The use of LA-ICP-MS in a pilot study for determining the concentration of selected trace elements in rudist shells

F. Sánchez-Beristain[1], K. Simon[2], L. Pérez-Cruz[3], P. García-Barrera[1], L. López-Esquivel Kranksith[4], J. Urrutia-Fucugauchi[3] and J. P. Duda[5]

(1) Museo de Paleontología, Facultad de Ciencias, Universidad Nacional Autónoma de México (UNAM).
Circuito Exterior S/N. Coyoacán 04510 DF, Mexico.
sanchez@ciencias.unam.mx
(2) Geowissenschaftliches Zentrum Göttingen. Abt. Geochemie. Goldschmidstraße 5. D-37077 Göttingen, Germany.
(3) Instituto de Geofísica, Universidad Nacional Autónoma de México (UNAM). Circuito Exterior S/N. Coyoacán 04510 DF, Mexico.
(4) Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México (UNAM).
Circuito Exterior S/N. Coyoacán 04510 DF, Mexico.
(5) Geowissenschaftliches Zentrum Göttingen. Abt. Geobiologie. Goldschmidstraße 3. D-37077 Göttingen, Germany.

ABSTRACT

A protocol for the determination of the concentration of selected elements in two rudist shells was developed using Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). Element analysis in rudists has never been performed beyond including major and some minor elements, and thus this work presents the first results in this field. The concentrations of 35 isotopes were analyzed. Low iron and manganese concentrations reflect the absence of a diagenetical imprint on both shells. There is a negligible amount of crust-associated elements, which reveal little evidence of terrigenous input. Phosphorus amount is also low; however, it is high enough to mask reliable Rare Earth + Yttrium (REY) pattern measurements. Strontium and magnesium concentrations in the inner layers of a shell of *Titanosarcolites* show relicts of an original aragonitic composition. On the contrary, concentrations of these elements in a shell of *Biradiolites rudissimus* reveal an original low Mg-calcite mineralogy in its outer layers. The two shells were selected, considering their apparently *a priori* good preservation, based on the petrological examination of thin sections. No significant concentrations of elements such as chromium, cobalt, nickel, copper, zinc, molybdenum or antimony could be found. The concentrations of vanadium and barium may reflect evidence of biological activity, since they apparently do not correlate significantly with silicon, aluminium or sulphur. The low cost and precision of this method in comparison to others such as the use of electron microprobe, or X-ray fluorescence, makes it an optimum alternative for geochemical analyses of fossils, thus opening a new line of research.

Keywords: Cretaceous, geochemistry, LA-ICP-MS, rudists, trace elements.

El uso de LA-ICP-MS en un estudio piloto para determinar la concentración de elementos traza selectos en conchas de rudistas

RESUMEN

Se desarrolló un protocolo para la determinación de elementos selectos en conchas de rudistas por medio de la técnica de Espectrometría Plasma-Masa Inductivamente Acoplada con Ablasión Láser (LA-ICP-MS). El análisis de elementos en rudistas no ha sido realizado con fines más allá de detectar ciertos elementos mayores y algunos menores, y jamás se ha utilizado el LA-ICP-MS. Se analizaron las concentraciones de 35 isótopos. Las concentraciones de magnesio y estroncio sugieren que la composición mineralogica original de calcita para las capas exteriores de la concha de Biradiolites rudissimus *Trechmann y de aragonito para las capas interiores de la concha de* Titanosarcolites *se conservan. Las concentraciones de hierro y manganeso reflejan la ausencia de influencia diagenética. Existe evidencia mínima de contaminación por terrígenos y fósforo; no obstante, la cantidad de este último es suficiente como para enmascarar mediciones confiables de patrones REY. Las dos conchas fueron seleccionadas a partir de la examinación petrológica de láminas del-*

gadas. No se encontraron concentraciones significativas de elementos como cromo, cobalto, níquel, cobre, zinc, molibdeno o antimonio. Sin embargo, las concentraciones de vanadio y bario podrían reflejar evidencia de actividad biológica, dado a que estos elementos no se encuentran significativamente correlacionados con azufre, aluminio o silicio. Este método demostró ser confiable para la medición de los elementos selectos. Adicionalmente, su bajo costo y precisión en comparación con otros métodos como el uso de microsonda y fluorescencia por rayos X, lo torna una alternativa óptima para el análisis geoquímico de fósiles, abriendo así una nueva línea de investigación.

Palabras clave: Cretácico, elementos traza, geoquímica, LA-ICP-MS, rudistas.

