



## Distribution of major and trace elements in La Luna Formation, Southwestern Venezuelan Basin

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### Abstract

The La Luna Formation (Maraca section), Maracaibo Basin, was studied by means of V and Ni analysis of the bitumen, total organic carbon (TOC), total sulfur (St), major elements (Si, Al, Fe, Mg, Mn, Ca, Ti, Na, K, P), trace elements (V, Ni, Co, Cr, Cu, and Zn), and electron microprobe analysis (EPMA) of the whole rock, and St, major elements (Si, Al, Fe, Mg, Mn, Ca, Ti, Na, K, P), trace elements (V, Ni, Co, Cr, Cu, Zn, Mo, Ba, U, Th) and rare earth elements (La, Ce, Nd, Sn, Eu, Th, Yb, Lu) of the carbonate-free fraction. The results are discussed based on the organic and inorganic association of trace elements and their use as paleoenvironmental indicators of sedimentation. An association between V and organic matter is suggested by means of correlation between V and Ni vs. TOC, the use of EPMA (whole rock) and V and Ni concentrations (carbonate-free fraction), whereas Ni is found in the organic matter and the sulfide phase. Fe is present as massive and framboidal pyrite, whereas Zn precipitates into a separate phase (sphalerite), and Ni, Cu and, in some cases, Zn, can be found as sulfides associated with pyrite. Concentrations of V and Ni (bitumen), TOC, St, V, Ni, Cr, Cu and Zn (whole rock), U, Th, Mo (carbonate-free fraction) are indicative of changes in the dysoxic sedimentation conditions in the chert layers (TOC, St, V, Ni, Cu and low Zn and V/Cr <4) to euxinic anoxic conditions in the argillaceous limestone (TOC, St, V, Ni, Cu and high Zn and V/Cr >4). In the sequence corresponding to the argillaceous limestone, variations in the concentrations of TOC, St, V, Ni, Zn, Cu and Cr (whole rock) can be observed, also suggesting variable sedimentation conditions. The following is proposed: (i) sedimentation intervals under euxinic conditions associated with high contribution and/or preservation of organic matter, allowing a high concentration level of V and Ni in the organic phase and the accumulation of Cu, Zn and Ni (in a smaller proportion) in the sulfide phase; (ii) sedimentation intervals under anoxic conditions and in the presence of relatively lower H<sub>2</sub>S, which allowed lower concentrations of V and Ni in the organic phase and higher concentrations of Cu, Zn, and Ni in the sulfide phase. Rare earth elements (REE) concentrations exhibit a marked increase in Ce, Nd, Sm, Eu, Y and Lu for the QM-3 interval, relative to Post-Archean Average Shale (PAAS). REE enrichment in shales has been related to the presence of phosphate minerals such as monazite or apatite. However, these minerals were not detected through XRD or EPMA in the whole rock or in the carbonate-free fraction. The association of REE with organic matter is suggested due to the absence of phosphate minerals, although assessment of these elements require further analysis.

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### 1. Introduction

The presence of trace elements in the organic matter (bitumen and kerogen) of a source rock depends mainly on the following factors: (1) metals used in metabolic

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processes of living organisms (biogenic elements), (2) the pH and Eh of the sedimentary environment, especially the existence of sulfate-reducing conditions, (3) metals in the sedimentary environment; this is related to the chemical composition of the fluid phase interacting with the sediments during diagenesis, (4) the mineralogy of the sedimentary rock (carbonate or siliciclastic), especially the type and amount of clay minerals of which the clays from the smectite group (expanding clays) have the largest sorption capacity, (5) the type of organic matter related to the presence of functional groups that can form organometallic complexes. The last three points are very important for the distribution of trace elements in a system comprising a sulfide phase, organic matter, and clay minerals.

Trace elements present in crude oils and source rocks (bitumen, kerogen and whole rock) have been used in geochemical interpretations related to oil–oil and oil–source rock correlation (Hitchon and Filby, 1984; Ellrich et al., 1985; Simoza et al., 1985; Filby, 1994; Frankenberger et al., 1994; Alberdi et al., 1996; López et al., 1998); Nd isotope ratios ( $^{143}\text{Nd}/^{144}\text{Nd}$ ) have been proposed for correlating source rocks and oils (Manning et al., 1991), as well as specific metal ratios ( $\text{V}/\text{V} \pm \text{Ni}$ ) and ( $\text{Mo}/\text{Mo} + \text{Cr}$ ) to correlate kerogen and bitumen (Odermatt and Curiale, 1991). Other applications are in the study of primary and secondary migration (Al-Shahrstani and Al-Atyia, 1972; Greibrokk et al., 1994). Trace elements also serve as indicators of thermal maturity (López et al., 1991). The study of paleoredox conditions has been carried out on the whole rock (Jones and Manning, 1994; Mongenot et al., 1996; Garban et al., 1997; Alberdi and Tocco, 1999). However there are few studies on the determination of organic (kerogen and bitumen) and inorganic (minerals) association of trace elements (Hirner and Xu, 1991; Mercer et al., 1993) and its application to paleoenvironmental studies. This paper presents the study of the distribution of major and trace elements in organic (kerogen and bitumen) and inorganic (minerals) matter in rocks from the La Luna Formation (Maraca section), Venezuela. The study is based on the determination of major and trace elements in the whole rock, carbonate-free residue, and bitumen by means of different techniques such as XRD, ICP, ICP/MS and EPMA in order to establish their association with organic or inorganic phases. From these results inferences are made regarding the sedimentation conditions for La Luna Formation in the section studied.

## 2. Study area

The La Luna Formation constitutes the most characteristic lithological unit of the Cretaceous (Cenomanian–Campanian) of Venezuela's Western Basin, corresponding to the main source rock of the Mar-

acaibo Basin's oils (Talukdar et al., 1985, 1986). The unit is located throughout the whole Basin of the Maracaibo Lake, Zulia State, in Falcón, Lara, Trujillo, Mérida, Táchira, and Barinas States and in the Guajira Peninsula, Colombia. The La Luna Formation typically consists of limestone and argillaceous limestone, with an abundance of laminate and finely dispersed organic matter, thinly stratified (González et al., 1980). This formation was deposited in marine environments under anoxic euxinic conditions, which allowed the preservation of the organic matter (González et al., 1980). Erlich et al. (2000) reported that deposits of intervals rich in organic carbon in the La Luna Formation were controlled by the development of paleobathymetric barriers (the Santa Marta and Santander Shields, the Paraguaná Block and the old Andes in Mérida) which favored the development of an anoxic environment causing circulation of restricted waters and limited ventilation. These anoxic conditions are also attributed to a high level of evaporation and low precipitation (high salinity bottom water).

The section of the La Luna Formation under study is located in the Maraca Ravine in the Negro River, Perijá District, Zulia State (Fig. 1). Sampling was carried out in a 300-m thick section, consisting of alternating massive and finely laminated limestone, with intercalations of thin chert layers.

## 3. Samples and methods

A total of 15 samples from the La Luna Formation, was analyzed. Samples were ground and mineralogical composition was determined by means of X-ray diffraction (Siemens XD-8 Advance); concentrations of total organic carbon (TOC) (LECO C-144), inorganic carbon or carbonatic carbon were determined using Bernard's calcimeter method (Hesse, 1971) and total sulfur (St) (LECO SC-432). Bitumen was extracted with dichloromethane in a Soxhlet extractor, and quantified; V and Ni elements were analyzed by means of inductively coupled plasma atomic emission spectrometry (ICP-AES Jobin-Yvon-24).

Major elements (Si, Al, Fe, Mg, Mn, Ca, Ti, Na, K, P) and trace elements (V, Ni, Co, Cr, Cu, Zn) in the whole rock were analyzed by inductively coupled plasma atomic emission spectrometry (ICP, Thermal Jerrel Ash INVIRO).

The carbonate phase was eliminated using HCl (12 N) for 12 h. After carbonate dissolution, concentrations of total sulfur (St), major elements (Si, Al, Fe, Mg, Mn, Ca, Ti, Na, K, P), trace elements (V, Ni, Co, Cr, Cu, Zn, Mo, Ba, U, Th), and some REE (La, Ce, Nd, Sn, Eu, Th, Yb, Lu) were determined by means of inductively coupled plasma-mass spectrometry (ICP/MS, Perkin Elmer Elan 6000).

