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## **Soft Inorganic Geochemistry: A New Concept for Unconventional Resources Modeling\***

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### **Abstract**

Soft inorganic geochemistry is defined as the spatial modeling of geochemical data, which prioritizes the amount of data, their spatial relationship and their relationship with other data types (geological and geophysical data) over the individual chemical analysis accuracy.

The method is based on the statistical concept of processing the entire rock samples population available in the geological formation to model. Thus, the method involves thousands of chemical analysis of cutting and cores samples, their processing using geostatistical techniques and the integration with well log and seismic data, to produce unconventional resources 3D models.

The workflow is made up of the following steps:

- Non-destructive analysis of the cutting using rapid handheld X Ray Fluorescence analysis (HHXRF).
- Selection of representative sample of entire data population (3 to 5% of data population) for destructive analysis of mineralogy (XRD) and organic geochemistry (TOC analysis).
- Statistical analysis of the relationships between HHXRF, XRD and organic geochemistry data.
- Integration of well log and HHXRF data using 1D Gaussian cosimulation (type II Markov model) to produce geochemical logs with an intermediate depth resolution.
- Integration of seismic data with geochemical logs using Bayesian approach of sequential indicator simulation.

The different sources of uncertainty are the accuracy of HHXRF method, cutting sample uncertainty (provenance depth, well bore collapse and mud contamination) and the vertical seismic resolution.

The HHXRF detection variance is known because it is measured by the equipment. Uncertainty of cutting sample depth is assumed to be uniformly distributed in the sampled interval. In most cases, uncertainty of sample depth is smaller than vertical seismic resolution. Uncertainty related to cutting contamination is analyzed with the comparison of HHXRF data with chemical element background values of different rock types. Finally, the seismic data used to guide the population of inter-well space is the largest source of uncertainty.

This concept was applied to build integrated 3D geochemical models for several marine and lacustrine oil source rocks of Argentina sedimentary basins. In mature oil fields with a large number of wells, this tool allowed to determine source rock intervals and high brittleness zones due to rock mineralogy. Results allow to modify the stimulation method used, having high impact on overall cost and time.

## **Introduction**

The aim of this paper is to present the progress made in the implementation of a new geochemical inorganic modeling concept oriented to model unconventional reservoirs. The concept is based on the combination of rapid chemical analysis, processing and integration with other kind of data and final spatial modeling using geostatistical techniques in one and three dimensions (Larriestra, 2011).

The method is mainly based on the acquisition of nondestructive chemical data using rapid handheld X Ray Fluorescence equipment (HHXRF). It allows both making many chemical analyses in a short time without sample destruction and calculating measurement variance for each element. A small percentage of the population (3% to 5% of the samples) is processed with destructive methods for mineralogy (X Ray Diffraction) and Total Organic Content (pyrolysis) analysis. The method being introduce here, is mainly oriented to cutting samples processing, which is the largest data available in source rock intervals, but can also be applied to scan samples from outcrops and cores.

The study of Black Shale presents new scientific challenges; therefore, we must look for unconventional methods and tools in order to understand, its genesis, petrophysical properties and to forecast its future productive performance. It is thanks to the investigation of different data processing methods applied to a large database of chemical analyzes of source rocks belonging to Argentina sedimentary basins, that we can introduce the concept develop in this work.

In order to apply this concept, it is necessary to overcome certain paradigms related to methods of acquisition and data processing.

1. The first paradigm questioned is the statistical principle of sampling population: "We must process all existing cutting, cores or outcrops samples and not just a small portion of them". Thereby, we proposed to analyze the entire population with nondestructive methods (HHXRF), because its simplicity allows making a large number of chemical analyses in a short time.
2. The second paradigm questioned is the accuracy of geochemical analysis: "More important is the amount of data and its spatial behavior than the individual accuracy of chemical analysis". This appears to be an absurdity for analytical methods, but it turns out a key issue, because the analysis of all available data will reveal black shale sedimentary and geochemical evolution and therefore the following productive development.

3. The third paradigm questioned is the importance of cutting samples and its associated uncertainty: "The application of stochastic simulation methods are used to quantify the uncertainty associated with cutting to generate major, minor and trace element geochemical logs". These logs have many advantages over geochemical wire line logs (registered with radioactive indirect methods), since they are the product of a chemical analysis applied directly to the rock.

Finally, the large-scale integration of geochemical logs with seismic attributes (amplitude, frequency, curvature, etc.) should produce black shale three-dimensional models, together with geomechanical data should be used in the detection of sweet spots. These sweets spots should link both volumes with more organic matter and more brittleness condition. This is accomplished by model methods as Bayesian Indicator, Plurigaussian Truncated Fields or Multipoint simulation. These methods would integrate sedimentology, structure, geochemistry and geophysics data in a single predictive model.

## **Methodology**

### *Chemical Elements Analysis using Hand Held X-Ray Fluorescence equipment*

The major, minor and trace elements record on rock samples (cutting, cores or outcrops) is performed by portable X-Ray Fluorescence equipment as shown in [Figure 1](#). The analysis is performed without any destruction or sample modification. Generally, this type of equipment is able to detect most of the elements, but it is programmed to analyze a set of the most significant components of sedimentary and volcanic rocks. In the experiment conducted here were detected major elements Fe, Mn, Ca, K, S, minor elements Zr, Sr, Rb, Ti, Ba and trace elements as Mo, U, Th, Pb, Au, Se, As, Hg, Zn, W, Cu, Ni, Co, Cr, V, Sc, Cs, Te, Sb, Sn, Cd, Ag, Pd.

Such devices have a lower accuracy (ability to reproduce a pattern) than lab X Ray Fluorescence equipment, but it has a very low variance of mean detection values (low variability of repetitions performed on the same sample), so it is perfectly suitable for measuring differences between samples. In this way, you can investigate formation heterogeneity with a non-destructive, simple and fast method. The data obtained is organized in LAS format files for subsequent geochemical interpretation. The equipment can be moved to sample's deposit to save recording time and sample movement.

