

The neglected history of Oceanic Anoxic Event 1b: insights and new data from the Poggio le Guaine section (Umbria–Marche Basin)

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ABSTRACT: The upper Aptian to lower Albian interval (~114–109 Ma) represents a crucial period during Earth's history, with a major evolution in the nature of mid–Cretaceous tectonics, sea level, climate, and marine plankton communities. Interestingly, it also includes multiple prominent black shale horizons that are the sedimentary expression of oceanic anoxic event (OAE) 1b. However, due to a set of geological, stratigraphic, and taxonomic challenges, difficulties constraining this OAE may sometimes result in inaccurate correlation.

At Poggio le Guaine (central Italy), a continuous and undisturbed section of central western Tethyan pelagic sediments deposited during the latest Aptian and earliest Albian, complete with black shale horizons that record the OAE1b carbon cycle perturbations, has provided a unique opportunity to address the shortcomings referred to above. High-resolution geochemical proxies (CaCO₃, TOC, and $\delta^{13}\text{C}$), along with planktonic foraminifera and calcareous nannofossils, were used to establish an integrated and robust global stratigraphic framework in order to: (1) precisely correlate the prominent black shale horizons of OAE1b in different marine environments (the Vocontian Basin in southeast France, Deep Sea Drilling Project Site 545 and Ocean Drilling Program Hole 1049C in the eastern and western North Atlantic, respectively); and (2) provide an effective tool to reconstruct, in high resolution, the paleobiological, paleoceanographic and paleoclimatic changes across the upper Aptian to lower Albian interval.

The Poggio le Guaine section stands out as a valuable reference section for OAE1b, its constituent subevents, and the $\delta^{13}\text{C}$ record for the uppermost Aptian to lower Albian interval. The exceptional chemo- and biostratigraphic control allow direct comparison to the proposed candidate for the GSSP for the base of the Albian Stage at the Col de Pré-Guittard section in France.

INTRODUCTION

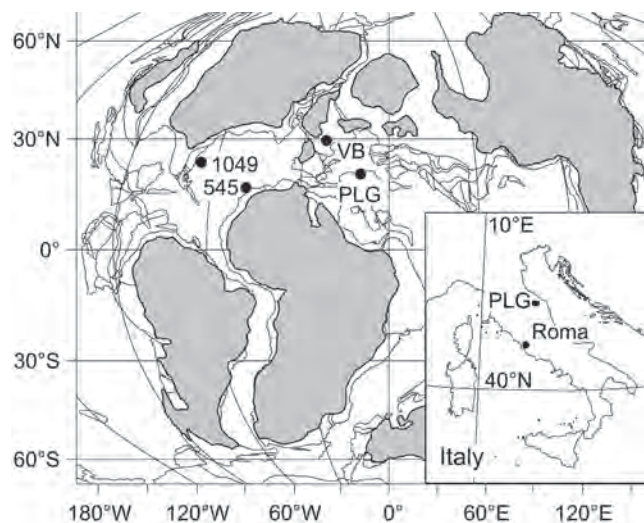
The upper Aptian to lower Albian interval (~114–109 Ma) of the Tethys and Atlantic Ocean contains several prominent black shale horizons which, with different definitions, are known in the literature as OAE (oceanic anoxic event) 1b (e.g., Arthur et al. 1990; Barlower et al. 1993; Leckie et al. 2002; Herrle et al. 2004; Trabucho Alexandre et al. 2011).

Although this OAE is probably one of the least significant in terms of the perturbation of the global carbon cycle, as testified by the lack of large CIEs (carbon isotope excursions), it has received more focus over time with research in the western Tethys and in the North Atlantic because the time interval during which the OAE1b takes place represents a significant reorganization of tectonics, climate, and biota (e.g., Coccioni et al. 1987B; 1989a; 1990a; 1990b; 2006; 2012; Tornaghi et al. 1989; Arthur et al. 1990; Coccioni 1990; Barlower et al. 1993; Bréhéret 1994; 1997; Erbacher et al. 1998; 1999; 2001; Barker et al. 2001; Hofmann 2001; Holbourn and Kuhnt 2001; Holbourn et al. 2001; Kuypers et al. 2002; Herrle 2002; 2003; Leckie et al. 2002; Herrle and Mutterlose 2003; Herrle et al. 2003a; 2003b; 2004; Tsikos et al. 2004; Friedrich et al. 2005; Arnaboldi and Meyers 2006; Wagner et al. 2007; Friedrich et al. 2005; Heimhofer et al. 2006; Wagner et al. 2007; 2008; Browning and Watkins 2008; Hofmann et al. 2008; Mutterlose et al. 2009; Friedrich 2010; Huang et al. 2010; Huber and Leckie 2011; Huber et al. 2011; Trabucho Alexandre et al. 2011; Petrizzo et al. 2012; 2013; McAnena et al. 2013; Kennedy et al. 2014).

However, stratigraphic incompleteness across the the upper Aptian to lower Albian interval, biostratigraphic problems, including limited resolution, ambiguous or inaccurate taxonomic identification and stratigraphic range of some species, and the different number of organic matter-rich horizons in the stratigraphic record of each basin imply that the multi-event OAE1b is not yet well-defined and its poor definition may sometimes lead to inaccurate correlations (e.g., Kennedy et al. 2000; Huber and Leckie 2011; Trabucho Alexandre et al. 2011).

Because the issues outlined above, the available bio-, chrono- and isotope stratigraphic framework around the upper Aptian to lower Albian interval that provides the basis for discussing and understanding (1) the respective roles of tectonics, sea level, climate, and ocean circulation in controlling the late Aptian–early Albian depositional environments, (2) the major biotic, chemical and climatic perturbation of the ocean and the atmosphere that marks this period in Earth's history, (3) the still debated forcing mechanisms that led to the formation of the organic-rich black shale horizons corresponding to the OAE1b, (4) the biotic, oceanographic and climatic changes associated with those mechanisms, and (5) the global modelling investigating climatic consequences and biogeochemical feedbacks that occurred around the OAE1b, remain poorly constrained.

The central–western Tethyan pelagic section outcropping at Poggio le Guaine in the Umbria–Marche Basin of central Italy (text-figure 1), with its complete and undisturbed record is recognized as a reference section for the Aptian–Albian throughout the area (Coccioni and Cocon 1987; Coccioni et al.



TEXT-FIGURE 1

Paleogeographic map at 113 Ma modified after Huber and Leckie (2011) showing location of Poggio le Guaine (PLG) section (lat. 43°32′29.06″N, long. 12°34′51.09″E), Vocontian Basin (VB), DSDP Site 545 and ODP Hole 1049C that are discussed in this study.

1987a; 1987b; 1989a; 1989b; 1990a; 1990b; 1991; 2006; 2012; Coccioni and Battistini 1989; Erba et al. 1989; Coccioni 1990; 1996; Ingram et al. 1994; Baudin et al. 1998; Turchyn et al. 2009). This section, with its excellent geochronological control and the remarkable occurrence of all of the prominent black shale horizons that are linked to OAE 1b (text-figures 2–3), provides an exceptional opportunity to address the shortcomings referred to above and may serve as a corner-stone when it comes to studying the global oceanographic, climatic and evolutionary changes linked to OAE1b.

Despite sharing a common set of global forcing mechanisms, the deposition of organic-rich sediments during OAE1b appears to be the result of several equifinal processes acting on a local scale as a function of many local environmental variables. Such variables include: sedimentation process, sedimentation rates, terrigenous input, surface productivity, carbonate dissolution and diagenesis (Trabucho Alexandre et al. 2011). Thus, the exact processes that have led to the enrichment of organic matter during OAE1b and their subsequent preservation in the geological record are still matter of discussion and, sadly, lie outside the scope of this work.

The major objectives of this study are (1) expanding the known record of the multi-event OAE1b to the central-western Tethys; (2) presenting the results of a high-resolution planktonic foraminiferal and calcareous nannofossil biostratigraphy in combination with a detailed carbon isotope record leading to an integrated and robust stratigraphic framework; (3) providing more precise constraints on the record and timing of the different OAE1b sub-events and the associated major biotic turnovers; (4) contributing to an improved stratigraphic correlation between the Poggio le Guaine reference section, the Vocontian Basin (southeast France), the DSDP (Deep Sea Drilling Project) Site 545 (Mazagan Plateau, eastern North Atlantic) and the ODP (Ocean Drilling Program) Hole 1049C (Blake Nose, western North Atlantic); and (5) providing new insights into the upper Aptian to lower Albian interval.

GEOGRAPHICAL, GEOLOGICAL, AND STRATIGRAPHIC SETTING

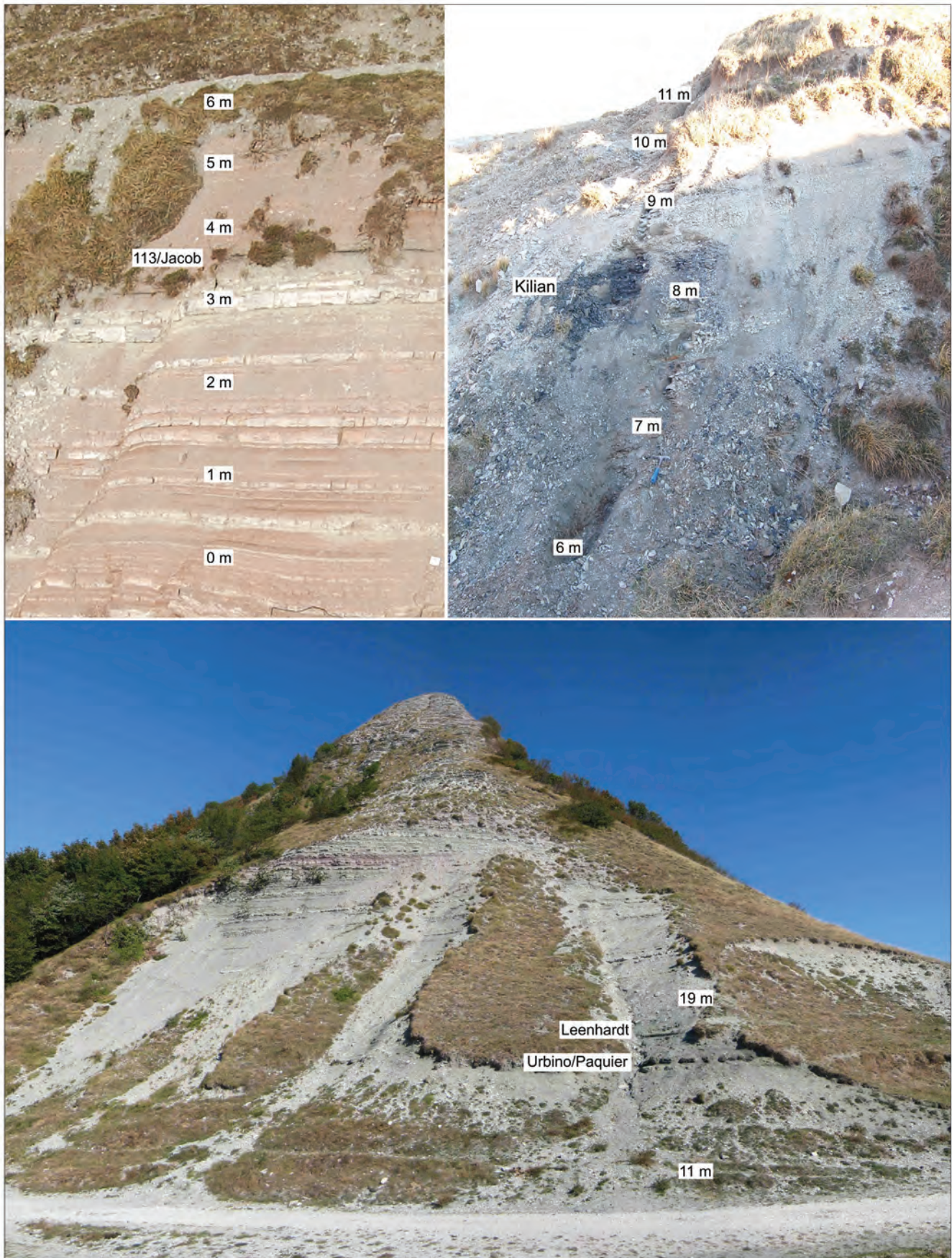
The Poggio le Guaine section (lat. 43°32′29.06″N, long. 12°34′51.09″E) is located on the Monte Nerone ridge of the Umbria–Marche Basin of central Italy, 6 km west of the town of Cagli (Marche Region) (text-figure 1).

The varicolored strata of the Marne a Fucoidi Formation of the Umbria–Marche Basin present a remarkably complete and well-preserved Aptian–Albian pelagic succession. This succession, and especially the distinctive intercalated organic-carbon-rich shales, have been the focus of three decades of dedicated and detailed stratigraphic research (Arthur and Premoli Silva 1982; Coccioni and Cocon 1987; Coccioni et al. 1987a; 1987b; 1989a; 1989b; 1990a; 1990b; 1991; 2006; 2012; Erba 1988; 1992; Coccioni and Battistini 1989; Erba et al. 1989; Coccioni 1990; 1996; Tornaghi et al. 1989; Coccioni and Galeotti 1993; Ingram et al. 1994; Baudin et al. 1998; Fiet and Masure 2001; Satolli et al. 2008; Tiraboschi et al. 2009; Turchyn et al. 2009). Individual black shale horizons in the Umbria–Marche Basin have been correlated with varying degrees of success with black shale horizons in other parts of the world.

The studied exposure representing the upper Aptian and lower Albian interval at Poggio le Guaine lies below and above the dirt road at spot height 880m above sea level and comprises pale reddish brown to dark reddish brown and pale olive to greyish olive argillaceous limestones and calcareous marlstones, marlstones, slightly calcareous mudstones to argillaceous mudstones with several cyclically alternating organic-rich black shales and mudstones (text-figures 2 and 3), some of which have been identified as the regional to global sedimentary expression of OAE1b (Coccioni et al. 1987a; 1989a; 1990a; 1990b; 2006; 2012; Coccioni and Battistini 1989; Erba et al. 1989; Coccioni 1996; Leckie et al. 2002; Trabucho Alexandre et al. 2011; Petrizzo et al. 2012; 2013; Kennedy et al. 2014).

