



Major element analysis in sedimentary rocks from the Middle Mississippian– Middle Pennsylvanian La Joya section in Sierra Agua Verde, Sonora, Mexico

Análisis de elementos mayores en rocas sedimentarias de la sección La Joya del Misisípico Medio-Pensilvánico Medio en Sierra Agua Verde, Sonora, México

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Abstract

The Sierra Agua Verde is a significant paleontological site in northwestern Mexico. While numerous stratigraphic and paleontological studies have been conducted in this area, a lack of geochemical research has hindered a complete understanding of its paleoenvironmental context. Our study primarily focused on examining the fossiliferous limestone from the Middle Mississippian to Middle Pennsylvanian periods in the region. By utilizing X-ray fluorescence (XRF), we measured major element oxide concentrations in bulk rock limestone samples. This analysis helped us infer the paleoenvironmental conditions through elemental ratios and correlation coefficients. The samples displayed calcium enrichment, with some also exhibiting high magnesium/calcium (Mg/ Ca) ratios. The silicon/aluminum (Si/Al) ratio, akin to Si/Ca, was interpreted as indicative of productivity, potentially attributed to the presence of siliceous sponges. Nevertheless, elevated silicon values could also result from continental weathering processes. Peaks in elemental values apart from calcium may indicate episodes of riverine influx onto the carbonate platform where these sediments settled. We related the curve of major elements to previous stable isotope studies to determine if detrital element input aligned with global or regional climate conditions. Our hypotheses were corroborated by statistical analysis, yielding dendrograms that highlighted associations between elements such as Al and K, as well as Fe and Ti (Morisita Index). This could suggest the precipitation of minerals like orthoclase/illite and ilmenite. Moreover, the increasing divergence between Mg and Mn in comparison to the Al-K phenon, along with Si, might explain the strong Fe-Ti connection, reflecting the tendency of both Mn and Ti to form oxides. The co-precipitation of Si and P might also be linked to productivity episodes. However, the Si content could indicate either quartz input or biogenic silica contribution.

Keywords: Carboniferous, Mexico, paleoenvironment, Si/Al, Si/Ca, Sonora, X-ray fluorescence.

Resumen

La Sierra Agua Verde es un importante sitio paleontológico en el noroeste de México. Si bien se han realizado numerosos estudios estratigráficos y paleontológicos en esta área, la falta de investigación geoquímica ha dificultado una comprensión completa de su contexto pa-

Cómo citar / *How to cite*: Villanueva-Olea, R., Sánchez-Beristain, F., Palafox-Reyes, J. J., Buitrón-Sánchez, B. E. (2025). Major element analysis in sedimentary rocks from the Middle Mississippian–Middle Pennsylvanian La Joya section in Sierra Agua Verde, Sonora, Mexico. *Paleontología Mexicana*, *14*(1), 29–44.

Manuscript received: February 18, 2024. Manuscript corrected: May 29, 2024. Manuscript accepted: June 4, 2024.



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leoambiental. Nuestro estudio se centró principalmente en examinar calizas fosilíferas del Misisípico Medio-Pensilvánico Medio en la región. Utilizando fluorescencia de rayos X (FRX), medimos las concentraciones de óxidos de elementos mayores en muestras de caliza en roca total. Este análisis nos ayudó a inferir las condiciones paleoambientales a través de proporciones elementales y coeficientes de correlación. Las muestras presentan un enriquecimiento de calcio, y algunas también mostraron altas proporciones de magnesio/calcio (Mg/Ca). La relación silicio/aluminio (Si/Al), similar a Si/Ca, se interpretó como indicativa de productividad, potencialmente atribuida a la presencia de esponjas silíceas. Sin embargo, los elevados valores de silicio también podrían deberse a procesos de intemperismo continental. Los picos en los valores elementales distintos del calcio pueden indicar episodios de aporte fluvial hacia la plataforma carbonatada donde se asentaron estos sedimentos. Relacionamos la curva de elementos mayores con estudios previos de isótopos estables para determinar si la entrada de elementos detríticos se alineaba con las condiciones climáticas globales o regionales. Nuestras hipótesis fueron corroboradas mediante análisis estadístico, arrojando dendrogramas que resaltaron asociaciones entre elementos como Al y K, así como Fe y Ti (Índice de Morisita). Esto podría sugerir la precipitación de minerales como ortoclasa/illita e ilmenita. Además, la creciente divergencia entre Mg y Mn en comparación con el clado Al-K, junto con el Si, podría explicar la fuerte conexión Fe-Ti, reflejando la tendencia de Mn y Ti a formar óxidos. La coprecipitación de Si y P también podría estar relacionada con episodios de productividad. Sin embargo, el contenido de Si podría indicar entrada de cuarzo o una contribución de sílice biogénica.

Palabras clave: Carbonífero, México, paleoambiente, Si/Al, Si/Ca, Sonora, fluorescencia de rayos-X.

1. Introducción

The Late Paleozoic was a time of great climatic change that started in the Late Devonian and ended in the early Permian. These changes represent the development of a series of glaciations in the Gondwana supercontinent, which ultimately led to the formation of the northern hemisphere cyclothems (Isbell et al., 2003). It was also a time of extended continental collisions, mountain building, and fluctuating sea levels (Wicander and Moore, 2010). The Paleozoic stratigraphic record extends through the world since it constitutes the base over which younger strata of Mesozoic and Cenozoic ages lie. Particularly, the Paleozoic has been long studied in North America, with a paleoclimatic and paleoenvironmental perspective, which has allowed the correlation of these patterns found in the region with those present in other parts of the world like the Paleotethys (Mii et al., 2001). In the same way, the Late Paleozoic shows lower eustatic levels compared with those of the Early Paleozoic, a phenomenon that can be attributed to the so-called Late Paleozoic Ice Age (LPIA) (Haq and Schutter, 2008). Paleozoic exploration geology in search of hydrocarbon reservoirs has broadened in recent vears (e.g. Xiangzheng et al., 2019; Yuan et al., 2019). Regarding geochemistry, there is a scarcity of studies comprising Paleozoic materials; most geochemical studies are focused on several stages in the Mesozoic and Cenozoic.