RESUMEN EXTENDIDO EN CASTELLANO

Introducción y Metodología

Los Rudistas son moluscos bivalvos sésiles extintos que dominaron los ambientes arrecifales del Jurásico Superior hasta el Cretácico Superior (Alencáster, 1995). Sus conchas consisten principalmente de una capa externa con una mineralogía de calcita baja de magnesio y de capas internas de aragonito (Skelton, 1974; Steuber, 1999). Han sido objeto de estudio con una gran diversidad de enfoques, que incluyen a la Sistemática (Alencáster, 1995), así como a la Paleobiología (Götz and Stinnesbeck, 2003), la Paleoecología (Götz, 2007; Götz and Stinnesbeck, 2003) y la Bioestratigrafía (Sari and Özer, 2009). No obstante, a pesar de que se han estudiado en el ámbito de numerosos puntos de vista, es apenas hasta hace más de una década que se han aplicado análisis geoquímicos en ellos. Estos trabajos han proporcionado datos que han prestado una valiosa información paleoecológica. La mayoría de las investigaciones se han abocado a la obtención de la tasa de crecimiento de ciertas especies de rudistas, así como a la determinación de patrones de estacionalidad con ayuda de isótopos estables (Steuber, 1996; Steuber et al.*, 1998; Steuber, 1999; Steuber* et al.*, 2005; Huang* et al.*, 2006). En todos los casos, la exactitud de los resultados ha sido atribuida a la escasa diagénesis como producto de la mineralogía de las conchas (calcita baja en magnesio).*

En investigaciones más recientes, Hennhöfer y colaboradores (2012) llevaron a cabo análisis de isótopos de oxígeno en conchas seleccionadas de rudistas dentro de un pequeño bouquet de la especie Biradiolites mooretownensis. Estos autores obtuvieron valiosa información paleobiológica, al concluir que un ciclo reproductivo se llevó a cabo cada año y que también podría haber estado relacionado con la estacionalidad.

A pesar del gran número de publicaciones recientes con respecto a la geoquímica de conchas de rudistas, pocas abordan el análisis de elementos. El contenido de elementos traza no relacionados con la contaminación se ha investigado ampliamente en los bivalvos modernos (Reinfelder et al.*, 1997; Risk* et al.*, 2010).*

La técnica de Espectrometría de Masas Inductivamente acoplada a Plasma (ICP-MS, por sus siglas en inglés) es un método de alta resolución que permite la detección de concentraciones de elementos traza en el rango de ppm (Schäfer, 2006). El acoplamiento de este equipo con un sistema de ablación por láser (LA-ICP-MS) permite el análisis de todas las muestras sin disolverlas previamente. La ablación con láser tiene una resolución más alta que los métodos de dilución, ya que estos últimos requieren mucho más material que el anterior, lo que implica una mezcla de facies (Delecat, 2005). Esta técnica ha sido utilizada con éxito en diversos campos dentro de las geociencias, en particular en vulcanología (Yang et al.*, 2009), la petrología de la corteza oceánica (Kelley* et al.*, 2003), y más recientemente en la geoquímica de carbonatos. (Blumenberg* et al.*, 2011; Sánchez-Beristain and López Esquivel–Kranksith, 2011; Sánchez-Beristain* et al.*, 2011; Rodríguez-Martínez* et al.*, 2011). Muy pocos son los trabajos que abordan aspectos geoquímicos mediante LA-ICP-MS en fósiles provenientes de facies carbonatadas (Burla* et al.*, 2009; Evans and Müller, 2013), pero ninguno lo ha hecho con rudistas. Esta es la razón por la cual decidimos proponer este protocolo.*

Dos secciones pulidas provenientes de valvas inferiores de conchas de rudistas fueron analizadas. Estas conchas pertenecen a un ejemplar de "Titanosarcolites sp.nov. 1 pendiente de denominación" Oviedo-García del Maastrichtiense de Chiapas, México (Figura 1), y a un ejemplar de Biradiolites rudissimus Trechmann del Campaniense?–Maastrichtiense, también de Chiapas, México (Figura 2). La selección de las conchas fue llevada a cabo a través del análisis petrológico de láminas delgadas, entre cinco conchas del género Titanosarcolites y tres del género Biradiolites

La ablación con láser se realizó utilizando un sistema Excimer de 193 nm COMPEX 110 (Lambda Physik, Göttingen, Alemania) equipado con un potenciador de forma del haz óptico GEOLAS (MicroLas , Göttingen , Alemania) a aproximadamente 3 J/cm² y 26 kV de energía interna láser, con un diámetro de línea de ablación de 120 micras. El material extraído fue transportado en el plasma ICP-MS RDC II (Perkin-Elmer, Canadá) usando argón como gas acarreador. Las mediciones se realizaron en las dos secciones pulidas de las conchas de rudistas, con los siguientes parámetros para la serie de tiempo: 35 isótopos se analizaron en tiempos de barrido de 0.65s; el tiempo de duración de las mediciones varió de acuerdo a la longitud deseada, que compren-

día una cantidad variable de puntos de lectura (RP, por sus siglas en inglés). Las mediciones comenzaron después de 30 segundos de pre-calentamiento y terminaron 10 segundos antes del final de la macro. La normalización y cuantificación fueron llevadas a cabo con el estándar NBS610; el estándar interno para los isótopos fue 43Ca, asumiendo que tiene una concentración constante en carbonatos (400000 ppm). El procedimiento para obtener las muestras consistió en efectuar la ablación con láser a lo largo de una línea continua, a modo de determinar las variaciones espaciales a lo largo de las distintas zonas de las conchas. Este método de "ablación en línea" (Schäfer, 2010) ha demostrado ser útil en comparación con el método puntual (Kamber and Webb, 2007), tratándose de la medición de concentraciones de elementos en zonas contiguas con diferente composición.

