
H.A. Leanza, A. Mazzini, F. Corfu, E.J. Llambías, H. Svensen, S. Planke, O. Galland

Servicio Geológico Minero Argentino and CONICET, Av. Julio A. Roca 651, 1322 Buenos Aires, Argentina
Department of Geological Processes, University of Oslo, PO Box 1047 Blindern, 0316 Oslo, Norway
Centro de Investigaciones Geológicas, Universidad Nacional de la Plata, Calle 1 - # 644, 1900 La Plata, Argentina
Volcanic Basin Petroleum Research (VBPR), Oslo Research Park, 0349 Oslo, Norway

A R T I C L E   I N F O

Article history:
Received 23 August 2011
Accepted 31 July 2012

Keywords:
Radiometric ages
Pliensbachian/Toarcian boundary
Early Jurassic
Chachil Limestone
Precuyano Cycle
Neuquén Basin

A B S T R A C T

New radiometric U–Pb ages obtained on zircon crystals from Early Jurassic ash layers found within beds of the Chachil Limestone at its type locality in the Chachil depocentre (southern Neuquén Basin) confirm a Pliensbachian age (186.0 ± 0.4 Ma). Additionally, two ash layers found in limestone beds in Chacay Melehue at the Cordillera del Viento depocentre (central Neuquén Basin) gave Early Pliensbachian (185.7 ± 0.4 Ma) and earliest Toarcian (182.3 ± 0.4 Ma) U–Pb zircon ages. Based on these new datings and regional geological observations, we propose that the limestones cropping out at Chacay Melehue are correlatable with the Chachil Limestone. Recent data by other authors from limestones at Serrucho creek in the upper Puesto Araya Formation (Valenciana depocentre, southern Mendoza) reveal ages of 182.16 ± 0.6 Ma. Based on these new evidences, we consider the Chachil Limestone an important Early Jurassic stratigraphic marker, representing an almost instantaneous widespread flooding episode in western Gondwana. The unit marks the initiation in the Neuquén Basin of the Cuyo Group, followed by widespread black shale deposition. Accordingly, these limestones can be regarded as the natural seal of the Late Triassic–earliest Jurassic Precuyano Cycle, which represents the infill of halfgrabens and/or grabens related to a strong extensional regime. Paleontological evidence supports that during Pliensbachian–earliest Toarcian times these limestones were deposited in western Gondwana in marine warm water environments.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

The Neuquén Basin is located in the foothills of the Andes between parallels 32° and 42° S and is exposed in the Cordillera Principal as a narrow N–S belt that broadens out south of parallel 36° S into the eastern foreland where it is termed the Neuquén Embayment (Ramos, 1999, 2009; Arregui et al., 2011). The basin was formed during fragmentation of Gondwana and the subsequent opening of the South Atlantic Ocean. In the Triassic and Early Jurassic a series of halfgrabens trending NNW–ESE were developed and filled by volcanic and sedimentary sequences (the Precuyano Cycle) at separate depocentres, some of them cropping out and others detected only in subsurface (Fig. 1A). The rifting stage was followed by an Early Jurassic widespread marine transgression from the Panthalassic Ocean, thus changing from localized rifting to a generalized subsidence (Legarreta and Gulisano, 1989; Legarreta and Uliana, 1999; Vergani et al., 1995; Franzese and Spalletti, 2001). As a result, these depocentres, located to the east of the arc and trench system, became progressively inter-connected, and were integrated during Pliensbachian times into an extensive area of marine sediment deposition located between the volcanic arc to the west and the South American foreland to the east. The expansion of a broader basin coincided with the initiation of a long-term stage of subsidence, during which a number of marine units ascribed to the Cuyo Group were deposited (Groeber, 1946; Gulisano, 1981; Gulisano and Pando, 1981; Gulisano et al., 1984; Leanza, 2009; Arregui et al., 2011). Although intensive research on the Precuyano Cycle has been undertaken in recent years in the Neuquén Basin (Franzese and Spalletti, 2001; Pángaro et al., 2002a, 2002b, 2009; Franzese et al., 2006, 2007; Muravchik et al., 2008, 2011; Schiuma and Llambías, 2008; Cristallini et al., 2009; D’Elia et al., 2012a,b), until now its upper limit remained uncertain. As a matter of fact, the first marine sediments interbedded within
volcanic materials were included into the Cuyo Group, although they are forming part of a synrift context.

The aim of this paper is to investigate the possibility that the Early Jurassic limestones of the Cuyo Group outcropping at the Chachil, Cordillera del Viento and Valenciana depocentres (Fig. 1A) can be chronologically correlated to a single event affecting a large area. For this purpose we present new zircons isotopic U–Pb dating and field observations which shed light on the age, distribution and paleogeography of the first widespread marine transgression from the Panthalassic Ocean on western Gondwana. According to recent paleogeographic maps, the Early Jurassic (Pliensbachian–earliest Toarcian) marine transgression penetrated into the Neuquén Basin in southern Mendoza through the Curiepto–Atuel seaway (Vicente, 2005; Arregui et al., 2011). As it will be demonstrated in this paper, the significance of these Early Jurassic thin bedded and highly silicified limestones (“Chachil Limestones”) is not only relevant with regard to previous paleogeographic designs, but its occurrence also sheds light on the controversial upper limit of the Precuyano Cycle. Finally, the meaning of these limestones as a paleoclimatic event of regional significance is also highlighted.

2. Geological framework

The Neuquén Basin is part of an extensional system which was developed in a retroarc context along the active margin of South America. Its history has been controlled by a changing tectonic setting of the western margin of Gondwana. It contains Late Triassic to Early Paleogene marine and continental sequences several thousand meters thick accumulated in a variety of conditions, mostly as a result of important marine transgressions from the Panthalassic Ocean (Legarreta and Gulisano, 1989; Legarreta and Uliana, 1991). It is bounded to the NE by the San Rafael Block and to the SE by the Nord Patagonian massif. The western margin of the Basin is defined by an almost continuous volcanic arc.

