

DOES “BLACK SHALES” SUFFICE FOR LITHOLOGICAL CHANGES IN TRANSGRESSIVE FACIES? THE CASE OF THE AGUA DE LA MULA MEMBER (AGRIO FORMATION), NEUQUEN BASIN, ARGENTINA

Marcos Comerio^{1,2}, Pablo José Pazos¹, Patricia Eugenia Zalba^{2,3}

1: Inst. de Estudios Andinos “Don Pablo Groeber”, Depto. de C. Geológicas, Ftad. de Ciencias Exactas y Naturales, UBA, Pabellón II, Cdad. Universitaria, 1428 Bs. As., Argentina. CONICET. comerio@gl.fcen.uba.ar, pazos@gl.fcen.uba.ar

2: CETMIC-CIC. Centro de Tecnología de Recursos Minerales y Cerámica. Cno. Centenario y 506, (1897).

Manuel B. Gonnet. comerio@gl.fcen.uba.ar, zalba@yahoo.com.ar

3: School of Geosciences, Monash University, Melbourne, Australia. zalba@yahoo.com.ar

Keywords: shales variability, microfabric, Lower Cretaceous, Agua de la Mula Member, Neuquén Basin

RESUMEN

“Black shades” ¿Es suficiente para denotar cambios litológicos en facies transgresivas? Caso del Miembro Agua de la Mula (Formación Agrio), Cuenca Neuquina, Argentina

Se estudió, por medio de microscopía óptica y electrónica de barrido, así como por difracción de rayos X y contenido de carbono orgánico, la variabilidad de litofacies correspondiente a la etapa transgresiva basal del Miembro Agua de la Mula de la Formación Agrio, a escala de cuenca. Se pudieron diferenciar tres grupos de sedimentitas de grano fino: (i) un grupo dominados por componentes intracuencales derivados de la producción orgánica y carbonática, (ii) otro con altos porcentajes de componentes terrígenos y (iii) un tercer grupo con predominio de minerales autigénicos. Además de procesos de baja energía, como el de decantación a partir de material en suspensión, se documentaron corrientes tractivas, desarrollo de matas microbianas y bioturbación. Los procesos sedimentarios reconocidos sugieren que durante la depositación los escenarios fueron dinámicos y variables a distintas escalas, tanto en sentido lateral como vertical, y no relativamente estables como antes se presumía.

INTRODUCTION

As it has already been mentioned in the existing geological literature, a number of terms are used to describe fine-grained sedimentary rocks (*e.g.* calci-mudstones, claystones, mudrocks, phylsils, shales, siltstones, etc). For instance, shale is the generally accepted class name for fine-grained rocks which are characterized by its finely laminated structure and where clay minerals, clay-size carbonates, kerogen and silica are their main components (*cf.* Potter *et al.* 1980; Bates and Jackson 1987). Nevertheless, Macquaker and Adams (2003) have provided a descriptive scheme suggesting “mudstone” as the most appropriate general term for these rocks, composed predominantly of

material (whatever the mineralogy) with a grain size lesser than 64 μm . The term includes three constituents with different origins in varying proportions: i) allochthonous (detrital), ii) productivity (autochthonous) and iii) authigenic (diagenetic) derived materials.

For mudstones in distal marine settings, recent works have demonstrated a great textures variability which reflects that not only pelagic settling of fine grained material occurs as the main sedimentary process in these scenarios (O'Brien 1996; Schieber 1999; Ghadeer and Macquaker 2011; Trabucho-Alexandre *et al.* 2012). In a study of mudstones from a wide range of ages O'Brien (1996) identified bottom flowing currents, low-density turbidity currents and microbial mat development besides suspension settling indicating that erosion, sediment transport, and deposition take place in environments where relatively low energy conditions dominate. In high resolution sequence stratigraphy analysis of mud-dominated successions, it is important to highlight the role of optical and electron microscopy, combined with geochemical and field data, to provide details about the cryptic variability documented at thin-section scale where individual genetic beds (<10 mm) are common (Macquaker *et al.* 2007; Trabucho-Alexandre *et al.* 2012).

The Neuquén Basin, located on the central-western of Argentina, is a prolific petroleum basin for both, conventional and unconventional oil and gas reservoirs and where excellent examples for the study of "muddy" successions related to transgressive stages are present.

