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Inorganic Geochemistry as Technique to Preliminary Assessment of Shale Plays in Cretaceous Source Rocks in the Eastern Cordillera Basin, Colombia*

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Abstract

The Colombian Cretaceous source rocks in the Eastern Cordillera Basin have been of particular relevance to geoscientists and exploration companies in the oil industry during the last decades, because of its high conventional hydrocarbons potential. Moreover, the urgency of developing unconventional hydrocarbons in Colombia today has increased the need for new techniques and models that not only define unconventional shale plays, but also evaluate and predict rock properties. We present here, detailed elemental geochemistry analysis using the XRF technique, on outcrop samples of the Upper Valanginian to Turonian-Coniacian succession of source rocks, including limestone and marlstones of the Rosablanca Formation, black shales of the Paja, Simití and Simijaca Formations, and finally siliceous siltstone and limestones of the La Frontera Formation and shales with some siltstone intercalations of Conejo Formation, all deposited in a mixed clastic-carbonate ramp. Within the succession studied, trace elements concentrations and paleoredox proxies were identified and then grouped in chemofacies and these, in turn, provided chemostratigraphic criteria to correlate stratigraphic sections distant from each other geographically, coupled with sedimentological descriptions. The potential most prolific chemofacies are characterized by high enrichment factor (EF) for U, V, and Mo that outlines paleoredox conditions, and EF's for Ni, Cu which in turn, indicate areas of high amounts of organic matter preservation and are interpreted as anoxic, related closely to OAE I and II and transgressions. On the other hand, chemofacies with lower amounts redox sensitive trace elemental EF's, suggests dysoxic to oxic conditions that allowed the development of benthic fauna, which precluded conservation of organic matter. In order to establish the potential targets within the succession, semi-quantitatively TOC values were predicted, using well-known strong correlation between Mo and TOC. Higher TOC values and EF for Ca, related to brittleness, are indicative of potential zones to produce a huge amount of unconventional hydrocarbons. Thus, the black shales of Paja, Simijaca and Conejo Formations matches the main characteristics of a shale play such as deposition in anoxic environments, good preservation of organic matter, higher TOC associated with good relative fracability. Finally, this study open the way to researchers interesting in similar topics in Colombian basins.

Introduction

The Colombian Eastern Cordillera basin is a NNE-SSW – trending Mesozoic extensional basin inverted during the Cenozoic (Figure 1), and their cretaceous succession represent a major transgressive-regressive cycle with the maximum flooding surface close to the Cenomanian-Turonian boundary (Villamil, 1996). The latter sedimentary succession corresponds to one of the most prolific petroleum province of Colombia and recently positioned as an important exploratory target for unconventional petroleum resources. In spite of this effort, however, many uncertainties remain with regard to their accurately depositional environment (paleo-redox conditions and preservation of organic matter), TOC index and potential fracability. We present here, detailed elemental geochemistry analysis using the x-ray fluorescence (XRF) technique, on outcrop samples of the Upper Valanginian to Turonian-Coniacian succession of source rocks, including limestone and marlstones of the Rosablanca Formation, black shales of the Paja and Simití Formation, which represents an earlier maximum flooding surface distal facies, the organic-rich and shale facies of Simijaca Formation, siliceous siltstone and lidites of the La Frontera Formation, meanwhile, they represents a later maximum flooding surface facies deposited during a global anoxic event (Villamil, 1999) and shales with some siltstone intercalations of Conejo Formation all deposited in a mixed clastic-carbonate ramp. The results of this study will allow better our understanding about the key features to consider in unconventional shale plays assessment and decrease its inherent associated uncertainty.