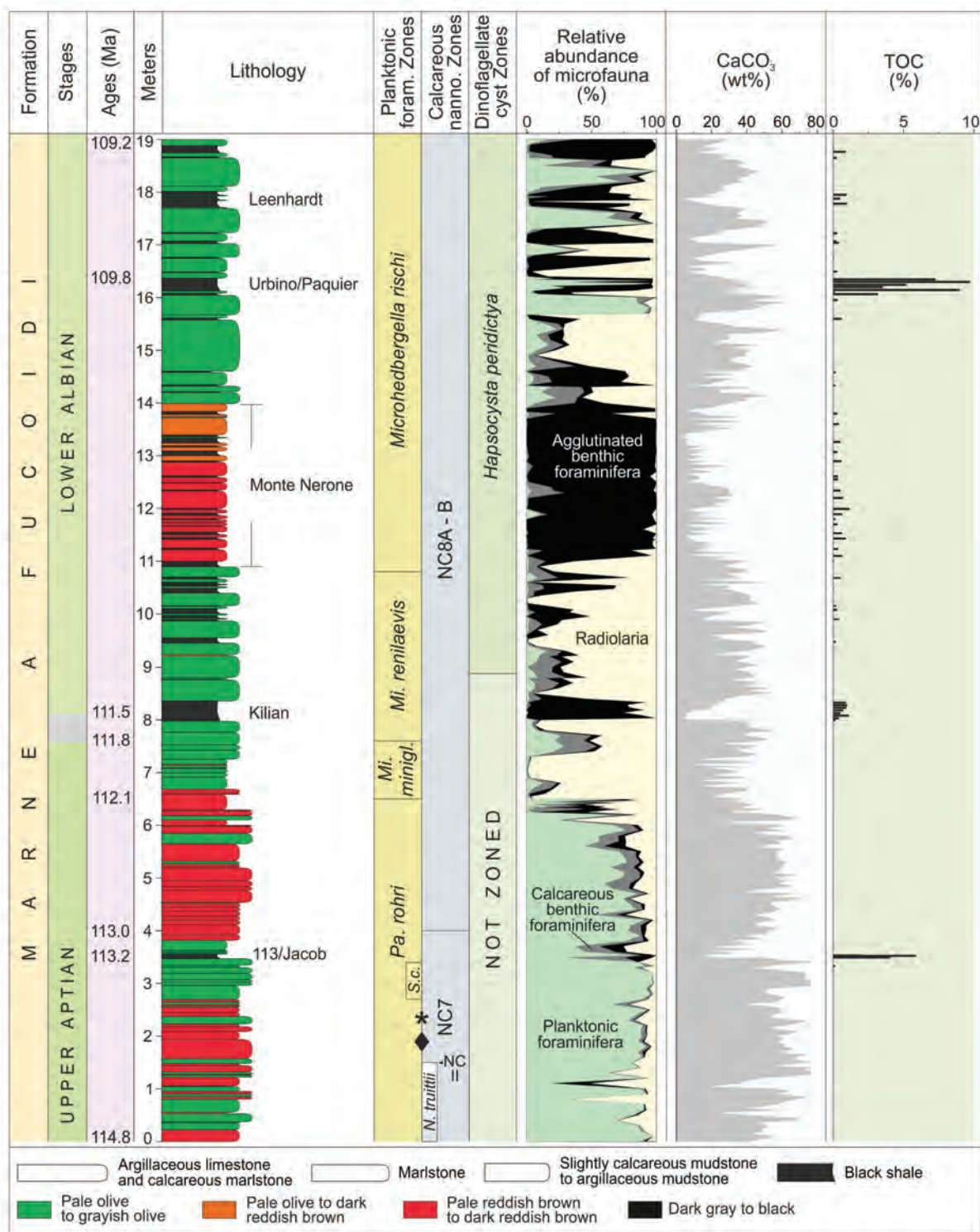
All the lithotypes originated as nannofossil-planktonic foraminiferal ooze, deposited above the calcite compensation depth at a paleolatitude of ~20°N according to the Ocean Drilling Stratigraphic Network Plate Tectonic Reconstruction Service (<http://www.odsn.de>) and at middle to lower bathyal depths of about 1000–1500m (Coccioni 1990), in a relatively quiet pelagic setting. Similar to observations made in the core drilled in 2010 in close proximity to the Poggio le Guaine section (Coccioni et al. 2012), no physical evidence of unconformable surfaces is obvious, thus confirming the stratigraphic continuity of the studied section.

Four black shale horizons are prominent at the Poggio le Guaine section (text-figure 3). The oldest of them is 8cm-thick (from meter stratigraphic level, msl, 3.47 to msl 3.55) and corresponds to the ‘113 level’ of Coccioni et al. (1987a; 1989a; 1990a; 1990b), Coccioni and Battistini (1989) and Erba et al. (1989). Above it a 40cm-thick (from msl 7.97 to msl 8.37) black shale characterized by very fine laminations, without bioturbation, occurs. The overlying 25cm-thick (from msl 16.12 to msl 16.37) distinctly laminated black shale corresponds to the ‘Urbino level’ of Coccioni et al. (1987a; 1989a; 1990a; 1990b), Coccioni and Battistini (1989) and Erba et al. (1989). Finally, a 29cm-thick black shale (from msl 17.71 to msl 18) is found at the top of the studied section.



TEXT-FIGURE 2

The Poggio le Guaine section in outcrop. The locations of the black shale horizons that are the sedimentary expression of the four sub-events of OAE1b are also shown.



TEXT-FIGURE 3

Stratigraphy of the studied interval at Poggio le Guaine plotted against relative foraminiferal and radiolarian abundance, calcium carbonate, and total organic carbon (TOC) content. The diamond and asterisk respectively mark the highest occurrence of *Pseudoplanomalina cheniourensis* and the lowest occurrence of *Pleurostomella subnodosa* which, in the absence of significant planktonic foraminiferal events, was used by several authors to identify the Aptian/Albian boundary (see Huber and Leckie 2011). The short stratigraphic interval, yielding a large number of the elongated chambered planktonic foraminifera *Schakoina cepedai* and likely correlated with the similar interval recognized by Huber and Leckie (2011) in the late Aptian at ODP Hole 1049C, is also shown. NCII corresponds to the end of the *Nannoconus truitii* Acme that is the second Aptian nannoconid crisis of Herrle and Mutterlose (2003), and marks the late Aptian cold snap of Mutterlose et al. (2009). In the absence of a formal definition of the base of the Albian Stage and following Petrizzi et al. (2012, 2013) and Kennedy et al. (2014) we have placed the Aptian/Albian boundary at the Poggio le Guaine section within the thin stratigraphic interval spanning from the LO of *Mi. renilaevs* to the significant, short-lived negative CIE falling in the middle part of the black shale that spans from msl 7.97 to msl 8.37 (i.e., the Kilian level equivalent). Estimated ages for the studied section are inferred after Grippo et al. (2004), Huang et al. (2010), and Ogg and Hinnov (2012). Key to planktonic foraminiferal and calcareous nannofossil abbreviations: *Pa.* = *Paraticinella*, *Mi.* = *Microhedbergella*, *minigl.* = *miniglobularis*, *S.* = *Schackoina*, *c.* = *cepedai*, *N.* = *Nannoconus*.

MATERIAL AND METHODS

A 19m-thick section was logged in detail (text-figure 3 and Appendix 1) and a total of 572 bulk-rock samples were collected with an average resolution of ~3.3cm, corresponding to ~9.7 kyr. Some intervals were more densely sampled in order to refine the position of important biohorizons.

Samples were collected from trenches at least 20cm deep to obtain fresh rock. To ensure precision in sampling level some beds were taken in their entirety and then split in the laboratory. All the materials studied are housed in the laboratory of the DiSTeVA (Dipartimento di Scienze della Terra, della Vita e dell'Ambiente, Università di Urbino).

All samples were analyzed for foraminiferal biostratigraphy and microfauna. Samples were treated following the cold acetolysis technique of Lirer (2000) by sieving through a 63µm mesh and drying at 50°C. The cold acetolysis method enabled extraction of generally easily identifiable foraminifera even from indurated limestones. This technique offered the possibility of accurate taxonomic determination and detailed analysis of foraminiferal assemblages. Planktonic and benthic foraminiferal and radiolarian abundances were calculated in the > 63µm fraction of two hundred and fifty-seven selected samples that were divided using an Otto microsplitter from a representative split of at least 300 specimens. Tests showing > 50% fragmentation were excluded from the specimen counts. The abundance counts are shown in Appendix 1. The planktonic foraminiferal framework used and the species concepts adopted in this study follow Huber and Leckie (2011), Petrizzo et al. (2012) and the CHRONOS online Mesozoic taxonomic dictionary located at <http://portal.chronos.org> with references therein. Additional reference to the taxonomic notes of Ando et al. (2013) was also made. Herein we use the terminology of lowest occurrence (LO) and highest occurrence (HO) to delineate the appearance and disappearance of taxa.

A total of one hundred and thirty samples were selected throughout the section and investigated for calcareous nannofossil biostratigraphy. Overall, sampling density was 50cm although some intervals were more densely sampled (10cm) in order to refine the position of important biohorizons. Bulk sediment was processed following the standard techniques of pipette-strew slide preparation at constant concentration. Calcareous nannofossil analysis was performed using a Zeiss Imaging II light microscope with a magnification of 1500x. All the specimens belonging to key biostratigraphic taxa were counted in 1mm² according to the procedure of Backman and Shackleton (1983). About 300 FOV (fields of view) per sample were examined to check for nannofossil species richness. Calcareous nannofossil preservation was evaluated using the visual criteria of Roth and Thierstein (1972), Roth (1984) and SEM (Scanning Electron Microscope) observations. Lowest Occurrence (LO) and Highest Occurrence (HO) of index species could be used to establish a nannofossil biostratigraphic framework following Sissingh (1977; amended Perch-Nielsen 1985) and Roth (1983; amended Bralower et al. 1993; 1995). However, since the succession, the taxonomy and the calibration of some biohorizons are not yet well established worldwide or even from one basin to another, we preferred to avoid the rigid application of the zonal scheme allowing us to focus on the biohorizons themselves, in order to test their applicability and reproducibility at a supra regional scale. The distribution and composition of calcareous nannoplankton assemblages are, in fact, controlled by local and regional paleoenvironmental conditions such as

nutrients, temperature, terrigenous input, marginal versus open oceanic depositional setting (e.g., Thierstein and Young 2004). Paleoenvironmental changes influence the ecology of some key species and, together with changes in the preservation state, may affect their applicability and reproducibility. These factors are likely responsible for the (apparent?) diachronic LOs and HOs of biostratigraphically important species observed worldwide.

Foraminiferal and calcareous nannofossil events and zonal and subzonal boundaries recorded in the Poggio Le Guaine section and their respective meter stratigraphic levels are shown in Table 1 and zonal foraminiferal and calcareous nannofossil marker species and significant species are illustrated in Plates 1–5.

The dinocyst zonation is after Fiet and Masure (2001) (text-figure 3).

Calcium carbonate analyses were performed on nearly all samples (text-figure 3 and Appendix 1) at the geochemistry laboratory of the DiSTeVA. The bulk rock samples were crushed to fine powder in an agate mortar. Calcium carbonate content measurements were obtained using a Dietrich-Frühling calcimeter, a method based on the measurement of CO₂ volume produced by the complete dissolution of pre-weighed samples (300±1 mg each) in 10% vol. HCl. Total carbonate content (wt.% CaCO₃) was computed with a precision of 1% using formulae that take into account pressure and temperature of the lab environment, amount of bulk sample used, and the volume of CO₂ developed in the calcimeter. Standards of pure calcium carbonate (i.e., Carrara Marble) were measured every ten samples to ensure precise calibration.

TOC (total organic carbon) content was measured on 62 selected samples (text-figure 3 and Appendix 1). Bulk sediment samples were powdered and ca. 15 mg was decarbonated using HCl 1M in silver cups for 24 h at ambient temperature, then dried in an oven at 60°C and analysed using a Thermo Electron Flash EA 1112.

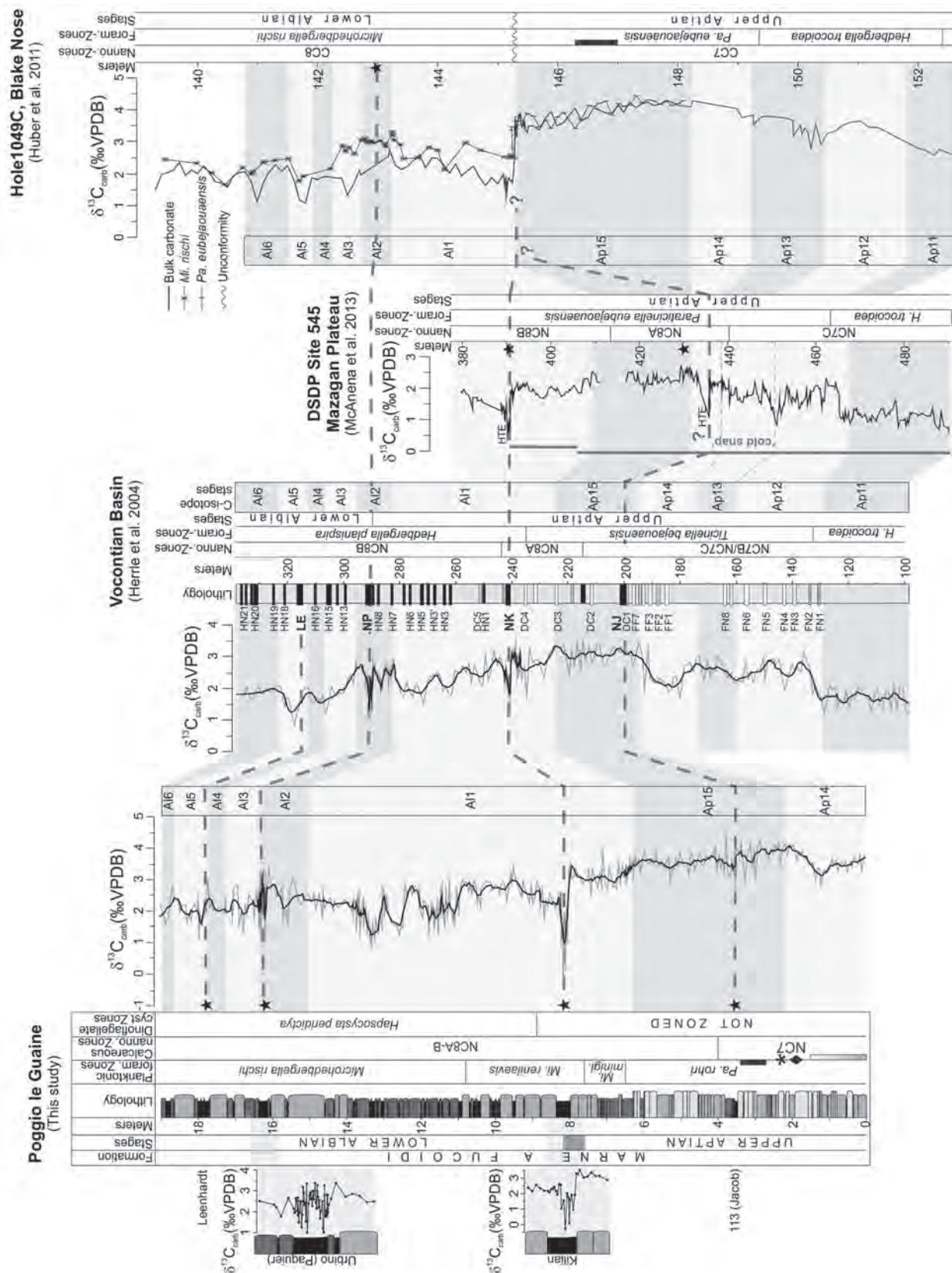
Stable isotope analyses ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) were conducted on 487 bulk samples (text-figure 4 and Appendix 1) using an automated continuous-flow carbonate preparation GasBenchII device (Spötl and Vennemann 2003) and a ThermoElectron Delta Plus XP mass spectrometer in the geochemistry laboratories at the IAMC-CNR (Istituto per l'Ambiente Marino Costiero-Consiglio Nazionale delle Ricerche), Institute of Naples. Acidification of samples was performed at 50°C. Again, to ensure precise calibration, every 6 samples, an internal standard (Carrara Marble with $\delta^{18}\text{O} = -2.43\text{‰}$ versus VPDB, Vienna Pee Dee Belemnite, and $\delta^{13}\text{C} = 2.43\text{‰}$ versus VPDB) was run and every 30 samples the NBS19 international standard was measured. Standard deviations of carbon and oxygen isotope measures were estimated at 0.1 and 0.08‰, respectively. All the isotope data are reported in $\delta\text{‰}$ versus VPDB.

MICROPALEONTOLOGY AND BIOSTRATIGRAPHY

Microfaunal abundance and preservation and remarks

Our detailed documentation of microfaunal content and abundance across the continuous uppermost Aptian-lower Albian sedimentary sequence exposed at Poggio le Guaine permits a reliable description of the magnitude and rate of microfaunal turnovers despite some diagenetic alteration of the microfaunal assemblages.

Most of the samples from the Poggio le Guaine section yielded foraminifera and radiolaria with fluctuations in relative



TEXT-FIGURE 4

Combined carbon isotope stratigraphy for the upper Aptian-lower Albian interval from the Poggio le Guaine section, Vocontian Basin, DSDP Site 545 and ODP Hole 1049C, with black shale horizons plotted against biochronostratigraphy. Time-equivalent black shale horizons are marked by black stars and correlated with dashed grey lines. The isotope carbon stages are from Herrle et al. (2004). The late Aptian cold snap and the HTEs (high-thermal events) from McAnena et al. (2013) are highlighted at DSDP Site 545. The *Shackoina cepedai* intervals (black bar) recognized at Poggio le Guaine (this study) and at ODP Hole 1049C (Huber and Leckie 2011) are also shown. Key to planktonic foraminiferal abbreviations: Pa. = *Paratitella*, Mi. = *Microhedbergella*, minigl. = *miniglobularis*, H. = *Hedbergella*.

