential cause-and-effect relationships between CAMP volcanism, the initial negative CIE, and extinction on land and in the oceans are not rigorously established, given that existing data from below-CAMP continental sedimentary successions only suggest that the initial negative CIE and extinction stratigraphically preceded the initial outpouring of CAMP basalt.

To constrain the relative timing between CAMP volcanism and the perturbation of the carbon cycle and thus elucidate further the possible role of the CAMP in triggering the end-Triassic environmental disruption and, by association, the mass extinction, two continental sedimentary successions cropping out below the oldest CAMP flood basalts in the Central High Atlas (Morocco) were investigated. Combined δ¹³C_TOC (δ¹³C of total organic carbon), palynology, major and trace elements, and mineralogy of the sediments precisely constrain the sequence of end-Triassic events.

**Geological setting**

The geology of Morocco can be divided into four main domains: from south to north, the Anti-Atlas (Palaeozoic to Precambrian...
terranes), the High and Middle Atlas (Mesozoic rift zones uplifted during the Cenozoic), the Mesetas (a mainly Palaeozoic region), and the Rif (an Alpine belt). In the Anti-Atlas domain, Palaeozoic and Precambrian rocks are exposed up to 2000 m, in response to the marginal up-doming of the West African craton that occurred as the African plate impacted with the Eurasian plate. The earliest magmatic activity is Palaeoproterozoic to early Palaeozoic in age and is preserved as sparse mafic to silicic intrusive and extrusive rocks (e.g. Koyate et al. 2013; Youbi et al. 2013). The Meseta domain is mainly composed of Palaeozoic series, strongly deformed by the Hercynian Orogeny, which created a heterogeneous basement prior to Triassic rifting. Carboniferous magmatism occurred in the Hercynian (Variscan) Meseta domains (central Morocco) and is represented mainly by intermediate–acid and sparsely mafic–ultramafic intrusions (Michard et al. 2008). The Carboniferous mafic–ultramafic intrusions, which have been covered by up to 2000 m of Permian and Triassic sedimentary and volcanic rocks, were exhumed during the Late Jurassic–Early Cretaceous interval (Saddiqi et al. 2009). Triassic to Lower Jurassic continental sedimentary rocks were deposited in extensional intracontinental basins formed prior to and during the breakup of Pangaea. The Upper Triassic red beds (Hofmann et al. 2000) were deposited under a semi-arid to arid climate (Hay et al. 1982) in fluvial, lacustrine and lagoon environments. These red beds were covered by widespread basaltic lava flows of the CAMP, preserved in all Triassic–Jurassic basins in Morocco (Youbi et al. 2003; Marzoli et al. 2004; Verati et al. 2007). Hofmann et al. (2000) indicated the presence of meter-scale asymmetric cycles in the Triassic to Lower Jurassic continental red beds of the Argana Valley (western Morocco), which they attributed to palaeoclimatic and palaeohydrological fluctuations within the Milankovitch frequency. More recently, Deenen et al. (2010) provided a detailed magnetic susceptibility record and suggested distinct frequencies that were tentatively linked to orbitally forced cycles (precession, obliquity and eccentricity). By assuming a 100 kyr eccentricity forcing for one of the magnetic susceptibility frequencies, an average sedimentation rate of c. 6 (±1) cm ka⁻¹ has been calculated (Deenen et al. 2010).

Material and methods

Studied sections and sampling

Two sections from Morocco were sampled in detail (Figs 2 and 3): the Tiourjdal section in the southern Central High Atlas (31°07'45"N, 7°22'70"W) and the Oued Lahr section in the northern Central High Atlas (31°36'45"N, 7°22'53"W). The sedimentary succession in both the studied localities consists of a series of black to grey and olive-green claystones and red siltstones that were probably deposited in a lagoon to playa environment (Hofmann et al. 2000) and are overlain by up to c. 300 m of CAMP basalt lava piles (Fig. 3; Marzoli et al. 2004). According to combined bio-, magneto- and chemostratigraphic analyses, the oldest outcropping CAMP flood basalts in Morocco (lower unit) may represent the first known eruptive phase of this LIP (Marzoli et al. 2004; Deenen et al. 2010; Blackburn et al. 2013). In particular, a Late Triassic (Norian–Raetian) age for the continental sequences and, by extension, for the overlying CAMP basalts is provided by previously published palynological data for the Tiourjdal and Oued Lahr sequences (Marzoli et al. 2004).

