

**Ammonoid
multi-extinction
crises**

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Ammonoid multi-extinction crises during the Late Pliensbachian – Toarcian and carbon cycle instabilities

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Five crises affecting ammonite evolution occurred during the Late Pliensbachian to Late Toarcian stages (Early Jurassic). The first two (Gibbosus and end-Spinatum zones) occurred during highly cold and regressive conditions which were followed by a global anoxic event generated during a supergreenhouse warm event (Levisoni subzone) concomitant with a worldwide transgressive event. The last two (Late Variabilis and Late Insigne zones) are related to regressive events. We present new carbon isotope data from Southern Peru that demonstrate that most of the major Toarcian crises affecting ammonite evolution can be correlated with the variations affecting the $\delta^{13}\text{C}$ during that unstable period. The morphogenetic reactions of the ammonites during the five different upper Liassic critical episodes are analysed, showing how this group can be used as stress indicators.

1 Introduction

The Toarcian Stage has been the subject of a multitude of papers, focusing mainly on the identification and interpretation of a major anoxic event (OAE) affecting global oceans during extreme greenhouse conditions (Jenkyns, 1985, 1988; McArthur et al., 2000; Hesselbo et al., 2000; Guex et al., 2001; Morard et al., 2003; Svensen et al., 2004, 2007; van de Schootbrugge et al., 2005; Wignall et al., 2005, 2006; Cohen et al., 2007; Mattioli et al., 2008; McArthur et al., 2008; Littler et al., 2009; Suan et al., 2008, 2011; Gröcke et al., 2011; Caruther et al., 2011; Sandoval et al., 2012, etc.). A sharp negative carbon isotope excursion (CIE) associated with the OAE in both marine and continental organic matter record, as well as in carbonates, has been interpreted as evidence of an immense injection of light ^{12}C in the oceanic-atmospheric carbon reservoirs. To explain this negative CIE, rapid release of methane from gas hydrate contained in marine continental-margin sediments, due to global warming induced by volcanic has been supposed (Hesselbo et al., 2000). Alternatively oxidation of methane

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gas generated by subsurface thermal metamorphism during magmatic intrusion of the Karoo-Ferrar traps has been proposed (McElwain et al., 2005; Svensen et al., 2007).

More recently, several papers refer to a cooling phase, probably related to a brief glaciation, that preceded the OAE during the latest Pliensbachian (Guex et al., 2001; Morard et al., 2003; Dera et al., 2010). The Pliensbachian-Toarcian transition is also characterized by a small negative CIE, related to a very different environmental scenario (regression and cooling) when compared to the Early Toarcian CIE (transgression, super-greenhouse, ocean anoxia). Both the Late Pliensbachian and Early Toarcian (Semicelatum Zone) intervals are characterized by two successive extinction crises, which affected several different groups of microfossils (Bartolini et al., 1992; Wignall et al., 2006; Mailliot et al., 2009; Arias, 2009; Mattioli et al., 2009) and macrofaunas (Vörös, 2002; Aberhan and Fürsich, 2000; Macchioni and Cecca, 2002; Dera et al., 2010; Garcia Joral et al., 2011). The benthic fauna was touched by the Early Toarcian OAE, while the nektonic fauna such as ammonites was affected by double extinction events, the Late Pliensbachian event being much more severe than the Early Toarcian one (Morard et al., 2003).

Essentially the entire Toarcian stage was a time interval punctuated by environmental instabilities, as highlighted by two further ammonite extinction crises at the Variabilis-Thouarsense and Insigne-Levesquei boundaries. However, these two crises episodes have been the subject of only a very few paleontological and geochemical studies (Guex, 1992; Sandoval et al., 2012).

