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Chemostratigraphy of the Pliensbachian, Puesto Araya Formation (Neuquén Basin, Argentina)

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---| **A B S T R A C T** |---

In a preliminary attempt to establish an isotope stratigraphy, strontium, carbon and oxygen isotope ratios were determined from marine biogenic carbonates of Pliensbachian age, in the context of scheme of local ammonite Zones correlatable to the European Standard Zonation. Two sections, río Atuel and arroyo Serrucho, of the mainly siliciclastic Puesto Araya Formation, Neuquén Basin, south-western Mendoza, Argentina, were studied. Specimens of the bivalve genera *Weyla* Bhöm and *Gryphaea* Lamarck were selected for the isotopic determinations because of their low-Mg calcite original mineralogy and widespread presence. Scanning electron microscopy, X-ray diffraction and X-ray fluorescence spectrometry techniques were used to control the good degree of preservation of most of the biogenic material, as evidenced by pristine fabrics, 100% calcite composition and Sr, Mn and Fe concentrations. Although strontium isotope ratios are slightly scattered, it is possible to compare them with those of the Early Jurassic seawater reference curve. Carbon isotope signals show two relative maxima, correlatable with those recorded for the upper part of the *Ibex* Zone and the middle part of the *Margaritatus* Zone in various European sections, indicating the possible global significance of these events. $\delta^{18}O$ values were found to be unreliable for isotope stratigraphy, as they are largely depleted in comparison to those of coeval unaltered marine carbonates.

KEYWORDS | Chemostratigraphy. Ammonite Zonation. Bivalve shells. Pliensbachian.

INTRODUCTION

Fluctuation in carbon, oxygen and strontium isotopic compositions in carbonates for biostratigraphically well-dated successions, has been used to construct seawater isotope variation curves through geological time. Thus, isotope stratigraphy has become a good tool for correlat-ing and dating marine sedimentary successions. The variation of geochemical parameters has also been used as a proxy for determining palaeoceanographic changes.

Strontium isotope stratigraphy is based on three principles. First, the oceanic $^{87}Sr/^{86}Sr$ ratio has been homogeneous at any time as a consequence of the long residence

time of strontium compared to the short mixing time of the ocean. Second, the seawater $^{87}Sr/^{86}Sr$ ratio has varied systematically through geological time and, third, the $^{87}Sr/^{86}Sr$ value is recorded in biogenic calcium-bearing minerals, precipitated from the ocean water, without fractionation. Since the publication of Burke's strontium curve (1982), strontium isotope stratigraphy (SIS) has become a useful method to date marine sediments. A high resolution strontium isotope curve for the Early Jurassic has been constructed by Jones et al. (1994) and Jones and Jenkyns (2002) on the basis of British marine successions. Jenkyns et al. (2002) presented a general curve for the Jurassic including additional data from Europe, Canada and New Zealand.

Carbon isotope stratigraphy (Kaufman and Knoll, 1995; Veizer et al., 1999; Jenkyns et al., 2002) is based on isotopic fractionation associated with partitioning of the global carbon pool between reduced (organic carbon) and oxidized (carbonate - bicarbonate - carbon dioxide) reservoirs due to continental weathering, global sedimentation rates, primary productivity, organic carbon burial and ocean circulation mode.

Oxygen isotope stratigraphy (Podlaha et al., 1998; Jacobsen and Kaufman, 1999) is based on isotopic fractionation related to changes in palaeotemperatures and evaporation-precipitation balance in seawater.

In the Aconcagua-Neuquén Basin of west-central Argentina, or in short, the Neuquén Basin, the Lower Jurassic, and especially the Pliensbachian, is well represented, and biostratigraphic studies have shown a succession of local ammonite Zones (Riccardi et al., 2000) correlatable to the European Standard Zonation. Thus, the Neuquén Basin provides an excellent opportunity to study the Early Jurassic seawater isotopic variation of sections in the Southern Hemisphere.

This work includes new strontium, carbon and oxygen isotope ratios measured on bivalve shells from the Pliensbachian marine succession of Puesto Araya Formation. Data were obtained from two sections with a detailed biostratigraphical control, based on ammonite Zones. This is the first attempt to establish an isotope stratigraphy for the Jurassic of Argentina.