Forty-three samples from the thickest section (Tiourjdal; c. 6 m of sediments cropping out below the basalts) were collected at a sampling interval of c. 0.15 m to obtain high-resolution mineralogical data (by X-ray diffraction (XRD) analysis); and the dark grey to black levels (22 samples) were analysed for organic carbon isotopes. In the Oued Lahr section only dark grey to black levels (cropping out c. 2.5 m below the basalts) were sampled and analysed, both for XRD and C-isotopes. Twenty-four samples were selected from the Tiourjdal section and six samples from the Oued Lahr section and processed for elemental X-ray fluorescence (XRF) analysis.

Analytical methods

Samples for palynological analysis were processed using standard techniques, using HCl (37%) and HF (45%), as described by Cirilli et al. (2009). The same nomenclature as used by Cirilli et al. (2009) is adopted here. For carbon isotope analyses of TOC, powdered rock samples were repeatedly acid-washed with 10% HCl for 3 h at 70°C in a water bath to remove carbonates and pyrite, and neutralized with deionized water. An aliquot of 10 mg of sample was analysed for δ¹³C_TOC at the University of Oxford (Research Laboratory for Archaeology and the History of Art) with a Carlo Erba NA 1108 elemental analyser coupled to a SERCON Geo 20/20 IRMS running in continuous flow mode with a He carrier gas. The accuracy of isotope analyses (σ = ±0.14‰) was calculated using an alanine in-house standard routinely checked against international standards IAEA-CH-6 and IAEA-CH-7 and traceable back to the VPDB standard.

The bulk mineralogy of fine-grained sediments was studied by XRD, following standard semi-quantitative approaches (Schultz 1964) to allow comparison between samples. XRD analyses were carried out at the University of Padova (Dipartimento di Geoscienze)
using a Philips X’Pert Pro diffractometer in Bragg–Brentano geometry equipped with a Cu X-ray tube and solid-state detector (RTMS, X’celerator). Whole-rock XRF major-element analyses were carried out at the University of Padova (Dipartimento di Geoscienze) with a wavelength-dispersive spectrometry sequential Philips PW2400 spectrometer using standard techniques (Marzoli et al. 2011). Trace element analyses were performed by inductively coupled plasma mass spectrometry at AcmeLabs (http://acmelab.com).

Results

Sporomorph biostratigraphy

According to present and previous analyses, the palynological assemblage of the investigated sedimentary successions suggests a Late Triassic age (Marzoli et al. 2004). Triassic sporomorphs characterize the sediments up to the contact with the basalts (Marzoli et al. 2004). This biostratigraphy is confirmed by the sample OL2 analysed here (0.2 m below the contact with the basalt) from the Oued Lahr section, which yielded a palynological assemblage marked by the presence of Enzonalasporites vigens, Staurosaccites quadrifidus and cf. Samaropollenites speciosus, in association with Patinasporites densus, Classopollis torosus, Classopollis meyerianus and Tsugaepollenites pseudomassulae (Fig. 4). Sample HAJ18, taken from a level c. 1.7 m below the contact with the basalt at Tiourjdal, contains similar, though not very well-preserved sporomorphs, among which are rare Classopolis spp., Patinasporites densus and bisaccates (mostly represented by Alisporites spp.). The presence of the Circumpolles group (e.g. Classopollis murphyae, Classopollis torosus, Classopollis meyerianus), which first appeared in the Norian, and of Patinasporites densus is consistent with a Rhaetian age for the investigated sections (Cirilli et al. 2009; Cirilli 2010; Kürschner & Waldemar Herngee 2010). Palynological studies allow correlation of the onset of CAMP volcanism with sedimentary rocks of other circum-Atlantic basins. A similar Upper Triassic sporomorph assemblage to that identified at Tiourjdal and Oued Lahr was found in sediments up to the contact with the basalts from the Argana Basin, Morocco (Marzoli et al. 2004). In contrast, the last occurrence of Patinasporites densus, which mainly defines the end-Triassic extinction of Blackburn et al. (2013), occurs at c. 0.45 m below the first (oldest) CAMP basalt in the Fundy Basin, Canada (Fowell & Traverse 1995; Cirilli et al. 2009) and c. 10 m below the first CAMP basalt flow in the Newark Basin (e.g. Fowell & Olsen 1993). In accordance with recent U–Pb ages for CAMP basalts (Blackburn et al. 2013), palynological data suggest a slightly diachronous onset of CAMP activity, being slightly older in the Moroccan than in the North American basins. The sub-CAMP stratigraphic sections in the Central High Atlas (Marzoli et al. 2004; this study) appear to be older than the end-Triassic extinction in the Newark Basin, which is marked also by the disappearance of Patinasporites densus (Blackburn et al. 2013).