In this paper (1) we present new carbon isotope data from carbonates ($\delta^{13}\text{C}_{\text{carb}}$) covering part of the Toarcian, starting from the Tenuicostatum Zone up to the lower Insigne Zone constrained by precise new ammonite biochronology from southern Peru; (2) we correlate this new Toarcian Pacific $\delta^{13}\text{C}_{\text{carb}}$ curve with the European record (Sandoval et al., 2012) to evaluate its potential for global use; (3) we match the carbon isotope fluctuations with the ammonite taxonomic richness curve (Dera et al., 2010) recalibrated according to our new biochronological data and interpretations; (4) we evaluate whether the Middle-Late Toarcian ammonite extinction event coincides with a

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major carbon cycle perturbations such as the Late Pliensbachian and the Early Toarcian ones; (5) we discuss ammonite morphogenetic reactions during all intervals of environmental instability during the Toarcian because ammonites can, in fact, develop atavistic morphologies during episodes of environmental stress (Guex, 1992); and finally; (6) we propose a new scheme for correlating the Peruvian ammonite sequence, and the Canadian and European ammonite zonations. The latter has implications for the calibration of Late Pliensbachian to Late Toarcian events from diverse sedimentary sequences dated by fossils, previously addressed by Palfy et al. (1997); Palfy and Smith (2000); Palfy (2008); Ogg et al. (2008); Jourdan et al. (2005, 2008); and Mazzini et al. (2010).

The ammonite biological crises and carbon cycle perturbations cannot be accurately correlated with the currently published geochronological ages established in the Karoo-Ferrar province, with one exception: the age of the lower Toarcian CIE proposed by Svensen et al. (2007) and Polteau et al. (2011), 182.7 ± 0.4 Ma.

2 Litho and biostratigraphy of the Palquilla section (southern Peru)

The stratigraphic section presented in this paper is located near the village of Palquilla, close to Tacna in southern Peru (GPS coordinates: $17^{\circ}36.703' S$, $70^{\circ}00.860' W$; Fig. 1). It belongs to the upper levels of the Pelado Formation defined by Wilson and García (1962). Paleogeographic significance and position of the section within the Arequipa Basin was discussed by Vicente (1981, 1989, 2005) and by Vicente et al. (1982). The stratigraphy of the Cerro Taracollo area, which includes the section of Palquilla, was first studied by Salinas (1986). This study demonstrated that the local stratigraphic sequence, mainly carbonate, corresponded to a transgressive event initiated during the Sinemurian, starting with slope deposits that culminated during the Middle Toarcian and was followed by deep calcilutites deposited during the upper Toarcian (San Francisco Formation). These local deposits are intercalated by important levels of

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resediments and by tephra produced by a magmatic arc located to the SW of the studied area.

The Palquilla section, illustrated in Fig. 2, starts with a thick and massive Late Pliensbachian condensed limestone bed full of brachiopods and bivalves. This bed is overlain by white laminated shales (bed 2) yielding a thin shelled bivalve, *Bositra*, and a finely ribbed *Dactylioceras* (*D. kanense*) (see Jakobs, 1997, Pl. 1, Figs. 19 and 20) belonging to the Tenuicostatum zone. In beds 3 and 13 we found *Hildaites striatus* (Guex, 1973, Pl. 3, Fig. 10), with a few intercalated *Dactylioceras* and *Eodactylites* indet., assigned to the Levisoni subzone. bed 20c provided *Porpoceras* (cf. *vortex*: see Buckman, 1911, Pl. 29A) and *Dactylioceras* with quadrangular whorl section. Higher in the section (bed 30c) we found the last local representatives of the family Dactylioceratidae (sp. indet. and *Porpoceras*). About 100 cm below bed 70, we collected well preserved fragments of *Grammoceras*, *Podagrosites* and *Hammatoceras*, and bed 83 produced one specimen of *Yakounia* (Jakobs et al., 1994, Pl. 5, Fig. 11) assigned to the Thouarsense zone. Typical *Pseudogrammoceras* and *Hammatoceras* have been found about 40 m above *Yakounia*, still indicating a lower Insigne zone age, and *Dumortieria* of the Levesquei zone occur about 100 m above. In summary the Toarcian sequence at Palquilla is mostly complete, but there is a gap corresponding to the lowermost Toarcian where the Mirabile and a part of Semicelatum subzones are probably very condensed if not partially missing. Note that lower Toarcian black-shales which are often associated to the CIE are not present in the section.