GEOLOGICAL SETTING

The Neuquén Basin (Fig. 1) is a roughly north-south oriented back-arc basin comprising a Mesozoic-Cenozoic sedimentary succession at least 7 km thick (Gulisano and Gutiérrez Pleimling, 1995; Legarreta and Uliana, 1999). The basin was formed due to extensional tectonics in the Early Mesozoic. Sedimentation began in the Triassic as
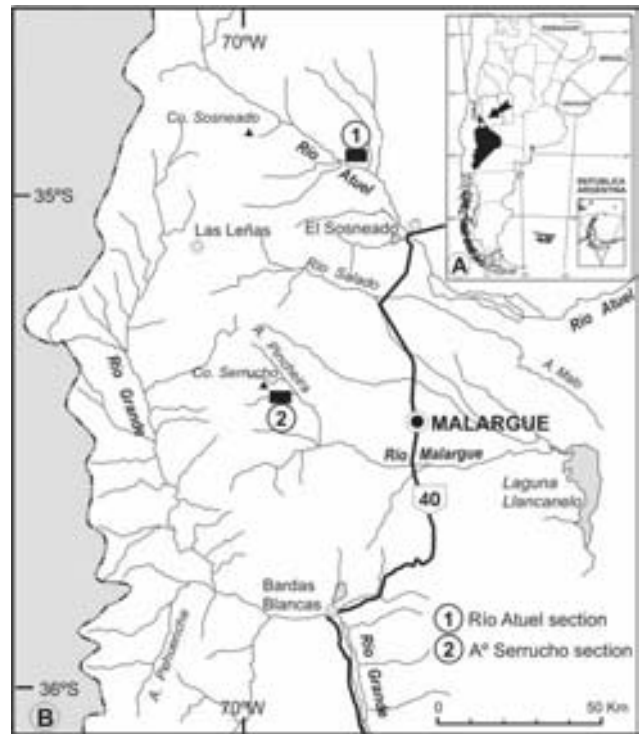

FIGURE 1 | **Location map: A) Neuquén Basin. B) Studied sections of the Puesto Araya Formation in the northern area of the Neuquén Basin.**

volcanic and coarse-grained continental deposits, and from the Late Triassic onwards a narrow marine corridor was established in the northern area of the basin. This sea expanded in the Pliensbachian-Toarcian, producing a westwards prograding clastic system and deep basin turbidites. Ammonites of the Andean region, present throughout, are especially well represented, and have been used to produce a detailed biozonation (Riccardi et al., 1999, 2000) that, even if partly based on endemic East

FIGURE 2 | **Ammonite Zonation for the Pliensbachian - Toarcian in the Neuquén Basin. After Riccardi et al. (2000).**

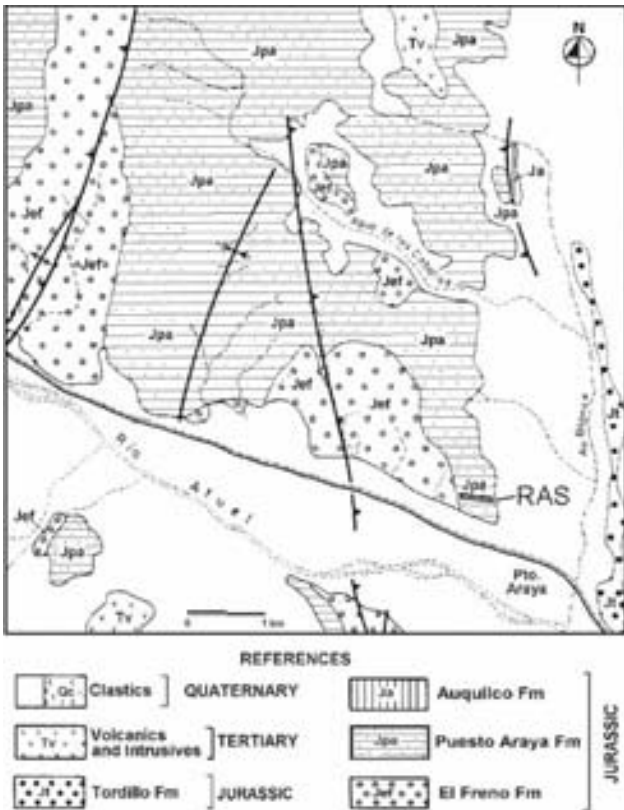Pacific fauna, is correlatable with the European Standard Zonation (Fig. 2).