### **Sequential Gaussian Simulation (SGS)**

The sequential Gaussian simulation consists in obtaining artificial realizations of a random field, so that they reflect the expected random function statistical properties. Similar function statistical properties are not precisely known, these are inferred through sets of realizations, by drawing values from statistical distribution. In this case, a random function is the chemical element spatial distribution in a stratigraphic interval. SGS is a simulation method for continuous data (Deutsch, C., 2002). This method uses the different variants of Kriging to estimate the shape of the spatial distribution (mean and variance) in unsampled points. This variance tends to zero as the point to be simulated is close to data points, and the variance is equal to zero when geographical overlap exists (strict observance of hard data). The simulation may be performed in one dimension (spatial data series), two-dimensional (map) and in three dimensions (three-dimensional model).

## Sequential Gaussian Simulation Steps

Firstly, the data should be normalized by transformation from real to Gaussian domain if their distribution is different from normal. Once the simulation process is finished, such data is back transformed to original domain. In the second step, we analyze the data spatial behavior by calculating the experimental variograms for each chemical element. From the analysis of experimental variograms, we can choose the theoretical function (theoretical variogram) that best represents the data spatial variability. The theoretical variogram is the essential component in the estimation process (different kriging algorithms) of statistical distribution at unsampled points.

[Figure 2](#) illustrates an example with vertical variograms for the elements Ca, Ba and Mo in a calcareous rock interval. Both Ca and Ba are present in almost every sample and show background values belonging to carbonate rocks. These elements show vertical experimental variograms (dot plot) matching almost perfectly with exponential theoretical models (line plot).

This is due to data spatial continuity because both elements are detected in all samples. However, molybdenum, which responds to the presence of hydrocarbons in the rock, presents a more irregular vertical distribution and the experimental variogram does not have a good adjustment to a spherical theoretical model as shown in [Figure 2](#).

Anyway, in addition to identifying the theoretical models that respond to each chemical element, we can determine vertical ranges of variability. The range is the distance at which the variogram does not continue to grow and stabilizes at a maximum value (sill). The range gives a quantitative idea of the degree of spatial data continuity. Calcium has a vertical range of 32 m and for barium is 26 m, indicating that both elements are more continuous than molybdenum, because it has a vertical range of 9 m in this example.

### Gaussian cosimulation in one dimension (vertical direction)

If there are significant correlations between wire line and chemical logs, the former can be used to guide the stochastic simulation in areas where there is no hard data (chemical analysis) helping to reduce total system uncertainty. The calculation of statistical distributions at unsampled points is made using a kriging variant known as collocated cokriging. This method combines the hard data weights (chemical analysis) with the soft variable (wire line log) to perform the estimation of statistical distribution at unsampled point. The hard data weights are more important in proximity of points while soft data weights are more important where the unsampled point is far from the data points.

Type II Markov model variant is used with the placed cokriging in which the variogram is estimated from a linear transformation of soft data variogram. It applies when soft data has an areal distribution (or vertical continuity in this case) greater than the hard data (Journel, 1999, Deutsch, 2002, among others). Therefore, we only must know the soft variable variogram and the correlation coefficient between soft and hard data ([Figure 3](#)).

### **Considerations about cutting vertical uncertainty**

Geostatistics assumes that the geographical coordinates (x, y, z) of hard data are known. In the case of cutting sample, there is uncertainty about sample provenance depth. We must assign a single depth value within the range of depths represented by the sample. The selection of this depth is performed by simulation assuming a uniform distribution in the interval represented by the sample. Finally, this depth is assigned to the point and it is entered in the simulation process.

The result of 100 realizations is shown in [Figure 4](#). These realizations shown the uncertainty associated with depth (i.e. peaks of simulated logs do not match exactly) and the frequency content is higher (4th and 5th track). The average of 100 realizations (third track) is smoother than individual realizations, because it tends to represent the average value at each depth. However, the frequency content of average log and its vertical resolution is greater than the original Calcium log made using cutting data only (second track). Notably, the average of 100 Calcium realizations (third track) includes unsampled intervals (upper part of the well) because they are estimated by simulation process where only the soft variable (Density log) is present.

Thus, the average curve of Calcium has both hard (chemical data) and soft information (density log) geostatistically combined and it has an intermediate vertical resolution between cutting and wire line log.

### **Comparison of geochemical logs derived from cutting and wire line tool**

For a 60 m sandy interval, cutting geochemical log of Iron shows a good correlation with Iron recorded on geochemical wire line tool ([Figure 5](#)), while for titanium there is no significant relationship ([Figure 6](#)). [Figure 7](#) shows the correlation of calcium (logging tool) and calcium (XRF) for interbedded clastic and carbonate rocks. There is an improvement of the correlation, but the correlation appears to be weak for values less than 10,000 ppm of Ca and it is better if they are over 30,000 ppm. These examples would suggest that logging tool response is directly related to the concentration (and thus the volume) of the detected chemical element.

### **Gaussian Simulation and 3D Modeling**

When cutting samples have no vertical continuity it is feasible to use three-dimensional modeling of chemical elements from cutting samples even with a very irregular distribution. The only caveat is that uncertainty in the z position is considered negligible within the three-dimensional modeling. The product of this process is three-dimensional models of chemical elements from which it is feasible to extract geochemical logs and detect the possible presence of outliers ([Figure 8](#)). Due to cutting contamination problems, outliers that deviate from the expected geochemical background are identified by their lack of stratigraphic continuity ([Figure 9](#)).

### **The geochemical well logs and Black Shale**

Black Shale has a pattern of certain chemical elements that are invariably repeated and help to characterize the genesis of euxinic sedimentary environments. Nawratil et al. (op. cit.), Tonner et al. (2012), Smith and Malicse (2010), Potter et al (2005), Lash and Blood (2012), among

others reports the presence of molybdenum, vanadium, chromium, nickel and arsenic. Some of them show good correlation with organic matter content and therefore it is feasible to estimate the amounts of TOC using the best correlation with trace metals. These relationships can be used to produce geochemical logs by simulation ([Figure 10](#)).

The rock brittleness estimation can be established from the sedimentary relationship between quartz and zircon (Zr silicate) and Zirconium mineralogical log can be built using stochastic simulation. [Figure 11](#) shows TOC, calcium and zirconium logs for Vaca Muerta Formation black shale (Neuquén Basin, Argentina).

