Integrated stratigraphy of the Upper Hauterivian to Lower Barremian Agua de la Mula Member of the Agrio Formation, Neuquén Basin, Argentina

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ABSTRACT:

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The Upper Hauterivian to Lower Barremian Agua de la Mula Member of the Agrio Formation (Neuquén Basin, Argentina) was studied applying an integrated stratigraphic approach and facies analysis. The ammonite biostratigraphy of the member has been improved based on bed-by-bed collecting. The already defined biozones (*Spitidiscus riccardii, Crioceratites schlagintweiti, Crioceratites diamantensis* and *Paraspiticeras groeberi*) were recognized, precisely related to the succession, and further refinement was proposed. Sequences of different order are built by stacked starvation/dilution (S/D) sequences, regarded here as sixth-order sequences with only two components that can be unequivocally distinguished: the lower starvation hemisequence and the upper dilution hemisequence. Pro- and retrogradational stacking pattern of S/D sequences define supra-ordinate sequences. The sequence-stratigraphic analysis resulted in the subdivision of the member into four main depositional sequences (DSAM-1 to -4) and several subordinate sequences. Previously published sequence stratigraphic charts of the Neuquén Basin did not relate sedimentary sequences to biozones, and are hence not comparable to the scheme presented here and other charts. Our study shows a good agreement with the sequence-chronostratigraphic scheme of European basins, thus arguing in favour of a predominantly eustatic control on sequence development during the Late Hauterivian to Early Barremian. A latest Early Barremian age is proposed for the almost ammonite-barren upper part of the Agrio Formation, based on correlations of sequence boundaries.

Key words: Lower Cretaceous; Southern America; Neuquén Basin; Bio- and sequence stratigraphy; Anoxic events.

INTRODUCTION

The stratigraphy and palaeontology of the highly fossiliferous Late Valanginian–Early Barremian Agrio Formation of the Neuquén Basin (Argentina) have been subject of several studies since the end of the nineteenth century (Behrendsen 1891; Behrendsen 1892; Haupt 1907; Lazo, 2004; Leanza 1945; Leanza 1981a; Leanza 1981b; Leanza 2003; Leanza *et al.* 1977; Leanza *et al.* 2006; Veiga *et al.* 2005; Weaver 1931). However, these studies are often focused only on specific topics such as ammonite biostratigraphy (Aguirre Urreta 1995; Aguirre Urreta *et al.* 1993; Aguirre Urreta and Rawson 1997; Aguirre Urreta *et al.* 2005; Leanza 1981a; Leanza 1981b; Leanza *et al.* 1977; Leanza and Wiedmann 1980), trigoniid taxonomy and stratigraphy (Leanza 1993; Lazo, 2003), facies analysis and sequence stratigraphy (Legarreta and Gulisano 1989; Sagasti 2005; Spalletti *et al.* 2001a; Spalletti *et al.* 2001b; Veiga *et al.* 2005; Veiga *et al.* 2002; Veiga and Vergani 1993) as well as the study of organic facies and anoxic events (Doyle *et al.* 2005; Tyson *et al.* 2005). However, an integrated approach in order to unravel the geological history of the unit was still missing.

The aim of this paper is to assess the stratigraphy of the Upper Hauterivian to Lower Barremian Agua de la Mula Member of the Agrio Formation from the integration of ammonite biostratigraphy, sequence stratigraphy and event stratigraphy, following a detailed facies analysis (Archuby and Fürsich 2010). Palaeoecology and taphonomy of benthic marine invertebrates also provided valuable information for the interpretation of stratigraphic patterns (Archuby 2009).

Geological setting

The Neuquén Basin

The Neuquén Basin is located on the eastern side of the Andes of Argentina and Chile, between a latitude of 32° and 40°S (Legarreta and Uliana, 1991; Text-fig. 1A). It extends for approximately 700 km from north to south and more than 400 km from west to east. The basin contains a Late Triassic to Cenozoic sedimentary succession comprising continental and marine siliciclastic, carbonate, and evaporitic deposits, which are at least 7 km thick and cover an area of over 160,000 km² (Vergani *et al.* 1995).

The basin has been characterized as an ensialic back-arc basin placed east of the Andean magmatic arc, which developed in response to the subduction of the Nazca Plate below the South American Plate (Textfig. 1B). It is limited by cratonic areas to the northeast (Sierra Pintada System) and southeast (North Patagonian Massif). In the study area it crops out as a series of N–S-oriented fold and thrusts belts (Aconcagua, Malargüe, and Agrio; Howell *et al.* 2005).

The predominantly marine Jurassic and Cretaceous fill of the Neuquén Basin (Text-fig. 2) consists of thick and widespread successions deposited during protracted thermal subsidence and regional back-arc extension. They include a complex series of transgressive-regressive cycles of different magnitude, controlled by the combined effects of changes in subsidence rates, local uplift, and eustatic sea-level oscillations (Howell *et al.* 2005; Sagasti 2001). Although the Andean magmatic arc was a prominent N– S striking positive feature, by the time of deposition of the Agrio Formation the Neuquén Basin was connected to the west with the Pacific Ocean through gaps in the volcanic arc (Spalletti *et al.* 2000). Uplift and inversion of the Andes during the Cretaceous finally isolated the basin from the Pacific Ocean and, after further compression, it evolved from a back-arc into a foreland basin (Veiga *et al.* 2005).

Lithostratigraphy and depositional environment of the Agrio Formation

The Agrio Formation is widely exposed along the Agrio Fold and Thrust Belt in the Andean sector of the Neuquén Basin. It extends from the vicinity of La Mala Dormida in southern Mendoza southwards to Catán Lil, a few kilometres south of Cerro Marucho in southern Neuquén. To the west, the boundary of present-day outcrops coincides with the foothills of the Andes (Text-fig. 1A). Towards the eastern and southern margins of the basin, the marine rocks of the Agrio Formation interfinger with the Centenario Formation. The formation overlies marine deposits of the Mulichinco Formation (Text-fig. 3A) and is covered unconformably by siliciclastic, carbonate, and evaporitic rocks of the Huitrín Formation.

The unit was defined by Weaver (1931) for a thick succession of marine shales overlying the Mulichinco Formation. Weaver divided the Agrio Formation into lower and upper divisions separated by a thin but laterally persistent unit, the Avilé Sandstone. The three lithostratigraphic elements are considered as members. The Pilmatué (lower) Member (Leanza et al. 2001) is composed of up to 600 m of marine shales and mudstones associated with thin sandstone beds and carbonates (wackestones and packstones; Aguirre Urreta and Rawson 1997). The middle unit, the Avilé Member, consists of up to 100 m thick sandstones with fine conglomerates and subordinate mudrocks interpreted as aeolian and arid fluvial deposits. It represents a major drop in sea level across the basin (Veiga et al. 2002). The Agua de la Mula (upper) Member (AMMb) is a marine succession, up to 1000 m thick, composed of shales, mudstones, sandstones and bioclastic carbonates (Spalletti et al. 2001b). Leanza (2003) placed the Chorreado Member, previously considered as a Hutrinian unit, in the Agrio Formation. The Agua de la Mula Member is thus sandwiched between two continental lithostratigraphic units that represent important regressive packages: the Avilé Member below and the Huitrín Formation above (Text-fig. 3 B and C).

The Jurassic–Cretaceous fill of the Neuquén basin was subdivided into three supersequences named Lower, Middle and Upper (Legarreta and Gulisano 1989; Text-fig. 2). The Middle Supersequence is represented by the lithostratigraphic unit Mendoza Group (Tithonian–Early Barremian). It was in turn divided



Text-fig. 1. Localities and geological setting. A – Geographic position of the Neuquén Basin with the localities studied, Agua de la Mula (AML) and Bajada del Agrio (BAL). B – Schematic diagram across the Pacific margin of Gondwanaland. Not to scale. (modified from Legarreta and Uliana 1991). 1 – Minor accretionary wedge (or tectonic erosion). 2 – Ridged forearc. 3 – Magmatically active half-graben or graben depressions. 4 – Backarc basin under extension and strike-slip conditions. 5 – Continental interior (foreland)

into three subordinate sequences, i.e., Lower, Middle and Upper Mendoza mesosequences (Text-fig. 2). Each of these three mesosequences starts with continental and/or marginal marine sedimentary packages, deposited in the inner portion of the basin (Legarreta and Gulisano 1989). The Agua de la Mula Member of the Agrio Formation together with the underlying Avilé Member are interpreted as a second-order sedimentary sequence (Upper Mendoza Mesosequence, Legarreta and Gulisano 1989). The Avilé Sandstone occurs in most of the Neuquén Basin (Weaver 1931). It represents deposition during a major drop in the relative sea level and is interpreted as a lowstand systems tract (Legarreta and Gulisano 1989; Legarreta et al. 1993; Legarreta and Uliana 1991; Veiga et al. 2002; Veiga and Vergani 1993). The overlying Agua de la Mula Member of the

Agrio Formation shows the re-establishment of marine conditions, which persisted until the end of the deposition of the Upper Mendoza Mesosequence.