The two studied stratigraphical sections of the Puesto Araya Formation (Fig. 1) are located, approximately 60 km from each other, in the northern area of the Neuquén Basin, in south-western Mendoza: one at río Atuel (RAS) and the other at arroyo Serrucho (ASS). Figures 3 and 4 show the geological maps of these areas. The Puesto Araya Formation is made up of estuarine and marine deposits, mainly composed of massive or cross-bedded normally graded coarse- to fine-grained sandstones. Subordinate thin limestones are present in ASS. Both successions bear a rich bivalve fauna, associated with ammonites, brachiopods, gastropods, corals, foraminifera and ostracods. The Puesto Araya Formation attests to a shallower water shelf with occasional storms. Variety of benthic fauna, epifauna, and trace fossils indicate lower sedimentation rate in well-oxygenated waters. Towards the top of the succession a decrease in grain size and storm generated sedimentary structures, associated with an increase in organic matter contents, indicate a deeper sedimentation in less oxygenated (dysaerobic) waters (Lanés, 2002). The Puesto Araya Formation is Sinemurian-Toarcian in age (Damborenea and Manceñido, 1993).

METHODS

Specimens of the bivalve genera *Weyla* Bhöm and *Gryphaea* Lamarck were selected for isotopic determinations because their original low-Mg calcite mineralogy is the most resistant to diagenesis, and because they are common in the two studied sections. Shells were collected from different strata without preferred size or orientation, articulated or not and sometimes fragmented.

To assess the state of preservation of each sample they were examined by scanning electron microscopy (SEM). Microstructural analyses showed that shells retained their pristine fabrics: complex cross foliated (CCF) and cross foliated (CF) in *Gryphaea* Lamarck and CCF in *Weyla* Bhöm (Carter, 1990). Slight microdissolutions in calcite fibres were observed in all samples. Well-preserved material was then cleaned to remove detrital contamination, following techniques described in Cagnoni et al. (2001). Samples were also evaluated for mineral homogeneity by X-ray diffraction and it was determined that shells are composed by 100% calcite. Trace element analyses were performed by X-ray fluorescence at the Instituto de Geocronología y Geología Isotópica (INGEIS) with a wavelength dispersive Philips PW 1410 spectrometer. Sr, MnO and total Fe_2O_3 concentrations were determined on compacted powered samples, free of organic matter. International standards NBS-1b, NIST-1c, NIST-88b, JLs-1 and JDo-1 were used as reference materials. Analytical uncertainties are 2% for Sr, 7% for total Fe_2O_3 and 12% for MnO. Precision of the analyses is better than 2% for Sr and total Fe_2O_3 and 5% for MnO.
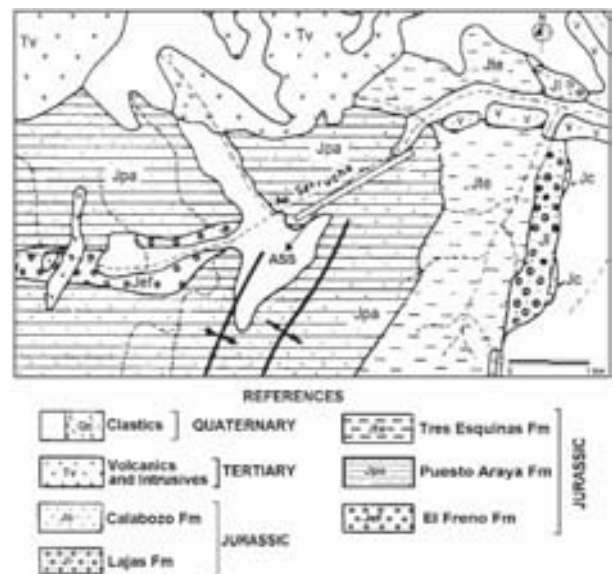
Sr isotopic determinations were performed at the INGEIS and at the Centro de Geociencias, Universidad Federal do Pará, Belem, Brazil with a Vg 54 R double collector and a Vg 54 E single collector mass spectrometer respectively. All results were normalized to the Eimer and Amed standard (0.708000).