In the state of Sonora, the Sierra Agua Verde has the most complete sequence of the Paleozoic in northwestern Mexico and has deposits from the Neoproterozoic (?) to the Pennsylvanian period in two different groups. Stewart et al. (1984, 1988, 1999) were among the first to recognize the presence of Paleozoic rocks. The deposits of San Jose Group represent only the Cambrian period, whereas the Agua Verde Group represents lithologies from the Ordovician to Lower Permian systems (Ochoa-Granillo and Sosa-León, 1993). Many of the strata of the Agua Verde Group are highly fossiliferous. Previous studies have focused on the identification of crinoids and taphonomic patterns of encrinites (Buitrón-Sánchez et al., 2007); the discovery of Pennsylvanian fusulinid foraminifera and calcareous algae (Gómez-Espinosa et al., 2008); the identification of a varied Carboniferous biota of phylloid algae and invertebrates like coralline chaetetid sponges, brachiopods, bryozoans, tabulate and solitary corals, fusulinid foraminifera and several paragenera of crinoids (Buitrón-Sánchez et al., 2015); and the description of mid-Carboniferous conodont associations (Navas-Parejo et al., 2017). These conodont associations are typical of shallow-water carbonate platforms found in other parts of the North American craton.

The Sierra Agua Verde range has not been studied from a geochemical approach. Recently, Villanueva-Olea *et al.* (2019) expanded the study of this group by generating more data

on microfacies and by involving new geochemical analysis of a section representing the Middle Mississippian-Middle Pennsylvanian interval. Geochemical characteristics were obtained through the excursions of $\delta^{13}C$ and δ^{18} O of limestones of the La Joya section and were interpreted in terms of paleo-depositional environments that varied from the margin-platform reefs to a restricted-circulation lagoon. A paleo-bathymetric curve reconstructed from the microfacies analysis and distinctive patterns of $\delta^{13}C$ and $\delta^{18}O$ infers that the changes observed were due to regional as well as local factors, such as varying inputs of ¹²C-enriched continental fresh water, regional upwelling and residence times of the seawater in the shallow restricted platform. Nevertheless, the global climatic patterns also forced the isotopic behavior as well (Villanueva-Olea et al., 2019). Geochemical characteristics go beyond the characterization of stable isotope compositions and involve differentiation among lithologies through the major element analysis (Craigie, 2018). For example, Herron (1988) introduced a parameter (i.e. log Fe/K ratio) for the classification of arkoses, which is one of the most commonly used geochemistry-based classification schemes for sandstone. Similarly, many other geochemical studies have focused on paleoenvironmental interpretations using major oxides as biomarkers (e.g. Ross and Bustin, 2009; Hakimi et al., 2015; Hu et al., 2017), showing the viability of using these proxies for interpreting depositional environments. For example, Hakimi et al. (2015) interpreted the high Ca and moderate Si and Al contents in their samples from Late Jurassic-Early Cretaceous sediments of Iraq as indicators of a deposit in Ca-rich waters but with clear inputs of quartz and clay minerals. The finding of low- to moderate levels of P concentrations was interpreted as input of mixed organic matter, which led to the formation of a reducing depositional environment favorable for preservation of organic matter.

In this work, we further discern aspects regarding geochemistry of the Middle Mississippian-Middle Pennsylvanian limestones exposed at Sierra Agua Verde of northwestern Mexico (state of Sonora) by determining the concentrations of the major element oxides through the X-Ray Fluorescence technique (XRF) to identify the lithologies as well as to complement the previously reported paleoclimatic and paleoenvironmental interpretations for this area.

2. Study area and stratigraphy

The Sierra Agua Verde is a mountain range in the state of Sonora in northwestern Mexico. The works of Stewart et al. (1984, 1988, 1999) were among the first to recognize the presence of Paleozoic rocks in this area. Other studies have also contributed to the understanding of the regional stratigraphy (Repetsky et al., 1985; Poole et al., 1995). Ochoa-Granillo and Sosa-León (1993) disserted on Ordovician, Devonian, Carboniferous, and Permian strata. The area (Figure 1) is distinguished for its richness in Paleozoic biota (Minjárez-Sosa et al., 1993; Ochoa-Granillo and Sosa-León, 1993). The lithological group with the same name includes the informal Santiago formation of the Mississippian age and it is composed of limestone, dolomitized limestone, and sandstone in a platform with calcareous banks of colonial organisms (Ochoa-Granillo and Sosa-León, 1993). Overlying it and in a transitional contact, the informal La Joya formation, of the Pennsylvanian age, can be found. It consists of limestone intercalated with calcareous lodolites and sandy lenses, and was deposited in a shallow platform, with development of calcareous banks with terrigenous input (Ochoa-Granillo and Sosa-León, 1993, p. 35-38). The paleontological study of Gómez-Espinosa et al. (2008) reported the presence of fusulinids and calcareous algae. Recently, Buitrón-Sánchez et al. (2007, 2015) mentioned the presence of numerous other species such as phylloid algae, fusulinids, chaetetids, tabulate and solitary corals, gastropods, fenestellid bryozoans, productid and spiriferid brachiopods, crinoids, and conodonts in the La Jova formation. Navas-Parejo et al. (2017) conducted a biostratigraphic study based on conodonts, in which they reported the presence of some index fossils that allowed the location of the mid-Carboniferous boundary within the mid-sequence of the La Joya section, being composed in the lower part of Meramecian and Chesterian (Middle–Upper Mississippian: Visean–Serpukhovian) strata, and in the upper part of a Morrowan (Bashkirian, Lower Pennsylvanian) sedimentary sequence. Traditionally, this section had been considered part of the Pennsylvanian system (Atokan: Upper Bashkirian–Lower Moscovian) (Buitrón-Sánchez *et al.*, 2007, 2015; Gómez-Espinosa *et al.*, 2008). We studied the lithologies of a sequence of deposits of *ca.* 270 m thick of Meramecian– Atokan (Middle Mississippian–Middle Pennsylvanian) age within the section (Figure 2). The base of this section (about 50 m thick) corresponds to sandy limestones and poorly fossiliferous grayish limestones. It is overlain by light to dark gray limestones between 50–180 m (from the base) and intercalations of pale volcanic tuff, and a coquina layer composed of brachiopods at 80 m (Navas-Parejo *et al.*, 2017). The Pennsylvanian La Joya formation starts at 131 meters over the base, which means the previously described Mississippian lithology