## Conclusions

The concept developed in this work, is embodied in a new chemical-mathematical tool producing intermediate resolution geochemical logs. These logs can characterize sedimentary facies within the black shale, analyze their origin, allow genetic correlations between wells, investigate and predict indirectly hydrocarbon potential fragility of the rock from its mineralogical composition. This can also be used to calibrate and/or correct the response of geochemical wire line tools together with other logs related to the rock, such as the gamma ray spectral and photoelectric factor logs. Moreover, the method presented here, allows building geochemical curves from cutting in old wells with no conventional logs, where curves like zirconium may be similar to SP and the association K-U-Th similar to spectral gamma ray log. The Mo and V logs can be compared with the oil saturation, according to the concepts of Marakushev and Marakushev (2002) and personal experiences (and Larriestra Schiuma, 2011, Larriestra et al, 2010), regarding the chemical composition of oils.

Finally, it is presumed that this tool will be a valid and important technology to be used for a long time before wire line tools can detect key trace elements for black shale analysis. The models made for Vaca Muerta formation with this methodology (Nawratil et al., 2012) allowed to modify stimulation treatments, with high impact on cost and time.

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[http://www.searchanddiscovery.com/documents/2012/41110tonner/ndx\\_tonner.pdf](http://www.searchanddiscovery.com/documents/2012/41110tonner/ndx_tonner.pdf)

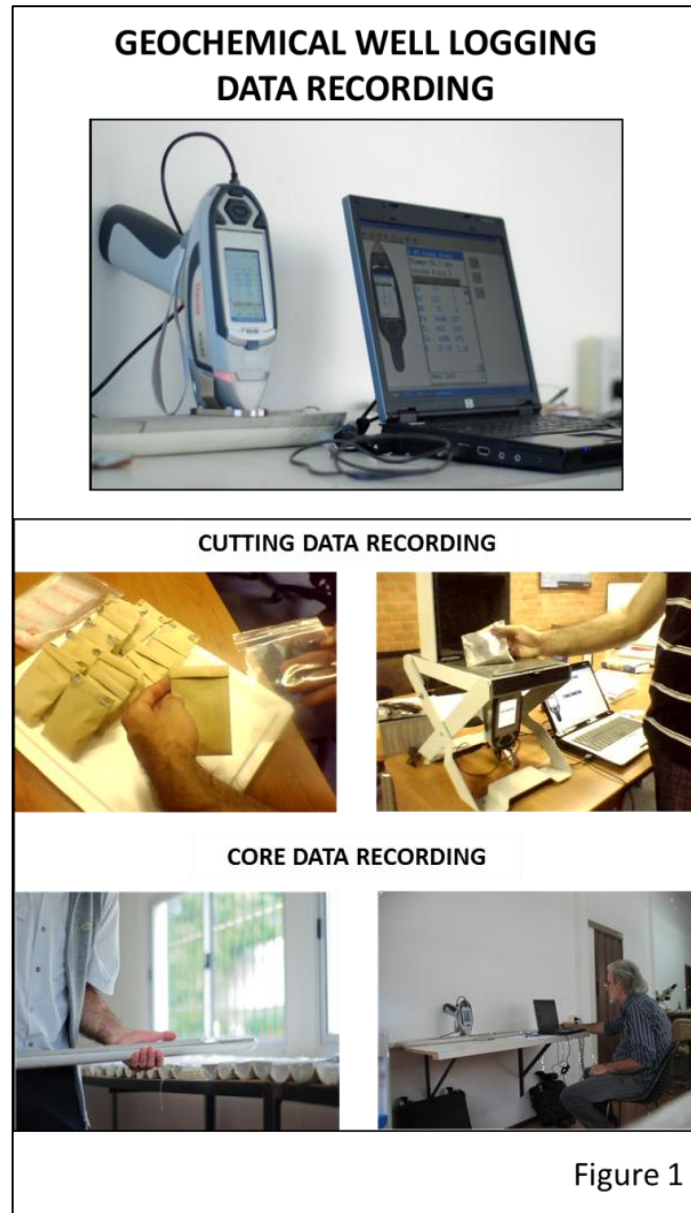


Figure 1. Geochemical well logging data recording.