C-isotope data

The C-isotope signature of organic matter of the 22 samples analysed at Tiourjdal varies from –27.3 to –20.1‰ (versus VPDB). At the
base of the section, δ¹³C_TOC values increase from –24.7 to –20.1‰ and then remain stable up to 1.5 m below the sediment–basalt contact. Negative–positive shifts occur, with minima as low as –27.3‰ followed by 5–6‰ positive rebounds to background values, in the 0.3 m below the base of the basalts (Fig. 3a). The C-isotope signature of organic matter at Oued Lahr varies from –24.3 to –20.3‰. A c. 3‰ negative shift occurs 0.9 m below the base of the basalt (Fig. 3b). The δ¹³C_TOC curve from Oued Lahr (Fig. 3b) does not show the peculiarities of Tiourjdal section, which makes correlation difficult. However, the c. 3‰ negative shift occurring c. 1 m below the base of the basalt can be tentatively correlated with the δ¹³C_TOC negative perturbation occurring c. 1 m below the base of the basalt at Tiourjdal, where the content of trioctahedral sheet silicates is also similar (Fig. 3).

**Whole-rock mineralogy and chemical composition**

A dominant mafic source rock for the continental claystones and siltstones underlying the CAMP basalts can be illustrated through chemical and mineralogical analyses (Figs 3, 5 and 6). Besides diocahedral (low-Mg) sheet silicates (relative abundance 15–52%) and Generally minor quartz (1–30%), both sections are characterized by large amounts (11–84%) of high-Mg trioctahedral sheet silicates (Fig. 3). At Tiourjdal, the percentage of trioctahedral sheet silicates shows irregular changes (Fig. 3a): it first gradually decreases from the bottom of the section to 1.5 m below the sediment–basalt contact (from 35–40 to 20–25%, Fig. 3a) and then shows two distinct peaks, at 1.5 m (81%) and 0.2 m (84%) below the contact. At Oued Lahr, the percentage of trioctahedral sheet silicates is relatively constant (28–41%), with the highest values at 1.6 m below the sediment–basalt contact (Fig. 3b).

Consistent with the described mineralogical compositions is the chemistry of claystones and siltstones from the studied sections, which indicates a high MgO content ranging from c. 10 to c. 33 wt% (Fig. 3). At Tiourjdal, MgO reaches maximum values (up to 32.7 wt%) in two major peaks, at c. 1.5 m and c. 0.3 m below the sediment–basalt contact (Fig. 3a). At Oued Lahr, the MgO content varies from 12.7 to 24.9 wt%, with the maximum value at 1.9 m
below the base of the basalt (Fig. 3b). From the 1.9 m level toward the top of the section, MgO wt% decreases (Fig. 3b). MgO contents are negatively correlated with elements such as SiO₂, K₂O and Rb, which are lower in triocahedral than in dioctahedral sheet silicates. In contrast, no correlation is observed between Mg and other trace elements, which generally display high values (e.g. Ce 15–100 ppm; Zr c. 100–400 ppm) but, Rb excepted, show no systematic variation with stratigraphic position. Light REE are enriched with respect to heavy REE (Fig. 5) when normalized to chondritic values (McDonough & Sun 1995).

Other sub-CAMP sedimentary strata have been previously analysed in the Argana Basin (Morocco) and the Hartford Basin (USA). The Argana section (Daudui & Pot de Vin 2002; Daudui et al. 2007) shows concentrations of chloride + talc + chlorite-smectite mixed layers in the clay fraction (<2 μm) that increase from about 10% at more than 20 m below the basalt contact to 20–90% at 0–9 m below the basalt contact. Talc contents are high (up to 30%) in the c. 2 m below the Argana basalt and decrease upwards to the contact with the basalt. In the same topmost 2 m, c. 10% kaolinite is present, whereas illite occurs throughout the section and tends to decrease upwards, having its highest content (60%) at more than 20 m below the basalt.