During the Triassic to Early Jurassic, many NNW–ESE trending halfgrabens (Fig. 1A) were generated (Uliana and Biddle, 1988; Uliana et al., 1989, 1995) and filled up by volcanic and sedimentary
sequences, mostly grouped in the Precuyano Cycle (Gulisano, 1981), the Precuyo Mesosequence (Lagarreta and Gulisano, 1989) or Saníco Subsynthem (Riccardi and Gulisano, 1993) with variable thickness ranging from zero up to a few thousand meters (Lagarreta and Gulisano, 1989; Gulisano, 1993; Riccardi et al., 1992; Vergani et al., 1995). The rifting stage was followed by the Early Jurassic marine ingress of the Cuyo Group, thus changing from localized rifting to a generalized subsidence (Lagarreta and Gulisano, 1989; Lagarreta and Uliana, 1999; Pángaro et al., 2009).

The Neuquén Basin maintained an almost continuous subsidence rate until the Late Cretaceous, which is represented by synorogenic deposits of the Neuquén Group that define the beginning of the flexural subsidence and the establishment of the Neuquén foreland basin (Ramos et al., 2011b). The next stage corresponds to the first Atlantic transgression into the basin represented by the Malignué Group displaying a regional change in the foreland slope associated with a eustatic sea level rise (Barrio, 1990). After that, a stage of uplift and non-deposition (Eocene hiatus) was followed by compressional tectonics during the Oligocene to the Late Miocene, until the basin reached its current structural configuration (Ramos, 1995, 2009; Cobbold and Rosello, 2003; Ramos et al., 2011a).

2.1. The Chachil Limestone: history, regional distribution and correlations

The term “Chachil Limestone” was introduced by Weaver (1942) to identify regularly bedded and highly silicified fossiliferous micritic limestones cropping out in the southern slope of the Chachil range. However, as stated by Manceñido and Leanza (1993), this term remained unused in the geological literature for many years, until it was restored by Leanza (1985, 1992), during geological mapping of the Chachil region. At the time Weaver (1942) introduced the name, this unit was still considered of Triassic age based on the finding by Groeber (1924) of a species of the bivalve genus Myophoria supposedly similar to those present in the German Muschelkalk (e.g. Myophoria neuquensis Groeber, 1924). Later on, Leanza (1948) noted that the Groeber’s species was found in association with Early Jurassic bivalves and therefore its Triassic age was discarded. Ammonites in this unit were first recorded by Leanza and Blasco (1991) at the Nireco creek (S 39° 04' 09"—W 70° 30' 10''), in the eastern flank of the Chachil range, and later on they were grouped in the Austromorphites behrendseni Assemblage Zone (=Davoei Standard Zone) of late Early Pliensbachian age (Riccardi, 2008; Riccardi et al., 2011).

Apart from its original record at the southern extremity of the Chachil range (Weaver, 1942; Leanza, 1992; Cucci and Leanza, 2000), the Chachil Limestone was found in the eastern flank of the cited range at Nireco creek (Leanza and Blasco, 1991), as well as in the La Atravesada hill (S 35° 57' 08"—W 70° 38' 03''), where it occurs interfingering with the Sierra Chacaico Formation in association with manganese deposits (Leanza et al., 1990; Zanettini et al., 2010; Zappettini et al., 2011a).

In subsurface, in the Anticlinal Campamento oil field (S 38° 58' 41"—W 69° 43' 46'') around the Dorsal de Huincul area in southern Neuquén Basin (Fig. 1A), Schiuma and Llambias (2008) described Pliensbachian limestones interfingering with coarse conglomerates, whereas Pángaro et al. (2009) also mentioned that these limestones were excellent reflectors in seismic lines. Other subsurface limestones at the base of the Los Molles Formation were recently reported (Schiuma et al., 2011) from the Cupen Mahuida oil field (S 38° 44' 43"—W 68° 55' 20'') located in the eastern region of the Neuquén Basin (Fig. 1A). These limestones, overlying a thick volcanic sequence, may be correlated with the Chachil Limestone suggesting their widespread distribution throughout out the basin.

In the northwestern flank of the Cordillera del Viento range, Algoma type deposits of jaspilites developing Banded Iron Formation (BIF) were described in the Colomichicó Formation (Zappettini and Dalponte, 2009) with U–Pb SHRIMP ages of 185 ± 1.9 Ma and 185.7 ± 2.3 Ma (Zappettini et al., 2011b). Although these Algoma type deposits were almost coeval with the here described limestones, they were ascribed by those authors to the Precuyano Cycle, as they still occur in a synrift context.

3. Description of the Chachil Limestone in its stratigraphic context

In order to highlight the significance of the Chachil Limestone during the Late Triassic–Early Jurassic evolution of the Neuquén Basin, a brief description of the Chachil, Cordillera del Viento and Valenciana depocentres, in which new U–Pb ages were obtained, is given below (for location see Fig. 1A).

3.1. The Chachil depocentre

Mapping of the Chachil region (Fig. 1D) was carried out by Lambert (1946, 1948, 1956), Leanza (1985, 1992), Cucci and Leanza (2000) and García Morabito and Ramos (2011), while considerations regarding its infill were made by Leanza et al. (2005), Franzese and Spalletti (2001), Franzese et al. (2006, 2007), Muravchik et al. (2008) and Carbome et al. (2011). Studies related to the main rift-related faults systems of this depocentre were made by Franzese et al. (2006) and García Morabito and Ramos (2011). Here the Precuyano Cycle is represented by volcanic and continental sedimentary infill comprised between the Huarpican and Rioatuelican unconformities (Leanza, 2009). A brief description of the units which constitute the infill of this depocentre is given below (Fig. 2).

