V/Ni ratio as a parameter in palaeoenvironmental characterisation of nonmature medium-crude oils from several Latin American basins

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ABSTRACT

Statistical descriptive analyses were performed taking into account sulphur, vanadium and nickel concentrations in several nonmature crude oil samples collected in the last few years from various Venezuelan and Spanish basins. Techniques used included flame atomic absorption spectrometry and energy-dispersive X-ray fluorescence spectroscopy. The results allow us to obtain a generic diagram in which four zones are well defined by their limit V/Ni ratios or Ni contents. Although previous works established intervals with reference to V/Ni ratios, this is nonetheless one of the first times that data are statistically considered with the aim of obtaining and evaluating the validity of a diagram plot to make it possible to determine the type of environment in which organic matter was deposited prior to any crude oil. Such a diagram is useful in establishing the palaeoenvironmental redox conditions that prevailed in the corresponding source rocks during their deposition. It is important to emphasize that this diagram can be applied as a geochemical exploration tool in medium-crude oils from other petroliferous basins in order to significantly reduce the costs and time of oil prospecting.

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1. Introduction

Geochemical indicators commonly used in the characterisation of oil seeps, crude oils and bitumens include concentrations of trace elements, particularly vanadium and nickel. Despite the fact that the concentrations of these metals can be influenced by processes of thermal alteration, deasphalting, biodegradation and washing water or during migration, the V/Ni ratio itself tends to be constant due to the structural similarities among organometallic compounds that contain vanadium and nickel. This trait means the ratio is one of the most useful parameters for determining both the origin of precursor organic materials and oil–oil or oil–source rock correlations (Lewan, 1984; Hunt, 1996), in addition to other indicators related to different chemical elements (Quinby-Hunt and Wilde, 1996; Wilde et al., 2004).

Nevertheless, based on the lithofacies, these parameters may vary widely. In siliciclastic facies, for instance, the high concentration of iron ions leads to reactions with sulfide ions, thus forming pyrite, whereas nickel ions tend to form organometallic compounds, which leads to low V/Ni ratios. However, in most carbonatic facies, the low concentration of iron ions means that nickel ions react with sulfide ions and that it is unlikely to form organometallic compounds, meaning high values for this ratio. Moreover, the V/Ni ratio is used as an indicator in order to determine which physicochemical conditions

control the formation of organometallic compounds, such as redox potential (Eh), the concentration of hydrogen ions (pH) and the activity of sulfide ions.

Like several preceding geochemical research works (Escobar, 1987; Itriago, 1999; Mata, 2001; among others), this work is based on data from vanadium and nickel total concentrations, V/Ni ratio and sulphur content. These data were obtained from four medium-crude oil series from an equal number of previously selected areas in the three main Venezuelan basins (Fig. 1): the Urdaneta district and Ceibita area (Maracaibo–Falcón Basin), the Hamaca area (Eastern Venezuelan Basin), and the Silvestre field (Barinas–Apure Basin). These areas were selected according to the three above-defined medium-crude oil types (Lewan, 1984).

After studying Eh and pH vanadium and nickel diagrams, a generic graph (Fig. 2) was proposed (Lewan, 1984), applicable only to slightly altered crude oils with specific gravity values of 22–39° API. Lewan's diagram reveals the existence of three distinctive types (represented by symbols I, II and III, respectively) based upon the physicochemical conditions of deposition for their corresponding source rocks. This also allows crude oils from several depositional facies to be identified as deriving from the same source rock.

Labastidas (1997) analysed thirty-four crude oil samples from various oil fields (Silvestre, Sinco, Maporal, Mingo, Hato, La Victoria and Guafita) with the aim of studying both the source-rock palaeoenvironmental conditions and the physicochemical characteristics of crude oils from wells in the Barinas–Apure Basin. Other crude