Figure 1. Study area, in the state of Sonora, northwestern Mexico.

Major Element Analysis of La Joya Section, Sierra Agua Verde, Sonora, Mexico



Figue 2. Stratigraphic column of the La Joya section in the Sierra Agua Verde, Sonora, Mexico (Modified from Navas-Parejo *et al.*, 2017).

continues over the Pennsylvanian. The upper part of the section (180–270 m from the base) has pink limestone with intercalations of white and dark chert nodules. This interval is highly fossiliferous with a biota consisting of green algae, coralline sponges (*Chaetetes*), foraminifers, brachiopods, bryozoans, and crinoids (Buitrón-Sánchez *et al.*, 2007, 2015; Gómez-Espinosa *et al.*, 2008).

3. Material and methods

A total of 67 samples from this section were evaluated through petrographic microscopy in thin sections looking for those with minimal diagenesis (*i.e.* dolomitization, silicification, stylolitization, and presence of iron oxides). Finally, we selected 31 samples for this study. All of them were ground to <72 μ m particles in a Spex SamplePrep 8000 M mill in tungsten carbide vials. The powdered samples were further dried in an oven up to 110°C for 24 hours and about 0.8 g of the dried samples were mixed with a flux containing lithium metaborate (LiBO₂), lithium tetraborate (Li₂B₄O₇), and lithium iodide (LiI), maintaining a sample/flux ratio of 1:9 for estimation of major element oxides in an X-ray fluorescence (XRF) spectrometer (*e.g.* Lozano-Santa Cruz *et al.*, 1995; Lozano and Bernal, 2005). Loss on ignition (LOI) was determined by heating 1 g of sample at 950°C for 1 hour, and this data was added to the elemental concentrations obtained in the spectrometer to obtain the total mass of the sample.

Subsequently, the sample and flux mixing was fused in Pt/Au (ratio of 95:5) melting pots using a Claisse Fluxy-10 fluxer and the disc-shaped glass pearls generated were placed into a ZSX Primus II Rigaku wavelength-dispersive X-ray fluorescence spectrometer (WD-FRX), housed at the Laboratorio de FRX (Instituto de Geología, UNAM), which detected different wavelengths typical of each element and estimated the concentrations of SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, and P₂O₅, by using the inhouse and external reference materials (USGS). The threshold of detection was 0.002% or 20 ppm.

4. Results

Due to the ease to work with elements, we decided to convert the values of elemental oxides to elements by eliminating the corresponding percentage of oxygen on each value. Hence, Table 1 shows the concentrations once converted to percentage elements in the calcareous samples. In general, calcium with 15.4% – 40.1% is the most abundant, and is followed by silicon with 0.1% - 28.5%, magnesium with 0.08% - 6.9%, iron with 0.03% - 0.5%, titanium with 0.01% - 0.15%, and phosphorus with 0.003% - 0.12%. Most of the concentrations of some elements remained below the detection limit. For example, aluminium had a range

between <0.002% - 0.6%; potassium showed values between <0.002% - 0.28%, whereas manganese between <0.002% - 0.01%. Sodium could not even be detected by the equipment.

The Santiago formation represents the limestones of the Mississippian epoch and has a total of 17 samples, which range from LJ 2 to LJ 38 (Table 1). The ranges (in percentage) for each element are: calcium with 15.38 - 40.11, silicon with 0.23 - 28.52, magnesium with 0.08 - 2.13, aluminum with <0.002 - 0.59, iron with 0.03 - 0.35, potassium with 0.01 - 0.28, titanium with 0.01 - 0.15, phosphorus with 0.003 - 0.117, and manganese with <0.002 - 0.01.

For the La Joya formation, which is defined by the Pennsylvanian part of the section, a