A)

Boundary stage (Kennedy et al. 2014)		APTIAN		ALBIAN	
Marker beds		J	K	P	L
Vocontian Basin	(Kennedy et al. 2000)	<i>Ticinella bejaouaensis</i>		<i>Hedbergella planispira</i>	
	(Herrle et al. 2004)	<i>Ticinella bejaouaensis</i>		<i>Hedbergella planispira</i>	
	(Petrizzo et al. 2012; Kennedy et al. 2014)	<i>Paraticinella rohri</i>		<i>Microhedbergella renilaevs</i>	<i>Mi. rischi</i>
	ODP Site 1049C (Huber et al. 2011)	<i>Paraticinella eubejaouaensis</i>		<i>Microhedbergella rischi</i>	
Umbria-Marche Basin (This study)		<i>Paraticinella rohri</i>	<i>Mi. minigl.</i>	<i>Mi. renilaevs</i>	<i>Microhedbergella rischi</i>

B)

Boundary stage (Kennedy et al. 2014)		APTIAN		ALBIAN	
Marker beds		J	K	P	L
Vocontian Basin	(Kennedy et al. 2000)	CC7	CC8		
		NC7	NC8A-B		
	(Herrle et al. 2004)	NC7B/NC7C	NC8A	NC8B	
	(Petrizzo et al. 2012; Kennedy et al. 2014)	CC7	CC8A-B*	CC8A	
		NC7	NC8A-B*	NC8A-B	
ODP Site 1049C (Huber et al. 2011)		CC7	⚡	CC8	
Umbria-Marche Basin (This study)		NC7	NC8A-B		

TEXT-FIGURE 5

Comparison of the planktonic foraminiferal (A) and calcareous nannofossil (B) zonal and subzonal sequence for the upper Aptian to lower Albian interval of the Poggio le Guaine section of the Umbria–Marche Basin with those from the Vocontian Basin as provided by different authors and from ODP Site 1049C in the same time interval. The position of the Aptian/Albian boundary stage according to Kennedy et al. (2014) is also indicated. The asterisks mark the Jacob (J), Kilian (K), Paquier (P) and Leenhardt (L) sub-events of OAE1b. Key to planktonic foraminiferal abbreviations: *Mi.* – *Microhedbergella minigl.* – *miniglobularis*.

abundance throughout, which are generally accompanied by significant changes in the carbonate content (text-figure 3).

Planktonic foraminifera occur in almost all samples. From the base of the section up to msl 6.2 planktonic foraminifera dominate the faunal assemblages (up to 97%, with an average of 76%) except at the msl 0.8 and msl 1.1 and within and slightly above the black shale horizon spanning from msl 3.47 to msl 3.55. Two sudden major decreases in their abundance are recorded at msl 6.25 and msl 6.5 with the percentage declining from 67.2% to 3.6% and from 68.5% to 4%, respectively. Similar decreases in abundance in the uppermost Aptian are also recorded in the Col de Pré-Guittard section of the Vocontian Basin (Petrizzo et al. 2012) and at DSDP Site 511 in the South Atlantic (Huber and Leckie 2011). In the stratigraphical interval between the two major decreases observed at Poggio le Guaine the number of planktonic foraminifera fluctuate markedly throughout with percentages that vary from 0.3% to 68.5% and an average value of 21.2%. In the overlying stratigraphic levels planktonic foraminifera are absent or occur in low to very low percentage with some temporary rapid increase in abundance (up to 28.2% at msl 7.5). A distinctive increase in their general abundance (up to 99.5% at msl 18.4) starts slightly below the Urbino level of Coccioni et al. (1987a; 1989a; 1990a; 1990b), Coccioni and

Battistini (1989) and Erba et al. (1989) that spans from msl 16.12 to msl 16.37 and continues up to the top of the section, with marked drop in the total number of specimens across the carbonate poor black shale beds.

From the base of the section up to msl 6.5 planktonic foraminifera are generally moderately to well-preserved whereas from this stratigraphic level up to the base of the Urbino level the preservation of planktonic foraminifera is generally poor to moderate, with most of the specimens showing diagenetic alteration with different degrees of test recrystallization. Preservation progressively improves from the base of the Urbino level upwards.

Benthic foraminifera are consistently present throughout the section with variable abundances except for a couple of samples within the Urbino level. From msl 6.25 up to the top of the section they are generally more abundant than planktonic foraminifera and along with radiolaria are a consistent component of faunal assemblages. Benthic foraminifera dominate the faunal assemblages from msl 11 to msl 13.9 and also within most of the black shales recorded from msl 14.33 up to the top of the section. The upper Aptian to lower Albian interval at Poggio le Guaine as well as throughout the Umbria–Marche Basin is marked by a

Foraminiferal bioevents, biozonation, and remarks

Planktonic foraminiferal distribution and changes in species composition and abundance across the studied section permits the identification of four biozones along with a precise placement of the zonal boundaries and enable the identification of some secondary biostratigraphic data that are potentially very useful for global correlation (text—figures 3–4).

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Calcareous nannofossil biohorizons, biozonation, and remarks '*Nannoconus truittii* Acme'

The end of the '*Nannoconus truittii* Acme' (Mutterlose 1989), which marks the second Aptian nannoconid crisis (NCII of Herrle and Mutterlose 2003) and a global cooling episode (the 'Late Aptian cold snap' of Mutterlose et al. 2009), is recognized at msl 1.5, in the lower part of the planktonic foraminiferal *Paraticinella rohri* Zone, which is in agreement with the data from the Vocontian Basin (Herrle and Mutterlose 2003) (text–figure 3 and Table 1).

LO of *Prediscosphaera columnata* (NC8A)

The appearance of genus *Prediscosphaera* has long been used as a proxy for the Aptian/Albian boundary in many publications. In particular, the base of *Prediscosphaera columnata* nannofossil Zone has been assumed to closely approximate the base of the Albian (Barrier 1977; Perch-Nielsen 1979; Bralower 1992).

Kennedy et al. (2000) made an accurate description of the different *Prediscosphaera* morphotypes (from elliptical to sub-circular to fully circular) appearing across the uppermost Aptian/lower Albian. According to their study, the first *Prediscosphaera* occurring in the uppermost Aptian sediments of the Col de Pré-Guittard section are the elliptical *P. spinosa*, immediately followed by the sub-circular forms. Both biohorizons were observed slightly above the Jacob level (e.g., Herrle et al. 2004). True circular forms known as *P. columnata* made their appearance later. In their discussion they reached the conclusion that "the exact level of the lowest *P. columnata*, as reported in the literature, is somewhat compromised by taxonomic imprecision and inconsistency". Herrle and Mutterlose (2003) who studied other Vocontian sections, reached different conclusions: the first *Prediscosphaera* to appear are undetermined species (no description and no illustration is provided) and this event lies in the lower-upper Aptian of Serre Chaitieu section, before the Fallot level (e.g., Herrle et al. 2004) which is well constrained by the LOs of *P. spinosa* and *P. columnata*, the last comprising sub-circular to near circular morphotypes.

The appearance of the genus *Prediscosphaera* thus seems discrepant between the Herrle and Mutterlose (2003) and Kennedy et al. (2000) studies, probably because the latter did not go as deep as the lower-upper Aptian and missed the first occurrences of the genus which is very rare. It is important to stress, however, that the base of *Prediscosphaera columnata* and NC8A Zone is agreed between these two papers, being fixed by the first occurrences of sub-circular, near circular morphotypes above the Jacob level.

In this study we did not encounter any *Prediscosphaera* sp. in the lower part of the section before the Jacob level as in Herrle et al. (2004). The first *Praediscosphaera* observed at msl 4, just above the 113 level, are sub-circular morphotypes (text–figure 3 and Table 1). *Prediscosphaera spinosa* was sporadically found higher up in the section, together with true circular specimens. *Prediscosphaera* is always very rare and small-sized (about 4µm) at the beginning of its range.

LO of *Hayesites albiensis* (NC8B)

The LO of *H. albiensis* was used as subzonal marker by Bralower et al. (1993) for the uppermost Aptian, after the LO of *P. columnata*.

Kennedy et al. (2000) studied material from the Vocontian Basin, where a true separation between *H. albiensis* and *Hayesites*

irregularis was not made although *H. albiensis*-like specimens were observed throughout the stratigraphic range of the studied sections. Herrle and Mutterlose (2003) observed the LO of *H. albiensis* slightly above the Kilian level in the Vocontian basin. In the North Atlantic ODP Site 1049C, Browning and Watkins (2008) reported a fairly enlarged stratigraphic range for *H. albiensis*, starting well before the LO of *P. columnata*. The use of this biohorizon seems problematic for two main reasons: (1) the occurrence of transitional forms between *H. albiensis* and its ancestral form *H. irregularis* and (2) bad preservation (etching overgrowth) can obliterate the stellate, thinner rays that characterize the species, thus preventing its correct diagnosis. This greatly detracts from the reliability of this taxon as a marker species.

In our study we found transitional forms between *H. albiensis* and *H. irregularis* in agreement with Bown (in Kennedy et al. 2000) while true *H. albiensis* were observed from msl 16.3, within the upper part of the Urbino level (text–figure 3 and Table 1). It results that the diachronic behavior of this species, whether real or its rareness and/or poor preservation, represents an obstacle for correlation even at a basin scale. We preferred therefore to avoid the strict application of this biohorizon to split Subzones CC8a and b and NC8A and B (text–figures 3–4 and Table 1).

LO of *Tranolithus orionatus* (NC8C)

The LO of *T. orionatus* (= *T. phacelosus*) was proposed as a marker at subzonal level by Perch-Nielsen (1979; 1985) and Applegate and Bergen (1989). No study precisely cites its position which has been given as middle Albian (Thierstein 1973) and top *mammillatum* ammonite Zone (Jeremiah 1996). Its LO is reported well after the Leenhardt level in the Vocontian Basin (Herrle 2002; Herrle and Mutterlose 2003). It was not encountered in the studied section.

Other biohorizons were used in previous studies to refine the biostratigraphic framework. Their applicability and reproducibility is however still limited to regional supra regional scale.

The LO of *Cylindralithus nudus* was reported by Bown (1998) after the LO of *P. columnata*. In this work *C. nudus* is consistently recorded from msl 0.5, well before the LO of *P. columnata* (Table 1).

The LO of *Rhagodiscus achlyostaurion* as a secondary marker was reported by the literature at different stratigraphic levels: after the LO of *Axopodorhabdus albianus* by Erba (1988), thus in the upper Albian, or before the LO of *P. columnata* thus in the uppermost Aptian according to Bralower (1992) and Kennedy et al. (2000). At the Poggio le Guaine section *R. achlyostaurion* occurs sporadically from msl 1 to msl 17 where it is commonly and consistently recorded (Table 1). The discontinuous occurrence of this taxon prevents a faithful utilization for biostratigraphy.

The LO of *Eiffellithus hancockii* followed by that of *Cribrosphærella ehrenbergii* were reported by Herrle (2003) in the Vocontian Basin above the LO of *P. columnata* and before the Kilian level, while Kennedy et al. (2000) reported it from the base of the Col de Pré-Guittard section. In this study *E. hancockii* is recognized from msl 2.5 while *Cribrosphærella* sp. is recorded from msl 4.5, which is below and above the 113 level, respectively (Table 1).

The HO of large *Assipetra/Rucinolithus* is a biohorizon proposed by Tremolada and Erba (2002) and Tiraboschi et al. (2009) lying between the LOs of *P. columnata* and *C. ehrenbergii*. At the Poggio le Guaine section *Assipetra/Rucinolithus* drastically decrease from msl 18, above the Urbino level, where we fixed its common top (Table 1).

The last occurrence of *Micrantholithus hoschulzi* reported by Erba was not fixed in this work, with *M. hoschulzi* being present throughout the studied section.

Comparing the biohorizons found in this study with those reported in previous literature we highlight more discrepancies than agreements. This can be due to several factors (sample density, preservation, ecology, etc.) that are important to carefully evaluate before any correlation attempt.

A comparison of the planktonic foraminiferal and calcareous nannofossil zonal and subzonal sequence for the upper Aptian to lower Albian interval of the Poggio le Guaine section with those from the Vocontian Basin as provided by different authors and from ODP Site 1049C in the same time interval is shown in text–figure 5.

Dinoflagellate cysts

Following Fiet and Masure (2001), the middle-upper part of the succession belongs to the *Hapsocysta peridictya* dinocyst Zone.

THE APTIAN/ALBIAN BOUNDARY AT POGGIO LE GUAINÉ

The placement of the Aptian/Albian boundary has a convoluted history and is currently undecided although an array of options are being considered as potential definitions for the base of the Albian Stage (Ogg and Hinnov 2012).

According to the most current reliable criteria to define the base of the Albian Stage as those reported by Ogg and Hinnov (2012, with references therein), the Aptian/Albian boundary should be placed within the stratigraphic interval spanning from the Jacob level to the Paquier level of the Vocontian Basin or their equivalents and related coeval carbon–13 isotopic excursions (e.g., Herrle et al. 2004).

The extinction of the planktonic foraminifera *Pa. rohri* has been traditionally used to approximate the Aptian/Albian boundary, especially in the absence of macrofossils, because of its distinctive morphology and size, and its continuous stratigraphic distribution documented in a wide range of environmental settings (e.g., Sliter 1989; Cobianchi et al. 1997; Premoli Silva and Sliter 1999; Bellier et al. 2000; Coccioni et al. 2006; Huber and Leckie 2011; Petrizzo et al. 2012). In addition, the lowest occurrence of the benthic foraminifera *Pl. subnodosa*, calibrated here for the first time relative to the extinction of *Pa. rohri*, has been used by several authors (e.g., Moullade 1966; 1974; Sigal 1977; Hart et al. 1996) to identify this stage boundary in absence of significant planktonic foraminiferal events.

Herrle et al. (2004) proposed an alternative non-biostratigraphic criterion to define the Aptian/Albian boundary at the onset of the pronounced negative shift of $\delta^{13}\text{C}$ values in early *Hayesites albiensis* NC8B calcareous nannofossil Subzone.

In Geologic Time Scale (GTS)2012 (Ogg and Hinnov 2012), the base of the Albian Stage is placed in correspondence of the LO of sub-circular forms of the calcareous nannofossil *P. columnata*,

which marks the NC7/NC8 zonal boundary of Roth (1978) and Bralower et al. (1993) with an age of ~113 Ma following Selby et al. (2009).

More recently, the Col de Pré-Guittard section has been proposed by Kennedy et al. (2014) as a candidate Global Boundary Stratotype Section and Point (GSSP) for the base of the Albian Stage, which fulfils many, but not all, of the requirements set out by Remane et al. (1996). The candidate boundary can be identified using the LO of the planktonic foraminifera *Mi. renilaevs* as recorded by Petrizzo et al. (2012; 2013) within the Kilian level and coinciding with a significant, though short-lived negative CIE that can be traced into the Atlantic region (Herrle, 2002; Herrle et al. 2004; Petrizzo et al., 2012; 2013; Trabucchi Alexandre et al. 2011).

Remarkably, the sequence of the planktonic foraminiferal events recorded at the Poggio le Guaine section is similar with that reported by Huber and Leckie (2011) from deep-sea Atlantic and Indian Ocean records and by Petrizzo et al. (2012) and Kennedy et al. (2014) from the Vocontian Basin with only minor discrepancies which probably are due to a sampling bias. Thus, as also pointed out by Petrizzo et al. (2012), the extinction of *Pa. rohri*, the planktonic foraminiferal turnover, and the appearance of *Mi. miniglobularis* and *Mi. renilaevs* appear to be synchronous and are effective bioevents for global correlations that combined with carbon–isotope stratigraphy could be used as reliable primary and/or secondary criteria to define the GSSP for the base of the Albian Stage in stratigraphically complete successions.

However, in the absence of a formal definition of the base of the Albian Stage and following Petrizzo et al. (2012, 2013) and Kennedy et al. (2014) we have placed the Aptian/Albian boundary at the Poggio le Guaine section within the thin stratigraphic interval spanning from the LO of *Mi. renilaevs* to the significant, short-lived negative CIE falling in the middle part of the black shale that spans from msl 7.97 to msl 8.37 (text–figures 3–6).

