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$^{87}Sr/^{86}Sr$ Late Miocene age of fossil molluscs in the 'Entrerriense' of the Valdés Peninsula (Chubut, Argentina)

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Abstract

$^{87}Sr/^{86}Sr$ analysis on calcitic shells of pectinids (*Chlamys actinodes* and *Chesapecten crassus*) and oysters (*Ostrea* sp.) shows that the 'Entrerriense' sequence belonging to the Puerto Madryn Formation, Valdés Península (Chubut), was deposited at about 10.0 ± 0.3 Ma. Thus, a middle Tortonian age is assigned to the sequence. Within the sequence, the pectinids better retain their original $^{87}Sr/^{86}Sr$ ratio, whilst the oysters are altered and yield older-than-real ages. The latter is the result of greater susceptibility to interaction with diagenetic fluids bearing Sr derived from the alteration of tuffaceous materials and volcanic rocks of intermediate and basic composition.

Resumen

Análisis de $^{87}Sr/^{86}Sr$ en conchillas calcíticas de pectínidos (*Chlamys actinodes* y *Chesapecten crassus*) y ostras (*Ostrea* sp.) demuestran que la secuencia 'Entrerriense' correspondiente a la Formación Puerto Madryn, de Península Valdés (Chubut), fue depositada alrededor de los 10.0 ± 0.3 Ma. Por lo tanto esta secuencia es de edad tortoniana media. Los pectínidos retienen mejor la relación original de $^{87}Sr/^{86}Sr$ mientras que las ostras se alteran más fácilmente e indican edades más antiguas que las reales. Esto se debe a que son más susceptibles a interactuar con fluidos diagenéticos portadores de Sr derivado de la alteración de materiales tobáceos y rocas volcánicas de composición intermedia y básica.

Keywords: Entrerriense; Coquinas; Late Miocene; Cool water carbonates; Patagonia; $^{87}S./^{86}Sr$

1. Introduction

The 'Entrerriense' or 'Paranense' Sea, that flooded a large part of South America during the Neogene, deposited sediments identified as the Puerto Madryn Formation (Haller, 1978) in northeastern Patagonia, Argentina, as the Paraná Formation (Yrigoyen, 1969) in the Paraná River area of Entre Ríos Province, Argentina, and as the Camacho Formation (Goso and Bossi, 1966) in Uruguay. The age of these beds has been controversial since d'Orbigny (1842) assigned them to the Tertiary, with modern estimates of age ranging from Middle to Late Miocene. Here we show that measurement of $^{87}Sr/^{86}Sr$ in fossils from the 'Entrerriense' deposits yield precise ages for sections exposed in northern Patagonia and allow a Late Miocene age to be assigned to the unit.

2. Geological setting and previous age determinations

The Puerto Madryn Formation crops out in northeastern Patagonia around the Valdés Península (Fig. 1A,B). The unit comprises a flat-lying, 200 m-thick sequence of coquinas, cross-bedded sandstones with mud drapes, mudstones with heterolithic lamination, and laminated or massive, totally bioturbated mudstones (Fig. 1C). This sequence spans a transgressive–regressive cycle within an overall

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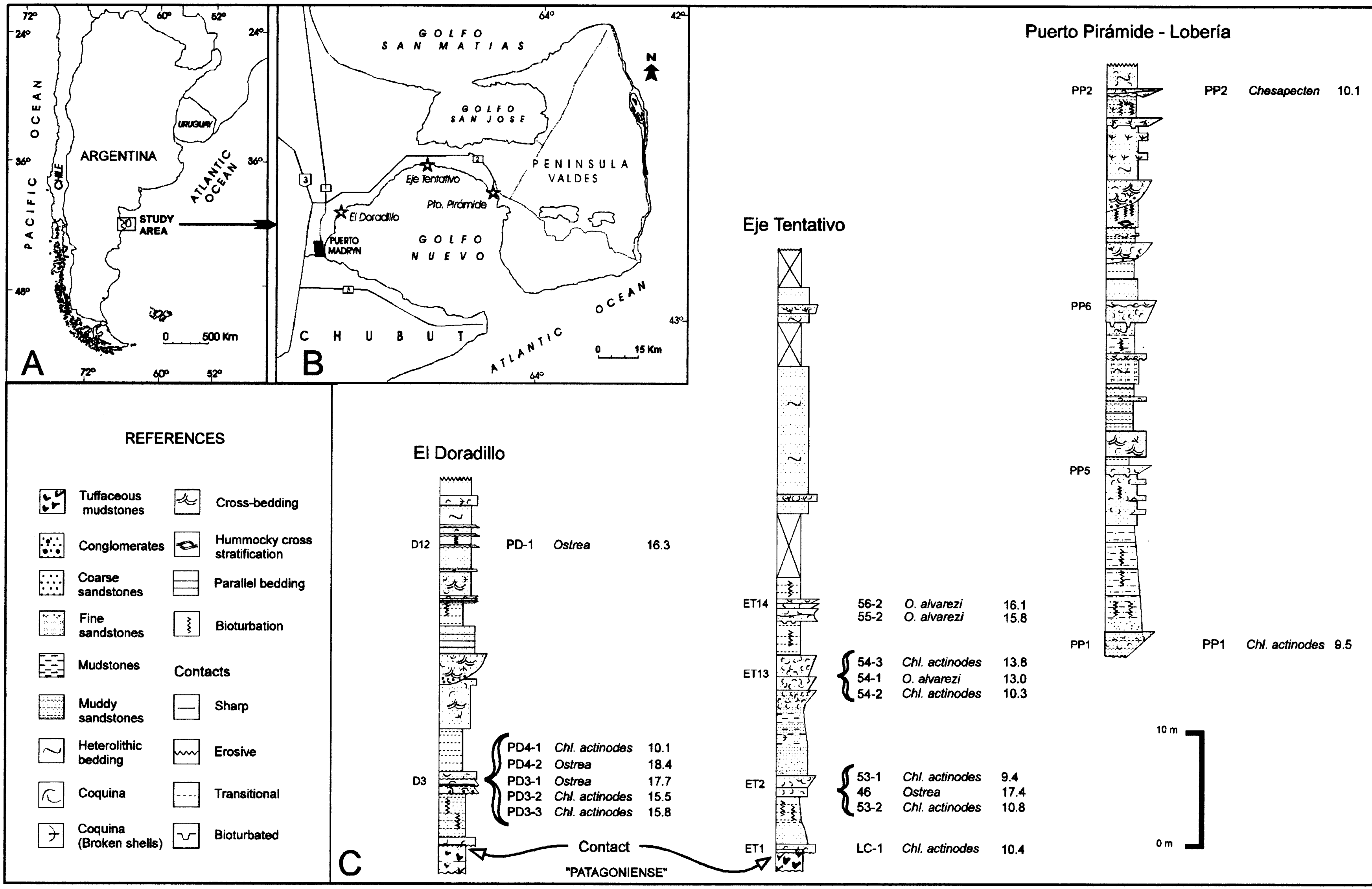