The black shales associated to the last major flood-event from the paleo-Pacific ocean which widespread over most of the Neuquén basin were lithostratigraphically included in the Agua de la Mula Member (Leanza *et al.* 2001), Agrio Formation (Weaver 1931), that locally are source rocks for oil in the subsurface (Legarreta and Villar 2012). A synthesis for this unit has been made by Spalletti *et al.* (2011, and references therein).

A late Hauterivian age for the base of the Agua de la Mula Member (*Spitidiscus riccardii* ammonoid zone) was corroborated by zircons analyzed in a tuff layer (U-Pb SHRIMP: 132 ± 1.3 Ma) and possibly reaching the basal Barremian (Aguirre-Urreta *et al.* 2008). The basal contact with continental facies of the Avilé Member, Agrio Formation, is sharp and represents a transgressive surface. Instead, the stratigraphic contact with the overlaying Huitrín Formation is controversial and documents a disconformity or a master sequence boundary according to Veiga *et al.* (2005, see for more details).

Northward of the basin, in the Mendoza province, the Agua de la Mula Member was well studied by Sagasti (2000, 2005), but in outcrops of the Neuquén realm, the muddy facies of this unit have been locally analyzed (Spalletti *et al.* 2001). In outcrops of the Neuquén province, the thickness of the Agua de la Mula Member ranges from 470 to 250 m. Nevertheless, in the Mendoza region the succession ranges from 140 to 100 m (Sagasti 2000, 2005).

To shed light upon lithofacies variability of black shales, informally named *Spitidiscus* shales, we have investigated them using field data, optical and electron microscopy, X-ray diffraction (XRD) and total organic carbon in six stratigraphic sections. The gathered information allowed us

to recognize a great variety of textures being differentiated on the basis of composition, fabric and diagenesis which response to changes in: i) extrabasinal input (terrigenous fraction), ii) carbonate production, iii) organic carbon production, iv) bioturbation, v) authigenic minerals. This study illustrates the different rock types present in a mud succession which reflects changes in bottom conditions and sedimentological processes operating during a transgressive phase throughout different parts of the basin.

METHODOLOGY

The Agua de la Mula Member was sampled in six different areas of the Neuquén Basin, Neuquén province, in order to determine lithofacies variability (Figure 1). During the field work detailed sedimentologic columns (1:100) were measured and described. Also, bed geometries, faunal compositions and lithologic contacts were described for each lithofacies found.

Optical petrography was performed on 50 thin sections, some of them stained with Alizarin Red-S to discriminate ferroan and non-ferroan calcite and dolomite (Dickson 1965). Also, depositional and diagenetic fabrics were examined using a JEOL SEM/EDAX. A scheme for fine-grained sedimentary rocks (Macquaker and Adams 2003) was useful to describe texture features, where

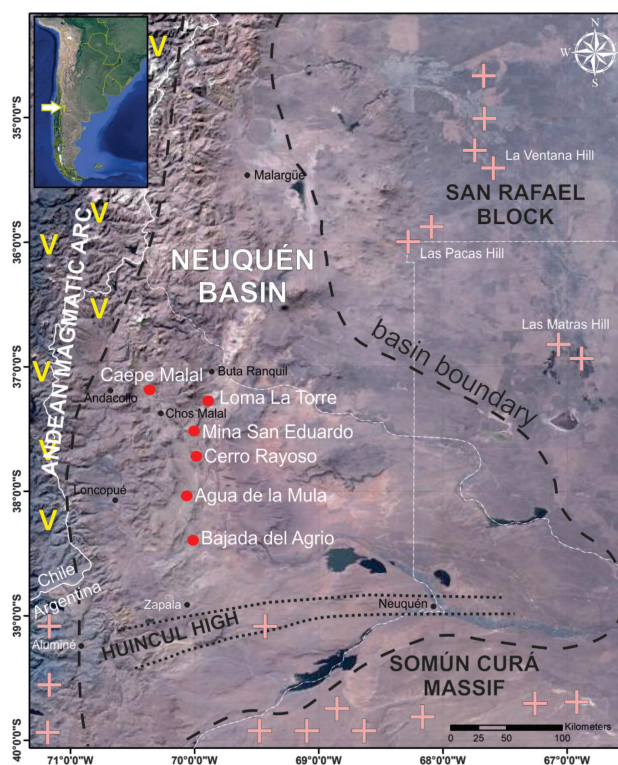


Figure 1. Satellite image of the Neuquén basin (adapted from Naipauer *et al.* 2014). Red dots indicate the stratigraphic sections where the Agua de la Mula Member was studied.

irrespective of their origin (allochthonous, autochthonous or diagenetic), a mudstone containing more than 90% of a particular component is described as being “dominated”, between 50-90% “rich” and 10-50% “bearing”. In addition, their laminae and bedding geometries were described (Cole and Picard 1975 in Potter *et al.* 1980).