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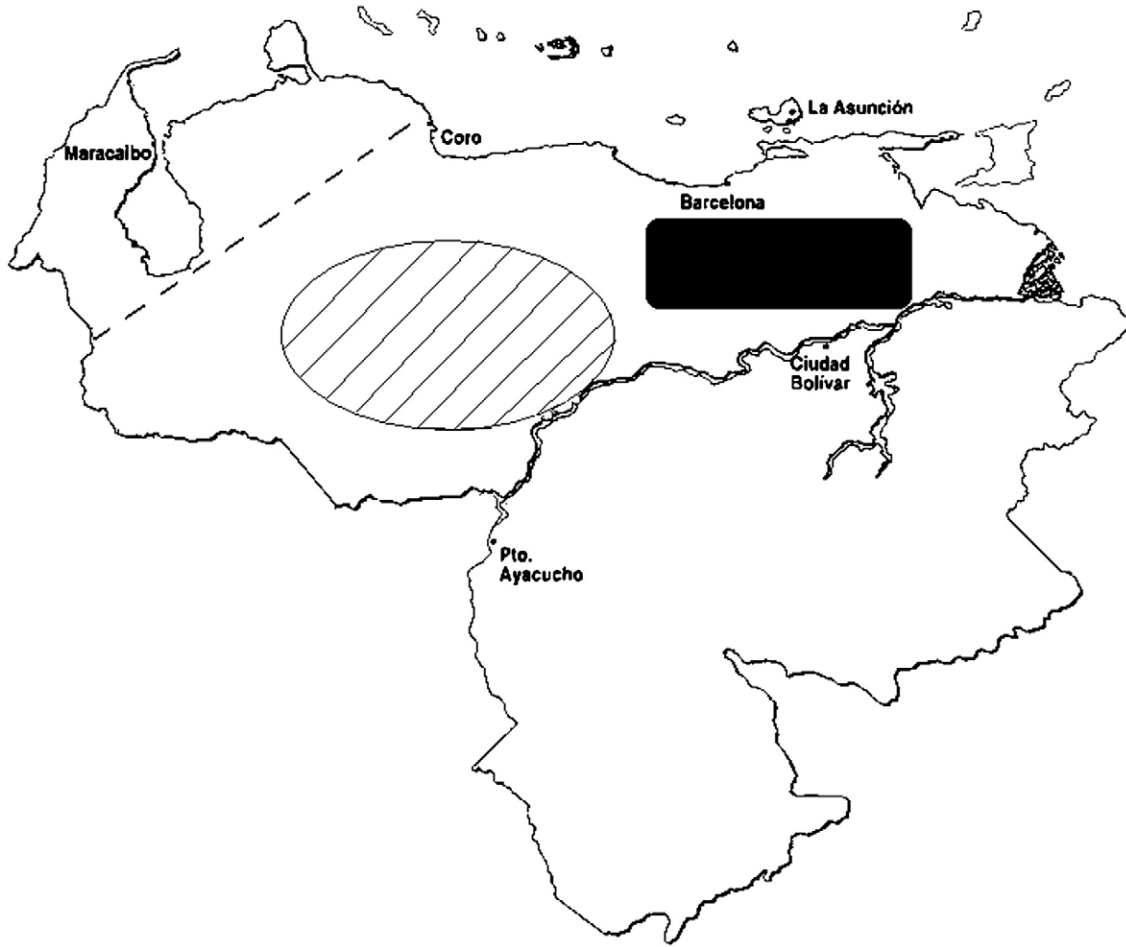 E-mail address: gmarmar@us.es (G. Márquez).