3.1.1. Precuyano Cycle

3.1.1.1. Nireco Formation (Leanza et al., 2005). This name replaces the former Choiyoi Formation (sensu Groeber, 1946) and its type locality is at the head of the Nireco creek (S 39° 02' 44"—W 70° 32' 29''), where it attains 867 m in thickness. Together with the Lapa Formation, it is considered part of the synrift succession of the Precuyano Cycle (Gulisano et al., 1984; Franzese and Spalletti, 2001; Leanza et al., 2005; Schiuma and Llambias, 2008). It consists of an alternation of andesitic and andesitic–dacitic flows with intense violet color, together with dacitic and rhyodacitic tuffs, as well as breccias and lithic tuffs with porphyritic texture. Basic lavas are extremely rare. Its lowermost portion contains gray siltstones with fossil wood. It unconformably overlies the Chachil Plutonic Complex of Permian age, actually considered to form part of the Choiyoi Group (sensu Llambias et al., 2007; Llambias and Sato, 2011). It is covered, also unconformably, by the Lapa Formation (Upper Triassic), or by the Chachil Limestone (Fig. 3a) where the former unit is absent.

3.1.1.2. Lapa Formation (Groeber, 1958). This unit includes sedimentary and volcanic rocks first described by Lambert (1946). Its type locality is at the northern slope of the Lapa hill (S 39° 23' 59"—W 70° 26' 32''), where it attains 290 m in thickness (Leanza, 1992). It consists of fanglomerates, conglomerates, sandstones and tuffaceous sandstones, interbedded with sporadic basaltic flows. The unit ends with thick tuff layers of ignimbritic nature. It is unconformably covered (Rioatuelican unconformity) by the Chachil Limestone. This unit is considered to form the upper part of the synrift suite of the Precuyano Cycle. On the basis of floristic remains of Telemachus elongatus Anderson and Pagiophyllum sp. its age is ascribed to the Late Triassic (Spalletti et al., 1992).
3.1.2. Cuyo Group

3.1.2.1. Chachil Limestone (Weaver, 1942). In this region it constitutes the basal unit of the Cuyo Group (sensu Gulisano, 1981). It consists of regularly bedded, strongly silicified dark gray micritic limestones, with yellowish-pink weathering surfaces, displaying a maximum thickness of 50 m (Leanza, 1992; Manceñido and Leanza, 1993). The unit unconformably overlies basement plutonic rocks (Chachil Plutonic Complex) and/or synrift deposits.
3.1.2.2. Los Molles Formation (Weaver, 1931). Its type locality was established by Volkheimer (1973) along the Maihuén creek (S 39°02'45"–W 70°18'02") in the Ñireco creek area, on the eastern flank of the Chachil range, were grouped by Riccardi (2008) in the Austromorphites behrendseni Assemblage Zone (=Davoei Standard Zone) of late Early Pliensbachian age. Two samples (C-09-1 and C-09-2) were collected for U–Pb dating from a tuff layer located 2.5 m above the base of the unit (Fig. 3b); the results are reported below.

3.1.2.2.1. Los Molles Formation (Weaver, 1931) has been described by various authors, including Volkheimer (1973), Leanza and Hugo (1997), Leanza et al. (2005), and Llambías et al. (2007). The formation comprises marine sediments that are primarily composed of black and gray shales, with occasional sandstone and conglomerate layers. These deposits are associated with volcanic and sedimentary rocks, indicative of temperate waters (Leanza, 1992, 1993).

3.2. The Cordillera del Viento depocentre

3.2.1. Precuyano Cycle

3.2.1.1. Cordillera del Viento Formation (Leanza et al., 2005). This formation is composed of marine sedimentary deposits that range from the Pliensbachian to the late Early Pliensbachian (Giebeli Standard Zone) (see Riccardi, 2008). In the Bajo de Lapa area (S 39°22'34"–W 70°28'41"), Gómez Pérez (2001) reported stromatolitic buildups related with volcanic venting through boundary faults related to synrift depocentres.

3.2.1.2. Milla Michicó Formation (Freytes, in Digregorio, 1972). This formation is composed of marine sediments that range from the Pliensbachian to the late Early Bajocian (Giebeli Standard Zone) (see Riccardi, 2008). In the Bajo de Lapa area, it attains nearly 400 m in thickness. It was previously described as the Chachil Limestone by Leanza and Hugo (1997). It lies between the Chachil Limestone and/or the Sierra Chacaicó Formation (Volkheimer, 1973) and is covered by prograding near-shore sandstones of the Lajas Formation (Weaver, 1931). It is mainly composed by black and gray shales, mostly deposited in an anoxic environment, and is considered to be Late Triassic to possibly earliest Jurassic (Llambías et al., 2005). In the Bajo de Lapa area, it unconformably overlies the Cordillera del Viento Formation, and consists of mesosilicic and basic volcanics, displaying a bimodal character. It is unconformably overlain by La Primavera Formation. No radiometric age or fossils were found in the Milla Michicó Formation. However, considering that this unit is bounded by similar unconformities present at the Chachil depocentre (Leanza et al., 2005), the correlation with the Lapa Formation is sustained, and its age is considered to be Late Triassic to possibly earliest Jurassic (Llambías et al., 2007).

3.2.1.3. La Primavera Formation (Suárez and De la Cruz, 1997). This formation is composed of marine sediments that range from the Pliensbachian to the late Early Pliensbachian (Giebeli Standard Zone) (see Riccardi, 2008). In the Bajo de Lapa area, it unconformably overlies the Milla Michicó Formation. No radiometric age or fossils were found in the Milla Michicó Formation. However, considering that this unit is bounded by similar unconformities present at the Chachil depocentre (Leanza et al., 2005), the correlation with the Lapa Formation is sustained, and its age is considered to be Late Triassic to possibly earliest Jurassic (Llambías et al., 2007).