Carbon and oxygen isotopic analyses were carried out at the INGEIS following the usual techniques (McCrea, 1950 and later modifications) and measured in a Finnigan MAT triple collector Delta S mass spectrometer. All data are reported in the conventional per mil deviation (δ‰) and referred to the V-PDB standard. The analytical error is 0.1 ‰ ($\pm 2\ \sigma$) for both δ^{13}C and δ^{18}O.

RESULTS

Trace elements

Sr, Mn and Fe concentrations are used as indicators of diagenetic changes, evidenced by depletion in Sr and increase in Mn and Fe contents (Brand and Veizer, 1980; Anderson et al., 1994). The Sr contents (Table 1) of the studied samples are within determined ranges for bivalves (Anderson et al., 1994). The pronounced difference in the Sr contents between specimens of *Gryphaea* Lamarck (*ca*. 500 ppm) and *Weyla* Bhöm (*ca*. 800 ppm) is probably associated to biological control (Morrison and Brand, 1988). Some samples show slightly higher concentrations of Mn and Fe (Table 1). Mn contents up to *ca*. 400 ppm would be related to facies control (oxygen depleted

waters) and not to diagenetic modifications (Morrison and Brand, 1988). High Fe values (>500 ppm) are related to the presence of small quantities of pyrite and oxide coatings, that could not be eliminated completely from fossil surfaces. Considering trace element contents, samples PA 29, PA 40 (RAS) and ASPA 33 (ASS) are the best preserved.

Strontium isotopes

In this work Sr isotope data were obtained for one sample from RAS and for seven samples from AAS (Table 1). The sample (PA 15d) from RAS (Fig. 5) comes from the lower part of the *Dubariceras* Zone (= Upper *Ibex* Zone) and its ^{87}Sr/^{86}Sr value is in agreement with those of the Jurassic isotope curve (Jones, 1994). The other strontium isotope data are from the arroyo Serrucho section (Fig. 6) where ammonites are less abundant. Isotopic signals show a monotonic falling trend from sample ASPA 85-1, which underlies ammonites of the *Dubariceras* Zone (= Upper *Ibex*—Lower *Davoei* Zones) to ASPA 26, which underlies ammonites of the *Dactylioceras hoelderi* Zone (= *Falciferum* Zone). Samples ASPA 69-70, ASPA 33 and ASPA 32 have been discarded since the Sr isotope ratios do not match the corresponding biostratigraphical position, indicating that the Sr isotope system did not remain closed to post-depositional processes. Although data are slightly scattered (Table 1), they are in agreement with the European reference curve (Jones et al., 1994; Jones and Jenkyns, 2001) and the obtained stratigraphic resolution is within one or two ammonite Zones.

TABLE 1 | **C, O and Sr isotope ratios and elemental concentrations.**

RIO ATUEL SECTION (RAS)

Sample	Genera	δ^{13}C	δ^{18}O	^{87}Sr/^{86}Sr	Sr ppm	Mn ppm	Fe ppm
PA 67	*Weyla*	1,6	-6,4	-	823	133	580
PA 51-1	*Weyla*	1,0	-6,7	-	701	385	802
PA 48-1	*Weyla*	1,1	-7,5	-	852	153	471
PA 40	*Weyla*	1,6	-7,1	-	864	238	236
PA 29	*Gryphaea*	2,7	-5,7	-	467	105	259
PA 18-19d	*Weyla*	0,6	-8,2	-	748	280	943
PA 15d	*Gryphaea*	2,1	-7,0	0.70732 ± 6	478	348	443

ARROYO SERRUCHO SECTION (ASS)