Table 1. Conter	nts of maior el	ements in samt	oles of the La I	ova section in	w/w units
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	Si	Ca	Al	Ti	Fe	Mn	Mg	К	Р	LOI
Samples	%	%	%	%	%	%	%	%	%	%
LJ 2	1.29	36.03	0.06	0.02	0.07	0	2.13	0.02	0.007	42.18
LJ 4	0.36	38.55	0	0.02	0.06	0	1	0.01	0.008	42.77
LJ 6	0.34	39.75	0	0.01	0.05	0	0.22	0.01	0.003	42.48
LJ 7	0.27	40.11	0.01	0.03	0.06	0	0.2	0.02	0.003	42.02
LJ 11	0.31	39.07	0.01	0.02	0.19	0.01	0.2	0.01	0.016	42.98
LJ 12	0.23	39.76	0.02	0.03	0.07	0.01	0.17	0.01	0.006	42.61
LJ 14	0.71	39.2	0.05	0.02	0.18	0.01	0.19	0.03	0.007	41.85
LJ 16	1.04	39.11	0.07	0.03	0.12	0.01	0.16	0.05	0.01	41.36
LJ 21	28.52	15.38	0	0.02	0.03	0	0.08	0.01	0.117	16.04
LJ 24	7.23	31.78	0.59	0.15	0.35	0.01	0.34	0.28	0.054	34.49
LJ 27	2.95	37.22	0	0.01	0.05	0	0.4	0.01	0.028	40.02
LJ 29	1.43	38.81	0	0.03	0.05	0	0.22	0.01	0.081	41.06
LJ 30	8.76	31.27	0.25	0.04	0.16	0.01	0.34	0.13	0.01	34.51
LJ 32	6.31	34.09	0.15	0.08	0.06	0.01	0.21	0.09	0.013	36.7
LJ 34	3.56	36.74	0.1	0.07	0.05	0.01	0.18	0.06	0.038	39.09
LJ 36	0.66	39.56	0.01	0.02	0.05	0.01	0.18	0.02	0.037	41.91
LJ 38	0.49	39.65	0	0.03	0.07	0.01	0.15	0.01	0.027	42.2
LJ 40	3.66	36.97	0.06	0.04	0.07	0	0.16	0.04	0.014	38.92
LJ 41	0.74	39.19	0	0.02	0.08	0	0.22	0.01	0.008	42.28
LJ 42	0.29	40.01	0.03	0.02	0.06	0	0.15	0	0.007	42.19
LJ 44	0.83	39.17	0.02	0.02	0.05	0	0.23	0.02	0.007	42.11
LJ 45	0.78	38.62	0.01	0.02	0.07	0	0.63	0	0.009	42.34
LJ 48	0.6	33.36	0.01	0.03	0.1	0	4.34	0.01	0.043	43.65
LJ 50	2.22	37.98	0	0.02	0.04	0	0.22	0	0.033	40.82
LJ 52	1.13	38.87	0.01	0.01	0.05	0	0.21	0	0.028	41.92
LJ 54	2.57	37.58	0.01	0.02	0.06	0	0.23	0.01	0.012	40.63
LJ 55	6.92	28.82	0.19	0.05	0.48	0.01	3.1	0.11	0.041	36.52
LJ 57	6.94	31.53	0.14	0.06	0.17	0.01	1.46	0.07	0.035	36.55
LJ 60	14.06	16.1	0.63	0.12	0.51	0.01	6.93	0.28	0.12	30.02
LJ 63bis	1.01	39.75	0	0.02	0.05	0	0.23	0	0.004	41.02
LJ 64	0.11	40.1	0	0.02	0.04	0	0.26	0	0.003	42.47

total of 14 samples were analyzed. The ranges (in percentage) for this formation are: calcium with 16.1 - 40.1, silicon with 0.11 - 14.06, magnesium with 0.15 - 6.93, aluminium with <0.002 - 0.63, iron with 0.04 - 0.51, potassium with <0.0002 - 0.28, titanium with 0.01 - 0.12, phosphorus with 0.003 - 0.12, and manganese with <0.002 - 0.01.

When we plot the abundance of Si and Ca as oxides (Figure 3), it is evident that there is a reverse relationship between them. Major element analyzes suffer from the closure limitation (*e.g.* Johansson *et al.*, 1984; Pingitore and Engle, 2022). Since calcium is the most represented element in limestones, it suffers a concentration decrease as the concentrations of the other elements increase. Complementarily, the nature of our samples is reflected in the LOI fraction (comp. Török *et al.*, 2010), as revealed by similar LOI and CaO plots (Figure 3).

As a method to elucidate the paleoenvironmental signal, we pursued the analysis of



Figure 3. SiO_2 (blue) vs CaO (red) variation plots of strata from the La Joya formation. The dotted line interval is characterized by the occurrence of diagenetic events, such as silicification. LOI plot (green) displays similarities with CaO, as expected, due to the original calcitic mineralogy. See text for further information.

elemental ratios. The main ratios utilized were Si/Ca, Si/Al, Al/Ca, Fe/Ca, Ti/Ca, K/Ca, and Mg/ Ca (Table 2).

For the Si/Ca ratio, all values except LJ 21, are found below 1, meaning that Si concentrations are lower in relation to Ca. In contrast, for the Si/Al ratio, Si is enriched in relation to Al. For the remaining ratios (Al/Ca, Fe/Ca, Ti/Ca, K/Ca, and Mg/Ca) values are less than 1 and, in several samples, equal 0.

These data were then plotted (Figure 4). These ratios compared against calcium show a similar

Table 2. Relations between different major elements with calcium and silicon, coming from samples of Sierra Agua Verde, Sonora. Values in asterisk were calculated based on the lower threshold of the equipment detection (0.002%), therefore, the value shown here is underestimated for the Si/Al ratios.