References

Fig. 4. Generalized stratigraphic column of the Cordillera del Viento depocentre.
“Liásico tobáceo” (Zöllner and Amos, 1973), “Unnamed Unit” (Gulisano and Gutiérrez Pleimling, 1995) or Lista Blanca Formation (Iglesia Llano and Riccardi, 2000). The La Primavera Formation is fairly well exposed to the north of the gas pumping Rajapalo station (S 37° 16′ 36″–W 70° 34′ 30″) (Fig. 5a), and consists of a volcanioclastic succession interbedded with marine deposits with invertebrate fossils (bivalves, brachiopods, gastropods, corals) and fossil wood. It unconformably overlies the Milla Michicó Formation and is covered, across a sharp contact, by the Chachil Limestone. The base of the unit exhibits basaltic flows parallel to the stratification planes, whereas in its medium to higher levels it consists of silicic explosive volcanic rocks (volcanogenic sandstones and breccias) interbedded with marine fossiliferous beds, high density flow deposits and well-laminated ignimbrites (Fig. 5b). The pyroclastic input was probably generated by subaerial to subaqueous volcanoes – likely great calderas – located near the shore-line (Suárez and De la Cruz, 1997). The bimodal volcanism in marine waters suggests that sedimentation was still severely influenced by an extensional tectonic regime. On the basis of its faunal content it was roughly ascribed to the Pliensbachian/Toarcian (Damborenea and Manceño, in Gulisano and Gutiérrez Pleimling, 1995). Suárez et al. (2008) provided an SHRIMP age of 183 ± 1.3 Ma for La Primavera Formation, but without specifying the horizon in which the sample was taken.

3.2.2. Cuyo Group

3.2.2.1. Chachil Limestone (Weaver, 1942). It overlies La Primavera Formation and is covered by anoxic black shales of the Los Molles Formation (Fig. 5c). The unit is fairly well exposed at Chacay Melehue creek in Vega del Tero (S 37° 15′ 09″–W 70° 30′ 25″) where it attains 29.5 m in thickness. It consists of regularly thin-bedded gray limestones, with yellowish-pink weathering surface (Fig. 6a). Some tuff layers were sampled in between the stratification planes, and zircon ages are reported below for a tuff layer 9 m above the base of the unit (Fig. 6b) and a further tuff layer 4.5 m below the top of the unit (Fig. 6c). The obtained ages confirm that the Chachil Limestone developed through the Pliensbachian/Toarcian boundary. Other outcrops of this limestone with similar
stratigraphic relationships occur just north of the Rajapalo station, where it attains 12 m in thickness. At this locality the base of the Chachil Limestone overlies through a sharp surface, the ignimbrites and the high density flow deposits of the La Primavera Formation (Fig. 5c). Other important outcrops of this unit occur at the top hill (S 37° 16’ 22”–W 70° 36’ 39”e) located 1.3 km to the southwest of La Primavera pass in direction to Andacollo, where it attains 18 m in thickness.

3.2.2. Los Molles Formation (Weaver, 1931). In the Chacay Melehué area this unit attains more than 800 m in thickness, and is confined between the Chachil Limestone and the Tábanos Formation (Stipanicic, 1966). Where this unit is eroded (Rajapalo area), it is unconformably overlain by the prograding fluvial conglomerates of the Lotena Formation. It mainly consists of black shales, with a high content of organic matter, deposited in a turbiditic regime. Based on its ammonite content, its age is regarded as Early Toarcian (Tenuicostatum Standard Zone) (Riccardi, 1993; Gulisano and Gutiérrez Pleimling, 1995; Riccardi, 2008). At the Toarcian/Aalenian boundary there are andesitic lahars intercalated within black shales, thus indicating that volcanism, although of andesitic nature, was still active at that time (Llambías and Leanza, 2005).

3.3. The Atuel and Valenciana depocentres

In recent years detailed structural and sedimentological studies of the Late Triassic–Early Jurassic infill of the Atuel depocentre (Fig. 1A) have been carried out by several authors (Lanés, 2005; Lanés et al., 2008; Giambiagi et al., 2005, 2008; Bechis et al., 2005). It includes, from base to top, mixed marine and non-marine deposits of the Arroyo Malo, El Freno, Puesto Araya and Tres Esquinas Formations. The oldest deposits of the Arroyo Malo Formation in the western part of the Atuel depocentre include the Triassic–Jurassic boundary in marine facies (Riccardi et al., 1997) followed by the fluvial El Freno Formation. The Puesto Araya
Formation was divided by Giambiagi et al. (2005, 2008) into a lower and an upper section, the first one related to synrift processes, whilst the uppermost one evolved to a carbonate-rich content in relationship with the initiation of the sag stage in the basin, followed by widespread black shale deposition. According to recent paleogeographic maps, the Early Jurassic (Pliensbachian–earliest Toarcian) marine transgression is thought to penetrate into the basin in southern Mendoza through the Curepto–Atuel seaway (Vicente, 2005; Arregui et al., 2011).

The infill of the Valenciana depocentre (Fig. 7a and b), located nearly 70 km to the south of the Atuel depocentre (Fig. 1D), was studied in detail by Gulisano and Gutiérrez Pleimling (1995). Of concern for the present paper, the Serrucho (S 35° 26’ 32”–W 69° 54’ 12”) and Calabozo (S 35° 29’ 16”–W 69° 54’ 48”) creeks composite section presented by the cited authors reveals that the depth of this depocentre is much less than the Atuel depocentre. The oldest unit in the Serrucho creek area is represented by nearly 120 m of coarse fluvial conglomerates of the El Freno Formation, whose base above the Choiyoi Group can only be observed 60 km to the north-west in the Portezuelo Ancho section (S 35° 05’ 23”–W 70° 07’ 40”) (see Fig. 25 in Gulisano and Gutiérrez Pleimling, 1995). The succession is interpreted to continue with nearly 150 m of the upper Puesto Araya Formation, followed up the 350 m of the Tres Esquinas Formation mostly composed of black shales.