Detailed macro- and microfacies analyses provided strong bases for the stratigraphic interpretation (Archuby and Fürsich 2010). It allowed the recognition of different types of facies characteristic of the sedimentary environments in which the sediments and fossils were deposited. Facies analysis (Archuby and Fürsich 2010) indicates that the Agua de La Mula Member of the Agrio Formation was deposited in an open marine ramp setting. There are no indications of departures from normal salinity. The oxygen content was lowered during some periods but total depletion, if it happened at all, occurred only briefly. Nutrient levels were probably high during the deposition of the member.



Text-fig. 2. Stratigraphic chart of the Neuquén Basin. Modified after Groeber (1946), Legarreta and Gulisano (1989), and Sagasti (2001)

METHODS

During spring and autumn of 2002, 2003, and 2004 the Agua de la Mula Member of the Agrio Formation was studied in detail at two localities (Text-fig. 1A). The first section, Bajada del Agrio (BAL) (S 38° 03'; W 70° 02'), is situated 64 km north of the town of Zapala on National Road 40. The other one, Agua de la Mula (AML) (S 38° 26'; W 70° 04'), is located 104 km north of Zapala and around 3 km to the east of the National Road 40.

The unit crops out almost completely in Bajada del Agrio and the beds can be followed for several hundred

metres. The ammonite fauna is abundant and present in most of the section, which allows a good biostratigraphic control. Outcrops in the Agua de la Mula area are generally poorer. Apart from some portions of the section that are not exposed, the upper 100–150 m are faulted and were not surveyed.

Fieldwork involved detailed measurement and description of sections including: type of lithology, sedimentary structures, bioturbation including trace fossil identification, and observations of taphonomic features of shell concentrations. In addition, all sedimentological attributes were recorded at a 1:100 scale.



Text-fig. 3. A – Schematic stratigraphic section of the Mendoza Group (modified from Aguirre Urreta and Rawson 1997). B – Contact between the Ayilé and the Agua de la Mula members. Bajada del Agrio (BAL) section. C – Contact between the Agrio and the Huitrín formations. Bajada del Agrio (BAL) section

The ammonite fauna was sampled in both sections and an additional intensive bed-by-bed sampling was carried out in the BAL section. Ammonites were taken to the lab for preparation and identification. The successions have been biostratigraphically subdivided by means of the ammonites collected; the zones and subzones established have been compared and correlated with previous ammonite zonal schemes for the area and with the standard West Mediterranean ammonite zonal scheme. The taxonomic treatment and illustration of the ammonites will be published separately (Archuby *et al.* in prep.).

SECTIONS

The Agua de la Mula Member is well defined in the study area. It overlies the Avilé Member conformably with a sharp contact (Text-fig. 3 B). At the locality of Agua de la Mula, sandy calcareous argillaceous shales overlie the medium- to coarse-grained sandstones of the Avilé Member. At Bajada del Agrio, the marly shales cover fine-grained sandstones and siltstones with ripple cross-lamination and desiccation cracks, deposited on top of the fluvial sandstones of the Avilé Member. At the same locality, the top of the unit is well marked by an erosion surface underlain by a marine oolitic and bioclastic grainstone bed, and overlain by fluvial coarse-grained sandstones (Troncoso Member) and a gypsum layer of the Huitrín Formation (Text-fig. 3C). As mentioned above, the upper 150 metres are poorly exposed at Agua de la Mula and therefore were not included in this study.

Bajada del Agrio

The Agua de la Mula Member at the Bajada del Agrio (BAL) section is completely exposed (Text-fig.

4). The Avilé Member is an almost 10 m thick medium- to coarse-grained sandstone unit with trough cross-stratification. Its erosional base represents a second-order sequence boundary (Text-fig. 3B). Ten metres below the base of the Avilé Sandstone, intercalated into siliciclastic mudstones of the Pilmatué Member, a thin shell-bed has yielded the ammonite Weavericeras vacaense of Early Hauterivian age. On top of the Avilé Member at BAL, there is a 1 m thick transitional set of beds with fine- to medium-grained sandstones with desiccation cracks and vertical burrows. These beds are sharply overlain by offshore marls and marly clays. The section can be subdivided into four segments. The first 165 m are dominated by dark, fine-grained siliciclastic sediments (clay to silt) with thin intercalated shell-beds, showing a long-term subtle progradational pattern. Abundant ammonites (e.g. Spitidiscus riccardii and Plesiospitidiscus gutierrezi) indicate an earliest Late Hauterivian age for these beds. Between 165 and 210 m, there is a strongly progradational sedimentary package that ends with an important erosional surface. The third segment comprises a thick sedimentary pile characterized by numerous high-frequency sequences (Pl. 1, Fig. 1), each composed of a basal starved shell-rich hemisequence usually overlying an erosion surface, and a siliciclastic-dominated and markedly progradational upper part. Bundles of these basic sequences compose sequences of different hierarchies (intermediate and main sequences). Facies typically fluctuate in these basic sequences from offshore to shoreface settings. Starved portions of these sequences have thick and complex shell beds with abundant and well preserved fossil invertebrates (Archuby 2009). Crioceratitid ammonites of Late Hauterivian age are abundant in these shell beds. On





Text-fig. 4. Stratigraphic logs of the sections measured at Bajada del Agrio (BAL) and Agua de la Mula (AML). (c – claystone; s – siltstone; f, m and c – fine, medium and coarse sandstone; g – gravel. m – mudstone, w/fl – wackestone/floatstone, p – packstone, g – grainstone, rm – micritic rudstone, rs – sparitic rudstone)



Plate 1. 1 – Agua de la Mula section (AML) from ca. 250 m (to the left of the photograph) to 350 m (to the right) showing the sequence boundary Agua de La Mula-0 (SBAM-0), the Avilé Member (LST-1), the transgressive surface-1 (TSAM-1), the SBAM-2 and the high frequency starvationdilution (S/D) sequences. 2 – Agua de la Mula section (AML) from the Avilé Member up to the conspicuous transgressive bed overlying TSAM-1

top of this third segment, *Paraspiticeras groeberi* of latest Hauterivian–Early Barremian age was recorded. Siliciclastic input was low to moderate during the deposition of this part of the section. In the fourth segment, although basic sequences are present, sedimentary trends are characterized by higher hierarchy (i.e., intermediate) sequences. Only at the top of these sequences are progradational patterns present and siliciclastic facies reach shallow settings. Transgressive beds consist of pure limestones, and coral patch reefs are present.

Agua de la Mula

The Agua de la Mula locality (AML) is situated 40 km north of BAL, approximately 5 km east of the National Route 40 (Pl. 1, Fig. 2). The contacts between the Pilmatué, Avilé, and Agua de la Mula members are very well exposed, as are the first 20 m of the latter. From there onwards, outcrops show some gaps or poorly exposed segments for approximately 150 m. From 170 to 450 m the section is fairly well exposed. However, the dip of the beds is low (ca. 13°) which makes it difficult to observe some sedimentological features. Above 450 m, the AML section is strongly faulted and was not measured. The section can be subdivided in a similar way to the BAL section. The lowermost part bears early Late Hauterivian ammonites. Fine-grained siliciclastic rocks with thin intercalations of shell beds predominate. The second part of the section is well exposed although its facies is more uniform than in the BAL section The features of the third segment are similar to those described for BAL. The fourth segment of the BAL section is very poorly exposed at AML, although thick oolitic and bioclastic grainstone beds and coral reefs indicate similar depositional environments.