Fig. 1. (A) and (B) Location maps. Star symbols in (B) indicate the locations of the studied sections. (C) Sedimentologic logs of the 'Entrerriense' beds that crop out in the cliffs along the north coast of Golfo Nuevo, Chubut (only the lower 50 m of the Puerto Pirámide–Lobería section is shown). Stratigraphic levels of the samples and $^{87}Sr/^{86}Sr$ ages (Ma) are indicated.

regressive sequence (Scasso and del Río, 1987). It was deposited in a shallow shelf with storm influence, evolving upwards into a tide-dominated estuarine environment. Thick fossiliferous coquinas occur throughout the sequence and yield a diverse and abundant molluscan fauna of bivalves and gastropods, together with brachiopods, bryozoans, and echinoids. The Puerto Madryn Formation overlies the Upper Oligocene–Lower Miocene Gaiman Formation (Mendía and Bayarsky, 1981; Scasso and Castro, 1999). The bounding surface between these units is interpreted as a coplanar transgressive-ravinement surface (Scasso et al., 1999; del Río et al., 2001). A marked erosive surface separates the Puerto Madryn Formation from the overlying ?Pliocene to Recent fluvio-glacial gravels ('Rodados Patagónicos').

The age of the 'Entrerriense' deposits has been discussed since the middle of the 18th century and, up to now, estimates of age have been based mainly on the widespread and characteristic malacological content in the shallowest deposits of the 'Entrerriense' sequence. The Paraná Formation was placed in the Eocene by d'Orbigny (1842), whereas Philippi (1893) and Borchert (1901) considered it to be of Pliocene age. By assessing the percentage of Recent taxa present in the units (Lyellian percentages), Ihering (1907) concluded that the molluscan fauna from the Paraná Formation as well as that contained in the Puerto Madryn Formation were of Early Miocene age.

The ostracod fauna in the 'Entrerriense' of Patagonia allowed García (1970) to assign a Miocene age to the beds that crop out at Puerto Pirámide, whilst a Late Miocene age was proposed by Malumián and Masiuk (1973), based on the presence of the benthic foraminiferal species *Prothelphidium tuberculatum* — a taxon recognised in the Paris Basin and widely dispersed in the Argentine 'Entrerriense' deposits. On the basis of correlations from borehole data (370–55 m in the oil well YPF Ch P.V. es-1) Masiuk et al. (1976) established an age of Middle to Late Miocene, whilst a Middle Miocene age has been also accepted by Malumián and Náñez (1996).

del Río (1988, 1989, 1992) discussed the age of the Puerto Madryn Formation and, according to palaeontological, palaeogeographic, and palaeoclimatic evidence from molluscan faunas, a probable late Middle Miocene age was suggested. Subsequently, Martínez (1994) stated that, although a Middle Miocene age could be considered for the Argentine 'Entrerriense' deposits, a Late Miocene age should not be dismissed.

Vertebrates have been also studied. Cione (1978, 1988) and Cione and Tonni (1981) placed the 'Entrerriense' beds in the Late Miocene, mainly based on its shark and ray content. However, Cozzuol et al. (1993) and Riva Rossi (1996) accepted the Middle Miocene age provided by molluscs.

3. Samples

We have measured $^{87}Sr/^{86}Sr$ in biogenic carbonate from 16 pectinid valves and seven oyster valves, and in two whole-rock samples comprising a carbonate-cemented clastic matrix. Samples were collected from eight coquinas of the Puerto Pirámide–Lobería, Eje Tentativo, and El Doradillo sections at the Valdés Península (Fig. 1C). These sections were correlated by tracing the almost horizontal beds along the cliffs on the north coast of the Golfo Nuevo. All the fossil shells were from assemblages of shells that are well preserved, entire, randomly oriented, and with disarticulated valves in shell-supported and matrix-supported, highly porous, poorly lithified beds. The samples were extracted from the auricular and hinge areas of the pectinid and oyster valves, respectively. These areas are mainly composed of prismatic and foliated calcite in both *Chlamys* and *Ostrea* groups (Carter, 1990a,b). Details of samples and sample localities are given below.

3.1. Puerto Pirámide–Lobería section

The stratigraphically lower sample is contained in a 3 m thick hard bed (PP1 in Fig. 1C) of the Puerto Pirámide section, which crops out in the intertidal area at the base of Cerro Olazábal, east of Puerto Pirámide. The strongly bioturbated and highly fossiliferous coquina was deposited on a marine inner-shelf environment that grades upwards from matrix-supported to shell-supported beds. At the top is an assemblage of unsorted entire valves, mainly well preserved and disarticulated, of the bivalves *Amusium paris*, *Chlamys actinodes*, *Aequipecten paranensis*, *Ostrea patagonica*, and *Ostrea alvarezi*. Also the crab *Chaceon peruvianus* and scarce gastropods such as *Trophon geversianus*, *Epitonium borcherti*, *Spirocolpus pyramidesia*, and the brachiopod *Pachymagas pyramidesia* are recorded.

