PS Geochemistry of Ordovician and Silurian Black Shales, Cantabrian Zone, Asturias and Leon Provinces, Northwest Spain*

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Abstract

The Cantabrian Zone is defined as the area to the east of exposed Precambrian rocks of the Narcea Antiform, north of the Cenozoic Duero Basin, and west of the Mesozoic-Cenozoic Basque-Cantabrian Basin. Rocks within the Cantabrian Zone are mostly sedimentary of Paleozoic age, namely Cambrian through Carboniferous.

Organic rich Ordovician and Silurian black shales are important source rocks throughout the world. According to Klemme and Ulmishek, 9% of the worlds' original petroleum product, including both gas and oil, were generated from rocks of Silurian age. Their presence has been well established on the Iberian Peninsula on outcrops and in boreholes. Time equivalent shales are currently targets for shale gas exploration in other European countries such as Sweden, Poland and Romania. A recent AAPG publication described organic rich Silurian shales in the Lusitanian Basin of northern Portugal; however, a literature search did not uncover any published reports describing the geochemistry of Silurian shales in the Cantabrian Zone. Field samples were therefore required in order to evaluate the source rock potential of lower Paleozoic black shales in northwestern Spain.

Twenty four new samples were gathered from twelve different outcrop locations in the provinces of Asturias and Leon during a May, 2010 field trip. Twenty samples from the Lower Silurian Formigoso Formation and four samples from the middle Ordovician Sueve Formation were analyzed. Tests included X-Ray Diffraction, Pyrolysis, Conodont Alteration Index, Vitrinite-Like Reflectance, Rock/Eval, Dispersed Organic Matter, Kerogen Type and Total Compositional Analysis. The data from these analyses will be shown along with the sample locations.

Successful shale gas plays in the United States display TOC values above 2%. Unfortunately, no Cantabrian Zone samples recorded TOC's above 2%; in fact, nineteen of the twenty four samples had TOC's under 1%. In addition, the kerogen type was overwhelmingly inertinite, meaning not only that there is no organic material left to be generated and produced through the process of desorbtion.

Based upon the exceedingly poor results of the geochemical work, the conclusion reached was that the Lower Paleozoic black shales in the Cantabrian Zone have very poor potential for the production of shale gas. In addition, the extremely rugged nature of the local terrain and poor road infrastructure would make drilling and completion operations very difficult.

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REGIONAL GEOLOGY, CANTABRIAN ZONE

The purpose of this section is to describe the geology of the Cantabrian Zone in a very general manner. The shale gas potential of the area will be emphasized, especially with respect to Lower Silurian black shales of the Formigoso Formation and to the middle Ordovician black shales of the Luarca and Sueve Formations.

Cantabrian Zone Description

The Cantabrian Zone is the northern part of the Variscan Iberian Massif, mostly composed of sedimentary rocks of Paleozoic age, namely Cambrian through Carboniferous (figure 1). It is limited to the west by exposed Precambrian rocks of the Narcea Antiform, to the south by the Cenozoic Duero Basin, and to the east by the Mesozoic-Cenozoic Basque-Cantabrian Basin.

Structural Evolution

The Cantabrian Zone is a part of "Variscan" Spain, containing soley Precambrian through Paleozoic rocks and usually but not everywhere only mildly affected by the Alpine Orogeny. The area was part of the proto-African northern portion of Gondwana during Paleozoic time. The passive shelf Gondwanan sediments were thrusted in an eastern direction as a result of the collision between the continents of Laurussia and Gondwana during the Variscan Orogeny (late Carboniferous). The present day Cantabrian Mountains south of the Cantabrian Zone were subsequently formed during Alpine tectonism.

The structural architecture of the basin is represented by a thin skinned fold and thrust belt with foreland basin propagating deformation. The Narcea Antiform (figure 2) has Precambrian rocks exposed at its core. It was thrust onto the Paleozoic rocks of the Cantabrian Zone forming characteristic folds and nappes. The thrust units are Carboniferous in age and were subsequently folded into north-south arcuate trends. The main detachment has been mapped to take place in the Lower Cambrian. Similar decollements in other worldwide basins, such as the Appalachian basin, are concentrated within organic rich zones which "grease" the faults into movement. This process was believed to be active within the Cantabrian Zone.

There is evidence to show that metamorphism did not take place within the Cantabrian Zone as a result of this thrusting. Illite crystallinity data points to an end to metamorphic history in the southwest Cantabrian mountains during the late Ordovician. This is an important point with respect to a potential Silurian shale play. The shales would not have been metamorphosed in such as manner as to destroy desorbtion sites and effective permeability.

STRATIGRAPHY

There are marked facies differences between the Lower Paleozoic of the Narcea Antiform and of the Cantabrian Zone, the former consisting mainly of terrigenous sediments and the latter being mainly a shallow marine environment.

The Cambrian in the Cantabrian Zone is divided into three units, those being the Herrería, the Láncara, and the Oville Formations, plus the uppermost Barrios Formation that conformably continues into the lower Ordovician (figure 3). The Herrería rests unconformably on the Precambrian Narcea formation, consists of siliclastics and rare dolomites, and is thought to represent a transitional fluvial-marine environment. It is between 900m and 1700m locally. The Láncara Formation is 150 – 225m thick and consists mainly of carbonates and interbedded shales of a shallow marine origin.

The Cambrian continues conformably with the alternating shales and sandstones of the Oville Formation. The entire succeeding Cambrian to Lower Ordovician section is represented by the mostly sedimentary quartzites of the Barrios Formation. However, dark shales of Middle Ordovician age named the Luarca or Sueve Formations are found in some areas of the Cantabrian Zone, especially in outcrops along the Fold and Nappes region as well as to the east of the Central Coal Basin. This fossiliferous black shale unit has been known to be up to 350m thick along the northern coast, and up to 150m thick in the southern Fold and Nappes region. It has been proposed that the Sueve dark shales were deposited in a series of sub-parallel grabens along the margin of North Gondwana. Finally, an Upper Ordovician volcaniclastic 400-500m interval known as the Castro Formation has been described along the coast at Cape Penas and concludes the Ordovician. Exceptionally, in some parts of the southern Fold and Nappes region, as at Los Barrios de Luna, the top few meters of the Barrios Formation, known as "Luna Quartzite", could represent another formation of Upper Ordovician? to Lower Silurian? age.

The Silurian conformably overlies the Upper Ordovician along the coast, and is unconformable with the Middle Ordovician elsewhere. It is mostly subdivided into two formations, namely the Formigoso and the Furada/San Pedro formations. The Formigoso is Llandovery through Wenlock in age. It consists of 70m to 200m of dark gray to black graptolitic shales. The overlying Furada-San Pedro Fm. is 5-250m thick section containing grey to red sandstones which are believed to be of nearshore marine origin. The entire Silurian becomes sandier to the east in the Manto del Pongo area, or is completely absent through Variscan erosion. The lowermost Devonian is conformable with upper Silurian sediments. The subsequent Rañeces-La Vid Group represents an abrupt environmental change from a siliceous dominated to a calcareous dominated setting of both nearshore to shallow marine environments. Reefal deposits are occasionally present, representing a tropical climate. The remainder of Devonian units in the Cantabrian Zone continue to show marine, carbonate facies, until increasing clastic input in Late Devonian mostly ended reefal development. In total, the Devonian in the Cantabrian Zone can be found up to and exceeding 2000m in thickness. The Silurian and the Devonian become sandier in the Folds and Nappes region close to the Central Coal Basin, and are nearly absent through Variscan erosion in the Manto del Ponga area.

Carboniferous deposition was concurrent with the Variscan Orogeny, and differed from older Paleozoic rift to passive margin settings by being a foreland thrust basin. Bearing mainly foredeep siliclastic rocks over a wide
range of depositional environments, the Carboniferous basins were more unstable than earlier basins, resulting in fewer correlatable beds over regional distances. Total Carboniferous thickness in the Central Carboniferous Coal Basin is up to 6000m.

Economically important coals have been mined locally, mainly from Westphalian aged beds bearing good quality bituminous coals. Anthracite is found in small Stephanian aged post-Variscan basins.