CLARIFYING THE LATEST APTIAN-EARLY ALBIAN OAE1b

Arthur et al. (1990, and references therein) first introduced the OAE1b sub-event (OAE-1 of Jenkyns 1980) to denote the Aptian–Albian black shales widely distributed in the Pacific Basin and in allochthonous terrains in California and Oregon, throughout the Tethyan Province from Pakistan to France, in India, Israel and the Middle East, and also as the apparent source for much of the petroleum reservoirs in giant fields in the Zagros fold belt and other areas, in eastern South America and the circum-South Atlantic. In particular, careful analyses of Aptian–Albian sections in the hemipelagic Vocontian Basin of the Tethyan domain have revealed the occurrence within the upper Aptian to lower Albian interval of four levels (i.e., the upper Aptian ‘Jacob’ and ‘Kilian’ levels and the lower Albian ‘Paquier’ and ‘Leenhardt’ levels of Bréhéret 1983; 1988) of regional extent that are particularly rich in organic carbon and well dated using ammonites.

At the same time, Coccioni et al. (1987a; 1989a; 1990a; 1990b), Coccioni and Battistini (1989) and Erba et al. (1989) recognized across the upper Aptian to lower Albian interval within the cyclic pelagic Marne a Fucoidi Formation of the Umbria–Marche Basin (central Italy) some distinct black-shales horizons of regional extent within the *Ticinella bejaouensis*, the *Hedbergella planispira* and the *Hedbergella rischi*–*Ticinella*

Within the past two decades, in agreement with Bralower et al. (1993), many authors assigned the term OAE1b to the lower Albian Paquier level and its equivalents (e.g., Erbacher et al. 1996; 1999; 2001; Erbacher and Thurow 1997; Bralower et al. 1999; Holbourn and Kuhnt 2001; Holbourn et al. 2001; Herrle 2002; 2003; Kuypers et al. 2002; Herrle and Mutterlose 2003; Herrle et al. 2003a; 2003b; 2004; 2010; Tsikos et al. 2004; Friedrich et al. 2005; Reichelt, 2005; Karakitsios and Agiadi-Katsiaouni, 2007; Wagner et al., 2007, 2008; Browning and Watkins, 2008; Hofmann et al. 2008; Tiraboschi et al. 2009; Ben Fadel et al. 2011; Gale et al. 2011; McAnena et al. 2013; Peybernes et al. 2013).

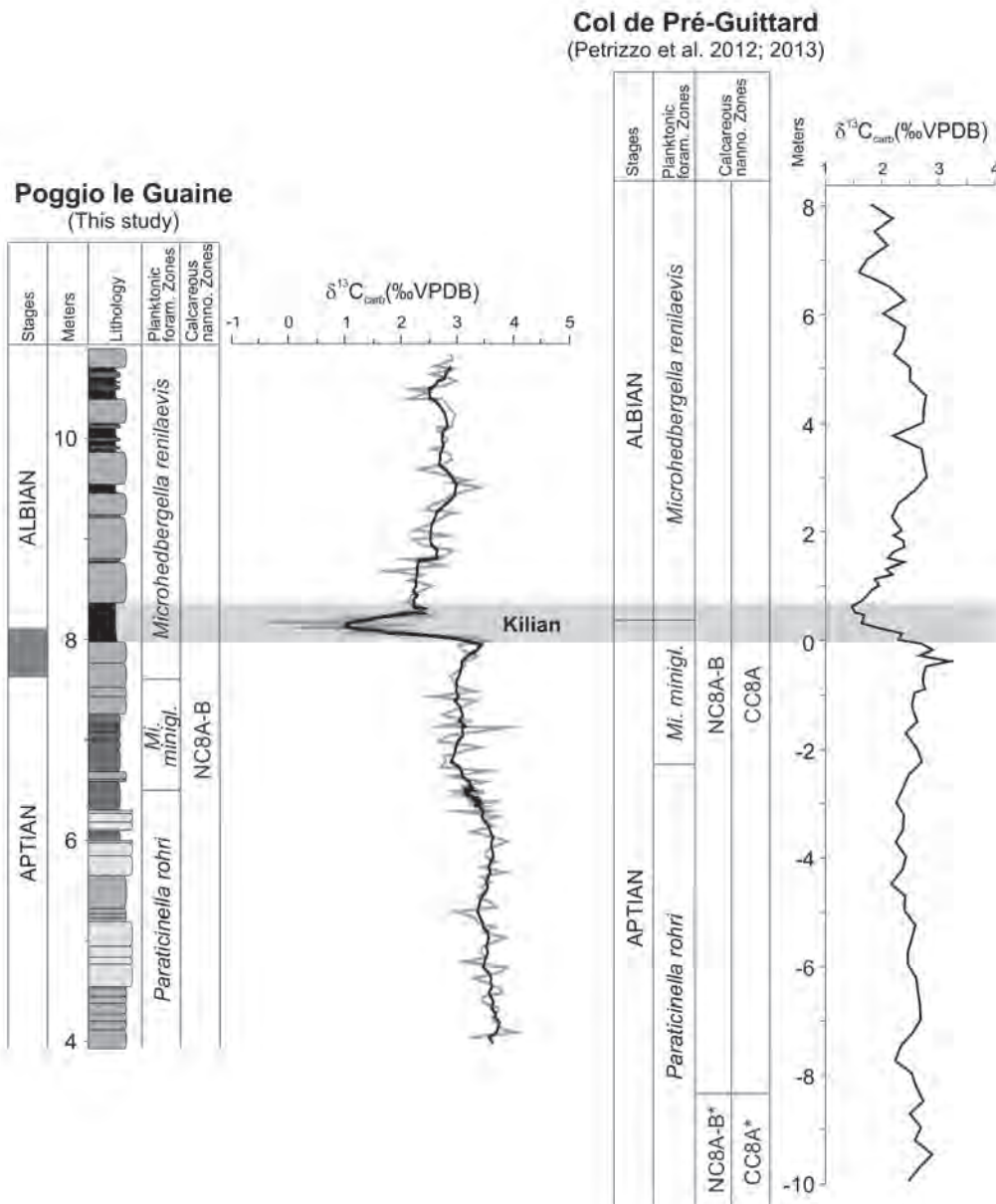
More recently, Trabucho Alexandre et al. (2011) have stated that OAE1b contains the record of several perturbations in the global carbon cycle and multiple black shale horizons, which correspond to four discrete sub-events (i.e., Jacob, Kilian, Paquier and Leenhardt) and are defined by negative excursions in the composite carbon isotope record that has been proposed as a standard reference curve for the Aptian to the lower Albian (Herrle et al. 2004).

DEFINING OAE1b AT THE POGGIO LE GUAINÉ SECTION AND A COMPARISON OF ITS RECORD AND TIMING IN TETHYS AND THE NORTH ATLANTIC

A comparison among the studied carbon isotope record and the $\delta^{13}\text{C}$ curves from the Vocontian Basin, the DSDP Site 545 Mazagan Plateau and the ODP Site 1049C is shown in text-figure 4. The combination of high resolution carbon-isotope stratigraphy and biostratigraphy allows a correlation of main black shale horizons and isotope stages as defined by Herrle et al. (2004). There is good correspondence in shape and absolute values between the different records, even if slight differences in isotope values can be observed and primarily explained in terms of the differential effects of local diagenesis or dissimilar paleoceanographic conditions, resulting in a different response to global carbon perturbations.

Sub-event 1 (113 or Jacob sub-event)

256



TEXT-FIGURE 6

Comparison between the calcareous plankton and carbon stable isotope stratigraphy through the Aptian/Albian boundary at the Poggio le Guaine and Col de Pré-Guittard sections, the latter candidate GSSP for the base of the Albian Stage as proposed by Kennedy et al. (2014). Key to planktonic foraminiferal abbreviations: *Mi.* – *Microhedbergella*, *mi.*, *minigl.* – *miniglobularis*.

and paleo-water depth between 500 and 1500m according to Friedrich et al. 2005) (e.g., Herrle 2002; Herrle et al. 2004). In the Tarendol section (Vocontian Basin) this level is ~75cm-thick with a TOC content up to 2.5% and includes organic matter of terrestrial origin (e.g., Bréhéret 1994; Herrle 2002; Heimhofer et al. 2006). According to Herrle (2002) and Herrle et al. (2004), the Jacob level lies in the upper part of the *Ticinella bejaouensis* planktonic foraminiferal Zone (currently the *Paraticinella eubejaouensis* Zone or the *Paraticinella rohri* Zone following Petrizzo et al. 2012, or this study, respectively) and of the *Rhagodiscus angustus* NC7B/NC7C calcareous nannofossil Zone, between the first appearances of calcareous nannofossils *Prediscosphaera spinosa* and *P. columnata* (text-figure 4).

At the Poggio le Guaine section, the 113 level exhibits a TOC content up to 5.9% and is defined by a weak negative CIE of ~0.7‰ (text-figures 2–4). It is located in the upper part of the *Paraticinella rohri* planktonic foraminiferal and of the NC7 calcareous nannofossil Zones. The 113 level therefore, can be regarded as the sedimentary expression of the first sub-event (~113.2 Ma) of OAE1b, and is thus equivalent to the Jacob level which, according to Huang et al. (2010), would have lasted for ~40 kyr (text-figures 3–4). In addition, we suggest that the lower of two negative carbon isotope excursions labeled HTE (high thermal event) by McAnena et al. (2013) at DSDP Site 545 could be a North Atlantic equivalent of the Jacob sub-event (text-figure 4). It occurs in the middle of the *Paraticinella rohri*

TABLE 1

Foraminiferal and calcareous nannofossil event recorded in the Poggio le Guaine section and their meter stratigraphical level and zonal boundaries according to different biozonations. The zonations of Huber and Leckie (2011) and Petrizzo et al. (2012) with the recent taxonomic notes of Ando et al. (2013) for planktonic foraminifera and Sissingh (1977; amended Perch-Nielsen, 1985), and Bralower et al. (1995) for calcareous nannofossils were applied. LO = lowest occurrence, HO = highest occurrence.

Events	Meter stratigraphic levels
LO? <i>Cylindralithus nudus</i>	0.5
LO <i>Rhagodiscus achlyostaurion</i>	1
Top Acme <i>Nannoconus truittii</i>	1.5
HO <i>Pseudoplanomalina chenourensis</i>	1.9
LO <i>Pleurostomella subnodosa</i>	2.3
LO <i>Eiffelithus hancockii</i>	2.5
<i>Schackoina cepedai</i> Acme	2.7–3.4
NC7/NC8A–B zonal boundary	4
LO <i>Predicosphaera columnata</i> sub-circular	4
LO <i>Cribrophaerella</i> sp.	4.5
LO <i>Microhedbergella miniglobularis</i>	6.42
<i>Paraticinella rohri</i> / <i>Microhedbergella miniglobularis</i> zonal boundary	6.5
HO <i>Paraticinella rohri</i>	6.5
LO <i>Predicosphaera columnata</i> near-circular	6.5
LO <i>Predicosphaera spinosa</i>	6.5
<i>Microhedbergella miniglobularis</i> / <i>Microhedbergella renilaevis</i> zonal boundary	7.6
LO <i>Microhedbergella renilaevis</i>	7.6
LO <i>Microhedbergella rischi</i>	10.8
<i>Microhedbergella renilaevis</i> / <i>Microhedbergella rischi</i> zonal boundary	10.8
LO <i>Microhedbergella praepianispira</i>	11.53
LO <i>Microhedbergella pseudoplanispira</i>	12.1
LO <i>Predicosphaera columnata</i> circular	15.5
LO <i>Hayesites albiensis</i>	16.3
LO <i>Rhagodiscus achlyostaurion</i> (common)	17
HO "big" <i>Assipetra/Rucinolithus</i>	18

(recorded by these authors as *Paraticinella eubejaouensis*) planktonic foraminiferal Zone and in the lower NC8A calcareous nannofossil Zone.

At ODP Hole 1049C the Aptian/Albian boundary has been interpreted as an unconformity based on the sharp lithologic contact and the lack of transitional planktic foraminiferal species seen in the lowermost Albian in other boundary sections (Huber and Leckie 2011; Huber et al. 2011). The related hiatus, spanning 0.8–1.4 Myr according to Huber et al. (2011), may include the Jacob level equivalent. Both the Poggio le Guaine and ODP Hole 1049C sections include thin upper Aptian intervals yielding the elongated chambered planktonic foraminifera *Schackoina cepedai*. At Poggio le Guaine, the interval is slightly below the Jacob level equivalent, at ODP Hole 1049C this interval is just below the unconformity.

Sub-event 2 (Kilian sub-event)

The Kilian level is the organic-rich expression of the second sub-event of OAE1b. In the Col de Pré-Guittard section of the Vocontian Basin this level is ~74cm-thick with a TOC content up to 3.3% and also includes organic matter of terrestrial origin (e.g., Bréhéret 1994; 1997; Herrle 2002). According to Herrle (2002) and Herrle et al. (2004) the Kilian level falls in the lowermost part of the *Hedbergella planispira* planktonic foraminiferal Zone and in the uppermost part of the *Predicosphaera columnata* NC8A calcareous nannofossil Subzone (text-figure 4). However, according to Petrizzo et al. (2012; 2013) and Kennedy et al. (2014), the Kilian level currently spans from the uppermost part of the *Microhedbergella miniglobularis* planktonic foraminiferal Zone to the lowermost part of the *Microhedbergella renilaevis* planktonic foraminiferal Zone. A comparison between the calcareous plankton and carbon stable isotope stratigraphy through the Aptian/Albian boundary at the Poggio le Guaine and Col de Pré-Guittard sections is shown in text-figure 6. The Col de Pré-Guittard section has recently been proposed by Kennedy et al. (2014) as candidate section for the GSSP for the base of the Albian Stage.

Conversely, a recent detailed study of planktonic foraminifera in sediments from several Atlantic localities (Huber and Leckie 2011) has shown that at DSDP Site 545 (paleolatitude ~20°N and paleo-water depth ~2000m according to Huber et al. 2011) the sediments that were hitherto regarded as lower Albian, including the black shale identified as the early Albian OAE1b Paquier sub-event (e.g., Bralower et al. 1993; 1997; Herrle 2002; Leckie et al. 2002; Herrle et al. 2004; Friedrich et al. 2005; Wagner et al. 2007; 2008; Hofmann et al. 2008; Friedrich 2010; McAnena et al. 2013) are currently considered latest Aptian in age because of the presence of a major unconformity spanning from the latest Aptian *Paraticinella eubejaouensis* (currently *Paraticinella rohri*) planktonic foraminiferal Zone through the late Albian *Pseudothalmanninella subtacinensis* planktonic foraminiferal Zone. In addition, at DSDP Site 545 the co-occurrence of the last *Pa. eubejaouensis* with *Ps. blakenosensis* (Leckie 2011, pers. comm. in Petrizzo et al. 2012), the latter species previously identified as *Gubkinella graysonensis* by Leckie (1984; 1987) at this site, is recorded by Petrizzo et al. (2012) at Col de Pré-Guittard up to the base of the Kilian level and according to this study up to the base of the prominent black shale spanning from msl 7.97 to msl 8.37 at Poggio le Guaine. All these biostratigraphic findings consistently show that the black shale at DSDP Site 545, which was 60 to 80 cm-thick with a TOC content up to ~5% and characterized by a distinct negative carbon isotope excursion from approximately 2‰ prior to the organic-rich interval to, on average, 0.75‰ during the event and a gradual return to isotopic values in the order of 1.2‰ at its termination (e.g., Herrle 2002; Herrle et al. 2004; Friedrich et al. 2005; Wagner et al. 2008; Trabucho Alexandre et al. 2011), has to be regarded as a Kilian level equivalent as also pointed out

by Trabucho Alexandre et al. (2011) and Petrizzo et al. (2012) (text-figure 4). On this basis the black shale horizon at DSDP Site 545 previously regarded by Herrle (2002), Herrle et al. (2004), Friedrich et al. (2005), Hofmann et al. (2008), Wagner et al. (2007; 2008) and McAnena et al. (2013) as a Paquier level equivalent (i.e., the third sub-event of OAE1b) should be viewed from different timing, paleoecological, paleoenvironmental and paleoclimatic perspectives.