3 Correlation with Canadian and Europe ammonite standard zonations

The correlation of the Palquilla Toarcian ammonite sequence described above, the Canadian zonation of Jakobs et al. (1994) and the zonation used in Europe is given in Fig. 3.

Most of the ammonite correlation is easy because Jakobs et al. (1994) collected very diagnostic taxa. In Canada, the base of the Kanense zone contains finely ribbed

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Dactylioceras (group of *D. kanense*, see above), followed by *Hildaites* from the Levisoni subzone. *Rarenodia planulata* Venturi (1975, Pl. 1, Fig. 7), occurring in the Planulata zone, is known from the top of the Falciferum zone to the base of the Bifrons zone. *Denckmannia crassicosta* (= *Phymatoceras crassicostata* Merla in Jakobs et al., 1994, Pl. 3, Figs. 5 and 6) and *Merlaites* (Crassicostata zone) are restricted to the Variabilis zone and *Podagrosites* first occurs in the upper part of this zone. *Grammoceras* spp characterizes the Thouarsense zone. The upper Toarcian Yakounensis zone is more difficult to interpret because some ammonites assigned to *Dumortieria* and *Pleydellia* by Jakobs et al. (1994) are in fact related to *Grammoceras* and *Pseudolillia* which occur in the Insigne/Dispansum subzones. In other words they are older than the Levesquei zone. In particular, the Canadian "*Pleydellia*" *maudensis* (Jakobs et al., 1994, Pl. 5, Figs. 1 and 2) is a typical *Pseudolillia* with a clearly tabulated ventral area (Guex, 1975, Pl. 8, Fig. 7). *Dumortieria* assigned to *D. cf. dumortieri*, *cf. levesquei* and *insignisimilis* are true *Dumortieria* of Levesquei age but *Dumortieria? phantasma* (Jakobs et al., 1994, Pl. 5, Figs. 19 and 20) is a smooth Grammoceratid and "*Pleydellia*" *crassiornata* (Jakobs et al., 1994, Pl. 5, Figs. 3 and 4) is interpreted as a strongly costate and bifurcate Grammoceratid, with a trend to develop weak umbilical nodes. Such bifurcate Grammoceratids are known in the Thouarsense zone in Europe (e.g. *G. aff. comptum* sensu Gabilly, 1975, Pl. 18, Figs. 9 and 10).

4 Carbon isotope record at Palquilla and global correlations

Carbon and oxygen isotope analyses of aliquots of whole rock samples were performed using a Thermo Fisher Scientific Gas Bench II carbonate preparation device connected to a Delta Plus XL isotope ratio mass spectrometer (IRMS) at the University of Lausanne (Switzerland). The CO₂ extraction was done by reaction with anhydrous phosphoric acid at 70 °C. The stable carbon and oxygen isotope ratios are reported in the delta (δ) notation as the per mil (‰) deviation relative to the Vienna Pee Dee belemnite standard (VPDB). The standardization of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values relative to the

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international VPDB scale was done by calibration of the reference gases and working standards with IAEA standards. Analytical uncertainty (2 s), monitored by replicate analyses of the international calcite standard NBS-19 and the laboratory standards Carrara Marble is no greater than $\pm 0.05\%$ for $\delta^{13}\text{C}$ and $\pm 0.1\%$ for $\delta^{18}\text{O}$.