The fauna shows a wide range of preservation state. While brachiopods are in life position and crabs are entire and articulated, pectinids and ostreids may be represented either by disarticulated or articulated valves as well as by entire or fragmented shells with well preserved ornamentation, no size or right/left valves sorting and no preferred orientation. Different rates of exhumation are evidenced by perforations and infestation by epibionts and endoliths.

This coquina is the deepest-water facies for the 'Entrerriense' in this area and it probably represents a sea level highstand (del Río et al., 2001). It would correspond to a Type I coquina (sensu Kidwell, 1986). It consists of a complex coquina that grades upwards from a matrix-supported multi-event time-averaging within-habitat assemblage to a shell-supported environmentally condensed assemblage.

Sample PP2 is a valve of *Chesapecten crassus*. It was collected from a 1 m-thick coquina that crops out in the cliffs close to Lobería Punta Pirámide, 2 km west of and 50 m stratigraphically above the first sample. The coquina (PP2 in Fig. 1C) is a complex, amalgamated Type IV–I (sensu Kidwell, 1986) coquina with an erosive base. At

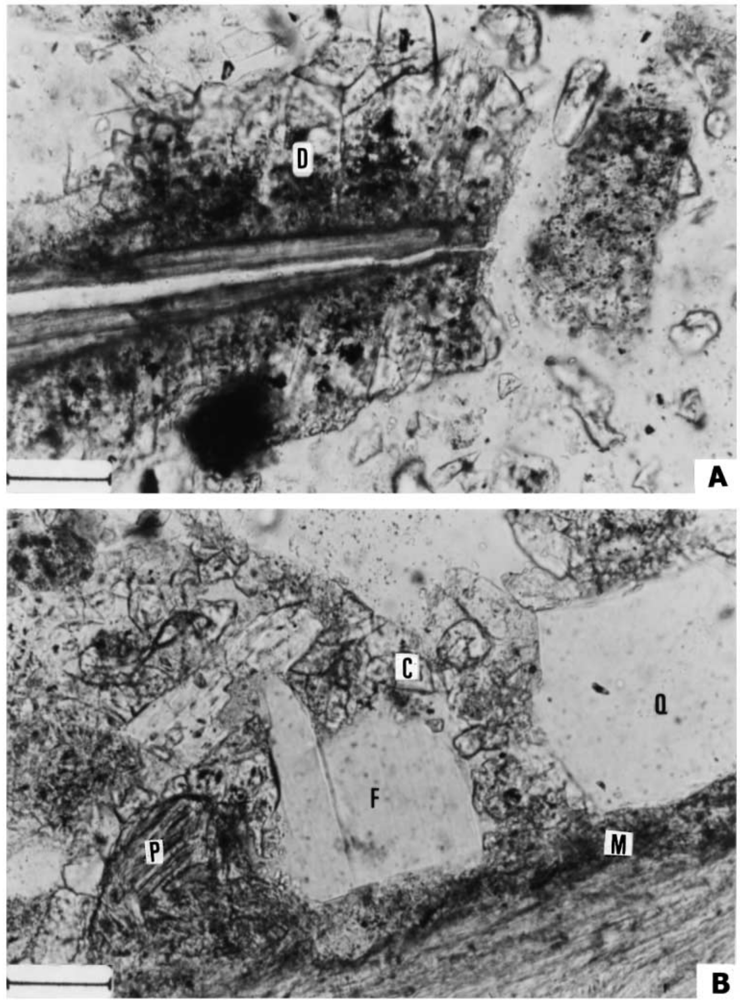

Fig. 2. (A) Drusy calcite crystals (D) surrounding a valve. Scale bar = 0.15 mm. (B) Blocky microsparite calcite cement (C) in a sandy coquina. Lower right a valve with calcite lamellae structure and micritised borders (M). Clasts: Q, quartz; F, feldspar; P, pyroxene. Scale bar = 0.1 mm.

least five depositional events can be recognised within it, the last represented by a highly concentrated shell-supported bed, 0.2–0.6 m thick, that suggests a single high-energy hydraulic process of concentration: the unit has an erosive base, contains highly-fragmented valves, and is topped by a pavement yielding entire and well-preserved disarticulated valves of the pectinids *Amusium paris* and *Chesapecten crassus*. This complex coquina was probably deposited in a tide dominated external estuarine environment.

PP5 and PP6 are whole-rock samples comprising calcite cement and sand-sized matrix of two matrix-supported coquinas (Fig. 1C). The cement (50%) is composed of blocky microsparite or drusy calcite which, together with its low-magnesium–calcite composition, are evidence of meteoric origin (Fig. 2). The mixed clastic–carbonatic matrix is mainly composed of feldspar, quartz, lithic fragments, and calcitic bioclasts.

3.2. Eje Tentativo section

The ET1 horizon at Eje Tentativo (Fig. 1C) is a 2.5 m-thick complex coquina with at least three amalgamated events with erosive base on the Patagoniense strata. This is a shell-supported bed with sandy matrix and well-preserved, disarticulated, mainly entire valves of *Chlamys actinodes*, *Ostrea patagonica*, *Ostrea alvarezi*, glycymerids, turritellids, and briozoans.

The coquina ET2 consists of a 1.5 m-thick, sandy, matrix-supported fossiliferous bed with erosive base, made up by two events. The basal event is dominated by hash and a pavement of *Ostrea patagonica* and *Glycymerita magna* at the top; the other event is dominated by an assemblage of well-preserved, disarticulated and entire valves of *Ostrea patagonica*, *Chlamys actinodes*, *Aequipecten paranensis*, and turritellids.

