High Resolution Non-Destructive Chemostratigraphy of Vaca Muerta Formation, Argentina: New Evidence of Black Shale Sedimentary Features*

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Abstract

The detection of hydrocarbon generation potential in black shales and the existence of potential reservoir zones within them are key features that conventional well logs fail to adequately define. We present a method that allows the integration of chemical data (X-Ray Fluorescence analysis from cutting and cores) with well logs using Geostatistic Simulation algorithms. The well analyzed belongs to Cerro Vagón block and it is located in the south margin of Neuquén Basin, Argentina (Figure 1).

The stratigraphic framework (Figure 2) is composed of three source rock levels ranging from Jurassic to Lower Cretaceous, where the Jurassic Vaca Muerta Formation is the most important (red arrow). The rest of the stratigraphic column is composed of clastic and carbonate beds ranging from Jurassic to Tertiary ages. Some of these beds are reservoirs and claystone, while limestone and anhydrite are the most important seals.

Methodology

This article is based on soft inorganic geochemistry principles (Larriestra, 2013). 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 sample population available. It involves thousands of chemical analysis of cutting and core samples, their processing using geostatistical techniques and the integration with well log and geophysical data to produce an unconventional resources model.

Data Acquisition

The chemical element analysis was performed using rapid hand held X-Ray Fluorescence (HHXRF) equipment in a non-destructive registration process. The analysis consisted of the detection of 32 chemical major and trace elements, from 80 cutting samples belonging to Vaca Muerta Formation. and two cores from its bottom beds. Cores were analyzed by 180 readings each separated by 10 cm from the other. Finally, all samples were processed for XRD and TOC destructive analysis.

Data processing and geochemical log construction is based on selection of best correlations between the chemical elements and the set of wireline logs available in the well, whether recorded or calculated by petrophysical analysis. Then Gaussian co-simulation with Markov model type II is performed, using the well log as co-variable. After the simulations are performed, the average value of the *n* realizations is the expected log of the chemical element (Nawratil et al.; 2012, Larriestra, 2011; Larriestra, 2013).

This method allows creation of chemical element logs of vanadium, molybdenum, sulfur, chromium and nickel, useful to assess the potential hydrocarbon generation of source rocks. Moreover, geochemical logs as zirconium and titanium (related to clastic episodes) allow identifying areas with better reservoir conditions in black shale.

Results

Vaca Muerta Formation Sedimentology and Geochemistry

Vaca Muerta Formation rocks can be described as marine organic-rich mudstones with a minor siliciclastic component at the base that gradually passes to limestone towards the top. The lower part of the formation (lower 60-70 m) is characterized by clastic sediments deposited in an anoxic environment with high contents of TOC, hydrogen index and anomalous concentrations of molybdenum, vanadium, nickel and chromium.

The graph of TOC versus S1 + S2 shows the source rock potential level of the Vaca Muerta bituminous rocks. If we add the molybdenum concentration as a bubble map (Figure 3), we can see positive correlation of the three variables. The same behavior may be observed when we add the vanadium concentration values to the TOC / S1+S2 cross plot (Figure 4). Furthermore, in the cross plot of Figure 5, the regression of TOC versus molybdenum concentration shows a strong correlation of 0.89.

Similar to the case presented by Nawratil et al. (2012), the zirconium (zircon) content is proportionally related to quartz, common in siliciclastic sedimentary episodes. Additionally, zirconium and titanium show high correlation (indicating heavy minerals presence), and both elements share high correlation with molybdenum concentration too (Figure 6). This fact allows us to conclude that the anoxic lower beds have an important clastic composition (very fine sand to silt). Finally, the relationship between zirconium and calcium shows a strong negative correlation (Figure 7), interpreted as the gradual passage of environments dominated by clastic sedimentation (high Zr) at the bottom, to environments where chemical (organic) sedimentation prevails (high Ca) at the top.

Core High Resolution Chemostratigraphy

The result of the core high resolution chemostratigraphy is shown in Figure 8. In the first track, the curves plotted are potassium (blue), zirconium (brown) and gamma ray (dash line). In the first 12 m measured from the top, the curves show high correlation between themselves and a remarkable stratigraphic cyclicity. In the second track, short, medium and deep resistivity curves are shown in black and calcium concentration is plotted in blue. Again, a strong correlation between those curves and a characteristic cyclicity is observed in this section of Vaca Muerta.