Two features distinguish the sections. First, the section at Agua de la Mula was deposited in a more basinward position compared to Bajada del Agrio. The facies at AML represent deeper sedimentary environments than in the BAL section at equivalent positions. Thick successions of nearshore sandstones at the top of major regressive cycles, observed at AML, are missing in the BAL section, probably because of erosion or non-deposition due to sediment bypassing. These features coincide with the assumed palaeogeographic position of the sections in the basin. The second aspect that differentiates AML from BAL is the higher amount of terrigenous sediment in most parts of the section, indicating a higher extrabasinal input and/or higher availability of accommodation space.

RESULTS AND DISCUSSION

Biostratigraphy

The Agua de la Mula Member of the Agrio Formation in the study area includes four ammonite biozones, in ascending order: the *Spitidiscus riccardii* Zone of early Late Hauterivian age (Aguirre Urreta 1995; Aguirre Urreta *et al.* 2005; Leanza and Wiedmann 1992); the *Crioceratites schlagintweiti* and *Crioceratites diamantensis* zones of the early to late Late Hauterivian, respectively (Aguirre Urreta and Rawson 1993); and the *Paraspiticeras groeberi* Zone of latest Hauterivian to early Barremian age (Aguirre Urreta and Rawson 1993; Aguirre Urreta *et al.* 2005). Background knowledge of the Hauterivian–Barremian ammonite biozonation of the Neuquén Basin and West Mediterranean Tethys is summarized in Text-fig. 5.

Patterns found in this study

Weavericeras vacaense Zone. A thin shell-bed with a ferruginous bioclastic matrix containing several well preserved specimens of *Weavericeras vacaense* Weaver was found in the Pilmatué Member, 10 m below the Avilé Member. This species indicates a late Early Hauterivian age for the topmost portion of the Pilmatué Member (Aguirre Urreta *et al.* 2005). This biozone ends with the erosional base of the fluvial sandstones of the Avilé Member (Coihuequican Unconformity of Leanza *et al.* 2006).

Spitidiscus riccardii Zone. Several specimens of Spitidiscus riccardii Leanza and Wiedmann were found in the Agua de la Mula Member in both sections, indicating an earliest Late Hauterivian age of the basal part of this member (Aguirre Urreta et al. 2005). In the BAL section, this biozone extends up to 166 m above the Avilé Member. The first occurrence coincides with the first fossil concentration level of the unit. These ammonites normally occur flattened or, less commonly, preserved in three dimensions, usually as fragments of whorls, but also as almost complete specimens. In the AML section, specimens of S. riccardii have been found from the base of the unit up to 140 metres. Some fragments found at this locality show weak ornamentation between widely developed constrictions, displaying features close to those of Plesiospitidiscus gutierrezi Leanza and Wiedmann, which has also been assigned to this biozone. No vertical patterns were detected in the ranges of these two species but this may also be related to the scarcity of P. gutierrezi.

Crioceratites schlagintweiti Zone. This biozone was defined by Aguirre Urreta and Rawson (1993) for

the occurrence of the crioceratitid species Crioceratites schlagintweiti Giovine and C. apricus Giovine, assigned to the early Late Hauterivian. Aguirre Urreta and Rawson (1997) defined the base of this zone at the first appearance of crioceratitid ammonites. In the BAL section, a juvenile ammonite whorl from 170 m above the base shows well developed radial ribs that do not change throughout the shell. This specimen has been tentatively identified as Crioceratitidae indet., and its appearance marks the base of the C. schlagintweiti Zone in this section. It is worth mentioning that the last occurrence of specimens of S. riccardii is four metres below the first appearance of crioceratitid remains, making the contact between these two biozones very sharp at this locality, especially when concerning the enormous thickness of the section.

Two different types of specimens of *C. schlagintweiti* have been found. Type A resembles in ornamentation the descriptions and illustrations of Giovine (1950), but the shell is larger (sometimes more than 30 cm in diameter) and not uncoiled. Type B fully coincides with the original description of the species. *C. schlagintweiti* type A is abundant in both sections. In the BAL section, it was observed between 225 to 255 m above the base. Type B, however, is lacking in Bajada del Agrio and rare in Agua de la Mula, where it occurs together with type A. The top of this biozone is indicated by the first occurrence of *C. diamantensis* of the eponymous zone. *C. apricus* has not been observed in any of the sections.

Crioceratites diamantensis Zone. According to Aguirre Urreta et al. (2005), this biozone comprises the beds above the C. schlagintweiti Zone and is characterized by the presence of the crioceratitid ammonite C. diamantensis, which can occur together with C. andinus. In the BAL section, C. diamantensis and C. andinus occur between 255 and 347 m above the base. The first occurrence of C. diamantensis is a few metres above the last occurrence of C. schlagintweiti, forming a sharp contact. A local subdivision of the biozone is possible considering that between 255 and 283 m, C. diamantensis and C. bederi (sensu Gerth, 1925) occur together and are replaced up-section by C. andinus and C. perditus, species that range up to the top of the zone. It is worth noting the presence of uncoiled shells of C. bederi at the top of the lower proposed subzone. This fact indicates the presence of two uncoiling events, one in the C. schlagintweiti Zone and a second in the C. diamantensis Zone. In the AML section, specimens of both C. diamantensis and C. perditus have been collected.

Paraspiticeras groeberi Zone. Two beds with abundant fragments of *Paraspiticeras groeberi* have been found between 381 m and 392 m above the base in the BAL section. This ammonite species has not yet been recorded at AML, where the section is incomplete and beds of this biozone probably could not be sampled.

Level with ammonite indet. At BAL, there are almost no ammonites from 392 m up to the top of the section. The exception consists of a single specimen of a probably new species collected at 499 m. The taxonomic determination of this specimen will probably improve the knowledge of the age of the unit because of its stratigraphic position. Aguirre Urreta *et al.* (2005) also mentioned the find of a new species around this level. These authors described an as yet unstudied open-coiled ammonite species, which differs from the aforementioned specimen.

Biostratigraphic discussion

The Spitidiscus ricardii Zone is well developed, and its lower and upper boundaries are sharp. The age of this biozone is assumed as earliest Late Hauterivian (Aguirre Urreta et al. 2005), based on the similarity with species of the Mediterranean region. In this study, the base of the biozone is inferred to coincide with the erosion surface below the Avilé Member even though the lowermost 2.1 metres lack ammonites in the BAL section (they consist of unfossiliferous marginal marine facies). These 2.1 metres are assigned to the S. riccardii Zone in view of the stratigraphic continuity between the top of the Avilé Member and the first occurrence of Spitidiscus. The erosion surface at the base of the Avilé Member is a second-order sequence boundary (Coihuequican Unconformity of Leanza et al. 2006). The Avilé Member is thus genetically linked with the overlying Agua de la Mula Member and not with the underlying Pilmatué Member. The Avilé Member is therefore assigned here to the Spitidiscus riccardi Zone and, hence, to the earliest Late Hauterivian ammonite biozone of the Neuquén Basin.

The ammonite fauna of the C. schlagintweiti Zone has been linked to mid-Hauterivian ammonites of the Mediterranean region based on the uncoiled nature of the shells (Aguirre Urreta and Rawson 1997). In the present study, open-coiled crioceratitid ammonites were found in this as well as in the C. diamantensis Biozone, which renders the correlation criteria currently used between these regions open to question. Ammonites of the C. diamantensis Biozone are correlated with latest Hauterivian forms of the Mediterranean region because of the more compressed and involute nature of the shells, observed in Pseudothurmannia (Aguirre Urreta and Rawson 1997; Aguirre Urreta et al. 2005). In the present study, these features were observed in C. andinus and C. perditus, both characterizing the proposed upper biosubzone. In this way, the correlation with the Plesiospitidiscus ligatus Zone of the Mediterranean region



Text-fig. 5. Ammonite biostratigraphy of the Hauterivian–Lower Barremian of the Neuquén Basin, and standard West Mediterranean zonation (modified after Aguirre Urreta and Rawson 1997 and Aguirre Urreta *et al.* 2005)

Hu Forr	uitrín Ammonite species nation ranges	Uncoiling	Zones/sub-zones this study New zone/s ?		Zones Aguirre Urreta et al. (2005)	Age
500 m-	* Ammonite indet.				?	arremian
400 m-	⊥Paraspiticeras groeberi		P. gro	eberi	P. groeberi	ä
300 m-	C.perditus C.andinus C.bederi + C.diamantensis C.schlagintweiti	*	Crioceratites diamantensis	andinus + perditus diam + beden	C. diamantensis	luterivian
200 m-			C. schlagintweiti		C. schlagintweiti	Late Ha
100 m-	Spitidiscus riccardii		S. riccardii		S. riccardli	
0 m Avile	* Weavericeras vacaense		W. vacaer	ISE	W. vacaense	E. Haut.