Bed ET13 is placed at the top of a near 5 m-thick complex coquina that grades upwards from scarcely dispersed valves in a sandy matrix to a high concentration of disarticulated, non-oriented and non-size-sorted valves of *Chlamys actinodes*, *Ostrea alvarezi*, turritellids, and briozoans in a highly bioturbated mudstone matrix with abundant hash.

ET14 is a 0.5 m-thick, shell-supported coquina with

Table 1
$^{87}Sr/^{86}Sr$ ratio, calculated age and age uncertainty (in Ma) of 'Entrerriense' samples

Group	Location	Species	$^{87}Sr/^{86}Sr$		Ma		
			Chlamys	*Ostrea*	*Chlamys*	Uncertain	*Ostrea*
1	*Puerto Pirámide–Lobería*						
	PP2	*Chesapecten crassus*	0.708894		10.1	0.8	
			0.708898		9.9	0.8	
	PP1	*Chlamys actinodes*	0.708908		9.5	0.9	
			0.708925		8.7	1.0	
	Eje Tentativo						
	56-3	*Chlamys actinodes*	0.708893		10.1	0.8	
			0.708897		10.0	0.8	
	54-2	*Chlamys actinodes*	0.708888		10.3	0.7	
	53-2	*Chlamys actinodes*	0.708874		10.8	0.6	
			0.708874		10.8	0.6	
	53-1	*Chlamys actinodes*	0.708911		9.4	0.9	
	LC-1	*Chlamys actinodes*	0.708885		10.4	0.7	
	Playa Doradillo						
	PD-4-1	*Chlamys actinodes*	0.708894		10.1	0.8	
			Mean age		10.0		
			2SD			1.2	
			2SE			0.3	
2	PD-3-2	*Chlamys actinodes*	0.708762		15.5		
			0.708773		15.1		
	PD-3-3	*Chlamys actinodes*	0.708749		15.8		
			Mean age		16.6		
			2SD			0.7	
			2SE			0.4	
3	*Playa Doradillo–Eja Tentativo*						
	54-3 (altered)	*Chlamys actinodes*	0.708802		13.8		
	56-2 (repick)	*Ostrea*		0.708735			16.1
	55-2	*Ostrea*		0.708747			15.8
	54-1	*Ostrea*		0.708817			13.0
	48	*Ostrea*		0.708655			17.4
	PD-1	*Ostrea*		0.708727			16.3
	PD-4-2	*Ostrea*		0.708572			18.4
	PD-3-1	*Ostrea*		0.708630			17.7
				0.708630			17.7

erosive base and fine sandy matrix. At the base, it is almost exclusively dominated by *Ostrea patagonica* and *Amusium paris*, whereas upwards it is dominated by *Ostrea alvarezi*, *Ostrea patagonica*, *Aequipecten paranensis*, *Amusium paris*, and only a few *Chlamys actinodes*. Articulated shells are very common and ornamentation is exceptionally well preserved.

3.3. El Doradillo section

Coquina D3 is a 5 m-thick, amalgamated, shell-supported horizon made up of at least four depositional events with erosive bases. The coquina contains abundant casts of *Glycymerita magna*, *Retrotapes ninfasiensis*, turritellids, and randomly oriented, large, entire, well preserved and disarticulated valves of *Ostrea alvarezi* and *Chlamys actinodes* in a sandy matrix.

The uppermost coquina (D12) is a 0.5 m-thick, sandy matrix-supported coquina with erosive base and abundant hash and only a few entire disarticulated valves of *Ostrea patagonica* and *Aequipecten paranensis*.

4. Methods

Apparently altered portions of each macrofossil were removed using diamond cutting tools; the remainder of each sample was broken into fragments of sub-mm size. The fragments were cleaned by brief immersion in 1.2 M hydrochloric acid solution, then in ultrapure water and they were dried in a clean environment. Fragments for analysis were then picked under the binocular microscope. Alteration was assessed by optical microscope, scanning electron microscope (SEM) and chemical analyses. Chemical

Table 2
Chemical analyses of 'Entrerriense' samples (VP: preservation index as determined by examination of shell fragments under the optical microscope (scale: 1: very poorly preserved, to 5: very well preserved). Sr/Ca and Fe/Mn expressed as atomic ratio × 1000

Group	Location	Species	VP	CaO (%)	Mg (ppm)	Sr (ppm)	Na (ppm)	Fe (ppm)	Mn (ppm)	Sr/Ca	Fe/Mn
1	*Puerto Pirámide–Lobería*										
	PP2	*Chesapecten crassus*	2.5	39.12	751	652	2209	66	178	1.10	0.37
				38.96	673	625	2770	65	180	1.06	0.36
	PP1	*Chlamys actinodes*	3.5	39.42	808	805	2023	188	537	1.35	0.35
				39.74	604	712	1770	119	430	1.19	0.28
	Eje Tentativo										
	56-3	*Chlamys actinodes*		40.57	765	900	2070	73	220	1.47	0.33
				40.57	765	900	2070	73	220	1.47	0.33
	54-2	*Chlamys actinodes*	3.5	38.31	1013	718	1935	169	223	1.24	0.76
	53-2	*Chlamys actinodes*	4.0	38.95	654	760	1959	61	181	1.29	0.34
			4.0	39.24	654	702	2220	50	178	1.18	0.28
	53-1	*Chlamys actinodes*	3.5	38.50	736	803	2037	104	128	1.38	0.81
	LC-1	*Chlamys actinodes*	3.5	38.79	820	792	1807	104	204	1.35	0.51
	Playa Doradillo										
	PD-4-1	*Chlamys actinodes*	4.0	38.32	657	805	2336	110	363	1.39	0.30
2	PD-3-2	*Chlamys actinodes*	3.5	39.90	820	620	1270	65	95	1.03	0.68
			3.0	39.90	820	620	1270	65	95	1.03	0.68
	PD-3-3	*Chlamys actinodes*	3.5	40.00	860	820	1830	56	111	1.36	0.50
3	*Playa Doradillo–Eja Tentativo*										
	54-3 (altered)	*Chlamys actinodes*	2.0	39.85	430	525	2190	83	290	0.87	0.29
	56-2 (repick)	*Ostrea*	3.0	38.55	1710	368	3170	135	270	0.63	0.50
	55-2	*Ostrea*	4.0	39.13	912	487	1990	183	153	0.82	1.20
	54-1	*Ostrea*	3.0	39.33	1178	470	2685	74	220	0.79	0.34
	48	*Ostrea*	4.0	39.82	1288	412	2310	95	86	0.69	1.10
	PD-1	*Ostrea*	2.5	39.12	825	499	2887	49	134	0.84	0.37
	PD-4-2	*Ostrea*	3.5	38.85	1037	340	1929	121	168	0.58	0.72
	PD-3-1	*Ostrea*	2.5	39.46	2791	309	950	490	1191	0.52	0.41
				39.47	1600	312	1223	282	957	0.52	0.29