Fig. 7. a) Generalized stratigraphic column of the Valenciana depocentre, southern Mendoza, Neuquén Basin; b) outcrop aspect of the uppermost beds of the Puesto Araya Formation in contact with the Tres Esquinas Formation at Serrucho creek, where Mazzini et al. (2010) calculated its age as Early Toarcian (182.16 ± 0.6 Ma).
and sandstones, displaying just at its base the Toarcian Oceanic Anoxic Event (TOAE) recently described by Mazzini et al. (2010).

4. Methods and results

4.1. Field work

Field work was undertaken by the authors in the Neuquén Basin during March–April 2008 to conduct regional studies and sampling. One of the crucial goals was to identify tuff layers in the logged sections for dating by the U–Pb method. Sampling was done at the type locality of the Chachil Limestone (Chachil depocentre) and Chacay Melehue creek (Vega del Tero) and Rajapalo localities (Cordillera del Viento depocentre) (Fig. 1A, C and D). Further observations and U–Pb ages were also obtained at the Serrurcho creek locality (Valenciana depocentre) in southern Mendoza (Fig. 1A and B), with results already published by Mazzini et al. (2010).

4.2. Zircon dating

Dating was carried out by the ID-TIMS U–Pb method on zircon. The initial tuff material was nearly unconsolidated, in part clay-rich and generally friable. It was therefore comminuted using a mortar and pestle, with subsequent flotation and progressive decanting of the light minerals, followed by sieving and enrichments by magnetic and heavy liquid methods. The further steps of the procedures follow essentially Krogh (1973) with modifications described in detail in Corfu (2004). Decay constants are those of Jaffey et al. (1971). Data plotting and calculations were done using the program ‘Isoplot’ (Ludwig, 2003).

The zircon grains were selected under a binocular microscope, primarily trying to separate crystals formed during the volcanic event from potential xenocrysts, the main criteria being sharp euhedral and ideally prismatic shapes together with the identification of one main coherent type. The final verification of the validity of the ages is based on the reproducibility of the individual ages. The identification was very successful in sample AR08VT-14 (S 37° 15’ 09” – W 70° 30’ 25”), which comprises one main homogenous population (Fig. 8a), and, with one exception, in sample AR08VT-56 (S 37° 15’ 11” – W 70° 29’ 58”), which comprises both short- and long-prismatic crystals (Fig. 8b), but it did not work very well with the other two samples, whose populations are dominated by xenocrystic zircon grains (see below).

The second task was to eliminate the effects of Pb loss before analyzing the zircons. This turned out to be rather difficult with sample AR08VT-14, where a first selection of the dominant prismatic zircons (Fig. 8a) was subjected to mechanical abrasion (Krogh, 1982). The resulting analyses of single grains (8–11) are all clustered together (Table 1; Fig. 9a) but distinctly discordant. In a second step, zircon grains from this sample were annealed at 900 °C for 3 days, followed by partial dissolution in HF at 194 °C overnight before final selection, based on the ‘chemical abrasion’ technique of Mattinson (2005). This approach was much more successful in removing domains affected by Pb loss, and more efficient at isolating pure zircon by mining out the many inclusions that characterize the population. Analysis 4 (Table 1), representing one of the solutions removed after the overnight partial dissolution step, shows that the more soluble zircon underwent a much higher degree of Pb loss and was also much more rich in common Pb than the residue. The analyses obtained by chemical abrasion are distinctly older than those obtained after mechanical abrasion, although some dispersion in the U–Pb ratios remains (Fig. 9a). The age that we report (185.7 ± 0.4 Ma) is based on the two oldest and most precise analyses (2–3) deemed to be free of Pb loss. Analysis 1 is yet somewhat older, but much less precise because of high common Pb level, either from accidental contamination or some residual Pb-rich inclusion. This analysis was obtained from two short-prismatic grains, and it is suspected that they contained a xenocrystic component.

For sample AR08-VT56 there was no obvious distinction between grains treated by chemical or mechanical abrasion, with five analyses (13–17) clustered together, giving a concordia age of 182.3 ± 0.4 Ma (Fig. 9b). Just one grain (18) yields a younger age, reflecting Pb loss, whereas a second fraction (12) has an older age likely due to an inherited component.