Bulk rock samples XRD were examined in order to determine mineralogy in a Philips 3020 goniometer (Ni-filtered CuK α , 35 Kv, 40 Ma, without secondary monochromator). For non-oriented samples step-scan data were taken from 3 to 70° 2 θ , with a step width of 0.04° and a counting time of 2 s/step. Mineral phases were recognized and quantified with the FULLPROF program (Rodríguez Carvajal 2001), which is a multipurpose profile-fitting program including Rietveld refinement (Rietveld 1969). Clay minerals were studied on oriented samples (< 2 μ m) for routine analyses (air dried, glycolated overnight and heated for 2 hours at 550°C).

Total organic-carbon (TOC) analyses were performed by GeoLab Sur (Argentina). The total carbon contents of untreated, powdered samples were obtained using a Leco C/S analyzer after removal of any inorganic carbon by acidification.

RESULTS

A great mudstone lithofacies variability was found through the six stratigraphic sections where the Agua de la Mula Member was studied (Figure 1). Different textures and sedimentary structures, including parallel lamination, scour surfaces, bioturbation, microbial mat development, concretinarian dolomite beds, together with para/autochthonous to allochthonous fauna were found. The mudstone descriptions, using the nomenclature of Macquaker and Adams (2003) based on the relative abundance of autochthonous, allochthonous and authigenic components, are presented below.

Mudstones dominated by autochthonous components

Laminated, organic matter-rich mudstones (between 50-90% of organic components) were detected in the first 10 m meters of the study section. In outcrops, these units are generally less than 0.5 m thick. Under optical microscopy organic compacted masses (medium to dark red-brown, 7.5R4/14) with diffuse outlines predominates. Such microlithofacies shows millimeter-thick bedding where thin to medium individual units (< 5 mm) are present. Internally, organic matter-rich laminae show even discontinuous to discontinuous wavy parallel geometries and graded to laminae dominated by flat lens-like micritic calcite pellets (Figure 2a). In some cases, irregular laminae rich in authigenic minerals such as dolomite are present. Non-parallel limits between laminae record microrelief surfaces which resembles both, scour surfaces (erosional) and load structures (deformational). Also, microbial mats, like sheath structures and extracellular

polymeric substance (EPS) were recognized under SEM images. Total organic carbon contents range from 1.28 to 5.80% and one sample contains 16.52% (kerogen type II predominates over I and III).

Other production-derived components include test of coccolithophores, radiolarian and foraminifers. For instance, XRD analyses reveal that many samples are composed mainly of calcite (85%), with minor silt-quartz and feldspar (10%), clay-size illitic material (2%), pyrite (2%) and organic matter (TOC 1%). Under optical microscopy calcite occurs as a fine crystalline aggregate which in part is recrystallized into microspar calcite. Nevertheless, under SEM it was possible to determine an allomicritic matrix represented by calcareous nannoplankton (Figure 2b). This observation indicates primary carbonate production in the photic zone, then transported through the water column to the sea floor. Besides, autochthonous fauna, characterized by well-preserved foraminifers recrystallized into macrospar calcite are present. Quartz and feldspar grains are redistributed and concentrated as a result of bioturbation of infaunal organisms. The sample is described as bioturbated, calcite cement, calcareous nannoplankton-dominated mudstone.

Mudstones dominated by allochthonous components

Mudstones dominated by extrabasinal components are rich in clay minerals including 2M1-illite. Also, mixed layer illite-smectite (< 15% of expandable layer) and chlorite predominates over kaolinite constitute important phase minerals in the clay fraction. Silt-size components are mostly quartz and minor feldspars (plagioclase over K-feldspar) and micas. Besides, autochthonous components represented by clay-sized calcite and amorphous organic matter are present.

Under optical microscopy some mudstones present wavy non-parallel limits and exhibit neither lamination nor bedding, where bioturbation evidence, as oriented grain and organized in circular form, is abundant and indicative of disrupted original depositional fabric (Figure 2c). They probably represent 3D structures being the fill more clay-rich than the host rock. According to the nomenclature scheme this microlithofacies is described as highly bioturbated, sand, silt and clay-bearing mudstone.

