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Bridging the Faraoni and Selli oceanic anoxic events: short and repetitive dys- and anaerobic episodes during the late Hauterivian to early Aptian in the central Tethys

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Abstract

A detailed stratigraphical and geochemical analysis was performed on the upper part of the Maiolica Formation outcropping in the Breggia (southern Switzerland) and Capriolo sections (northern Italy). In these localities, the Maiolica Formation consists of well-bedded, partly siliceous, pelagic, micritic carbonate, which lodges numerous thin, dark and organic-rich layers. Stable-isotope, phosphorus, organic-carbon and a suite of redox-sensitive trace-metal contents (RSTE: Mo, U, Co, V and As) were measured. Higher densities of organic-rich layers were identified in the uppermost Hauterivian, lower Barremian and the Barremian-Aptian boundary intervals, whereas the upper Barremian interval and the interval immediately following the Barremian-Aptian boundary interval are characterized by lower densities of organic-rich layers. TOC contents, RSTE pattern and C_{org}:P_{tot} ratios indicate that most layers were deposited under dysaerobic rather than anaerobic conditions and that latter conditions were likely restricted to short intervals in the latest Hauterivian, the early Barremian and the pre-Selli early Aptian.

Correlations are possible with organic-rich intervals in central Italy (the Gorgo a Cerbara section) and the Boreal northwest German Basin, and with the facies and drowning pattern in the evolution of the Helvetic segment of the northern Tethyan carbonate platform. Our data and correlations suggest that the latest Hauterivian witnessed the progressive installation of dysaerobic conditions in the Tethys, which went along with the onset in sediment condensation, phosphogenesis and platform drowning on the northern Tethyan margin, and which culminated in the Faraoni anoxic episode. This brief episode is followed by further episodes of dysaerobic conditions in the Tethys and the northwest German Basin, which became more frequent and progressively stronger in the late early Barremian. Platform drowning persisted and did not halt before the latest early Barremian. The late Barremian witnessed diminishing frequencies and intensities in dysaerobic conditions, which went along with the progressive installation of the Urgonian carbonate platform. Near the Barremian-Aptian boundary, the increasing

density in dysaerobic episodes in the Tethyan and northwest German Basins is paralleled by a change towards heterozoan carbonate production on the northern Tethyan shelf. The following return to more oxygenated conditions is correlated with the second phase of Urgonian platform growth and the period immediately preceding and corresponding to the Selli anoxic episode is characterized by renewed platform drowning and the change to heterozoan carbonate production. Changes towards more humid climate conditions were likely the cause for the repetitive installation of dys- to anaerobic conditions in the Tethyan and Boreal basins and the accompanying changes in the evolution of the carbonate platform towards heterozoan carbonate-producing ecosystems and platform drowning.

1 Introduction

The Early and early Late Cretaceous represents a time interval of considerable paleoenvironmental change, which found its expression in the repeated installation of widespread dysaerobic to anaerobic conditions in outer-shelf and basinal settings (Schlanger and Jenkyns, 1976; Jenkyns, 1980; Weissert and Erba, 2004). One of the oldest “oceanic anoxic episodes” (OAE) of the Cretaceous dates from the latest Hauterivian and is known as the “Faraoni event” (Cecca et al., 1994). This episode was originally identified in the central Italian Apennines, where it is preserved in the form of a well-distinguishable interval of thin and closely spaced organic-rich mudstone layers in pelagic carbonate (Cecca et al., 1994; Coccioni et al., 1998, 2006; Baudin et al., 2002; Baudin, 2005). A coeval equivalent of the Faraoni Level was subsequently found in northeast Italy (eastern part of the Trento Plateau and Lessini Mountains; Cecca et al., 1996; Faraoni et al., 1997; Baudin et al., 1997; Cismon, Venetian Alps; Erba et al., 1999; Tremolada et al., 2009) and in the southern Swiss Alps (Breggia; Bersezio et al., 2002). In the following, other Faraoni equivalents were identified outside the central Tethyan realm, such as in the Vocontian Basin (Vergons; Baudin et al., 1999), Ultrahelvetic Basin (Veveyse de Châtel St. Denis; Busnardo et al., 2003), and in the Rio Argos section of the Subbetic unit in Spain (Company et al., 2005).

The early Aptian oceanic anoxic "Selli event" (Coccioni et al., 1987) was first identified as part of the broadly defined, Aptian-Albian OAE (Schlanger and Jenkyns, 1976), which was in the following labelled as OAE 1a (Arthur et al., 1990). OAE 1a is generally characterized by a large, positive excursion in δ^{13}C values associated with enhanced organic matter burial (Weissert, 1981a). Organic-rich sediments associated with the OAE 1a have been documented from different marine basins, such as the Vocontian Basin (Bréhéret, 1988), the northwest German Basin (Kemper and Zimmerle, 1978; Mutterlose et al., 2009), the southern Tethyan realm (Heldt et al., 2008), the central and southern Atlantic (Bralower et al., 1994) and the middle and northwestern Pacific (Sliter, 1989; Bralower et al., 2002). Together with the Late Cenomanian "Bonarelli event", the Selli episode represents a model OAE for a wide range of investigations (e.g., Menegatti et al., 1998; Erba et al., 2010; Tejada et al., 2010; Stein et al., 2011a).

In the central Tethys and northern Atlantic, the pelagic sediments between the Faraoni and Selli OAEs are characterized by the presence of a series of thin, organic-rich mudstone layers, which have been interpreted as the result of short-lasting and cyclically reappearing anoxic episodes (Weissert et al., 1979, 1985; Weissert, 1981a; cf. also Herbert, 1992; Bralower et al., 1994; Bersezio et al., 2002). Intermittent anoxic conditions spanning the latest Hauterivian to the early Aptian time interval have also been documented from the northern German Lower Saxony Basin (Mutterlose et al., 2009, 2010). Brief anoxic episodes predating the Selli event have equally been established from the southern Atlantic and Mid-Pacific (e.g., Bralower et al., 1994). These short-lived anoxic episodes bridging the Faraoni and Selli OAEs are generally less well characterized in terms of their geochemistry, and their implications for the general paleoceanographic and paleoenvironmental conditions during this time interval are less well established. It is for example not known, if these short episodes have their expression in shallow-water sediments, and if they had a larger-scale, inter-basinal impact or if they were only of regional importance.

In this contribution we present new insights on the time interval spanning the late Hauterivian and earliest Aptian based on data from the Breggia and Capriolo sections

in southern Switzerland and northern Italy, respectively (Fig. 1). These two sections are complementary with regards to their age ranges and offer the possibility to cover the time interval between the late Hauterivian and earliest Aptian. Based on our data and their interpretation, we suggest that (1) these brief anoxic events are widespread within the Tethys, (2) can be correlated with their counterparts in the boreal northwest German Basin, and (3) are correlated with changes in the ecology of carbonate-producing benthos on adjacent shallow-water carbonate platforms.