Methodology

Data Acquisition

A total of ca. 2000 measures have been recorded from seven stratigraphic sections (measured in 50cm intervals along of 903.5 stratigraphic meters that comprise sections: QSJ, CCC, QLB, QLP, CVL, CGS and CSR, in the Eastern Cordillera Basin, using the handheld Thermo Scientific Niton XL3t series x-ray fluorescence (XRF) analyzer, following a calibration procedure to obtain optimal results on pressed powder pellets with the use of a He purge system. The measures were made on soil mode, counting times were 30 seconds each on the low, main and high energy filters (for analyzing minor and trace elements in ppm), and 90 seconds on the light filter setting (for analyzing major elements in wt.%) for a total analysis time of 180 seconds and additionally 2-3 system checks daily. The samples are from outcrops, which were collected from fresh surfaces and later washed to remove surficial contamination and obtain precision errors in the order of 3-5%.

Data Processing and Chemostratigraphic characterization

The trace metals used in this study to show the trends and chemostratigraphic characterization are Mo, Mn, Ni, Zn, U, Cu and V, and these metal concentrations are expressed in term of their enrichment factors (EF) which represent the enrichment or depletion of an element relative to an average crustal or average shale composition and concentration of elements according to Whedepohl (1971), this average shale has low organic matter and TOC values less than 1%. To normalize the concentrations, Ti is used instead Al because of its coefficient variation is too large, which is generally the case with studies involving high-resolution sampling (Tribovillard et al., 2006), however, Ti content in shales is 4600 mg*kg⁻¹ (Mielke, 1979), and is resistant to weathering and has very low mobility under almost all environmental conditions (Brookins 1988), proving further evidence to be minutely affected by biological or diagenetic processes, also is deposited into the system by colloidal transport and higher concentrations are present in organic rich water (Skrabal, 1995) suggesting detrital origins. The normalized elemental

concentrations were plotted versus depth in each stratigraphic column to display the changes in the EF's of elemental concentrations through the section, thus, if EF's is greater than 1, then there is enrichment and if EF's is less than 1, then there is depletion. Exploratory data analysis together with Principal component analysis (PCA) were incorporated to this study in order to assessing elemental associations based on depositional proxies and understanding the geologic control on the elemental distribution in the sediments. PCA reduces the multivariable data into orthogonal mutual factors by plotting a grouping cloud of all the points. The input variables should to be standardized (i.e. mean equal 0 and variance equal 1), this operation allows all input variables, which initially could be expressed in different units and have very different ranges, are expressed in a dimensionless comparable scale.

Results and Discussion

Due to the large amount of information (charts, tables, etc.) processed and columns profiled in this study, and to avoid excessive detail, we describe only the main feature assemblages that represents the most relevant behaviour of each geological formation studied.

Descriptive and Multivariate Statistics analysis

Regarding trace elements relationships of samples from all stratigraphic sections ([Table 1](#)) shows that Cr, Th, Rb, Zr and K are positively correlated to Ti but in QLP and CGS shows negative correlations suggesting that these sections underwent important dilution process. U, V, Ni, Cu, As shows significant positive correlation with Ti in almost all sections and some negative correlations, which is evidence of these elements has a probable detrital origin and does not totally authigenic enrichment due to dilution of organic matter caused by the clastic fraction, evidence of the latter is the negative correlation of Mo, Zn, Co, S with respect to Ti but these elements are associated effectively with the organic or authigenic fraction. A good negative correlation of Ca, Sr with respect to Ti was observed, pointing the development of carbonate factory in the absence of detrital input, which is expected. No marked relation between Fe and Ni, Cu, Mo, evidencing no significant incorporation of the trace metals to iron sulphide.