Zircon grains in the two samples from the Chachil Limestone (C-09-1 and 2; S 39° 13’ 17” – W 70° 33’ 37”) did not seem to be affected so strongly by Pb loss as those from AR08VT-14. In this case the grains were treated directly with chemical abrasion. The main problem with these populations, however, turned out to be the identification of the youngest, volcanic zircon component. The tested grains (Fig. 8c; Table 1) provide a wide range of apparent ages from the Mesoproterozoic to the Jurassic. The two oldest ages
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>sp in CA [2]</td>
<td>8</td>
<td>66.1</td>
<td>10.3</td>
<td>22.6</td>
<td>62</td>
<td>0.2094</td>
<td>0.0146</td>
<td>0.02963</td>
<td>0.00025</td>
<td>0.10</td>
<td>0.0036</td>
<td>1.6</td>
</tr>
<tr>
<td>2</td>
<td>lp in CA [4]</td>
<td>27</td>
<td>87.6</td>
<td>0.78</td>
<td>3.2</td>
<td>1345</td>
<td>0.2011</td>
<td>0.0012</td>
<td>0.02929</td>
<td>0.00009</td>
<td>0.62</td>
<td>0.04978</td>
<td>0.0023</td>
</tr>
<tr>
<td>3</td>
<td>lp in CA [5] RES</td>
<td>20</td>
<td>76.6</td>
<td>0.86</td>
<td>3.1</td>
<td>910</td>
<td>0.2007</td>
<td>0.0012</td>
<td>0.02918</td>
<td>0.00008</td>
<td>0.46</td>
<td>0.04987</td>
<td>0.0027</td>
</tr>
<tr>
<td>4</td>
<td>lp in CA [5] DISS</td>
<td>63</td>
<td>2.50</td>
<td>510.3</td>
<td>20</td>
<td>1.202</td>
<td>0.0069</td>
<td>0.0034</td>
<td>0.01</td>
<td>0.13</td>
<td>0.15</td>
<td>0.188</td>
<td>0.004</td>
</tr>
<tr>
<td>5</td>
<td>tip in CA [1]</td>
<td>3</td>
<td>94.9</td>
<td>0.91</td>
<td>2.5</td>
<td>227</td>
<td>0.2022</td>
<td>0.0058</td>
<td>0.02905</td>
<td>0.00012</td>
<td>0.46</td>
<td>0.0505</td>
<td>0.0014</td>
</tr>
<tr>
<td>6</td>
<td>lp in CA [3]</td>
<td>12</td>
<td>77</td>
<td>1.11</td>
<td>2.9</td>
<td>597</td>
<td>0.1992</td>
<td>0.0020</td>
<td>0.02887</td>
<td>0.00009</td>
<td>0.46</td>
<td>0.0506</td>
<td>0.0045</td>
</tr>
<tr>
<td>7</td>
<td>lp CA [2]</td>
<td>25</td>
<td>103.6</td>
<td>1.17</td>
<td>4.9</td>
<td>971</td>
<td>0.1977</td>
<td>0.0010</td>
<td>0.02880</td>
<td>0.00009</td>
<td>0.55</td>
<td>0.04979</td>
<td>0.0022</td>
</tr>
<tr>
<td>8</td>
<td>lp in A [1]</td>
<td>7</td>
<td>83.9</td>
<td>0.97</td>
<td>2.3</td>
<td>457</td>
<td>0.1879</td>
<td>0.0028</td>
<td>0.02720</td>
<td>0.00013</td>
<td>0.40</td>
<td>0.0501</td>
<td>0.0011</td>
</tr>
<tr>
<td>9</td>
<td>lp A [1]</td>
<td>1</td>
<td>165.1</td>
<td>1.01</td>
<td>0.9</td>
<td>337</td>
<td>0.1879</td>
<td>0.0045</td>
<td>0.02720</td>
<td>0.00013</td>
<td>0.40</td>
<td>0.0501</td>
<td>0.0011</td>
</tr>
<tr>
<td>10</td>
<td>lp A [1]</td>
<td>1</td>
<td>365.0</td>
<td>1.00</td>
<td>0.8</td>
<td>763</td>
<td>0.1861</td>
<td>0.0021</td>
<td>0.02692</td>
<td>0.00013</td>
<td>0.51</td>
<td>0.05014</td>
<td>0.0004</td>
</tr>
<tr>
<td>11</td>
<td>lp in A [1]</td>
<td>3</td>
<td>323.0</td>
<td>1.30</td>
<td>0.9</td>
<td>1852</td>
<td>0.0603</td>
<td>0.0090</td>
<td>0.02686</td>
<td>0.00092</td>
<td>0.50</td>
<td>0.05022</td>
<td>0.0023</td>
</tr>
<tr>
<td>12</td>
<td>Tuff, 9 m above base of Chachil Limestone; Vega del Tero, Chacay Melehue (AR08VT-14)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Tuff, 4.5 m below top of Chachil Limestone; Vega del Tero, Chacay Melehue (AR08VT-56)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Tuff in Chachil limestone, Mirador del Chachil Neúquen, Cuyo Group (C-09-1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Tuff in Chachil limestone, Mirador del Chachil Neúquen, Cuyo Group (C-09-2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Tuff, 9 m above base of Chachil Limestone; Vega del Tero, Chacay Melehue (AR08VT-14)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Tuff, 4.5 m below top of Chachil Limestone; Vega del Tero, Chacay Melehue (AR08VT-56)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>Tuff in Chachil limestone, Mirador del Chachil Neúquen, Cuyo Group (C-09-1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>Tuff in Chachil limestone, Mirador del Chachil Neúquen, Cuyo Group (C-09-2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Zircon: sp = short prismatic (l/w = 2–4); lp = long prismatic (l/w > 4); in = inclusions; bi = biotite; cld = cloudy interior; A = mechanical abrasion; CA = chemical abrasion; [1] = number of grains in fraction; DISS = dissolved zircon and residue after partial dissolution.

b Weight and concentrations are known to better than 10%, except for those near and below the ca. 1 µg limit of resolution of the balance.

c Th/U model ratio inferred from 208/206 ratio and age of sample.

d Pbc = total common Pb in sample (initial + blank).

e Raw data corrected for fractionation.

f Corrected for fractionation, spike, blank and initial common Pb; error calculated by propagating the main sources of uncertainty.

g Weights before partial dissolution step, thus exact U-concentration is uncertain.
are extrapolations from discordant analyses, whereas the other data are concordant indicating ages of 350 Ma (28), 300–296 Ma (20, 21, 29), and 192–188 Ma (22, 23, 31; Fig. 9c and d). Four of the grains from sample C-09-1 (24–27) and one from C-09-2 (32) plot in a tight cluster at the bottom of the dispersed array, yielding concordia ages of 186.0 ± 0.5 Ma and 185.9 ± 0.7 Ma, respectively (Fig. 9d). Because of their coherence, the latter data are considered to represent zircon crystals indigenous to the tuff, and hence to date the volcanic event. The two results combine into a weighted average age of 186.0 ± 0.4 Ma for extrusion of this tuff.