2 The Breggia and Capriolo sections

The Breggia section is located in southern Switzerland, in an abandoned quarry near the Breggia Gorge, close to Balerna (canton Ticino; Fig. 1). The Capriolo section has been measured in the upper part of an abandoned quarry northeast of Capriolo, southwest of the Lago d'Iseo, in northern Italy (Fig. 1). In both sections, the upper part of the Maiolica Formation has been sampled, which consists of a light-coloured pelagic, micritic carbonate including siliceous levels and nodules, and thin and dark-coloured mudstone interlayers.

For both sections, the magnetostraphies by Channel et al. (1987, 1993, 1995, 2000) and Channel and Erba (1992) were projected onto the measured sections. In addition, a crosscheck was performed by the analysis of calcareous nannofossils on selected mudstone samples. We used the last appearance of *Lithraphidites bollii* as a fix point to correct for apparent differences in measured thicknesses between the published and our sections. The resulting stratigraphies indicate that for the Breggia section, the upper Hauterivian and lower Barremian intervals are quite complete and that the top of the Maiolica Formation is marked by a major hiatus, which starts in the early late Barremian. The overlying Scaglia variegata is already of Aptian age.

The Maiolica Formation in the Capriolo section extends well into the lower Aptian. Unfortunately, its Barremian interval is incomplete and cannot be confidently subdivided by magnetostratigraphy, as was already stated by Channell and Erba (1992).

Based on the first appearance of *Rucinolithus irregularis* (Channell and Erba, 1992) we assume that the normal magnetochron underneath CMO represents at least in part CM1. As such most of the upper Barremian interval may have been preserved, whereas the lower Barremian interval appears largely reduced. Also the uppermost Hauterivian succession shows slumped intervals. The lowermost Aptian interval appears, on the contrary, well preserved.

Besides for its magnetostratigraphy and nannofossil biostratigraphy, the Hauterivian to Barremian interval in the Breggia section was also investigated for its facies and sedimentology by Weissert (1979, 1981b) and Weissert et al. (1979); stable carbon-isotope composition by Weissert et al. (1985); clay-mineral composition by Deconinck and Bernoulli (1991); organic matter by Arthur and Premoli-Silva (1982) and Bersezio et al. (2002); ammonites by Rieber (1977); and aptychi by Renz and Habicht (1985). The Hauterivian to lowermost Aptian interval in the Capriolo section was furthermore described by Weissert (1981b).

Here we provide detailed stratigraphic logs and records of stable carbon and oxygen isotopes, organic-matter and phosphorus contents, and redox-sensitive trace element distributions for both sections. These data were acquired in the framework of three bachelor theses, which were completed at the University of Neuchâtel (Jammet and Froidevaux, 2008; Bôle, 2009).

3 Methods

3.1 Organic-carbon analysis

The total organic carbon (TOC) content of preserved organic matter was analyzed on a Rock Eval™6 (Espitalié et al., 1985), with an instrumental precision of <2 %. Approximately 70 mg of powdered sample was first pyrolyzed and subsequently completely oxidized. The amount of hydrocarbon released during pyrolysis was measured by a FID detector, whereas the amount of CO_2 and CO during both steps was measured by

infrared absorbance. A standard cycle was applied, in which pyrolysis started isothermally at 300 °C for three minutes (S1: hydrocarbons released during the isothermal phase). The sample was then heated to 650 °C (S2: hydrocarbons released between 300 and 650 °C). The oxidation step started isothermally at 400 °C for three minutes (S3: CO_2 released) and subsequently, the sample was heated up to 850 °C. Obtained TOC contents are expressed in weight % (wt %). The hydrogen and oxygen indices ($HI = S2/TOC \times 100$ in mg hydrocarbons per g TOC; $OI = S3/TOC \times 100$ in mg CO_2 per g TOC) were plotted in a Van Krevelen-type diagram and used to characterize preserved organic matter (Espitalié et al., 1985). Two standards (IFP 160000 and VP143h) were applied to calibrate the measurements. The error relative to standard IFP 160000 is 0.77, 0.25 and 1.5 % for TOC, HI and OI, respectively.

3.2 Total phosphorus analysis

Total phosphorus (P) contents were measured on powdered bulk-rock samples. 1 ml of 1 M $MgNO_3$ was added to 100 mg powder and the resulting solution was dried in an oven at 130 °C during 30 min. The sample was then heated at 550 °C during two hours to oxidize the organic matter. After cooling, 10 ml of 1N HCl was added to the sample to liberate P and the solution was placed in a shaker during 16 h. The solution was then filtered, diluted 10 times and mixed with 100 µl molybdate mixing reagent to form phosphomolybdic acid (Eaton et al., 1995). In the following, 100 µl of ascorbic acid was added to reduce the acid and colour the solution blue. The intensity of the blue colour is a function of the P concentration. The total P content was measured by a UV/Vis spectrophotometer (Perking Elmer UV/Vis Spectrophotometer Lambda 10; $\lambda = 865$ nm). Selected samples were measured three times and the obtained precision is better than 5 %.

The C_{org}:P_{tot} ratio was calculated in mol mol^{-1} units for all measured samples.

3.3 Stable carbon- and oxygen isotope analysis

Stable carbon- and oxygen-isotope ratios were measured on powdered bulk-rock samples using a Thermo Fisher Delta V Advantage at the University of Berne, and a Thermo Fisher Delta Plus XL at the University of Lausanne, both equipped with an automated carbonate preparation line. The results were calibrated to the Vienna Pee Dee Belemnite (V-PDB) scale with a standard deviation better than 0.05 ‰ for δ^{13}C and 1 ‰ for δ^{18}O.

3.4 Redox-sensitive trace-element analysis

Carbonate samples were analyzed for molybdenum (Mo), uranium (U), cobalt (Co), vanadium (V), and arsenic (As) contents. These elements are considered as redox-sensitive trace elements (RSTE), which are used as indicator of the presence and intensity of oxygen depletion at the site of sediment deposition (Algeo and Maynard, 2004; Tribovillard et al., 2006; Bodin et al., 2007).

10 ml suprapur nitric acid (HNO_3) was added to 250 mg of rock sample reduced to powder in a PFA vessel and subsequently digested in a microwave oven (MSL-Ethos plus, Milestone; heating program EPA 3051). The solution was cooled, filtered (0.45 µm) and diluted to 100 ml with ultrapure water (Bodin et al., 2007). Dissolution percentages determined after filtration were between 89 and 94 wt % for all carbonate samples. Westermann et al. (2010) showed for comparable pelagic carbonates of Valanginian age from the same Breggia and Capriolo sections that RSTE contents and dissolution percentages are not positively correlated. This suggests that the RSTE are present in the soluble carbonate phase and not derived from partial leaching of the detrital fraction (cf. also Bodin et al., 2007). The RSTE data were, therefore, not normalized by aluminum contents.