Discussion

C-isotope data and correlation with existing end-Triassic δ¹³C_TOC curves

The δ¹³C_TOC variations of the analysed organic matter at Tiourjdal and Oued Lahr need to be discussed in terms of whether they reflect primary or secondary signatures. Thermal alteration owing to contact metamorphism could have resulted in fractionation of the organic C isotopes. Thus, the recorded shifts in the δ¹³C_TOC below the CAMP basalts could reflect thermal alteration of the organic matter rather than changes in the C-isotope composition of the global carbon cycle. Experimental isotopic studies have shown that ¹³C–¹²C bonds are destroyed more rapidly than other C–C bonds during thermal heating of organic matter, resulting in the production of ¹³C-depleted gas and ¹³C-enriched residue (e.g. Sackett et al. 1970; Sackett 1978). Thermally altered shale and coal at a contact with a magmatic intrusion commonly can show an increase (Δδ¹³C is typically 1–2‰) in the δ¹³C signature (e.g. McKirdy & Powell 1974; Simonet et al. 1981; Saxby & Stephenson 1987; Cooper et al. 2007), in contrast to what is observed at Tiourjdal and Oued Lahr. However, it has been also observed that some thermally altered coals intruded by sills and dykes show an ambiguous δ¹³C pattern with a small ¹³C depletion (Δδ¹³C < 2‰) in organic matter at the very contact with the intrusions; this phenomenon is more difficult to explain and could be linked to the inability of the generated ¹³C-depleted volatiles to migrate and their consequent entrapment within a closed system and accumulation around the contact aureole (Meyers & Simonet 1999; Cooper et al. 2007; Schimmelmann et al. 2009). Such a process has clearly not taken place in the samples described here, as subaerially erupted CAMP basalt would have flowed above the Triassic lagoon-playa sediments, allowing the escape of the thermally produced gas. In fact, contact metamorphism produces δ¹³C variations (both positive or negative) in organic matter that are generally small to negligible in magnitude (<2‰) (e.g. Gröcke et al. 2009; Schimmelmann et al. 2009; Aarnes et al. 2010). Therefore, contact metamorphism cannot explain the large (up to 6‰) negative shifts observed in the analysed organic matter of the studied sections (Fig. 3). Further evidence that contact metamorphism did not occur is given by whole-rock mineralogy and chemical composition, and will be discussed below.

Variation in the δ¹³C_TOC could also depend on changes in the source of organic matter through time. However, previous palynological analyses of the studied Moroccan successions (Marzoli et al. 2004) do not show any noteworthy change in the composition of organic matter throughout the sub-CAMP stratigraphic succession in the Central High Atlas (i.e. the palynological assemblage in the below-CAMP black–grey claystones remained effectively constant through time).

The δ¹³C_TOC curve from the Tiourjdal section (Fig. 3a) parallels very closely the published δ¹³C_TOC curves from coeval sub-CAMP sediments in Morocco (Argana Basin) and the Fundy Basin, Nova Scotia, Canada (Deenen et al. 2010, 2011), showing a marked negative CIE (Fig. 7). In the Moroccan and Nova Scotia basins (Deenen et al. 2010, 2011), the c. −6‰ negative CIE occurs in sedimentary strata yielding a similar palynological assemblage (including P. densus, Marzoli et al. 2004; Cirilli et al. 2009; present data) and located just below the first CAMP basaltic flows in each basin. The sub-CAMP sediments in the Argana and Fundy Basins are also characterized by a brief event of reversed magnetic direction (Deenen et al. 2010, 2011) that is tentatively correlated with the E23r chron of the Newark Basin (Kent & Olsen 1999). C-isotope data for the sub-CAMP continental sediments from the Newark and Hartford Basins (USA) are provided by bulk organic matter (re-plotted in Fig. 1) and n-alkanes (Whiteside et al. 2010). Whiteside et al. detected relatively low isotopic values in the strata just underlying the first CAMP basalts in the North American basins (Fig. 1).

The general shape of the δ¹³C curves of the Tiourjdal, Argana and Fundy sections (Deenen et al. 2010, 2011) is surprisingly similar to the end-Triassic δ¹³C curves from marine sections (e.g. St. Audries Bay, SW England; Hesselbo et al. 2002; Fig. 7). In particular, the marked and sharp negative CIE at the top of the sub-CAMP sequences is equivalent in shape and size to the initial CIE (sensu Hesselbo et al. 2002) of the marine sequences. Notably, the initial CIE at Tiourjdal (Fig. 3) comprises a set of negative–positive shifts. Similar high-frequency δ¹³C shifts have been observed also at Csővár (Hungary), where C-isotope data from carbonates show that the initial CIE consists of up to five cycles of negative–positive shifts (Pálfy et al. 2007). The relatively negative values (down to −24.7‰) recorded at the bottom of the sub-CAMP sequences may correspond to the precursor CIE (sensu Ruhl & Kürschner 2011).