5. Discussion

The ages presented in this paper (ca. 182–186 Ma) are equivalent in a regional context with ages from different magmatic events in Patagonia and west-central Argentina, as follows: a) synrift magmatism related to the Precuyano Cycle, where ages between ca. 182–219 Ma were obtained (Rapela et al., 1983; Pángaro et al., 2002a; Franzese et al., 2006; Schiuma and Llambías, 2008); b) arc activity in the Subcordilleran Batholith in Patagonia which terminated at 180 Ma (Rapela et al., 2005); c) Chon Aike Magmatic Province, with ages between ca. 180–200 Ma (Pankhurst et al., 2000); and d) early stages of the Andean magmatic arc (Saini-Eidukat et al., 2002; Castro et al., 2011).

In the Neuquén province a volcanic arc coeval with the early stages of the Cuyo Group is recorded at Pliensbachian/Toarcian times represented by the Icalma Formation (nom. trans. Zanettini et al., 2010). This unit expands westwards into the Chilean territory where it is known as the Icalma Member of the Nacientes del Bío Bío Formation (Suárez and Emparan, 1997) where pillow lavas and basaltic breccias intercalated within marine sediments are recognized. This arc was likely the volcanic source of the ash material which persisted in the Chacay Melehue area fading out since the Pliensbachian up to the Toarcian/Aalenian boundary (Llambías and Leanza, 2005).

The new isotopic ages that we present in this paper are indeed useful for the time-calibration of the first marine transgression from the Pacific side in the southern Neuquén Basin. The first radiometric U–Pb data of the Chachil Limestone at the type locality, obtained on crystal zircons found in ash layers within limestone beds located 2.5 m above the base of the unit, confirm an Early Pliensbachian age (186.0 ± 0.4 Ma). This result matches with the Early Pliensbachian age ascribed by Riccardi (2008) to the Austro-morphites behrendseni Assemblage Zone introduced by Hillebrandt (1987, 2006). This Assemblage Zone is equivalent to the lower part of the Fanninoceras Assemblage Zone (Riccardi et al., 1990, 2000) and to the Davoei Standard Zone of Europe (Riccardi, 2008). The Chachil Limestone, or its time equivalent Sierra Chacaicó Formation, have so far been considered in the Chachil depocentre as the lowermost unit of the Cuyo Group (e.g. Leanza, 1992; Leanza and Hugo, 1997; Leanza et al., 2005; Franzese and Spalletti, 2001; Franzese et al., 2006, 2007; Muravchik et al., 2008; Carbone et al., 2011). This boundary coincides in the Chachil depocentre with the upper limit of the Precuyano Cycle.

In the Cordillera del Viento depocentre, the Chachil Limestone is reported here for the first time based on regional geological observations and new radiometric ages from Vega del Tero (Chacay Melehue area) allowing to confirm a Pliensbachian (185.7 ± 0.4 Ma) to earliest Toarcian age (182.3 ± 0.4 Ma). Taking into account that the latter age was obtained 4.5 m below the top of the Chachil Limestone, we infer that at this locality, the Pliensbachian/Toarcian boundary is recorded within the uppermost part of this unit.

Studies in the Atuel depocentre in southern Mendoza show that limestones of the upper section of Puesto Araya Formation are placed just at the base where the sag stage begins (Lanés, 2005;
Giambiagi et al., 2008; Lanés et al., 2008). At the Serrucho creek in southern Mendoza (Valenciana depocentre), Mazzini et al. (2010) calculated the age of the youngest limestones of the upper section of the Puesto Araya Formation (Fig. 7b) as Early Toarcian (182.16 ± 0.6 Ma). This last age is almost identical to the younger tuff layer within the Chachil Limestone at Chacay Melehue, with a U–Pb age of 182.3 ± 0.4 Ma. This undoubtedly allows correlation between the limestones of the upper Puesto Araya Formation (sensu Giambiagi et al., 2008) with the Chachil Limestone at Chacay Melehue.

Based on the new isotopic data and geological observations stated above, we consider the Chachil Limestone as a very important Early Jurassic stratigraphic marker of regional significance, representing an almost instantaneous flooding episode throughout the Neuquén Basin and marking the initiation of the Cuyo Group (Fig. 10), followed by widespread black shale deposition (e.g. Los Molles/Tres Esquinas Fms.).

The role of the Chachil Limestone proposed here as natural seal for the active rifting represented in the Precuyano Cycle is a key aspect of this contribution. Given the lively discussions on the upper limit of the active rifting stage in the Neuquén Basin by different authors (Franzese and Spalletti, 2001; Pángaro et al., 2002a; Leanza et al., 2005; Franzese et al., 2006, 2007; Muravchik et al. 2008, 2011; Carbone et al., 2011; García Morabito and Ramos, 2011; Arregui et al., 2011; D’Elia et al., 2012a,b, between others), the isotopic age calibration of this unit helps to delimit the uppermost age of the active rifting, at least in outcrops of the three depocentres treated here, including also subsurface occurrences at Anticlinal Campamento (Schiuma and Llambías, 2008) and Cupén Mahuida (Schiuma et al., 2011). It is still an open question to investigate what are the evidences that indicate that rift-related faults ceased prior to the deposition of the Chachil Limestone and/or if there is any influence of the rift topography over the accumulation of the lower Cuyo Group successions. According to subsurface information, especially at the Dorsal de Huincul area, it is clearly evidenced that synrift faulting has influenced the early accumulation of Los Molles Formation, at least up to the Late Toarcian (Silvestro and Zubiri, 2008; Carbone et al., 2011; Mosquera et al., 2011).

Although it is proved that the marine transgression into the Neuquén Basin begun in the Late Triassic (Riccardi et al., 1997) through the Curepto–Atuel seaway (Vicente, 2005), it is highly probable that the Pliensbachian flooding episode took place through new marine pathways opened across an early Jurassic dissected arc, which actually is covered by thick Cenozoic sequences.