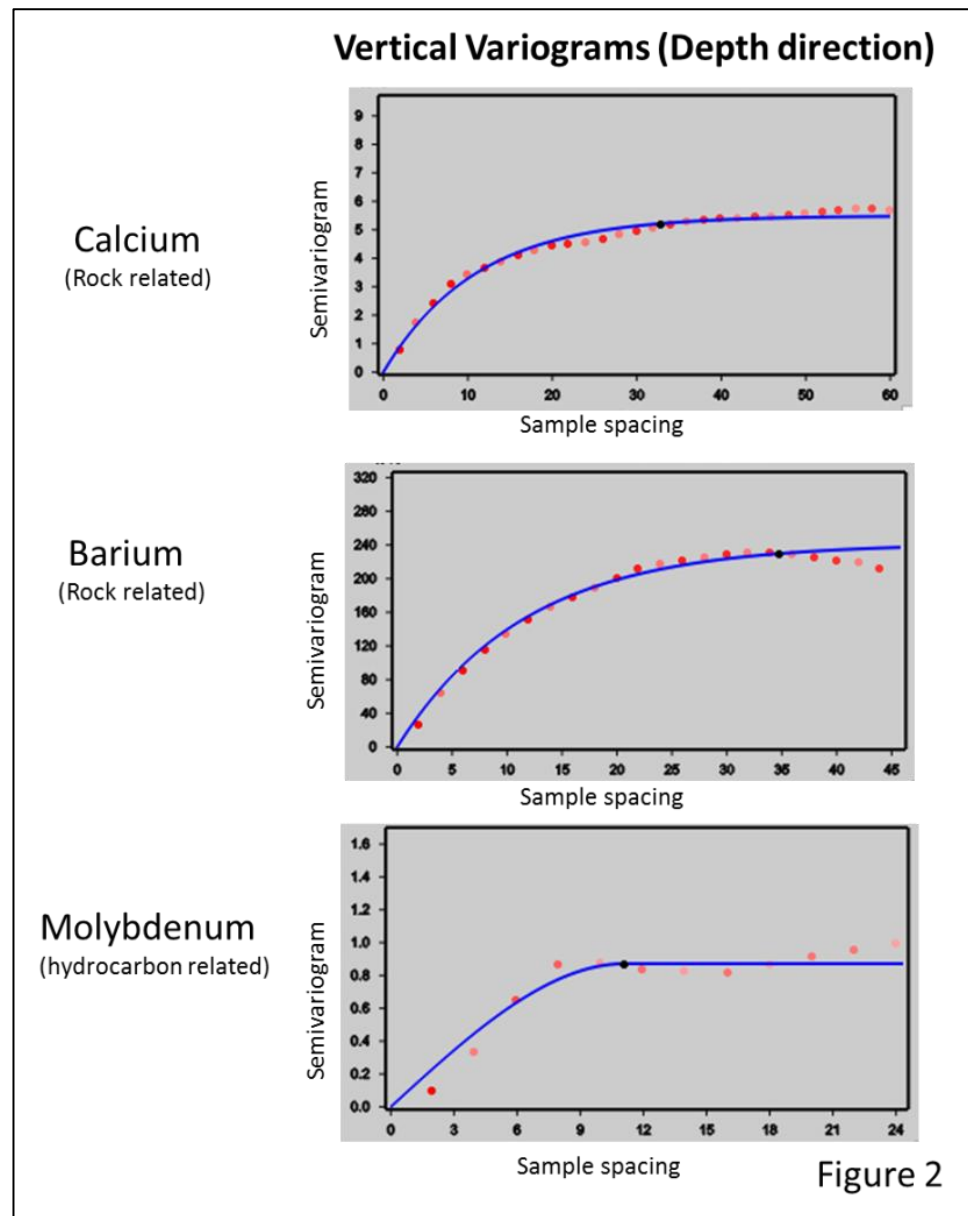


Figure 2. Vertical variograms (depth direction).

**Type II Markov Model of Collocated Cokriging  
Density Log (Soft Data)  
vs.  
Calcium logarithm (Hard Data)**

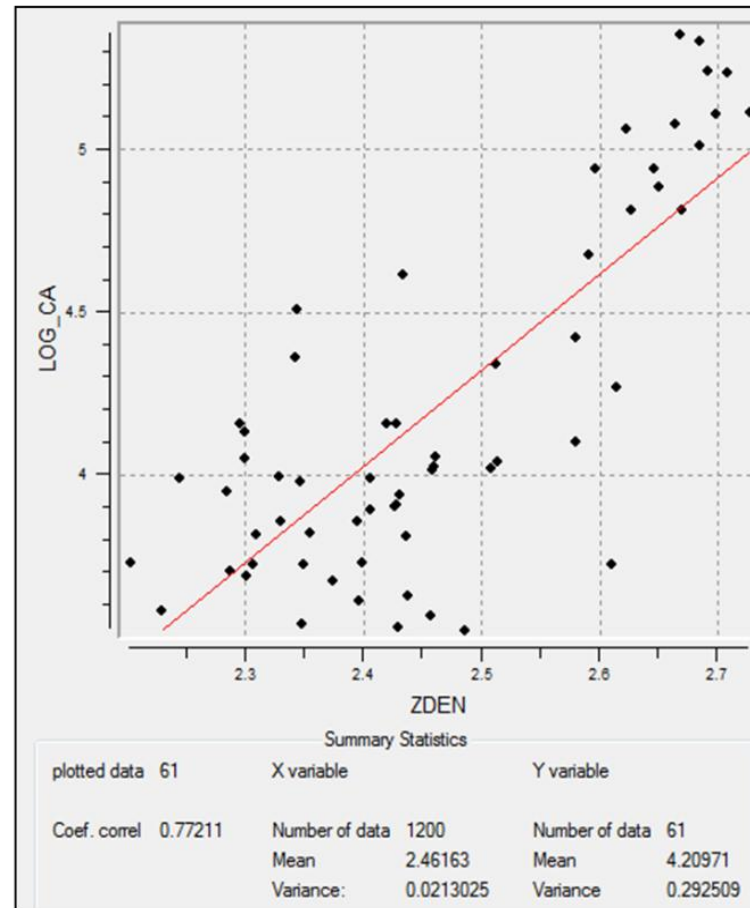


Figure 3

Figure 3. Type II Markov Model of Collocated Cokriging.