Clay-rich, carbonate-bearing mudstones show even discontinuous parallel lamination, lack of bedding structure and no disruption by bioturbation. Some of these units contain dispersed, reworked fragmentary shell debris and the fine silt grains are randomly distributed in the dark clay-carbonate-organic matrix. In other cases, diffuse transitions between silt-rich and clay rich laminae are present and are described as clay-rich, carbonate-bearing laminated mudstones (Figure 2d). SEM images show face-to-face clay minerals arrangement indicating their detrital origin (Figure 2e). Uninterrupted suspension settling may be the main sedimentary process responsible for deposition of these mudstones. Nevertheless, the laminated ones represent suspensions of distinct depositional events.

Mudstones that contain important authigenic components

Many samples contain a small proportion of diagenetic cements (less than 5%), but some of them present high percentage of such components (up to 20%). As framboidal aggregates, pyrite infill foraminifera chambers and also occurs as euhedral crystals among sedimentary matrix. Also, fluorapatite cement occurs as disseminated, discrete euhedral crystals (5 μm). Cement-rich mudstones are scarcely documented throughout the succession and are present as 1 to 0.3 m thick units, showing stratiform geometries with sharp and regular contacts. Ferroan dolomite is the predominant mineral phase in concretionary beds or bodies (Figure 2f). Under optical microscopy, these units are neither bedded nor laminated and bioturbation is absent. They are composed mainly of an interlocking mosaic of ferroan dolomite with minor silt, clay and organic matter in the residual matrix. Locally, the fine grained carbonate present aggrading neomorphism and some Fe-dolomite crystals are partially replaced by later non-ferroan calcite. This microlithofacies is described as a dolomite cement-rich mudstones.

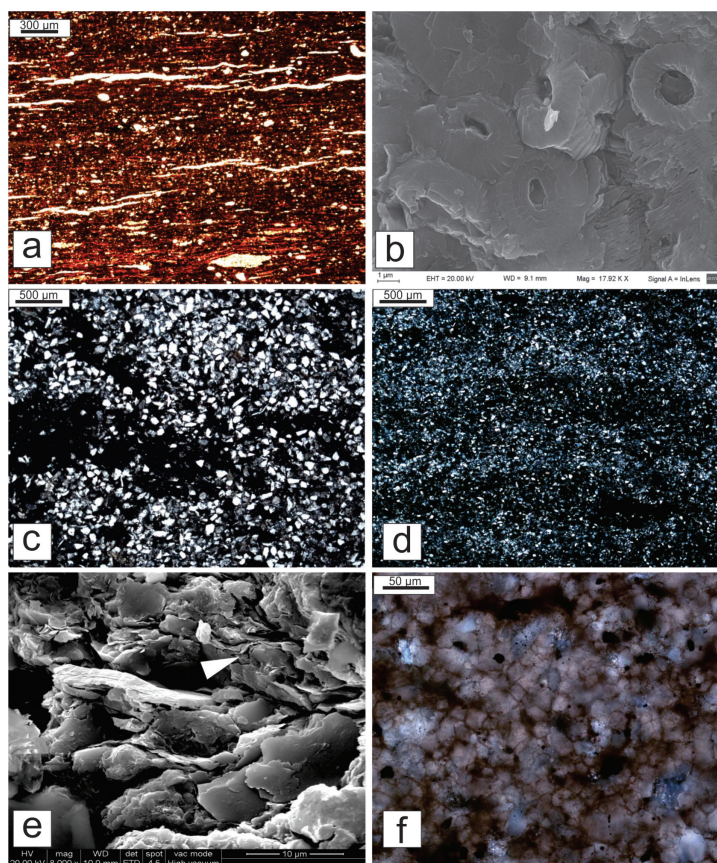


Figure 2. Light optical micrographs and secondary electron images. a) Laminated, organic matter-rich mudstones. The sample is composed mainly of algal-derived organic matter with micritic calcite and minor silt, illitic material and authigenic mineral phases (pyrite and dolomite). b) Bioturbated, calcite cement, calcareous nannoplankton-dominated mudstones. The alloimicritic matrix is dominated by coccoliths. c) Bioturbated, sand, silt and clay-bearing mudstone. The original fabric was reorganized by bioturbation processes. d) Alternating silt and clay size material dominated laminae with diffuse boundaries. e) Orientation of illitic particles as face-to-face aggregates (arrow). f) Dolomite cement-rich mudstones. Detrital clay and silt and organic matter are present among the cement crystal mosaic.