Interestingly, the NC8A/NC8B subzonal boundary defined by the LO of *Hayesites albiensis* at DSDP Site 545 lies well below the Kilian level equivalent and within the *Ticinella bejaouensis* (currently *Paraticinella rohri*) planktonic foraminiferal Zone (Bralower et al. 1993; Herrle 2002; Herrle et al. 2004). In contrast, in the Vocontian Basin this boundary has been placed by Herrle (2002) and Herrle et al. (2004) above the Kilian level and within the lowermost part of the *Hedbergella planispira* Zone (text-figure 4) (currently within the *Microhedbergella renilaevs* Zone following Petrizzo et al. 2012). It is unrecorded in the Les Oustaus section by Bown in Kennedy et al. (2000) and by Petrizzo et al. (2012; 2013) and Kennedy et al. (2014) in the Col de Pré-Guittard section (text-figure 5) and recognized only within the late Albian *Thalmanninella subticinensis* Subzone of the *Biticinella breggiensis* planktonic foraminiferal Zone by Gale et al. (2011) in the Col de Palluel section. All this, together with the difficulty in distinguishing between *H. albiensis* and its ancestral form *Haysites irregularis* as previously pointed out by Bown in Kennedy et al. (2000), greatly detracts from the reliability of *H. albiensis* as a marker species and the validity of the NC8A/NC8B subzonal boundary.

In summary, the Kilian level is documented in the western Tethys, in the eastern North Atlantic Mazagan Plateau at DSDP Site 545 (previously regarded there as a Paquier level equivalent), and in the western North Atlantic Newfoundland Basin at ODP Site 1276 (e.g., Bréhéret 1983; Herrle et al. 2004; Hofmann et al. 2008; Wagner et al. 2008; Trabucho Alexandre et al. 2011, and references therein). This level formed under increasing surface water productivity and enhanced preservation of organic matter at the sea floor associated with the early Albian sea-level rise (e.g., Herrle et al. 2004; Hofmann et al. 2008; Wagner et al. 2007; Huber and Leckie 2011; Trabucho Alexandre et al. 2011; McAnena et al. 2013; Peybernes et al. 2013). The second sub-event of OAE 1b is defined by a negative excursion in both marine carbonate (1.5‰) and organic matter (2 to 4‰) carbon isotope records (e.g., Herrle et al. 2004; Wagner et al. 2008; Trabucho Alexandre et al. 2011). The carbon isotope record of the Kilian level and its equivalents, including that regarded as a Paquier equivalent at DSDP Site 545, is remarkably similar between sites in the western Tethys and in the North Atlantic (Herrle et al. 2004; Friedrich et al. 2005; Hofmann et al. 2008; Wagner et al. 2007; 2008; Trabucho Alexandre et al. 2011; McAnena et al. 2013) and allows their correlation because it is generally assumed that the perturbations behind the development of such isotope signals are globally synchronous (text-figure 4).

Interestingly, at DSDP Site 545 a climate perturbation with a distinct rapid increase in ocean surface temperatures by ~3°C–3.5°C and severe perturbations in the hydrological balance have been documented by Hofmann et al. (2008) and Wagner et al. (2008) for the Kilian event (but are referred to the Paquier event or OAE 1b by these authors). Warm stable conditions prevailed during this event, suggesting that the emission of ¹³C-depleted carbon started abruptly but then continued over tens of thousands of years. The sea surface temperature then cooled by ~1–2°C at the end of the event, but did not reach pre-excursion

levels. This almost instantaneous warming was preceded in the late Aptian by cooler conditions (i.e., the late Aptian cold snap of Mutterlose et al. 2009) as shown by several authors (Kemper 1987; Frakes and Francis 1988; Weissert and Lini 1991; Jenkyns 1995; De Lurio and Frakes 1999; Price 1999; Herrle and Mutterlose 2003; Mutterlose et al. 2009; Hu et al. 2012; Price 2012; Maurer et al. 2012; McAnena et al. 2013; Bottini et al. 2014). This cooling was coincident with a positive CIE of ~2‰ in the carbonates and organic carbon that could have been caused by perturbations of the marine ecosystems and of carbon biogeochemical cycles during the upper Aptian to lower Albian interval (McAnena et al. 2013) (text-figure 4). This may have been triggered by large-scale volcanism in the southern Indian Ocean that is associated with the emplacement of the Kerguelen Plateau Large Igneous Province (LIP) during the late Aptian (~119–110 Ma according to Frey et al. 2003). The hydrothermal micronutrients originating from the emplacement of this LIP and the terrigenous nutrient element input could have played an important role in stimulating the primary productivity linked to the Kilian sub-event with consequent consumption of oxygen through organic matter and metal oxidation, hence promoting dysoxic conditions (Trabucho Alexandre et al. 2011).

The black shale that occurs at Poggio le Guaine from msl 7.97 to msl 8.37 and shows a TOC content up to 1.1% is located in the lower part of the planktonic foraminiferal *Microhedbergella renilaevs* planktonic foraminiferal Zone and, according to this study, in the lower part of NC8A–B calcareous nannofossil Subzones (text-figures 3, 4, and 6). It is defined by a prominent negative CIE of 3.7‰ (text-figures 4 and 6). Therefore this horizon can be regarded as a Kilian level equivalent lasting for ~120 kyr according to Huang et al. (2010) and as the sedimentary expression of the second sub-event (~111.5 Ma) of OAE 1b (text-figures 3–4). Remarkably, this is in agreement with Bottini et al. (2014) that identified the same black shale as a Kilian level equivalent in the Piobbico core (Erba 1988; 1992; Tornaghi et al. 1989) drilled 7km north of the Poggio le Guaine section.

Sub-event 3 (Urbino or Paquier sub-event)

The Paquier level, that is the organic-rich expression of the third sub-event of OAE 1b, is documented in the western Tethys, the western North Atlantic and in Mexico (Bréhéret 1983; 1994; Tribouillard and Gorin 1991; Bralower et al. 1999; Erbacher et al. 1999; 2001; Herrle et al. 2003B; 2004; Tsikos et al. 2004; Wagner et al. 2008; Trabucho Alexandre et al. 2011). It was formed under increasing surface water productivity and the enhanced preservation of organic matter on the sea floor associated with the early Albian sea level rise (e.g., Herrle et al. 2004; Friedrich et al. 2005; Browning and Watkins 2008; Wagner et al. 2008; Huber and Leckie 2011; Huber et al. 2011; Trabucho Alexandre et al. 2011). This sub-event of OAE 1b is defined by a negative excursion in both marine carbonate (1.5–2‰) and organic matter (~3‰) carbon isotope records that can be significantly different between basins or when measured in different (in)organic compounds due to different palaeoceanographical settings, variations in the source of organic matter or diagenetic effects (e.g., Bralower et al. 1999; Erbacher et al. 2001; Kuypers et al. 2002; Herrle et al. 2004; Tsikos et al. 2004).

In the L'Arboudeysse section (Vocontian Basin), the Paquier level is 1.63 m-thick with mean TOC content generally above 3% and maximum values of 8% and with terrestrial and marine organic matter in variable proportions (e.g., Bréhéret 1985; Tribouillard and Cotillon 1989; Herrle 2002). This level lies in the middle part of the *Hedbergella planispira* planktonic foraminiferal Zone (currently the *Microhedbergella rischi* planktonic foraminiferal

Zone of Huber and Leckie 2011) and of the *Haysites albiensis* NC8B calcareous nannofossil Subzone (Herrle 2002; Herrle et al. 2004) (text-figure 4).

The Paquier level equivalent at ODP Hole1049C (paleolatitude ~25°N and paleo-water depth between 800 and 1500m according to Huber et al. 2011) is 46cm-thick with a TOC content up to 12.3% and contains organic matter of predominantly of marine origin (Erbacher et al. 1999, 2001; Kuypers et al. 2002; Friedrich et al. 2005; Huber and Leckie 2011; Huber et al. 2011; Trabucho Alexandre et al. 2011). It falls within the *Microhedbergella rischi* planktonic foraminiferal Zone and the CC8 calcareous nannofossil Zone (Huber and Leckie 2011; Huber et al. 2011). Also a distinct rapid increase in ocean surface temperatures as that recorded for the Kilian sub-event of OAE 1b at DSDP Site 545, with an almost instantaneous warming by ~2°C along with the marine isotope shifts (Wagner et al. 2008) is documented at this Paquier level equivalent.

At the Poggio le Guaine section, the Urbino level shows TOC values up to 9.8% (text-figures 2–4). It is located in the middle of the *Microhedbergella rischi* planktonic foraminiferal Zone and within the NC8A-B Subzones (text-figures 3–5). This sub-event is defined by a negative CIE of ~2.2‰ at the base and a second CIE at the top (text-figure 4). The Urbino level, therefore, can be regarded as an equivalent of the Paquier level that was estimated to have lasted for ~44–46 kyr (Herrle 2003) and as the sedimentary expression of the third sub-event (~109.9 Ma) of OAE1b (text-figures 3–4).

The stratigraphic interval between the equivalents of the Kilian and the Paquier levels at Poggio le Guaine section includes numerous black shale horizons several of which belonging to the Monte Nerone level of Coccioni et al. (1990b) (text-figure 3). These last can be correlated with the black shales Haute Noir 1 to Haute Noir 8 (HN1 to HN8, see text-figure 4) of the Vocontian Basin that according to Herrle (2002) and Herrle et al. (2004) punctuate the same stratigraphic interval (text-figure 4). However, the carbon isotope stratigraphy and biostratigraphy available for this interval do not provide a valuable means to correlate single black shale horizons.

Sub-event 4 (Leenhardt sub-event)

Prior to the current study, organic-rich expression of the fourth sub-event of OAE1b known as the Leenhardt level has only been documented in the Vocontian Basin. In the Col de Palluel section it is ~92cm-thick with a TOC content up to 3% and contains organic matter of marine origin (e.g., Bréhéret 1994; Herrle 2002). According to Herrle (2002) and Herrle et al. (2004), the Leenhardt level occurs in the upper part of the *Hedbergella planispira* planktonic foraminiferal Zone (currently the *Microhedbergella rischi* planktonic foraminiferal Zone of Huber and Leckie 2011) and the middle part of the *Haysites albiensis* NC8B calcareous nannofossil Subzone (text-figure 4).

At the Poggio le Guaine section, a 29cm-thick black shale horizon with a TOC content up to 0.95% spans from msl 17.71 to msl 18 and falls within the upper part of the *Microhedbergella rischi* planktonic foraminiferal Zone and the NC8A–B calcareous nannofossil Subzones (text-figures 3–4). This black shale horizon defined by a negative CIE of ~1‰, can therefore be regarded as a Leenhardt level equivalent and as the sedimentary expression of the fourth sub-event of OAE1b (text-figure 4).

Interestingly, a marked increase in the abundance of radiolaria, benthic foraminifera, and fish debris, in conjunction with a fall in planktonic foraminiferal abundance and diversity, is recorded across the the upper Aptian to lower Albian interval at the Poggio le Guaine section (Coccioni et al. 1990b, and this study), suggesting enhanced productivity in the surface waters (text-figure 3). Moreover, the benthic foraminiferal distribution pattern throughout this section provides evidence that fully anoxic conditions were established only occasionally during the Urbino/Paquier sub-event of OAE1b, which is in agreement with previous data from the Vocontian Basin, DSDP Site 545 and ODP Site 1049 (e.g., Erbacher et al. 1998; 1999; Holbourn and Kuhnt 2001; Holbourn et al. 2001; Herrle et al. 2003a; 2003b; Friedrich et al. 2005).

It is noteworthy that a number of other thin black shale horizons, which have been identified between the four main sub-events and are generally characterized by slightly negative carbon isotope values and TOC values <1%, definitively document a

PLATE 1

Scanning electron photographs of selected foraminifera from the upper Aptian–lower Albian Poggio le Guaine section (central Italy).
Scale bars are 50µm for Figures 2, 4 and 5, and 100µm for all the other Figures.

1a-c. *Globigerinelloides aptiensis*, msl 2.6.

2a-c. *Globigerinelloides duboisi*, msl 7.6.

3a-c. *Globigerinelloides ferreolensis*, msl 3.4.

4a-c. *Globigerinelloides maridalensis*, msl 7.4.

5a-c. *Globigerinelloides paragottisi*, msl 7.9.

6a-c. *Hedbergella praetrocoidea*, msl 0.1.

7a-c. *Hedbergella trocoidea*, msl 0.3.

8a-c. *Hedbergella rhinoceros*, msl 2.7.

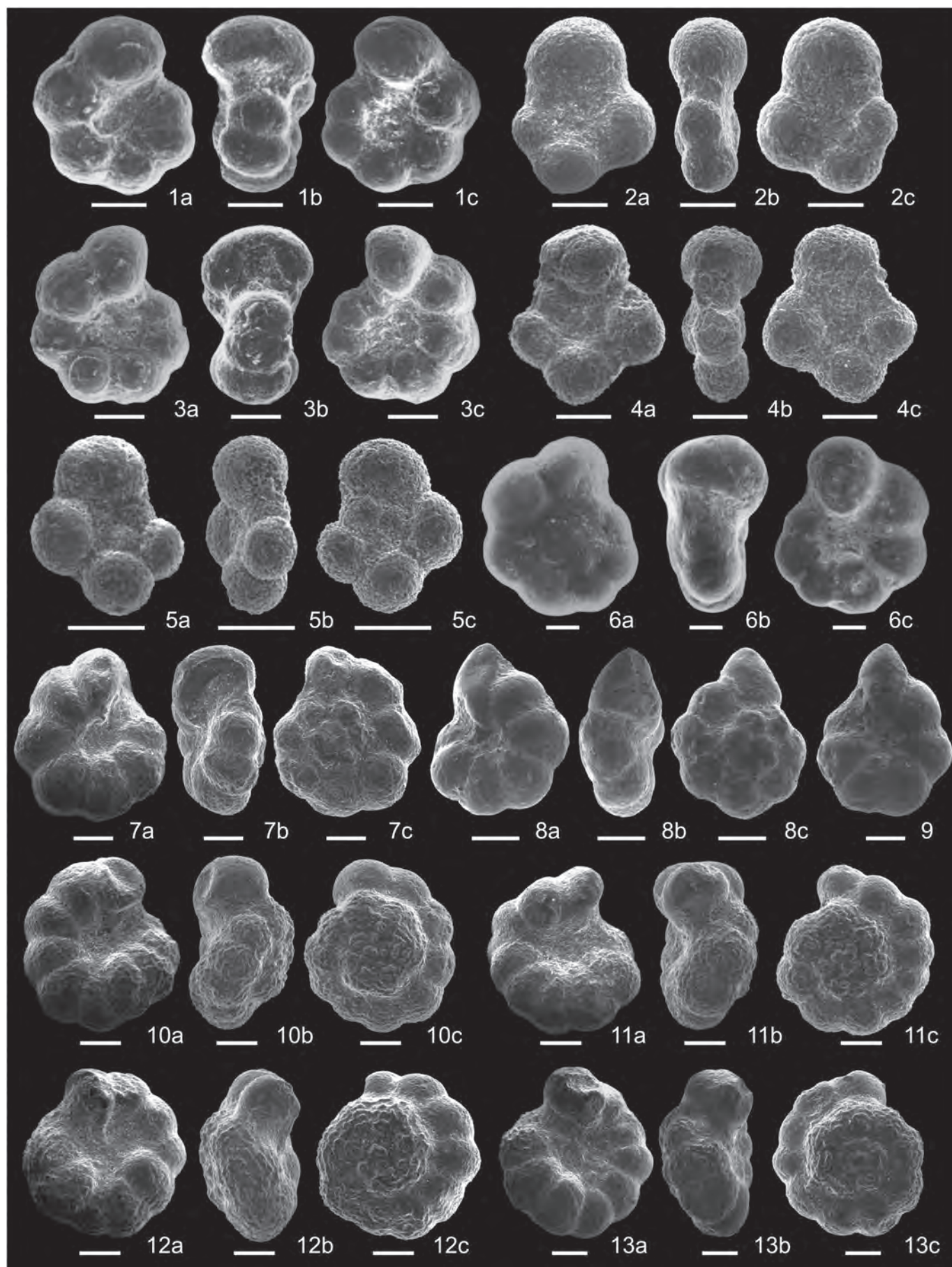
9. *Hedbergella rhinoceros*, msl 2.7.

10a-c. *Paraticinella rohri*, msl 0.5.

11a-c. *Paraticinella rohri*, msl 1.9.

12a-c. *Paraticinella rohri*, msl 3.2.