FIGURE 1: CANTABRIAN ZONE STRUCTURAL ELEMENTS

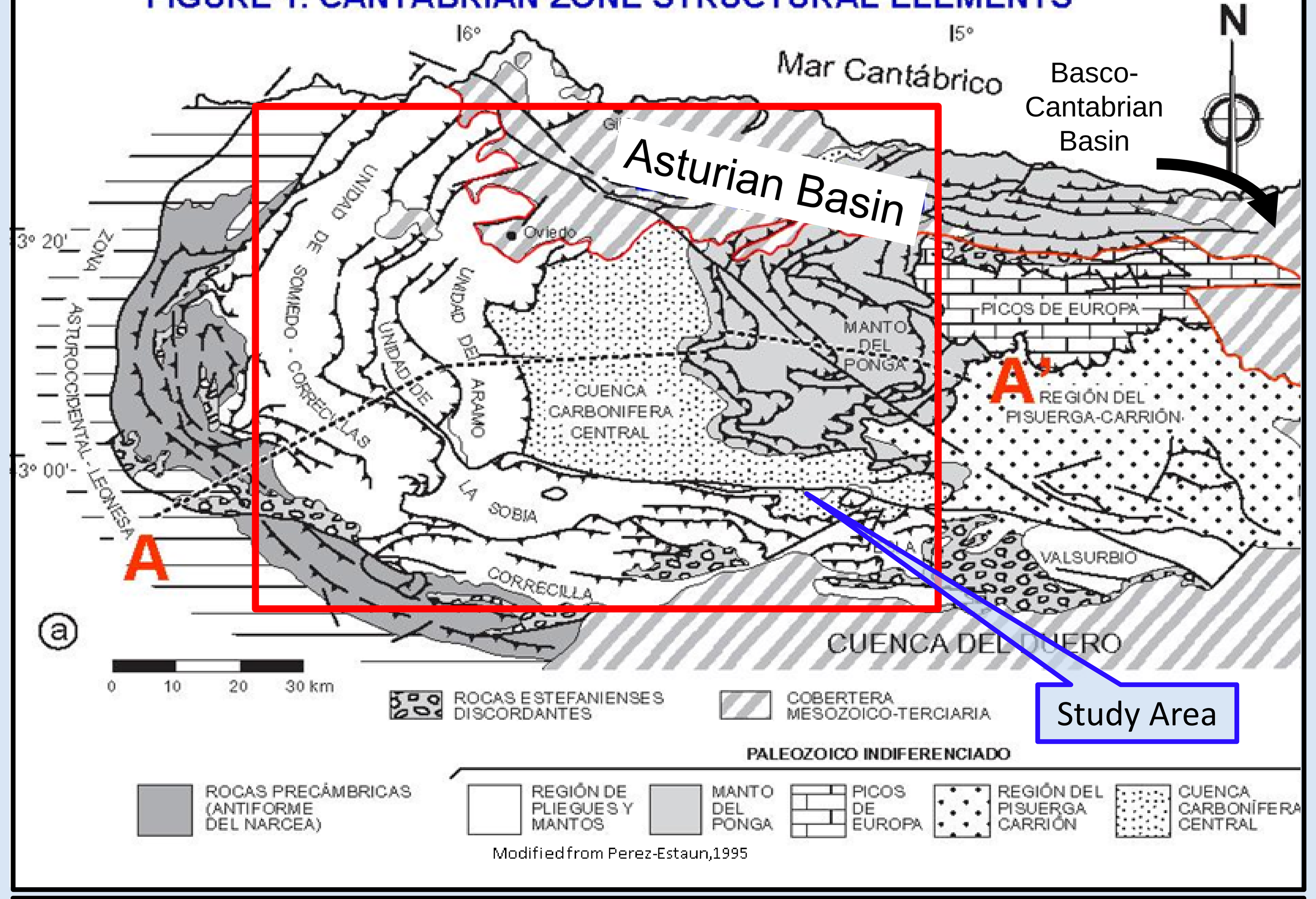


FIGURE 2: STRUCTURAL CROSS SECTION

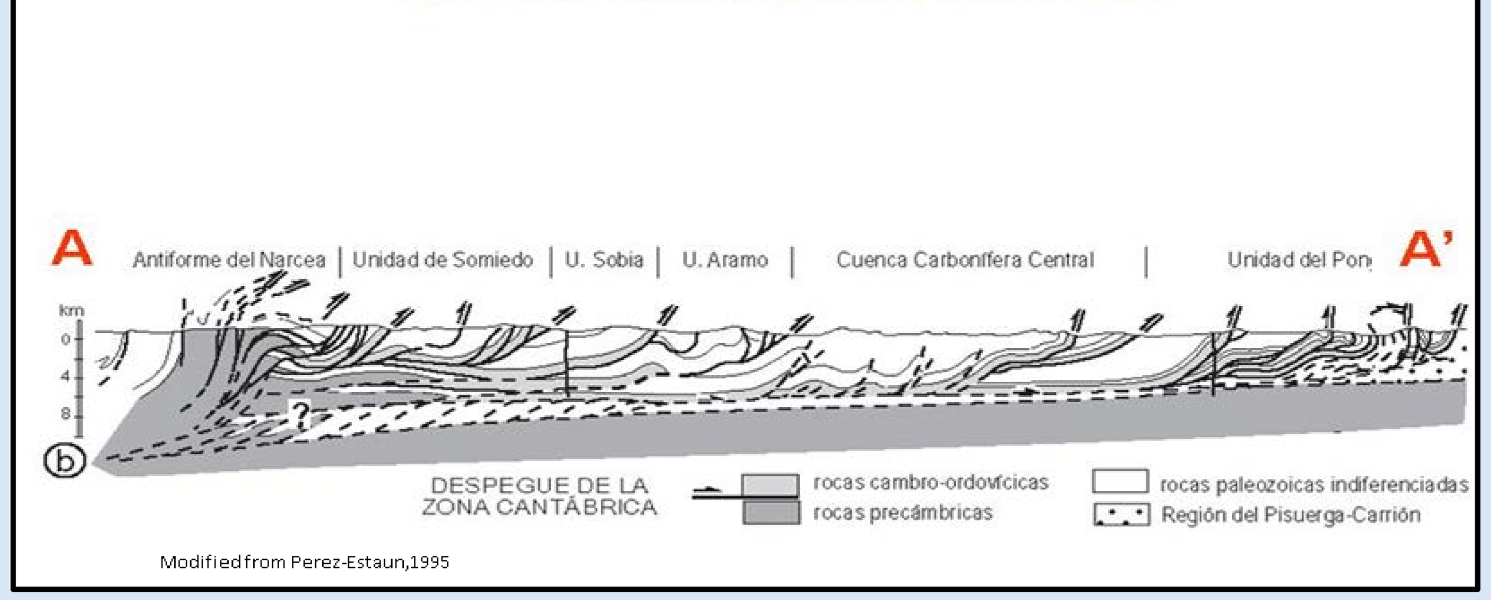


FIGURE 3
Alba Syncline Column

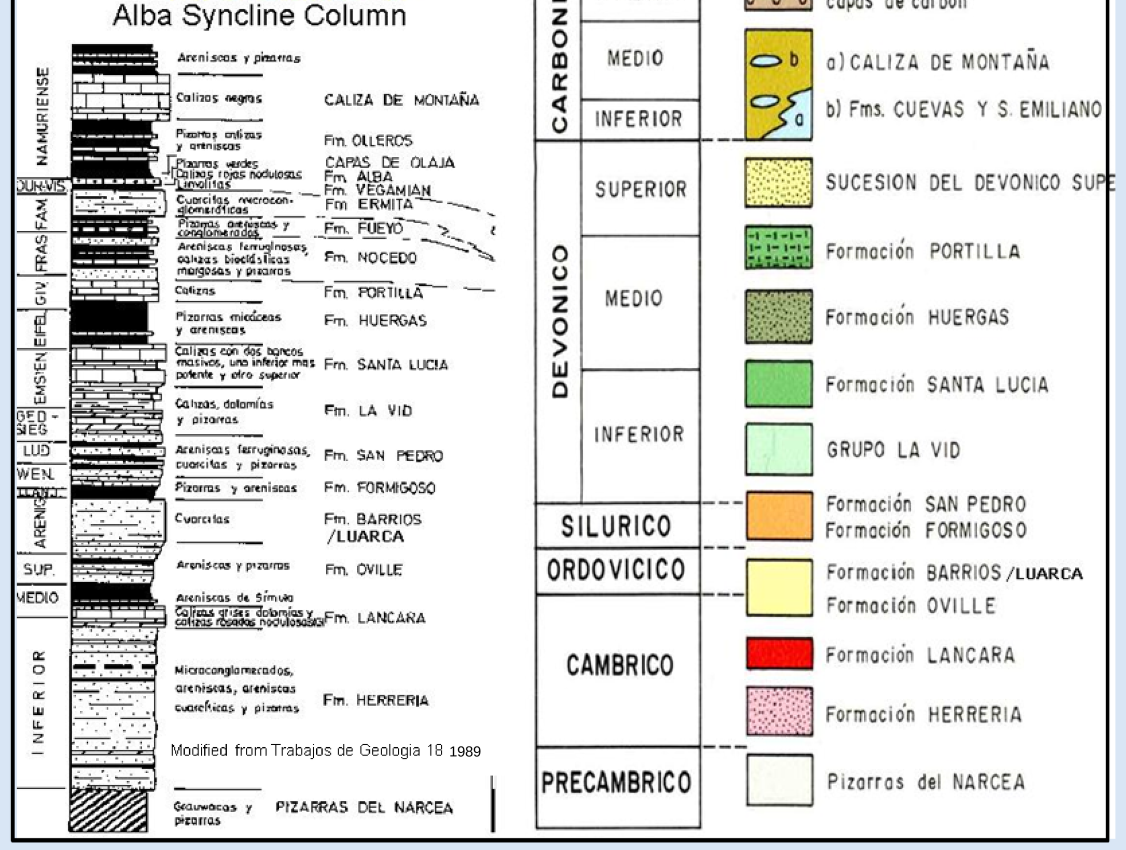
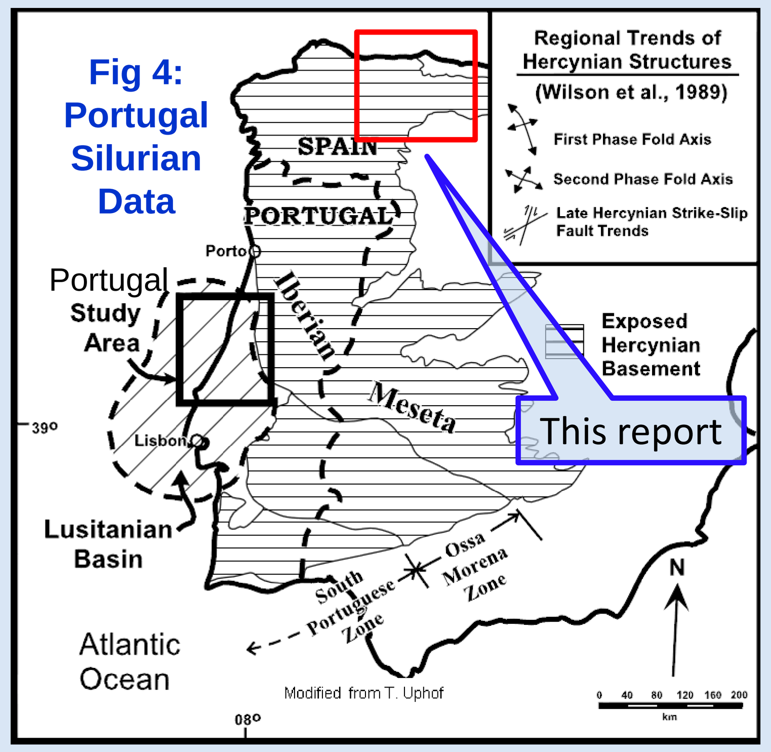


Fig 4: Portugal Silurian Data



Shale Gas (Unconventional) Objectives

The Silurian black graptolitic shales present in the Cantabrian Zone correlate to the organic rich facies that have provided hydrocarbons for the giant and super giant Middle Eastern and North African oil and gas fields. According to Klemme and Ulmishek, 9% of the worlds original petroleum product, both gas and oil, were generated from rocks, especially graptolitic shales, of Silurian age. In northwest Spain, the Lower Silurian Formigoso Formation has been measured on outcrop to be as thick as 300m, an interval that could generate large amounts of natural gas. There were no published geochemical data on these shales from within the Cantabrian Zone prior to this report. However, very good quality organic rich shales have been studied on the Silurian outcrops in the Iberian Massif on the edge of the Lusitanian Basin, Portugal (figure 4). TOC of 7.29% at 1.23% Ro and 8.60% TOC at 2.70% Ro have been measured in this basin from outcrops. The beds are equivalent in age to the Formigoso Fm. If similar organic rich beds could be found in the Cantabrian Zone, then they could provide excellent targets for shale gas exploration.