VP = preservation index as determined by examination of shell fragments under the optical microscope (scale: 1 = very poorly preserved, to 5 = very well preserved). Sr/Ca and Fe/Mn expressed as atomic ratio × 1000.

analyses for Na, Ca, Mg, Sr, Fe, and Mn were determined by ICP-AES on samples dissolved in 1.8 M acetic acid; the precision of the analyses was better than ±5%. In order to assess the contribution to $^{87}Sr/^{86}Sr$ from radioactive decay of ^{87}Rb, concentrations of Rb were measured by furnace-AAS and found to be less than 0.5 ppm.

For the $^{87}Sr/^{86}Sr$ analyses, cleaned macrofossil fragments were evaporated to dryness in 6 M HNO_3 in order to oxidise organic matter and were then converted to chloride salt by subsequent evaporation to dryness with ultra-pure 6 M HCl. Samples were taken up in 2.5 M HCl and Sr separated by standard methods of column chromatography. Values of $^{87}Sr/^{86}Sr$ were determined with a VG-354 mass spectrometer using the multidynamic routine SrSLL (Thirlwall, 1991) that includes corrections for isobaric interference from ^{87}Rb. Data have been normalised to a value of 0.1194 for $^{86}Sr/^{88}Sr$. The data were collected between July 1997 and March 1999. During data collection, the measured value for NIST 987 was within 0.000030 of the value 0.710248. Data reported in Tables 1 and 2 have been adjusted to a value of 0.7102480 ± 0.0000025 (2SE, $n = 19$) for NIST 987 which corresponds to a value of 0.7091746 ± 0.0000032 (2SE, $n = 19$) for EN-1 in our laboratory. Based upon replicated analysis of NIST 987, the precision of our measurements (2SE) was ±0.000015 for single determinations, ±0.000011 for duplicates, and ±0.000009 for triplicates. Total blanks were <2 ng of Sr; analysed subsamples were about 10 mg in mass and thus contained about 7 μg of Sr. Concentrations of Rb were found to be too low to require corrections for radiogenic Sr. Data are presented in Tables 1 and 2. The $^{87}Sr/^{86}Sr$ values of the samples have been converted to numerical age using Version 2:1/98 of the Look-Up Table of Howarth and McArthur (1997); for details of V2:1/98, see McArthur and Howarth, 1998). The $^{87}Sr/^{86}Sr$, numerical age, and chemical composition of the samples are given in Tables 1 and 2 and plotted in Fig. 3.

Two samples (PP5 and PP6) of a mixture of cement and clastic–carbonatic matrix were treated with concentrated hydrochloric acid in order to leach Sr from clastic

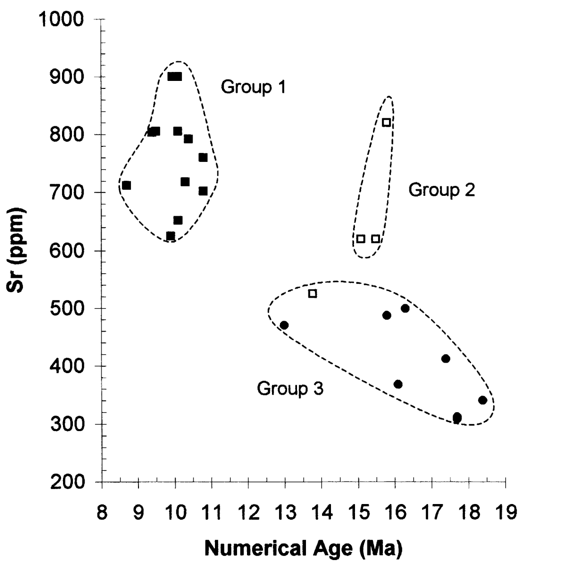

Fig. 3. Sr versus numerical age ($^{87}Sr/^{86}Sr$) plot from all the studied localities. The three groups of values correspond to unaltered *Chlamys* (solid squares), altered *Chlamys* (open squares), and altered oyster (solid circles) samples. Pectinids seem to better retain their original $^{87}Sr/^{86}Sr$ ratio than oysters. The latter are probably altered by recrystallisation or replacement of the original calcite by deposition of secondary calcite containing Sr with an isotope ratio lowered by interaction of diagenetic fluids with basic volcanic matrix.

components. The residue was discarded and Sr was separated from the leachate by standard methods of ion exchange chromatography. This procedure was undertaken to discover whether Sr contributed by diagenesis of clastic components would increase or decrease the Sr isotopic composition of fossils that might be altered by diagenetic processes.