Sample	Genera	δ^{13}C	δ^{18}O	^{87}Sr/^{86}Sr	Sr ppm	Mn ppm	Fe ppm
ASPA 26	*Gryphaea*	1.8	-14.5	0.70722 ± 3	476	240	532
ASPA 33	*Gryphaea*	2.3	-14.7	0.70738 ± 9	522	46	259
ASPA 32	*Weyla*	0.9	-14.9	0.70729 ± 3	818	112	595
ASPA 69	*Weyla*	2.0	-16.0	0.70726 ± 5	803	185	468
ASPA 69-70	*Weyla*	2.2	-15.3	0.70760 ± 6	783	476	352
ASPA 80a	*Weyla*	2.2	-15.4	0.70725 ± 3	790	216	447
ASPA 85-1	*Weyla*	2.6	-16.6	0.70734 ± 6	840	209	643

Carbon isotopes

First we analysed δ^{13}C variations (Table 1) from samples in RAS (Fig. 5), where abundance of key ammonites, between the lower part of the *Dubariceras* Zone (= Upper *Ibex* Zone) and the *Fanninoceras disciforme* Zone (= *Spinatum* Zone) supports a more accurate biostratigraphy than in arroyo Serrucho section. In this interval, we find a carbon isotope composition of 2.1‰ in the lower part of the *Dubariceras* Zone, followed by a rise to a maximum of 2.7‰ in the upper part of the *Dubariceras* Zone (= Upper *Ibex*—Lower *Davoei* Zones). Then values decay away from the boundary between *Fanninoceras behrendseni* and *fannini* Zones (= Lower *Margaritatus* Zone) to *Fanninoceras disciforme* Zone (= *Spinatum* Zone) to reach a minimum of 1.0‰ in a *Weyla* shell located slightly higher up in the section. A new rise in δ^{13}C values begins in levels that, although ammonites were not recorded, are close to the Pliensbachian-Toarcian boundary.

In the arroyo Serrucho section (Fig. 6) ammonites indicate the *Dubariceras* Zone (= Upper *Ibex*—Lower *Davoei*) to *Falciferum* Zone (= *Dactylioceras hoelderi* Zone). The C isotope record (Table 1) has a maximum of 2.6‰ in levels (ASPA 85-1) immediately underlying ammonites of the *Dubariceras* Zone. Going up in the stratigraphic succession, δ^{13}C values remain almost constant through the *Dubariceras* Zone to *Fanninoceras fannini* Zone (= Mid-Upper *Margaritatus Zone)*, with values rounding 2.2‰. A minimum of 1.8 ‰ (ASPA 26) is registered towards the *Dactylioceras hoelderi* Zone (= *Falciferum* Zone).