Because the correlation with the initial CIE is of crucial importance, this possibility is explored further. Following Deenen et al. 2010, 2011)
(2010, 2011), magnetostratigraphic data seem to support such a correlation, given that the reversed polarity interval detected just below the sharp negative CIE from the Argana and Fundy Basins can be matched with reversed polarity intervals from the St. Audries Bay section (Hounslow et al. 2004). Furthermore, radiotopic age data confirm the correlation; the second oldest lava flow unit from Morocco and the Fundy Basin CAMP basalt has been dated at 201.564±0.054 Ma and 201.566±0.031 Ma (Blackburn et al. 2013), both ages being c. 0.2 Ma older than the U–Pb dated Triassic–Jurassic boundary (201.3±0.43 Ma; Schoene et al. 2010). A time gap of c. 0.2 myr is consistent with the estimated age difference between the Triassic–Jurassic boundary and the initial CIE based on astronomically tuned cyclostratigraphy (Deenen et al. 2010; Ruhl et al. 2010; Blackburn et al. 2013). If the astrochronological results of Blackburn et al. (2013) are accepted, the sub-CAMP CIE predates the CAMP basalts (at least in the Fundy and Argana basins) by less than 10 kyr. Considering the combined astrochronological and radioisotopic data, as well as the evidence that the investigated sub-CAMP strata contain an Upper Triassic pollen assemblage, it is concluded that the sub-CAMP negative CIE could most probably correspond to the global end-Triassic initial CIE as defined by Hesselbo et al. (2002).

Based on the same magnetostratigraphic and cyclostratigraphic data, the positive shift at the base of the Moroccan sections in the Central High Atlas and in the Argana Basin (Deenen et al. 2010) is identified as the positive rebound of the precursor CIE that has been recognized also at St Audries Bay, in SW England, in the Tethys realm, and in the Danish Basin (Ruhl & Kürschner 2011; Lindström et al. 2012).

**Origin of the mafic signature of studied sediments**

The whole-rock compositions and mineralogy of the studied sediments below the first CAMP basalts in Morocco indicate a major contribution from a mafic source rock. The analysed claystones and siltstones have an MgO content that is markedly higher (MgO >10%) than those of average clays from various geological settings and average continental crust (Gromet et al. 1984; Wedepohl 1995; Fig. 6).

A metamorphic origin for mafic sheet silicates? It may be argued that the abundance of mafic sheet silicates coupled to high MgO values observed in the Oued Lahr and Tiourjdal sections is due to metamorphism induced by heating from the overlying lava flows and/or by infiltration of Mg-rich hydrothermal fluids from the overlying basalt. Such an interpretation has been favoured to explain the high levels of mafic sheet silicates in the Argana Basin, Western High Atlas, Morocco (Daoudi & Pot de Vin 2002) and in claystones near the contact with the CAMP Hampden basalt flow in the Hartford Basin, Connecticut Valley, USA (April 1980). In this latter basin, the red beds were thermally metamorphosed by the c. 14 m thick Hampden basalt (a simple flow, considering the terminology of Self et al. 1997) and were also infiltrated by mafic hydrothermal fluids. Evidence of circulation of hot fluids in the Newark Basin was provided by Puffer & Laskowich (2012), who recognized diapirc structures that formed probably by hot fluids originating from sediments and intruding the overlying basalt (Orange Mountain Basalt, CAMP, Newark Basin, USA).