RSTE contents (in ppm) were determined by a quadrupole ICP-MS (ELAN 6100, Perkin Elmer) in a semi-quantitative mode (totalQuant^{TM}), with a precision of 5 %. The

calibration was based on two certified reference materials (LKSD-1 lake sediment and NIST-1640 natural water).

4 Results

4.1 Total organic carbon

Samples of the dark, laminated and organic-rich layers in the Breggia section show TOC values between 0.9 and 12.6 wt %, whereas those of the Capriolo section vary between 0.2 and 14.7 wt % (Figs. 2 and 3). The TOC values in the Breggia section are generally higher (mean value = 3.7 wt %, $n = 24$) than those in the Capriolo section (mean value = 2 wt %; $n = 25$). The highest TOC values in the Breggia section are registered in two layers below the Hauterivian-Barremian boundary. Generally, the Barremian mudstone layers in the Breggia section are somewhat richer than their upper Hauterivian counterparts. In the Capriolo section, both the upper Hauterivian and Barremian mudstone layers show relatively low TOC values, whereas the lower Aptian layers contain higher TOC values (Figs. 2 and 3).

HI and OI of the organic matter preserved in the mudstone layers of both sections range between approximately 90–370 mg HC g^{-1} TOC and 20–120 mg CO_2 g^{-1} TOC (Breggia), and 30–300 mg HC g^{-1} TOC and 30–120 mg CO_2 g^{-1} TOC (Capriolo). In a Van Krevelen-type diagram, the preserved organic matter plots mostly within or nearby the type III field (Fig. 4).

4.2 Total phosphorus

Total P contents were measured on a series of carbonate and mudstone samples. In samples of the Breggia section, total P contents for carbonates and mudstones vary between approximately 100 and 250 ppm, and 250 and 1000 ppm, respectively, whereas in the Capriolo section, total P contents range between approximately 70 and

280 ppm in carbonate samples and 100 and 1000 ppm in mudstone samples (Figs. 2 and 3). Sporadic outliers are noted in Figs. 2 and 3, but are not further considered.

The stratigraphic evolution in total P contents in carbonates of the Breggia section is marked by two maxima around 250 ppm within the upper Hauterivian and a further maximum around 250 ppm in the middle lower Barremian interval. In the Capriolo section, carbonate P contents are generally higher in the Barremian and lower Aptian interval, in comparison to the upper Hauterivian interval. In both sections, the mudstone samples display rather disparate spreads of values, and trends are difficult to be discerned.

In the Breggia section, the C_{org}:P_{tot} molar ratios show departures above 300 in mudstone levels with higher TOC values (>4 wt %; Fig. 2) dating from the latest Hauterivian and middle early Barremian. Similar departures are observed in two layers above the Hauterivian-Barremian boundary and one layer within the lower Aptian interval of the Capriolo section. There, the Barremian levels are not necessarily those with the highest TOC levels, whereas the lower Aptian level is the one which possesses the highest TOC value of the entire measured section (14.7 wt %).

4.3 Stable-carbon and oxygen isotopes

The δ^{13}C record of the Breggia section shows comparable values and a consistent trend for both the carbonate and mudstone samples (Fig. 2). It is characterized by rather stable values for the upper Hauterivian interval at around 1.5 ‰. The δ^{13}C record rises to maximal values around 1.8 ‰ in the Hauterivian-Barremian boundary interval. In the following, the δ^{13}C values slowly decrease to near 1.5 ‰ and increase again to fluctuate around 1.8 ‰ for the remainder of the lower Barremian interval. Just above the boundary between the lower and upper Barremian, the δ^{13}C record increases by approximately 1 ‰ to values of 2.5 ‰.

The δ^{13}C record of the Capriolo section is only shown for the carbonate samples (Fig. 3), since the mudstone samples show systematic negative offsets of up to 0.8 ‰ relative to the carbonate samples, probably because of diagenetic overprint. The

carbonate samples of the upper Hauterivian interval are characterized by a gentle trend towards more negative values from near 2 ‰ to 1.8 ‰, followed by a short-lasting positive trend to around 1.9 ‰ and a renewed negative trend towards a minimum of 1.5 ‰ near the Hauterivian-Barremian boundary. δ^{13}C values in the lower part of the Barremian interval are rather stable and fluctuate between 1.5 and 1.8 ‰, whereas in the upper part, they move to a maximum of near 2.2 ‰. The Barremian-Aptian boundary interval shows a negative excursion to a minimal value of near 1.8 ‰, which is followed by an irregular positive trend towards values of 2.2 ‰ near the top of the section (Fig. 3).

In the Breggia section, the δ^{18}O values for the marlstone samples are approximately 1–2 ‰ lower compared to the carbonate samples. We therefore opted to only display and discuss the carbonate values (Fig. 2). In the upper Hauterivian part of the section, the δ^{18}O record fluctuates between values of −1.5 and −2.5 ‰, with two minima within the upper Hauterivian interval. Immediately underneath the Hauterivian-Barremian boundary, the δ^{18}O record rises to values of −1.5 ‰ and descends in the following to values of −1.8 ‰. From the middle lower Barremian to the top of the section, the δ^{18}O record remains stable around values of approximately −1.8 ‰ (Fig. 2).

The δ^{18}O values of mudstone samples in the Capriolo section are up to 3 ‰ lower than the values in nearby carbonate samples and are not further discussed here. The δ^{18}O record of Capriolo starts with rather stable values around −1.8 ‰ to −1.9 ‰, and shows in the following an irregular negative trend towards the lowest value (−2.6 ‰) measured in the entire section, near the Hauterivian-Barremian boundary (Fig. 3). This is followed by a rapid positive trend towards values near −1.8 ‰ and the remainder of the Barremian interval shows rather stable δ^{18}O values around −1.8 ‰ to −2 ‰. The Barremian-Aptian boundary interval shows decreasing values towards −2.2 ‰ and the lower Aptian interval is again characterized by an increase to −1.8 ‰, a slight decrease to 2 ‰ and a renewed increase to −1.4 ‰ (Fig. 3).

4.4 Redox-sensitive trace elements

Selected carbonate samples in the Breggia section show Mo, U, Co, V and As contents between 0–471 ppb, 0–2655 ppb, 1105–11493 ppb, 1243–3763 ppb, and 0–4912 ppb, respectively (Fig. 2). Mean values for Mo, U, Co, V and As are 108 ppb, 500 ppb, 2976 ppb, 2252 ppb, and 936 ppb ($n = 19$). Departures of these mean values are seen for levels underneath the Hauterivian-Barremian boundary (for all measured RSTE) and in the upper Barremian interval (for U and Co).

In carbonate samples of the Capriolo section, Mo, U, Co, V and As contents range between 0–545ppb, 43–3557 ppb, 964–8127 ppb, 1219–13941 ppb, and 0–2883 ppb, respectively (Fig. 3). The mean values for Mo, U, Co, V and As are 71 ppb, 451 ppb, 2051 ppb, 2618 ppb, and 442 ppb ($n = 42$). Excursions in RSTE contents are observed for carbonates underneath the Hauterivian-Barremian boundary and within the lower Aptian interval.