Carbon isotopic values of samples PA 18-19d (RAS) and ASPA 32 (ASS) were not considered in the isotope stratigraphy since they have chemical and isotopic evidences of diagenetic changes. No isotopic fractionation was found between specimens of both bivalve genera, *Weyla* Bhöm and *Gryphaea* Lamarck.
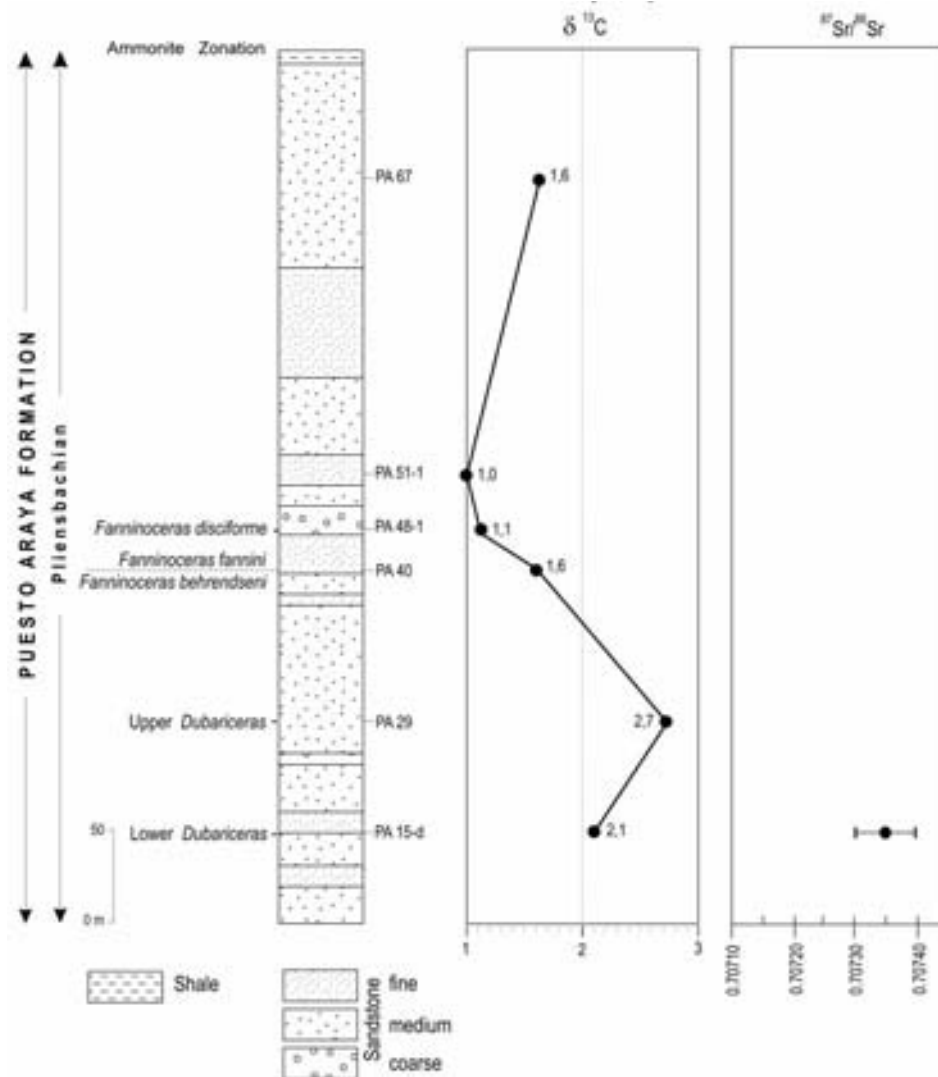

FIGURE 5 | **Lithological section of Puesto Araya Formation at the río Atuel section (RAS) (simplified and modified after Lanés, 2002) with C and Sr isotope data and ammonite Zones.**
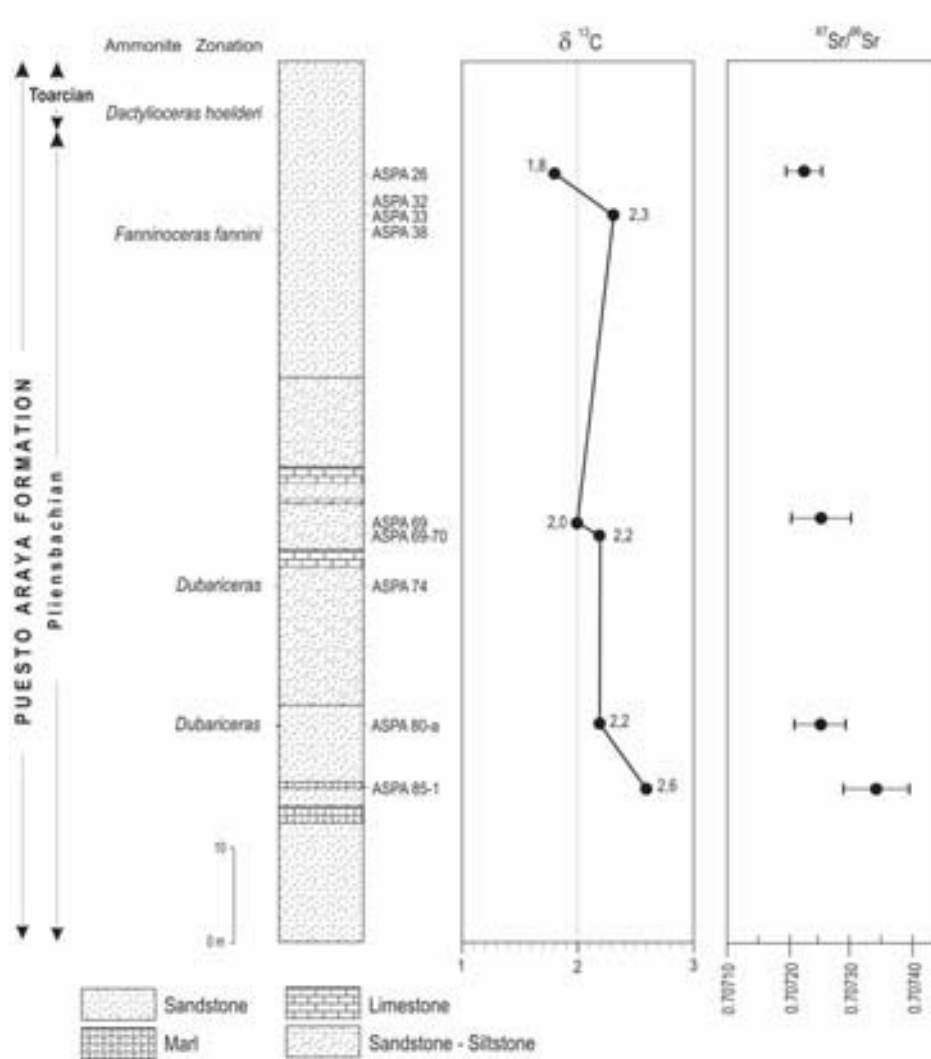
FIGURE 6 | **Simplified lithological section of Puesto Araya Formation at arroyo Serrucho section (ASS) with C and Sr isotope data and ammonite Zones.**