In the sedimentary strata at Tiourjdal and Oued Lahr, there is no evidence of significant contact metamorphism with the overlying basalt flows or of fluid infiltration. Unlike the Hartford red beds, MgO contents at Tiourjdal and Oued Lahr are high (>10 wt%) throughout the entire sections; that is, down to more than 6 m below the basalt (Fig. 3). Similarly, triocahedral sheet silicates are persistently high (>20%) and reach the highest levels near the contact with the basalt at Tiourjdal (Fig. 3). Persistently high contents of mafic sheet silicates to a depth of at least 6 m (Tiourjdal) or more than 20 m (Argana), and fluctuations in the amounts of these mafic sheet silicates throughout the section at Tiourjdal (as described above, there is a gradual decrease from the bottom of the section to 1.5 m below the sediment–basalt contact and there are two distinct peaks, at 1.5 and 0.2 m below the contact; Fig. 3), are inconsistent with a contact metamorphic event. Indeed, contact metamorphism
would induce a decreasing effect in terms of temperature, and thus of new mineral formation, away from the basalt contact. Contact metamorphism is hampered particularly by the development of a basal crust at the base of compound pahoehoe lava flows (Self et al. 1997), such as those of the lowest CAMP flows in Morocco (El Hachimi et al. 2011), which isolates the hot lava interior and allows lava inflation and flow for several tens of metres to tens of kilometres. Moreover, in the Tiourjdal section, the basalt–sediment contact is characterized by injections of basalt into sediment (‘load casts’; Marzoli et al. 2004). These load casts form as a result of the rapid deposition of basalt onto a water-saturated sediment and indicate that the underlying deposits were still soft or only slightly consolidated at the time of emplacement of the volcanic rock, further suggesting that the first lava flows were contemporaneous with the deposition of the Upper Triassic sediments. In this case, the water would have played an important role by cooling the basalt quickly and reducing its thermal effect on the sediment. Furthermore, in the Oued Lahr section, the basalt–sediment contact is characterized by a volcanic breccia, typical of the base of pahoehoe-like lava flows (Self et al. 1997), which has acted as an insulator between basalt and sediment.

In addition, the chemical and mineralogical profiles at Tiourjdal and Oued Lahr argue against a significant fluid infiltration from the basalt into the underlying sedimentary strata. For example, the MgO content (10–32 wt%; Fig. 3) of the sedimentary succession at Tiourjdal and Oued Lahr is persistently higher than in the overlying basalts (c. 6–10 wt%; Bertrand et al. 1982; Marzoli et al. 2004). Such a composition would require fluxing of Mg-rich fluids from a very thick lava pile, to elevate the observed MgO content from a pristine value comparable with those of the Hartford Basin red beds (c. 3 wt%; April 1980) or of average clays of typical continental derivation (Fig. 6). Even without considering that hydrothermal fluids would probably rise rather than sink and that there is no field evidence for the presence of fluid pipes that might have induced infiltration of hydrothermal fluids, fluxing of any such fluids would undoubtedly have caused a localized alteration, rather than widespread chemical and mineralogical modification.

The colour of grey to black levels in the Hartford Basin, Connecticut Valley (USA), has been interpreted before as the result of hematite reduction to magnetite under reducing conditions linked to contact metamorphism (April 1980). April (1980) suggested that hematite reduction acted as a source of Fe$^{2+}$, thereby explaining the high Fe content of interstratified chlorite–vermiculite found within the 0.5 m below the Hampden basalt (Newark). Such reducing conditions are thought to be restricted to the baked zone. However, the grey to dark levels in the studied sections in Morocco are laterally continuous on a kilometre scale and are observed down to 10 m below the oldest CAMP basalts. In fact, the grey levels correspond to intertidal lacustrine sediment, whereas the red beds were deposited in a more oxidizing supratidal environment such as a playa lake. Therefore, the absence of hematite and the consequent grey colour is not a result of overprinting by hydrothermal reducing fluids but of variation in physico-chemical redox conditions during sedimentation.

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**Fig. 7.** Correlation between $\delta^{13}$CTOC curves of Morocco, Canada and the UK, and temporal relationships between C-isotope perturbations, end-Triassic mass extinction and CAMP volcanism. The St Audries Bay, SW England (Hesselbo et al. 2002), Fundy Basin, Canada (Deenen et al. 2011) and Argana Basin, Morocco (Deenen et al. 2010) sections have been previously correlated based on magnetostratigraphic data (Deenen et al. 2010, 2011). The initial negative CIE occurs stratigraphically just below the first CAMP basalts and above the short reverse polarity interval both in the Argana Basin (Deenen et al. 2010) and in the Fundy Basin (Deenen et al. 2011) and is coincident with the end-Triassic mass extinction interval (horizontal bar). (For the position of the Triassic–Jurassic boundary at St Audries Bay see Fig. 1.)
**Mafic source rocks of sub-CAMP sediments.** Given that the geochemical compositions of the studied claystones and siltstones probably reflect a primary signature it is apparent that the dominantly clay-grade sheet-silicate mineralogy requires a significant contribution from a mafic source rock (see Wilson 2004), probably an early erupted CAMP volcanic rock, which underwent alteration, erosion, transport and deposition in the High Atlas basins. Notably, whole-rock compositions (Fig. 6) of High Atlas sediments investigated here fall between the composition of clays from various worldwide geological contexts (clays derived from typical continental crust) and the trioctahedral sheet silicates that typically form from altered mafic rock, as observed also in the hydrothermally modified CAMP basalts in Morocco (Dekayr et al. 2005; Fig. 6).