Sample	Si/Ca	Si/Al	Al/Ca	Fe/Ca	Ti/Ca	K/Ca	Mg/ Ca
LJ 2	0.036	21.55	0.002	0.002	0.001	0.001	0.059
LJ 4	0.009	*675.69	0	0.002	0.001	0	0.026
LJ 6	0.009	*649.20	0	0.001	0	0	0.006
LJ 7	0.007	18.88	0	0.002	0.001	0.001	0.005
LJ 11	0.008	21.17	0	0.005	0.001	0	0.005
LJ 12	0.006	12.7	0	0.002	0.001	0	0.004
LJ 14	0.018	14.28	0.001	0.005	0.001	0.001	0.005
LJ 16	0.027	14.2	0.002	0.003	0.001	0.001	0.004
LJ 21	1.854	5988.99	0	0.002	0.001	0	0.005
LJ 24	0.228	12.31	0.018	0.011	0.005	0.009	0.011
LJ 27	0.079	*5573.37	0	0.001	0	0	0.011
LJ 29	0.037	337.07	0	0.001	0.001	0	0.006
LJ 30	0.28	35.17	0.008	0.005	0.001	0.004	0.011
LJ 32	0.185	43.23	0.004	0.002	0.002	0.003	0.006
LJ 34	0.097	36.01	0.003	0.001	0.002	0.002	0.005
LJ 36	0.017	56.61	0	0.001	0	0	0.004
LJ 38	0.012	*933.61	0	0.002	0.001	0	0.004
LJ 40	0.099	60.86	0.002	0.002	0.001	0.001	0.004
LJ 41	0.019	*1407.03	0	0.002	0	0	0.006
LJ 42	0.007	8.98	0.001	0.002	0	0	0.004
LJ 44	0.021	54.03	0	0.001	0.001	0	0.006
LJ 45	0.02	105.04	0	0.002	0	0	0.016
LJ 48	0.018	62.76	0	0.003	0.001	0	0.13
LJ 50	0.058	*4191.07	0	0.001	0.001	0	0.006
LJ 52	0.029	141.91	0	0.001	0	0	0.005
LJ 54	0.068	421.97	0	0.002	0	0	0.006
LJ 55	0.24	36	0.007	0.017	0.002	0.004	0.107
LJ 57	0.22	48.42	0.005	0.005	0.002	0.002	0.046
LJ 60	0.873	22.32	0.039	0.032	0.007	0.018	0.43
LJ 63bis	0.025	*1913.14	0	0.001	0.001	0	0.006
LJ 64	0.003	*199.62	0	0.001	0	0	0.007



Figure 4. Logarithmic relationships between different elemental ratios of the La Joya section compared with the paleobathymetric curve and δ^{13} C and δ^{18} O values previously published in Villanueva-Olea *et al.* (2019). Asterisks indicate some of the elements in the ratio yielded a value below detection equipment limit (<0.002%), which implies the corresponding peak is more accentuated than that shown in the plot. The values of δ^{13} C follow the standard of VPDB, whereas those for δ^{18} O are in VSMOW.

pattern. Only the first curve (Si/Al) does not exactly match the others in some parts, having several peaks scattered through the entire column, which could be attributable to low Al concentrations at the corresponding points.

For the Mg/Ca ratio curve (Figure 4), the lower half of the section (the Santiago fm. and the base of the La Joya fm.) presents comparatively lower values than the upper half and until LJ 45, where an increase starts until LJ 60, which has the higher value. After this rise, a fall in the last two samples was recorded, with values like those of the lower half of the section.

To recognize the source of the main elements analyzed, we used the Pearson correlation coefficient (r; Pearson, 1895) between any major element (*i.e.* K, Mg, Fe, etc.) and Ti or Al (Table 3). High correlations (close to 1) between any major element and Ti-Al (low solubility elements) are considered proxies of continental erosion, because the elements were transported in the detrital fraction together with the Ti-Al from the continent. Hence, r values close to 0, might indicate *in situ* precipitation at the sea bottom. To complement these analyses, dendrograms were additionally designed with the aid of the MVSP software (licensed to FSB), in order to strengthen the inferences obtained through the Pearson Correlation coefficient (Figure 5). Four experiments were carried out, using two algorithms and two coefficients. The

Table 3. Correlation coefficients of various elements from the La Joya section. p-values are indicated above the diagonal, whereas the coefficients are below it. Values highligted in bold overpass the confidence level of 0.05.

	Si	Ti	Al	Fe	Mn	Mg	Ca	Κ	Р
Si		0.04	0.02	0.08	0.43	0.16	0	0.02	0
Ti	0.37		0	0	0	0.02	0	0	0.01
Al	0.42	0.92		0	0	0	0	0	0.01
Fe	0.32	0.68	0.81		0	0	0	0	0.02
Mn	0.15	0.55	0.51	0.55		0.44	0.23	0	0.44
Mg	0.26	0.41	0.55	0.68	0.14		0	0	0
Ca	-0.92	-0.51	-0.6	-0.57	-0.22	-0.6		0	0
Κ	0.43	0.93	0.99	0.82	0.55	0.52	-0.6		0.01
Р	0.75	0.45	0.48	0.43	0.14	0.5	-0.82	0.47	

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Figure 5. Dendrogram using both UPGMA and WPGMA clustering methods coupled with the Pearson Coefficient. Ca is independent of other elements, pointing to a calcitic mineralogy. The strong Al-K phenon depicted here (with values close to 1) can provide evidence the presence of illite/orthoclase. In addition, the progression from Ti towards Mn (encompassing Fe and Mg) can be related to silicates. Finally, the phenon Si-P could point to some sort of biogenic precipitation. See text for further details.



Modified Morisita's Similarity Figure 6. Dendrogram using both UPGMA and WPGMA clustering methods coupled with the Morisita Similarity Index. Note the similar topology compared with Figure 5, except for the phenon Fe-Ti (with values close to 0.85), which could indicate the precipitation of minerals such as ilmenite. See text for further explanation.

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algorithms used were WPGMA (Weighted Pair Group Method with Arithmetic Mean) and UPGMA (Unweighted Pair Group Method with Arithmetic Mean), both of them developed by Sokal and Michener (1958). These algorithms were coupled with both the Morisita Similarity Index (Morisita, 1959; Figure 6) and with the aforementioned Pearson Correlation Coefficient. Results were very similar, showing only slight topological variations in the obtained dendrograms (Figures 5 and 6).