CONCLUDING REMARKS

The transgressive facies of the Agua de la Mula Member, Agrio Formation were studied by detailed petrographic analysis, in conjunction with XRD and organic carbon data. A great variety of microlithofacies, that differ in the relative proportions of organic material, carbonate production, detrital silt and clay minerals and authigenic phases as well are present. Besides, bioturbation processes, not often observed in hand specimens, disrupted the sediment and were responsible for the original depositional fabric change.

Commonly viewed as homogeneous, the informally named Spitidiscus shales, which include marlstones to more consolidated beds (*e.g.* mudstones) are useful terms at a macroscopic scale. The actual knowledge deserves a detailed study, whereas those terms are so far to represent the complexity of sedimentary processes that take place during deposition of this muddy succession. In the present study, sediment transfer processes include both suspension settling and advective sediment transport (Schieber *et al.* 2007)

Another important item is the role of X-ray diffraction in the study of muddy facies. Even though, it is an excellent technique to know the mineral phases present in mudstone samples and the possibility to quantify them quickly and with a slightest error, if it is used in isolation, XRD can introduce some mistakes. For instance, in mudstones dominated by autochthonous components, laminated organic matter-rich mudstones contain in average calcite (75%), with minor quartz and feldspar (13%), clay minerals (7%) and pyrite, dolomite (5%) which are similar to those obtained in calcite cement, calcareous nannoplankton-dominated mudstones (see above in results).

As one might expect percentages obtained from the quantification of XRD-analyses do not reflect anything about textural and fabric relations and the cryptic lithofacies variability is documented only by optical petrography. However, it is an important tool to split mudstones dominated by extrabasinal components (allochthonous) from autochthonous ones which if variations are systematic, probably correspond to changes in the balance of production relative to dilution.

In the Agua de la Mula Member, lateral and vertical mudstones facies changes occur which will be interpreted in a sequential stratigraphic framework. The implications of this variability for unconventional resources explorations should be taken in mind.

ACKNOWLEDGMENTS

This research was supported by the Instituto de Estudios Andinos Don Pablo Groeber and by the Centro de Tecnología y Recursos Minerales y Cerámica, where the author (M.C.) is currently carrying out his Ph.D. investigations. Special thanks to Héctor Villar (GeoLab Sur) for the TOC analyses. To Diana E. Fernández and David Tineo for their help during the field work. Also, the

authors are grateful to the reviewers for their comments and suggestions. This is the contribution C-88 of the Instituto de Estudios Andinos Don Pablo Groeber.