5. Results and discussion

All the samples examined by binocular microscope and SEM showed well-defined, small areas that underwent dissolution and growth of calcite and iron and manganese oxides, inside cavities and between laminae of the shell structure (Figs. 4D and 5A). Out of these areas, the shell structure appeared well preserved (Figs. 4A, B and 5B–D) and the altered parts were easily avoided during sampling. However, evidence of slight recrystallisation was found sporadically (Figs. 4C and 5C) in apparently well-preserved parts of the shells. Studied valves are composed of pure, low-magnesian calcite as demonstrated by X-ray diffraction and chemical analysis (Tables 1 and 2). Ca, Sr, Na, and Mg contents, and their atomic and molecular ratios, are in general agreement with the sparse published data for these fossil groups and their Recent equivalents (e.g. Turekian and Amstrong, 1960; Stenzel, 1971; Dodd and Stanton, 1981; Morse and Mackenzie, 1990).

Data from recent specimens of both groups show relatively low Sr and Mg contents in comparison with most molluscs and other fossil groups (see Morse and Mackenzie, 1990, pp. 189, 212, and 213). Our oyster samples show higher Mg content than the pectinid ones. In addition, most oyster samples have Sr/Ca (atom ratio $\times$ 1000) between 0.52 and 0.84, mostly below the range for Recent *Crassostrea virginica* and other fossil oysters (1.01–1.90 and 0.81–1.83, respectively: Stenzel, 1971). Oyster samples showing more intense alteration (not analysed/not included in Tables 1 and 2), in turn, showed still lower Sr/Ca ratios. As a consequence, pectinid samples with lower Mg and higher Sr and Sr/Ca ratios probably lack any diagenetic alteration, although it must be taken into account that Sr and Mg content is not only dependent on diagenetic alteration but also on temperature, chemistry of sea-water, and physiology of the organisms (Morse and Mackenzie, 1990).

In Fig. 3, numerical age is plotted against Sr concentration of the samples. Three populations are apparent: (1) valves of *Chlamys* with ages between 8.7 and 10.8 Ma and Sr content above 600 ppm; (2) two valves (one was analysed twice) of *Chlamys* with ages of 15.1–15.8 Ma and Sr content above 600 ppm; (3) one valve of *Chlamys* and seven valves of *Ostrea* with ages between 13.0 and 18.4 Ma and Sr content below 600 ppm.

The concordance of $^{87}Sr/^{86}Sr$ data (and thus numerical ages) for *Chlamys* samples of Group 1 and their low Mg and relatively high Sr content (Fig. 3) suggest that they are well preserved in comparison with Groups 2 and 3. Nevertheless, the Mn/Fe ratio of all samples is >1 (Tables 1and 2). We interpret this fact as indicating that the samples were subject to post-oxic, but not sulphidic, conditions of diagenesis after burial. We believe that these ratios do not indicate significant alteration, but mobilisation of these elements during diagenesis has resulted in their deposition on cavities and crystal surfaces between laminae and not in the mineral structure (Figs. 4D and 5A; cf. McArthur, 1994), which is well preserved as has been clearly observed by examination of shell fragments under the optical microscope and SEM. On the other hand, the $^{87}Sr/^{86}Sr$ data are concordant (within the total range of expected analytical uncertainty of ± 0.000030).

The $^{87}Sr/^{86}Sr$ and Sr concentrations for Groups 2 and 3 are difficult to interpret (see above). The valves of *Chlamys* of Group 2 seem reasonably well preserved and show only slightly local recrystallisation (Fig. 4C). This might indicate that the basal units at Playa Doradillo are 15.5 ± 0.2 Ma in age (Tables 1 and 2), where if not for the fact that Sample PD-4-1, from the upper part of the same complex bed, has an age of 10.0 ± 0.3 Ma. Reworking from older deposits can be ruled out, because *Chlamys* valves are fragile and they are often preserved entire and without evidence of abrasion. The *Chlamys* ages that average 15.5 Ma could therefore result from alteration which, in the 'Entrerriense' units, lowers $^{87}Sr/^{86}Sr$ by exchanging original Sr with Sr of a lower isotopic ratio. Fine tuffs and tuffaceous mudstones,