Fig. 1. Three main Venezuelan petroliferous basins. Note: Eastern Basin (shaded surface area), Maracaibo–Falcón One (white surface area) and Barinas–Apure Basin (lined surface area).
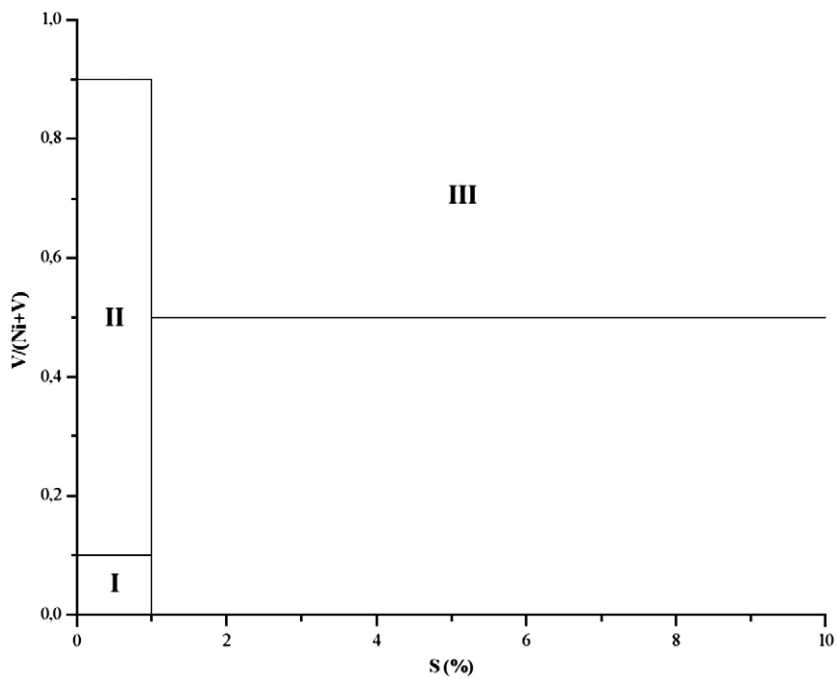

Fig. 2. Graph (V/V + Ni) in comparison to sulphur content in percent of weight.

Table 1
Linear regressive parameters for V and Ni content data from each study area

	Pearson's coefficient	Slope	Intercept
Hamaca area	0.92	4.44	−100
Silvestre field	0.95	2.51	2.35
Ceibita area	0.75	0.57	0.93
Urdaneta district	0.98	8.75	6.52
Ayoluengo field	0.99	3.24	110

oil samples from the Hamaca area in the Orinoco Oil Belt have also been analysed (Alberdi et al., 1996). Similarly, a geochemical characterisation has been carried out on about one hundred crude oils, oil seeps and bitumens from several areas in the Maracaibo–Falcón Basin (Del Ollo, 1993; Escobar, 1987). Our research work attempts to include some of these data (V and Ni concentrations) to establish a new generic diagram that would allow an easy and rapid determination of the type of environment in which the organic matter prior to the medium-crude oils was preserved. In addition, and with the aim of evaluating the validity of the afore-mentioned diagram, this same diagrammatic representation is applied to a series of crude oil samples from the Ayoluengo field (Basque–Cantabrian Basin, Spain).

2. Geological setting

The Maracaibo–Falcón Basin is located in north-western Venezuela, which comprises mainly the states of Zulia and Falcón and, to a lesser extent, those of Mérida, Táchira and Trujillo. The Maracaibo sub-basin (containing 700 oil-producing fields after drilling about 16,500 wells) covers an area of approximately 50,000 km^2, with an estimated sediment volume of 250,000 km^3 over a pre-Cretaceous basement. The main petroleum source rock is La Luna Formation, although other source rocks also generate hydrocarbons (González de Juana et al., 1980). The similarity in sulphur contents, expressed as a percentage by weight, and V/(V+Ni) ratios from numerous studies (For example, López et al., 1991) have allowed us to conclude that most crude oils extracted from the Maracaibo sub-basin were generated from the same source rock, as physicochemical conditions remain almost constant throughout the entire sub-basin. In the eastern part of this basin is the Falcón sub-basin, with a surface of 35,000 km^2 and a sediment volume of 161,000 km^3 (Martínez, 1976). This sub-basin produces high-quality crude oils and has enormous gas accumulations (González de Juana et al., 1980).

The Eastern Venezuelan Basin includes two major oil fields, El Furrial, which covers the northern part of this basin, and the Orinoco Oil Belt, located on the southern boundary of the basin. The principal source rock in this basin is associated to the Guayuta Group, which comprises the Querecual and San Antonio Formations. The formations were deposited during the maximum transgression in the late Cretaceous. This group has a sequence of calcareous shales and sandstones from the deposition of organic sediments under anoxic conditions (Casani, 1985); its organic facies display horizontal and vertical variations as well.