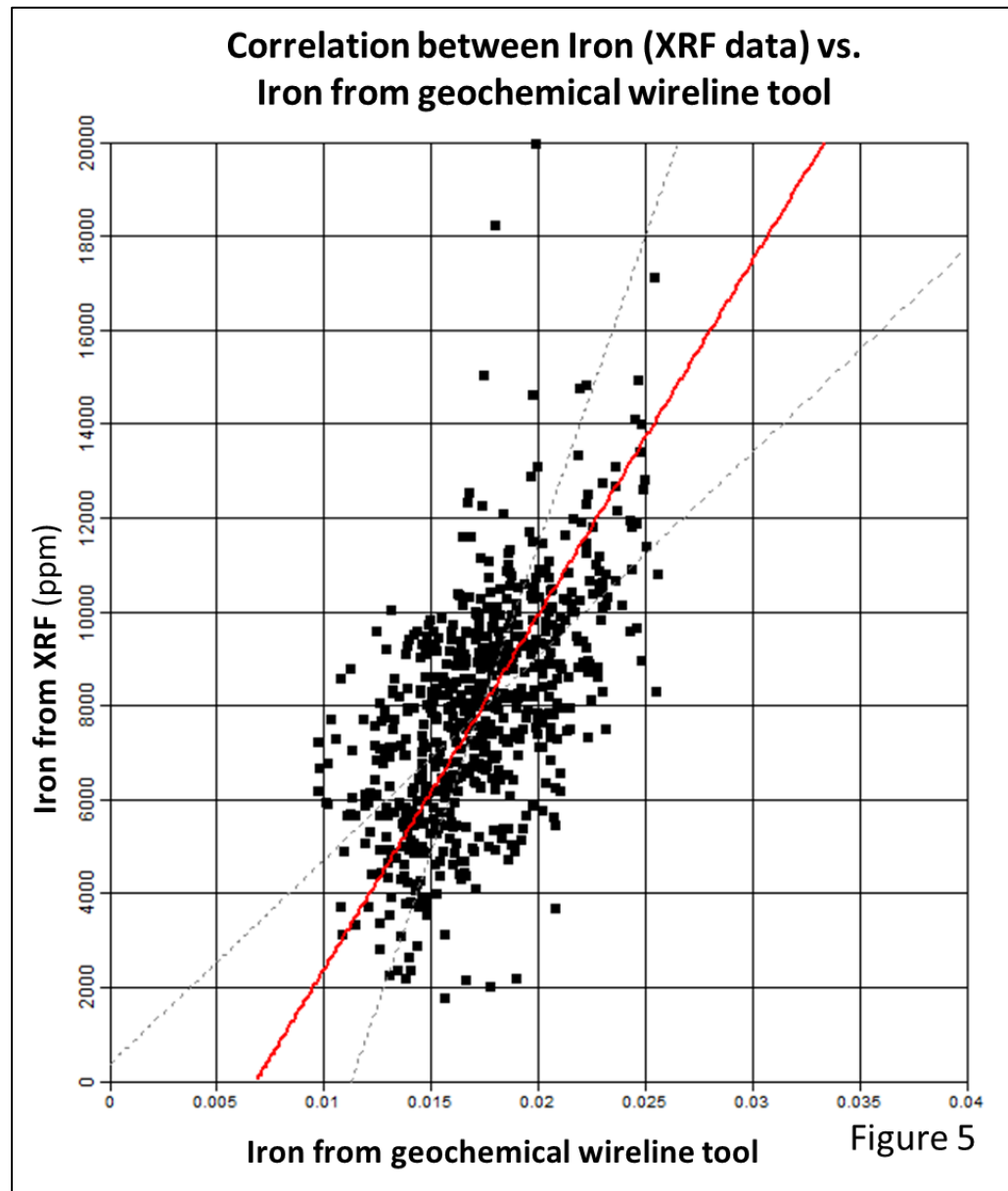


Figure 5. Correlation between iron (XRF data) vs. iron from geochemical wireline tool.

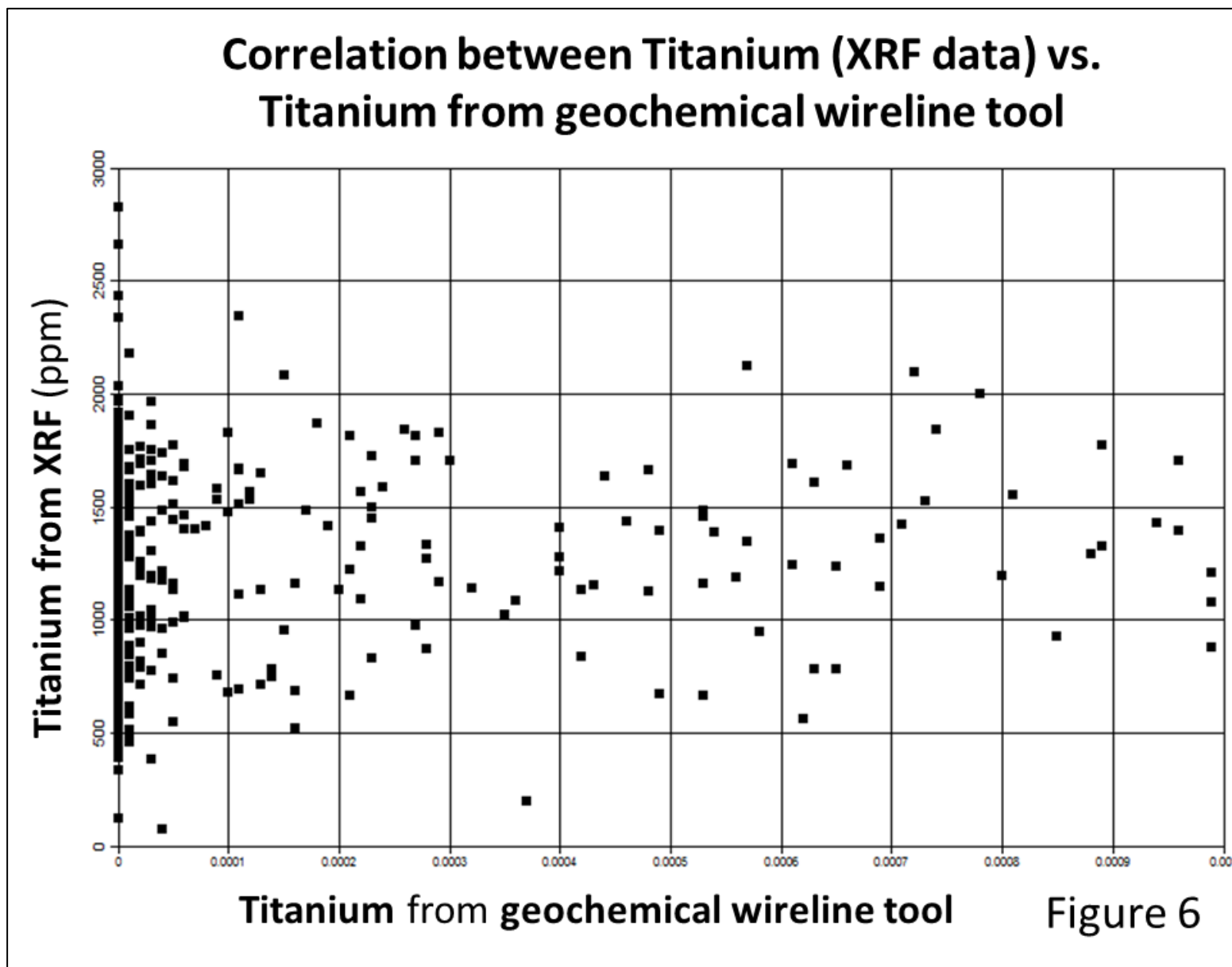


Figure 6. Correlation between titanium (XRF data) vs. titanium from geochemical wireline tool.