Resultados y Discusión

Los resultados observados para ambas conchas son similares en cierta medida (Figuras 3,4). Las concentraciones de estroncio en ambas conchas son consistentes con la mineralogía de las mismas; esto es, aproximadamente 4500-5000 ppm para las capas internas aragoníticas en Titanosarcolites *y alrededor de 500 ppm para la capa externa de calcita baja en magnesio de* Biradiolites. *En contraparte, las concentraciones de magnesio oscilan alrededor de 500 ppm y 5000 respectivamente, respaldando lo anterior. El contenido de manganeso (menor a 250 ppm en ambas conchas) refleja una huella diagenética baja (Figuras 3-4). Lo anterior es respaldado por el contenido de hierro (menor a 300 ppm en ambos casos). En general, no hay evidencia de contaminación por terrígenos en las conchas.*

Las concentraciones de azufre y fósforo en ambos conchas no reflejan ninguna correlación con terrígenos. Los valores de azufre oscilan entre 600 y 1200 ppm, mientras que el fósforo oscila entre 10 y 50 ppm. El fósforo, al tener influencia en la deposición y precipitación de Tierras Raras e itrio (REY), impide una interpretación confiable de las concentraciones de estos elementos. Por lo tanto, los datos REY no fueron tomados en cuenta para el análisis.

Elementos como el molibdeno, zinc, cobre, antimonio y cromo no tienen concentraciones significativas en las conchas. El caso del vanadio es, sin embargo, de especial importancia. Sus concentraciones se sitúan entre 5 y 100 ppm en los dos conchas. En la actualidad, organismos como las ascidias son capaces de metabolizar el vanadio con el fin de producir sustancias proteínicas que disuaden a los depredadores potenciales (Brusca and Brusca, 2003; Michibata et al.*, 2002). Sin embargo, las funciones vitales de este elemento no se han deducido en cualquier otro tipo de organismos. Al descartarse la contaminación antropogénica por razones obvias en los bivalvos fósiles, se plantea un escenario importante para futuras investigaciones.*

Las dos conchas muestran diferencias en sus concentraciones de bario (Figuras 5-6). En Titanosarcolites *los picos de bario oscilan entre 25 y 160 ppm, mientras que en* Biradiolites*, entre 15 y 180 ppm. De lo contrario, las concentraciones de Ba permanecen cerca de 0 ppm a lo largo de los transectos de ablación. Si bien la diagénesis generalmente tiende a aumentar las concentraciones de bario (Henkel* et al.*, 2012), las concentraciones de estroncio y magnesio revelan que las mineralogías originales se conservan. Esto se ve reforzado con las bajas concentraciones de elementos relacionados con diagenesis, como hierro y manganeso, que no exhiben correlación alguna con el bario. Los picos en la concentración de este elemento pueden por lo tanto ser el resultado de su absorción de fitoplancton ingerido, particularmente de diatomeas (Thebault* et al.*, 2009). Por otra parte, Gillikin y colaboradores (2006) sugirieron que la causa de picos de Ba / Ca puede no estar relacionado a la ingestión de fitoplancton, sino a la presencia de barita. En* Titanosarcolites, *no existe una correlación entre las concentraciones de Ba y S a lo largo del transecto ($r^2 = 0.003$), por lo que el escenario de la ingesta de fitoplancton puede ser plausible. Por otra parte, la correlación media entre el bario y azufre en la concha de* Biradiolites *($r^2 = 0.31$) puede indicar que el origen de bario esté en parte relacionado con la presencia de barita.*

Introduction

Rudists are extinct sessiles, mostly erect bivalves which dominated reef environments from the Upper Jurassic until the Upper Cretaceous. They were the most important reef builders during the Cretaceous (Alencáster, 1995). Their shells generally consist of an external layer made of low-magnesium calcite and internal layers of aragonite (Skelton, 1974; Steuber, 1999).

They have been the subject of studies with numerous approaches, including systematic studies (Alencáster, 1995; García-Barrera *et al.,* 1998, Oviedo-García, 2006), as well as paleobiological (Götz, 2003; Götz and Stinnesbeck, 2003), paleoecological (Götz, 2003; 2007) and biostratigraphical ones (Mitchel and Gunther, 2002; Vicens *et al.*, 2004; Sari and Özer, 2009). More recently, they have also been considered in studies with geochemical perspectives. Steuber (1996) obtained the growth rate of two species of rud-

ists and concluded that seasonality was present in the Late Cretaceous with the aid of stable isotope analyses. In addition, he measured the concentrations of minor elements in the shells. Following his research, Steuber (1999) analyzed the distribution of four elements and the values of isotopic $\delta^{13}C$ and $\delta^{18}O$ of several rudist shells from the Mediterranean and Eastern Africa. He conferred the accuracy of his results to the low-Mg calcite mineralogy of the shells.