The variations of $\delta^{13}\text{C}_{\text{carb}}$ isotopes at Palquilla are given in Fig. 2. The values stay low around 0‰ across the Pliensbachian-Toarcian boundary. Similar low values have been documented for the well expanded Peniche section in Portugal, GSSP of the Pliensbachian/Toarcian boundary (Hesselbo et al., 2007). A minor negative inflexion in coincidence with the first *Hildaites striatus* beds (base of Levisoni subzone) is correlative with the Early Toarcian OAE negative CIE. This event corresponds at global scale with an increase in marine organic matter, well documented in several sections in Western Europe and elsewhere, and very recently also from the Southern Hemisphere Neuquén Basin in Argentina (Al-Suwaidi et al., 2010) and at high polar latitudes (Suan et al., 2011). However, at the Palquilla section, this negative CIE does not co-occur with black-shales in the outcrop. The fact that in the Palquilla area conditions during the Early Toarcian were not anoxic, could explain the lesser amplitude of the negative shift (only 1‰). In NW Europe basins where high organic matter content (up to 10% in wt) and strong anoxic conditions were documented, the negative shift can attain up to 6‰ (Sandoval et al., 2012). In this case, early diagenetic recycling of organic matter may be responsible for a ^{12}C enrichment (Küspert, 1982) and consequently for the amplification of the negative CIE. The negative CIE is likely a global perturbation, but its different amplitudes probably reflect local responses due to various paleogeographic settings and hydrographic conditions. Alternatively, the fact that in Palquilla section the lower part of the negative excursion is not so pronounced, is probably due to the presence of a gap, as mentioned above.

When completely documented, the Early Toarcian CIE culminating in the Levisoni subzone is preceded by a positive excursion starting in the Early Tenuicostatum zone (Hesselbo et al., 2007). At Palquilla this positive excursion is missing. However, the major positive shift of the Falciferum subzone is well represented in that locality. We

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observe a trend towards negative values starting with beds containing *Porpoceras* (Bifrons Zone). The uppermost part of the $\delta^{13}\text{C}$ curve is characterized by a steep negative shift that may have been amplified by diagenetic impact. In this part of the curve, very low $\delta^{13}\text{C}$ values correspond with very low values of $\delta^{18}\text{O}$. In any case a negative excursion occurring in the Middle-Late Toarcian transition (Variabilis and Thouarsense zones) has also been documented in Southern France and is discussed in a general synthesis of the Toarcian $\delta^{13}\text{C}$ correlations by Sandoval et al. (2012) (see Fig. 4 for comparison). In Europe this episode is related to a major regressive event, often associated with a gap. This shows that the negative excursion documented for the same age interval at Palquilla is not an artefact of diagenesis and is certainly of global significance. Note that this Middle-Late Toarcian negative shift is possibly correlative with the negative excursion observed by Mazzini et al. (2010) in the Neuquen Basin (Argentina).

5 Multi-extinctions crises during the Late Pliensbachian and Toarcian

The variations in ammonite biodiversity, expressed as species richness, from the Pliensbachian-Toarcian boundary up to the lower part of the Late Toarcian (Dera et al., 2010) are calibrated to our ammonite field data and biochronological revision (Fig. 2). A first extinction event is discussed by Meister (1988, 1989; Meister and Stampfli, 2000; see also Dera et al., 2010) at the transition between the Gibbosus and Spinatum zones in the Late Pliensbachian, below the stratigraphic interval studied at Palquilla. This is followed by a more marked extinction at the Pliensbachian-Toarcian boundary (C1), and is succeeded by a minor event (C2) coincident with the Early Toarcian AOE, and a major ammonite biotic crisis during the Middle-Late Toarcian transition in the upper part of the Variabilis and Thouarsense zones (C3). All ammonite biotic crises coincide with low values of $\delta^{13}\text{C}_{\text{carb}}$. In NW Europe, extinction crises C1 and C3 are clearly associated with regressive events while the crisis C2 is associated with transgression and anoxic conditions. In the Pacific setting of Palquilla, extinction crisis C1 is strongly

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covariation and external stress has been the topic of very few papers (see e.g. Guex, 1992).