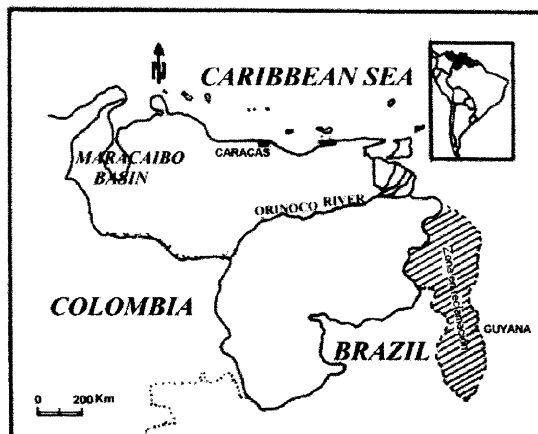
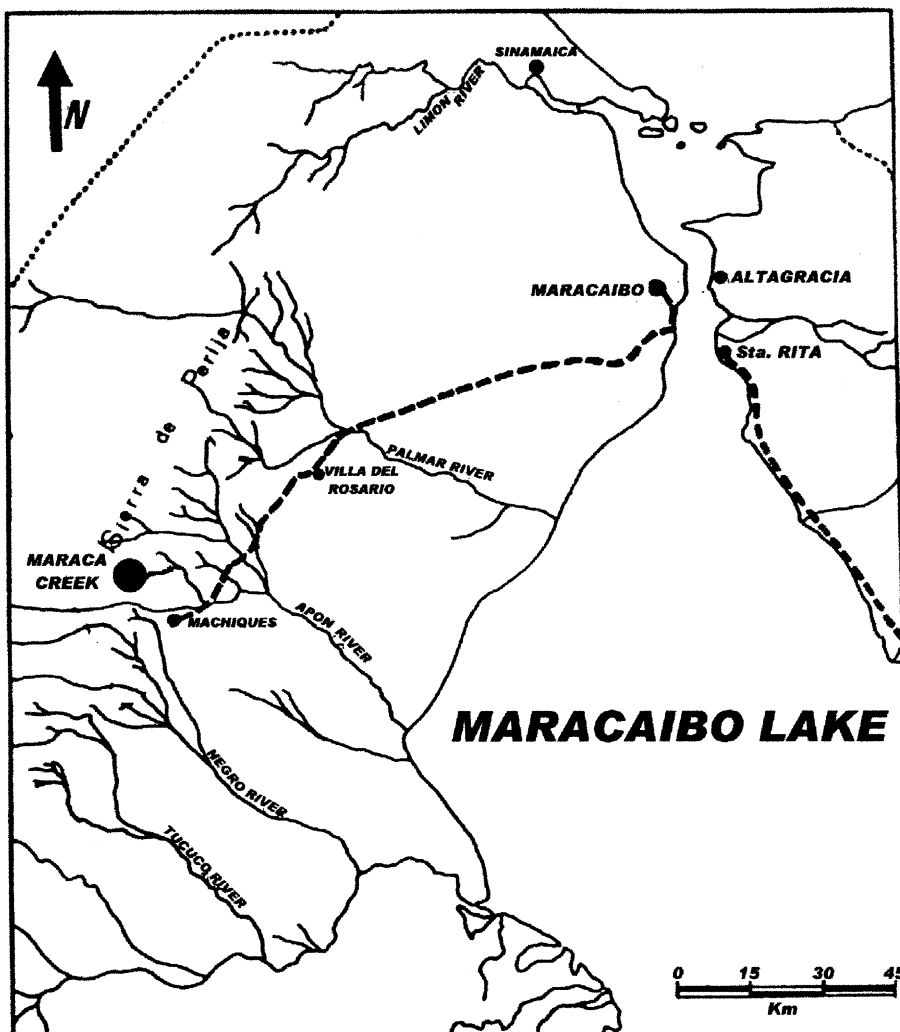


Fig. 1. Location of the region under study.

The distribution of major and trace elements in the rock's organic and inorganic fraction was determined using electron microprobe analysis (EPMA, Jeol 8900R). This equipment has two types of X-ray detectors (WDX and EDX), which allow simultaneous analysis of the elements. It is also equipped with a detector of backscattering electrons (BSE), capable of qualitatively obtaining compositional (average atomic number-COMPO) and topographic (TOPO) information. Rock sections were cut and embedded in phenolic resin and then polished with diamond paste. X-ray maps were developed in every section for the following elements: S, Ca, Si, Al, K, Fe, V, Ni, Cu, Zn.

#### 4. Results and discussion

##### 4.1. Bitumen

The presence of V and Ni in the organic matter as tetrapyrrolic complexes has been extensively researched (Lewan and Maynard, 1982; Lewan, 1984; Filby, 1994). Therefore these two elements, whose relationship with organic matter has been well established, were analyzed in the bitumen extracted from the La Luna Formation. Bitumen concentrations are over 4000 ppm, except for the two chert layers with concentrations equal to or less than 1000 ppm. V concentration is between 141 and 1750 ppm and Ni ranges between 9 and 100 ppm (Table 1). In addition, no significant differences are found in the concentration of V and Ni in the bitumen of the argillaceous limestone and cherts. However, when V vs. Ni is compared, an acceptable correlation is observed for argillaceous limestone, but not for chert

Table 1  
Concentration of V and Ni, V/V + Ni ratio in bitumen

Samples	V (ppm)	Ni (ppm)	V/V + Ni
QM-1	438	13.4	0.970
QM-2	926	23.0	0.976
QM-3	705	18.6	0.974
QM-4	608	18.3	0.971
QM-5	707	16.0	0.978
QM-6	1330	20.6	0.985
QM-7 (Chert)	719	78.7	0.905
QM-7A	636	9.87	0.984
QM-8	729	16.3	0.978
QM-8A (Chert)	141	32.6	0.812
QM-9	312	8.04	0.975
QM-10	738	11.1	0.985
QM-11	231	13.1	0.946
QM-12	1740	38.5	0.978
QM-14	1750	68.1	0.963

layers (Fig. 2). This is reflected in the V/V + Ni ratio, which averages 0.974 for argillaceous limestone and 0.859 for cherts. Even though extracted bitumen can correspond to a mixture of indigenous and migrated bitumen, the similarity of the V/V + Ni ratio for the argillaceous limestone and its difference relative to cherts suggests that in the bitumen this ratio is not altered as a result of migration in the studied stratigraphic interval. The V/V + Ni ratio in bitumen has been used to identify changes in lithofacies. Odermatt and Curiale (1991) reported that this ratio is higher in siliceous intervals as compared to carbonatic intervals in rocks in the Monterey Formation (Santa María Basin,

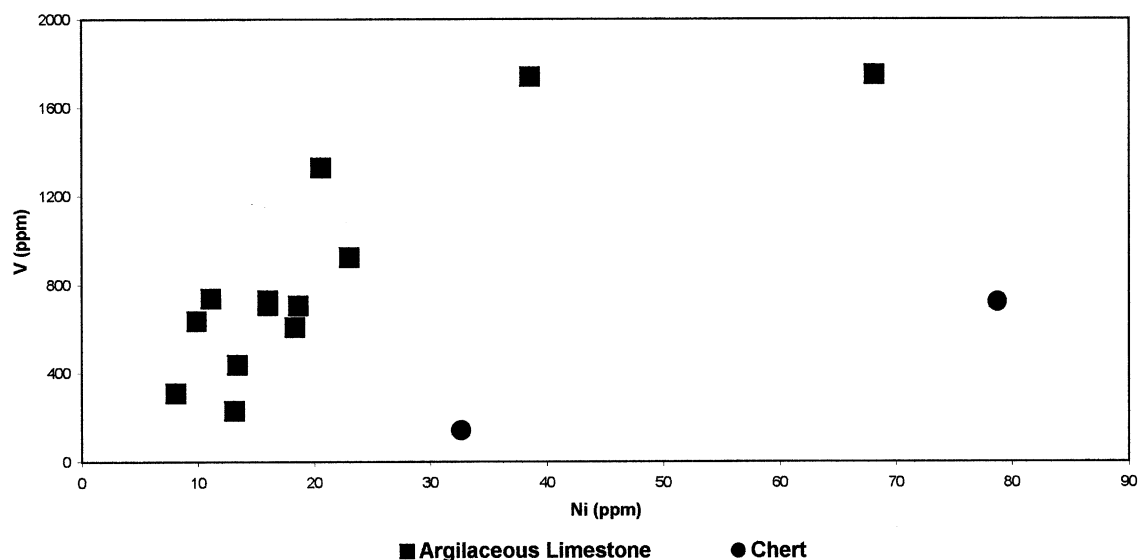


Fig. 2. Concentration of V (ppm) vs. Ni (ppm) for bitumen.