5 Discussion

5.1 Organic-carbon contents and preservation

TOC contents reach values above 10 wt % in two mudstone layers below the Hauterivian-Barremian boundary in the Breggia section and in one layer within the lower Aptian interval in the Capriolo section (Figs. 2 and 3). All other measured intervals possess TOC contents below 10 wt %. These values are generally lower than the values measured for the Faraoni interval in central Italy (e.g., Baudin, 2005), whereas they are higher than the ones measured in organic-rich layers immediately underneath the Selli Level in central Italy (Stein et al., 2011a). In comparison to the Breggia section, the TOC values in Capriolo are generally lower, probably due to a higher degree of tectonic overprint. This is also indicated by the somewhat higher T_{max} values in Capriolo (average value = 430 °C) relative to Breggia (average value = 427 °C) (Espitalié et al., 1985).

The HI and OI values plot within or nearby the type-III field (Fig. 4), and no real trends are discernable between TOC contents and HI/OI values, except for very low values underneath 0.5 wt %, which tend to have very low HI and higher OI values. These values suggest that preserved organic matter in both sections is partly altered by its tectonic history and aerial exposure, but may also include a terrestrial component. The levels close to the Hauterivian-Barremian boundary in the Breggia and Capriolo sections show systematically lower HI values than the Faraoni level in central Italy (with values up to 600; Baudin, 2005).

5.2 Phosphorus contents and C_{org}:P_{tot} molar ratios

Trends in P burial rates are used as a proxy for temporal changes in the amount of P transferred into the basin (Föllmi, 1995, 1996; Bodin et al., 2006a), assuming steady-state conditions over time periods covering several residence times of reactive P in the ocean (approximately 10 000–20 000 yr in modern oceans; e.g., Filippelli, 2008). Lacking a major detrital fraction, total P in pelagic carbonate sections may be used as a proxy for reactive P, which was transferred into an authigenic phase, became adsorbed onto reactive mineral surfaces, or remained associated with organic matter (e.g., Ruttenberg, 2004). Under dysaerobic conditions, buried P may be preferentially released and returned to bottom waters, and P burial rates may tend to lower, thereby masking the initial P flux rates into the basin (e.g., Slomp et al., 2004; Mort et al., 2007). Evidence for this is provided by the C_{org}:P_{tot} molar ratios in organic-rich layers, which tend to be significantly higher than the Redfield ratio (106:1) under dysaerobic conditions (e.g., Algeo and Ingall, 2007; Mort et al., 2007).

In both sections, P contents in carbonates and mudstone layers are generally higher in those intervals, where mudstone layers are more frequent and characterized by higher TOC contents (Figs. 2 and 3). The overall P contents are relatively low and comparable to those of other sections in the Maiolica Formation (e.g., Gorgo a Cerbara, Stein et al., 2011a) or in older intervals of the Maiolica Formation in the same sections (Westermann et al., 2011). In the Breggia section, P contents in carbonate samples show a maximum in the upper Hauterivian interval and tend to become lower in the Hauterivian-Barremian boundary interval. The P values are higher again in the lower Barremian interval. The Capriolo P values tend to decrease in the upper Barremian interval and remain low in the lower Aptian interval, except for a small maximum. These trends are comparable to those compiled by Bodin et al. (2006a) and Föllmi (1995).

In the Breggia section, the C_{org}:P_{tot} molar ratios are larger than 300 for mudstone interlayers with the highest TOC values (underneath the Hauterivian-Barremian boundary and in the higher part of the lower Barremian interval; exception is a mudstone layer just above the boundary between the lower and upper Barremian intervals: Fig. 2). In the Capriolo section, this relationship holds only for one mudstone interlayer within the lower Aptian interval.

5.3 Stable-carbon isotope records

For the purpose of this contribution, only the carbon-isotope records will be discussed, since they serve as correlation tools. In the Breggia section, the general trend is similar to trends in other sections of the central and northern Tethys (Fig. 5). Minimal δ^{13}C values in the upper Hauterivian interval, the increase in the uppermost Hauterivian and lowermost Barremian interval, the trend to slightly more negative values in the lower part of the lower Barremian interval, the positive trend followed by the negative trend in the upper part of the lower Barremian interval, and the sharp increase in δ^{13}C values in the lower part of the upper Barremian interval are well correlated (Godet et al., 2006).

The long-term trends in the δ^{13}C record in the Capriolo section appear also correlatable, with minimal values near the Hauterivian-Barremian boundary, followed by a trend towards more positive values, which are typical for the late Barremian. The δ^{13}C record seems to confirm that most of the lower Barremian interval is missing (Fig. 5). The trend towards more negative values during the upper part of the Barremian interval and the minimum in the δ^{13}C record near the Barremian-Aptian boundary is also known from the Cismon Apticore in northeastern Italy (Erba et al., 1999), the Gorgo

a Cerbara section in central Italy (Godet et al., 2006; Sprovieri et al., 2006), and the Angles section in southeastern France (Wissler et al., 2002; Godet et al., 2006).

It is clear from the correlations shown in Fig. 5 that the accumulation rates of the Breggia and Capriolo sections are much lower compared to those of other sections from the central and northern Tethyan realms.

5.4 Redox-sensitive trace-element records

Stratigraphic distributions of RSTE (here: Mo, U, Co, V and As) and enrichments therein are widely used as a tracer of the presence and intensity of oxygen-depletion within the water column during sediment deposition. The here-investigated suite of RSTE appears preferentially in dissolved form under oxidizing conditions, and tends to form organo-metal complexes or precipitate as oxides, hydroxides and sulfides under anoxic conditions (Algeo and Maynard, 2004; Tribovillard et al., 2006; Brumsack, 2006; Bodin et al., 2007; Westermann et al., 2010).

The RSTE contents discussed here have been measured on carbonate samples, and the absolute values are generally depleted relative to those for post-Archean average shale (PAAS; Mo = 1 ppm, U = 2.8 ppm, Co = 17 ppm, V = 107 ppm, As = 1.5 ppm; Taylor and McLennan, 1985, 1995). This implies that enrichments in RSTE relative to the background values in the carbonates of both sections are not of a magnitude, which would allow for the definite identification of dysaerobic or anaerobic conditions. It is only in combination with the other parameters used here (TOC, C_{org}:P_{tot} ratios) that certain observations can be made.