5. Discussion

5.1. General interpretations of r values and elemental ratios

The most abundant element in rocks of the La Joya section was Ca, which was expected, since most of the rocks in the area are limestones. Si was the second most abundant element, which might have different sources. Dendrograms confirm that Ca concentrations are independent of those of other elements (Figures 5 and 6). This makes sense, because in limestone, the most abundant element is Ca (Flügel, 2010). On the other hand, silicon is essential to form silicates and feldspars, and it can thus carry other elements such as Al, K, Mg, Fe and Mn. The partial decoupling of Si regarding these elements is possibly linked to the fact that its source might be either quartz or biogenic silica (White, 2013), which may also account for its abundance, second to Ca. Furthermore, it must also be stressed that the coupling between silicon and P (Figures 5 and 6), despite the low concentrations of the latter, could be related to organic precipitation events, since the silicon concentration can be related to productivity episodes (Kristiansen and Hoell, 2002). Likewise, the interaction of silicon with phosphorus has been successfully studied in aquatic environments, to assess bioproductivity (Conley and Malone, 1992; Tallberg et al., 2008). Nevertheless, more studies involving more elements, such as Ba (Liguori et al., 2016) and its

relation to Mn (Carter *et al.*, 2020), would be required to sustain this assertion.

When we plot the r coefficients of the different elements, a negative correlation (r = -0.6) is observed between Al and Ca, which is attributed to the association of aluminum with clay and other clastic minerals. Conversely, positive correlations are found between Al, Fe, K, and Ti, which means all these elements constitute the clastic fraction of the samples. Complementarily, dendrograms with clustering algorithms between UPGMA/WPGMA and the Morisita Similarity Index (C_{λ}) indicate an association between Fe and Ti (Figure 6). This could mean a coprecipitation of these elements in minerals like ilmenite (Anthony et al., 2005). However, this is not reflected in UPGMA/WPG-MA-Pearson dendrograms (Figure 5). Therefore, to confirm this association, more studies would be necessary.

In all dendrograms (Figures 5 and 6), Mg and Mn are progressively more distant from the Al-K phenon, and from Si. This can serve as a complement to the explanation that Fe and Ti could be associated with each other, in addition to the fact that Mn can, like Ti, form oxides (White, 2013).

The strong positive correlation between Al and Ti implies that these elements have the same continental source and were transported as particles through continental runoff. The low positive correlation between Si-Al, Si-K, and Si-Fe (<0.43) indicates that not all the silicon in the platform results from chemical weathering of continental rocks, supporting the idea of a partly biogenic origin for Si. The same is true for Mg, when it is compared with Ti and Al: not all the Mg was carried in the insoluble fraction of weathering products, it could also be the product of precipitation at the sea bottom in Mg-enriched waters (*e.g.* Warren, 2000).

In any case, it must be stressed that Si concentrations are considerably high ($\bar{x} = 3.54$), when compared to other sources. This would imply that silicon must have another origin additional to silicates/feldspars (*e.g.* Tucker and Wright, 1990) which would include a biogenic source (comp. Reitner, 1992).

The concentrations of Na below the detection limit of the XRF equipment suggests a lack of deposition of Na-bearing plagioclase in the platform or chemical weathering of most of the plagioclase during the transportation from the continent into the platform. On the other hand, K-bearing minerals (potassium feldspars) are present in the platform and are more resistant to chemical weathering compared to plagioclases (Pye, 1986). K might also have been present in clay minerals deposited in the platform and it is similar to the abundance of Al. Furthermore, all dendrograms suggest a strong association between K and Al, forming a strong phenon (C_{λ} = 0.983; Figures 5 and 6), which reinforces the theory that supports orthoclase as a possible source of origin of these elements. However, another possibility could be that the cause of this association, as indicated by the dendrogram, could be the presence of illite, as this would explain the more or less strong correlation that exists between the K-Al phenon and elements such as Mg and Fe. Nevertheless, its rather low C_{λ} value (ca. 0.57 using UPGMA and 0.52 using WPGMA; Figure 6) in comparison with the K-Al value, in addition to the presence of other elements like Ti and Mn, which are not typical of illite, leads us favor orthoclase as the most likely option for the coprecipitation of K-Al.

Different proxies were used to evaluate the fluctuations of some variables in the platform, like biogenic productivity, using the Si/Al ratio; and erosion using Al/Ca, Fe/Ca, Mg/Ca, Ti/Ca, and K/Ca ratio and total carbonate content of the samples. Mg/Ca is a proxy that enables the abundance of magnesium in calcite to be seen, or the abundance of low magnesium calcite compared to high magnesium calcite or dolomite (Warren, 2000; Sánchez-Beristain et al., 2016). It might also be used as a proxy of salinity of the water (Hönisch et al., 2013). The r for Mg and Al has a value of 0.55, whereas this value for Mg and Ca is -0.60. Both r coefficients are interpreted as Mg found mostly in the clastic fraction rather than being part of high magnesium calcite or dolomite. Therefore, the Mg/Ca

ratio can be regarded as a proxy of continental erosion, as are all previously mentioned ratios.

The K/Ca, Fe/Ca, and Al/Ca ratios with minimum values close to 0 (Table 2) mean a depletion of these elements in the carbonates. Low Fe/Ca ratios can be explained because of the absence of ferromagnesian minerals (Creamean *et al.*, 2014), whereas low Al/Ca values mean a reduced input of Al-rich clays (Kraft *et al.*, 2013).