The Late Pliensbachian minor extinction event is characterized by an increase in polymorphism within the genus *Amaltheus* (covariation within the *margaritatus*- > *gibbosus* plexus; see Guex et al., 2003, Fig. 2) and by the appearance of the evolute *Pleuroceras*, derived from typical involute Amaltheids.

During the Pliensbachian-Toarcian boundary major regressive event the Dactylioceratidae reacted similar to other groups by a marked increase in variability with extreme forms leading from the depressed and strongly spinose *Dactylioceras crosbeyi* group to serpenticone forms with simple ornamentation of the *Eodactylites* morphogroup, another case of typical covariation.

The Early Toarcian OAE major extinction event is characterized by the same kind of variability increase within the *Dactylioceras semicelatum* group which develops spinose forms with cadicone internal whorls, well described by Howarth (1973, Pl. 8, Figs. 1–3). This episode is also characterized by the appearance of evolute Hildoceratids known as *Hildaites*, derived from the relatively involute Protogrammoceratids. However the complete transition between the two groups is not well recorded.

During the Middle-Late Toarcian transition, an exceedingly important faunal turnover is observed with the disappearance of the Hildoceratids, Dactylioceratids and Phymatoceratids which are replaced by the Hammatoceratids and Grammoceratids in the ammonite populations.

This crisis, like the others, is marked by a strong increase in polymorphism of the ammonites (e.g. covariation of the *Haugia-Denckmannia* and the *Pseudogrammoceras-Podagrosites* plexus illustrated in Guex, 2001, Fig. 5 and Guex, 2006, Fig. 6): as noted above, such variability increases are particularly important during major environmental stress episodes (see Guex, 1992, 2001 and 2006 for details).

The same kind of biotic situation occurs once more during the Late Insigne-Early Levesquei crises (Guex, 1975; Dera et al., 2010) where we observe the disappearance of abundant *Osperleioceras*, most typical Hammatoceratids, *Alocolytoceras*,

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Buckmanites and *Oxyparoniceras*. In the topmost abundantly fossiliferous beds of the Late Insigne Zone (Dispansum subzone) we observe again a huge polymorphism in the *Osperleioceras reynesi* group with typical *Osperleioceras* like *O. alterans-wunstorfi* (Guex, 1975, Pl. 8, Fig. 3) giving rise to simplified *O. reynesi* (Guex, 1975, Pl. 8, Fig. 2),
5 a form characterized by an evolute coiling and simple, strong and almost straight lateral ribs (Guex, 1992, Fig. 4; Morard and Guex, 2003, Fig. 1). The same is observed in *Hammatoceras* of the *bonarellii* group (Guex, 1975, Pl. 9, Fig. 12) which gives rise to serpentine *Catullocceras* (Guex, 1975, Pl. 2, Fig. 4), the direct ancestor of the *Dumortieria* and *Pleydellia* leading to all the Haplocerataceae of the Middle and Upper
10 Jurassic (Guex, 1992, Fig. 5).

7 Possible relationships between the Toarcian crises and the Karoo Ferrar CFB

In the late 80s, general opinion held that major regressive events were responsible for the major biotic changes in the marine environments (see Sandoval et al., 2001 for discussion). More recently, many major extinctions events have been correlated
15 with significant volcanic activities (Courtilot, 1995; Courtilot and Renne, 2003). In the case of the Pliensbachian – Toarcian, a correlation between the biotic events and the onset of the Karoo Ferrar LIP has been invoked by Palfy and Smith (2000); Wignall (2001) and several others. Most geochronological data concerning the Karoo and Lesotho province are due to Jourdan and colleagues and are summarized in Jourdan
20 et al. (2005, 2008). These author's ages are based on K-Ar analyses and they cannot be strictly compared with the approximate U-Pb ages established by Palfy and Smith (2000). Taking the ca. 0.8% systematic age bias between Ar-Ar and U-Pb dates into account (Min et al., 2000; Renne et al., 2010), the Karoo expected U-Pb age may be situated in between 178.5 and 184.5 Ma. Palfy et al. (1997, 2000) estimated the age
25 of the Pliensbachian-Toarcian boundary at about 183.6 +1.7/-1.1 Ma and the age of the Canadian Crassicostrata zone (approximately equivalent to the Variabilis zone) at 181.4 Ma (± 1.2 Ma).