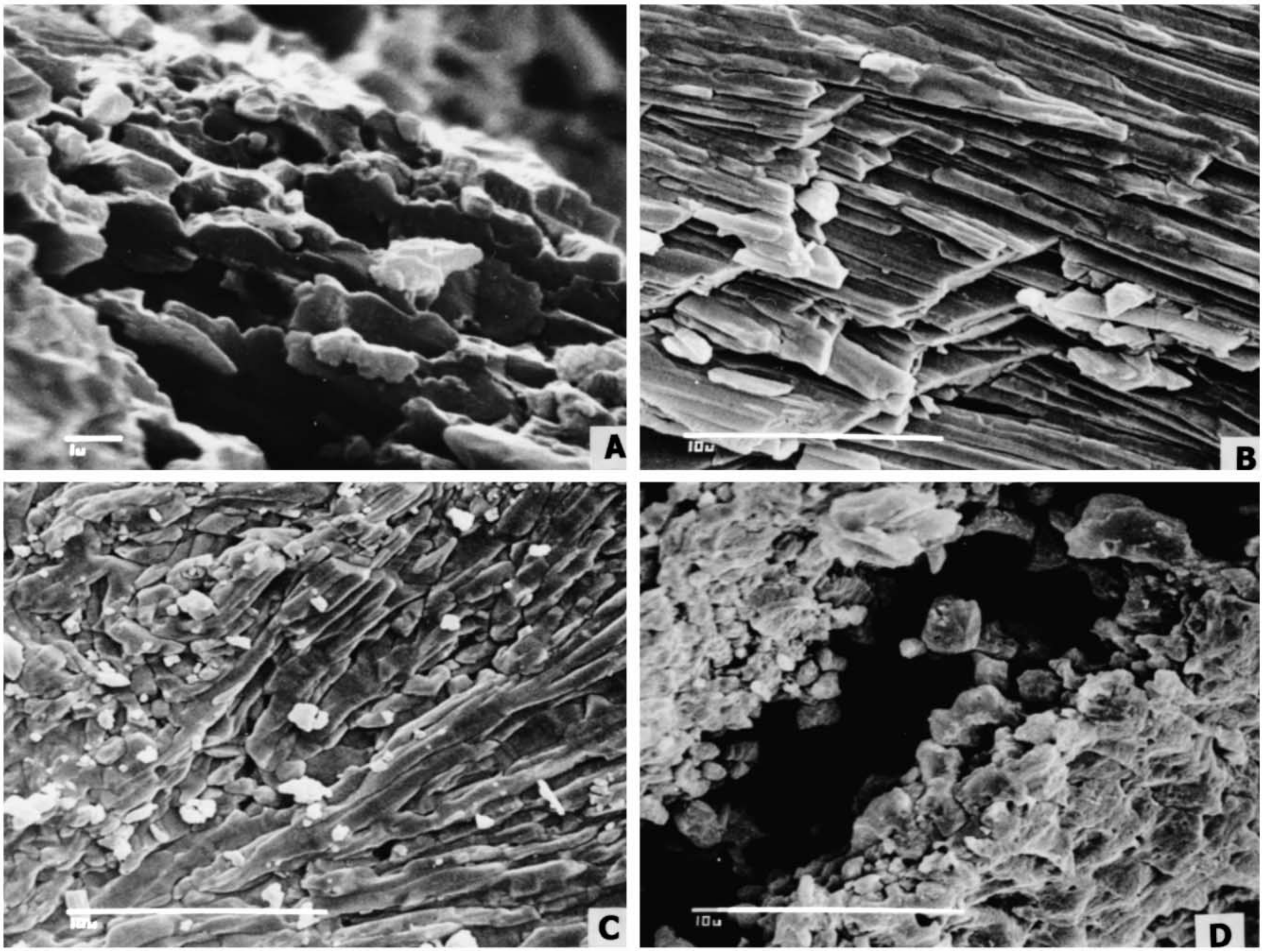

Fig. 4. SEM photomicrographs of fragments of the auricular area of *Chlamys* shells, from the 'Entrerriense' at the Valdés Peninsula. (A) Well-preserved irregularly polygonal, calcite-simple-prismatic layers typical of the *Chlamys* shells, sample PP2, age = 10.0 Ma, scale bar = 1 μm. (B) Well preserved calcite crystals from a crossed foliated part of the shell, sample PD3-2, age = 15.5 Ma, scale bar = 10 μm. (C) Partially recrystallised calcite crystals showing low-angle crossed foliated microstructure, sample PD 3-2, age = 15.5 Ma, scalebar = 10 μm. (D) Drusy growth of iron and manganese oxides within elongated cavities along altered and partially dissolved calcite layers. The original prismatic structure of the shell is still visible to the lower right, sample PD3-3, age = 15.8 Ma.

with fresh or little altered volcanic glass shards, are commonly interbedded with the coquinas; lithic fragments from basic to mesosilic volcanics, together with andesine and labradorite grains, are the main components of intercalated sandstones (Scasso and del Río, 1987; Marengo, 1998). The main sources were most probably basic to intermediate contemporaneous volcanism northwest of the studied region, together with highly explosive acid and calc-alkaline volcanism in Central Patagonia (Salani and Page, 1990; Salani et al., 1994) and in the Andes.

Dissolution of volcanic material in pore water would have given diagenetic fluids with a $^{87}Sr/^{86}Sr$ ratio much lower than that in the biogenic carbonate (cf. Elderfield and Gieskes, 1982). This is consistent with ratios from acid leaches of clastic matrix and calcite cements (Fig. 2), which yielded values of 0.707865 and 0.707281. As a consequence, ages derived from $^{87}Sr/^{86}Sr$ of Group 2 are most probably older than real ages as a result of subtle alteration of the original calcite, and this extends to samples of Group 3, mainly oyster valves.

Chlamys and *Ostrea* shells are mainly built of prismatic calcite layers and, in consequence, they should be adequate for Sr dating. In our case, however, *Ostrea* seem to do poorly at retaining an original Sr signal. This may be due to the presence of irregular and chalky deposits or the porous shell layers that can be developed in the shells. As an adaptive strategy for existence on soft substrates, some oysters have porous structures (Carter, 1990a; Chinzei, 1995) that are susceptible to infilling with diagenetic calcite (Fig. 5C,D). The clear evidence of diagenesis under post-oxic conditions (Mn/Fe values > 1) and of a volcaniclastic matrix and cement with low $^{87}Sr/^{86}Sr$ ratio show that porous *Ostrea* may have low Sr concentrations and low $^{87}Sr/^{86}Sr$ as a result of diagenetic alteration. The SEM study of the oyster microstructure proves that alteration is not always clearly detected, mainly due to the complex structural