13a-c. *Paraticinella rohri*, msl 5.5.



long-interval (~3.8 Myr) of global carbon cycle perturbation, with periods of paroxysmal carbon burial during the 113 or Jacob, Kilian, Urbino or Paquier and Leenhardt sub-events. Consequently, the definition of OAE1b encompasses a longer and more dynamic perturbation (including several short-term changes) of carbon burial compared to the other Cretaceous OAEs.

Following Grippo et al. (2004), Huang et al. (2010), and Ogg and Hinnov (2012), the studied interval spans approximately 5.6 Myr, from ~114.8 Ma to ~109.2 Ma (text-figure 3). A comparison between Poggio le Guaine section and the Vocontian Basin (see Herrle et al. 2004) shows that the mean sedimentation rate, through different stratigraphic intervals, may be estimated as follows: from the Jacob level to the Kilian level = 0.26cm/kyr and 2.35cm/kyr, respectively; from the Kilian level to the Paquier level = 0.47cm/kyr and 2.94cm/kyr, respectively. These data agree with the two different palaeoenvironment settings, oceanic for the Poggio le Guaine section and neritic for the Vocontian Basin, with an increased input of terrigenous material, more or less organic-rich, during the early Albian, as testified by a marked change of the sedimentation rate.

CONCLUSIONS

The multi-proxy investigation of the uppermost Aptian–lower Albian continuous and undisturbed pelagic section at Poggio le Guaine (central Italy) provided a unique chance to produce a high-resolution reconstruction of the sedimentary dynamics in the western Tethyan Realm during the OAE1b (~3.8 Myr) which is the longest and least-studied Cretaceous OAE. Investigations of the short-term perturbations of the global carbon cycle, reflected by numerous black shale horizons, are comprehensive enough to encompass the well-known four sub-events and offer an unprecedented opportunity to investigate rapid climate changes in a greenhouse world. The new integrated and robust global stratigraphic framework established at Poggio le Guaine, based on carbon-isotope stratigraphy calibrated with planktonic foraminiferal and calcareous nannofossil biostratigraphy provides

an effective tool with which to precisely correlate OAE1b and its short-term phases in different marine environments.

Moreover, the Poggio le Guaine section has been also compared with the Col de Pré-Guittard section, proposed as a candidate GSSP for the base of the Albian Stage, showing only a minor discrepancy with the placement of the Aptian–Albian boundary. On the basis of the exceptional chemo- and biochronostratigraphic control, including the remarkable occurrence of all the sub-events linked to the latest Aptian–early Albian OAE1b, the studied section can be therefore considered as a new reference section for this OAE as well as for the $\delta^{13}\text{C}$ record for the uppermost Aptian to lower Albian interval.

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PLATE 2

Scanning electron photographs of selected foraminifera from the upper Aptian–lower Albian Poggio le Guaine section (central Italy). Scale bars are 100µm for Figures 1 to 10, 50µm for Figures 11 to 16, and 2µm for Figures showing wall details.

1a-c. *Paraticinella transitoria*, msl 5.5.

2a-b. *Pseudoplanomalina cheniourensis*, msl 1.7.

3. *Pleurostomella subnodosa*, msl 2.5.

4a-c. *Shackoina cepedai*, msl 2.8.

5a-c. *Shackoina cepedai*, msl 3.1.

6. *Shackoina cepedai*, msl 3.2.

7. *Shackoina cepedai*, msl 3.4.

8. *Shackoina cepedai*, msl 3.4.

9. *Shackoina cepedai*, msl 3.4.

10a-c. *Shackoina cepedai*, msl 3.4.

11a-c. *Microhedbergella miniglobularis*, msl 6.42.

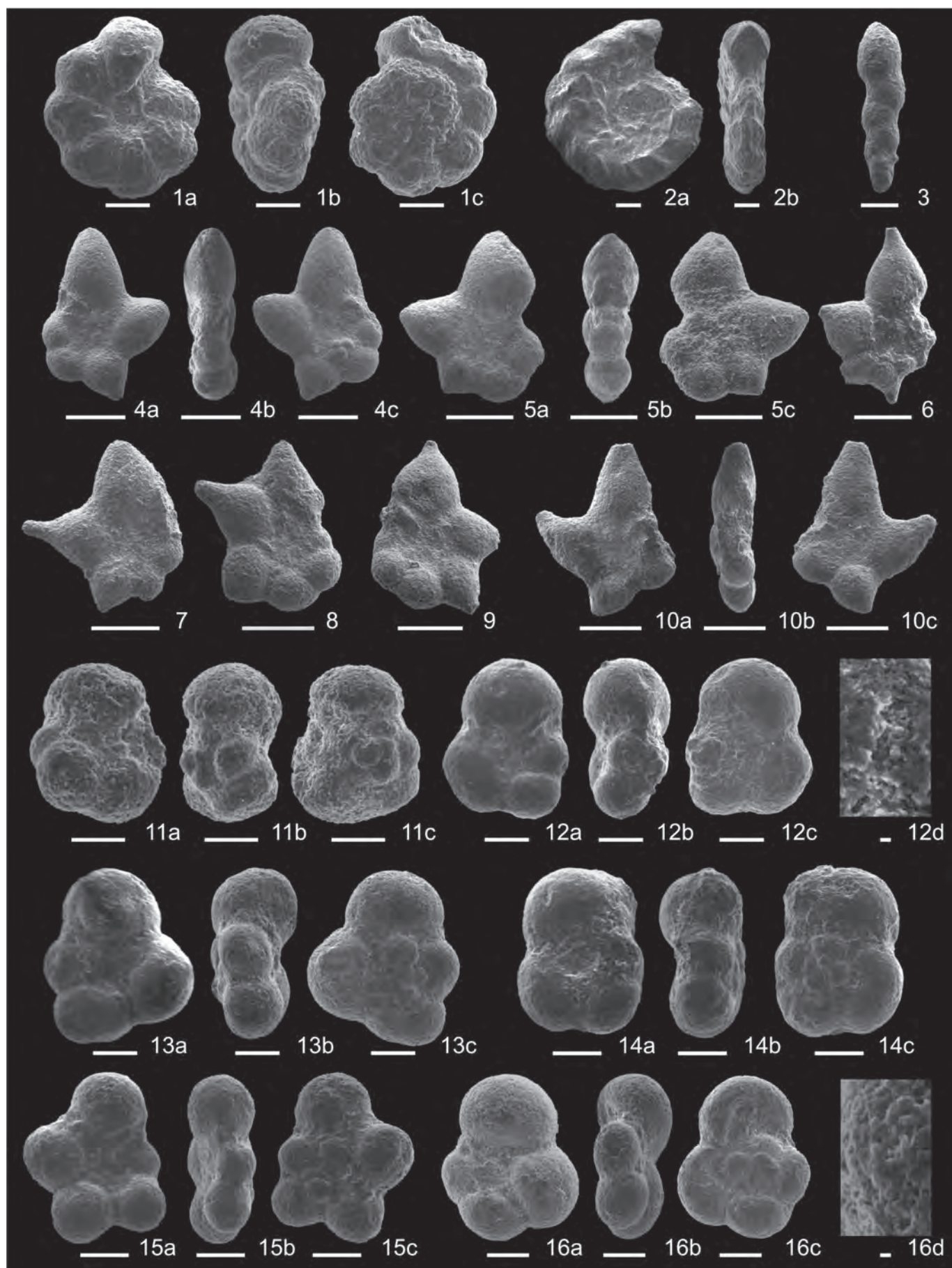
12a-d. *Microhedbergella miniglobularis*, msl 14.1; d = magnified view of the microperforate wall surface of the spiral side of penultimate chamber.

13a-c. *Microhedbergella miniglobularis*, msl 16.322.

14a-c. *Microhedbergella miniglobularis*, msl 6.8.

15a-c. *Microhedbergella renilaevs*, msl 16.322.

16a-d. *Microhedbergella renilaevs*, msl 16.322; d = magnified view of the microperforate wall surface of the spiral side of penultimate chamber.



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PLATE 3

Scanning electron photographs of selected foraminifera from the upper Aptian–lower Albian Poggio le Guaine section (central Italy). Scale bars are 2µm for Figure showing wall details and 50µm for all the others Figures.

1a-c. *Microhedbergella renilaevis*, msl 17.5.

2a-d. *Microhedbergella renilaevis*, msl 17.6; d = magnified view of the microperforate wall surface of the spiral side of penultimate chamber.

3a-c. *Microhedbergella renilaevis*, msl 14.1.

4a-c. *Microhedbergella renilaevis*, msl 14.1.

5 a-c. *Microhedbergella renilaevis*, msl 7.97-8.02.

6a-c. *Microhedbergella renilaevis*, msl 7.8.

7a-c. *Microhedbergella renilaevis*, msl 17.

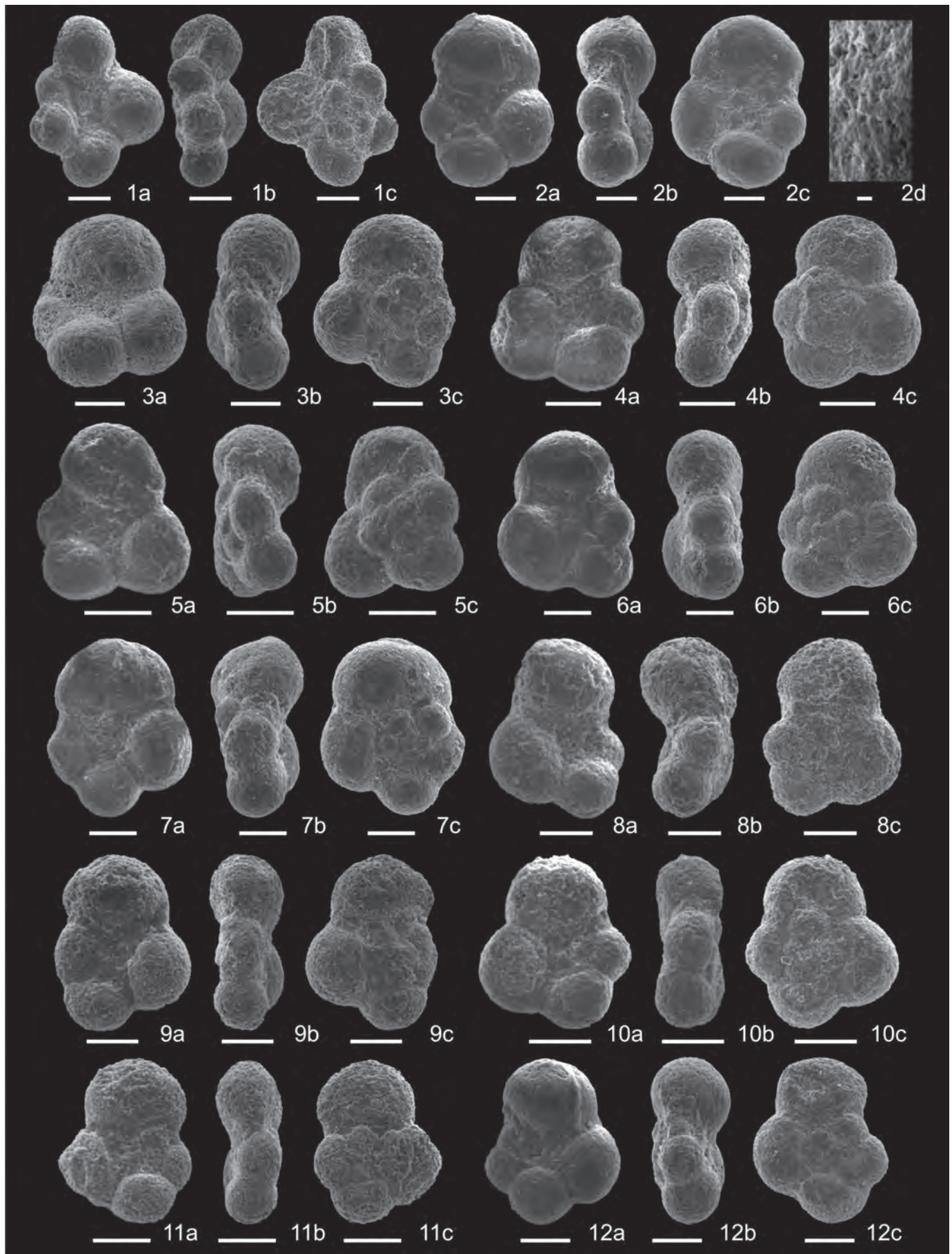
8a-c. *Microhedbergella renilaevis*, msl 17.

9a-c. *Microhedbergella renilaevis*, msl 17.

10a-c. *Microhedbergella renilaevis*, msl 7.6.

11a-c. *Microhedbergella renilaevis*, msl 7.7.

12a-c. *Microhedbergella renilaevis*, msl 16.9.



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PLATE 4

Scanning electron photographs of selected foraminifera from the upper Aptian–lower Albian Poggio le Guaine section (central Italy). Scale bars are 50µm for Figures 1, 5, 6 and 11, and 100µm for all the other Figures.

1a-c. *Microhedbergella renilaevs*, msl 7.9.

2a-c. *Microhedbergella rischi*, msl 16.322.

3a-c. *Microhedbergella rischi*, msl 15.8.

4a-c. *Microhedbergella rischi*, msl 10.8.

5a-c. *Microhedbergella praeplanispira*, msl 11.53.

6a-c. *Microhedbergella praeplanispira*, msl 13.

7a-c. *Microhedbergella pseudoplanispira*, msl 12.3.

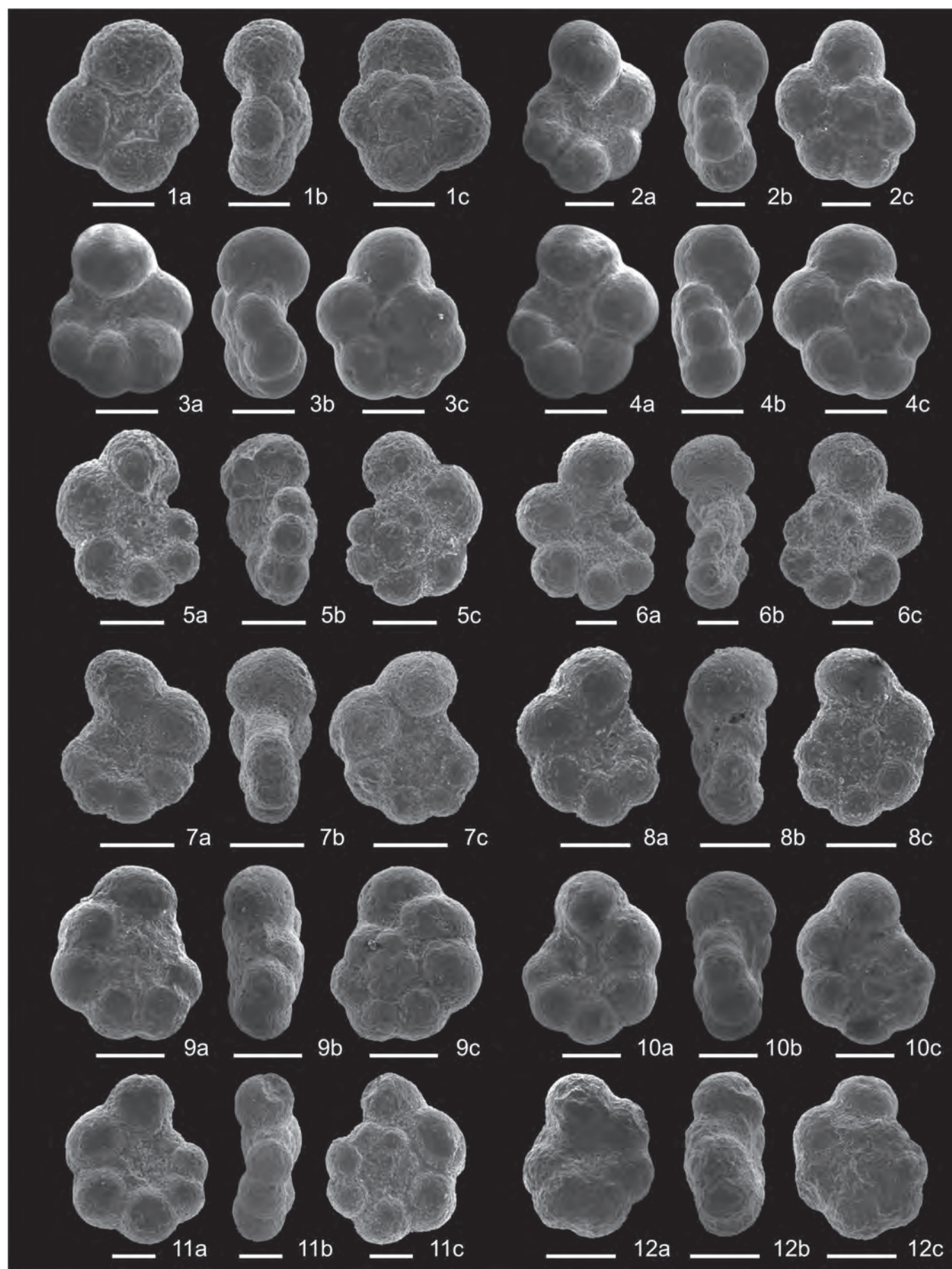
8a-c. *Microhedbergella pseudoplanispira*, msl 13.6.