Cross plots of U, V and Mo ([Figure 2](#)) shows no relationship with respect to Ti, indicating that these trace metals can be used for interpreting paleoredox conditions, contrary to Th and K which matches with trend line, thus, likely indicating their overwhelmingly association with terrigenous-source clay minerals, however, some slight deviations from the best fit line exist, evidencing a possible separate source. The relationship between Ca and Ti, reflects different origins for these elements, as indicated above. PCA results ([Figure 3](#)) are conclusive separating the elements into 3 distinctive groups, thus, QLB section has 59.59% for variance accountability and the factor loadings grouped in Ti, Th, Fe, Cr, Rb, Pb, K, Zr, Co and U representing the terrigenous input and mixed origin for U; Mo, Zn, Ni, V, Cu, As and S for the Authigenic enrichment; Ca and Sr representing the Carbonate elements properly. In QJS section F1 and F2 explains the 51.17% of variance and the factor loadings are grouped in Ti, Th, K, Rb, Pb, Cr representing the terrigenous input; S, Zn, Mo, Ni, Cu, U, As, V for the Authigenic enrichment; Ca and Sr for the Carbonate elements. Some variations to the grouping of elements e.g., Fe, Co and Zr indicates different source than expected. V, Sr, Fe, Pb and Mo in CGS (52.54% variance accountability) section, confirms the foregoing assumption and highlights the strong dilution process for this section. PCA results of the CSR section (50.65% of variance accountability) are quite conspicuous because of inclusion of a new group, as yet not recorded. The terrigenous group remains uniform with Ti, K, Zr, Rb as expected, but also Sr was added. Authigenic enrichment keeps V, Ni and Mo, but U reflects strong evidence of dilution processes and / or detrital origin. The new group

comprise Cr, Pb, Cu, Fe, S, Zn, As, Co and Ca, these combinations of elements suggests a strong relationship with a magmatic sulphide source, linked to magmatic segregation processes on immiscible liquids (Maksaev, 2001). The fact that their opposite projection to the terrigenous data cloud on the correlation circle plot, asserts its distinction as a new group.

Chemofacies and Potential Production Zones

Determining chemofacies based on inorganic geochemistry involves interpreting the oxygen levels in the water at the time of deposition (Tribovillard et al., 2006), these oxygen levels were grouped in Oxic, Dysoxic, Suboxic, Anoxic and Euxinic according to Tyson and Pearson (1991). The oxic facies represented by yellow color (Figure 4), composed mainly of fine-grained sandstone, siltstone and limestone and scarce marlstone, is characterized by abundance of benthic fauna, low Ca content but in some cases variable. EF's of V, Ni, Cu, Mo and U are depleted, however some isolated peaks of Mo and Cu exist. A large influx of terrigenous is interpreted due to higher EF's for Th, K and Ti and leaching of U and Cu. The dysoxic facies represented by magenta color, shows significant influence of terrigenous input with EF's of Th, K and Ti enriched, but lesser than oxic facies; EF's of paleoredox elements evidencing a very variable behavior, however, U in most cases appear depleted to leached, probably linked to postdepositional reoxygenation (Tribovillard et al., 2006) caused by relatively environmental abruptly changes such as turbidity currents deposited in low-oxygen settings, tempestites or hyperpycnal flows. Lithologically is composed mainly by marlstone, siliceous shales and siltstone. The Suboxic and anoxic facies share certain features such as marked enrichment of V, Ni, Mo and U and terrigenous input strong depleted, nevertheless, the difference points in a strong enrichment of Cu in the anoxic facies, suggesting greater amounts of well-preserved organic matter. The euxinic facies shows abrupt enrichment peaks of U, V and Mo, these facies together with the foregoing described, comprise the finest lithology associated to pyrite horizons. Two marked (marked with stars in Figure 4) absence of U, V enrichment and a more modest one in Cu in the presence of a prominent Mo and Ni enrichment are observed in Suboxic facies, invoke a possible "basin reservoir effect" (Algeo, and Lyons, 2006) evidencing moderately to strongest restricted deep-water masses renewal.

A semi-quantitatively analysis to predict TOC values from Mo concentration by using two linear regressions equations shows good correlations with TOC reported for the formations studied here. Thus, the uppermost part of Rosablanca Formations shows an average 1.56% TOC value and maximum 1.77% TOC value that matches with the anoxic facies. The Paja Formation shows an average 1.79% TOC value and maximum 2.58% TOC that matches with the euxinic facies. Simití Formation presents an average 1.66% TOC value and maximum 3.11% TOC value that matches with anoxic facies. Simijaca and La Frontera Formations shows very closed results, average 1.89% TOC with maximum 4.48% TOC values and 2% TOC with maximum 4.59% TOC values respectively. Finally, the basal part of Conejo Formation shows a relative decrease value, with an average 1.72% TOC and maximum 2.9% TOC values that matches with dysoxic facies.