Steuber *et al.,* (1998) analyzed several rudist shells from the Campanian of north-central Turkey. They measured stable isotope profiles in shells of the three dominating species and found a cyclic variation in $\delta^{18}O$, which was in turn attributed to seasonal variations in temperature. In addition, they obtained information on the individual life spans and the vertical growth rates of the shells. Later, Steuber *et al.* (2005) presented valuable information on the temperature variation in low paleolatitudes. They analyzed the intra-shell content of $\delta^{18}O$ in valves of different rudist species, and concluded that a low seasonal variability existed, along with higher maximum temperatures. However, they were also able to find episodes of cooling (high seasonal temperature variability), which they related to the possible existence of polar ice sheets.

Huang *et al.,* (2006) measured carbon and oxygen isotopes, along with Mn and Sr concentrations in rudist shells from southern Tibet and also assessed the importance of the low-Mg mineralogy of the outer layers in rudists shells to conduct geochemical analyses.

In one of the most recent studies, Hennhöfer *et al.,* (2012) conducted oxygen isotope analyses on selected shells within a small bouquet of the rudist species *Biradiolites mooretownensis.* They obtained valuable information which provided an insight into rudist palaeobiology, by concluding that a reproductive cycle took place every year and might have also been related to seasonality.

Despite the relative large number of publications regarding the intra-shell geochemistry of rudist shells, most of them deal with isotope geochemistry and few with element analyses. The contents of trace elements non-related to pollution have been extensively investigated in modern bivalves (Reinfelder *et al.*, 1997; Carrol and Romanek, 2008; Eisler, 2009; Risk *et al.*, 2010). Of particular interest is barium, since it may be associated to phytoplankton dynamics and to the ingestion of diatomean phytoplankton (Thébault *et al.*, 2009).

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a high-resolution method that allows detection of trace element concentrations in the ppm range (Schäfer, 2006). Coupling this equipment with a Laser-Ablation system (LA-ICP-MS) makes it possible to analyze all samples without previously dissolving anything. It is of special importance that this method allows a high spatial resolution sampling, by permitting located ablations at determined places, which in turn renders sublimates consisting of single phases, and is therefore adequate for complex rock samples consisting of various phases of minute size. Laser ablation has a higher resolution than dilution methods, since the latter require much more material than the former, thus implying a mixture of facies (Delecat, 2005).

LA-ICP-MS has been used successfully in diverse fields within geosciences, in particular in volcanology (Yang *et al.,* 2009), petrology of the ocean crust (Kelley *et al.*, 2003), and more recently in carbonate geochemistry. Sánchez-Beristain *et al.* (2011) measured the contents of 26 elements in microbialites from the St Cassian Formation (Upper Triassic, NE Italy). They concluded that the primary mineralogy of these microbialites was composed of high Mg-calcite. In addition, high contents of Fe and Mn were detected, which they attributed to a formation in a reductive environment rather than to meteoric diagenesis. Trace elements, such as Cu and Mo were also found in this work. The concentrations of these elements would possibly be due to the relics of a biological activity, as no correlation existed within them and elements such as Si or Al. Finally, a high content of terrigenous matter was assessed. This was inferred by the presence of Ti, Zr and Rb, which showed a high correlation to Si and Al.

Rodríguez-Martínez *et al.* (2011) analyzed the geochemistry of a stromatolite from the Upper Turonian in Spain. They detected a considerable siliciclastic input associated with accretion stages of the microbial fabric.

Sánchez-Beristain and López Esquivel-Kranksith (2011) added a new insight to the microbialites from the St. Cassian Formation. They determined the redox state of the Upper Triassic with aid of V, Cr, Co and Ni, and concluded that reductive conditions prevailed in some settings within the St. Cassian Formation.

Blumenberg *et al.* (2011) measured by means of LA-ICP-MS high contents of manganese in shale formed by microbial activity from the Precambrian of Mauritania. They observed this element forming crystals and causing a very strong luminescence.

These four works are the only ones dealing with LA-ICP-MS and carbonate geochemistry. No single publication deals with the determination of the concentration of any element in carbonate fossils, for example.

Despite many aspects of the palaeobiology and palaeoecology of rudists having been studied (Alencáster, 1995; Götz and Stinnesbeck, 2003; Götz, 2007), only a few papers deal with their geochemical aspects (Steuber, 1996; Hennhöfer *et al.*, 2012), and none with the distribution of minor or trace elements within their shells. This is the reason why we decided to propose this protocol.

We present the results of the measurement for the first time of selected elements obtained through LA-ICP-MS in rudists: one shell of "*Titanosarcolites* sp. nov.1 denomination-pending" Oviedo-García and one shell of *Biradiolites rudissimus* Trechmann. Results from this pilot analysis will be presented and discussed later in this paper.