The early CAMP eruptions might have been explosive, at least in part, rather than effusive, as suggested by the discovery of a 2 cm hypothetical tuff layer preserved below the oldest lava flows in the Argana Basin (Olsen et al. 2012). The existence of early CAMP pyroclastic deposits remains to be confirmed, but if such existed, they would have been more easily transported and altered into sheet silicates than would massive lava flows. Mafic sources other than CAMP are unlikely. The rare pre-CAMP mafic rocks in central Morocco (i.e. mafic–ultramafic Carboniferous intrusions; Michard et al. 2005) are a highly improbable candidate as a source of the trioctahedral sheet silicates in Upper Triassic sediments. These Carboniferous intrusive rocks did not crop out at the surface during the Late Triassic because they were buried under up to 2000 m of Permian sedimentary and volcanic (mostly intermediate to acidic) rocks that were exhumed only during the Late Jurassic–Early Cretaceous interval (Saddiqi et al. 2009).

Therefore, it is suggested that the mafic component of the analysed claystones and siltstones derived from alteration, erosion, transport and redeposition within the basin of CAMP-derived rocks. Such processes would guarantee production of large amounts of secondary mafic minerals from CAMP basalts, but in particular the transport of material into the basins would preferentially select the ‘easily floating’ mafic sheet silicates as opposed to other secondary minerals. As a consequence, only part of the pristine CAMP geochemical signature would be registered in the High Atlas claystones and siltstones, whose concentrations of poorly soluble elements (Nb, Zr, REE) are different from those of unaltered CAMP basalts (Fig. 5).

**An early and slightly diachronous onset of CAMP volcanism**

The hypothesis that the claystones and siltstones from the Moroccan High Atlas sequences result from an early CAMP source requires eruption of these basalts at an earlier time than those at present preserved in this region and further implies that the beginning of volcanism was diachronous. A relatively early onset for the LIP is supported by the recognition of CAMP intrusive rocks in western Africa (Mali and Guinea) yielding an age (1202 Ma; Deckart et al. 1996; Verati et al. 2005; recalculated after Renne et al. 2010) significantly older than the Triassic–Jurassic boundary. Recently observed negative shifts of marine Sr and Os isotopes further support an onset of CAMP volcanism well before the beginning of the Jurassic Period (Cohen & Coe 2002, 2007; Kuroda et al. 2010; Callegaro et al. 2012). The likelihood of CAMP onset preceding the lowest preserved lava flows at Oued Lahr and Tiourjdal is reinforced by the probable rapid deposition of the investigated sedimentary sequences (within c. 100–200 kyr, according to Deenen et al. (2010) and Blackburn et al. (2013)) and by the slight diachronity suggested for the onset of CAMP volcanism by stratigraphic data and radioisotopic ages of basalts from circum-Atlantic basins (Marzoli et al. 2004, 2011; Deenen et al. 2010; Blackburn et al. 2013). The results documented here suggest that, even at the smaller scale of the Central High Atlas, there was diachronous onset of CAMP volcanism. Sediments of the Oued Lahr section do not record the initial negative CIE and, if the proposed chronostratigraphic correlation is correct, the first supra-sediment flood basalt at Oued Lahr could be slightly older than the one overlying sediments at Tiourjdal.

**Relative timing and cause-and-effect relationships between end-Triassic events**

The new data give for the first time crucial information bearing on the sequence of end-Triassic events and support CAMP volcanism as the main trigger for the complex C-isotope perturbations. The first important conclusion is that both precursor and initial CIEs occurred when the CAMP was already erupting, thus making the cause-and-effect relationship between volcanism and carbon cycle disruption more likely.

It is generally considered that volcanic CO₂ is insufficiently light isotopically (δ¹³C: −7 to −5%) to cause large negative CIEs in the reservoirs of the active carbon cycle, and that strongly ¹³C-depleted C must be provided to the system by other sources such as methane hydrates or thermally altered organic-rich sediments. Nevertheless, C-isotope analyses of some non-CAMP LIP basalts (Hansen 2006) and mantle xenoliths (Deines 2002) show relatively negative values (−25% average) that could explain LIP-related negative CIEs. However, no robust conclusions can be drawn because the C-isotope signature of CAMP-derived CO₂ is so far unknown. The problem of explaining the large end-Triassic negative CIEs remains open: CAMP activity and associated release of CO₂ may have triggered the multiple end-Triassic negative CIEs via repeated and rapid injections of (1) extremely ¹³C-depleted volcanic CO₂ and/or (2) CH₄ from destabilization of ocean-floor clathrates (δ¹³C as low as −60‰; Dickens et al. 1995) caused by volcanic CO₂-induced global warming and/or (3) thermogenic methane (δ¹³C −35 to −50‰; Svensen et al. 2004) from basaltic intrusions into subsurface organic-rich sediments. These hypotheses are not mutually exclusive. Indeed, the onset of CAMP volcanism could have triggered the release of both thermogenic and clathrate methane, thus amplifying the global climatic and environmental effects of increasing pCO₂ levels and promoting further global warming (McElwain et al. 1999), as well as causing ocean acidification (Martindale et al. 2012).