Oxygen isotopes

Oxygen isotope composition of bivalve shells in the two studied sections (Table 1), shows evidence of diagenetic interaction with isotopically light fluids (Popp et al., 1986). Thus, in both successions, obtained values are depleted in comparison to those of the coeval unaltered marine carbonates (Veizer et al., 1999) and do not reflect primary isotopic composition of ocean water.

In ASS signals vary between -16.6‰ and -14.5‰, indicating probable interaction with very depleted fluids under a strong altitude effect, like those of present Andean rivers (Panarello and Dapeña, 1996) at the same latitude.

On the other hand, $\delta^{18}O$ values in RAS evidence quite minor diagenetic changes. This might be related to the fact that isotopic equilibrium between oxygen of water and carbonate has not yet been attained as in ASS. Never-

theless, an equilibration with less negative local waters (Panarello and Dapeña, 1996) could also be considered as a probable cause for these more enriched values.

DISCUSSION

To construct the isotope stratigraphy for the Pliensbachian in the Neuquén Basin, south-western Mendoza, we have integrated Sr and C isotope values obtained from bivalve shells of Puesto Araya Formation (Figs. 5 and 6) with the Andean Zones and Standard Biozones based on ammonites (Fig. 2).

In the río Atuel section a Sr isotope value (sample PA 15d) was obtained in beds included in the lower part of the *Dubariceras* Zone (= Upper *Ibex* Zone) which is in agreement with the Sr isotope value of the Early Jurassic seawater reference curve (Jones, 1994; Jones and Jenkyns, 2001).

Higher up in the RAS succession, sample PA 29 (upper part of the *Dubariceras* Zone = Upper *Ibex*—Lower *Davoei* Zones) has a positive shift ($\delta^{13}C$=2.7‰) compared to sample PA 15d. Sample preservation of the former, as is evidenced by trace elements, indicates that its isotopic signal can be considered primary. A similar value ($\delta^{13}C$=2.6‰) was obtained on ASPA 85-1 from the arroyo Serrucho section. Shell preservation is also good in spite of the slightly high Fe content. Its Sr isotope value corresponds to that recorded for the *Ibex* Zone. Similar carbon isotope values were reported by Morettini (Jenkyns et al., 2002) in the pelagic-carbonate sections of the Upper *Ibex* Zone in the Apennines of Italy. The same relative maximum registered for this biozone was also identified by Rosales et al. (2001) on belemnite rostra in the Basque-Cantabrian Basin of northern Spain.