5.2. Geochemical interpretations for the Santiago formation

The Al/Ca, Fe/Ca, K/Ca, and Ti/Ca ratios show a similar pattern with low values through much of the Meramecian (Table 2). The low Fe/ Ca ratios are interpreted here as indicating no entrance of Fe-rich minerals, whereas the low Al/Ca values mean a reduced input of Al-rich clays. At the end of this stage, in the sample LJ 24, there is a conspicuous peak which is indicative of riverine influx with detrital input into the marine platform environment. That assumption is supported by the correlation of a negative excursion observed in δ^{13} C and δ^{18} O for the same sample.

The pattern of low continental inputs into the external marine platform environments is similar to the paleobathymetric curve which shows deeper sea levels for this time and, hence, a major distance from the coast, indicating a reduced river input. The paleobathymetric curve shifts from deeper to shallower conditions approximately when the elemental ratio curves peak in the final part of the Meramecian. The return to deeper conditions agrees with the return of low levels at the base of the Chesterian, even if the shallowing at the end of the Chesterian does not seem to cause another peak in the elemental ratios. This is interpreted as indicating no entrance of detrital sediments into the platform at that time. The behavior of the Mg/Ca ratio in the Mississippian part of the section is like that of the other erosion proxies, which proves the magnesium is part of the clastic fraction.

The Si/Ca curve (Figure 4) shows a slightly different pattern in relation to the other erosion curves already mentioned, but it is quite similar to the Si/Al curve, with a peak in LJ 21, a little before the peaks of the other elemental ratios. Since the Si/Al ratio indicates the abundance of continental quartz, biogenic silica or both, the peak in Si/Al, also present in Si/Ca but not displayed in the other elemental curves means that Si does have a biogenic source rather than continental and is considered a proxy of productivity. For the peak in LJ 30, the possible source of this biogenic silica could be attributed to the presence of sponge spicules seen in the microfacies analysis of the section (Villanueva-Olea et al., 2019).

A previous study on δ^{18} O (Villanueva-Olea *et al.*, 2019) shows that this proxy varied greatly throughout all the Meramecian, but, on average, the curve tends to higher values. This was interpreted as a period with cool temperatures (even if it was not glacial as such), with some warming periods. During this time, the values of elemental erosion ratios remained low and uniform, except for the peaks in the samples already mentioned, which does not seem to agree with the unstable pattern of the δ^{18} O curve.

A decrease in sea level causes the continental surface to be easily exposed to weathering and erosion. However, for this mechanism to happen, wet conditions must be present. This encourages the removal of chemically weathered sediment. Therefore, wetter and colder conditions are necessary to produce an increase in the riverine influx of major continental elements. Since we only have cold conditions for this time, no substantial increase in detrital input is seen in the platform.

By this time, the δ^{13} C isotopic signature has a slight and uniform tendency to higher levels (1-4‰) that begin at the base of the section (Meramecian) to the end of the Chesterian, except for two negative peaks in LJ 16 and in LJ 24 (Figure 4). This uniformity fits well with the patterns in elemental ratios with scarce input by this time. The interpretation here is a platform with nearly similar conditions, except for some environmental

shifts (from margin platform reef to more restricted, shallower lagoon) in a context of a cool climate, with low inputs of organic matter and detrital minerals from the continent. This is corroborated by other studies (e.g. Fielding et al., 2008) that bring evidence of short glaciation pulses during the Mississippian of Gondwana. Caputo et al. (2008) reported the occurrence of short-lived glacial events, one of them during the Visean (Meramecian) of South America and during the earliest Serpukhovian (Upper Mississippian: latest part of the Meramecian) of South America and Africa. These events had an impact on the water chemistry globally with higher δ^{13} C and δ^{18} O values during some part of the Mississippian (i.e. latest Tournaisian-latest Visean boundary sensu Frank et al., 2008).

5.3. Geochemical interpretation for the Mississippian–Pennsylvanian boundary

For the Mississippian-Pennsylvanian boundary (found in sample LJ 40), the Ti/Ca, K/Ca, Al/Ca, and Si/Ca ratios show a slight upturn towards higher values, whereas the $\delta^{13}C$ and δ^{18} O remain in low values related with those of the Mississippian (Figure 4). The slight increases of Ti, K, Al, and Si together with ¹⁸O impoverishment could indicate a major contribution of freshwater to the platform (Kulacki and Cardinale, 2012), which is ¹⁶O enriched. This means the establishment of warmer and more humid conditions in a regional scale, which promoted higher erosion rates of major elements and organic matter coming from land. Facies belts data from LJ 40 to LJ 42 (Morrowan) indicate a switch from lagoon to margin-platform close to the slope environments, as well as a decrease in δ^{18} O which are thought to respond to wetter and warmer conditions that enabled a rise in sea level.

This contrasts with a major event of glaciation, recorded at the Mississippian–Pennsylvanian boundary (Holz *et al.*, 2008) based on stratigraphical and paleontological evidence in Gondwana (Fielding *et al.*, 2008 and references therein) and δ^{13} C and δ^{18} O positive excursions recorded throughout the world (Mii *et al.*, 1999; Frank *et al.*, 2008). Only δ^{18} O shows a positive excursion that initiates slightly later than the M–P boundary, but the same positive tendency in δ^{13} C values is not recorded. This might be related to the closeness to the coastline because of sea-level changes which locally change the water chemistry in more restricted waters, not reflecting the immediate changes in δ^{13} C and δ^{18} O values.

5.4. Geochemical interpretations for the La Joya formation

After LJ 42, an upturn in δ^{18} O values is observed, which can be correlated with the previously mentioned glacial event occurring during the late Mississippian–early Pennsylvanian (Veevers and Powell, 1987; Crowell, 1999; Isbell *et al.*, 2003; Fielding *et al.*, 2008, among others). The element ratio curves support this pattern for much of the Morrowan (LJ 42 - LJ 54) for the occurrence of low levels of continental elements brought to the platform (Figure 4).