In sum up, Rosablanca formation deposited under dysoxic-Suboxic conditions with good OM conservation proxies and fair TOC values that not reaches the minimum value to be consider shale gas reservoir (2% TOC), their marlstone horizon could be a potential production zone because its high brittleness factor. Paja formation deposited in oscillating anoxic-suboxic conditions shows good OM proxies and fair to good TOC values also good fracability indicators, consequently could be a target of potential production. Simijaca and La Frontera formations even though that was deposited under dysoxic-suboxic conditions and shows no conclusive OM preservation proxies, fair to very good TOC values that matches with anoxic facies encourages to consider as a potential production zone. Likewise, the fact that volcanic ash layers coincide with the anoxic facies could hytoplankton biomass likely due to combination of an increase of P supplies together with a lowering of light intensities

(Modenutti et al., 2013), thus widespread oxygen depletion occur by bacterial populations that responded to increased nutrients levels, and the oxygen based system grades into one dominated by anaerobic heterotrophs. The basal part of Conejo formation was deposited under dysoxic conditions along with their fair to good TOC values and significant siliceous content could be consider a production zone further studies. The basal part of Conejo formation was deposited under dysoxic conditions along with their fair to good TOC values and significant siliceous contents could be considered a production zone.

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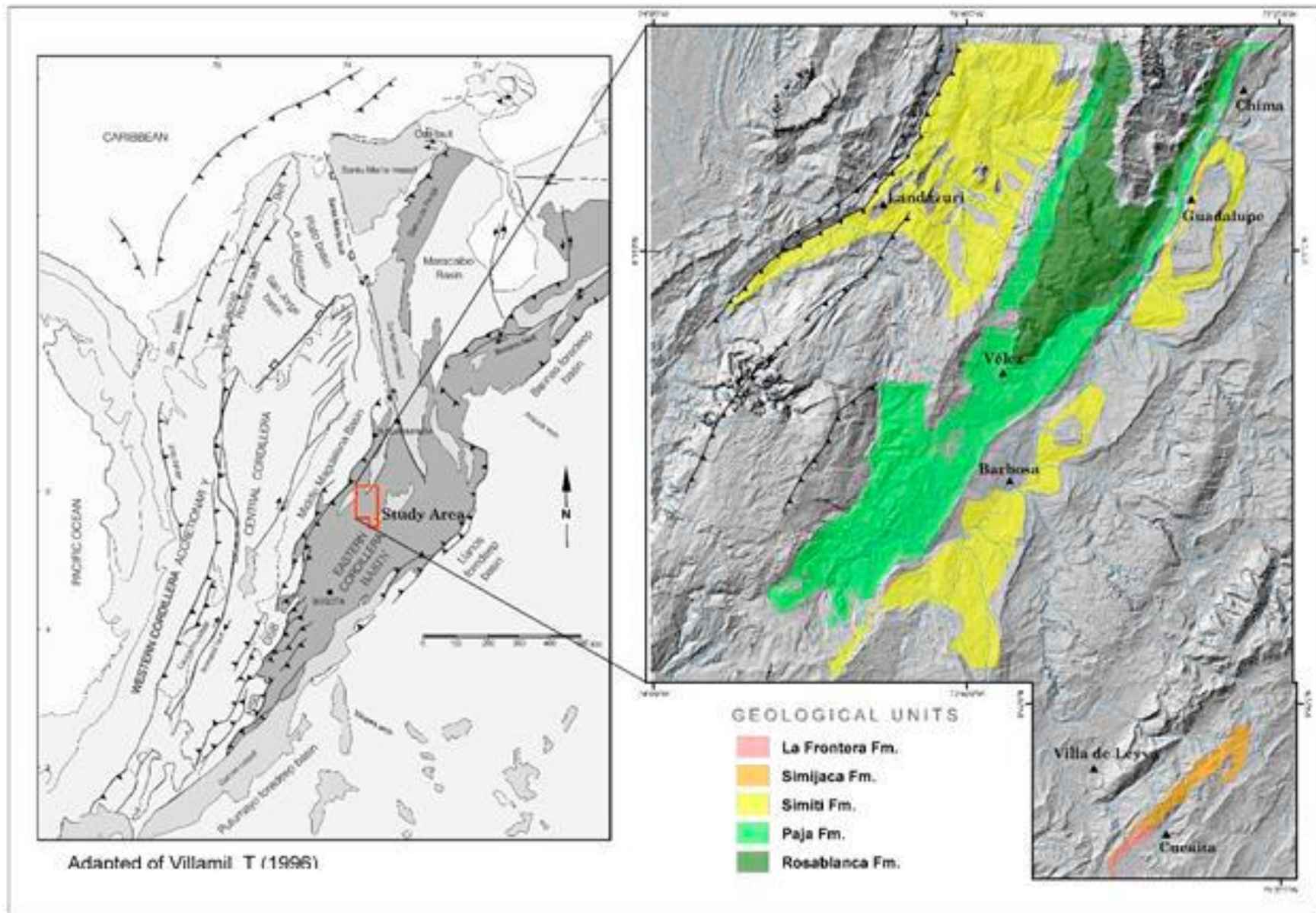