Text-fig. 6. Ammonite occurrences in the Bajada del Agrio (BAL) section, biozones and comparison with previous stratigraphic schemes. Shaded areas represent anoxic events. Rhombs indicate the occurrence of uncoiled ammonites

is proposed to extend up to the top of the *C. diamantensis/C. bederi* Biosubzone. *Paraspiticeras groeberi*, provisionally dated as Early Barremian (Aguirre Urreta and Rawson 1993; Aguirre Urreta *et al.* 2005), is now more confidently placed at the base of this stage after detection of the inferred expression of the uppermost Hauterivian Faraoni Event (for more information see the Anoxic events section below). The upper third of the section at BAL is poor in ammonites and thus exhibits a less reliable biostratigraphic zonation.

Our knowledge of the ammonite biostratigraphy of the Agua de la Mula Member is not entirely satisfactory. The basal biozone exhibits an as yet not understood succession of *Spitidiscus* and *Plesiospitidiscus* species. There is also confusion about the systematics of the crioceratitid species that compose the second and third biozones, and the upper third of the section yielded only two ammonite specimens, which have not yet been studied in detail (a systematic treatment of the ammonoids is underway; Archuby *et al.*, in prep.). Thus, precise biostratigraphic correlation with the West Mediterranean Province is still very difficult.

Biostratigraphic synthesis

The ammonite biostratigraphy of the Agua de la Mula Member of the Agrio Formation is more complex than previous studies indicate (Aguirre Urreta and Rawson 1997; Aguirre Urreta *et al.* 2005). Furthermore, crioceratitid systematics are in need of revision as has been already pointed out (Aguirre Urreta and Rawson 1997). However, these two problems are beyond the scope of this study.

Together with *Spitidiscus riccardii*, scarce remains of *Plesiospitidiscus gutierrezi* were collected. However, a possible vertical superposition of these two species remains unclear.

Specimens of *Crioceratites schlagintweiti* coinciding with Giovine's (1950) descriptions are rare in the Agua de la Mula section and absent at Bajada del Agrio. This biozone is well represented by large specimens that, although regularly coiled, share all other morphological features with the original description of *C. schlagintweiti*.

The finding of uncoiled specimens of *C. bederi* in the *C. diamantensis* Zone suggests that previous correlations of the *C. schlagintweiti* Zone by Aguirre Urreta and Rawson (1997) with the mid-Hauterivian based on uncoiled crioceratitids of Europe should be revised. Uncoiled forms occur in at least two different biozones in the section at Bajada del Agrio.

The *P. groeberi* Zone is now more confidently placed in the uppermost Hauterivian–lowermost Bar-

remian interval as it is developed immediately above the inferred uppermost Hauterivian equivalent of the Faraoni Event in the Neuquén Basin (see below).

The upper third of the BAL section has a very limited record of ammonites. However, these more than 100 m of sediments probably represent a significant amount of time and deserve a more intensive study in the future.

Sequence stratigraphy

During the Jurassic and Early Cretaceous, the Neuquén Basin passed through a sag evolutionary stage, behaving as a marginal basin (Mitchum and Uliana 1985). From the late Jurassic (Kimmeridgian) to the Late Cretaceous, the basin experienced thermal subsidence evidenced by the geometry of the mesosequences as well as their internal stacking pattern, which shows subtle facies changes (Legarreta and Gulisano 1989). Ramos (1977) and Zapata and Folguera (2005) indicated that during this period the Neuquén Basin was a back-arc basin strongly affected by tectonic and eustatic sea-level changes due to a narrow connection with the ocean towards the northwest (Text-fig. 1B). As the Neuquén Basin experienced a relatively simple thermal sag mode of subsidence, a low gradient depositional ramp developed in which the nature and extent of the facies were strongly influenced by variations in global sea level (Legarreta and Uliana 1991).

Most published information indicate that the Agua de la Mula Member was deposited in a tectonic setting characterized by a steady and slow subsidence (Legarreta and Gulisano 1989; Legarreta et al. 1993; Legarreta and Uliana 1991; Mitchum and Uliana 1985; Spalletti et al. 2001a; Spalletti et al. 2001b). Vergani et al. (1995), in turn, indicate that the Lower Cretaceous Mendoza-Rayoso succession is punctuated by several unconformities that define the stacking pattern of multiple transgressive-regressive sequences, reflecting intermittent subsidence and eustatic processes. In summary, while several authors support the dominance of eustatic sea-level changes over tectonics to explain most of the Lower Cretaceous sedimentary record of the Neuquén Basin (and in particular the Agrio Formation), others give tectonics a more important role.

There is no agreement on the number of third-order sequences that compose the Agua de la Mula Member. Many authors described three third-order (major) sedimentary sequences for the unit (Legarreta and Gulisano 1989; Legarreta and Uliana 1991; Spalletti *et al.* 2001b). Legarreta and Uliana (1991) report at least two short-lived episodes of shallowing that caused exposure of the shelf. The resultant abrupt basinward shift of the siliciclastic nearshore facies can be recognized in the widespread shelfal accumulation of the Agua de la Mula Member. Legarreta *et al.* (1993, their text-fig. 2) recognized at least eight (third-order) sequences for the Agua de la Mula Member of the Agrio Formation in the southern part of Mendoza Province. Sagasti (2000) found, in a deep basinal setting of southern Mendoza, five groups of bedding couplets, which were interpreted as the distal expression of five major sequences [third-order in Sagasti (2000); fourth-order in Sagasti (2001)].

The Agua de la Mula Member of the central Neuquén province has four segments that can be easily recognized from their sedimentological, stratigraphic and palaeontological features (see Sections chapter). They probably fit with the three third-order sequences described in the literature (Legarreta and Gulisano 1989; Legarreta and Uliana 1991; Spalletti *et al.* 2001b) in the following way: the first two segments mentioned here correspond to the first sedimentary sequence of the literature. The third and fourth in turn coincide with the other two third-order sequences respectively. However, based on detailed investigations a different scheme is proposed here.

The studied unit exhibits a very cyclic pattern, which can be followed throughout the sections (Pl. 1, Fig. 1). Lowest hierarchy (i.e. highest order) sequences develop in a wide variety of ways. In most cases, the sequences are composed of a starved lower hemisequence followed by a usually thicker, bioclast-poor and siliciclastic-dominated upper portion. These sequences have been previously named "Starvation/Dilution Sequences" or S/D sequences (Archuby 2009; Archuby and Fürsich 2010; see Text-fig. 7). Spalletti et al. (2001a, b) recognized the presence of low-hierarchy sequences (or high-frequency cycles) in the Agua de la Mula Member in the areas of Loma La Torre, south of Pampa Tril (in the north of the Neuquén province) and at Bajada del Agrio (central part of the same province). For these authors, the high-frequency cycles are particularly well developed in the highstand systems tracts of third-order sequences. Sagasti (2000, 2001) describes the development of bedding couplets for the same unit in the Mendoza province. Orbital forcing of Milankovitch cyclicity was used to explain the cycle origin in several articles (Sagasti 2000, 2001; Spalletti et al. 1990; Spalletti et al. 2001a, b).

Multiple-order cyclicity is evident throughout the sections (e.g. Text-figs. 4A, 8). According to Coe and Church (2003) sequences in these cases are more properly described as being composed of sequence sets instead of systems tracts (i.e. composed of transgressive,

highstand, etc. sequence sets). However, whether sequences are composed of parasequences or minor sequences is irrelevant, as the features that define the sedimentary product of each portion of a relative sea-level curve are the stacking patterns of sedimentary packages, and their position with respect to important surfaces. Consequently, systems tracts are named here as in classical sequence stratigraphic terminology.

Main sequences

Based on the stacking patterns of the basic S/D sequences, the studied unit has been subdivided into four main sedimentary sequences. In this study, main sequences are defined as those that delineate the major retrogradational/progradational trends built by numerous stacked S/D sequences. These sedimentary packages most likely correspond to third-order sequences, considering the amount of S/D sequences involved, their thicknesses, and their position with respect to ammonite biozones. Furthermore, a number of intermediate sequences building the main sequences have been recognized, being supra-ordinate to the basic S/D sequences and subordinate to the main sequences. In sequence hierarchy, they correspond to fourth- and/or fifth-order (high-frequency) sequences (Mitchum and van Wagoner 1991). There is no exact correspondence between former sequence stratigraphic schemes (Legarreta and Gulisano 1989) and this study. Consequently, the sedimentary sequences of the Agua de la Mula Member and their boundaries were named individually:

Main sequences: Depositional Sequence Agua de la Mula, plus a correlative number (e.g. DSAM-1).