For the Mg/Ca ratio curve, a conspicuous peak is observed only in the sample LJ 48 (Figure 4) and does not follow the pattern seen in the other curves, including the Si/Al ratio curve, meaning the magnesium for this sample, is a product of precipitation as high magnesium calcite or dolomite, and might represent more saline conditions. However, it would be necessary to carry out an analysis of sample LJ 48 by means of EDS to determine the original composition of the sample and the magnesium content in it.

Regarding LJ 50, Si/Al strongly rises (Figure 4), without a corresponding increase in the other elemental ratios, perhaps as a result of biogenic precipitation of Si, even if there is no evidence of a biogenic source for this sample (Villanueva-Olea *et al.*, 2019). Another possible explanation is a shift in provenance of the terrigenous material that comes to the platform in the form of volcanic glass, which might be correlated with active volcanic activity. Such activity can be associated with the orogenic event

Ouachita-Marathon-Sonora, when Gondwana collided with Laurentia to form Pangea (Poole *et al.*, 2005) or to the submarine volcanic activity due to the closeness to the mid-ocean ridge located in the Rheic Ocean by that time (Palafox-Reyes, 2011). However, aside from this possible shift in the source of silica, we did not find any other evidence of such correlation with this orogenic activity, except for the thin layer of tuff in LJ 23 from the Santiago fm. Alternatively, a simpler explanation could involve a major quartz input into the carbonates.

For the last part of the Morrowan some peaks are present which correlate with paleobathymetric changes (from LJ 50 to LJ 64). They could be assigned to wetter and warmer conditions; however, the δ^{13} C and δ^{18} O curves do not support this assumption, as δ^{13} C is maintained at relatively constant values and δ^{18} O has a positive tendency (Figure 4), which is evidence of a cooling climate. For this reason, we believe the rise in the deposit of detrital elements by freshwater streams must be on a local/regional rather than global scale.

However, in the case of the LJ 60 level, it appears with the most conspicuous peaks in detrital elemental ratios (except Si/Al). This behavior correlates to a shift to shallower conditions as evidenced by the paleobathymetric curve. This shallowing may be due to a regression in a context of glaciation, which is supported by δ^{13} C and δ^{18} O isotopic data, with positive peaks for this level (Figure 4).

6. Conclusion

The study of major element ratios in sediments from the La Joya section in the Sierra Agua Verde, Sonora, agrees with the previous work on the area about microfacies and stable isotope analyses. Some conclusions can be drawn:

1. Some of the higher Mg/Ca values are interpreted as high evaporation rates, but most of them are the result of Mg coming from the continent in the detrital fraction of the samples analyzed.

- 2. The ratio Si/Al, when similar in behavior to Si/Ca, has been interpreted as a proxy of productivity for the presence of siliceous organisms (*i.e.* sponges).
- 3. The use of correlation coefficients has shown that not all Si deposited in the platform was removed together with the Al, Fe, or K by chemical weathering of continental rocks, but one part of it must be of autochthonous biogenic source, which can be confirmed by means of the presence of siliceous sponges spicules.
- 4. Plotting dendrograms aided us in discerning the relationships between elements in a much clearer way, thus leading us to the conclusion that element pairs such as Al-K might be related to minerals like orthoclase. In addition, this method led to a possible association between Ti and Fe, linked to ilmenite, and to a Si-P phenon, possibly related to bioproductivity episodes. Si, however, might also in addition be related to quartz input.
- 5. Most of the Mississippian corresponds to low values of elemental ratio inputs, with some remarkable peaks that indicate weathering and erosion through riverine influx into the carbonate platform. This tendency is accompanied by high δ^{13} C and δ^{18} O values, which were decreasing until the end of the Mississippian, and are indicative of cooling conditions, but with some warming and wetter periods correlating with these elemental positive peaks, when weathering and erosion are enhanced.
- 6. Unlike the overwhelming evidence of the establishment of glacial conditions in the Mississippian–Pennsylvanian boundary of the La Joya section, slight increases of some continental elements are shown, together with lower δ^{13} C and δ^{18} O values, which are interpreted as a major influx of freshwater into the platform, perhaps because of warmer and more humid conditions regionally.
- 7. The isotopic evidence of a glaciation appears after LJ 42 (posterior to the M-P

boundary), where the δ^{18} O curve starts to change to more positive values, supported by the relatively low values in the detrital elemental ratios through much of the Morrowan. Some peaks could be attributed to a change in the source of Si derived from volcanic activity in a context of orogenic events, when Gondwana collided with Laurasia. Yet, more studies are necessary in order to fully ascertain the extent of such volcanic activity.

8. For the last part of the section corresponding to the end of the Morrowan and Atokan, an increased input of detrital elements is assigned to local or regional conditions, as this pattern is not replicated for δ^{13} C and δ^{18} O isotope values, which indicate cooler temperatures.

Acknowledgements

The authors wish to thank Rufino Lozano and Patricia Girón for the technical support at the X-ray fluorescence Laboratory, Instituto de Geología, UNAM. Funding was provided by CONACYT (Grant No. 165826) and ECOS Francia-México (Grant No. M13-U01 "Evolución de los Ecosistemas del Paleozoico de México"). Additionally, we would like to acknowledge Matthew Lovegrove and Andrea Caballero-Ochoa for reading and making comments on an early version of this manuscript, as well as for revising the English. Finally, we wish to express our gratitude to the two anonymous reviewers for their comments and suggestions, which significantly improved the quality of our manuscript. We also extend our thanks to Dr. Josep A. Moreno-Bedmar (Mexico City) for his assistance during the editorial process and to Sandra Ramos, M. Sc., for the technical editing of our manuscript.

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