An additional shale gas target was the Ordovician Sueve Formation which has been measured to be over 500m on outcrop. Again, no geochemical data have been published. An indication of the potential of Ordovician source rocks is an oil seep that has been discovered in Ordovician aged rocks while building El Tunel Ordovicico del Fabar, Ribadesella, Asturias. It was thought that these rocks could also be excellent shale gas objectives if buried deep enough to enter the gas window.

FIELD TRIP RATIONALE

Parameters that define successful shale gas plays in the United States include depth to target, thickness, porosity, permeability, pressure gradient, stress field (presence or absence of natural fractures), organic richness (measured as Total Organic Content or TOC in wt. %), thermal maturity (as measured by such means as vitrinite reflectance, conodant alteration index or Tmax), clay content, gas content, adsorbed gas, and presence or absence of top and/or bottom water barriers. Most of these parameters are obtained only after a great deal of effort and expenditure. Tasks include acquiring 2D and/or 3D seismic in order to define structural complexity, drilling and completing vertical wells to obtain rock properties, and drilling and completing horizontal wells in order to quantify gas productivity and ultimate reserves. Reserves are calculated using a formula that includes free gas (from porosity within the rock matrix and in fractures) and desorbed gas, which is gas flowing into the wellbore under certain conditions of temperature and pressure. Gas is chemically bonded to kerogen and is denoted as adsorbed gas before the bond is broken, at which point it is considered to be desorbed.

Organic richness is the most important parameter because there can be no exploration prospectivity without the ability of the target shale to generate and store natural gas. Fortunately this sort of data can be calculated from outcrop samples. Although outcrop data is notably less exact than can be extracted from core data, it can be relied upon for general purposes. Since there had already been positive indications of organic richness from Silurian rocks in Portugal, it was anticipated that similar rocks would be found in the Cantabrian Zone.

Parameters that can be measured at the outcrop or calculated in the laboratory from outcrop samples include thickness, vitrinite reflectance (or other thermal maturity measurements), and clay content. This last parameter is important as it effects the ability of frac water to open spaces into which gas can flow into the wellbore in an efficient manner. Shales within both the Formigoso and Sueve formations have been measured on outcrop to exceed the thickness of US shale plays, so it had been hoped to ascertain good values for organic richness, clay content and thermal maturity from outcrop samples. Thus it was suggested that the group obtain some initial outcrops samples from a local geologist. Therefore, in November, 2009, the group contacted Dr Carlos Aramburu, University of Oviedo, and requested him to gather a Silurian sample. Dr Aramburu kindly did so while taking his students on a field field trip. The sample was gathered adjacent to the dam of the Los Barrios de Luna Reservoir. Here the Silurian Formigoso rests on the Upper Ordovician?-Lower Silurian? Luna Quartzite.

The sample was sent to Weatherford Laboratories in Houston, Texas which was also where all subsequent samples were sent. The TOC was measured at 1.04% which was below average TOC's for US shales. Next, the issue of thermal maturity was addressed. Since vitrinite, an organic material associated with humic or peat material, did not evolve until post Silurian times, the commonly used measurement of vitrinite reflectance (Ro) could not be used in this Silurian sample. In addition, the low S2 peak (which will be discussed in more detail below) resulted in an inaccurate Tmax value. The samples were devoid of conodants, so a conodant alteration index (CAI) could not be determined. Finally, the organic material was visually examined and it was surmised that the sample had an Ro equivalent value of 3.56% which is in the upper dry gas window.

Although the organic richness was slightly below the values found in successful US shale gas plays, the facts that equivalent Silurian shales in Portugal were highly organic rich, the section is very thick, and was within the dry gas window led the group to organize a more through and extensive field trip. It was hoped that with more rock data good source rocks necessary for a successful shale gas play would more likely be discovered. Therefore, Dr Aramburu was asked if he could lead a group out into the field, and fortunately his schedule was open in early May, 2010, which is when the field trip took place.

The group asked Dr Aramburu to satisfy two main criteria: first, to gather mostly Silurian samples but not to ignore the Ordovician, and second, to spread the sampling out regionally so as to get data over a wide area. Dr Aramburu choose twelve outcrops to visit, with two being Ordovician and ten being Silurian. We would re-sample the Los Barrios de Luna area because due to spring rains the original sample area was now underwater. Ultimately, the group was successful at obtaining twenty four samples at eleven outcrops of which twenty were of Silurian age and four were Ordovician.

Besides Dr Aramburu, the attendees of the field trip were John Underwood and Frank Maio.

Poster II will display and describe the outcrops where the samples were obtained.

Poster III will show the results of the subsequent geochemical analyses.

SAMPLE LOCATIONS AND SURFACE GEOLOGY

OUTCROPS: LOCATIONS AND DESCRIPTIONS

The base map in the center of the poster shows the outcrop localities superimposed on a road and topographic map. The outcrop locations, sample numbers and latitude and longitude of each locality is displayed in the table in the upper right. Maps showing the location of the outcrops superimposed on the surface geology are shown. The surface geology maps were compiled from a series of reports published in Trabajos de Geologia, University of Oviedo. For explanation of the map stratigraphy see the strat column on the lower right.

Pico Gobia and Cerracin Outcrops

The Pico Gobia and Cerracin localities in Asturias Province were examined in order to gather samples from Ordovician black shales of the Sueve Formation. The 50 – 100m section has been described as consisting of two black shale members separated by a middle member with interbedded sandstones and shales. The Sueve rests unconformably on the Barrios Formation, the base of which is an ironstone band. Overlying the Sueve in an unconformable manner are sandstones of the Upper Devonian Ermita Formation.

A photograph displaying the entirety of the Sueve Formation at the Pico Gobia road cut is shown on the right. The middle sandstone member is clearly exposed, separating the upper and lower black shale members. Sample HOH 5A was taken from the lowermost Sueve just above the Barrios Formation.

The lowermost Sueve Formation resting unconformably on the ironstone member of the Barrios Formation. Samples 6A and 6B were taken at this exposure, and sample 6C was taken from the upper Sueve black shale further up the road from this photograph.

Las Ventas and Tuiza

The Las Ventas and Tuiza localities are in Asturias Province and were chosen because of exposures of the Silurian Formigoso black shales. The two sites are on opposing limbs of the Las Plaza syncline, the center of which consists of massive upper Carboniferous carbonates. The Formigoso Formation has been measured to be 65m thick at this locality, but only the middle of the formation is present. The shales range from black to medium gray in color, and contain graptolites.

The Tuiza locality resides on the western limb of the La Plaza Syncline on the side of a hill alongside a narrow and busy road. The Formigoso consists of black to medium gray shales. The shales are very heavily weathered so sample 8A was taken as shown on the photo as deeply into the outcrop as possible order to get a clean, unweathered rock.

The Barrios Formation underlies the Formigoso at this exposure. It consists of dense quartzarenites, white in color and densely cemented with quartz.

Pobladura De Luna, Los Barrios de Luna, and Aralla

These three locations are located in the province of Leon. Good exposures of the Formigoso Formation are to be found here on the steeply dipping limbs of the Alba and Aralla Synclines, which are filled with Carboniferous deposits.

The Formigoso exposure at Pobladura de Luna, consisting of medium gray to black shales, was heavily weathered. It rests on the Barrios Formation. Samples 9A and 9B were taken from this outcrop in progressively younger beds, i.e. 9A is the oldest sample. Again, the outcrop was dug into as much as possible in order to obtain fresh samples.

Fresh samples on the south side of the Embalse de Luna dam were difficult to find as the original Los Barrios sample site was now underwater. Sample 10A was taken from a very heavily weathered road cut in the lowermost Formigoso. However, a better, less weathered exposure just above the original site was discovered and this is where the middle Formigoso sample10B was taken.

At the Aralla locality a complete Formigoso Formation section was exposed. The site was less heavily weathered than the Tuiza, Pobladura de Luna and first Barrios de Luna sites.

From top to bottom the Formigoso Formation is 56m/181' thick. It consists of a lower black shale member, a middle sandy member, and an upper member composed of grey to black shales. Samples 11 A and 11B were taken from the lower member and sample 11C was taken from the upper member.

Pajares

This outcrop is in the province of Asturias. Structurally it is on the exposed northern limb of the east-west trending San Emeliano Syncline. The Formigoso Formigoso is represented by medium gray to black shales and is moderately weathered. Samples 1A, 1B and 1C were taken from this locality.