REFERENCES

- Aguirre-Urreta, M.B., P.J. Pazos, D.G. Lazo, C.M Fanning and V.D. Litvak, 2008, First U-Pb shrimp age of the Hauterivian stage, Neuquén Basin, Argentina, *Journal of South American Earth Sciences*, 26: 91-99.
- Bates, R. J. and J. A. Jackson, 1987, *Glossary of Geology*, American Geological Institute, Alexandria, Va., 788.
- Cole, R.D. and M.D. Picard, 1975, Primary and second structures in oil shale and other fine-grained rocks, Green River Formation (Eocene), Utah and Colorado, *Utah Geology*, 2: 49-67.
- Dickson, J.A.D., 1965, A modified technique for carbonates in thin section, *Nature*, 205: 587.
- Ghadeer, S.G. and J.H.S. Macquaker, 2011, Sediment transport processes in an ancient mud-dominated succession: a comparison of processes operating in marine offshore settings and anoxic basinal environments, *Journal of the Geological Society*, 168: 1121-1132.
- Leanza, H.A., C.A. Hugo and D. Repol, 2001, Hoja Geológica 3969-I, Zapala. Provincia del Neuquén, 128 pp. Instituto de Geología y Recursos Minerales, Servicio Geológico Minero Argentino, Boletín 275.
- Legarreta, L. and H.J. Villar, 2012 Las facies generadoras de hidrocarburos de la Cuenca Neuquina, *Petrotecnia*: 14-39.
- Macquaker, J.H.S. and A.E. Adams, 2003, Maximizing information from fine grained sediments: an inclusive nomenclature for mudstones, *Journal of Sedimentary Research*, 73: 735-744.
- Macquaker, J.H.S., K.G. Taylor and R.L. Gawthorpe, 2007, High-resolution facies analyses of mudstones: Implication for paleoenvironmental and sequence stratigraphic interpretations of offshore ancient mud-dominated successions, *Journal of Sedimentary Research*, 77: 324-339.
- Naipauer, M., M. Tunik, J.C. Marques, E.A. Rojas Vera, G.I. Vujovich, M.M. Pimentel, and V.A. Ramos, 2014, U-Pb detrital zircon ages of Upper Jurassic continental successions: implications for the provenance and absolute age of the Jurassic-Cretaceous boundary in the Neuquén Basin, in S. Sepúlveda, L. Giambiagi, L. Pinto, S. Moreiras, M. Tunik, G. Hoke and M. Farías (eds.), *Geodynamic Processes in the Andes of Central Chile and Argentina*, Geological Society, Special Publications 399, in press.
- O'Brien, N.R., 1996, Shale lamination and sedimentary processes, in A. E. S. Kemp, (ed.), *Palaeoclimatology and Palaeoceanography from Laminated Sediments*, Geological Society Special Publication 116: 23-36.
- Potter, P.E., J.B. Maynard and W.A. Pryor, 1980, *Sedimentology of Shale*. New York, Springer-Verlag, 306 p.
- Rietveld, H.M., 1969, A profile refinement method for nuclear and magnetic structures, *Journal of Applied Crystallography*, 2: 65-71.
- Rodríguez Carvajal, J., 2001, Recent development of the Program FULLPROF. Commission on Powder Diffraction (IUCr), *Newsletter*, 26: 12-19.

- Sagasti, G., 2000, La sucesión rítmica de la Formación Agrio (Cretácico inferior) en el sur de la provincia de Mendoza, y su posible vinculación con los Ciclos de Milankovitch, *Revista de la Asociación Argentina de Sedimentología*, 7: 1-22.
- Sagasti, G., 2005, Hemipelagic record of orbitally-induced dilution cycles in Lower Cretaceous sediments of the Neuquén Basin, in G.D. Veiga, L.A. Spalletti, J.A. Howell and E. Schwarz (eds.), *The Neuquén Basin: A case study in sequence stratigraphy and basin dynamics*. Geological Society of London, Special Publication 252: 231-250.
- Schieber, J., 1999, Distribution and deposition of mudstone facies in the Upper Devonian Sonyea Group of New York, *Journal of Sedimentary Research*, 69: 909-925.
- Schieber, J., J. Southard and K. Thaisen, 2007, Accretion of mudstones beds from migrating floccule ripples, *Science*, 318: 1760-1763.
- Spalletti, L.A., D.G. Poiré, E. Schwarz and G.D. Veiga, 2001, Sedimentologic and sequence stratigraphic model of a Neocomian marine carbonate-siliciclastic ramp: Neuquén Basin, Argentina, *Journal of South American Earth Sciences*, 14: 609-624.
- Spalletti, L.A., E. Schwarz and G.D. Veiga, 2011, La Formación Agrio (Cretácico Temprano) en la Cuenca Neuquina, in H.A. Leanza, C. Arregui, O. Carbone, J.C. Danieli and J.M. Vallés (eds.), *Geología y Recursos Naturales de la Provincia del Neuquén*, 18º Congreso Geológico Argentino, p. 145-160.
- Trabucho-Alexandre, J. R. Dirkx, H. Veld, G. Klaver, and P.L. De Boer, 2012, Toarcian black shales in the Dutch central graben: record of energetic, variable depositional conditions during an oceanic anoxic event, *Journal of Sedimentary Research*, 82: 104-120.
- Veiga, G.D., J.A. Howell and A. Strömback, 2005, Anatomy of a mixed marine-non-marine low-stand wedge in a ramp setting. The record of a Barremian-Aptian complex relative sea-level fall in the central Neuquén Basin, Argentina, in G.D. Veiga, L.A. Spalletti, J.A. Howell and E. Schwarz (eds.), *The Neuquén Basin: A case study in sequence stratigraphy and basin dynamics*. Geological Society of London, Special Publication 252: 139-162.
- Weaver, C.E., 1931. *Paleontology of the Jurassic and Cretaceous of West Central Argentina*, 417 Memoir University of Washington, 1: 1-469.