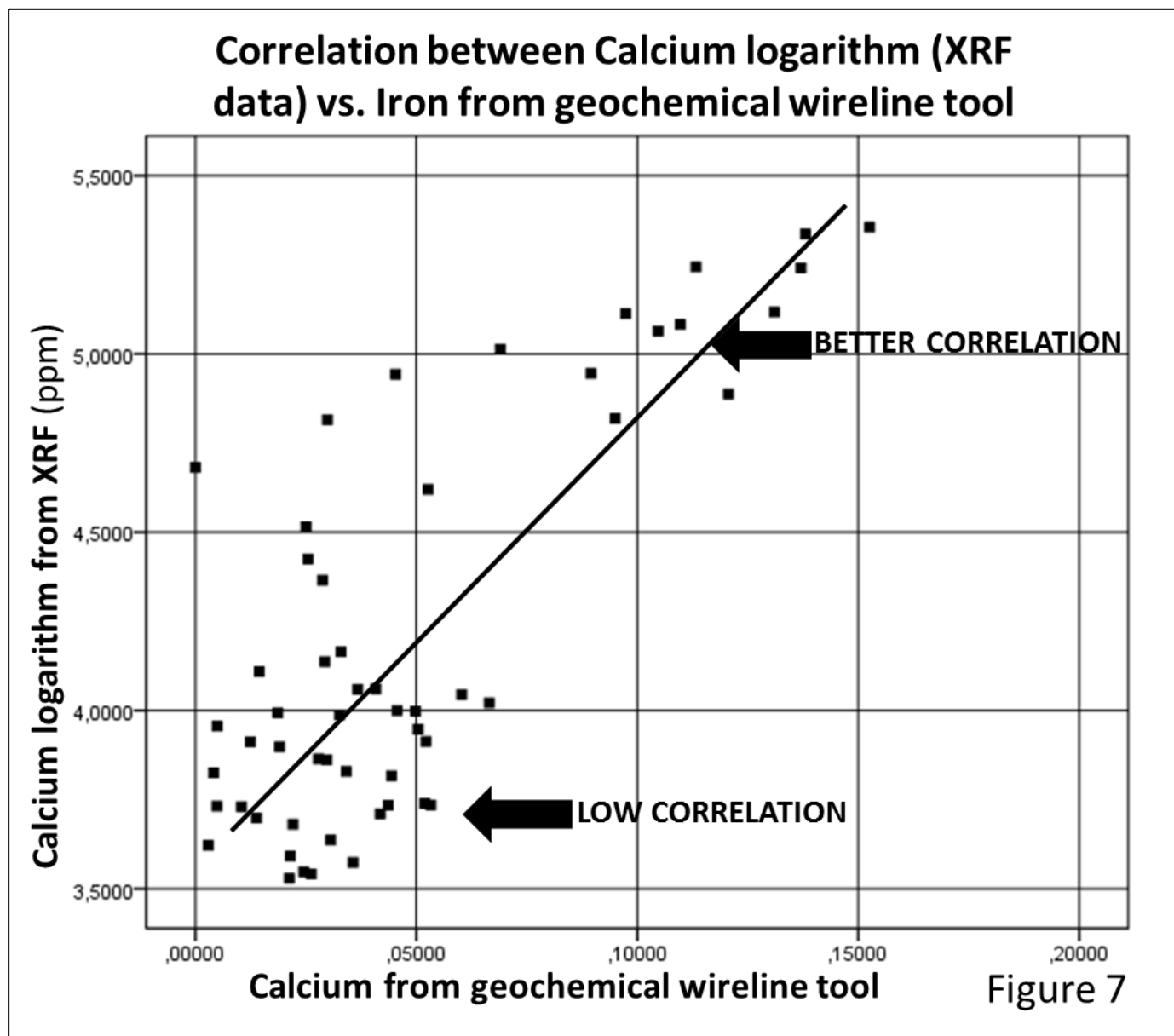
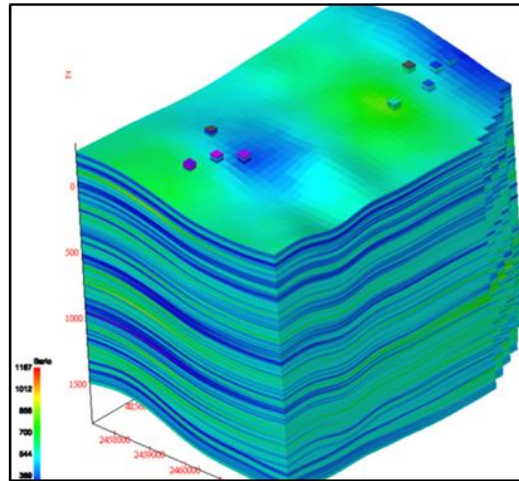


Figure 7. Correlation between calcium logarithm (XRF data) vs. iron from geochemical wireline tool.

### 3D model derived geochemical logs

(from Schiuma y Larriestra, 2011)

3D model of  
chemical element  
(Barium)



Geochemical XRF log: Rb/K<sub>2</sub>O relationship

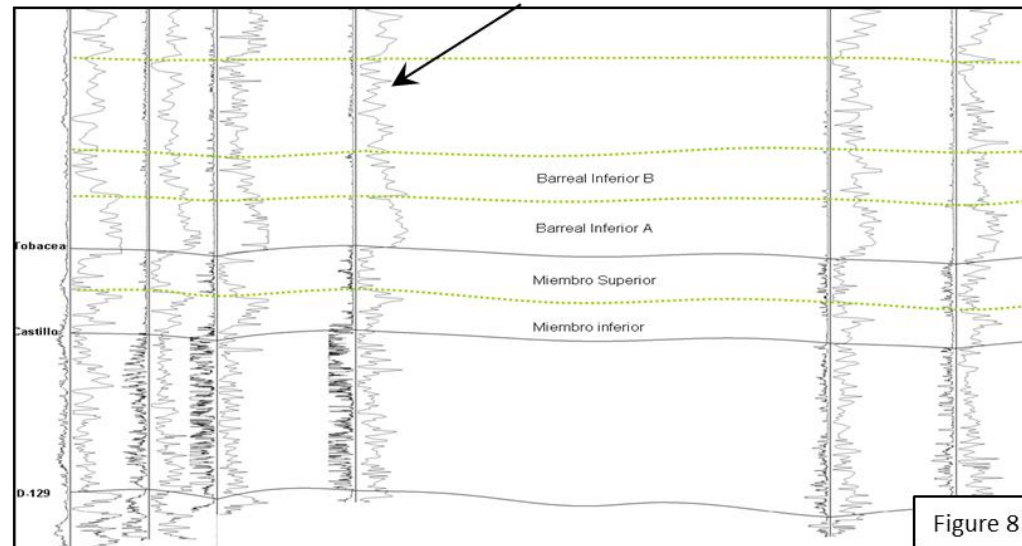


Figure 8

Figure 8. 3-D model derived geochemical logs (barium).