The appearance of limestones in the Neuquén Basin is sudden and of wide distribution, as evidenced by the Chachil Limestone. This is in contrast with scarcity of limestones in the Precuyano Cycle, where only very localized and thin lacustrine limestones were reported (Muravchik and Franzese, 2005). This means that a dramatic change took place in the paleogeography and paleoclimate in the Basin, which marks the initiation of the Cuyo Group.

Another aspect to have in consideration is that the halfgrabens at the time of the infill of the Precuyano deposits had in some places steep borders. As an example, in the Lapa area, coarse brecciated conglomerates are developed at the base of the Sierra Chacaico Formation which is time-equivalent to the Chachil

\[182.16 ± 0.6 \text{ Ma} \]

**Fig. 10.** Correlation of the Chachil Limestone indicating the new U–Pb age calibration from north to south in the Valenciana, Cordillera del Viento and Chachil depocentres. Note that in Valenciana depocentre the older unit cropping out is El Freno Formation (Early Jurassic), so further correlations with basement units could not be made. Abbreviations: Ñi, Ñireco Fm.; La, Lapa Fm.; Ch, Chachil Limestone; LM, Los Molles Fm.; CV, Cordillera del Viento Fm.; MM, Milla Michicó Fm.; LP, La Primavera Fm.; EF, El Freno Fm.; PA, Upper Puesto Araya Fm.; TE, Tres Esquinas Fm.
Limestone (Leanza, 1992; Leanza et al., 2005). This means that accumulation of limestones at the shorelines was not always continuous, as it was interrupted in certain places by sedimentary material delivered from the source area into the basin.

Although further regional and detailed studies are needed at other localities, our results lead to consider the Precuyano Cycle as the sedimentary (either continental or marine) and volcanic infill of halfgrabens and/or grabens dominated by a strong extensional regime (synrift), deposited between the Huarpican unconformity and up to the initiation of the sag stage at Plisensbacherian/earliest Toarcian times, in coincidence with the development of limestones. Units with interbedded marine sediments (e.g. La Primavera Formation, Cordillera del Viento depocentre) previously taken as a part of the Cuyo Group, are ascribed to the Precuyano Cycle. If the same view is applied to the Atuel depocentre, the Arroyo Malo, El Freno and the lower section of Puesto Araya Formations could be interpreted as forming part of the Precuyano Cycle, whereas the upper section of the Puesto Araya Formation can be ascribed to the Cuyo Group, in coincidence with the initiation of sag stage in the basin.

Finally, another interesting aspect of the Chachil Limestone is its paleoclimatological significance in the Early Jurassic history of the Neuquén Basin. At Plisensbacherian-earliest Toarcian times, a biodiversity peak either considering ammonites (Riccardi, 2008), or bivalves (Damborenea, 1987; Leanza, 1993) and brachiopods (Manceñido, 1990) as well as microfossils (Ballent and Whatley, 2000) in association with corals was recorded. Apart from this, paleomagnetic data from ammonite bearing marine sections in the Lower Jurassic at the Chacay Melehue area (Iglesia Llano et al., 2006; Iglesia Llano, 2008) suggest that South America was shifted to its northernmost position. These studies support that in western Gondwana deposits of limestones in marine warm water environments existed at that time, thus allowing to consider the Chachil Limestone as a paleoclimatic event of regional significance.

6. Conclusions

Regional observations and new radiometric data from the Chachil, Cordillera del Viento and Valenciana depocentres, show that the Chachil Limestone is an important Early Jurassic stratigraphic marker representing an almost instantaneous flooding episode throughout the Neuquén Basin (Fig. 10). The limestone marks the initiation of the Cuyo Group, followed by widespread black shale deposition (e.g. Los Molles/Tres Esquinas Formations). This conclusion is supported by zircon dating (ca. 182–186 Ma) of tuff layers deposited at about the same time as Plisensbacherian–Early Toarcian limestones present in the three depocentres (Fig. 10).

As it is represented in recent paleogeographic maps, the Early Jurassic (Plisensbacherian–earliest Toarcian) marine transgression is inferred to have penetrated into the basin in southern Mendoza through the Curepto–Atuel seaway (Vicente, 2005; Arregui et al., 2011). However, according to our interpretation, to explain an almost instantaneous flooding episode represented by the Chachil Limestone we suggest that other connections of the basin with the open sea through a dissected magmatic arc existed at that time.

With regard to still open nomenclatural problems in the Neuquén Basin, our findings suggest that the Precuyano Cycle should be considered as the sedimentary (either continental or marine) and volcanic infill of halfgrabens and/or grabens formed in an extensional regime in the period between the Huarpican unconformity and up to the initiation of the sag stage, in the Plisensbacherian to the earliest Toarcian, in coincidence with the Rioauelian unconformity (see Figs. 2, 4 and 7). As a result, the shallow marine volcanogenic deposits of La Primavera Formation at the Cordillera del Viento depocentre are ascribed to the Precuyano Cycle instead of being the lower part of the Cuyo Group, as up to now has been considered.

Finally, based on paleontological evidence and paleomagnetic data mentioned in the discussion, the Chachil Limestone is regarded as an important paleoclimatic event of regional significance.

Acknowledgments

This study was supported by a Centre of Excellence grant to PGP, by a Young Outstanding Researcher grant (180678/V30) to Henrik Svensen, both of them from the Norwegian Research Council and by the grant PIP 5222 CONICET (Argentinian Research Council) to Héctor A. Leanza. The authors would like to thank Carlos Portilla (Dirección General de Minería, Zapala) for authorizing works in the Neuquén province, Alberto Garrido (Dirección General de Minería, Museo Olsacher, Zapala) for his help in obtaining samples from the Chachil Limestone type locality, Claudia Negro (SEEGMAR, Buenos Aires) for helpful comments on the Valenciana depocentre, and José Mendía (Dirección de Geología Regional, SEEGMAR, Buenos Aires) for its support for making possible this study.

References