California). Our results are different, because the V/V + Ni ratio in chert is lower with respect to the argillaceous limestone. These results can be related to the TOC concentrations, which are lower for cherts, where the lowest V and Ni concentrations are found in the whole rock (Table 2). Our results also suggest that a smaller content of TOC reflects a smaller accumulation and/or preservation of organic matter during sedimentation of these strata, and, therefore, a reduced possibility of a V and Ni association with tetrapyrrolic complexes.

#### 4.2. Whole rock

Mineralogical analysis showed the presence of calcite, quartz, pyrite and illite. In general, TOC concentrations are over 1% for the argillaceous limestone and under 0.8% for chert layers, whereas St has concentrations under 1% (Table 2). Si concentration in chert layers is high and Ca, Al and K low, thus reflecting lithofacies changes in the section. On the other hand, except for the two chert layers, Al and K exhibit an acceptable correlation (Fig. 3), which can be attributed to the presence of illite in these samples.

Upon a detailed analysis of the concentrations of trace elements in the interval corresponding to the sedimentation of the two chert layers (samples QM-7 and QM-8A) a decrease in concentrations of V, Ni, Cr, Cu and Zn occurs; this decrease is also observed in QM-4 and QM-11 and corresponds to the intervals with lower TOC and St content (Table 2). Based on these results, trace element concentrations were normalized with respect to the Turekian and Wedepohl's (1961) average shale composition, according to Mongenot et al. (1996):

$$NC = \frac{(TEC/AIC)_{\text{sample}}}{(TEC/AIC)_{\text{shale}}}$$

where:

NC = Normalized concentration

TEC = Trace element concentration

AIC = Aluminium concentration

Our results (Table 3) show that trace elements V, Ni, Cu, Zn and Cr, are enriched in the argillaceous limestone with respect to the average shale of Turekian and Wedepohl (1961), whereas this enrichment is relatively lower for chert layers. These results are indicative of variations in the sedimentation conditions associated with the contribution and/or preservation of organic matter and to the sulfate-reducing conditions of the sedimentary environment. A smaller contribution or preservation of organic matter, together with a lower degree of sulfate-reducing conditions or the absence of H<sub>2</sub>S (suboxic conditions), leads to a reduced association of V and Ni elements with this phase of the sediments that exhibit an acceptable correlation with TOC (Fig. 4). This suggests that these elements are mainly associated with the organic matter (kerogen and bitumen). The intervals with high V content correspond to those containing high St concentrations where maximum euxinic conditions are proposed. According to Lewan (1984), V is enriched in H<sub>2</sub>S-rich carbonatic sediments, because these environment favor the formation of the vanadyl ion (V<sup>IV</sup>), a species capable of forming organometallic complexes of the tetrapyrrolic type. In those sediments with reduced content of free H<sub>2</sub>S, V is less available as vanadyl ion, thus decreasing its possibility of being linked to the organic matter. These results suggest that the environmental sedimentation conditions of the La

Table 2

Concentrations of major and trace elements and V/V + Ni and V/Cr ratios in the whole rock

Samples	TOC (%)	St (%)	SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	MgO (%)	CaO (%)	Na <sub>2</sub> O (%)	K <sub>2</sub> O (%)	TiO <sub>2</sub> (%)	P <sub>2</sub> O <sub>5</sub> (%)	Zn (ppm)	Cu (ppm)	Ni (ppm)	Cr (ppm)	V (ppm)	V/ V + Ni	V/Cr
QM-1	3.0	0.37	12.50	2.18	0.70	0.42	44.30	0.04	0.28	0.08	0.13	555	25	97	60	758	0.887	12
QM-2	5.1	0.67	17.50	2.11	0.79	1.22	39.60	0.05	0.29	0.07	0.29	797	33	221	79	1485	0.870	18
QM-3	5.7	0.45	29.30	8.41	2.12	0.50	27.80	0.05	0.88	0.27	0.35	808	46	186	117	1888	0.910	16
QM-4	2.4	0.21	14.40	2.03	0.47	0.37	43.90	0.03	0.26	0.07	0.16	451	31	74	26	712	0.906	27
QM-5	7.3	0.73	30.70	2.86	0.82	0.32	31.70	0.05	0.40	0.11	0.37	855	47	256	95	1675	0.867	17
QM-6	7.3	0.47	26.80	2.57	0.81	0.29	34.30	0.05	0.35	0.10	0.28	754	54	275	111	1908	0.874	17
QM-7 Chert	0.8	0.73	85.50	0.64	1.31	0.08	4.85	0.06	0.08	0.02	0.10	134	6	45	45	195	0.812	4
QM-7A	0.7	0.23	10.50	1.13	0.45	0.53	48.80	0.02	0.13	0.03	0.10	86	<5	23	20	319	0.933	15
QM-8	4.4	0.09	30.80	1.77	0.68	0.27	34.20	0.03	0.23	0.07	0.16	262	42	192	62	1175	0.859	19
QM-8A Chert	0.2	0.05	89.10	0.59	0.70	0.05	4.05	0.05	0.10	0.02	0.05	249	5	25	30	123	0.831	4
QM-9	3.2	0.22	23.80	3.38	0.90	0.95	37.50	0.04	0.38	0.10	0.17	1104	37	145	84	1075	0.881	12
QM-10	3.5	0.13	23.50	1.34	0.35	0.31	41.00	0.03	0.20	0.04	0.11	1130	37	145	53	1333	0.901	25
QM-11	1.1	0.06	7.96	0.75	0.26	0.35	51.90	0.03	0.11	0.03	0.24	498	22	150	35	554	0.789	15
QM-12	4.4	0.35	30.10	3.39	0.84	0.42	33.30	0.08	0.51	0.13	0.34	1145	46	205	91	1932	0.908	21
QM-14	3.6	0.45	26.60	2.10	1.14	2.47	38.2	0.07	0.78	0.09	0.10	981	45	141	126	1032	0.879	39

Mn and Co < 5 ppm.