The data presented here help also to improve understanding of the nature of the precursor negative CIE as defined by Ruhl & Kürschner (2011). Those researchers explained the precursor negative CIE as the effect of thermal alteration of subsurface organic-rich sediments by intrusion of CAMP dykes and sills, and suggested that the carbon cycle disruption preceded the onset of CAMP basalt deposition. However, the presence of mafic sheet silicates corresponding in depositional age to the positive limb of the precursor CIE (Figs 3 and 7) strongly suggests that the outpouring of CAMP basalt had already started at the time that the negative CIE took place. The new data equally suggest that eruption of CAMP basalts preceded the end-Triassic mass extinction (Fig. 7). Therefore, the release of volcanic gases by CAMP activity is a viable trigger mechanism for this mass extinction. SO₂ and halogens produce short-term effects such as global cooling and acid rain (Wignall 2001), whereas sudden injection of CO₂ could have quickly increased atmospheric pCO₂ levels and triggered a global rise in temperature with catastrophic consequences for terrestrial and marine fauna and flora. Therefore, long-term pollution
of the end-Triassic ocean–atmosphere system with CAMP-derived volcanic gases (plus possible positive feedback phenomena such as clathrate emissions) could have severely changed global biogeochemical cycles and environments (McElwain et al. 1999), leading to progressive loss of life in the oceans and on land, culminating in the mass extinction (Hallam 2002; Tanner et al. 2004; Pálfy et al. 2007; Lindström et al. 2012; Mander et al. 2013). The high abundance of mafic minerals at the top of Taurjdal sedimentary sequence (Fig. 3) could testify to a peak of basalt outpouring that was coincident with the initial CIE. We suggest that a strong peak of CAMP activity overwhelmed a fauna and flora that were already weakened by relatively long-term CAMP volcanism.

Conclusions

The new C-isotope, mineralogical, elemental and palynological data from two stratigraphic sections in Morocco that crop out below the oldest CAMP basalt flow give crucial new information about the links and the relative timing between end-Triassic volcanism, carbon cycle disruption and, by inference, mass extinction.

(1) The studied sections are biostratigraphically constrained to the Late Triassic owing to the presence of a distinctive norian–rhaetic sporomorph assemblage (e.g. Classopollis murphyae, Classopollis torosus, Classopollis meyeranus, Patinasporites densus).

(2) Immediately below the first CAMP flood basalt an up to c. 6% negative CIE has been recorded in organic matter and can be correlated with the initial end-Triassic CIE recognized worldwide in both continental and marine sections.

(3) The studied sediments are characterized by unusually high mafic clay-mineral (up to 84%) and MgO (up to 32 wt%) content with peaks at multiple levels. Given the geological history of the region, and excluding the possibility of contact metamorphism and hydrothermal alteration, the presence of these minerals is best explained by the alteration and transport of early erupted CAMP basaltic material into the Central High Atlas basins.

(4) The initial negative CIE in the Central High Atlas coincides with an abrupt increase in sedimentary levels of mafic CAMP-derived minerals. This relative maximum in mafic mineral abundance could correspond in time to a distinct peak of CAMP volcanism that exposed large areas of basalt to superficial weathering.

(5) The data show that CAMP volcanism was already active when the positive rebound from the precursor negative CIE and the initial negative CIE occurred. These results show that the outpouring of CAMP basalt preceded the end-Triassic carbon cycle disruption and, by inference, the mass extinction.

(6) This study supports the hypotheses that the end-Triassic carbon cycle disruption was triggered by CAMP volcanism, and that relative long-term pollution of the atmosphere and ocean by CAMP volcanic gases, such as CO2 and SO2, could have caused a progressive loss of marine and terrestrial species culminating in the end-Triassic mass extinction.

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