Main sequence boundaries: Sequence Boundary Agua de la Mula, plus a number (e.g. SBAM-1).

Sequences within other higher hierarchy sequences – intermediate within main – with an additional number after the main sequence to which they belong (e.g. DSAM-1/1).

Sequence boundaries of these subordinate sequences after the main sequence boundary below it (e.g. SBAM-0/1).

Similar nomenclature has been used for the maximum flooding zones and systems tracts. In Text-fig. 9, a scheme of main and subordinate sedimentary sequences is shown, together with ammonite biozones and other stratigraphic markers. Text-fig. 11 shows the inferred correlations between the Neuquén Basin and European sedimentary sequences.

All, even minor, facies changes were considered in order to identify progradational, aggradational and retrogradational sets. These, in turn, have been used to interpret to which part of the base level curve the sedimentary package was related. Sequences were considered as major after fulfilling three criteria: (1) clearly detectable changes in facies trends (e.g. progradation to retrogradation) through key surfaces such as sequence boundaries or maximum flooding; (2) important facies contrasts in sequences in terms of water depth; and (3) a relevant amount of time involved in the development of the sequence (e.g., Vail et al. 1991; approximately 1-1.5 myr per main sequence according to the timescale of Ogg et al. 2004). According to the sedimentary sequence model (Van Wagoner et al. 1988), sequence boundaries are composite surfaces consisting of the sub-aerial unconformity and its marine correlative conformity. The correlative conformity was afterwards placed at the end of the falling stage systems tract, i.e., at the end of base level fall (Hunt and Tucker 1992). Maximum flooding periods do not necessarily leave a surface but a zone (i.e. Maximum Flooding Zone or MFZ; cf. Wiese and Wilmsen 1999; Wilmsen 2003). In a homoclinal ramp setting, which was the situation in which the Agua de la Mula Member was deposited, sharp boundaries are not expected between the different regressive systems tracts (i.e. between HST-FSST and FSST-LST) in medial to distal positions. Hence, the depositional sequence boundary would be difficult to detect and the only clear boundary would represent the top of the progradational sedimentary packages, i.e. the Maximum Regressive Surface, equivalent to the transgressive surface. Therefore, at least in some cases, the progradational packages can only be considered as regressive systems tracts. This coincides with the transgressive-regressive (T-R) sequence model of Embry (1993) that responds to the transgressive-regressive curve (Catuneanu 2002).

Sedimentary sequences and sequence boundaries have been dated with ammonites. Nevertheless, it is important to consider that, as was described above, the Valanginian–Hauterivian biostratigraphy of the Neuquén Basin is still in flux (e.g., the different opinions concerning correlation). Furthermore, the systematics of crioceratitid species, on which two of the four biozones are based, awaits revision (Aguirre Urreta and Rawson 1997).

First Depositional Sequence (DSAM-1). DSAM-1 starts with sequence boundary SBAM-0 at the base of the Avilé Member (SBAM-0) and is terminated 210 m (BAL) and 269 m (AML) above the base of the Agua de la Mula Member, at the position of SBAM-1 (Textfig. 4A). In the study area, SBAM-0 represents a subaerial unconformity. Ten metres below the boundary there is a conspicuous level with *Weavericeras va*- *caense* of latest Early Hauterivian age. A few metres above the Avilé Member, the occurrence of *S. riccardii* indicates the earliest Late Hauterivian. Consequently, SBAM-0 is placed close to the boundary between Early and Late Hauterivian. In both sections, the transition from the fluvial sandstones of the Avilé Member to the deep marine argillaceous sandy micrite and marls (AML) and muddy micrites (BAL) is abrupt. This maximum regressive surface (i.e. transgressive surface) is separated from SBAM-0 by the lowstand deposits of the Avilé Member. In this case, the depositional sequence can be differentiated from the T-R sequence, as it is possible to distinguish between the subaerial unconformity and the maximum regressive surface.

SAM-1 can be subdivided into two intermediate (fourth-order) sequences (DSAM-1/1 and 2) indicated by two thick sets of progradational piles of S/D sequences. DSAM-1 and the fourth-order sequences occurring within it are highly asymmetric in nature, characterized by very short TSTs and thicker RSTs. The first ~15 m of DSAM-1 are characterized by an aggradation of basinal sediments of clay and micrite, punctuated by thin levels of tabular skeletal concentrations. This facies records the deepest conditions for all sequences, and is interpreted as the MFZ of the DSAM-1. From 15 m to 105 m (BAL) and 115 m (AML) there is a gentle progradational pattern from bioturbated silty clays to argillaceous silts, silts and sandy silts, more or less regularly interrupted by thin, tabular skeletal concentrations that represent the starvation hemisequences of S/D sequences. The skeletal remains show a poor state of preservation and shell beds more evidence of physical destruction up-section. At the top of this progradational set there is a short, minor retrogradation, followed by a thin (ca. 1 m) but conspicuous bed rich in micrite, which is easily recognisable from its orange colour. The progradational set of beds is interpreted as a fourth-order regressive systems tract (RST), probably composed of sediments that were deposited during the highstand, fall and early rise in base level. The top of this sequence (SBAM-0/1) probably represents the top of the LST, i.e., the maximum regressive surface, and falls within the S. riccardii Zone of early Late Hauterivian age. SBAM-0/1 is a T/R-type sequence boundary. The complete fourth-order sequence (DSAM-1/1) developed in an offshore setting (basin to middle ramp) and this may be the reason why there are no distinct facies contrasts. The finer and more calcareous beds deposited above it are interpreted as the TST and maximum flooding zone of the following fourth-order sequence (DSAM-1/2). The RST of the DSAM-1/2 consists of a gentle progradational pattern up to 165 m (in BAL) and 185



Text-fig. 7. Model of starvation-dilution sequences. TST – Transgressive Systems Tract; RST – Regressive Systems Tract. For symbols see legend in Text-fig. 4

m (in AML) characterized by a moderate to low sedimentation rate (high degree of bioturbation of dilution hemisequences), and a strongly progradational upper portion. Starvation hemisequences are thicker and were deposited in progressively shallower environments (middle to inner ramp) as evidenced by taphonomic features of the benthic fossils (Archuby 2009). The relevant characteristics of the upper part of DSAM-1 are the more pronounced progradation with respect to the sediments below and the high rate of siliciclastic sedimentation (interlayered and heterolithic bedding, hummocky and amalgamated hummocky cross-stratification). In BAL, this strongly prograding package is a single coarsening- and shallowing-upward set of beds, although internal cyclicity is apparent from the repeated occurrence of amalgamated hummocky cross-stratified beds. The lower portion of the regressive part of DSAM-1/2 is considered as the HST-1 and belongs to the S. riccardii Zone. The upper, highly prograding one represents the FSST of both the fourth- and the third-order sequences. This unit yielded a single specimen of a juvenile crioceratitid shell at its base and has been included into the Crioceratites schlagintweiti Zone of the middle Late Hauterivian (see above). Consequently, the capping sequence boundary of DSAM-1 (=SBAM-1) is placed in the C. schlagintweiti Zone. LST deposits are absent in this

case. The uppermost part of DSAM-1 is more complex at AML and it may be speculated that apart from the FSST, an LST is also present (due to its more basinward position; Archuby 2009). In this case, SBAM-1 would have to be placed close to the boundary between the *S. riccardii* and *C. schlagintweiti* biozones, i.e., in the early to middle Late Hauterivian. However, the erosional transgressive surface (ravinement) at the top of the regressive systems tract is a more reliable sedimentary surface for correlations due to the clear change towards a retrogradational stacking pattern above it in both sections. Thus, SBAM-1 is a T/R sequence boundary (cf. Embry 1993).