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in the Dunlap Formation in Nevada (USA) and in the top Pliensbachian of the Ururoa-Kawhia area, New Zealand, just below marine beds with ammonites that we identified as *Dactylioceras* aff. *semicelatum*. The cooling model is confirmed by several recent $\delta^{18}\text{O}$ data (Gomez et al., 2008) and by the discovery of glendonites across the entire Pliensbachian (Price, 1999).

The regression phase is followed by a worldwide transgression during the Early Toarcian, with the deposition of black shales (Toarcian OAE of Jenkyns, 1988; crisis C2 in Fig. 2) and very warm climate possibly related to the major intrusion of the Karoo sills, as mentioned above (Polteau et al., 2011). This widespread anoxic event is responsible for major extinctions in the benthic foraminifera (Bartolini 1992) and brachiopods (Garcia Joral et al., 2011) but the ammonites were only slightly affected, mostly by a moderate drop in diversity (Fig. 2).

If we except the C2 crisis of the Toarcian OAE at 182.7 Ma (see Polteau et al., 2011), the other datings are not precise enough to prove a one to one correlation between the multiple Pliensbachian to Toarcian crises and the different pulses of the Karoo Ferrar volcanism. However it is highly probable that the major regressive events observed during the crises C1 and C3 are indeed related to that volcanism, generated by cooling induced by major SO_2 injections occurring prior or during these extrusive episodes, while the Levisoni crisis C2 and the OAE are related to the large-scale intrusion of Karoo sills.

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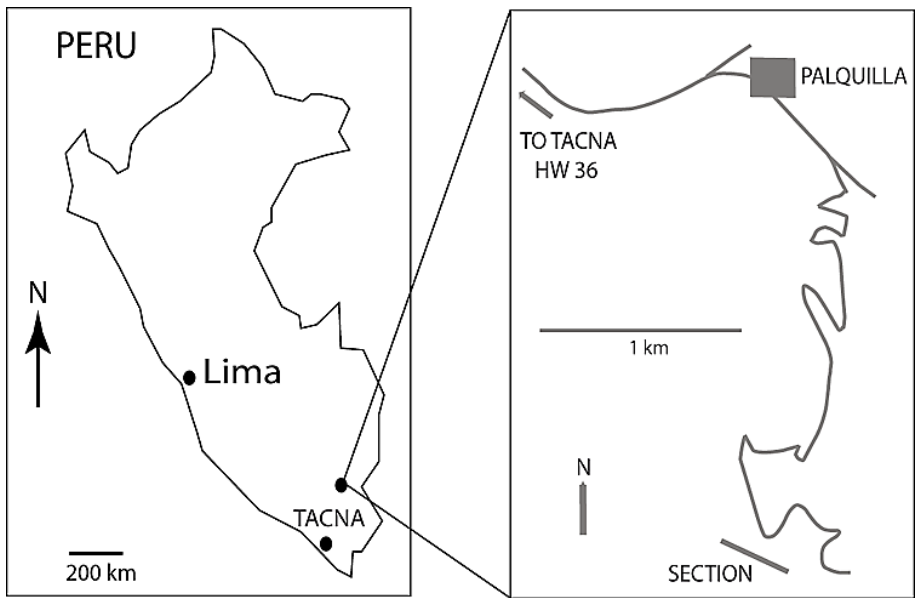


Fig. 1. Map showing the location of the Palquilla section.