Camplongo and Pontedo

These two outcrops lie within the province of Leon. They are essentially on the same outcrop, along strike on the northern edge of the Villamanin Syncline.

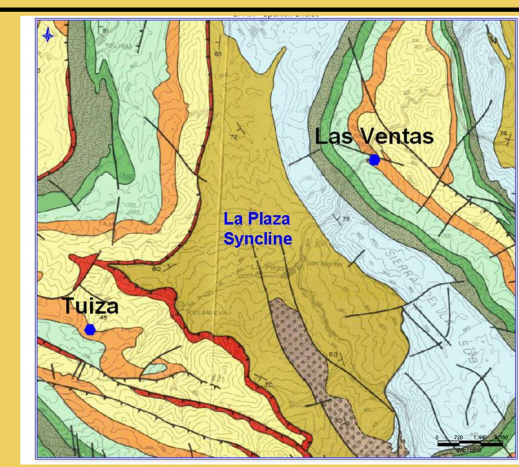
The Camplongo site is a long steeply dipping hill that has been heavily weathered. The Formigoso shales are mainly black with no middle member noted. It is not known if the section was upper or lower Formigoso. Samples 4A and 4B were taken from this site.

The Pontedo Silurian outcrop does not appear on published maps, and was discovered by Dr Aramburu. This was a very heavily weathered outcrop, but it was decided to take samples from this most eastern area of the trip. Samples 12A, 12B and 12C were taken at Pontedo.

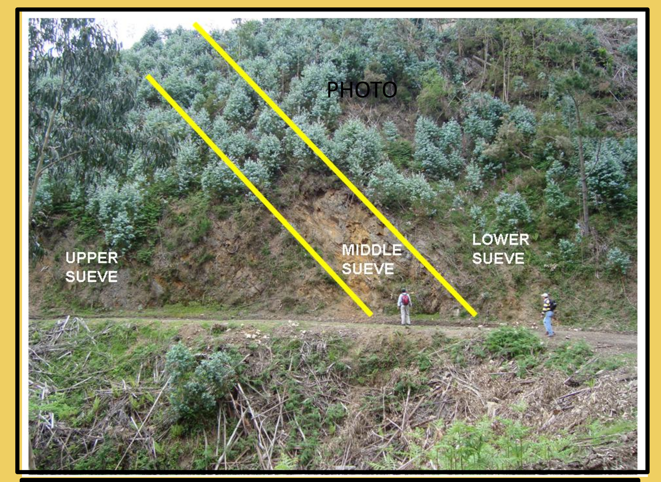
La Gotera

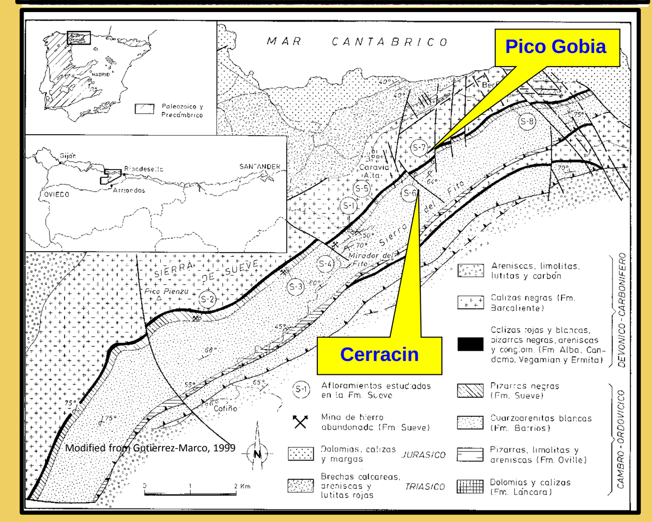
The site is located within the Aralla Syncline along strike with the Aralla sample locality. A complete Formigoso Formation is exposed above two road and rail tunnels. The steeply dipping Formigoso Formation overlies the Barrios formation. Samples 2A and 2B are from this site.

LAS VENTAS



CERRACIN and PICO GOBIA

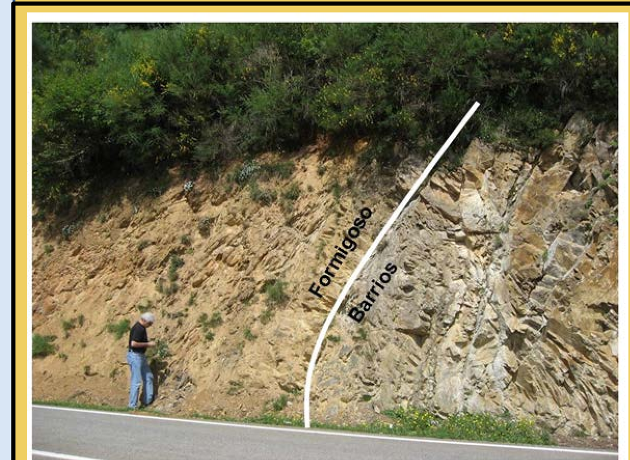




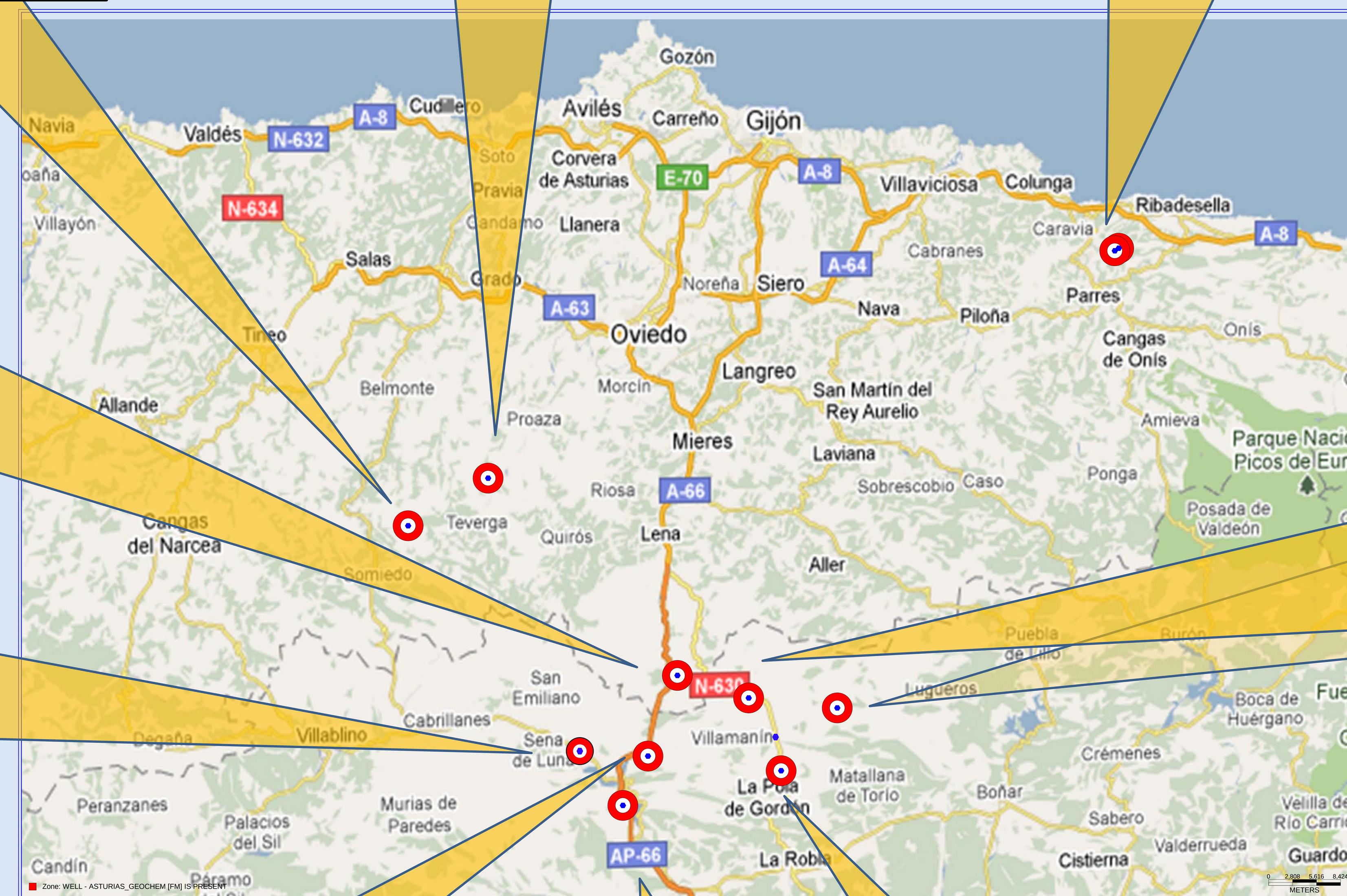
Outcrop locations latitude and longitudes

SAMPLE NAME	LATITUDE N DEG	MIN	SEC	LONGITUDE W DEG	MIN	SEC	OUTCROP NAME
HOH 1	43	0	0	5	47	8	STOP 1 - PAJARES
HOH 2	42	54	8	5	38	46	STOP 2 - LA GOTERA (TOP OF TUNNEL)
NONE	42	54	8	5	38	44	STOP 3 - VALLE BERNESGA
HOH 4	42	58	56	5	41	7	STOP 4 - CAMPLONGO
HOH 5	43	27	37	5	10	5	STOP 5 - PICO GOBIA
HOH 6	43	27	27	5	10	25	STOP 6 - CERRACIN
HOH 7	43	11	50	6	4	3	STOP 7 - LAS VENTAS
HOH 8	43	8	38	6	10	48	STOP 8 - TUIZA
HOH 9	42	54	11	5	54	58	STOP 9 - POBLADURA DE LUNA
HOH 10	42	51	0	5	51	27	STOP 10 - BARRIOS DE LUNA
HOH 11	42	54	37	5	49	26	STOP 11 - ARALLA
HOH 12	42	58	22	5	33	42	STOP 12 - PONTEDO