Material and methods

Two slabs from lower valves of rudist shells were obtained. These shells comprise one specimen of "*Titanosarcolites* sp. nov.1 denomination-pending" Oviedo-García from the Maastrichtian of Chiapas, Mexico (Fig. 1), and one specimen of *Biradiolites rudissimus* Trechmann from the Campanian?-Maastrichtian also of Chiapas, Mexico (Fig. 2). The shells were selected based on the good preservation
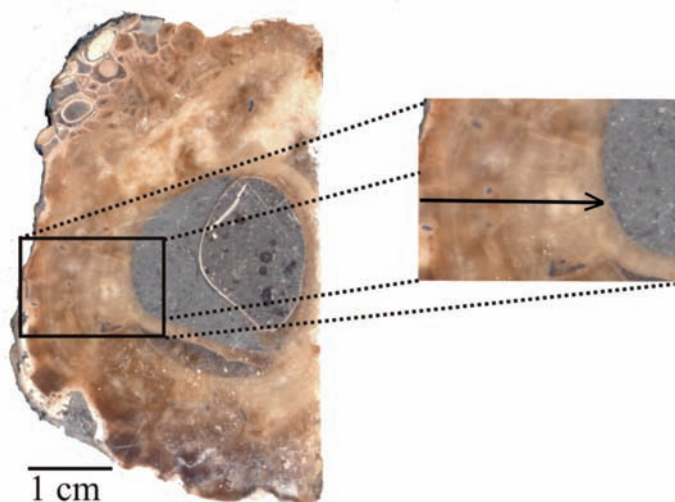

Figure 2. *Biradiolites rudissimus* Trechmann. Polished slab of a transverse section of a lower valve of the specimen. Detail shows the section where the LA-ICP-MS analysis took place (arrow).
Figura 2. Biradiolites rudissimus *Trechmann. Superficie pulida de una sección transversal de la valva inferior del especimen. El recuadro muestra la sección donde los análisis LA-ICP-MS fueron llevados a cabo (flecha).*
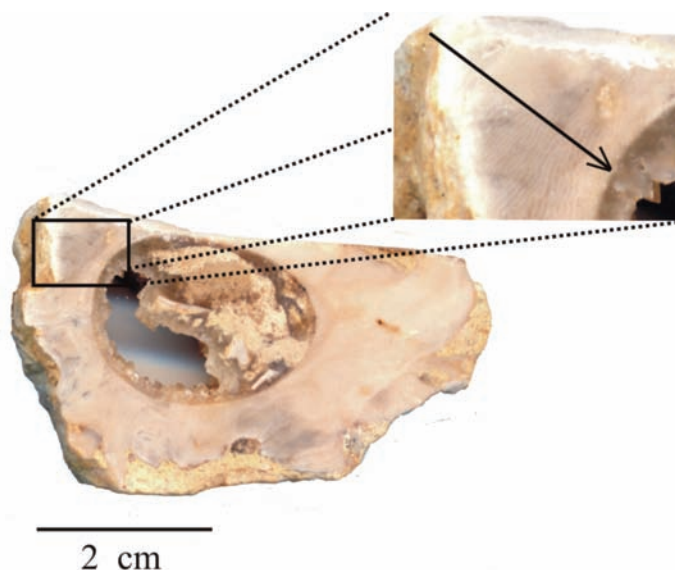

Figure 1. "*Titanosarcolites* sp. nov. 1 denomination-pending" Oviedo-García. Polished slab of a transverse section of a lower valve of the specimen. Detail shows the section where the LA-ICP-MS analysis took place (arrow).
*Figura 1. "*Titanosarcolites *sp. nov. 1 con denominación pendiente" Oviedo-García. Superficie pulida de una sección transversal de la valva inferior del especimen. El recuadro muestra la sección donde los análisis LA-ICP-MS fueron llevados a cabo (flecha).*

observed in the petrological examination of the corresponding thin sections, out of five *Titanosarcolites* and three *Biradiolites* shells. For more information regarding the geological settings where the samples come from, readers are referred to Alencáster (1995) and to Oviedo-García (2006).

Laser ablation was performed using an Excimer 193nm COMPEX 110 (Lambda Physik, Göttingen, Germany) equipped with an optical beam shape enhancer GEOLAS (MicroLas, Göttingen, Germany) at about 3 J/cm² and 26 kV of internal laser energy, with a line pit-diameter of 120 m. The ablated material was carried into the ICP-MS DRC II (Perkin-Elmer, Canada) plasma using Argon carrier gas. Measurements were made on the two polished slabs of the rudist shells, with the following parameters for the time-series: 35 isotopes were analyzed at sweep times of 0.65s. Time duration of measurements was variable, according to the desired length, which comprised a variable amount of reading points (RP). Measurements started after 30 seconds of pre-warming and ended 10 seconds prior to the macro end. This is made in turn to avoid peaks which do not reveal the real concentrations.