The RSTE enrichments in carbonates associated with mudstone layers underneath the Hauterivian-Barremian boundary in the Breggia section go along with high TOC values and elevated C_{org}:P_{tot} ratios (Fig. 2). To a lesser extent, the same coincidence is observed for the middle part of the lower Barremian interval in the Breggia section. For the Capriolo section, similar RSTE enrichments are observed for the carbonates near the mudstone layers underneath the Hauterivian-Barremian boundary; TOC and C_{org}:P_{tot} ratios of the same layers, are, however, not exceptionally high. The carbonates around a mudstone layer with high TOC and C_{org}:P_{tot} ratio within the lower Aptian interval are not enriched in RSTE (Fig. 3). Carbonate samples above this level are more enriched in RSTE, but the associated mudstone layers are not exceptionally enriched in TOC and their C_{org}:P_{tot} ratio is not increased relative to the Redfield ratio of 106:1.

For the Breggia section, these observations imply that anaerobic conditions may have prevailed during mudstone deposition in the latest Hauterivian and in the middle part of the early Barremian. For the Capriolo section, the data are less conclusive, and only hints can be made for a certain degree of oxygen depletion during the latest Hauterivian and eventually also for the early Aptian. For the remainder of the laminated organic-rich mudstone layers, depositional conditions were dysaerobic, rather than anaerobic. Given the paleogeographic proximity of both sections, the aforementioned discrepancy in terms of bottom-water oxygenation may reflect the development of local anaerobic pockets within larger dysaerobic bottom-water masses.

5.5 The Faraoni oceanic anoxic episode

In the Breggia section, the two organic-rich mudstone layers with TOC contents over 12 wt %, RSTE enrichment and C_{org}:P_{tot} ratios over 300 near the base of magnetochron CM4 are identified as an equivalent of the Faraoni level of central Italy. The correlation is confirmed by the nannofossil assemblages identified in the organic-rich mudstone interlayers, which consist of abundant large-sized *Assipetra terebrodentarius*, *Assipetra infracretacea,* and *Zeugrhabdotus embergeri*, and the last occurrence of *Lithraphidites bollii.*

In the Capriolo section, the identification of the Faraoni level is less conclusive with regards to the geochemical tracers. There are no levels within the upper Hauterivian interval, which are particularly enriched in TOC or P (relative to C_{org}). A level enriched in RSTE right underneath the last occurrence of *Lithraphidites bollii* is taken as the equivalent of the Faraoni level. This is confirmed by the presence of the same large-size nannofossil species as in the Faraoni level of the Breggia section.

In both sections, the Faraoni level is preceded by organic-rich layers, which appear approximately 5 and 3 m below the Faraoni level in the Breggia and Capriolo sections, respectively. The Faraoni level is also succeeded by a series of organic-rich mudstone interlayers, which extend well into the Barremian. These interlayers are thinner than the layers associated with the Faraoni event and their TOC contents are not higher than 2 wt %. Furthermore, they lack major departures in RSTE contents and C_{org}:P_{tot} ratios, which suggests that they are the product of dysaerobic rather than anaerobic conditions.

Overall, it appears that the Faraoni event is not a singular event, but rather a culminating episode of anaerobic conditions within a longer time interval of periodically resurfacing dysaerobic conditions leading to enhanced organic-matter preservation and/or diminishing carbonate deposition (cf. Bodin et al., 2006a).

5.6 Temporal pattern in organic-matter preservation during the latest Hauterivian to earliest Aptian time interval

In order to quantify the relative importance of organic-matter deposition and preservation per time unit, we established a density profile of the organic-rich mudstone layers. The profile was calculated as

$$\text{OML density} = \Sigma q_{\text{OML}}/t \tag{1}$$

where OML stands for organic-rich mudstone layer, t for time unit (corresponding to entire or parts of magnetochrons in the case of the Breggia and Capriolo sections; in my) and q_{OML} as parametrization for the thickness (h) of each layer, where $q_{OML} = 1$ ($h < 2$ cm), $q_{OML} = 2$ ($2\text{ cm} < h < 4$ cm), $q_{OML} = 3$ ($4\text{ cm} < h < 6$ cm), $q_{OML} = 4$ ($6\text{ cm} < h < 8$ cm), $q_{OML} = 5$ ($8\text{ cm} < h < 10$ cm), etc. Thicknesses greater than 20 cm have not been observed. Σq_{OML} corresponds to the sum of q_{OML}. For example, if an interval corresponding to 2my has five organic-rich interlayers with thicknesses of 1, 5, 11, 2 and 3 cm, respectively, the OML density would correspond to $(1+3+6+1+2)/2 = 6.5$ for this interval.

The results of this quantification are shown in Fig. 6 and suggest that periods of increased OML density occurred during the late Hauterivian, latest early Barremian and earliest Aptian. Periods of low OML density are identified for the late Barremian and the time interval just preceding the Selli episode.

5.7 Comparison with other regions

In addition to the central and northern Tethys, further possible expressions of the Faraoni anoxic episode have been observed in northwestern Sicily (Bellanca et al., 2002; Baudin, 2005; Coccioni et al., 2006), offshore Portugal and Morocco (DSDP Sites 370 and 398; Baudin, 2005), the North Sea area (Mutterlose and Ruffell, 1999), and in the central and northwestern Pacific (Resolution Guyot, ODP Sites 865 and 866; Baudin et al., 1995; Izu-Mariana margin, ODP Site 1149; Shipboard Scientific Party, 2000; Bodin et al., 2007). Evidence for the presence of a Faraoni equivalent was also not excluded for the Argentinean Neuquén Basin (Tyson et al., 2005).

For the Tethyan localities of the Faraoni level and its equivalents, the prevalence of anaerobic conditions has been shown based on paleontological (lack of benthos; Baudin, 2005), sedimentological (presence of laminated, organic-rich sediments with TOC values of up to 27 wt %; Baudin, 2005) and geochemical criteria (C_{org}–P_{tot} ratios; excursions in RSTE contents; Bodin et al., 2006a, 2007). The Faraoni anoxic episode coincides also with important evolutionary change in rudists (Masse and Fenerci-Masse, 2008), ammonite faunas (Hoedemaeker and Leereveld, 1995; Company et al., 2005), planktonic foraminifera (Venturati, 2006), radiolaria (O'Dogherty and Guex, 2002; De Wever et al., 2003), and calcareous nannofossils (Company et al., 2005; Tremolada et al., 2009).

With respect to the deposition of the younger, Barremian to lower Aptian organic-rich interlayers, we estimated the OML density for the Gorgo a Cerbara section in central Italy, using the stratigraphic plots of Fiet and Gorin (2000) and Stein et al. (2011a) (Fig. 6). The OML trends are comparable to those obtained from the Breggia and Capriolo sections, with the exception of the uppermost Barremian interval, which is

distinctly richer in organic-rich interlayers relative to the Capriolo section. Interestingly, a good correspondence is also given between the OML density curves for the central Tethys and the presence of laminated mudstone layers in the northwest German Basin (Mutterlose et al., 2009, 2010). We searched for further basinal records of this time interval; and indeed, the presence of organic-rich mudstone interlayers is known from different DSDP and ODP Sites from the central and northern Atlantic (e.g., Weissert, 1981a; Stein et al., 1988). The current age models for those deposits do, however, not allow for high-resolution correlations.