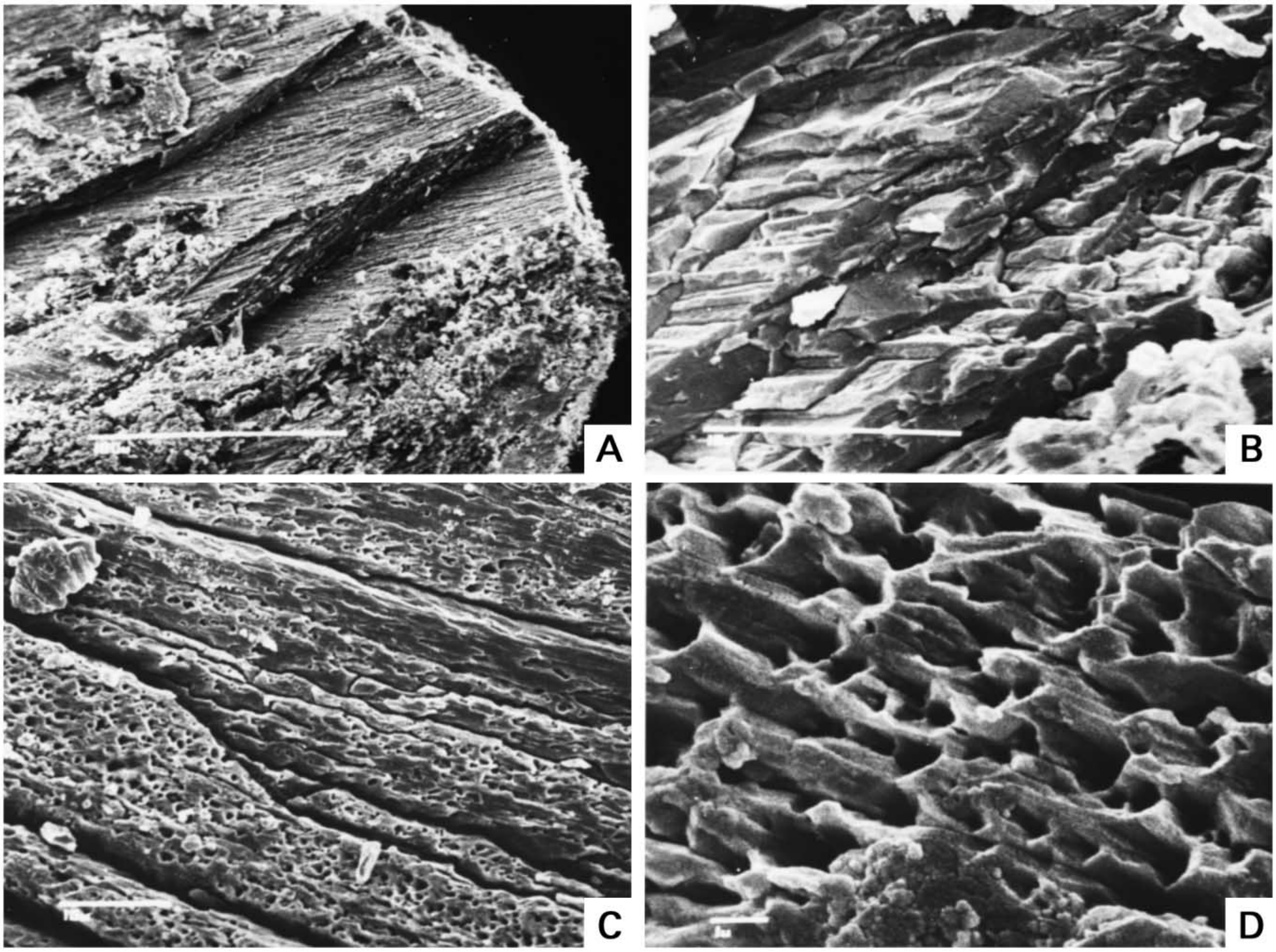

Fig. 5. SEM photomicrographs of fragments of the hinge area of *Ostrea* shells, from the 'Entrerriense' at the Valdés Peninsula. (A) Shell fragment showing crossed foliated structure of the shell and diagenetic, surficial growth of calcite together with iron and manganese oxides, sample PD3-1, age = 17.7 Ma, scale bar = 100 μm. (B) Fresh prismatic crystals from foliated calcite layers in a mainly altered oyster, sample PD3-1, age = 17.7 Ma, scale bar = 10 μm. (C) Highly porous (chalky) calcite layers intercalated with less-porous layers. Microfractures developed parallel to the layering, sample PD3-1, age = 15.8 Ma, scale bar = 10 μm. (D) Higher-magnification view of the 'chalky' calcite layers of (C), scale bar = 1 μm.

pattern of the shells and to the subtle nature of the recrystallisation processes in some carbonates (e.g. Mii et al., 1997; Scasso and Kiessling, 2001).

Modification of the diagenetic fluids and subtle diagenetic recrystallisation would be the cause of changes in the original $^{87}Sr/^{86}Sr$ ratio of the oysters, which show less Sr content than pectinids from the Group 1. Therefore, we believe that the $^{87}Sr/^{86}Sr$ ratio of samples from Group 1 is the value that represents the original isotopic ratio of the sea water, pointing to an age of about 10.0 ± 0.3 Ma for deposition of the 'Entrerriense'.

Three K/Ar dates by Zinsmeister et al. (1981) on glass concentrates from a tuff from the upper part of the unit at Bahía Cracker yielded numerical ages around 9.4 Ma (9.11 ± 0.1, 9.55 ± 0.3, 9.56 ± 0.3). This locality is 40 km to the south, yet stratigraphic and palaeogeographic work (Scasso and del Río, 1987) suggests it correlates with the uppermost beds of the section from Puerto Pirámide and Lobería Punta Pirámide. Our ages agree well with the dates of Zinsmeister et al. (1981), and the strontium ages suggest that the 'Entrerriense' sequence was deposited at 10.0 ± 0.3 Ma. Consequently, a middle Tortonian age corresponds to the sequence, which was deposited during the upper Magnetic Chron C5n (according to the time scale of Berggren et al., 1995), synchronically with the middle N16 planktonic foraminiferal zone of Blow (1969), and the lower NN10 to upper NN9 calcareous nannoplankton zones of Martini (1971).

6. Conclusions

Our results provide a well-constrained depositional age for the 'Entrerriense' deposits examined here. The strontium ages suggest that the 'Entrerriense' sequence was deposited at 10.0 ± 0.3 Ma. Pectinids retained their original $^{87}Sr/^{86}Sr$ ratio better than oysters. The latter were diagenetically altered by replacement by, or precipitation of, calcite in equilibrium with diagenetic fluids, with an isotope ratio lowered by interaction with intermediate and basic volcanic components of tuffs and sandstones. This process was probably favoured by the presence of irregular and chalky deposits or porous shell layers in the oysters.

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