Quantification of a single sweep, which has a dwell time of 0.65 s for all isotopes, is very erroneous. However, if 5 or more sweeps produce the same

results, the error of the mean average decreases dramatically. Standardization and quantification was done with NBS610; Internal Standard Isotope was ^{43}Ca, assumed to have a constant concentration (400000 ppm). Absolute concentrations are prone to have rather large errors, especially for those elements that have the most near-background concentrations. However, ratios can be measured more precisely, with errors of less than 2%. The procedure for obtaining samples was to allow laser ablation to go along a continuous line, in order to determine spatial variations along the different rudist shell areas.

The visual result is a surface where a line can be seen. The line-ablation method has proved to be useful while analyzing compositional variation along layered structures such as stromatolites and coralline sponges (Sánchez-Beristain, 2010; Rodríguez-Martínez *et al.*, 2011). This method has proved to be more efficient when compared to a punctual method (Kamber and Webb, 2007) for the measurement of element concentrations in contiguous areas with different microfacial composition in some stromatolites (Rodríguez-Martínez *et al.*, 2011).

The analyzed isotopes comprised ^{24}Mg, ^{27}Al, ^{29}Si, ^{31}P, ^{34}S, ^{49}Ti, ^{51}V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{85}Rb, ^{88}Sr, ^{90}Zr, ^{95}Mo, ^{121}Sb, ^{137}Ba, ^{178}Hf, and the 14 Rare Earth Elements plus ^{89}Y (REY).

Results and discussion

Strontium, Magnesium, Manganese, Iron

In the case of the *Titanosarcolites* sp. nov. 1 shell (Figure 1), the strontium content in the inner layers is around 5000 ppm, whereas the content of magnesium remains constant at about 600 to 1000 ppm. This is consistent with the shell mineralogy for the adult organisms of this species, possessing a thick series of inner aragonitic layers (Skelton, 1974). Furthermore, it shows little signs of diagenesis (Mn<100 ppm; White, 2013) (Fig. 3).

The results observed for *Titanosarcolites* sp. nov. 1 are to some extent similar to *Biradiolites rudissimus* (Figs. 2, 4). Nevertheless, slight differences can be seen. Strontium concentrations in the latter remain relatively constant throughout the shell (ca. 400 ppm), as does magnesium (ca. 2500 ppm; Fig. 4). These values are consistent with low-magnesium calcite mineralogy for the thick outer layer of the specimens of this genus, and for radiolitid rudists (Steuber, 1999). Manganese content (ca. 70 ppm) also reflects a low diagenetic imprint (Fig. 4).

The contents of manganese and iron are low in the whole transect of the laser ablated surface of both shells (ca. 70 -100 ppm for Mn and < 200 ppm for Fe
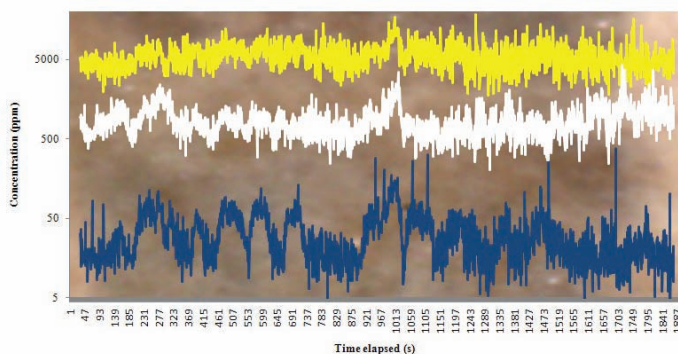

Figure 3. Results of LA-ICP-MS analyses on the shell of *Titanosarcolites* sp. nov. 1. Note the scarce concentrations of manganese (in blue) along the transect, which remain more or less constant, indicating a low degree of diagenetic effects. On the contrary, concentrations of strontium (yellow) and magnesium (white) point to an original aragonitic mineralogy. Image width: 1 cm.
Figura 3. Resultados de los análisis de LA-ICP-MS en la concha de Titanosarcolites *sp. nov. 1. Nótense las escasas concentraciones de manganeso (en azul) a lo largo del transecto que permanecen más o menos constantes, lo que indica un bajo grado de efectos diagenéticos. Por el contrario, las concentraciones de estroncio (en amarillo) y de magnesio (en blanco) apuntan a una mineralogía original aragonítica. Ancho de la imagen: 1 cm.*
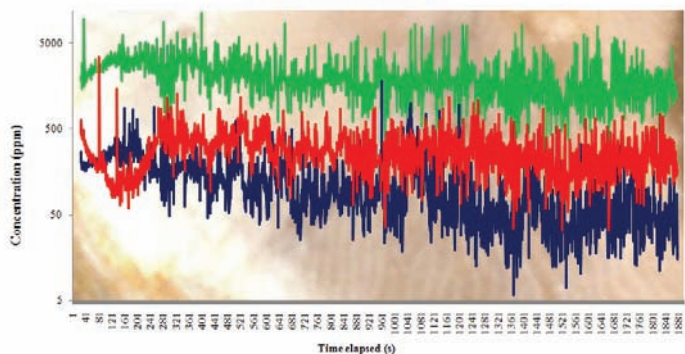