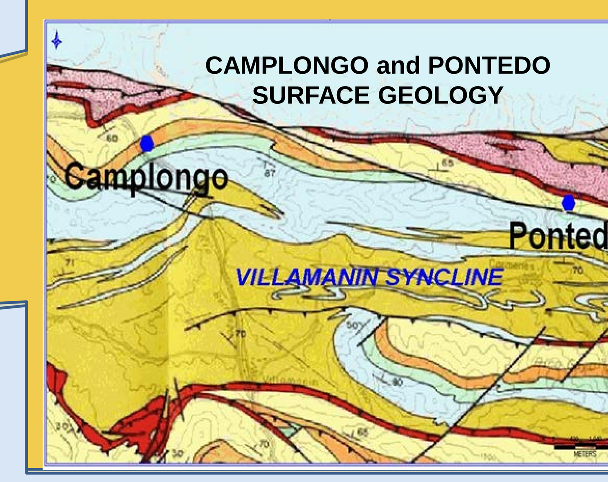
TUIZA



PAJARES



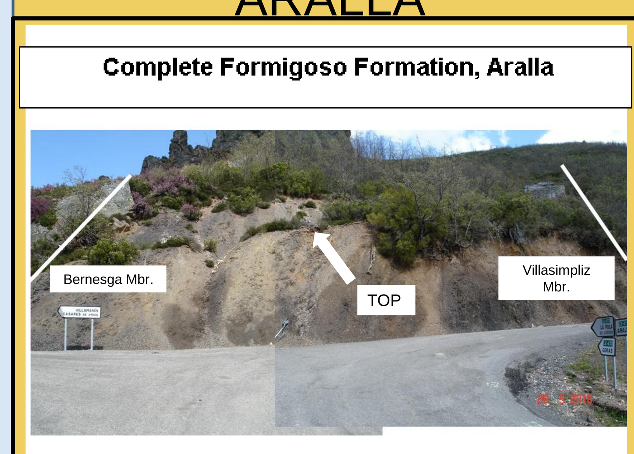
PONTEDO

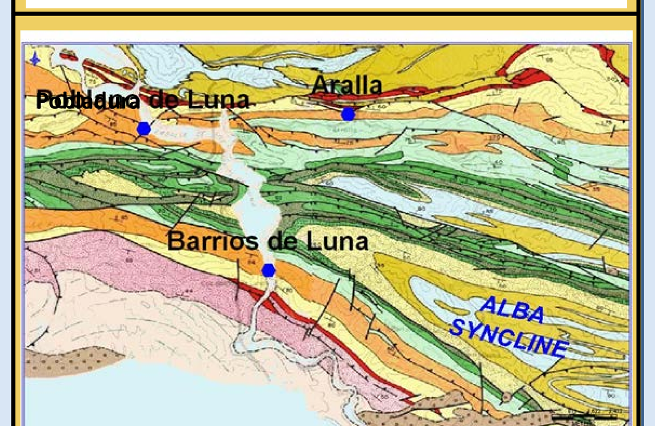


Surface Geology Maps and Strat Column from Trabajos de Geologia, Univ. de Oviedo n18, 1989. ISSN 0474-9588

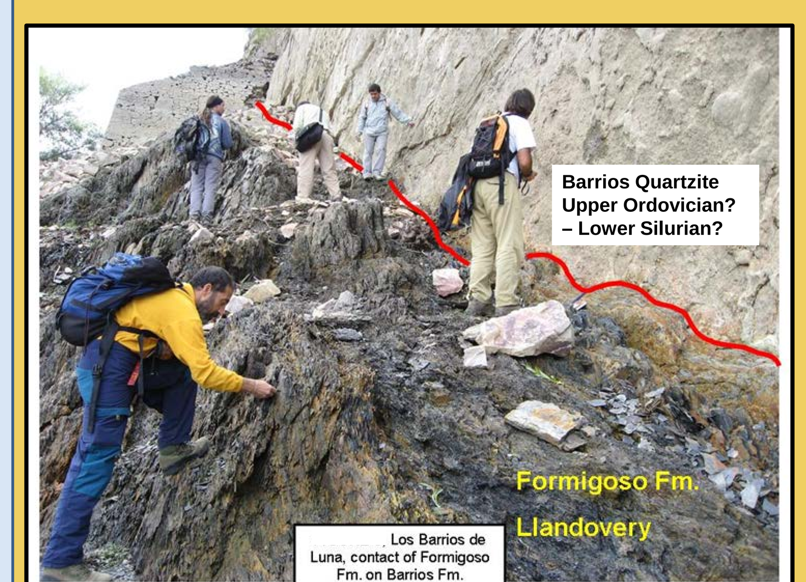
POBLADURA de LUNA

ARALLA

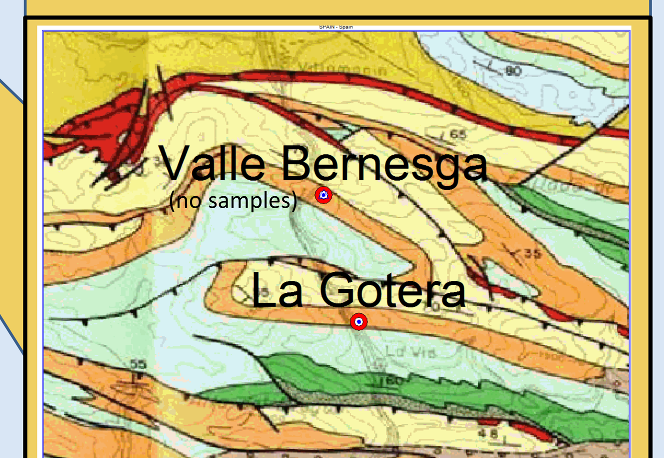




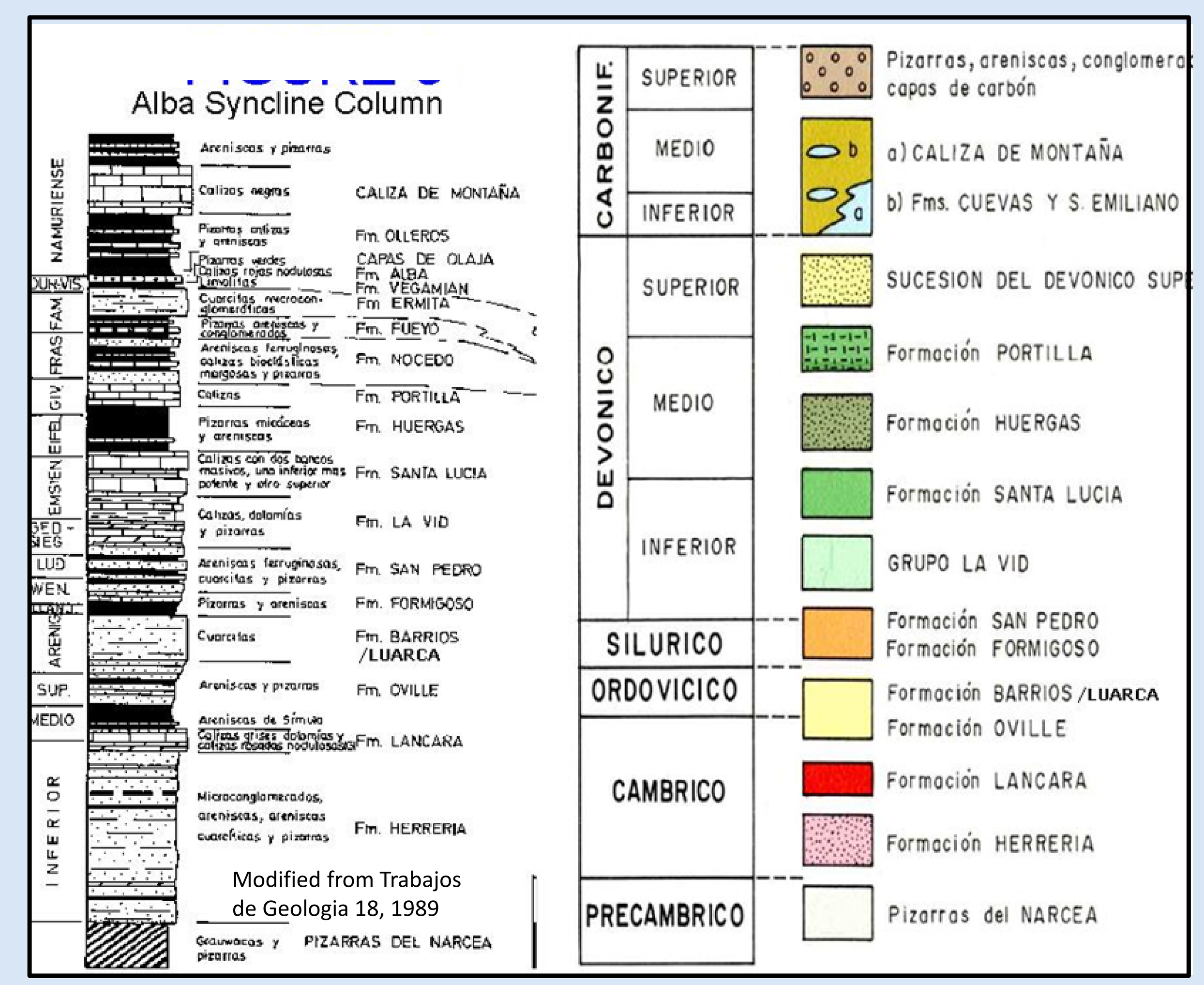
BARRIOS de LUNA



LA GOTERA



STRAT COLUMN



GEOCHEMICAL ANALYSES and CONCLUSIONS

GEOCHEMICAL ANALYSES

Procedure and tests

Tests were run on the samples in order to quantify the geochemical parameters of the rock samples in comparison to successful US gas shales. These tests included total organic carbon (TOC) content by weight percent, programmed pyrolysis, vitrinite reflectance analysis, and X Ray Diffraction. The TOC work would address organic richness, programmed pyrolysis would address kerogen type and thermal alteration, and vitrinite reflectance would place the samples within a specific thermal maturity rank. X Ray Diffraction would identify compositional material and percentages thereof.