Besides basin-to-basin correlations, we also observe interdependencies between the periods of enhanced organic-matter preservation and the evolution of the northern Tethyan platform presently outcropping in the Helvetic Alps (Fig. 6). A prolonged phase of platform drowning along the northern Tethyan margin has been documented from the Jura Mountains and Helvetic Alps, which started in the latest Hauterivian and lasted until the late early Barremian (Bodin et al., 2006b; Godet et al., 2010). The onset of this drowning episode slightly predates the onset of the Faraoni anoxic episode (Föllmi et al., 2006, 2007). The early late Barremian is characterized by the deposition of marly carbonate and carbonate-marl succession, which is interrupted by a short phase of condensation and phosphogenesis during the middle late Barremian. Thereafter, Urgonian-type shallow-water carbonates prograde and show the installation of a photozoan carbonate platform. The deposition of Urgonian carbonate is interrupted around the Barremian-Aptian boundary by a phase of heterozoan carbonate, marl and sand deposition ("Lower Orbitolina Beds": LOB). On top of the younger Urgonian unit overlying the LOB, a phase of platform drowning is observed, which is followed by heterozoan carbonate deposition ("Upper Orbitolina Beds": UOB), a second drowning phase (corresponding partly in time to the Selli oceanic anoxic event), and further heterozoan carbonate deposition (upper part of the UOB; Fig. 6). The periods of high OML density in the central Tethys realm correspond to periods of platform drowning and/or heterozoan carbonate deposition, whereas the phases of Urgonian photozoan carbonate deposition are correlated with phases of low OML density.

One of the environmental parameters, which may have changed conditions on the platform and in the basin, are variations in the nutrient flux, which interfere both with the composition and efficiency of shallow-water carbonate-producing ecosystems and the pelagic organic-matter export flux. P accumulation rates established for this time interval go rather well along with the contents measured in the Breggia and Capriolo sections and show an increase across the Hauterivian-Barremian boundary interval and higher values during the early Barremian, followed by lower values during the late Barremian (Bodin et al., 2006a) and higher values again for the early Aptian (Föllmi, 1995).

5.8 A scenario of paleoenvironmental change during the period from the late Hauterivian to the early Aptian

During the latest Hauterivian, the central and northern Tethyan basin witnessed short and repetitive phases of dysaerobic conditions and increased organic-matter preservation, whereas on its northern margin, the carbonate platform attached to the southern European margin started to drown. This phase of paleoceanographic change culminated in the Faraoni anoxic episode, which was probably not limited to the Tethyan realm, but may also have left its traces in other basins, probably as far as the Pacific. The late Hauterivian is characterized by a minimum in the Italian δ^{18}O whole-rock record (Fig. 6; Weissert and Erba, 2004; Godet et al., 2006; Bodin et al., 2009) and the onset in kaolinite deposition (in southeast France, Godet et al., 2008; Fig. 6; cf. Deconinck and Bernoulli, 1991), which may indicate humid and eventually warmer climate conditions.

The early Barremian is a period of generally increased organic-matter preservation, both in the Tethys as well as in the Boreal German Basin, and likely also in the central and northern Atlantic. The Helvetic and Jurassic segment of the northern Tethyan platform remained largely subjected to a halt in carbonate production, condensation and phosphogenesis, with a culmination in drowning pattern in the later part of the early Barremian (Bodin et al., 2006b). This time period is characterized by increasing

P burial rates and generally high kaolinite depositional rates (Fig. 6), which may indicate continuing humid climate conditions, with an increasing tendency towards the end of the early Barremian (Deconinck and Bernoulli, 1991; Godet et al., 2008). The δ^{18}O records in Italy and France show a tendency towards heavier values relative to the late Hauterivian, whereas the French belemnite record is characterized by a trend towards lighter values for most of the early Barremian (Fig. 6).

The late Barremian is characterized by lower rates of organic-matter preservation in the Tethyan basin and the progressive installation of the Urgonian carbonate platform on the northern Tethyan margin. P burial rates diminished during this time period and the same is true for kaolinite deposition, with the exception of a maximum in the middle late Barremian. The French δ^{18}O records are characterized by relatively positive values for a larger part of the late Barremian, which, in generally, is explained by a tendency towards cooler temperatures (cf. also Ruffell and Batten, 1990).

The renewed increase in organic-matter burial around the Barremian-Aptian boundary goes along with decreasing values in the δ^{18}O records and a change towards heterozoan carbonate production on the northern Tethyan platform. Even if the kaolinite record does not show a change in the Vocontian basin record, increases have been established on the adjacent carbonate platform (Godet et al., 2008; Stein et al., 2011b). This phase is followed by a decrease in organic-carbon burial and a second episode in Urgonian platform build up. The Selli OAE is finally preceded by a platform drowning phase and a change to heterozoan carbonate production, and goes along with a further platform drowning phase.

Our reconstruction of paleoenvironmental change during the period from the late Hauterivian to the early Aptian suggests that the Faraoni and Selli OAEs are culminations of longer periods of paleoenvironmental change with a widespread impact, and that the intervening periods of dys- to anaerobic conditions in the Tethys were related to those of other basins and had tele-connections with the evolution of the adjacent northern Tethyan carbonate platform. The higher frequency of dys- to anaerobic intervals in the pelagic realm and the vulnerability of the northern Tethyan carbonate platform to drowning during the late Hauterivian, Barremian and early Aptian can be seen as the expression of a regularly perturbed world.

6 Conclusions

We performed a detailed stratigraphic and geochemical analysis of two pelagic sections in southern Switzerland (Breggia) and northern Italy (Capriolo) and suggest that the latest Hauterivian, early Barremian and the Barremian-Aptian boundary interval were times of preferential organic-matter preservation under episodic dys- to anaerobic conditions, whereas the late Barremian and the period following the Barremian-Aptian boundary interval are characterized by a lower density in periods of organic-matter preservation. We compare this evolution to the section of Gorgo a Cerbara (central Italy), to the temporal pattern of organic-matter preservation in the northwest German Basin, and the evolution of the northern Tethyan shallow-water carbonate platform presently preserved in the Helvetic Alps, and observe synchroneity between the dysaerobic to anaerobic episodes in the Tethyan and Boreal Basins and a correspondence to the evolution of the northern Tethyan carbonate platform and its drowning phases. The paleoceanographic changes during the late Hauterivian and early Aptian are likely driven by changes towards more humid climate conditions.

This implies that the Faraoni and Selli anoxic episodes do not represent singular events in an otherwise unperturbed world, but are embedded in longer-lasting phases of environmental change preceding and following the anoxic episodes. They are bridged by a series of shorter-lasting dysaerobic and anaerobic episodes during the Barremian and early Aptian, which did not impact the world oceans in the same way as the Selli and probably also the Faraoni episodes. They are, however, more important than hitherto assumed, since a similar record is identified in the Boreal northwest German Basin and since relationships are seen between the frequency and intensity of the dys- to anaerobic episodes and the quality and quantity of carbonate production on the adjacent, northern Tethyan shallow-water carbonate platform.