Figure 4. Results of LA-ICP-MS analyses on the shell of *Biradiolites rudissimus.* Note the scarce concentrations of manganese (in blue) along the transect, which, as in *Titanosarcolites,* remain more or less constant. On the contrary, magnesium (green) and strontium concentrations (red) point to an original low-Mg calcitic mineralogy. Image width: 1.2 cm
Figura 4. Resultados de LA-ICP-MS análisis sobre la concha de Biradiolites rudissimus. *Nótense las escasas concentraciones de manganeso (en azul) a lo largo del transecto que, al igual que en el caso de* Titanosarcolites, *permanecen más o menos constantes. Por el contrario, las concentraciones de magnesio (en verde) y de estroncio (en rojo) apuntan a una mineralogía original de calcita baja en Mg. Ancho de la imagen: 1.2 cm.*

respectively). These values can be interpreted as indicators of a low diagenetic imprint, despite the relative medium content of strontium in the inner shell layers (Steuber, 1999). "Normal" aragonite content of strontium is around 12000-14000 ppm (Mastandrea and Russo, 1995). These strontium values are lower in the case of the diagenetic imprint, and are always associated with higher iron and manganese values (Laghi *et al.*, 1984; Sánchez-Beristain *et al.*, 2011).

Silicon, Aluminum, Hafnium, Rubidium, Zirconium, Titanium

In both shells, the contents of silicon and aluminum correlate with each other (not shown), and in turn with trace elements such as hafnium, rubidium, zirconium and titanium. Despite their negligible contents (<20 ppm Si; < 6 ppm Al), they can be related to sporadic terrigenous input, which may have been incorporated into the shell of the rudist by means of filtration. Occasionally, silicon values may be high due to an initial permineralization process (Flügel, 2010); however, crustal related trace element values do not rise along with them.

Sulfur, Phosphorus, Rare Earth Elements + Yttrium

Sulfur and phosphorus concentrations in both shells are rather low, and do not reflect any correlation with terrigenous material (Si or Al). Sulfur values range between 600 and 1200 ppm, whereas phosphorus ranges between 10 and 50 ppm. Regardless of the fact whether their signal come from relicts of biological activity or from terrigenous input (no correlation is visible with Si or Al), these elements, in particular P, have an influence on the deposition and precipitation of REY (Rare Earth Elements and Y), in that normalized patterns (REY patterns) would differ considerably to the interpretable ones (Byrne *et al.*, 1996). Therefore, we consider that REY data are not conclusive, and were thus not taken into account for the analysis.

Molybdenum, Zinc, Copper, Antimony, Chromium

Elements like molybdenum, zinc, copper, antimony and chromium do not have significant concentrations in any segment of the shells, and can seldom be found in isolated patches in them. Therefore, their concentrations can be interpreted as the product of occasional inclusions.

Vanadium

The case of vanadium is of special importance. Its concentration lies between 5 and 100 ppm in both shells. In modern times, organisms such as ascidians are able to absorb and metabolize vanadium through a specialized group of cells, the vanadocytes. These cells would have the function of producing proteinic substances which would deter potential predators (Brusca and Brusca, 2003; Michibata *et al.*, 2002). However, vital functions have not been inferred in any other kind of organisms. Some modern bivalves retain vanadium in their cells, most of which comes from a source of anthropogenic pollution. This not being the case for obvious reasons in fossil bivalves, poses an important scenario for further research.

Barium

The two shells show differences in their barium concentrations. In the *Titanosarcolites* sp. nov. 1 shell, Ba-peaks oscillate between 20 and 160 ppm (Figure 5). Otherwise, Ba concentrations remain close to 0 ppm along the ablation transect. The genus *Titanosarcolites* is included in the Family Caprinidae, whose members are characterized by possessing a shell composed of more or less thick internal aragonite layers and an external low-Mg calcite layer (Skelton, 1974; Steuber and Löser, 2000). Aragonite is
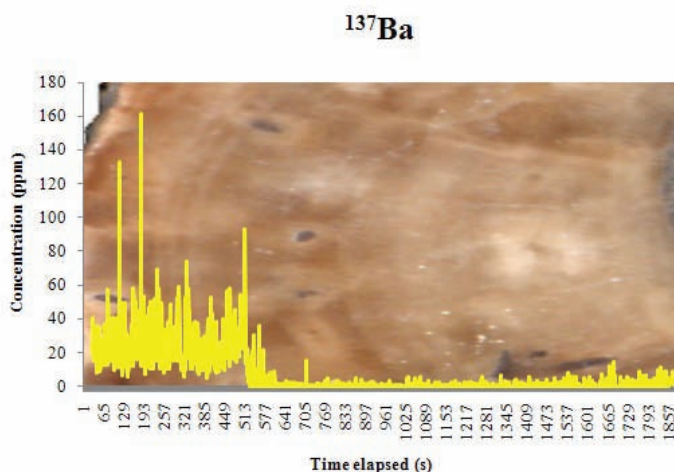