In order to create data with which to estimate parameters such as kerogen type, hydrogen index, and maximum temperature (or Tmax), the samples are evaluated with a procedure known as Rock-Eval. Weatherford Laboratories, the lab that conducted the experiments, uses the Leco method. Finely ground chemically treated and subsequently dried rock is placed in a furnace in an inert atmosphere and then raised to a temperature of 550^0C. The amount of hydrocarbon products evolved is recorded either by an infrared detector or a thermal conductivity detector as a function of time.

Source type, source quality, and maturation can be calculated from the three peaks, denoted as S_1, S_2, and S_3, during the pyrolysis procedure. Cross plotting of these values can also be used to determine source rock criteria.

The thermal maturity of the rocks is another important factor in assessing the hydrocarbon potential of source rocks. Indications of thermal maturity can be estimated as a function of the temperature at the S_2 generation peak, and through visual examination of vitrinite reflectance. Since vitrinite evolved in post Silurian times, a new technique has been established for such Paleozoic rocks and was used in this study and the results agreed with the pyrolysis work. In addition, alteration of conodont teeth (CAI) can be used as a thermal indicator, but unfortunately no conodont remains were found in selected samples.

Results

Weatherford Laboratories denoted the sample study as HOH 47795. Table 1 displays the TOC and programmed pyrolysis values

Organic Richness

The highest TOC value was 1.65% in the Silurian at Pobladura de Luna (sample 9A). Nineteen of the twenty four samples had TOC's under 1.0% . A distribution of the TOC values is shown on figure 1. Pobladura de Luna, Aralla, Los Barrios de Luna and Pontedo were the only Silurian samples with values above 1.0%. Only one Ordovician sample (Pico Gobia) out of four had a TOC value above 1.0%. These values alone would appear to preclude the ability of Lower Paleozoic shales in the Cantabrian Zone from supplying adequate gas for a shale gas play in a very rugged and remote area. However prior published work has shown that at high maturity levels present day TOC's can be much reduced as from the original TOC, therefore it was prudent to determine thermal maturity as efficiently as possible. The S_2 peak recorded very low values, the highest being 0.2. This indicates either very poor organic richness, or high thermal maturities.

Thermal Maturity and Kerogen Type

Three methods of determining thermal maturity of the rock samples were tried. An attempt was made on the original Luna sample to record a conodant alteration index but unfortunately no conodants were noted in the sample.

The second method involves Tmax calculation. Tmax (C) is the temperature at the highest yield of S_2 hydrocarbons. The S_2 values were very low, which would make the calculated Tmax values suspect. However, upon close examination of the pyrograms in figure 2 it can be seen for example that samples 2A, 4A, 12B as shown had characteristic "humps" which are indicative of the presence of organic material, therefore the Tmax values from those samples can be considered reliable. Those values ranged between a low of 488^0C and a high of 529C, meaning all of the samples has equivalent Ro's between ~1.8% and 3.25% which is firmly in the dry gas window. Figure 3 shows all the Tmax versus HI plotted, confirming that the samples are in the dry gas window.

Vitrinite was not evolved until post Silurian deposition. Nonetheless, Weatherford made a third attempt to estimate equivalent Ro's based upon visual examination of "vitrinite-like" particles. See table 2 to view the data. Four samples were sent to the labs, namely 12C, 11B, 9A and 10A. Their respective Ro's were 1.65%, 2.48%, 2.69%, and 3.74%, which agrees with the Tmax estimates of the samples being in the dry gas window. Figures 4 and 5 show cross plots of the %Ro with respect to S2 and HI. Many of the samples represented oxidized organic matter, which agrees with the Rock Eval determination of the preponderance of inertinite among the samples as shown in figures 4 and 5. Figure 6 shows a OI/HI cross plot; again Type IV kerogen is indicated.

Bitumen

Solid bitumen was identified in both the Luna sample and the four samples from the field trip. The age of all five samples was Silurian. Based on the presence of the bitumen it can be stated that oil has been generated and migrated into the Silurian rocks, and that it is possible that the oil was in fact generated in situ. Any local oil would have been generated at a very early stage. It is highly unlikely that any conventional closed structures formed early enough to trap oil could survive Variscan and/or Alpine orogenies.

Mineral Composition

Table 3 shows the results of the X-Ray diffraction tests on the Luna sample. It can be seen that the clay percentage is 63%, which compares unfavorably with the lower clay percentages of successful US shale gas plays. The significance of this data suggests that the Cantabrian Zone Silurian shales are not brittle enough for the type of completions that result in economic flow rates.

CONCLUSIONS

The Silurian and Ordovician samples were evaluated in order to determine their viability as shale gas targets. The results were that they compared unfavorably with the parameters of successful US shales. The most critical element, TOC, was too low (<1%) in most of the samples. The kerogen type was overwhelmingly inertinite. Both factors taken together mean that little to no free gas was ever generated and little to no desorbed gas remains; therefore gas reserves would be virtually non-existent. The clay content was also very high, meaning the shales would not react well to modern completion techniques that make shale gas plays economic. There was no other alternative but to abandon the concept of a shale gas play in the remote, topographically challenged region.

The one positive result was that bitumen was visually noted in some of the samples, meaning that oil was generated most likely at an early stage of deposition. It is well known that oil has been found seeping though an Ordovician section in a highway tunnel near Ribadesella (*www.elcomerciodigital.com/prensa/20070204/sociedad/tunel-sorpresas_20070204.html*). Unfortunately, it is highly unlikely that any local trap that had captured migrated oil could have survived intact after two mountain building orogenies. The low TOC's would also preclude the generation of significant quantities of oil.