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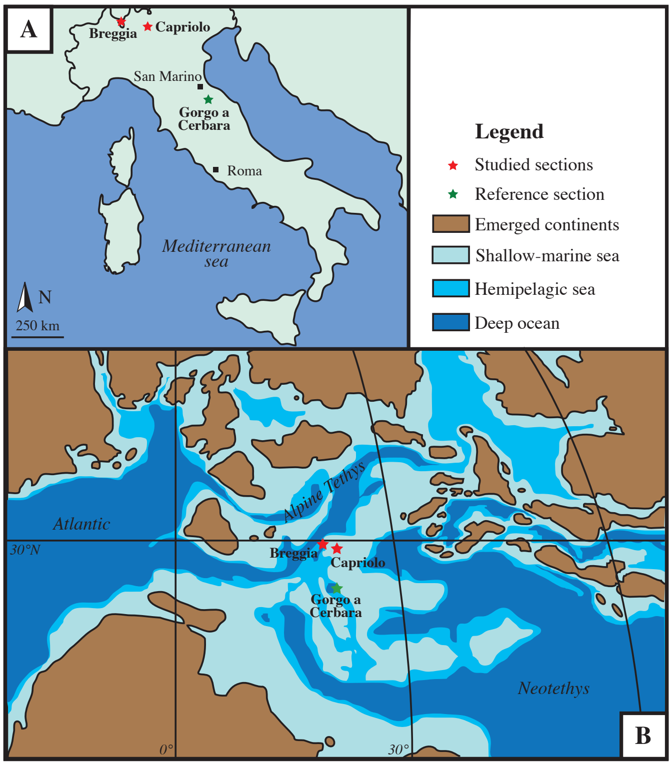

Fig. 1. Location of the studied sections and a reference section on a geographic map **(A)** and on a paleogeographic reconstruction for the early Aptian from Blakey (http://cpgeosystems.com/paleomaps.html) **(B)**. Modified from Stein et al. (2011).

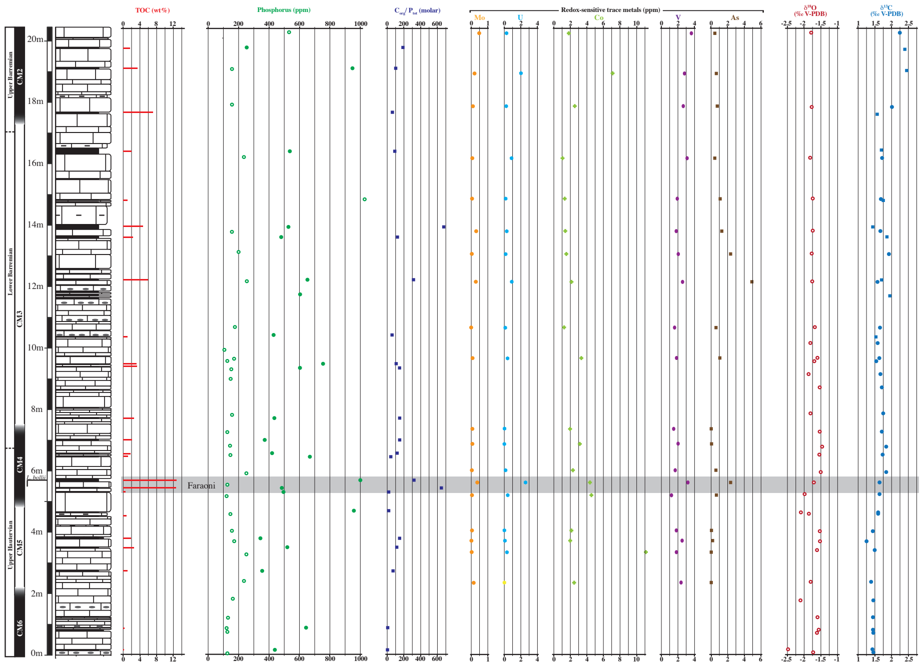

Fig. 2. The Breggia section: TOC contents in mudstone samples, phosphorus contents in carbonate (open circles) and mudstone samples (full circles), C_{org}:P_{tot} molar ratios, stable-carbon and oxygen-isotope values for carbonate (open and closed circles) and mudstone samples (rectangles), and redox-sensitive trace-metal distributions for molybdenum (Mo), uranium (U), cobalt (Co), vanadium (V) and arsenic (As) in carbonate samples. The gray band indicates the position of the Faraoni level. The magnetostratigraphy is after Channel et al. (1993).

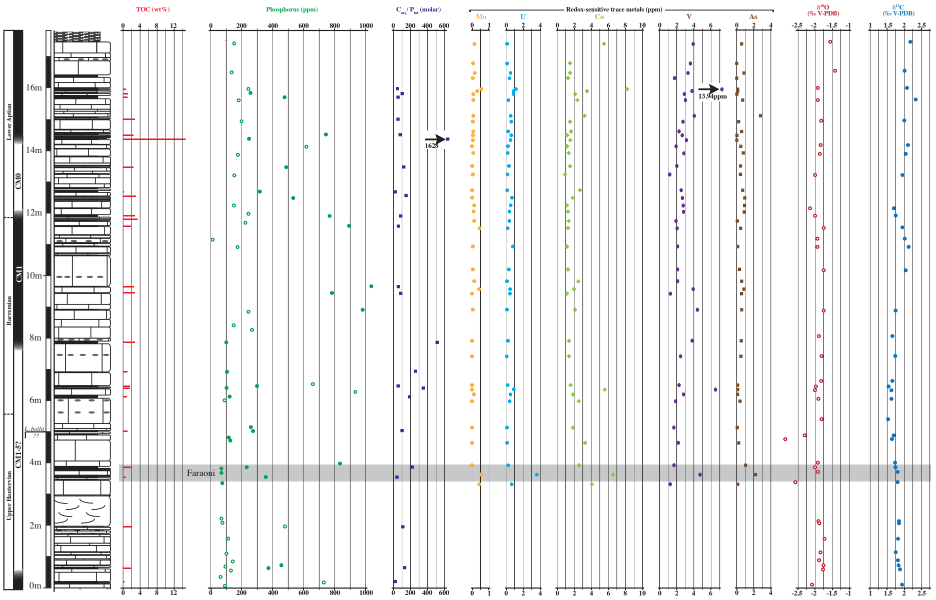

Fig. 3. The Capriolo section: TOC contents in mudstone samples, phosphorus contents in carbonate (open circles) and mudstone samples (closed circles), C_{org}:P_{tot} molar ratios, stable carbon and oxygen isotope values for carbonate samples, and redox-sensitive trace-metal distributions for molybdenum (Mo), uranium (U), cobalt (Co), vanadium (V) and arsenic (As) in carbonate samples. The gray band indicates the position of the Faraoni level. The magnetostratigraphy is after Channel et al. (1987) and Channel and Erba (1992).