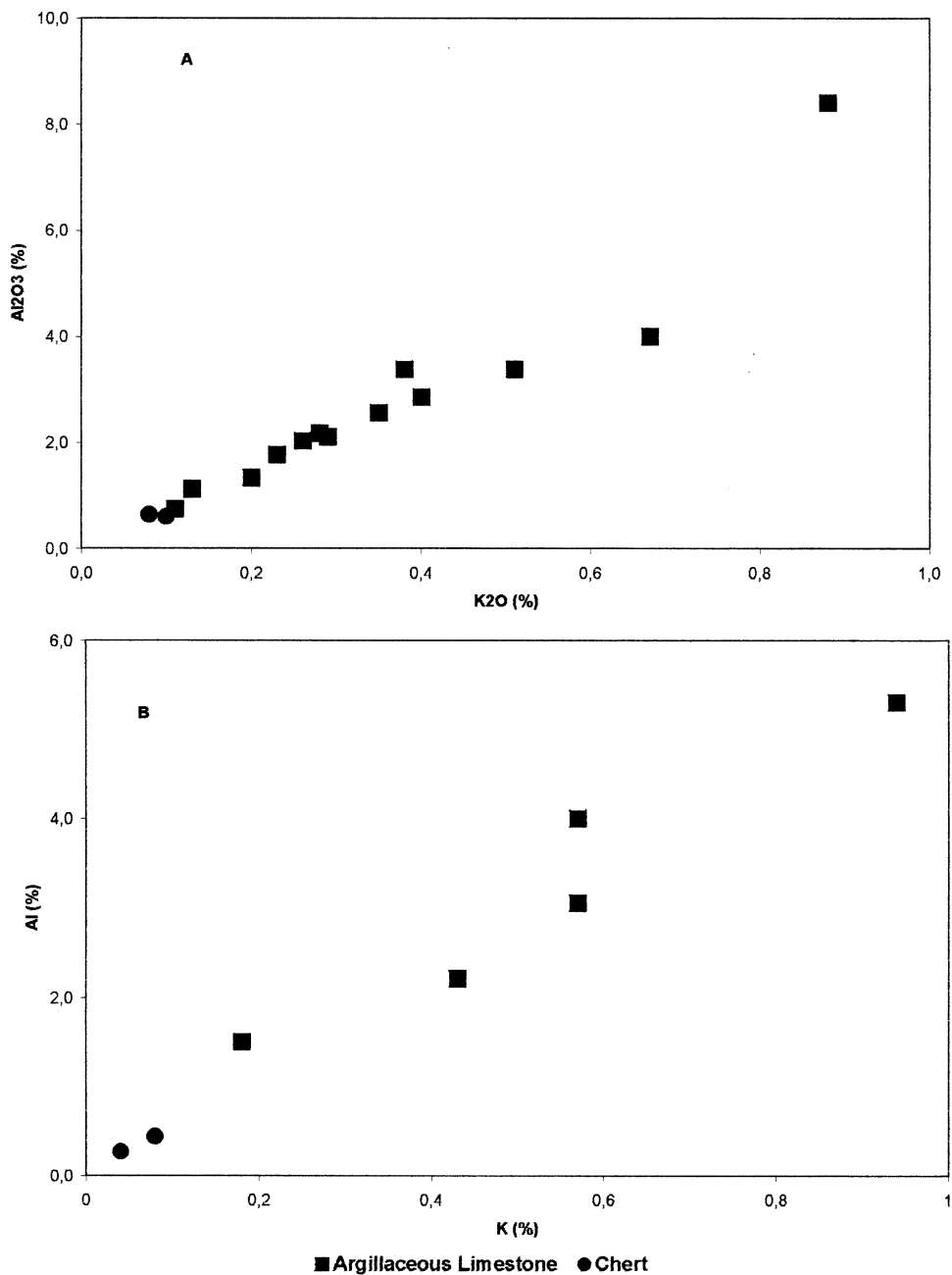


Fig. 3. Concentration of Al (%) vs. K (%) in the whole rock (A) and in the carbonate-free fraction (B).

Luna Formation vary from dysoxic conditions (less TOC, St, V, Ni, Cu and Zn content), corresponding to the chert layers, to euxinic anoxic conditions (higher content of TOC, St, V, Ni, Cu and Zn), corresponding to the argillaceous limestone.

Cr is incorporated into the clastic detrital fraction through Al replacement in clays (Jones and Manning, 1994); its concentration in rocks is not related to anoxic conditions during sedimentation. The V/Cr ratio has

been proposed as an index of paleoxygenation conditions (Dill, 1986; Dill et al., 1988). The values for the V/Cr ratio obtained in this study are  $\approx 4$  for chert layers and  $> 12$  for argillaceous limestones, which are higher than those reported by Jones and Manning (1994). However, for chert layers, where less euxinic sedimentation conditions are proposed, the V/Cr values coincide with the limit proposed by Jones and Manning (1994), i.e. 4.25, which plots between dysoxic and euxi-

Table 3

Normalized concentration of trace elements with respect to the average composition of shale of Turekian and Wedepohl (1961). N elements = normalized concentration

Sample	Zn (ppm)	ZnN	Cu (ppm)	CuN	Ni (ppm)	NiN	Cr (ppm)	CrN	V (ppm)	VN
QM-1	555	7.8	25	4.3	97	10.9	60	5.1	758	44.7
QM-2	797	8.0	33	5.8	221	25.7	79	6.9	1485	90.4
QM-3	808	4.9	46	2.0	186	5.4	117	2.6	1888	28.8
QM-4	451	5.5	31	5.7	74	8.5	26	2.4	712	45.1
QM-5	855	4.9	47	6.1	256	21.9	95	6.2	1675	75.2
QM-6	754	4.9	54	7.8	275	26.3	111	8.0	1908	95.4
QM-7 Chert	134	0.3	6	3.5	45	17.3	45	13.1	195	39.1
QM7-A	86	1.4	5	1.6	23	5.0	20	3.3	319	36.3
QM-8	262	1.5	42	8.8	192	26.6	62	6.5	1175	85.3
QM-8A Chert	249	0.5	5	3.2	25	10.4	30	9.4	123	26.8
QM-9	1104	8.2	37	4.1	145	10.5	84	4.6	1075	40.9
QM-10	1130	8.5	37	10.3	145	26.6	53	7.3	1333	127.8
QM-11	498	11.0	22	10.9	150	49.1	35	8.7	554	94.9
QM-12	1145	6.7	46	5.0	205	14.9	91	4.9	1932	73.2
QM-14	981	6.5	45	7.9	141	16.5	126	11.1	1032	63.1

nic conditions. For the rest of the column of sediments, corresponding to the sedimentation of carbonatic muds that generated the argillaceous limestone ( $V/Cr > 4$ ), sedimentation is said to occur under euxinic conditions. However, variations in the concentrations of TOC, St, V, Ni, Zn, Cu and Cr are observed within the sequence corresponding to the argillaceous limestone, which are smaller for some samples (for example QM-4 and QM-11). This suggests variable sedimentation conditions consisting of: (i) sedimentation intervals under euxinic conditions related to high contribution and/or preservation of organic matter that permitted a high V and Ni concentration in the organic phase, and the accumulation of Cu, Zn and Ni (in smaller proportion) in the sulfide phase; (ii) relatively shorter sedimentation intervals under anoxic conditions and in the presence of  $H_2S$ , which allowed a reduced concentration of V and Ni in the organic phase and of Cu, Zn and Ni in the sulfide phase.

On the other hand, Cu, Zn and Ni exhibit low concentrations in the intervals with reduced St content; these elements with chalcophile tendency should be associated with the sulfide phase in the rock, although they do not present an acceptable correlation with St. In order to study in a more detailed fashion the relationship of these trace elements analyzed in the whole rock with the sulfide phase or with the organic matter, elemental maps were developed using EPMA. Due to the high concentration of some trace elements in the sample QM-3, once the carbonate phase was eliminated (discussed below), a polished section of this sample (whole rock) was analyzed. As a result, pyrite framboids and massive pyrite were observed in the organic and inorganic matrix of the rock (Fig. 5). In the elemental mapping for S, Fe, V, Ni, Cu and Zn (Fig. 6), an association

between S and Fe elements is observed in the central part of the structure by means of the dot density diagram. In addition the dot density diagram shows an association between S and Zn around this structure, suggesting the presence of pyrite possibly surrounded by sphalerite, and also Ni in a smaller proportion. The presence of sphalerite framboids has been reported by Raybould (1973), while Mercer et al. (1993) indicate the association between Fe and Ni both in framboids as well as in massive pyrite, identical to or similar to that presented in Fig. 6, where according to the dot density diagram, Ni is associated to this pyrite in lower concentration in the structure. The lower concentration of Ni in the massive pyrite can be explained based on the mechanism proposed by Rickard (1970), where massive pyrite is formed from direct precipitation of  $Fe^{2+}$  by polysulfides [Eq. (1)]. According to Mercer et al. (1993), Ni cannot precipitate as polysulfide and thus should be in low concentrations in the massive pyrite that precipitates by means of this mechanism. In addition, the presence of sphalerite around the massive pyrite suggests a precipitation as a separate phase according to Eq. (2).



Zones with a strong correlation between S and Fe were also observed, where association with Zn is less with respect to Ni in the dot density diagrams (Fig. 7), thus confirming that Ni precipitates together with pyrite, but that in some cases Zn can form a separate sulfide phase (sphalerite) and in others precipitates together with the pyrite. In this case V and Ni are disseminated, meaning an association probably with the organic