Figure 1. Location map of Eastern Cordillera Basin and spatial distribution of geological formations studied. Note the reverse faulting at the west, suggesting the inversion of Mesozoic half-grabens.

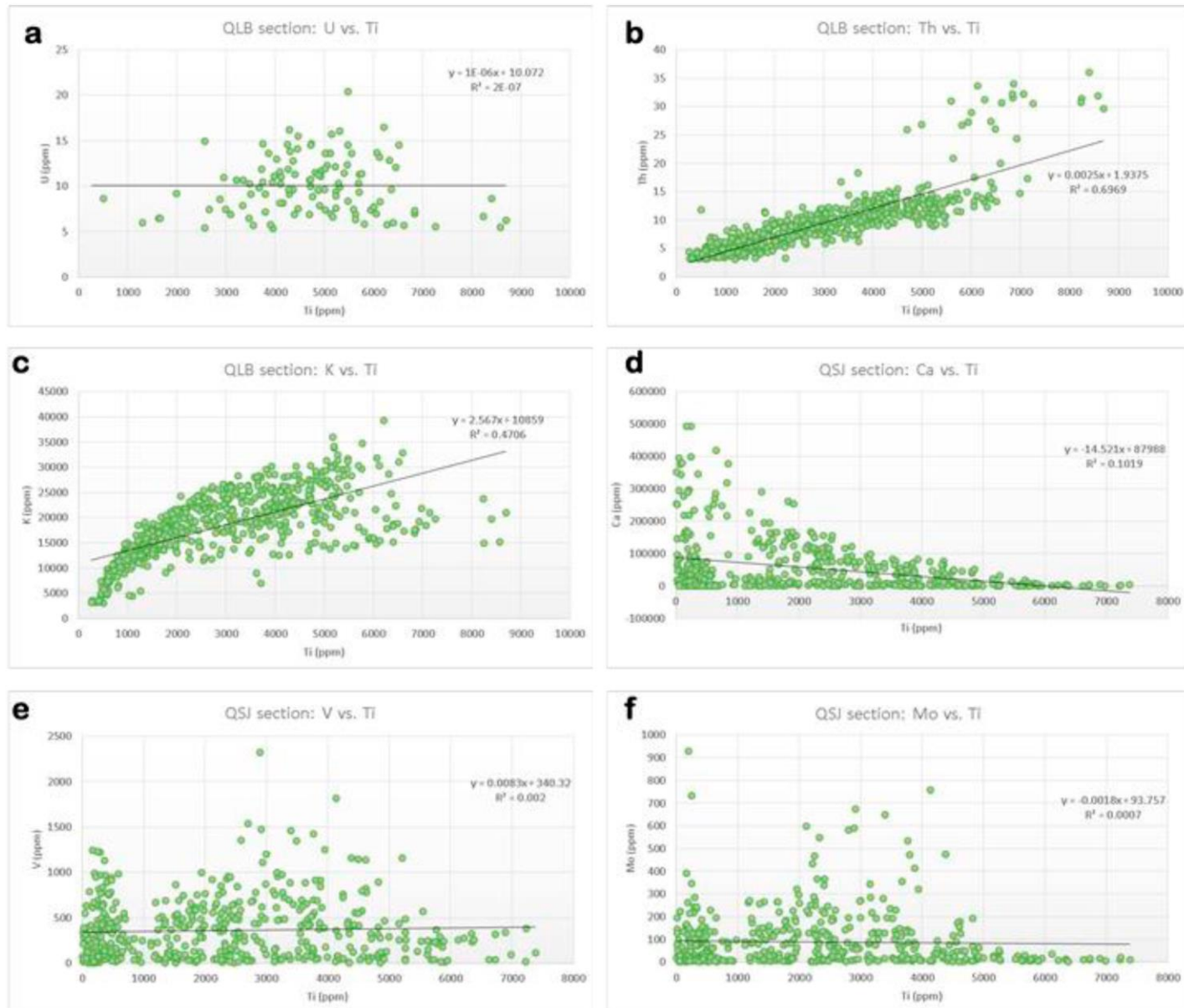


Figure 2. Cross plot of trace elements versus Ti, which is immobile during diagenesis. Thus, (a, e, f) shows no correlation with Ti, indicating good paleoredox proxy because their authigenic origin. (b, c) shows detrital origin of Th and K. (d) shows negative correlation suggesting a carbonate origin.