The Barinas–Apure Basin, located between the two states of the same names, is considered to be the third most important Venezuelan basin in regards to oil and gas reserves. The Maracaibo–Falcón Basin (Venezuela's most important basin) is located to the west, and the Eastern Basin lies to the east. The Apure and Arauca rivers mark the southern edge of the Barinas–Apure Basin, bordering the Colombian Llanos Basin (González de Juana et al., 1980). The Barinas–Apure Basin covers an area of about 162,000 km^2, with 500 m of Cretaceous and post-Cretaceous sediments. The basement comprises igneous-metamorphic pre-Cretaceous rocks and Jurassic and Palaeozoic sediments (Kiser, 1987). Oil production in the state of Barinas is mainly concentrated in a 3000 km^2 area that includes the Silvestre, Sinco, Mingo and Paez oil fields; this oil-producing zone is associated to the

Fortuna and Gobernador Formations. Likewise, in the state of Apure, the oil-producing zone comprises the Guafita and La Victoria oil fields and is associated to the Guafita Formation, subdivided in turn into the Arauca and Guardalito rocky formations (Labastidas, 1997).

The Basque–Cantabrian Basin, in northern Spain, is a Mesozoic basin folded and thrust during the Pyrenean orogeny in the Tertiary. The present structure of this sedimentary basin consists of a north-to-south verging thrust belt that constitutes the western portion of the Pyrenees (Quesada et al., 1997). Moreover, the Ayoluengo field, the only onshore oil field in Spain (covering 10 km^2), covers the southwestern part of this basin (Quesada et al., 1991). Several works (Quesada et al., 1995; Quesada and Robles, 1995) point to organic facies in the Late Jurassic sequence as the source rock for the whole Basque–Cantabrian Basin. This source rock is characterised as a transgressive sequence composed of carbonate shales with minor intervals of siliciclastic materials.

3. Materials and methods

Sulphur, vanadium and nickel concentrations were determined for different crude oils from the five cited areas in order to establish the above-mentioned V–Ni diagrammatic representation. The aim of this diagram is to classify medium-crude oils from any basin into one of several families according to the type of precursor organic material. Therefore, data were taken from fifty crude oils corresponding to an equal number of wells (Appendix): fourteen of them from the Silvestre field, twelve from the Hamaca area, another fourteen samples from the Urdaneta district, six from the Ceibita area, and the rest from some of the approximately fifty wells in the Ayoluengo field in Spain (Merten, 2006).

All crude oil samples have been analysed using different techniques. The sulphur contents were determined (according to the ASTM D-4294/98 method) by means of an energy-dispersive X-ray Panalytical spectrometer (model Axios), equipped with a digital signal processor and dual multi-channel analyser. Flame atomic absorption spectrometry allowed the quantitative analyses of vanadium and nickel concentrations (using norm ASTM D-5863/00) through a model 1100B Perkin-Elmer spectrometer. All the reagents were of analytical grade, and Mill-Q water was used.

The density or API gravity of the fifty samples was measured (in accordance with norm ASTM D-2041) using a Rice apparatus that included a set of necessary elements: a vibrator, a vacuum pycnometer, a vacuum pump, a filtration set, an electronic scale and a low pressure manometer composed of a U-shaped tube closed at one end and mounted on a glass blister connected to an evacuated tank.

Finally, a statistical analysis was done using all data corresponding to crude oils from the five areas mentioned above (Appendix), determining maximal and minimal values, averages and V–Ni Pearson's correlation coefficients. In order to obtain these statistical data, SPSS 13.0 package for Windows was used.