Second Depositional Sequence (DSAM-2). DSAM-2 is a 96 m (BAL) and 74 m (AML) thick package bounded by SBAM-1 of middle and the SBAM-2 of late Late Hauterivian age (*C. andinus /C. perditus* subzones of the *C. diamantensis* Zone). Two systems tracts of equivalent thicknesses can be recognized, a lower TST and an upper RST, the latter probably consisting chiefly of the HST. Three subordinate depositional sequences compose DSAM-2 (DSAM-2/1 to -2/3). A fourth sequence was probably truncated at the base of SBAM-2. This complex pattern of sequences is only evident in the BAL section (Text-fig. 4A). The TST-2 typically shows a retrogradational stacking pat-



Text-fig. 8. Intermediate sequence DSAM-3/1 in the Bajada del Agrio (BAL) section (304–330 m above the base of the section). For symbols see legend in Text-fig. 4

tern of S/D sequences. Up-section there is a tendency to more distal facies in the dilution hemisequences, from shoreface sandstones to offshore bioturbated siltstones (BAL) and argillaceous siltstones (AML). At the base of the systems tract there are S/D sequences without the starvation hemisequence and truncation (more than one S/D sequence represented only by the starvation hemisequence). Close to the maximum flooding zone, dilution-hemisequences have less clear or no coarsening/shallowing-upwards trends, and the S/D sequences are thinner, indicating greater distality and reduced sedimentation rate. The MFZ-2 consists of three thin S/D sequences characterized by thin starvation hemisequences with plenty of ammonites. The last occurrence of *C. schlagintweiti* and the first occurrences of *C. diamantensis* and *C. bederi* and, hence, also the biozone boundary are in the MFZ. The RST-2 is represented by a progradational stacking pattern altered by the presence of an intermediate sequence (DSAM-2/3). Dilution hemisequences range from offshore bioturbated mudrocks and siltstones to lower shoreface sand-dominated heterolithic and hummocky cross-stratified sediments, as well as bioturbated finegrained sandstones with amalgamated hummocky



Text-fig. 9. Sequences, sequence boundaries, ammonite occurrences, and biozones of the sections investigated. Shaded areas represent anoxic events. Rhombs indicate the occurrence of uncoiled ammonites

cross-stratification (in BAL). Starvation hemisequences are usually developed as thick, complex shellbeds, in some cases with a very well preserved benthic fauna (Archuby 2009). At the position of the MFZ of DSAM-2/3, the C. diamantensis/C. bederi Subzone is replaced by the C. andinus/C. perditus Subzone. The last C. bederi specimens are uncoiled, indicating the second event of ammonoid uncoiling in the unit. SBAM-2 is placed 306 m (BAL) and 343 m (AML) above the base, in the C. andinus /C. perditus Subzone of the C. diamantensis Zone, i.e., late Late Hauterivian. It is interpreted as the subaerial unconformity, modified by the following transgression. This means that it also represents the transgressive surface; the FSST and LST are absent and have been deposited in a more basinal position.

Third Depositional Sequence (DSAM-3). DSAM-3 measures 95 m at BAL and more than 90 m at AML. Its basal unconformity (SBAM-2) is represented by an erosional transgressive surface of late Late Hauterivian age (C. andinus /C. perditus Subzone of the C. diamantensis Zone). The upper unconformity, SBAM-3, is placed above the base of the Paraspiticeras groeberi Zone, provisionally dated as Early Barremian (Aguirre Urreta and Rawson 1993; Aguirre Urreta et al. 2005). A transgressive systems tract and a highstand systems tract of similar thicknesses compose the depositional sequence DSAM-3. Both systems tracts show strong retrogradational and progradational stacking patterns of S/D sequences respectively, and a conspicuous maximum flooding zone (MFZ-3) interpreted as the possible expression of the Faraoni OAE (see below). TST-3 is developed between 306 m and 351 m at BAL and 343 m to 396 m at AML, almost completely in the latest Late Hauterivian C. andinus /C. perditus Subzone. Facies in dilution hemisequences of the early TST-3 consist of bioturbated fine-grained sandstones, with hummocky cross-stratification and coarsely interlayered bedding, reflecting lower shoreface and upper offshore (i.e. inner and middle ramp) depositional environments. Characteristic late TST-3 sediments are bioturbated micritic silty clays and argillaceous siltstones, reflecting both, deep depositional settings (outer ramp) and general starvation. At BAL, in the lower part of the TST there is a well-developed subordinate sequence composed of four S/D sequences that clearly have a lower retrogradational TST and upper progradational RST (DSAM-3/1; Text-fig. 8). Thickly developed starvation hemisequences usually with a complex set of shell concentrations are another feature of the early TST-3. In AML, this systems tract has a different configuration: subordinate sequences are not unambiguously developed. The outstanding feature of the TST-3 at AML is the stacking of several starvation hemisequences without the respective dilution hemisequences, indicating phases of enhanced terrigenous starvation (see Text-fig. 4A, AML section, 343-353 m and Text-fig. 10). MFZ-3 is a conspicuous feature of the unit in both sections. It consists of an alternation of thin, bioturbated and muddy dilution hemisequences intercalated with variably thick starvation hemisequences composed of a homogeneous, densely-packed bioclastsupported shell bed (low-energy micritic rudstones facies of Archuby and Fürsich 2010). The starvation hemicycle in the middle of MFZ-3 reaches almost 1 m in thickness at BAL and more than 2 m at AML. Regardless of the differences of TST-3 between the two sections, MFZ-3 has very similar facies at both localities, with a comparable development. This fact makes this maximum flooding zone a useful stratigraphic feature for correlation, and it is interpreted here as the level of the Faraoni Event (see below).

The HST-3 is only partially exposed at AML. Nevertheless, its lower part shows a progradational trend. At BAL, there is a distinct coarsening- and shallowing-upward trend, together with the marked increase in the thickness of the S/D sequences. Dilution hemisequences range from offshore micritic mudrocks to lower shoreface bioturbated, fine-grained sandstones with hummockies and ripple cross-lamination. Specimens of *P. groeberi* occur in the middle part of the HST. Although the age of this species is not exactly known, it is reasonable to regard the beds containing *P. groeberi* as Early Barremian in age based on their conformable stratigraphic position above the inferred level of the Faraoni Event of latest Hauterivian age (Ogg *et al.* 2004).

The early HST-3 at BAL is characterized by an alternation of two kinds of cycles: normal S/D sequences with the dilution hemisequence showing a more or less pronounced coarsening-upward trend, and whose starvation hemisequences are mainly bioclastic limestones. The second (subordinate) type of cycle consists of thin intercalations of shell beds, one per dilution hemicycle of the S/D sequences. These shell beds are homogeneous, have a micritic and muddy matrix and are characterized by very well preserved, mainly disarticulated bivalves, gastropods, and scaphopods, in contrast with the less well preserved fauna in the starvation hemisequences of the main S/D sequences (Archuby 2009). The minor cycles are interpreted as subordinated (minor) starvation hemisequences that formed during deposition of the main dilution hemisequence. It has been proposed that these cycle couplets represent the expression of orbital cycles of obliquity (Archuby 2009).

SBAM-3 of Early Barremian age represents an erosional surface on top of a coarsening- and shallowingupward stacking of S/D sequences. It is interpreted as the subaerial unconformity, placed on top of the HST.

Upper part of the member (DSAM-4). The upper 150 m of the Agua de la Mula Member, above SBAM-3, exhibit a different and distinct stacking pattern of S/D sequences with more pronounced facies differentiation compared to SBAM-1 to -3. For instance, the facies changes from micritic, fissile argillaceous siltstones to a 2-m-thick sandstone bed of shoreface origin with amalgamated hummocky cross-stratification at the top of a regressive package, and a several-metres-thick bio-oo-grainstone, in only five S/D sequences (440-470m).