The Upper *Ibex* Zone relative maximum is followed in ASS by a fall in the carbon isotope values that remain almost constant from samples ASPA 80a to ASPA 69. A level (ASPA 74) located between the beds containing samples ASPA 80a and ASPA 69, bears *Eoamaltheus* sp. and indicates the *Dubariceras* Zone (= Upper *Ibex*—Lower *Davoei* Zones). Sr isotope values for ASPA 80a and ASPA 69 are consistent with those recorded for the Lower *Ibex*-Upper *Davoei* Zones.

The *Fanninoceras behrendseni – Fanninoceras fannini* boundary (= Lower *Margaritatus* Zone) in RAS is represented by sample PA 40, that shows the continuity in the decay tendency of $\delta^{13}C$ signal. In AAS, sample ASPA 33 evidences an increase in carbon isotope composition ($\delta^{13}C$=2.3‰) in comparison with lower levels. Geochemical data indicate that this sample is well preserved. Most probably it comes from the *Fanninoceras fannini* Zone (= Mid-Upper *Margaritatus* Zone), according to the ammonites found immediately below (ASPA 38). This value is consistent with the positive $\delta^{13}C$ excursion documented by Jenkyns and Clayton (1986) in the *Subnodosus* Subzone, *Margaritatus* Zone, for various pelagic-carbonate sections in the Alpine-Mediterranean (Tethyan) region. A similar positive shift was reported by Rosales et al. (2001) for the same biostratigraphic level in northern Spain. Higher up in the same section (ASS), sample ASPA 26, with a Sr isotope value in agreement with Upper *Ibex*—Mid *Margaritatus* Zones, has a carbon isotope signature that decays from the previous relative maximum attained.

In RAS ammonites coming from level PA 48-1 indicate the *Fanninoceras disciforme* Zone (= *Spinatum* Zone) where the decay in the carbon isotope signal continues. The same falling tendency is observed in sample PA 51-1 located upward in the same succession. This minimum in carbon isotopic composition is followed by a new enrichment in the carbon isotopic signal (sample PA 67; $\delta^{13}C$=1.6‰). This value probably preludes the way to the large positive excursion registered by Jenkyns and Clayton (1986) in the Lower *Falciferum* Zone.

The most conspicuous points in the carbon chemostratigraphic pattern are the two relative maxima registered in the Upper *Ibex* and Mid *Margaritatus* Zones. These minor positive excursions match both hemispheres and may be global in character. Jones and Jenkyns (2001) attributed their origin to unusual high storage rates of organic carbon in the sedimentary record, which left the ocean-atmosphere system enriched in isotopically heavy carbon.

CONCLUSIONS

This work is the first attempt to establish an isotope stratigraphy for the Jurassic of Argentina. Carbon and strontium isotopes determined from marine bivalve shells have proven to be useful for correlating and integrating two sections with a detailed ammonite Zonation of the Puesto Araya Formation, and in the correlation between them and the Early Jurassic seawater reference curves. These information allowed to outline the carbon and strontium isotope stratigraphy through the Pliensbachian, in the Neuquén Basin, southwestern Mendoza.

Strontium isotope data are in agreement with the European reference curve and the obtained stratigraphic resolution is within one or two ammonites Zones.

A quite good correlation was found between the carbon isotope variation pattern across the Pliensbachian in the Neuquén Basin and those established for various sections of the same age in the Alpine-Mediterranean region, Apennines of Italy and Basque-Cantabrian Basin of northern Spain. The most conspicuous points in the chemostratigraphic pattern are two carbon isotope relative maxima that match both hemispheres, one in the Upper *Ibex* Zone and the other in the Mid *Margaritatus* Zone. These minor positive excursions may be global in character.

Oxygen isotopes of the carbonatic shells are exchanged with isotopically depleted post-depositional fluids, making $\delta^{18}O$ values unreliable for isotope stratigraphy.

Taken into consideration the quite good textural preservation, the mineralogical homogeneity and the trace element contents together with the Sr, C and O isotopic signals by themselves, it could be assessed, as has been pointed out in Cagnoni et al. (2001), that the three isotope systems behaved differently under the same water/carbonate interaction. While O, the most sensitive indicator of diagenesis was largely exchanged, the Sr isotope system not always remained closed and the C has mostly retained the primary isotopic signature.

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