## 3D model derived geochemical logs

Anomalous data due to cutting contamination (Calcium)

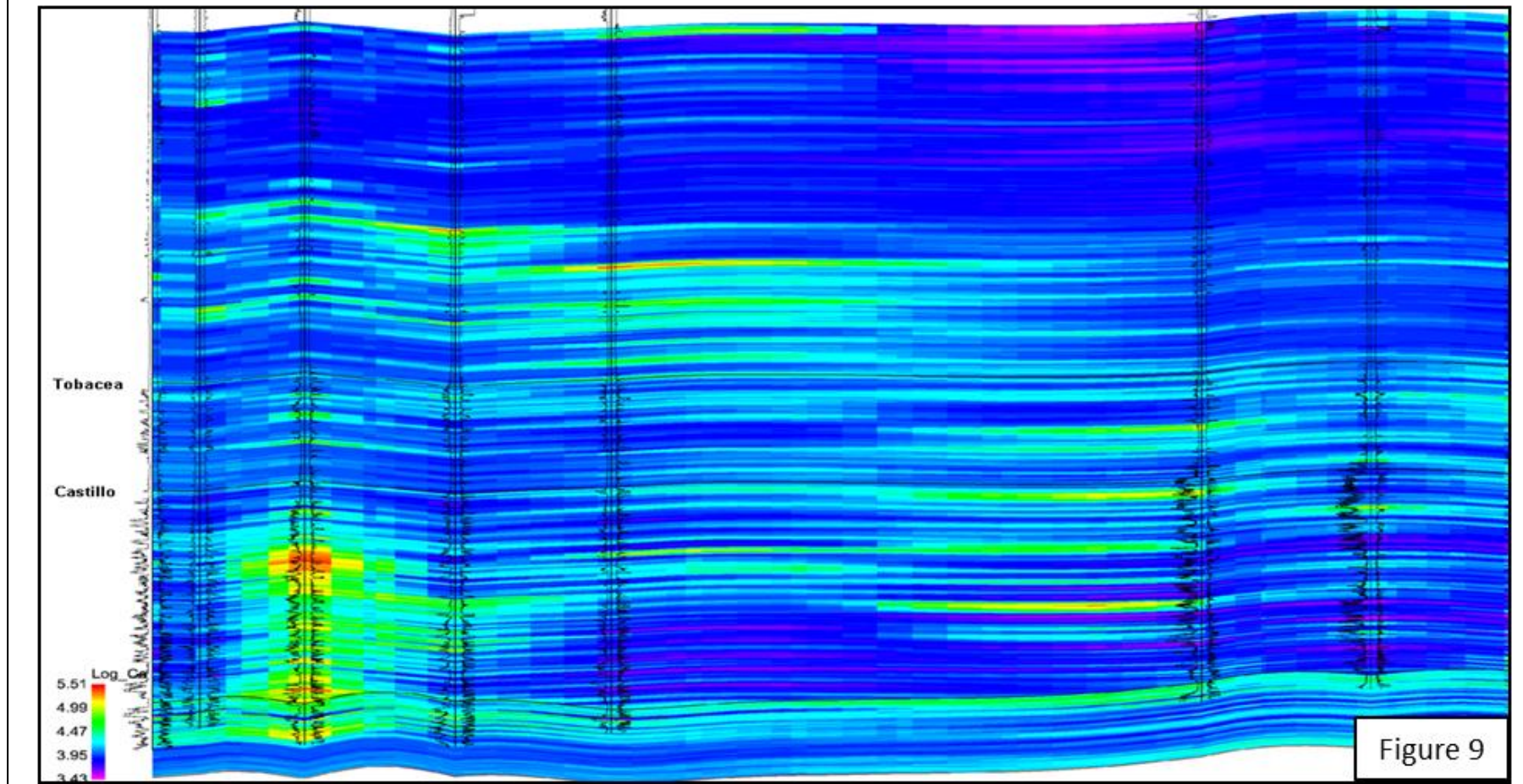


Figure 9. 3-D model derived geochemical logs (calcium).