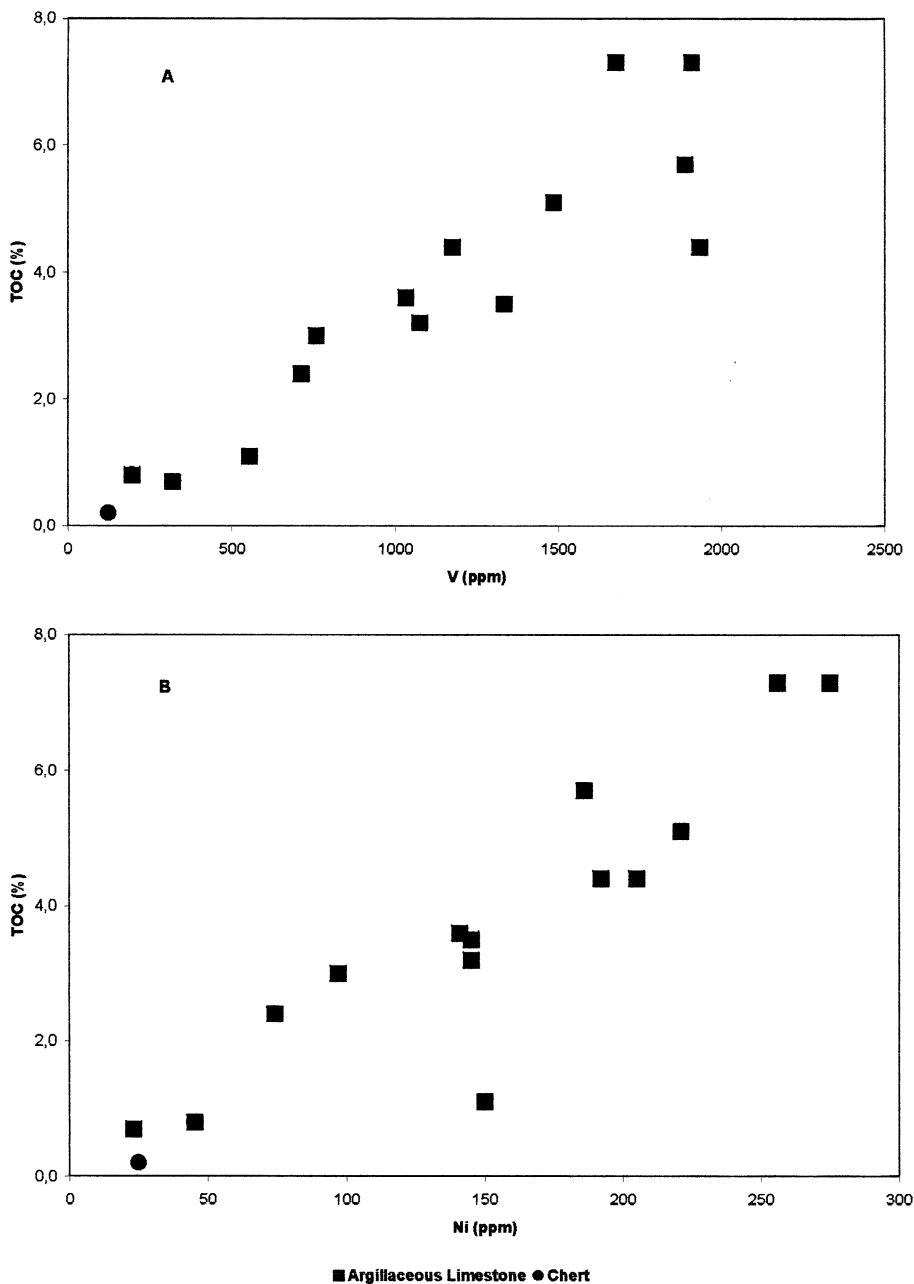


Fig. 4. Concentration of V (ppm) vs. TOC (%) (A) and Ni (ppm) vs. TOC (B) in the whole rock.

matter dispersed in the sample. These results support those obtained by means of elemental correlation: V and Ni associated with the organic matter, and Fe, Zn, Cu and Ni (in a smaller proportion) associated with sulfide phases.

#### 4.3. Carbonate-free residue

Once the carbonate phase was eliminated from the rock, mineralogical composition was again determined,

giving quartz, illite, caolinite and pyrite. Table 4 presents the major and trace element concentrations in the carbonate-free residue for some selected samples. Mass-loss correction due to carbonate elimination was carried out in these samples to obtain the concentration of trace elements with respect to the whole rock.

After this correction, V and Ni show a different relationship: V concentration appears to increase in the carbonate-free fraction, but after the weight loss

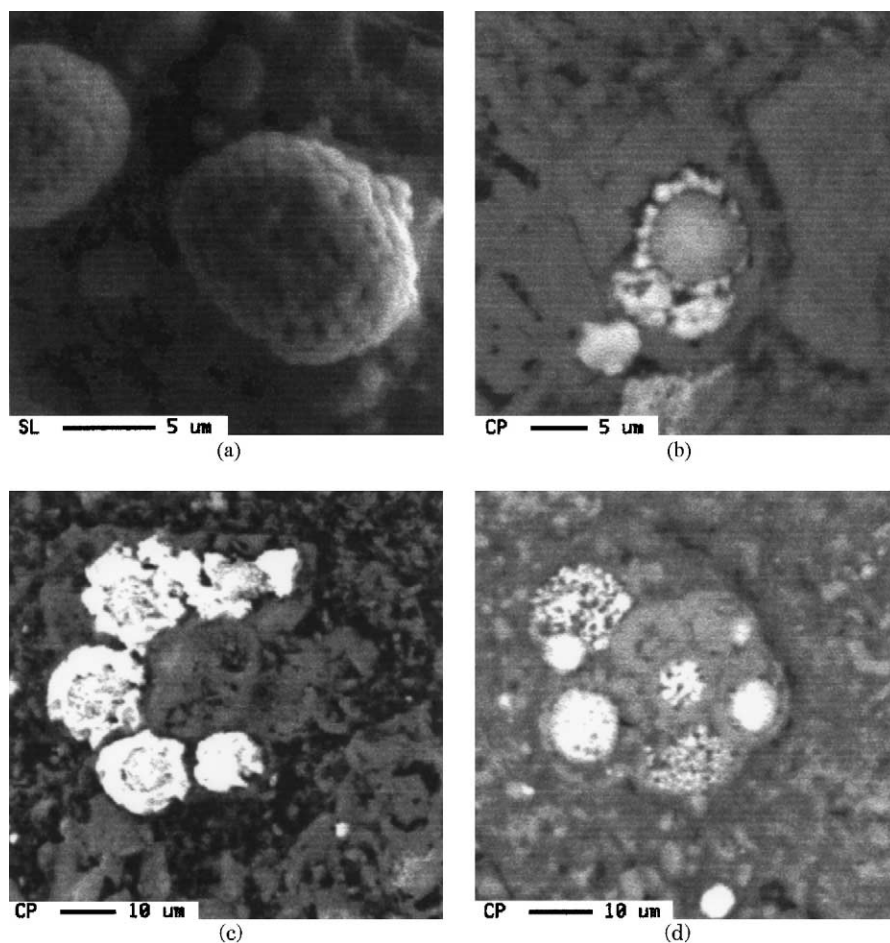


Fig. 5. Image of secondary electrons (SL) showing framboidal pyrite (a) and COMPO (CP) images (b, c and d) of different occurrences of pyrite and other massive sulfides.

Table 4

Concentration of major elements, trace, REE and V/Vi + Ni, U/Th and Sm/Nd ratios in the carbonate-free fraction

Samples	St (%)	Al (%)	Fe (%)	Mg (%)	Na (%)	K (%)	Ti (%)	P (%)	Mn (ppm)	Zn (ppm)	Cu (ppm)	Ni (ppm)	Cr (ppm)	V (ppm)	V/V + Ni
QM-1	2.6	5.31	3.10	0.34	0.08	0.94	0.21	0.021	24	533	89	263	224	2967	0.918
QM-3	3.8	1.50	3.11	0.74	0.16	0.18	0.20	0.002	5	60	40	300	76	4040	0.930
QM-5	1.7	3.06	1.25	0.20	0.05	0.57	0.13	0.012	11	170	77	312	202	3975	0.927
QM-7 Chert	1.9	0.44	1.21	0.02	0.05	0.08	0.02	0.002	5	35	8	34	26	350	0.911
QM7-A	2.5	4.00	2.70	0.20	0.05	0.57	0.13	0.006	10	12	24	115	70	1710	0.936
QM-8A Chert	0.4	0.27	0.29	0.01	0.04	0.04	0.01	0.002	5	98	5	23	16	183	0.888
QM-10	1.1	2.21	0.77	0.14	0.05	0.43	0.08	0.010	7	315	59	148	118	3520	0.959

Samples	Mo (ppm)	Ba (ppm)	Co (ppm)	U (ppm)	Th (ppm)	U/Th	Ce (ppm)	La (ppm)	Nd (ppm)	Sm (ppm)	Sm/Nd	Eu (ppm)
QM-1	80	480	4	6.2	3.3	1.88	62	39.5	23	2.4	0.104	0.4
QM-3	<1	9700	17	22.5	17	1.32	253	140	76	10.5	0.138	1.4
QM-5	150	390	7	5.3	1.8	2.94	24	16.9	8	1.1	0.138	0.3
QM-7 Chert	24	270	2	1.4	0.2	7	3	2.2	<5	0.2	–	<0.2
QM-7 A	31	210	8	0.5	1.6	–	27	17.6	17	1.3	0.076	<0.2
QM-8A Chert	18	310	<1	1.4	0.2	7	<3	1.4	<5	<0.1	–	<0.2
QM-10	46	390	5	3.5	1.7	2.17	14	11.5	6	0.7	0.117	<0.2