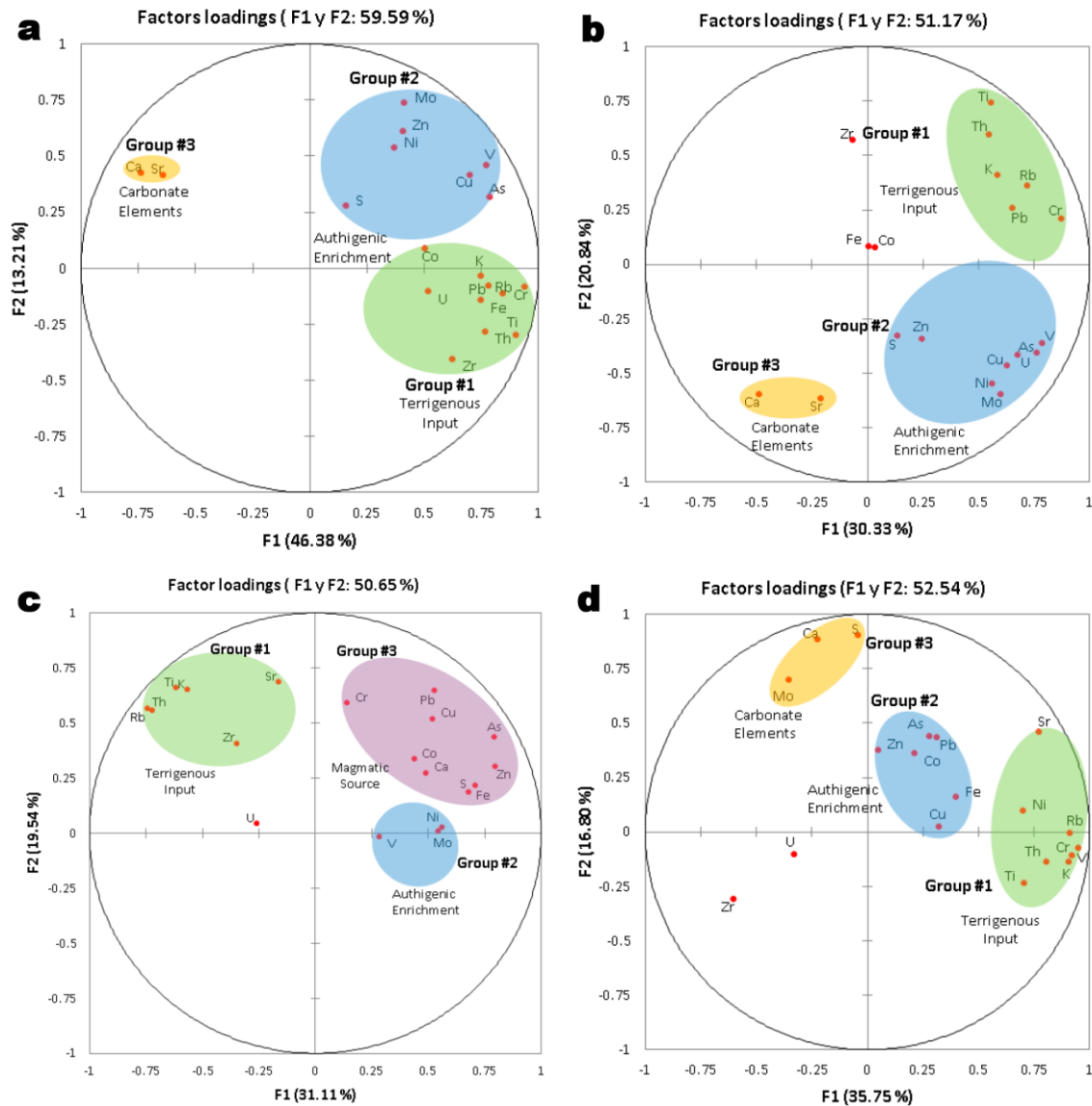


Figure 3. Circle plot of PCA correlations. (a) QLB section shows three properly distinctive groups: carbonate, terrigenous and authigenic. (b) QSJ section shows again the three formerly distinctive groups, however, Fe and Co were not taken into consideration due to their proximity to axis origin. (c) CSR section shows a new conspicuous group showing affinity with magmatic origin. (d) CGS section shows three distinctive groups: carbonate, terrigenous and authigenic. Nevertheless, carbonate group is high variable here.