4. Results and discussion

The statistical calculations corresponding to crude oil data from each study area are: the Hamaca area, V/Ni ratios from 3.24 to 4.03 (average equaling 3.54), Ni contents between 93.0 and 139 ppm (average 113 ppm); the Silvestre field, V/Ni ratios from 2.18 to 2.91 (average 2.53), Ni contents between 46.7 and 111 ppm (average 78.6 ppm); the Ceibita area, V/Ni ratios from 0.20 to 1.80 (average 0.77), Ni contents between 0.50 and 2.71 ppm (average 0.87 ppm); the Urdaneta district, V/Ni ratios from 5.64 to 11.4 (average 8.70), Ni contents between 5.10 and 148 ppm (average 49.4 ppm); and the Ayoluengo field, V/Ni ratios from 5.90 to 6.10 (average 5.99), Ni contents between 37.0 and 43.0 ppm (average 40.0 ppm). Table 1 shows the values of linear regressive parameters – Pearson's coefficient, slope and intercept – corresponding to V and Ni content
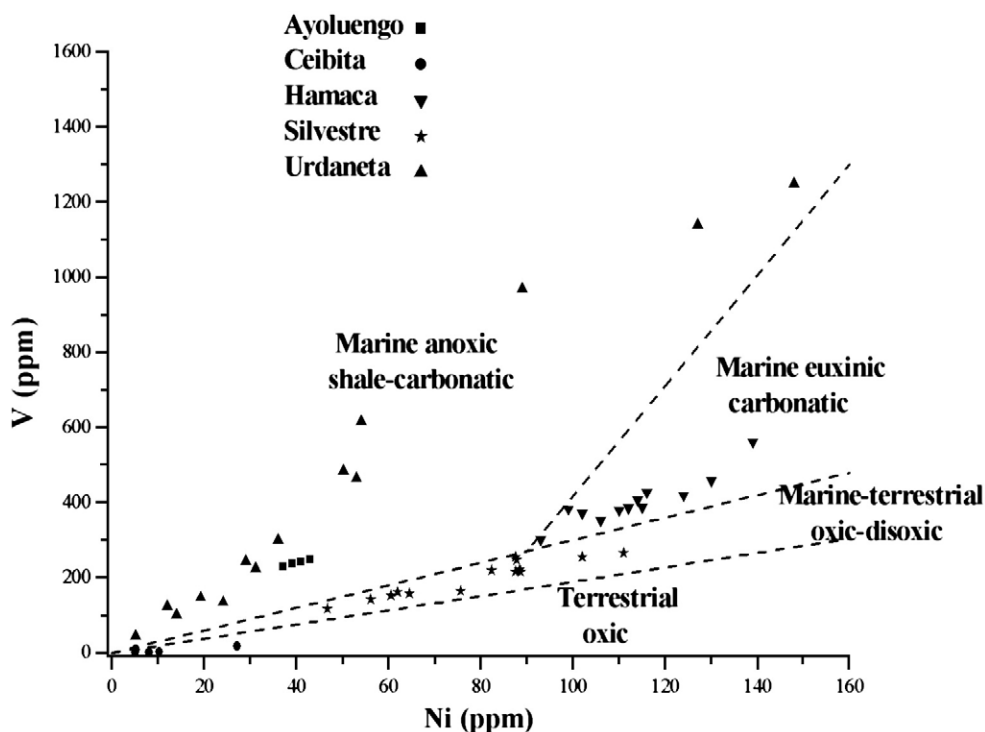
Fig. 3. Graphic zonation of V and Ni concentration values as tool for palaeoenvironmental interpretations.

data from each study area. It should be noted that the V and Ni concentrations refer to crude oils with a gravity range from 22° to 38° API, since such oils should not be significantly influenced by processes of thermal alteration, migration, or water-washing (Lewan, 1984).

Furthermore, crude oils from the two series from the Maracaibo–Falcón Basin have very different V/Ni linear regressive correlations: 0.97 for the Urdaneta district; by contrast, oils from the Ceibita area have a Pearson's coefficient value of 0.75. All the crude oils from these two series are nonmature, slightly altered by biodegradation, and genetically associated to a very reducing marine palaeoenvironment in this basin. An absence of sulphate ions reduces nickel ion concentrations in order to react with organic compounds, due to the fact that such ions form sulphur compounds; for this to occur, either the iron ion concentration must be low or sulphur ion content (bacterially generated) must be higher than the iron ion concentration (Lewan, 1984). However, the vanadyl ion content is high, hence the V/Ni ratios of over 3, which indicates that the source rock was deposited in a very reducing environment, characterised by the presence of sulphate-reducing bacteria (Quinby-Hunt and Wilde, 1994). Moreover, high sulphur contents measured in crude oils from the Urdaneta district make it possible to establish that these crude oils have their origin in carbonatic shales with a significant amount of siliciclastic sediments (Escobar, 1987).