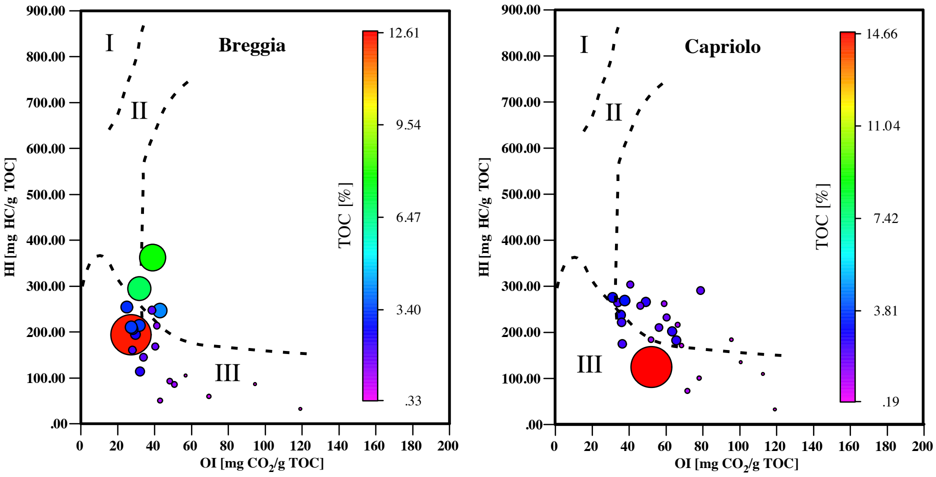

Fig. 4. Hydrogen index (HI) values versus oxygen index (OI) values in a Van Krevelen-type diagram for mudstone samples from the Breggia and Capriolo sections.

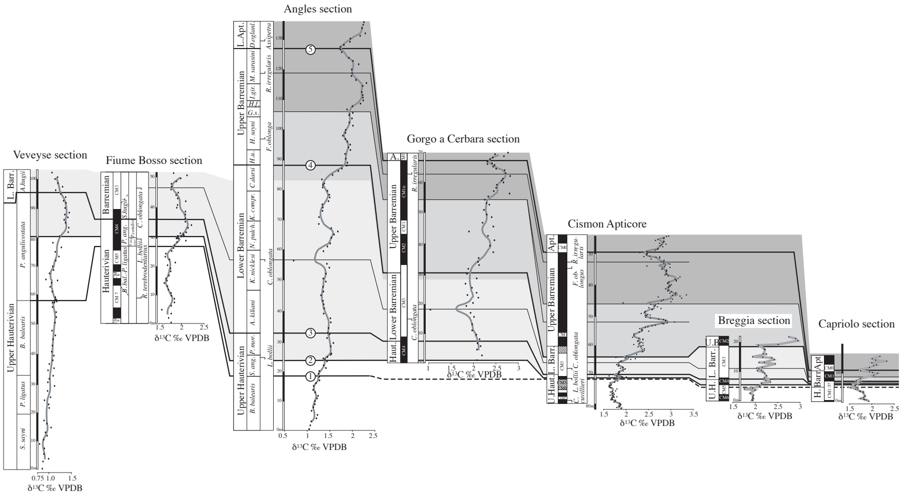

Fig. 5. Correlation of the δ^{13}C records of the Veveyse de Châtel Saint Denis, Fiume Bosso, Angles, Gorgo a Cerbara and Cismon Apticore sections and cores (modified from Godet et al., 2006) and the Breggia and Capriolo records.

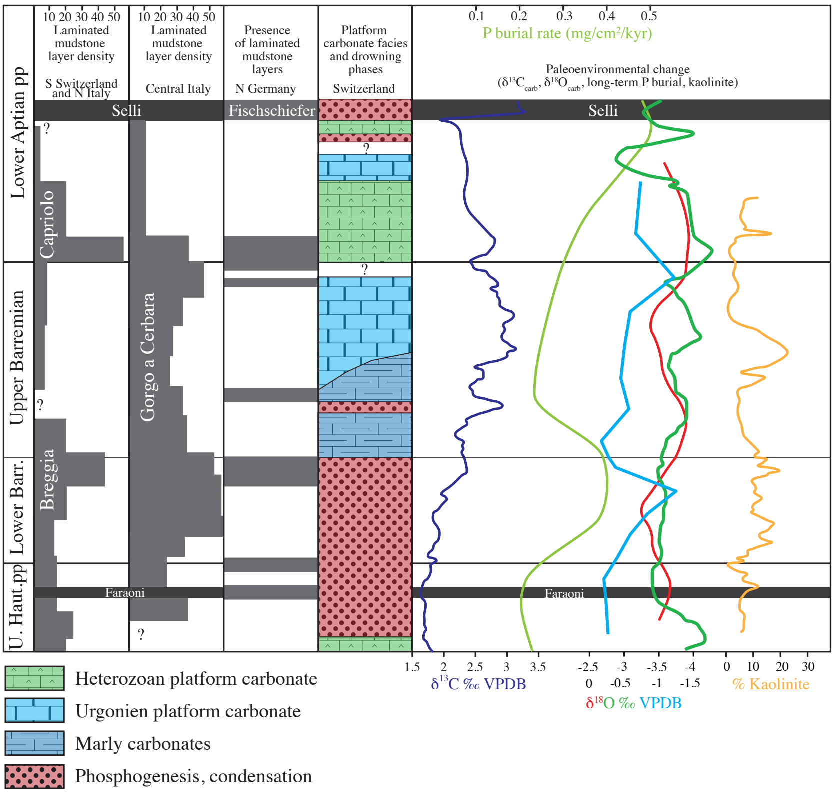

Fig. 6. Caption on next page.

Fig. 6. From left to right: laminated mudstone layer density for the Breggia and Capriolo sections; estimated laminated mudstone layer density for the Gorgo a Cerbara section using the stratigraphic log from Gorin and Fiet (2000) and Stein et al. (2011); age of laminated mudstone layers for the northwest German Basin: the Barremian and Aptian occurrences are from the basin margin (Mutterlose et al., 2010) and the Hauterivian occurrences from the basin centre (Mutterlose et al., 2009); evolution of the Helvetic segment of the northern Tethyan carbonate platform (modified after Föllmi et al., 2007); δ^{13}C record on whole-rock carbonate, from the Cismon outcrop and Cismon Apticore (Menegatti et al., 1998; Erba et al., 1999); low-resolution phosphorus burial record (Föllmi, 1995; Bodin et al., 2006a); δ^{18}O records from whole-rock carbonate from central Italy (in green; Sprovieri et al., 2006; Stein et al., 2011) and southeast France (in red; Godet et al., 2006; Bodin et al., 2009) and δ^{18}O record from belemnites from southeast France (in blue; Bodin et al., 2009); and kaolinite record from southeast France (Godet et al., 2008).