9a-c. *Microhedbergella pseudoplanispira*, msl 16.272.

10a-c. *Microhedbergella pseudoplanispira*, msl 16.322

11a-c. *Microhedbergella pseudoplanispira*, msl 17.99.

12a-c. *Microhedbergella pseudoplanispira*, msl 18.4.



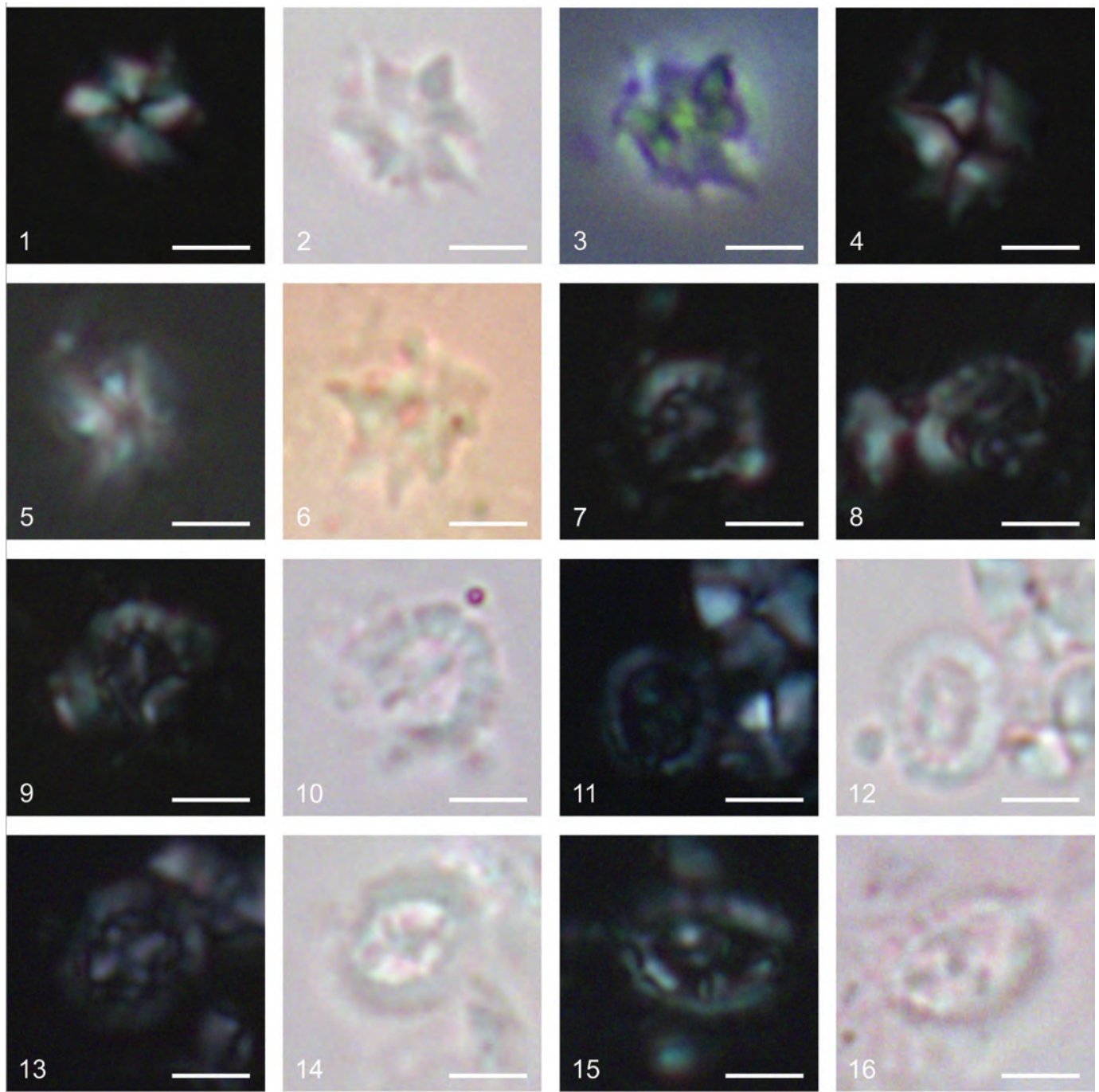
- In: Czarzar, G., and Kollmann, A., Eds., *Pelagic and flysch facies meeting (IGCP Project 262 “Tethyan Cretaceous Correlation”)*, Kraków, May 28–June 2, 1990:18–19. Kraków: Institute of Geological Sciences, Jagiellonian University.
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PLATE 5

Photographs of selected calcareous nannofossils from the upper Aptian–lower Albian Poggio le Guaine section (central Italy).

Scale bar = 2µm.

1. *Hayesites albiensis*, crossed nicols, msl 16.5.
2. Same specimen, natural light.
3. Same specimen as in 1 and 2 in phase contrast.
4. *Hayesites albiensis*, crossed nicols, msl 16.5.
5. Same specimen, high focus.
6. Same specimen, natural light.
7. *Prediscosphaera columnata* circular, crossed nicols, msl 16.
8. *Prediscosphaera columnata* circular, crossed nicols, msl 16.
9. *Prediscosphaera columnata* near-circular, crossed nicols, msl 10.
10. Same specimen, natural light.
11. *Prediscosphaera columnata* sub-circular, crossed nicols, msl 4.5.
12. Same specimen, natural light.
13. *Prediscosphaera columnata* sub-circular, crossed nicols, msl 4.5.
14. Same specimen, natural light.
15. *Prediscosphaera spinosa*, crossed nicols, msl 14.
16. Same specimen, natural light.



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APPENDIX 1

Dataset of planktonic, calcareous and agglutinated benthic foraminifera and radiolaria abundance, CaCO_3 , TOC and $\delta^{13}\text{C}$ of the Poggio le Guaine section plotted against meter stratigraphic levels.

Meter stratigraphic level at PLG section	Planktonic foraminifera	Calcareous benthic foraminifera	Agglutinated benthic foraminifera	Radiolaria	CaCO_3	TOC	$\delta^{13}\text{C}$
	(%)	(%)	(%)	(%)	(wt%)	(%)	(‰ vs. VPDB)
0.00	86.7	3.4	2.3	7.6	41.36		3.79
0.05					48.96		3.75
0.10	97	0	0	3	56.57		3.29
0.15					42.88		3.79
0.20	88	2.5	0	9.5	49.47		3.49
0.25					48.96		3.54
0.30	85	2.2	0	12.8	53.02		3.70
0.35					46.94		3.55
0.37					48.96		3.40
0.40	69	1.4	0	29.6	70.77		3.57
0.45					67.22		3.49
0.50	81.5	1.8	2.2	14.5	43.89		3.23
0.55					22.60		3.55
0.60	90	0.7	1.3	8	60.12		3.42
0.65					38.82		3.57
0.70	90	0.3	0.7	9	58.60		3.40
0.75					59.10		3.29
0.80	33	1	0	66	68.23		3.63
0.85					75.33		3.42
0.90	92	1	0.7	6.3	56.57		3.65
0.95					65.19		3.39
1.00	87.6	2.8	1.2	8.4	57.58		3.27
1.05					18.54		3.20
1.10	15.3	6.7	26.8	51.2	35.28		3.30
1.15					38.82	0.00	3.25
1.20	92	0.8	1.2	6	47.95		2.79
1.25					69.24		3.35
1.30	62	2	1	35	77.86		3.36
1.35					73.30		2.95
1.40	86	2	0	12	76.34		3.47
1.45					55.05		3.56
1.50	81	1	0	18	77.86		3.48
1.55					67.22		3.56
1.60	88.8	1.3	0.7	9.2	67.22		3.66
1.65					75.33		3.69
1.70	85.6	3.7	2.6	8.1	56.57		3.90
1.75					67.22		3.84
1.80	92	3	1	4	61.13		3.89
1.85					61.13		3.60
1.90	86.2	2.5	1.7	9.6	57.08		3.89
1.95					61.13		4.11
2.00	88.5	3.6	0.4	7.5	56.06		4.02
2.05					65.19		4.10
2.10	87.6	3.7	1.1	7.6	68.74		3.76
2.15					50.99		4.16
2.20	89.5	2.5	0.9	7.1	62.15		4.06
2.25					69.24		3.92
2.30	78	4	1	17	74.31		3.44
2.35					53.02		4.17
2.40	84.7	3.5	1.4	10.4	54.54		3.97
2.45					59.10		4.14
2.50	93	0.7	1.3	5	59.61		3.83
2.55					59.10		3.98
2.60	66	12	1	21	39.33		3.67
2.65					57.08		3.72
2.70	89	3	1	7	59.10		3.91
2.75					61.13		3.92
2.80	95	2	0	3	52.51		4.11
2.85					50.99		4.24
2.90	91.7	2	0.6	5.7	52.51		4.06

APPENDIX 1 *continued*

2.95					75.33		3.00
3.00	97	1	0	2	76.85		3.91
3.05					75.33		3.38
3.10	96	1	0	3	72.79		4.15
3.15					73.30		
3.20	97	0	0	3	73.30		3.64
3.25					61.13		2.95
3.30	83	4.7	0.3	12	42.88		
3.33	91.3	6.7	0.3	1.7	55.05	0.15	3.98
3.35					55.05		4.16
3.40	86	0.1	0	13.9	78.37		3.73
3.45					59.10		3.95
3.47-3.51	29	46	22	3			
3.49					48.96		3.90
3.50					30.71	4.09	3.75
3.51					16.52		2.87
3.52					18.54	5.90	3.09
3.51-3.55	84	5.6	10	0.4			
3.54					20.07	2.01	3.89
3.55					10.43		3.38
3.57					30.71		3.46
3.60	45.1	22.9	9.1	22.9	34.26		3.64
3.62					14.49		3.23
3.65					44.91		3.10
3.70	37.3	19.4	18	25.3	20.07		3.18
3.75					46.94		4.42
3.80	76	14	4	6	29.70		3.22
3.85					48.96		3.69
3.90	87	2	1.5	9.5	38.82		3.36
3.95					53.02		3.79
4.00	78	10	4	8	51.50		3.23
4.05					59.10		4.04
4.10	80.2	7.5	4.3	8	45.99		3.78
4.15					44.91		3.69
4.20	90.3	5.1	1.9	2.7	57.08		3.62
4.25					53.02		3.69
4.30	52.3	16.4	7.1	24.2	44.40		3.75
4.35					53.02		3.44
4.40	83.9	5.2	1.6	9.3	58.49		3.47
4.45					57.08		3.81
4.50	80	8	2.9	9.1	53.02		3.72
4.55					55.05		3.48
4.60	74.2	4.1	1	20.7	74.82		3.30
4.65					53.02		3.74
4.70	84.6	6.8	2.2	6.4	69.22		3.88
4.75					36.80		3.12
4.80	65.2	13.2	3.1	18.5	55.05		3.51
4.85					67.22		3.42
4.90	60.2	19.8	4	16	58.09		3.44
4.95					63.16		
5.00	73.1	14	1.4	11.5	55.05		3.85
5.05					69.24		3.46
5.10	75.9	11.3	3.4	9.4	54.03		3.67
5.15					59.10		3.37
5.20	64.7	17.5	3.7	14.1	60.12		3.30
5.25					61.13		2.96
5.30	77	10	3	10	62.65		3.69
5.35					57.08		3.59
5.40	75	9	2	14	57.58		3.36
5.45					57.08		3.49
5.50	71.3	12.9	3.9	11.9	57.08		3.43
5.55					61.13		3.59
5.60	44.9	14.8	16.3	24	44.40		3.42
5.65					59.10		3.84
5.70	56.2	14.6	5.6	23.6	57.08		3.45
5.75					67.22		3.69
5.80	55.3	15.3	5	24.4	62.15		3.50
5.85					40.85		3.50
5.90	76	10.3	3.4	10.3	60.63		3.63
5.95					50.99		3.89
6.00	67.2	13.8	4.5	14.5	63.67		3.70
6.05					20.57		3.24

APPENDIX 1 continued

6.10	24	4.7	1.3	70	67.72		3.64
6.15					67.22		3.48
6.20	67.2	12.4	5.4	15	56.57		3.73
6.25	3.6	3.6	39.6	53.2	29.69		3.61
6.30	0.3	43.4	27.3	29	53.02		3.32
6.31	9.7	33	16.3	41	44.91		3.48
6.32	5.8	33	27.3	33.9	40.85		3.37
6.33	5.2	23.2	26.7	44.9	34.77		3.23
6.34	0.3	13.7	42.9	43.1	36.80		3.24
6.35	16.3	20.9	23.3	39.5	40.85		3.29
6.36	11.9	21.5	23.1	43.5	36.80		3.40
6.37	26	16.5	9.5	48	42.88		3.23
6.38	7	31.4	13.7	47.9	42.88		3.29
6.39	6.7	20.2	17.6	55.5	42.88		3.42
6.40	10.9	22.8	16.7	49.6	42.88		3.13
6.41	34	10	9	47	40.85		3.24
6.42	45.6	7.3	16.1	31	38.82		3.34
6.43	31.9	16.8	15	36.3	30.71		3.00
6.44	4.4	15.7	24.3	55.6	36.80		3.13
6.45	59	10	8	23	39.84		3.01
6.46	18.5	19.4	19.1	43	34.77		3.05
6.47	34.3	20.5	29.8	15.4	26.66		3.20
6.48	63	6.1	8	22.9	36.80		3.28
6.49	68.5	9.4	7.5	14.6	38.82		3.14
6.50	4	0	0.4	95.6	36.29		3.10
6.55	0.6	1.8	0.7	96.6	20.57		3.49
6.60	0.7	1.6	11.8	85.9	28.18		2.87
6.65					38.82		3.55
6.70	5.3	13.2	2.8	78.7	41.36		2.70
6.75					12.46		2.80
6.80	12.5	10.6	3.3	73.6	37.81		2.77
6.85					10.43		
6.90	0.6	1.7	0.3	97.4	42.88		3.41
6.95					20.57		2.68
7.00	0.3	0.3	0.3	99.1	33.25		2.84
7.05					32.74		
7.09					16.52		3.88
7.10	0.4	0.3	0.3	99	41.87		2.72
7.15					7.90		3.21
7.20	1	1.7	0	97.3	50.49		2.73
7.25					9.93		
7.30	1.9	0.8	0.8	96.5	39.84		3.12
7.35					44.91		3.33
7.40	21	24	7	48	35.78		2.55
7.45					36.80		3.31
7.50	28.2	25.9	3.9	42	46.94		2.95
7.55					24.63		2.93
7.60	22.3	21.9	4.2	51.6	50.49		2.87
7.65					50.99		
7.70	25.9	23.9	8	42.2	38.82		3.14
7.75					38.82		3.13
7.80	7.5	2.3	4.6	85.6	57.58		3.36
7.85					40.85		3.10
7.90	3.6	2	0.4	94	42.37		3.03
7.95					35.78		3.52
7.97					49.98		3.25
7.97-8.02	5.6	3.9	1.6	88.9			
7.99					32.74	0.20	3.29
8.01					4.35		1.90
8.03					4.38	0.38	0.97
8.02-8.07	0.1	0	99.3	0.6			
8.05					4.35		1.92
8.07					6.38		1.60
8.08					5.87	1.11	0.09
8.09					4.35		1.74
8.07-8.12	0	0	88	12			
8.11					4.35		2.00
8.13					5.36	0.51	-0.38
8.15					8.40		1.56
8.12-8.17	1	0.3	73.4	25.3			
8.17					10.43		
8.18					4.86	0.70	1.02