Considering these facies changes as a proxy of the magnitude of the base level change alone, these internal "sequences" could be considered as of lower order (i.e., fourth- to third-order). However, they are composed of a maximum of nine S/D sequences, which suggests that they represent very little time (Archuby 2009), less than expected for typical third-order sequences (cf. Vail *et al.* 1991). Thus, the large shifts in sedimentary environment observed in the upper part of the member are more likely related to the fact that the basin was nearly filled, broad and shallow, with very low relief (end of Upper Mendoza Mesosequence). Facies analysis furthermore shows that there was low terrigenous input during that interval. In this setting, minor sea-level fluctuations, which formerly caused limited facies shifts, also result



Text-fig. 10. Stacking of several incomplete starvation-dilution sequences indicating enhanced starvation in the Agua de la Mula (AML) section at 350 m. A - Photograph of five starvation hemisequences stacked in a few metres of section. Sequence of TSTs and RSTs proposed indicated with triangles at the left. B - Segment of the section corresponding to the stacked beds. Note another stacking of incomplete starvation-dilution sequences a few metres below. For key to symbols see legend in Text-fig. 4

in large-scale lateral facies migrations and even emergence, giving the appearance of higher magnitude changes as beforehand (i.e., in DSAM-1 to -3). If this is accompanied by less siliciclastic input and more carbonates (possibly due to climate change), then the lithologically much more variable upper part of the Agua de la Mula Member may has been deposited in response to a single third-order sea-level cycle. Thus, it is regarded as a third-order sequence (DSAM-4), starting at sequence boundary SBAM-3 and capped by the major SBAM-4 at the base of the overlying Huitrin Formation. This interpretation is supported by the fact that three metres above SBAM-3 there is a conspicuous starvation hemisequence deposited in an inner ramp setting. Its sandy matrix, iron content, and the highly abraded nature of the predominantly large and thick-shelled benthic fauna (Archuby 2009) indicate deposition under high-energy conditions. All these features are shared with the first beds above the transgressive surfaces of the main sequences DSAM-1 and 2.

DSAM-4 is structured into three subordinate fourthorder sequences (DSAM-4/1 to -4/3). The boundaries of the fourth-order sequences are placed at the position of thickly developed oolitic grainstones (SBAM-3/1 and 3/2), which indicate important events of shallowing of the basin. There are no ammonites in these beds, with the exception of a single, not yet described specimen collected from the uppermost part of the member at BAL, and some fragments of another species mentioned in the literature (Aguirre Urreta *et al.* 2005).

Furthermore, it is possible to subdivide each fourthorder sequence in two subordinate sedimentary packages with more or less well developed lower retrogradational and upper progradational packages, identified as TSTs and RSTs, respectively. Boundaries are transgressive (ravinement) surfaces. MFZs are not clearly developed but starvation hemisequences close to MFZs are matrix-rich fine-grained bioclastic limestones (mudstones, wackestones, packstones, and floatstones), while closer to sequence boundaries coarser textures (grainstones and micritic rudstones) are common. Shells in fine-grained bioclastic limestones show different sizes and low quality of preservation due to high degrees of micritization. Shells in grainstones are highly abraded and rounded. Starvation hemisequences deposited in segments with higher proportion of terrigenous sediments and offshore settings are usually mixed rocks and contain well preserved benthic fossils.

Considering the fact that there are two orders of sequences between main (i.e., third-order) and basic S/D sequences, these intermediate sequences correspond to fourth- and fifth-order, respectively, and the basic sequences are of sixth-order.

Correlations with global and European sea-level charts

Sedimentary sequences described above were compared with global and European sequence stratigraphic charts (Haq *et al.* 1987; Hardenbol *et al.* 1998) in order to establish correlations between sequences, sequence boundaries, and maximum flooding surfaces. A detailed scheme of the sedimentary sequences of the Agua de la Mula Member is presented in Text-fig. 9. In Text-fig. 11 the main sequences recognized in the member are compared with the detailed sequence chronostratigraphic chart of Hardenbol *et al.* (1998). Only third- and fourth-order sequence boundaries have been used for correlation.

Early Hauterivian. SBAM-0 is placed at the boundary between the vacaense and riccardii zones. It is probably equivalent to the sequence boundary HA3 of Hardenbol et al. (1998) of latest Early Hauterivian age (Lyticoceras nodosoplicatum Zone). However, although both sequence boundaries may coincide in time, SBAM-0 represents one of the major sea-level falls in the history of the basin, a feature that does not fully correspond to the 'medium' nature of HA3. As has been mentioned before, SBAM-0 may represent a tectonically driven base-level fall or an eustatic, tectonically enhanced (uplift) fall. The sequence boundary of Haq et al. (1987) at the base of the third-order sequence LZB-2.5 does not coincide with SBAM-0, as the former is placed at the base of the L. nodosoplicatum Zone, i.e. it is older than the latter.

Late Hauterivian. The Late Hauterivian sequence boundaries HA4 to 6 coincide with the three main sequence boundaries described in this study for the same time segment: SBAM-0/1, SBAM-1, and SBAM-2 respectively. There are two more subordinate sequence boundaries between SBAM-1 and 2 (SBAM-1/1 and -1/2), separating three intermediate sequences that are of lower hierarchy than DSAM-2 and have no equivalents in the published charts. SBAM-2/1 also represents a minor sequence boundary. It may possibly coincide with the minor boundary HA7 of Hardenbol *et al.* (1998). The major maximum flooding surface coinciding with the Faraoni Event (*ohmni* Biozone of the European basins) has its equivalent in the MFZ-3 of the Neuquén Basin.

The two intermediate sequence boundaries proposed by Haq *et al.* (1987) for the Late Hauterivian may correspond to SBAM-0 and SBAM-2. If so, SBAM-1 would not have an equivalent therein. Conversely, if SBAM-1 were to be placed at the top of the HST (at

	oedemaecker et al. 2003)	Hardenbol et al. 1998	this study	Zones/sub-zones this study	
1	vanderheckii (pars)				
	caillaudianus	BARR 3	SBAM-4 SBAM-3/1		
	nicklesi	BARR 2	SBAM-3/2		
	hugii	BARR 1	SBAM-3	groeber	Ť
1	ohmni	HA 7			andinus
1.0	balearis	HA 6	SBAM-2	1	+ perditus
2	ligatus			diamantensis	diam + bederi
	[HA 5]	SBAM-1	schlagintweiti		
	sayni	[HA 4]	SBAM-0/1	riccardii vacaense	
Lairy	nodosplicatum	HA 3	SBAM-0		
		nicklesi hugii ohmni balearis ligatus sayni nodosplicatum	nicklesi hugii bhugii balearis ligatus ligatus HA 5 Sayni HA 4 HA 3 Sequence	nicklesi BARR 2 SBAM-3/2 hugii BARR 1 SBAM-3 ohmni HA 7 SBAM-2 balearis HA 6 SBAM-2 ligatus HA 5 SBAM-0 sayni HA 4 SBAM-0 nodosplicatum HA 3 Sequence boundaries	nicklesi BARR 2 SBAM-3/2 hugii BARR 1 SBAM-3/2 ohmni HA 7 Groeber balearis HA 6 SBAM-2 ligatus HA 5 SBAM-1 sayni HA 4 SBAM-0/1 nodosplicatum HA 3 vacaens

Text-fig. 11. Sequence correlation chart comparing sequence boundaries of the stratigraphic interval studied with the West Mediterranean Province (Hoedemaecker *et al.* 2003 in Aguirre Urreta *et al.* 2005) and the Hardenbol *et al.* (1998) chart of European basins

165 m at BAL and at 185 m at AML) and not on top of the FSST, it would belong to the *riccardii* Biozone, and would correlate with the oldest Late Hauterivian sequence boundary of Haq *et al.* (1987). In this case, the two main Hauterivian sequences boundaries of the Neuquén Basin would have equivalents in the sequence stratigraphic chart of Haq *et al.* (1987).

Barremian. SBAM-3, occurring in the *groeberi* Zone, is a relevant third-order sequence boundary that reliably correlates with the major sequence boundary BARR 1 of the European Basins. It represents the first sequence boundary above the Faraoni Event. From SBAM-3 to the top of the unit there is no biostratigraphic control (see Aguirre Urreta and Rawson 1997; Aguirre Urreta *et al.* 2005). Therefore, published sequence boundaries can be used provisionally to date the Barremian marine sediments of the Neuquén Basin until the biostratigraphy of this part of the succession is better understood. SBAM-4, which represents the top of the unit, is an eu-

statically driven major drop in base level overlain by fluvial and evaporitic sediments of the Huitrín Formation (Leanza 2003). It is correlated with the major sequence boundary BARR 4 of Hardenbol et al. (1998). In this way, sequence boundaries SBAM-3/1 and -3/2 correlate with boundaries BARR 2 and 3. The Early Barremian major MFS of the caillaudianus Zone in the chart of Hardenbol et al. (1998) has no unequivocal equivalent in the Neuquén Basin. The sequence boundary of Haq et al. (1987) below their sequence LZB-3.3 is inferred to correspond to the oldest Barremian sequence boundary SBAM-3. If the other two Barremian sequence boundaries of the chart (at the base of sequences 3.4 and 3.5) were to be correlated with the boundaries SBAM-3/1 and -3/2 described here, then SBAM-4 would have to be placed in the Aptian. This option does not seem to be justified, although it has been suggested in sequence chronostratigraphic charts previously published for the Neuquén Basin (Legarreta and Gulisano 1989; Legarreta et al. 1993). The first interpretation, shown in Text-fig. 11, is supported in this work. A better understanding of the ammonite biostratigraphy of this part of the succession will help in solving this problem.