Figure 5. Results of Ba-concentration obtained through LA-ICP-MS analyses along a transect on the shell of *Titanosarcolites*. Note that peaks do not exceed 160 ppm. Image width: 1.2 cm. See text for further details.
Figura 5. *Resultados de concentración de Ba obtenidos por medio del análisis con LA-ICP-MS a lo largo de un transecto en la concha de* Titanosarcolites. *Nótese que los picos no exceden las 160 ppm. Ancho de la imagen: 1.2 cm.Véase el texto para mayor información.*

more prone to diagenetic effects than calcite is (Flügel, 2010), and diagenesis usually tends to increase Barium concentrations (Dickson, 1985; Henkel *et al.*, 2012). However, Sr concentrations reveal that the original mineralogy is preserved to some extent. This is reinforced with low concentrations of late diagenesis-related elements such as Fe and Mn. Furthermore, no correlation exists between the concentrations of the two latter elements and barium (r^2= 0.003). The peaks in the concentration of this element may thus be the result of its absorption from ingested phytoplankton, particularly from diatoms (Thebault *et al.*, 2009). On the other hand, Gillikin *et al.* (2006) suggested that the cause of Ba/Ca peaks may be related not to the ingestion of phytoplankton, but rather to the presence of barite. However, no correlation exists between the concentrations of Ba and S throughout the whole time series, or at the Ba-peaks.

Biradiolites rudissimus Trechmann is a radiolitid rudist. The members of this family are characterized by possessing a thick calcitic outer layer, whereas the inner aragonite layer is reduced. The preservation is thus better, since the diagenetic imprint is lower. Low-Mg calcite mineralogy is reflected by the concentrations of magnesium and strontium. In addition, and as in *Titanosarcolites* sp. nov. 1, there is no correlation between these elements and barium. It is therefore inferred that the peaks observed for the barium concentration along the transect, which do not exceed 180 ppm (Figure 6) may reflect phenomena such as either the ingestion of phytoplankton or the absorption of barite. The medium correlation between barium and sulphur at the Ba-peaks (r^2= 0.31) may indicate that the origin of barium is in partly related to the barite.

Nevertheless, elevations in Ba concentrations in modern bivalves are sometimes related to ingestion of selected phytoplankton elements (particularly diatoms) through filtration (Thebault *et al.*, 2009). If this is the case in these shells, it could be a milestone in rudist palaeobiology and palaeoecology.

Barium concentrations have never been analyzed in rudists. Peaks in Ba concentrations could be assessed in both rudist shells. This element has been interpreted in modern bivalve shells as possible indicators of marine bioproductivity (Thebault *et al.*, 2009). They may be related to the ingestion of diatoms, which absorb this element into their shell. However, these concentration peaks may also be related to the absorption of barite ($BaSO_4$). Furthermore, as rudists comprise exclusively fossil material, they are prone to the effects of diagenesis, which may affect the content of barium in carbonates.
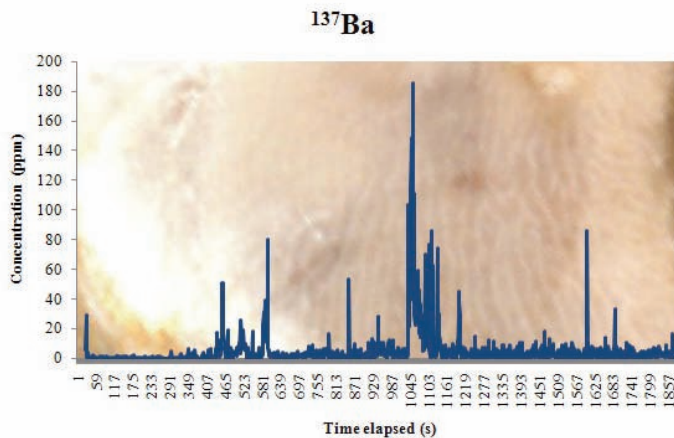

Figure 6. Results of Ba-concentration obtained through LA-ICP-MS analyses along a transect on the shell of *Biradiolites rudissimus*. Note that peaks do not exceed 180 ppm. Image width: 1.4 cm. See text for further details.
Figura 6. Resultados de concentración de Ba obtenidos por medio del análisis con LA-ICP-MS a lo largo de un transecto en la concha de Biradiolites rudissimus. *Nótese que los picos no exceden las 180 ppm. Ancho de la imagen: 1.4 cm.Véase el texto para mayor información.*

Conclusions

LA-ICP-MS revealed very important information on the distribution of selected elements in rudist shells. It proved to be a reliable method in determining their good preservation state, and thus their original mineralogy. Furthermore, it allowed the determination of the sporadic influence of terrigenous input and the presence of phosphorus, both of which hinder in turn the possibility of performing further analyses, such as the quantification of reliable REY patterns.

Some elements do not have a significant concentration pattern, and therefore it is not possible to elaborate any inferences based on them. However, selected trace elements, such as V and Ba may reflect certain instances of biological activity, such as the formation of specialized proteins, or the evidence of phytoplankton blooms.

This method can be used successfully in element analysis in fossil bivalve shells.

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