The high degree of dissimilarity between these two crude oil series in the Maracaibo–Falcón Basin can be explained by changes in organic facies, since organic material was deposited from west to east across the basin under very distinctive conditions. Results from crude oils originating in the Ceibita area indicate that oxic conditions prevailed in a terrestrial environment during sedimentation. Since vanadium is unstable under such conditions and does not react with porphyrins in order to form stable organometallic compounds, nickel ion reactions with porphyrins are favoured because of low concentrations of sulphur ions and high equilibrium constants of the corresponding nickel-containing organometallic compound formations (Barwise, 1990; Lewan and Maynard, 1982). Other geochemical parameters determined for the above-mentioned crude oils show precursor

organic matter from a terrigenous origin. As a result, high amounts of 18α(H) oleanane or low amounts of tricyclic terpane seem to indicate terrestrial sediments as precursors (Del Ollo, 1993).

In regards to unbiodegraded crude oil samples from the Eastern Basin (the largest Venezuelan basin in area), the corresponding crude oil family from the Hamaca area is characterised by a V/Ni Pearson's coefficient of approximately 0.92. This crude oil series derived from carbonatic source rocks under anoxic–euxinic conditions (Alberdi et al., 1996). Concentrations of sulphur and several trace metals such as V, Ni, Mo, and Cr in bitumens from the Hamaca area confirm that the Querecual Formation was deposited under very reducing conditions, characteristic of a sulphate-reducing marine environment (Garban, 1994).

Experimental results indicate a common origin for crude oils from the Barinas area; however, changes in the organic facies can also be noted. Regarding the kerogen prior to these crude oils, a mixture of continental and specially marine organic material was deposited in a transitional environment under suboxic to oxic conditions (Labastidas, 1997). Nevertheless, the linear regressive correlation coefficient for the data from the Silvestre field is not the lowest for the four studied Venezuelan crude oil series.

Fig. 3 shows a graphic representation of all data corresponding to the four crude oil families, each displaying a very different behaviour.

Lastly, different analyses reveal that the source rocks corresponding to Ayoluengo oils formed by deposition of organic sediments with a marine origin under anoxic or near anoxic conditions. The crude oils produced have specific gravity values ranging from 20° to 39° API and a low level of thermal maturation characteristic of all crude oils from the nonmature southern marginal part of the Basque–Cantabrian Basin (Quesada et al., 1997). The Pearson's correlation coefficient value of these crude oils is 0.99. Ni content and V/Ni average ratios indicate a carbonatic shale as source rock for the Ayoluengo oils, with a considerable amount of marine organic matter deposited under an anoxic environment. This fact confirms that subdividing these medium-crude oils into four different families based on their vanadium and nickel concentrations is a valid approach.

5. Conclusions

After analysing fifty crude oils, a new diagram plot can be proposed as a geochemical tool with the aim of quickly and easily correlating several parameters from undegraded crude oils to sedimentation redox conditions of the precursor source rocks and their lithological characteristics. It must also be stated that such a diagram is a useful instrument for reducing exploration costs and that it is applicable worldwide.

In summary, taking into account V and Ni concentrations, each of the four analysed crude oil series represents one particular generic group identified with the Urdaneta district (family A), the Silvestre field (family B), the Ceibita area (family C) and the Hamaca area (family D), respectively.

First, V/Ni ratios higher than 3 and Ni concentrations usually lower than 90 ppm (family A) suggest marine organic material and carbonatic shale or limestone as source rocks deposited under anoxic conditions. Second, V/Ni ratios ranging from 1.9 to 3 (family B) indicate that the corresponding source rocks were deposited under disoxic–oxic conditions with precursor organic matter of mixed origin: continental and, predominantly, marine. Third, V/Ni ratios lower than 1.9 (family C) show terrestrial organic material, with prevailing oxic conditions during the deposition of source rocks associated to such organic matter. Last, there is a fourth crude oil group (family D) characterised by V/Ni ratios higher than 3 and Ni concentrations higher than 90 ppm, where the corresponding source rocks were deposited in marine carbonatic environments under euxinic or very reducing conditions.

Finally, the main outcome of this research is that the aforementioned generic diagram can also be applied to V and Ni concentration data from oil seep and bitumen samples, in addition to medium-crude oils. This is most likely to be of great value to the oil industry, since it is much easier to obtain samples from crude oils than from their source rocks.