Anoxic events

Exceptional transgressions of global extent combined with local factors such as reduced circulation deposited organic-rich sediments (black shales) contemporaneously in different parts of the world. These global "oceanic anoxic events" (OAE) are useful stratigraphic levels as well as important marine source rocks. The combination of dysoxic-anoxic conditions and sediment starvation (i.e. good preservation of marine organic matter and low siliciclastic dilution) favoured the widespread deposition of organic-rich facies during the transgressive intervals of the Agrio Formation (Legarreta and Uliana 1991; Tyson et al. 2005; Uliana and Legarreta 1993). This unit includes organic-rich and bituminous black-shale facies (Leanza 1981b) that contributed to the 'Agrio' petroleum system that has a cumulative production of over 164 million barrels of oil (Tyson et al. 2005).

Important packages of bituminous black shales occur at two levels in the sections studied here. The first one is situated 15 to 20 m from the base of the unit in both sections within the lower Spitidiscus riccardii Zone. It is characterized by well-developed black, dark-bluish and dark-grey marls, micritic clays and micritic silty clays. Ammonites and benthic fauna occur scattered or in loosely packed shell-beds interpreted as the sediment-starved lower portion of orbitally induced precession cycles (Archuby 2009). The preservation of the fossils is excellent and there are little or no indications of physical disturbance, i.e., the sediments were deposited well below the storm wave base (Archuby and Fürsich 2010). The sediments are always bioturbated, albeit discrete trace fossils are rare (e.g., Chondrites). The benthic macrofauna consists of a diverse group of small, chiefly epifaunal and semi-infaunal bivalves and gastropods. Shallow infaunal bivalves are rare. There are two species of relatively deep infaunal lucinid bivalves (Recent lucinids are known to be well adapted to thrive in poorly oxygenated environments with the help of endosymbiotic chemo-autotrophic, sulphide-oxidizing bacteria; Reid and Brand 1986). This organic-rich set of beds has already been recognized in the literature and designed as the "Spitidiscus black shale" (Tyson et al. 2005). It was proposed that these sediments were deposited under anoxic to dysoxic conditions (Spalletti et al. 2001b; Tyson et al. 2005). However, bioturbation and the presence of benthic macrofauna indicate that the socalled "Spitidiscus black shale" probably did not experience total oxygen depletion at the sediment-water interface at any time. Instead, dysoxia and anoxia a few centimetres below the sediment-water interface can be deduced from the organic-rich nature of the sediments, the scarcity of infaunal species and the presence of lucinid bivalves.

Between 349 and 353 m above the base at BAL and 395 to 400 m at AML there is a distinct alternation of dark-grey and black mudrocks and marly mudrocks, and medium to thick, densely-packed shell-beds. This package represents the third major (third-order) maximum flooding zone (MFZ-3; see Text-fig. 4A). The shell beds are composed mainly of shells and shell fragments of small molluses (bivalves and gastropods) in densely-packed, bioclast-supported rocks (low-energy micritic rudstones in Archuby and Fürsich 2010). This facies is developed as particularly thick beds once in each section: almost 1 m at BAL (351 m above the base) and 2.5 m at AML (396-398 m above the base; Archuby and Fürsich 2010) respectively. The low-energy micritic rudstones are interpreted as amalgamated distal tempestites that accumulated over a long period, on the outer ramp. The interpretation of this set of beds as a distinct flooding event relies on two lines of arguments. Firstly, considering that the general trend of the unit is towards a progressive infill of the basin, this set of beds was deposited at a greater depth than the previous MFZ. Secondly, the same facies occurs in both sections at equivalent positions, even though sedimentation below and above these beds differed between the two localities. These facts suggest the occurrence of a widespread phenomenon proposed here as the Neuquén basin's equivalent of the "Faraoni Level" (Cecca et al. 1994). The Faraoni Level is the first widespread, latest Hauterivian dysoxic event in the European Cretaceous, whose Neuquén Basin equivalent had not yet been found (Tyson et al. 2005). It ranks among the seven most significant excursions in the carbon cycle during the Cretaceous (Ogg et al. 2004). If correctly identified, this event would indicate the top of the Hauterivian better than the ammonite biozones.

Other occurrences of dark mudrocks are found at the maximum flooding position of sequences in the last 150 m, for instance, at 432 to 450 m above the base at BAL (the equivalent part of the section is not properly exposed at AML). In this case, micritic mudrocks and marls alternate with fine-grained limestones. However, these occurrences are less conspicuous and their precise age is not known because of the poor ammonite record.

CONCLUSIONS

The ammonite biostratigraphy of the Agua de la Mula Member has been improved based on bed-by-bed collecting. The already defined biozones (*Spitidiscus riccardii*, *Crioceratites* schlagintweiti, *Crioceratites diamantensis* and *Paraspiticeras* groeberi) were recognized and precisely tied to the successions, and further refinement was proposed (e.g., two subzones in the *C. diamantensis* Zone). Nevertheless, a detailed study of the taxonomy of crioceratitid ammonites as well as of other new finds of cephalopods from the top of the section could substantially improve the knowledge of the biostratigraphy of this unit.

The change from uncoiled to normally coiled crioceratitid shells in the Neuquén Basin, previously placed between the *schlagintweiti* and *diamantensis* zones is here proposed to occur in the latter biozone, based on the find of uncoiled specimens of cf. *Crioceratites bederi*. Another important contribution of this study is the construction of an integrated bio-sequence stratigraphic scheme. Sequence boundaries described here and already mentioned in the literature have been linked to ammonite biozones, and biozones are related to sea-level changes and sequence-stratigraphic architectures (e.g., boundary of the *schlagintweiti* and *diamantensis* zones within the maximum flooding of depositional sequence DSAM-2).

Sequences of different order are built by stacked starvation/dilution (S/D) sequences. S/D sequences are the basic cycles and regarded here as sixth-order sequences with only two components that can be unequivocally distinguished: the lower starvation hemisequence and the upper dilution hemisequence. Pro- and retrogradational stacking pattern of S/D sequences define supraordinate sequences. These sedimentary packages were interpreted as either third- (main) and, fourth- or fifth-order (=intermediate), considering the amount of S/D sequences involved.

In this study, the depositional-sequence model cannot be strictly followed, because it is difficult to detect the features and surfaces that define the three regressive systems tracts (highstand, falling stage and lowstand). For the majority of the sequences recognized herein (except DSAM-1), the transgressive-regressive sequence model (Embry 1993) is more appropriate and was applied.

The sequence-stratigraphic analysis resulted in the division of the member into four main depositional sequences (DSAM-1 to 4). In turn, main sequences were subdivided in up to three fourth-order sequences in some cases. In this study, main sequences represent packages not included into higher order sequences.

Previously published sequence-stratigraphic charts of the Neuquén Basin did not relate sedimentary sequences to biozones, and are hence not comparable to the scheme presented here.

There is a good agreement between the sequencechronostratigraphic scheme developed in this study and sedimentary sequences of European basins (Hardenbol *et al.* 1998). A latest Early Barremian age is proposed for the almost ammonite-barren upper part of the Agrio Formation, based on correlations of sequence boundaries. Agreement with the chart of Haq *et al.* (1987) is less good.

An equivalent of the Faraoni Event, an important stratigraphic marker that indicates the top of the Hauterivian, was tentatively identified and related to other stratigraphic features, i.e. sedimentary sequences and ammonite biozones. Apart from the possible Faraoni OAE, two more anoxic/dysoxic events were detected in the course of the study: the basal "Spitidiscus" black shale of earliest Late Hauterivian age, and a series of dark mudrock beds that occur at different positions in the last 100 m.

The benefits of applying an integrated stratigraphic approach for the study of a sedimentary unit could be demonstrated by combining different stratigraphic tools, i.e. biostratigraphy, sequence stratigraphy and anoxic events. This is especially true for the upper part of the Agua de la Mula Member of the Agrio Formation where classical biostratigraphy was not applicable alone.

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