APPENDIX 1 *continued*

8.19					16.52		2.57
8.17-8.22	0	0	90	10			
8.21					18.54		2.60
8.23					20.07	0.92	1.94
8.22-8.27	0	1.3	77.7	21			
8.25					18.54		2.17
8.27					22.60		2.43
8.28					24.12	0.97	2.28
8.29					8.40		2.34
8.27-8.32	0.2	2.8	74.7	22.3			
8.31					24.63		2.27
8.33					23.61	0.88	2.08
8.32-8.37	0.5	0.9	90.1	8.5			
8.35					26.66		2.15
8.40	2.2	9.5	34.7	53.6	28.18		2.18
8.45					34.77		2.34
8.50	0.8	3.8	0.2	95.2	55.05		2.56
8.55					40.85		2.15
8.60	5.8	14.1	4.9	75.2	54.03		2.38
8.65					36.80		1.75
8.70	6.5	18.5	10.6	64.4	47.95		2.72
8.75					34.77		2.75
8.77					28.68		2.35
8.79	0.9	14.3	11.9	72.9	37.30		2.65
8.80	8.8	21.6	15.9	53.7	43.89		2.78
8.85					42.88		2.93
8.90	5.4	14	8.9	71.7	42.37		2.38
8.95					32.74		2.22
9.00	0.6	19.3	6	74.1	40.35		2.82
9.05					46.94		2.25
9.10	7.2	19.9	9.1	63.8	33.75		2.50
9.15					36.80		
9.20	9.2	8.6	9.2	73	41.87		2.81
9.23	9.7	13.4	17	59.9	34.77		2.97
9.25					20.57		2.44
9.30	15.5	11.3	3.5	69.7	38.82		2.56
9.35					46.94		2.77
9.40	1.9	3.8	1.3	93	50.49		2.89
9.45					42.88		
9.48	0	1	0.3	98.7	44.91	0.19	3.41
9.52	0.3	0.6	0.3	98.8	21.08		2.91
9.55					26.66		3.21
9.60	0	0	16.7	83.3	19.05		2.74
9.65					50.99		2.31
9.70	1.3	4.8	2.2	91.7	50.99		2.72
9.75					30.71		2.91
9.80	1.1	10.7	11.8	76.4	44.40		2.87
9.85					49.47		2.56
9.88	2.3	4.6	20.3	72.8	15.00	0.42	2.72
9.95	0	0	48.5	51.5	19.05	0.01	2.84
10.03	1.4	5.1	26.5	67	31.22		2.68
10.05					18.54		
10.08	0	1.6	34.4	64	6.88	0.25	2.89
10.15					34.77	0.22	
10.20	0	0.7	0	99.3	46.43		2.96
10.25					41.87		
10.30	0	0.7	0	99.3	41.87		2.81
10.35	0.5	5	6	88.5	41.62		2.74
10.42	0.8	4.9	31.4	62.9	34.77		2.49
10.45					30.71		2.22
10.47	1.2	12.2	53.6	33	27.67	0.06	2.72
10.54	0.7	11.7	56.6	31	30.21		2.97
10.55					8.404		2.89
10.60	0	1.7	0.2	98.1	53.52	0.03	2.54
10.65					14.49		2.94
10.68	8.5	15.7	55	20.8	36.80	0.54	2.60
10.75					28.68		2.93
10.80	0.5	13.6	7.2	78.7	39.84		2.87
10.85					36.82		2.99
10.90	1.6	5.8	2.5	90.1	26.68		2.74
10.95					32.74		1.94
11.00	1.6	12.9	21.9	63.6	41.36	0.06	2.72

APPENDIX 1 continued

11.05					18.54		1.65
11.07					30.71		1.86
11.09					16.52		1.90
11.10	0.3	0	96	3.7	15.00	0.67	1.64
11.11					6.38		
11.13					12.46		
11.15					38.82		
11.17					14.49		2.24
11.19					10.43		
11.20	1.2	11	68.6	19.2	27.67		2.93
11.21					10.43		
11.23	0	0	99.4	0.6	19.05	0.36	2.10
11.25					12.46		1.78
11.27					17.53		
11.29					22.60		
11.30	0.1	0.9	96	3	4.86		2.64
11.31					18.54		
11.33					16.52		1.55
11.35					20.57	0.03	1.76
11.37					10.43		1.78
11.39	0	0.2	96.8	3	8.404		2.80
11.40	0	1	98	1	15.00		2.61
11.41					8.40		1.98
11.43					7.39		2.79
11.44	0	0	97	3	7.39	0.91	1.90
11.45					8.40		1.98
11.47					6.38		2.21
11.49					5.36		
11.50	0	0	99.4	0.6	16.01		1.26
11.51					8.40		1.72
11.53	0.3	1	97.7	1	21.08	0.64	2.30
11.55					8.40		1.98
11.57					7.39		
11.59					14.49		1.56
11.60	0	0	90	10	12.46		2.07
11.61					20.57		1.39
11.63					20.57		2.00
11.65					8.40		2.20
11.67					8.40		1.90
11.69					6.38		2.18
11.70	0	0	99.9	0.1	6.38	0.31	1.82
11.71					30.71		
11.73					24.63		1.67
11.74					18.54		1.56
11.75					16.52		1.36
11.77					8.40		2.16
11.79					12.46		
11.80	0	0	98	2	5.87	0.18	2.10
11.81					30.71		1.99
11.83					22.60		2.28
11.85					6.38		
11.87					14.49		
11.89	10.8	4.8	80.9	3.5	9.42	0.64	2.32
11.91					22.6		1.78
11.93					12.46		
11.95					10.43		
11.97					6.38		1.98
11.99	0.3	0	99.4	0.3	5.86	1.14	2.60
12.01					12.46		2.03
12.03					14.49		2.53
12.05					26.66		2.64
12.10	0.2	1	98.6	0.2	20.57		2.79
12.15					32.74		2.75
12.20	0.2	1	98.6	0.2	20.57	0.67	2.50
12.25					32.74		2.77
12.30	1.4	27.6	70.5	0.5	29.70		2.47
12.34	3.6	17	77.2	2.2	30.21	0.58	2.56
12.40	0.7	18.3	79.9	1.1	28.18		2.87
12.45					16.52		1.46
12.49					16.52		1.56
12.50	0.2	1.4	98.2	0.2	5.36		
12.55					12.46	0.30	1.25

APPENDIX 1 *continued*

12.61	0	0	95	5	12.97	0.29	1.51
12.65					5.87		
12.70	0.2	1.4	98.2	0.2	21.59		
12.75					6.38		1.61
12.80	0.6	4	94	1.4	31.22		
12.85					5.36		1.97
12.89	0	0.1	99	0.9	19.05	0.54	2.52
12.91					6.38		2.50
12.93					6.38		
12.95					12.46		2.17
12.97					8.91		2.57
12.99					14.49		2.79
13.00	0.3	1.6	97.4	0.7	15.50		2.81
13.01					8.40		1.42
13.03					6.38		
13.07	0.2	0.4	99.2	0.2	16.52	0.28	1.94
13.09					7.39		
13.10	0.3	0.4	99	0.3	12.46		1.38
13.11					18.54		1.30
13.13					6.38		
13.15					10.43		
13.18	0	0	99.4	0.6	14.49		1.74
13.21					6.38		1.10
13.23					6.38		
13.25					5.36		
13.26	0	0	99.4	0.6	6.88	0.53	1.60
13.29					4.35		0.95
13.31	0	0	99.4	0.6	8.40		1.34
13.33					3.33		1.04
13.34					4.35		
13.38	0	0	99.4	0.6	4.35		1.82
13.41					5.36		1.32
13.43					4.35		
13.45					16.52		2.11
13.47					16.52		1.98
13.49					26.66		
13.50	0	0	99.4	0.6	11.45		1.57
13.51					30.71		2.41
13.53					30.71		2.35
13.55					18.54		
13.57					30.71		1.78
13.59					14.49		
13.60	0.3	0	99.4	0.3	9.93	0.39	1.40
13.61					12.46		1.27
13.63					26.66		2.70
13.65					36.80		2.18
13.67					26.66		2.40
13.69					16.52		
13.70	0	0	99.4	0.6	3.84		1.30
13.71					18.54		2.36
13.73					34.77		2.24
13.75					32.74		
13.77					13.47		2.39
13.79					18.54		1.90
13.80	1.6	20.7	43.1	34.6	15.50	0.25	2.21
13.829	0	0.3	98.7	1	11.95		1.97
13.83					7.39		
13.85					7.39		
13.87					8.40		
13.89					10.43		
13.90	0	0	98.7	1.3	13.98		2.20
13.91					18.54		2.29
13.93					22.60		2.25
13.95					24.63		2.20
14.00	6.7	30.4	22.3	40.6	30.21		2.38
14.05					40.85		
14.10	22	17.2	3.5	57.3	37.81		2.26
14.15					55.05		
14.20	11.3	32.8	7	48.9	24.63		2.11
14.25					24.63		
14.30	18.6	23.9	6.9	50.6	44.91		2.32
14.33	0	0	98.7	1.3	5.36	0.14	2.00

APPENDIX 1 continued

14.35					18.54		
14.40	4.5	14.8	53.2	27.5	22.09		2.41
14.45					34.77		
14.50	5.5	11	62.3	21.2	13.98		2.27
14.55					34.77		2.09
14.59	0	0.3	75.5	24.2	15.00	0.17	2.41
14.60	0	0.3	75.5	24.2	9.42		2.88
14.61					36.80		1.79
14.65					37.81		
14.70	7.2	29.8	10.7	52.3	44.40		2.53
14.75					37.30		
14.80	2.1	18.3	9.4	70.2	30.21		2.06
14.85					32.74		2.54
14.90	1.1	4.6	1.1	93.2	39.38		2.30
14.95					38.82		
15.00	8.3	10.5	3.6	77.6	42.37		2.54
15.05					30.71		
15.10	17	11.2	4.6	67.2	47.95		2.43
15.15					18.54		2.27
15.20	11.3	6.8	9.5	72.4	29.19		2.20
15.25					30.71		
15.30	6.9	9.4	12.5	71.2	27.16		2.48
15.35					55.05		
15.40	23.6	4.5	0	71.9	60.12		3.07
15.45					32.74		
15.50	13.7	10.8	4.9	70.6	27.16		2.70
15.55					14.49		1.59
15.59	2.4	0	38.1	59.5	8.91	0.56	2.05
15.63					14.49		2.00
15.67	0.1	0	4	95.9	13.47		1.70
15.70	90.6	2.9	0.9	5.6	12.46		2.79
15.75					34.77		2.59
15.80	94	2.2	0	3.8	48.48		2.49
15.85					46.94		2.46
15.90	85.2	3.6	0.8	10.4	62.15		2.78
15.95					40.85	0.29	2.86
16.00	84.3	14.2	1.2	0.3	61.64		2.72
16.07	9	0	27.3	63.7	43.89	3.17	3.38
16.10	3	3	28.2	65.8	23.61	0.13	2.62
16.123					38.82		1.94
16.125					42.88		2.80
16.128					34.77		2.82
16.130					38.82		1.82
16.132	5	0.5	77.9	16.6	38.82		1.98
16.134					32.74		2.08
16.137					24.63		1.76
16.142					31.73		1.84
16.147					30.71	8.97	2.76
16.148	14	0	74	12	40.85		
16.152					30.71		1.02
16.157					30.71		1.19
16.162					26.66		2.49
16.167					24.63		
16.172	25.6	0.1	71.1	3.2	28.68		2.03
16.177					32.74		1.68
16.182					36.80		2.56
16.187					43.89		2.20
16.192					42.88		2.71
16.197	29	0.2	67.8	3	43.64	3.58	2.98
16.202					40.85		2.15
16.207					34.77		2.45
16.212					44.91		3.37
16.217					36.80		
16.222	47.3	0.2	79.4	3	40.85		2.59
16.227					38.82		3.00
16.232					42.88		2.27
16.237					49.98		2.64
16.242					34.77		2.94
16.247	82	0	14	4	49.22	5.22	2.89
16.252					28.68		2.76
16.257					34.77		2.39
16.262					38.82		

APPENDIX 1 *continued*

16.267					42.88		1.02
16.272	96.3	0	0	3.7	40.85		3.35
16.277					42.88		1.54
16.282					36.80		2.42
16.287					18.54		2.32
16.292					21.59		2.92
16.297	31	0	66	3	30.21	9.76	2.50
16.302					36.80		1.85
16.307					44.40		1.25
16.312					36.80		2.48
16.317					44.91		2.51
16.322	96.9	0	0	3.1	24.63		1.98
16.327					32.74		1.50
16.332					40.85		1.83
16.337					34.77		2.06
16.342					32.74		2.53
16.347	4	0	93	3	31.22	7.31	2.64
16.352					44.41		1.98
16.357					34.77		1.94
16.362	20.7	0.2	75.8	3.3	16.52		2.14
16.367					28.68		
16.40	0.2	1.5	14.6	83.7	23.61		2.65
16.45					12.46		1.78
16.49	0	0	5	95	5.36	0.31	2.21
16.50	0	0	5	95	12.97		2.34
16.55					16.52		
16.60	0	2	49	49	5.2		2.51
16.65					35.78		1.91
16.70	0	0.2	94.8	5	13.47		2.18
16.75	0	0.4	94.6	5	8.91	0.07	1.35
16.80	0.4	5.3	15.9	78.4	18.04		2.03
16.85					24.63		1.57
16.90	37.3	8.8	1.3	52.6	35.78		2.80
16.95					46.94		2.81
17.00	12.5	4.6	1.6	81.3	59.61		2.73
17.04	0	1	97	2	9.42	0.39	1.58
17.06	0	0	97	3	12.46	0.21	2.16
17.10	0	0	97.9	2.1	7.90		2.00
17.15					10.43		
17.20	0	0.5	69.5	30	24.12		1.92
17.22	0.6	2.8	66.3	30.3	26.15	0.26	2.35
17.25					22.6		1.92
17.30	4.4	9.6	28.7	57.3	34.26		2.01
17.35					48.96		
17.40	91	5.7	1.2	2.1	47.44		2.11
17.45					53.02		
17.50	61.9	17.3	7	13.8	33.76		2.00
17.55					36.80		2.01
17.60	68.8	15.3	5.4	10.5	34.77		2.30
17.65					37.81		2.10
17.70	9.8	20.7	31.3	38.2	39.33		2.94
17.74	1.4	2	75	21.6	25.63		2.68
17.78	1	1.3	77.7	20	16.52	0.95	1.89
17.82	0.5	1	1	97.5	10.94		1.82
17.85	2	0	97	1	4.86		1.54
17.88	0	1	79	20	4.35	0.48	1.67
17.92	0.6	17	60.4	22	24.63		1.94
17.93	0	0.8	79.2	20	12.46		1.10
17.96	0.5	1	78.5	20	19.56	0.94	2.41
17.99	1.2	7.5	54.2	37.1	23.11		2.03
18.05					26.66		2.22
18.10	12.3	27.2	26.3	34.2	25.64		2.11
18.15					30.71		1.68
18.20	72.6	13.6	5.2	8.6	37.81		1.91
18.25					34.77		1.63
18.30	52.3	25.7	8.1	13.9	40.35		2.18
18.35					42.88		
18.40	99.5	0.1	0.1	0.3	45.92		2.18
18.45					38.82		1.95
18.50	11.1	39.5	14.1	35.3	34.77		2.34
18.55					38.82		
18.60	45.3	17	3.7	34	36.80		2.32

APPENDIX 1 continued

18.65	1.3	19.1	70.5	9.1	22.6	0.23	2.80
18.70	2.2	17	72.8	8	30.71		2.47
18.74					14.49		
18.77	0.1	2	94.9	3	13.47	0.86	1.81
18.83	0.1	2	96.9	1	25.64		1.70
18.85					14.49	0.06	1.58
18.90	0.6	2.1	96.8	0.5	19.05		1.92
19.00	16	20.8	59.2	4	29.70		2.21