FIGURE 2: SELECT PYROGRAMS

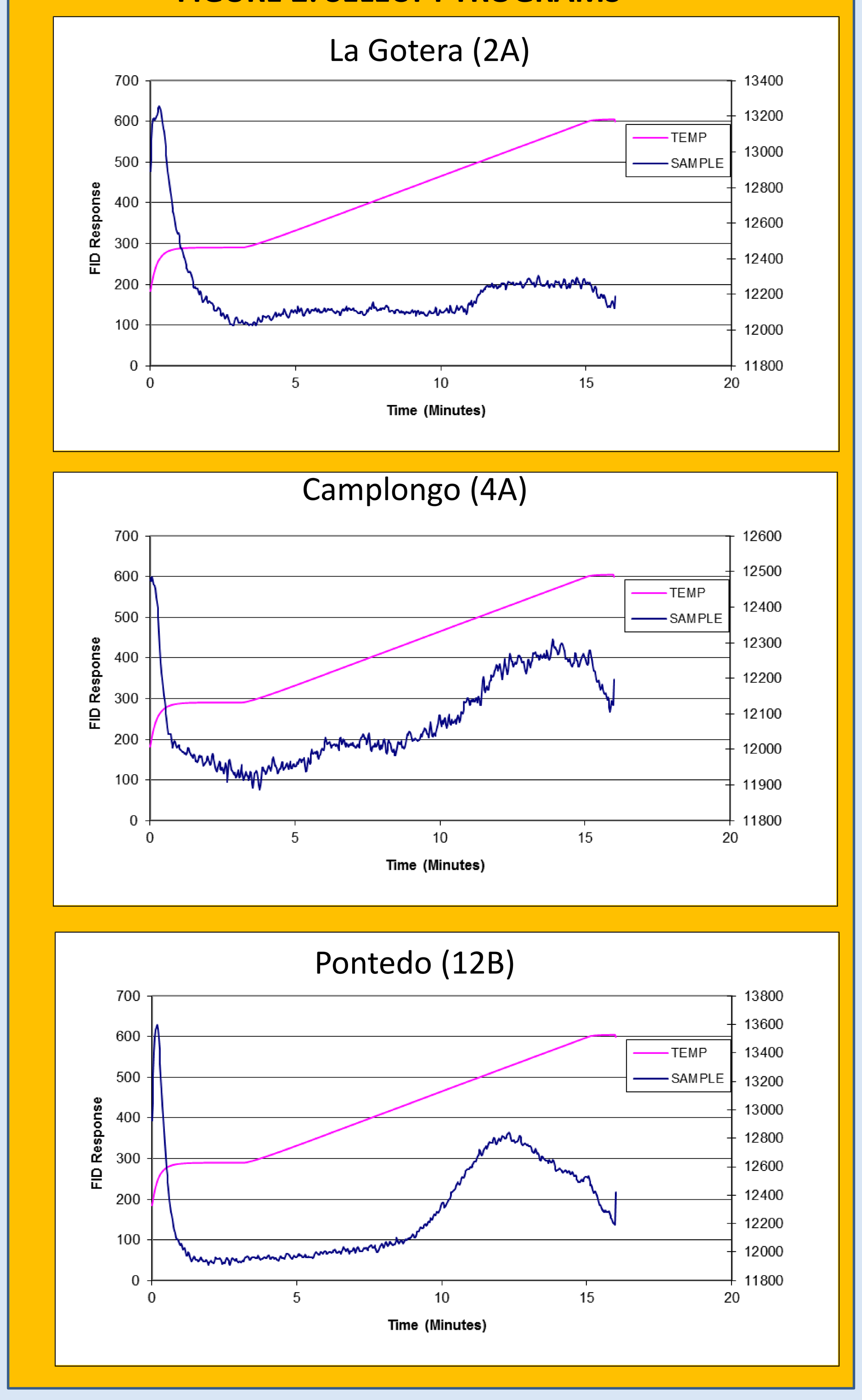


FIGURE 3: Kerogen Type and Maturity

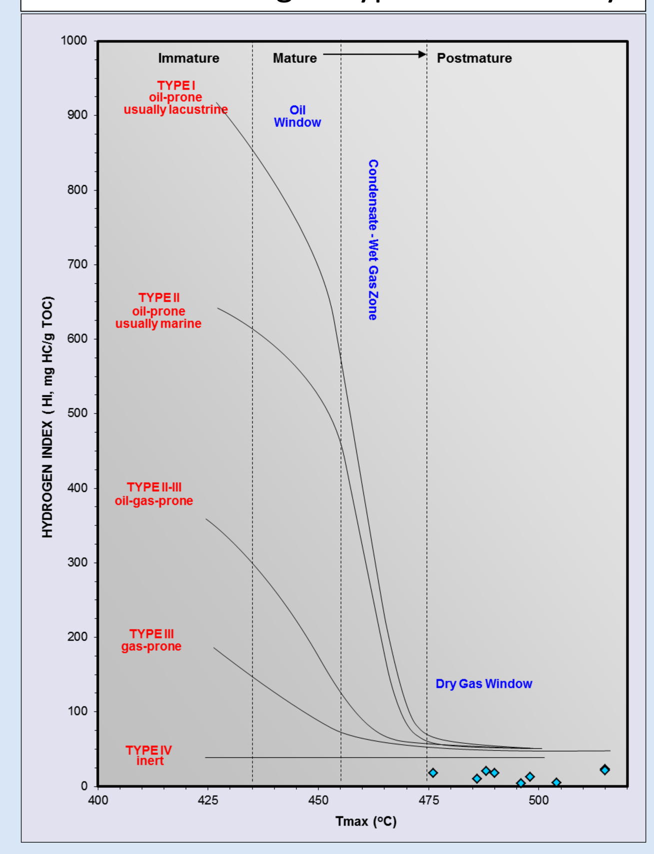


FIGURE 6: Kerogen Type

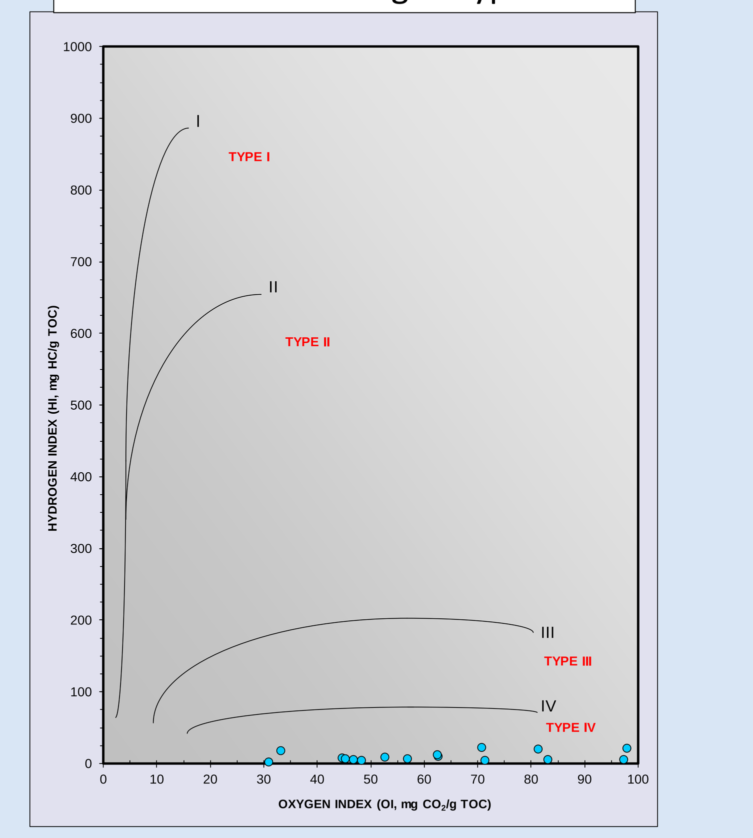


FIGURE 4: Kerogen Type and Organic Richness

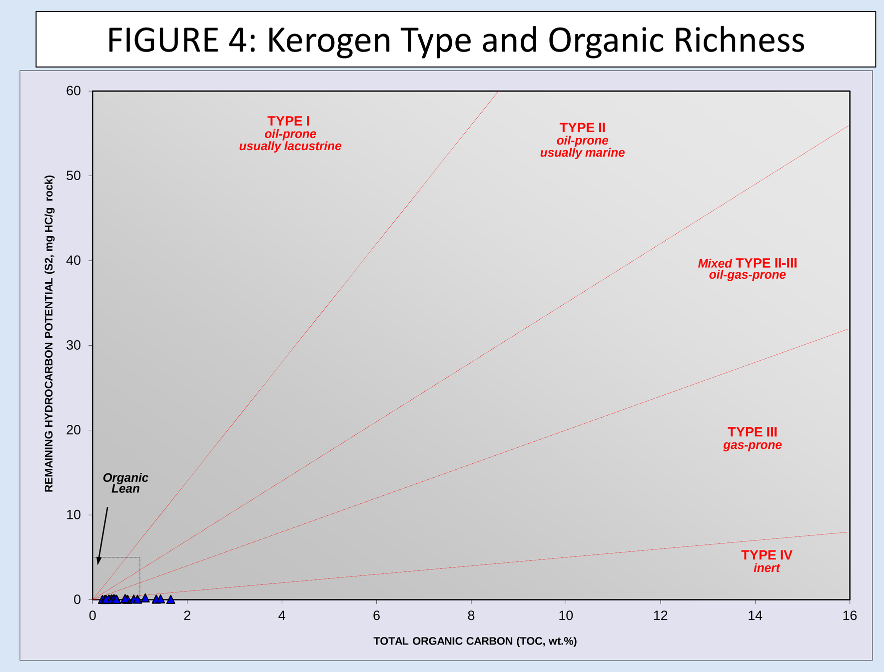


FIGURE 5: Kerogen Type and Richness

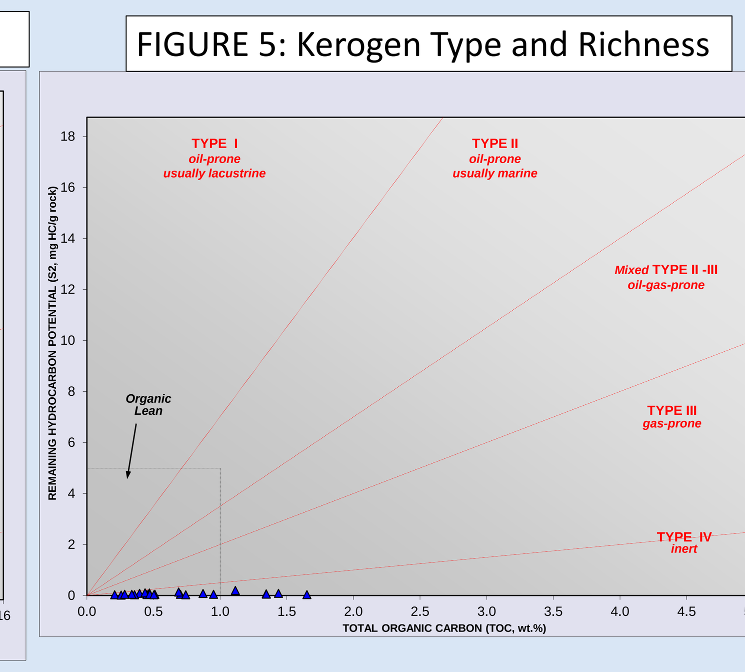


TABLE 1: TOC and Programmed Pyrolysis

Client ID	AGE	Locality	Sample Type	TOC	SRA S1	SRA S2	SRA S3	Tmax (°C)	HI	OI	S2/S3	S1/TOC*100	PI
HOH1 A	Silurian	Pajares	Outcrop	0.51	0.02	0.05	0.32	486	10	63	0	4	0.29
HOH1 B	Silurian	Pajares	Outcrop	0.46	0.02	0.06	0.29	498	13	62	0	4	0.25
HOH1 C	Silurian	Pajares	Outcrop	0.47	0.02	0.05	0.67	343	11	143	0	4	0.29
HOH2 A	Silurian	La Gotera	Outcrop	0.40	0.05	0.09	0.28	515	23	71	0	13	0.36
HOH2 B	Silurian	La Gotera	Outcrop	0.47	0.04	0.10	0.46	515	21	98	0	9	0.29
HOH4 A	Silurian	Camplongo	Outcrop	0.87	0.01	0.08	0.46	529	9	53	0	1	0.11
HOH4 B	Silurian	Camplongo	Outcrop	0.45	0.01	0.04	0.58	559	9	128	0	2	0.20
HOH5 A	Ordovician	Pico Gobia	Outcrop	1.35	0.02	0.07	0.63	523	5	47	0	1	0.22
HOH6 A	Ordovician	Cerracin	Outcrop	0.95	0.02	0.05	0.79	564	5	83	0	2	0.29
HOH6 B	Ordovician	Cerracin	Outcrop	0.70	0.01	0.05	0.40	558	7	57	0	1	0.17
HOH6 C	Ordovician	Cerracin	Outcrop	0.36	0.01	0.03	0.16	561	8	45	0	3	0.25
HOH7 A	Silurian	Las Ventas	Outcrop	0.44	0.04	0.11	0.48	359	25	110	0	9	0.27
HOH7 B	Silurian	Las Ventas	Outcrop	0.34	0.02	0.05	0.35	362	15	104	0	6	0.29
HOH8 A	Silurian	Tuiza	Outcrop	0.21	0.01	0.03	0.39	372	14	187	0	5	0.25
HOH9 A	Silurian	Pobladura de Luna	Outcrop	1.65	0.02	0.04	0.51	564	2	31	0	1	0.33
HOH9 B	Silurian	Pobladura de Luna	Outcrop	0.74	0.02	0.03	0.53	496	4	71	0	3	0.40
HOH10 A	Silurian	Barrios de Luna	Outcrop	0.47	0.04	0.05	0.81	352	11	172	0	8	0.44
HOH10 B	Silurian	Barrios de Luna	Outcrop	0.26	0.01	0.02	0.40	549	8	155	0	4	0.33
HOH11 A	Silurian	Aralla	Outcrop	1.35	0.02	0.06	0.65	504	4	48	0	1	0.25
HOH11 B	Silurian	Aralla	Outcrop	1.44	0.04	0.09	0.65	534	6	45	0	3	0.31
HOH11 C	Silurian	Aralla	Outcrop	0.50	0.01	0.03	0.49	551	6	97	0	2	0.25
HOH12 A	Silurian	Pontedo	Outcrop	0.29	0.01	0.05	0.47	490	18	165	0	4	0.17
HOH12 B	Silurian	Pontedo	Outcrop	0.69	0.03	0.14	0.56	488	20	81	0	4	0.18
HOH12 C	Silurian	Pontedo	Outcrop	1.12	0.04	0.20	0.37	476	18	33	1	4	0.17