Acknowledgments

Appendix A

Well	Area	V (ppm)	Ni (ppm)	S (%)	V/Ni	V/(Ni+V)
MFL1S	Hamaca	427	116	4.3	3.68	0.78
MFL6S	Hamaca	561	139	3.8	4.03	0.80
MFL50S	Hamaca	384	99.0	3.8	3.87	0.79
MFL38S	Hamaca	388	115	3.5	3.37	0.77
MFB-48	Hamaca	353	106	3.7	3.33	0.76
MFB-37	Hamaca	302	93.0	4.0	3.24	0.76
MFB-14	Hamaca	380	110	3.9	3.45	0.77
MFA-31	Hamaca	458	130	4.4	3.52	0.77
MFH-3	Hamaca	419	124	4.3	3.37	0.77
MFF-3S	Hamaca	372	102	4.3	3.64	0.78
MFD-5	Hamaca	386	112	4.6	3.44	0.77
MFK-1S	Hamaca	407	114	4.5	3.57	0.78
SHW-1	Silvestre	255	102	1.5	2.50	0.71
SHW-102	Silvestre	217	87.5	1.1	2.48	0.71
SHW-103	Silvestre	220	82.3	1.3	2.67	0.72
SHW-2	Silvestre	221	88.4	1.2	2.50	0.71
SHW-7	Silvestre	158	64.5	1.9	2.44	0.70
SMW-2	Silvestre	216	88.6	1.3	2.43	0.70
SMW-4	Silvestre	165	75.6	1.8	2.18	0.68
SMW-13	Silvestre	153	60.5	1.7	2.52	0.71
SMW-20	Silvestre	247	87.8	1.0	2.81	0.73
SMW-21	Silvestre	266	111	0.9	2.39	0.70
SMW-10	Silvestre	162	61.9	1.4	2.61	0.72
SMW-11	Silvestre	118	46.7	0.9	2.52	0.71
SMW-15	Silvestre	143	56.1	1.5	2.54	0.71
SMW-6	Silvestre	255	87.5	1.2	2.91	0.74
LCV-3	Ceibita	18.0	27.1	0.2	0.66	0.39

Appendix A (*continued*)						
Well	Area	V (ppm)	Ni (ppm)	S (%)	V/Ni	V/(Ni+V)
LCV-46	Ceibita	8.1	5.2	0.2	1.55	0.60
CG-23	Ceibita	9.2	5.1	0.2	1.80	0.64
CG-25	Ceibita	1.6	8.0	0.2	0.20	0.16
CG-43	Ceibita	2.2	10.2	0.2	0.21	0.17
CG-13	Ceibita	1.2	5.0	0.2	0.24	0.19
P-156K	Urdaneta	148	19.2	2.0	7.70	0.88
DM-43	Urdaneta	244	29	2.7	8.41	0.89
DM-54	Urdaneta	225	31.1	2.7	7.23	0.87
10C-3	Urdaneta	1250	148	2.1	8.45	0.89
14RN-1X	Urdaneta	465	53.0	1.6	8.77	0.89
14RN-2X	Urdaneta	617	54.1	1.6	11.4	0.91
23H-1X	Urdaneta	124	12.0	1.9	10.3	0.91
29G-2X	Urdaneta	136	24.1	2.3	5.64	0.84
B-148	Urdaneta	1140	127	2.4	8.97	0.90
ALP-4X	Urdaneta	485	50.2	1.9	9.66	0.90
ALP-6X	Urdaneta	102	14.0	1.8	7.28	0.87
11G-2	Urdaneta	970	89	2.2	10.9	0.91
ALP-9X	Urdaneta	300	36.0	1.8	8.33	0.89
SJL-2X	Urdaneta	44.9	5.10	3.0	8.80	0.89
AYO-1	Ayoluengo	230	37.0	0.2	6.10	0.85
AYO-14	Ayoluengo	238	39.1	0.2	6.08	0.85
AYO-5	Ayoluengo	242	40.9	0.2	5.91	0.85
AYO-9	Ayoluengo	250	43.0	0.2	5.90	0.85

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