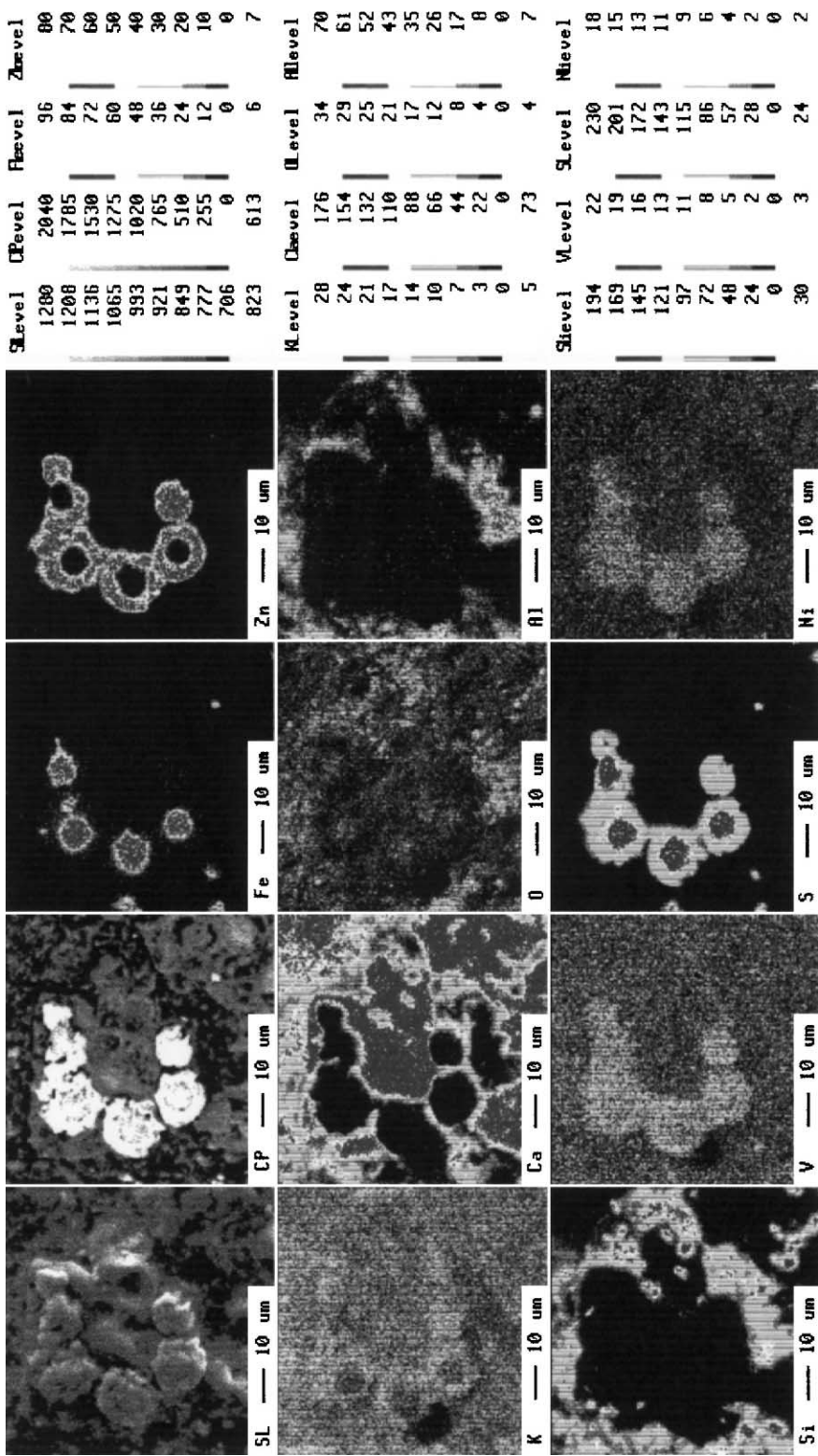


Fig. 6. X-ray dot maps.

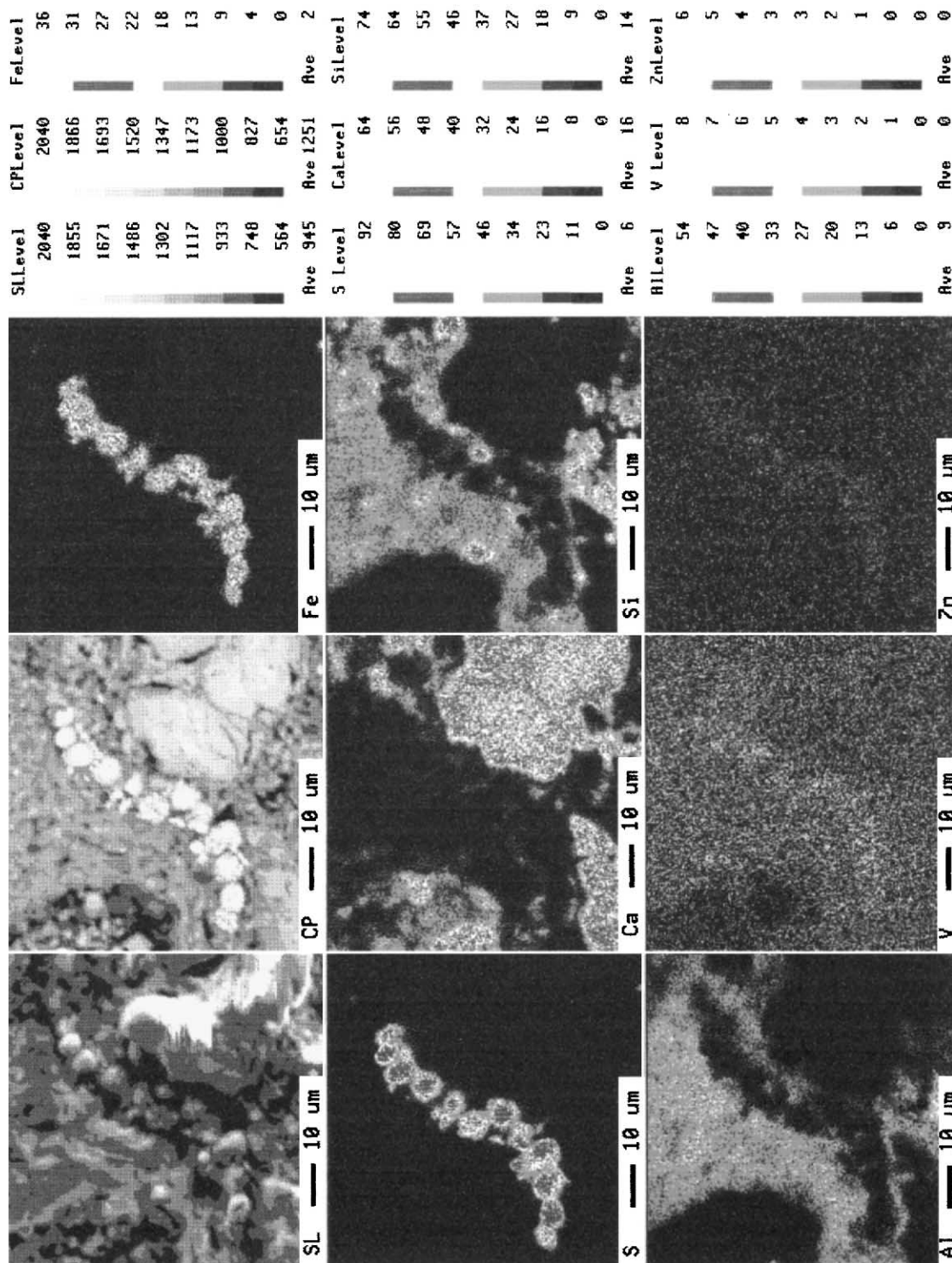


Fig. 7. X-ray dot maps.

correction, its concentration is similar to that obtained for the whole rock, whereas Ni concentration decreases by approximately 50%. This affects the correlation of V vs. Ni, which is 0.72 in the whole rock, and increases up to 0.88 in the carbonate-free residue. In addition, an increase is observed in the V/V + Ni ratio in the whole rock (Table 2) with respect to the carbonate-free fraction (Table 4), but both are smaller than those obtained in bitumen (Table 1). In general, the V/V + Ni ratio in bitumen is different from that obtained in the whole rock. These deviations in the values obtained in bitumen vs. rock reflect the presence of V and Ni in other phases of the rock (silicates, sulfides). The attack with HCl, in addition to removing carbonates, can also remove a smaller proportion of some sulfides (Mongenot et al., 1996). Our results suggest the elimination of Ni as sulfide during the acid attack; V concentration does not vary after the elimination of this phase because it does not show any association with carbonates. As a result the V/V + Ni ratio of the carbonate-free fraction increases. After elimination of the carbonate phase, graphic correlation between Al and K is maintained, again showing the close association of these elements in clay minerals, specifically illite (Fig. 3).