FIGURE 1: SAMPLE LOCATIONS AND TOC VALUES

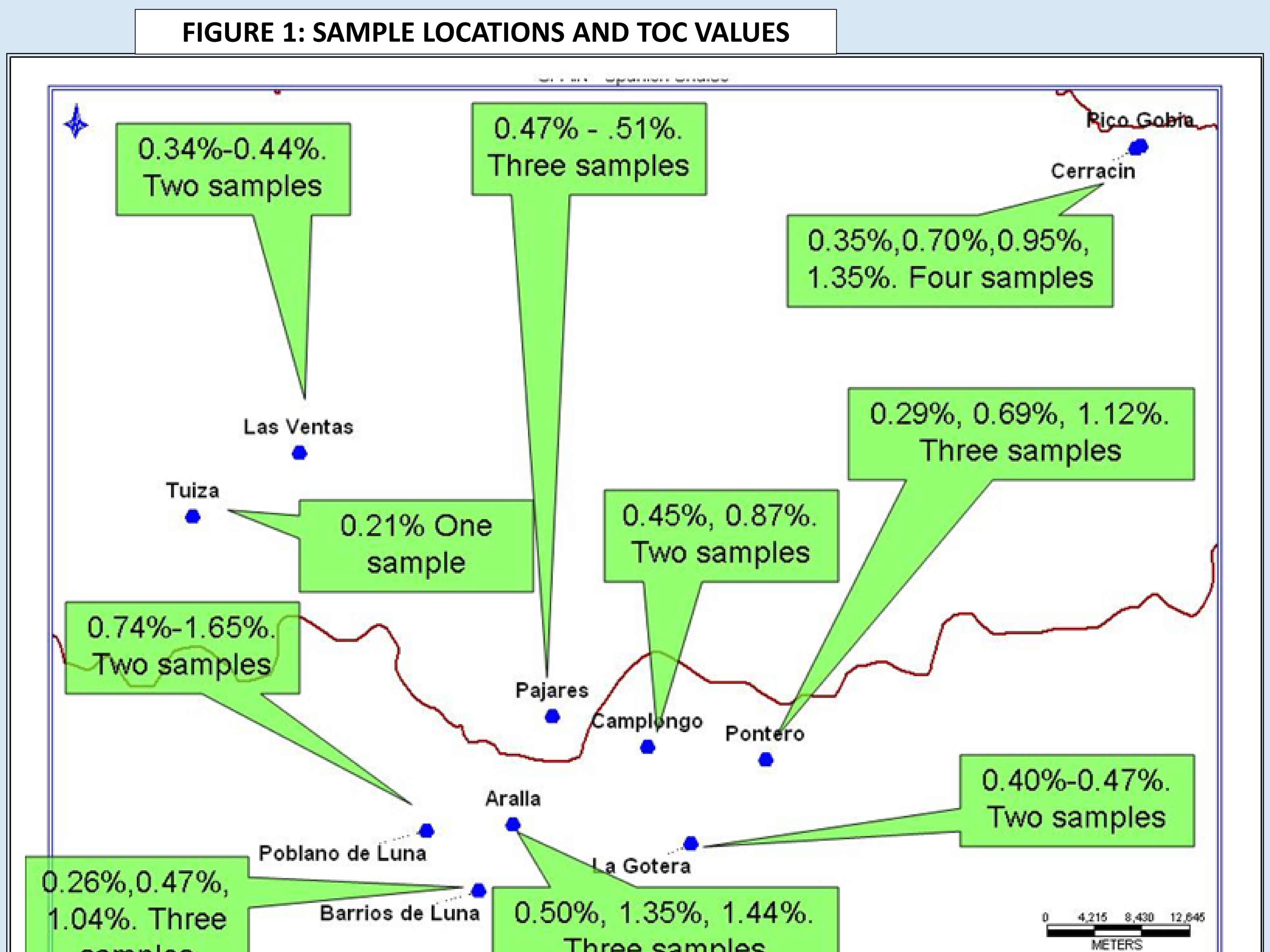


TABLE 2: Ro Readings "Vitrinite-like" particles

Sample ID	3401692245		3401692249		3401692255		3401692263	
Client ID	HOH Samples		HOH Samples		HOH Samples		HOH Samples	
Well Name	HOH Samples		HOH Samples		HOH Samples		HOH Samples	
Client ID	Pobladura de Luna		Barrios de Luna		Aralla		Pontedo	
	All Data	Indigenous Data	All Data	Indigenous Data	All Data	Indigenous Data	All Data	Indigenous Data
	2.5	2.56	3.11	3.58	2.03	2.3	1.47	1.51
	2.56	2.58	3.34	3.6	2.22	2.3	1.51	1.52
	2.58	2.59	3.34	3.6	2.25	2.3	1.52	1.54
	2.59	2.61	3.42	3.61	2.26	2.31	1.54	1.55
	2.61	2.62	3.45	3.62	2.3	2.31	1.55	1.56
	2.62	2.62	3.46	3.64	2.3	2.33	1.56	1.56
	2.62	2.62	3.52	3.64	2.3	2.34	1.56	1.56
	2.62	2.63	3.53	3.65	2.31	2.34	1.56	1.56
	2.63	2.63	3.54	3.68	2.31	2.36	1.56	1.57
	2.63	2.66	3.58	3.69	2.33	2.4	1.57	1.58
	2.66	2.67	3.6	3.7	2.34	2.4	1.58	1.58
	2.67	2.67	3.6	3.7	2.34	2.42	1.58	1.61
	2.67	2.68	3.61	3.75	2.36	2.44	1.61	1.61
	2.68	2.68	3.62	3.76	2.4	2.49	1.61	1.63
	2.68	2.68	3.64	3.79	2.4	2.49	1.63	1.64
	2.68	2.68	3.64	3.8	2.42	2.5	1.64	1.64
	2.68	2.68	3.65	3.82	2.44	2.51	1.64	1.64
	2.68	2.7	3.68	3.82	2.49	2.52	1.64	1.65
	2.7	2.72	3.69	3.84	2.49	2.52	1.65	1.65
	2.72	2.74	3.7	3.85	2.5	2.55	1.65	1.66
	2.74	2.75	3.7	3.87	2.51	2.55	1.66	1.67
	2.75	2.75	3.75	3.92	2.52	2.56	1.67	1.68
	2.75	2.76	3.76	3.92	2.52	2.57	1.68	1.68
	2.76	2.76	3.79	3.94	2.55	2.57	1.68	1.68
	2.76	2.77	3.8		2.55	2.57	1.68	1.71
	2.77	2.77	3.82		2.56	2.58	1.71	1.72
	2.77	2.78	3.82		2.57	2.59	1.72	1.72
	2.78	2.81	3.84		2.57	2.6	1.72	1.73
	2.81	2.82	3.85		2.57	2.61	1.73	1.74
	2.82		3.87		2.58	2.62	1.74	1.74
	2.89		3.92		2.59	2.64	1.74	1.76
	2.91		3.92		2.6	2.67	1.76	1.76
	2.91		3.94		2.61		1.76	1.77
	2.92		4		2.62		1.77	1.77
	2.93		4.01		2.64		1.77	
	2.96		4.26		2.67		1.97	
	3		4.32		2.83		2.04	
	3.11		4.37		2.87		2.12	
	3.32		4.62		2.96		2.17	
	3.78		4.67		2.97		2.2	
Average $\%R_o$	2.78	2.69	3.77	3.74	2.49	2.48	1.70	1.65
Standard Dev.		0.07		0.11		0.12		0.08
# of Points	40	29	40	24	40	32	40	34

TABLE 3: X-RAY DIFFRACTION (WEIGHT%)

WEATHERFORD LABORATORIES
X-RAY DIFFRACTION
(WEIGHT %)

Client:
Well: Luna Outcrop Sample
Area: Unknown
Sample Type: Outcrop
File No: HH-45715
Date: 01/15/10
Analyst: G. Walker

Sample Identity	CLAYS Chlorite	CLAYS Kaolinite	CLAYS Illite	CLAYS Mx I/S*	CARBONATES Calcite	CARBONATES Dolomite	CARBONATES Siderite	OTHER MINERALS Quartz	OTHER MINERALS K-spar	OTHER MINERALS Plag.	OTHER MINERALS Pyrite	OTHER MINERALS Zeolite	OTHER MINERALS Barite	TOTALS Clays	TOTALS Carb.	TOTALS Other
ACK000001	2	24	36	1	Tr	1	2	27	1	2	4	0	0	63	3	34
AVERAGE	2	24	36	1	Tr	1	2	21	1	2	4	0	0	63	3	34

* Ordered interstratified mixed-layer illite/smectite; Approximately 10-15% expandable interlayers