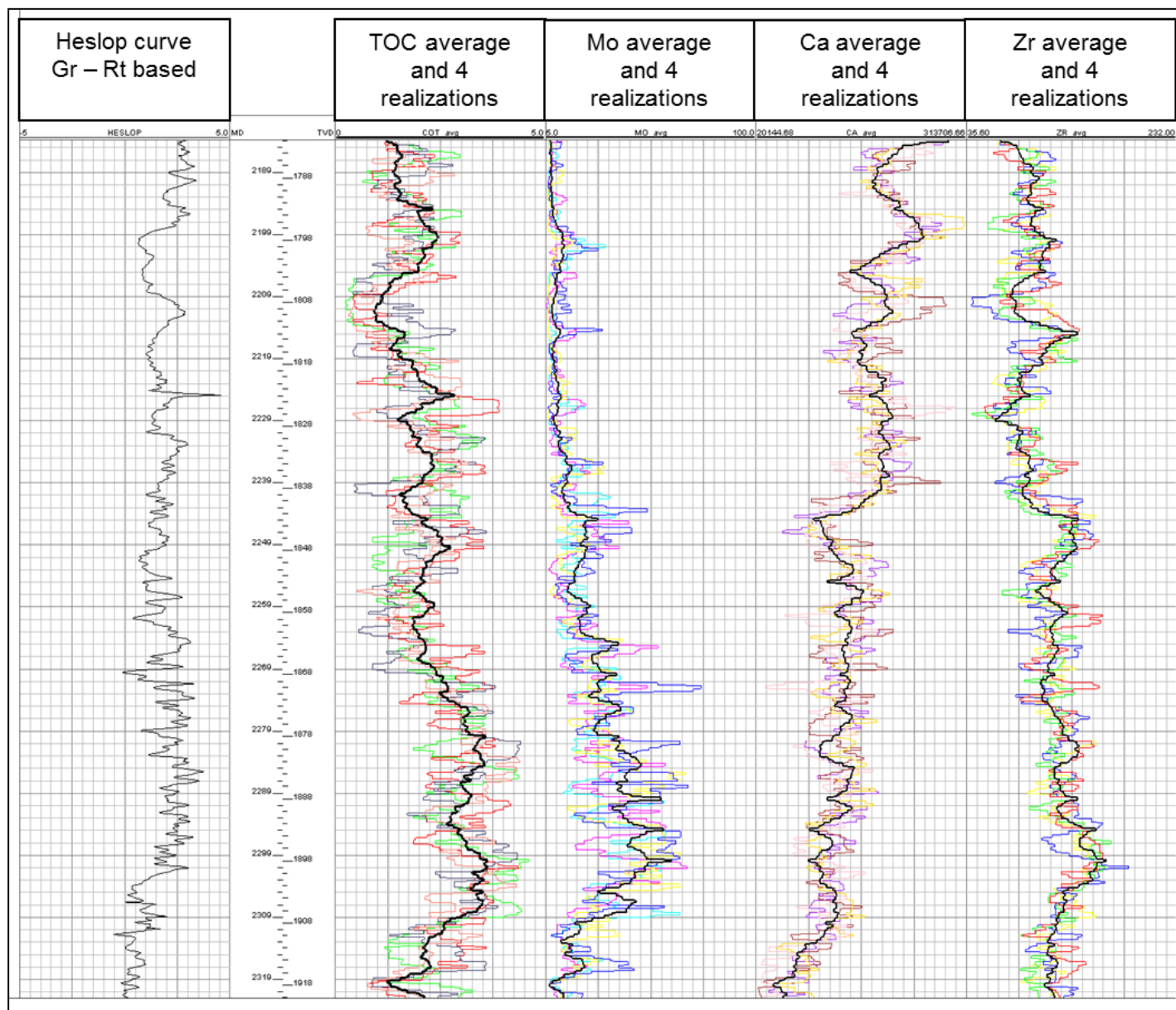


Figure 10. Geochemical log relationships.

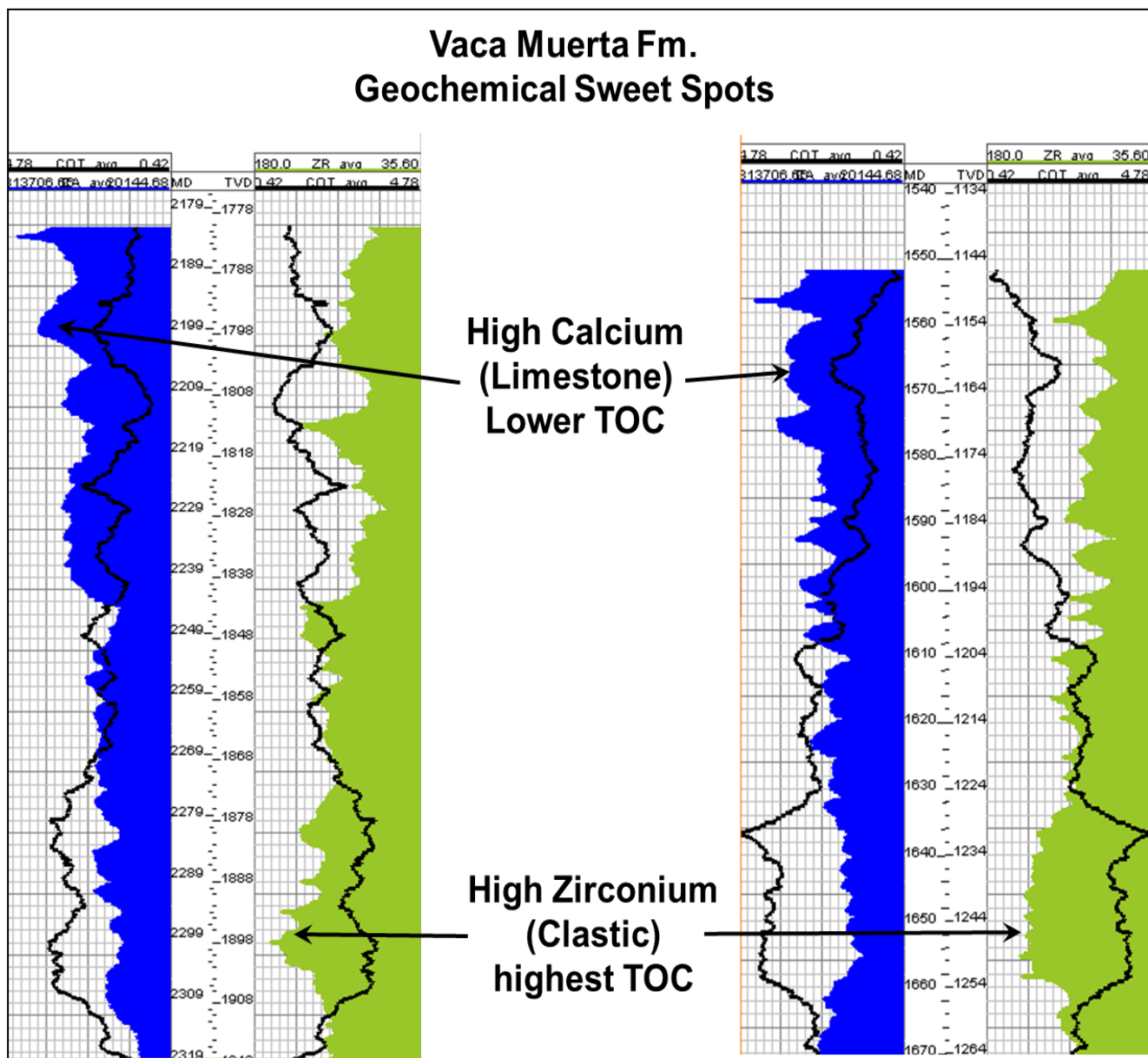


Figure 11. Vaca Muerta Formation geochemical sweet spots.