A detailed analysis of concentrations of trace elements in the carbonate-free fraction shows a relative increase in the concentrations of S, V, Ni, Ba, Co, Cr, Fe, U, Th, Ce, Nd, La, Sm, and Eu for the stratum designed as QM-3 (Table 4). Mongenot et al. (1996) report that sediments with high content of Ba, P and Cd are related to periods of high primary activity, but that Ba is not a good environmental indicator because it can be mobilized during diagenesis by sulfate-reducing reactions.

REE analysis (Table 4) shows a marked increase in Ce, Nd, Sm, Eu, Y, and Lu for the interval identified as QM-3 (Fig. 8), relative to PAAS shale (Post-Archean Average Shale; Yan et al., 2000). REE enrichment in shales has been associated with the presence of phosphate minerals such as monazite and apatite (Dill et al., 1988; Yan et al., 2000). However, these minerals were not detected by XRD or EPMA, either in the whole rock or the carbonate-free fraction of QM-3. The association of these elements with the rock in the absence of phosphate minerals has not been well established and no work on the REE analysis in the rocks of the La Luna Formation are found in the literature, except for that by Manning et al. (1991). They analyzed the Nd and Sm

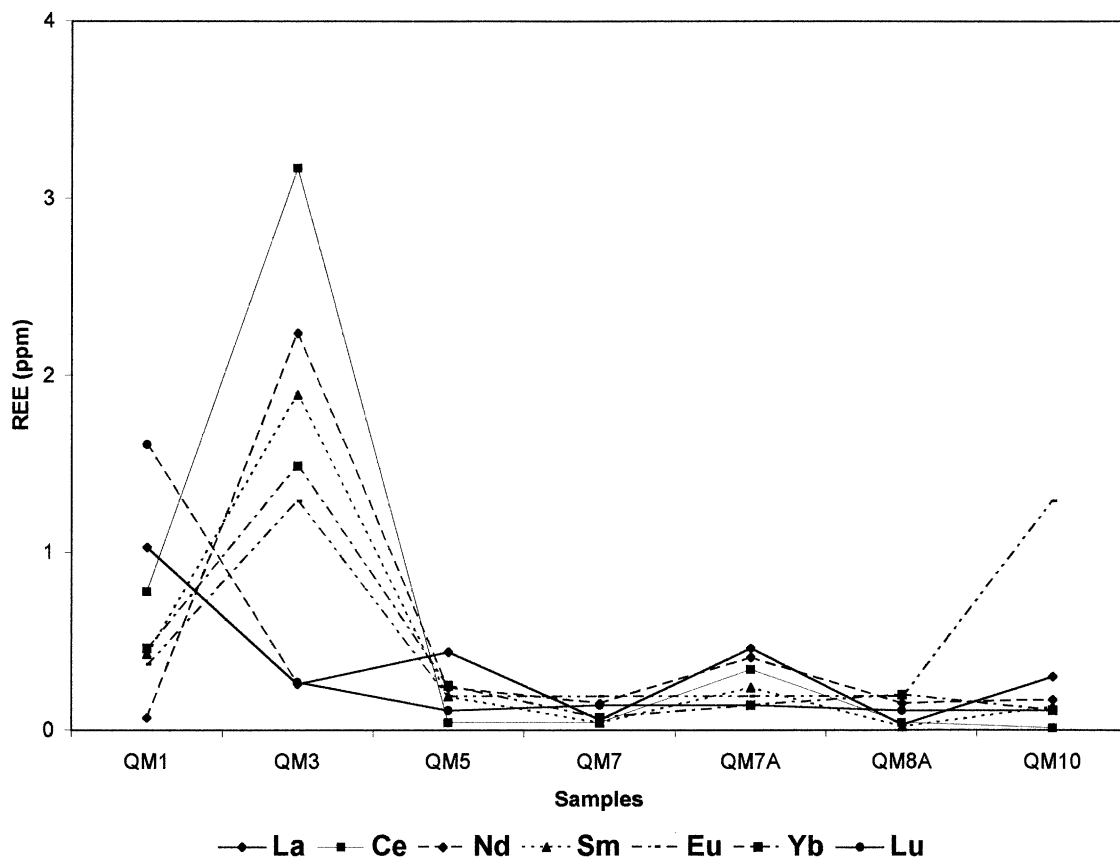


Fig. 8. Normalized concentration of REE with respect to average PAAS concentration.

elements in rocks of the La Luna Formation and in the asphaltene fraction of oils from Boscán Field (Southwestern Venezuelan Basin). As a result, they found that asphaltenes in Boscán oils are enriched in Nd with respect to the whole rock, and suggested that both elements are chelated with polar ligands of the organic matter—Nd in a greater proportion—and that REE can form stable, organometallic complexes with ligands different from porphyrins. Our results suggest the association of REE with the organic matter, although further research is required regarding these elements in the rocks in the La Luna Formation and in the carbonate and silicate-free fractions (kerogen + pyrite).

The Sm/Nd ratio was calculated for the carbonate-free fraction, and was found to be very similar for all samples (Table 4). This means that this relationship remains constant in the rock and indicates the possible application of these elements, by means of Nd isotopes in oil–source rock correlation studies (Manning et al., 1991).

The U/Th ratio, used as a redox conditions index (Jones and Manning, 1994), was calculated for the carbonate-free fraction. This ratio is  $>1$  for limestones and  $>7$  for cherts. The lower value of this ratio for argillaceous limestones can be related to the fact that Th is associated with the detrital fraction composed of heavy

minerals or clay in sediments of the mudstone type (Jones and Manning, 1994) and the samples from La Luna Formation contain clay minerals. On the other hand, the content of authigenic U was calculated following the Wignall and Myers method (1988), and values  $>2$  for argillaceous limestones, reaching 16 in QM-3, and  $<1$  for chert layers were obtained. Klunkhammer and Palmer (1991) report that sediments rich in organic matter can contain high concentrations of U (authigenic). The higher content of authigenic U in the argillaceous limestones supports our proposal of euxinic conditions and higher productivity and preservation during the sedimentation of carbonatic muds (argillaceous limestones) with respect to cherts, with variation in the  $H_2S$  content during sedimentation of carbonatic muds. In the section identified as QM-3 maximum euxinic conditions, productivity and preservation during sedimentation was observed.