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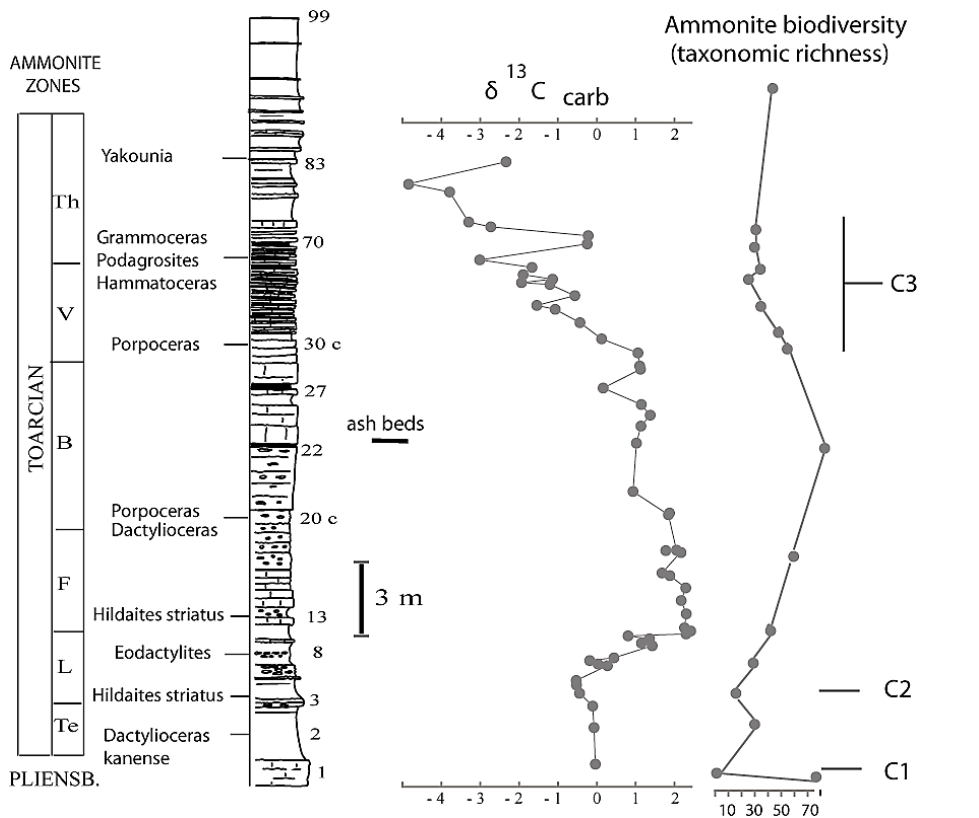


Fig. 2. Palquilla section with ammonite beds and $\delta^{13}\text{C carb}$ measurements. Ammonite zones: Th = Thouarsense, V = Variabilis, B = Bifrons, F = Falciferum, L = Levisoni, Te = Tenuicostatum. C1 to C3 = evolutionary crises discussed in the text. The taxonomic diversity (Dera et al., 2010) value at C1 corresponds to the number of taxa surviving the Pliensbachian-Toarcian boundary and the other values are calibrated to the stratigraphic section.