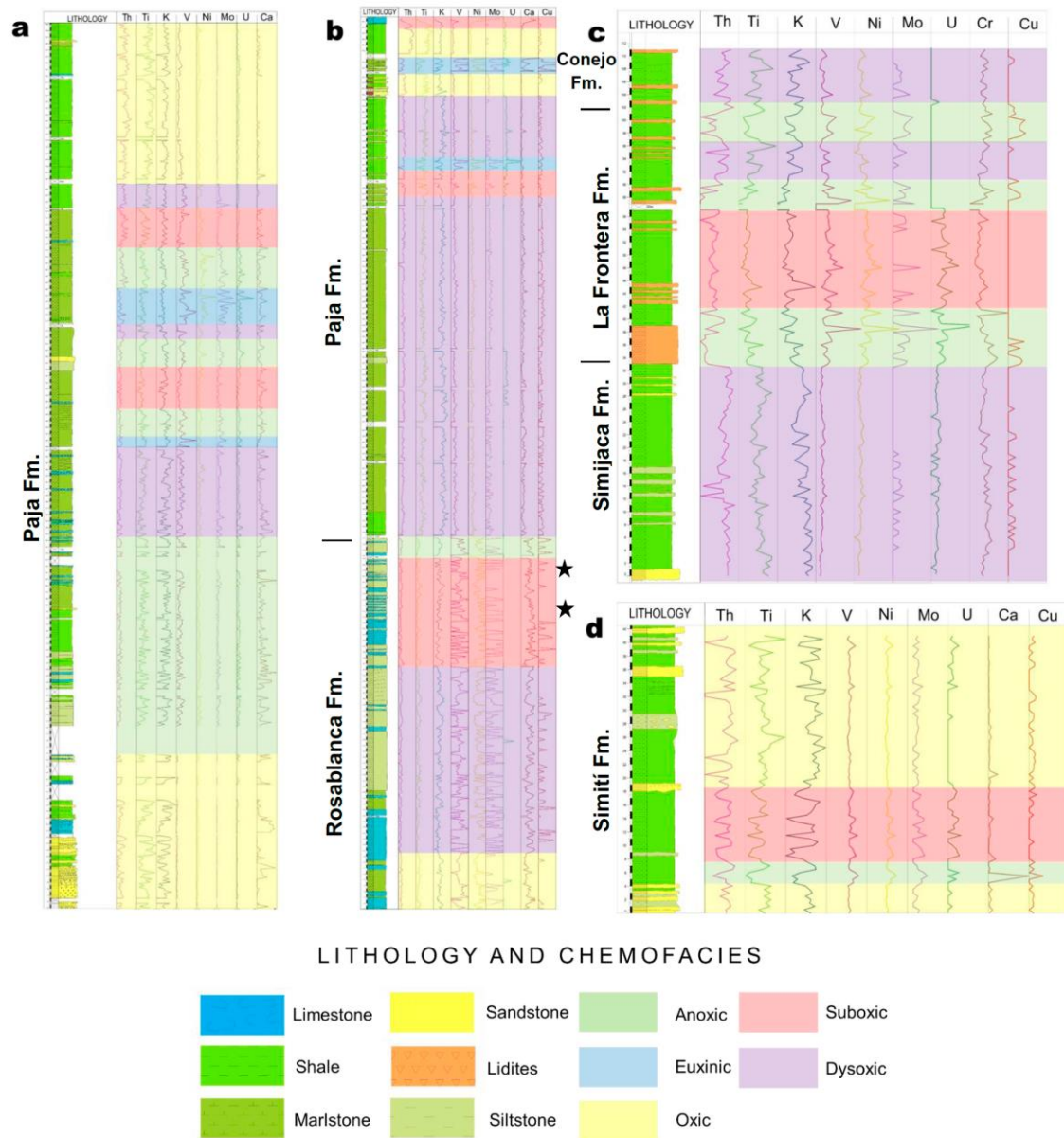


Figure 4. Chemostratigraphic analysis showing the main chemofacies defined in this study. (a) Corresponds to QJS section. (b) Corresponds to QLB section. Black star (◆) pointing out possible basin reservoir effect mentioned in the text. (c) Corresponds to CSR section. (d) Corresponds to CGS section.

Trace Elements	QLB	QLP	QSJ	CGS	CCC	CSR	CVL
Mo	0.108	0.076	-0.103	-0.161	-0.115	-0.215	-0.097
Zr	0.758	-0.496	0.437	0.010	0.765	0.599	0.349
Sr	-0.606	0.167	-0.464	0.429	-0.843	0.375	0.467
U	0.481	0.348	0.068	-0.192	0.375	0.153	0.516
Rb	0.752	0.517	0.634	0.499	0.864	0.786	0.775
Th	0.855	0.570	0.798	0.702	0.747	0.781	0.876
Pb	0.740	0.420	0.514	0.021	0.484	0.012	0.314
As	0.572	-0.230	0.086	0.092	0.595	-0.201	0.421
Zn	0.182	0.041	-0.112	-0.072	0.165	-0.251	0.141
Cu	0.509	0.063	-0.012	0.451	0.336	-0.070	0.368
Ni	0.277	0.120	-0.046	0.511	0.477	-0.190	0.422
Co	0.377	0.424	0.078	-0.018	0.286	-0.134	0.138
Fe	0.674	-0.143	0.069	0.074	0.765	-0.320	0.154
Cr	0.887	-0.303	0.640	0.692	0.910	0.379	0.847
V	0.555	0.568	0.169	0.711	0.955	-0.068	0.896
Ti	1	1	1	1	1	1	1
Ca	-0.695	0.172	-0.598	-0.289	-0.740	-0.131	-0.205
K	0.720	-0.248	0.680	0.756	0.884	0.865	0.890
S	0.058	0.509	-0.120	-0.133	0.236	-0.214	0.055

Table 1. Correlation matrix of trace elements respect to Ti, through all stratigraphic sections.