A significant correlation was observed in the carbonate-free fraction between the U and Mo elements (Fig. 9), which is in agreement with the results obtained by Bertine and Turekian (1973). In oxidizing environments, U is present as uranile ion ( $U^{VI}$ ); this soluble species is reduced and precipitates as uraninite ( $U^{IV}$ ) in reducing environments with an abundance of organic matter. On the other hand,  $Mo^{VI}$  is reduced to  $Mo^{IV}$

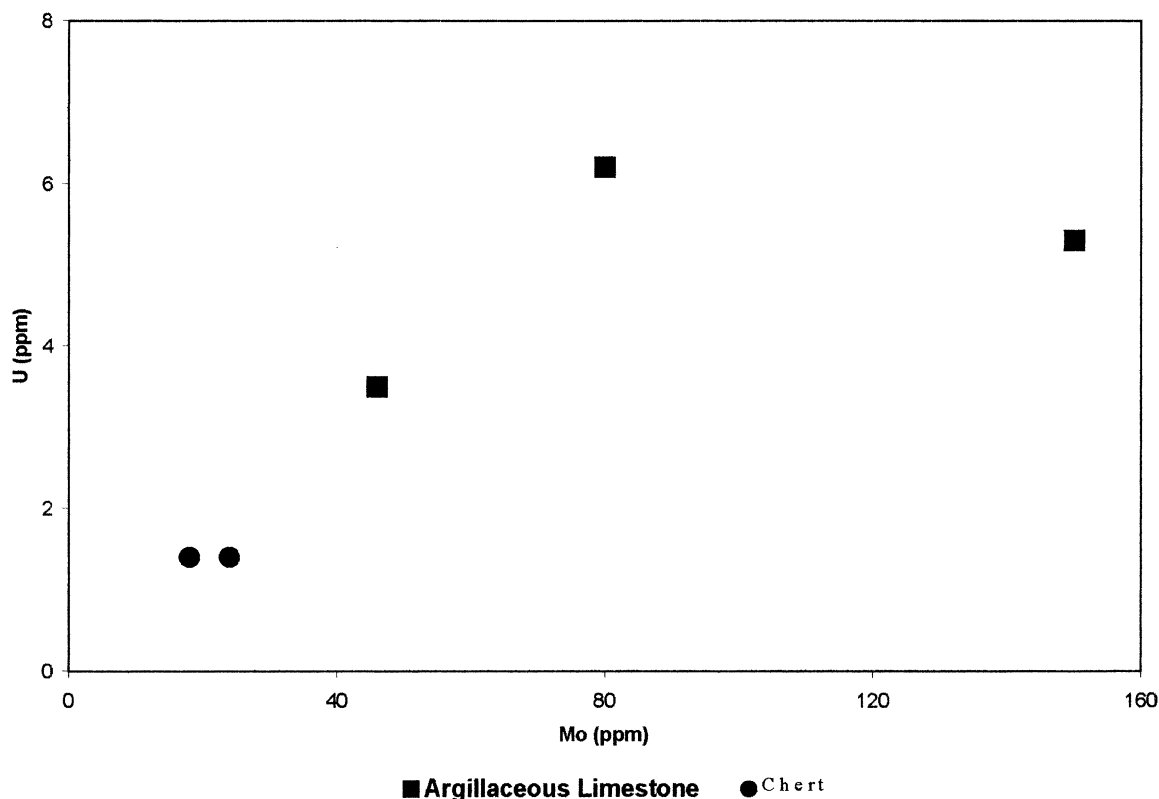


Fig. 9. Concentration of U (ppm) vs. Mo (ppm) in the carbonate-free fraction rock.

under sulfate-reducing conditions and is removed as sulfide from water by means of co-precipitation with Fe (Bertine, 1972). On the other hand, Pilipchuk and Volkov (1974) conclude that Mo enrichment in anoxic environments is the result of two processes: metal diagenetic fixation through the organic matter and precipitation with pyrite. The U/Mo correlation ( $r^2=0.63$ ) can be explained because both appear as soluble species in oxidizing environments and are reduced in environments rich in organic matter under sulfate-reducing

conditions (free  $H_2S$ ), forming insoluble authigenic species (uraninite and molybdenum sulfide).

Fe and S do not exhibit an appreciable correlation in the whole rock, but the correlation is acceptable ( $r^2=0.88$ ; Fig. 10) in the carbonate-free fraction. This suggests that Fe can be present in species such as carbonate (siderite), which are not associated with S in pyrite, and are solubilized during the acid attack, leaving a pyrite-enriched residue once they are dissolved, as confirmed by XRD and clearly observed

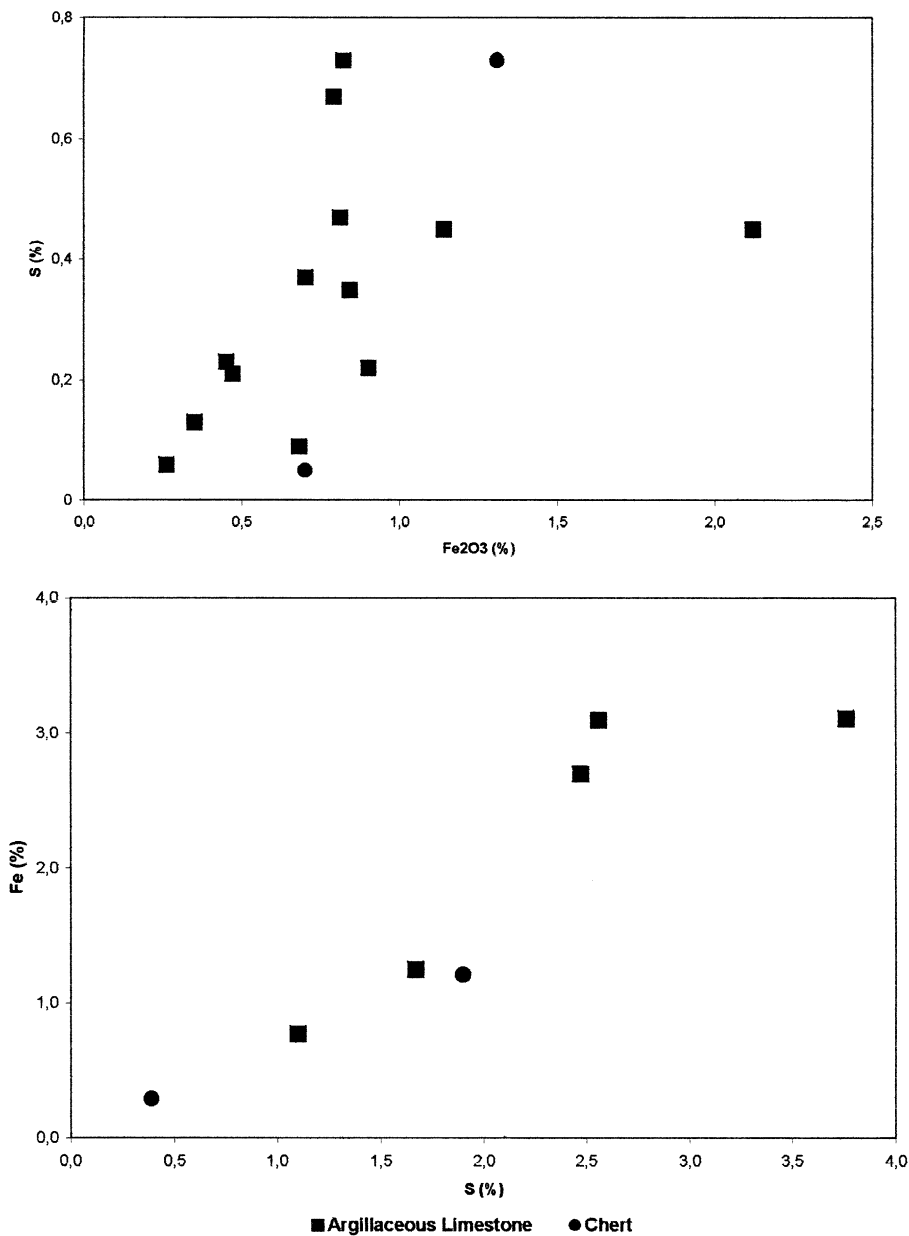


Fig. 10. Concentration of Fe (%) vs. St (%) in the whole rock (A) and in the carbonate-free fraction (B).

by means of EPMA, in the presence of abundant pyrite framboids.

## 5. Conclusions

V is associated with organic matter, while Ni is present both in the organic matter and in the sulfide phase, Fe appears as massive and framboidal pyrite, Zn precipitates in a separate phase (possibly sphalerite). Cu and Zn (in some cases) are found as associated sulfides.

Based on the concentrations of TOC, St, V, Ni, Cu and Zn, sedimentation under dysoxic conditions is suggested for the chert layers and under euxinic conditions for argillaceous limestones. These same parameters also indicate that in the sequence corresponding to the argillaceous limestones, there were variations in the sedimentation conditions of various intervals under euxinic conditions related to a high contribution and/or preservation of the organic matter at sedimentation intervals under relatively lower anoxic conditions and in the presence of H<sub>2</sub>S.

REE enrichment in the La Luna Formation, together with the absence of phosphate minerals (monazite or apatite) suggests the association of REE with organic matter, although these elements in rocks from the La Luna Formation and in the carbonate and silicate-free fractions (kerogen + pyrite) require further study.

The Sm/Nd ratio is very similar for all samples, thus confirming that this ratio remains constant in the rock and the possible application of these elements by means of the Nd isotopes in oil–source rock correlation studies.

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