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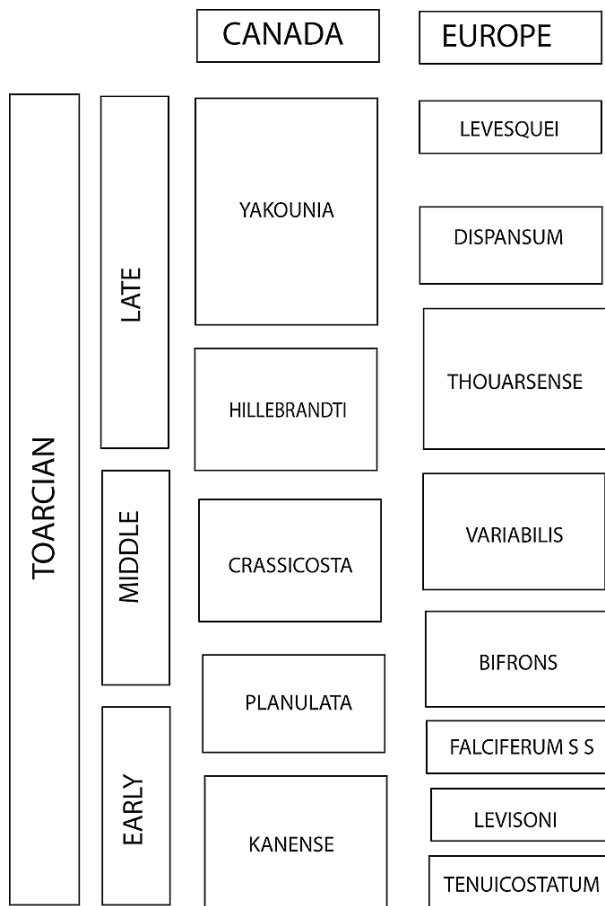


Fig. 3. Zonal correlations between Pacific realm and Europe.

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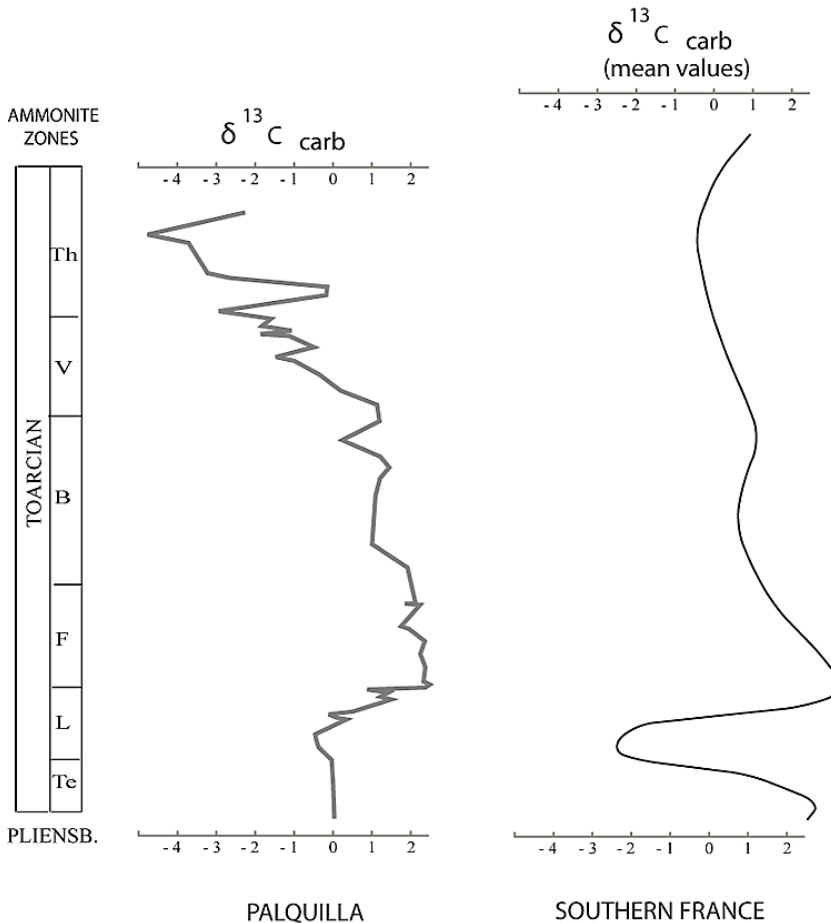


Fig. 4. Comparison between the carbon isotope curve measured at Palquilla and that of Southern France given in Sandoval et al. (2012). The correlation between the two curves is based on the ammonites.

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