In the third track, density log (dashed line), molybdenum (yellow) and TOC percentage (black circles) are plotted. As expected, the TOC percentage, indirectly measured by molybdenum concentration (as shown in Figure 5), shows an inverse behavior with density log, where high concentration of organic matter is accompanied by decreasing density values.

In the fourth track, potassium, thorium and uranium curves are drawn. Both first and second are well correlated with gamma ray log, while uranium (geochemically related to organic matter and molybdenum) was not detected with more frequency due to not enough detection level of the HHXRF equipment.

The fifth track shows manganese (black) and calcium (blue) concentrations, with a high remarkable correlation. The sixth track shows a photograph of the core, where the darkest colors are not necessarily related to high organic matter and molybdenum concentration. The seventh track shows sulfur and iron concentration where its high spatial relationship is explained by the presence of pyrite, enabling to quantify the volume of this mineral.

In the eighth track we can observe the spatial matching of molybdenum (yellow) and vanadium (red). The last one is the second most important trace element present in anoxic levels of Vaca Muerta.

The ninth track displays short and deep resistivity curves, TOC percentage (black dots) and pyrite percentage in yellow. We can see that resistivity lows match very well with pyrite and TOC peaks, going inversely to the Passey model (Passey et al., 1990, among others) where the resistivity is proportional to the content of organic matter. The tenth track shows nickel and chromium following the same trend and cyclicity of the other anoxic related metals showed in the previous tracks. The eleventh track displays the gamma ray (dashed line) and density logs showing a red area between them representing the best detection of TOC by these conventional logs.

Discussion

Most of methods of TOC estimation using common logs assume that organic matter volume is sensitive to density (Rhob is inversely related to TOC) and sonic wave transit time logs (direct relationship between DT and TOC). Moreover, in all TOC estimation methods a direct relationship between TOC and resistivity is assumed.

Obviously the last condition is not satisfied when we observe the ninth track of the geochemical log in Figure 8. In this case the increase of resistivity is proportional to the calcium content (almost a perfect correlation) and inversely proportional to organic matter content. Simultaneous lowering of the resistivity matches iron and sulfur peaks, i.e. with the pyrite concentration (in percentage). The resistivity is greatly influenced by the content of pyrite hiding the theoretical response of the organic matter, and therefore the Passey model cannot be applied in this case.

The most direct solution to evaluate the organic matter content is to analyze the molybdenum or vanadium concentration as shown in this work. In cases of sample unavailability for chemical analysis, an alternative solution is to use gamma ray and density logs. The gamma-ray profile is influenced by black shale uranium content and it matches with the molybdenum concentration due to geochemically affinity. The density log is very accurate in detecting organic material due to its low density, and the combination with gamma ray log gives the red area shown in the eleventh track of the geochemical log (Figure 8). This red area is a quantitative approach to organic matter percentage, and this method may be a better approximation to TOC evaluation, at least for the Vaca Muerta Formation in this area of Neuquén Basin.

Conclusions

The major existing cyclicity between thin beds with high organic matter and molybdenum content interbedded with beds showing important decrease in those concentrations is probably indicative of alternating anoxic and disoxic environments. Moreover, beds with low TOC show high calcium and manganesium concentration suggesting the possibility of sediment supply from basin margins carrying oxygenated sedimentary materials. This fact was observed by Potter, et al. (2005), among others authors, in the Devonian Canadway Formation, Pennsylvania, USA. This cyclicity between organic and non-organic rich periods resembles the atmospheric phenomenon known as El Niño-La Niña in activity since the Early Tertiary on the west coast of South America.

With regard to the evaluation of organic matter it is necessary to make some observations on conventional methods of TOC assessment. In the studied area of Neuquén Basin, the Passey model is not the most appropriate because of the pyrite content of Vaca Muerta rocks. However, Holmes et al. (2013) propose an interesting method to evaluate pyrite content using logs. We tried to use the same methodology but it was an unsuccessful, as the conductivity curve showed correlation only with pyrite in some intervals, as is displayed in Figure 9. Therefore, we conclude that the best indirect method for the evaluation of TOC content for Vaca Muerta Formation is the evaluation of molybdenum and vanadium derived from cutting chemical analysis.

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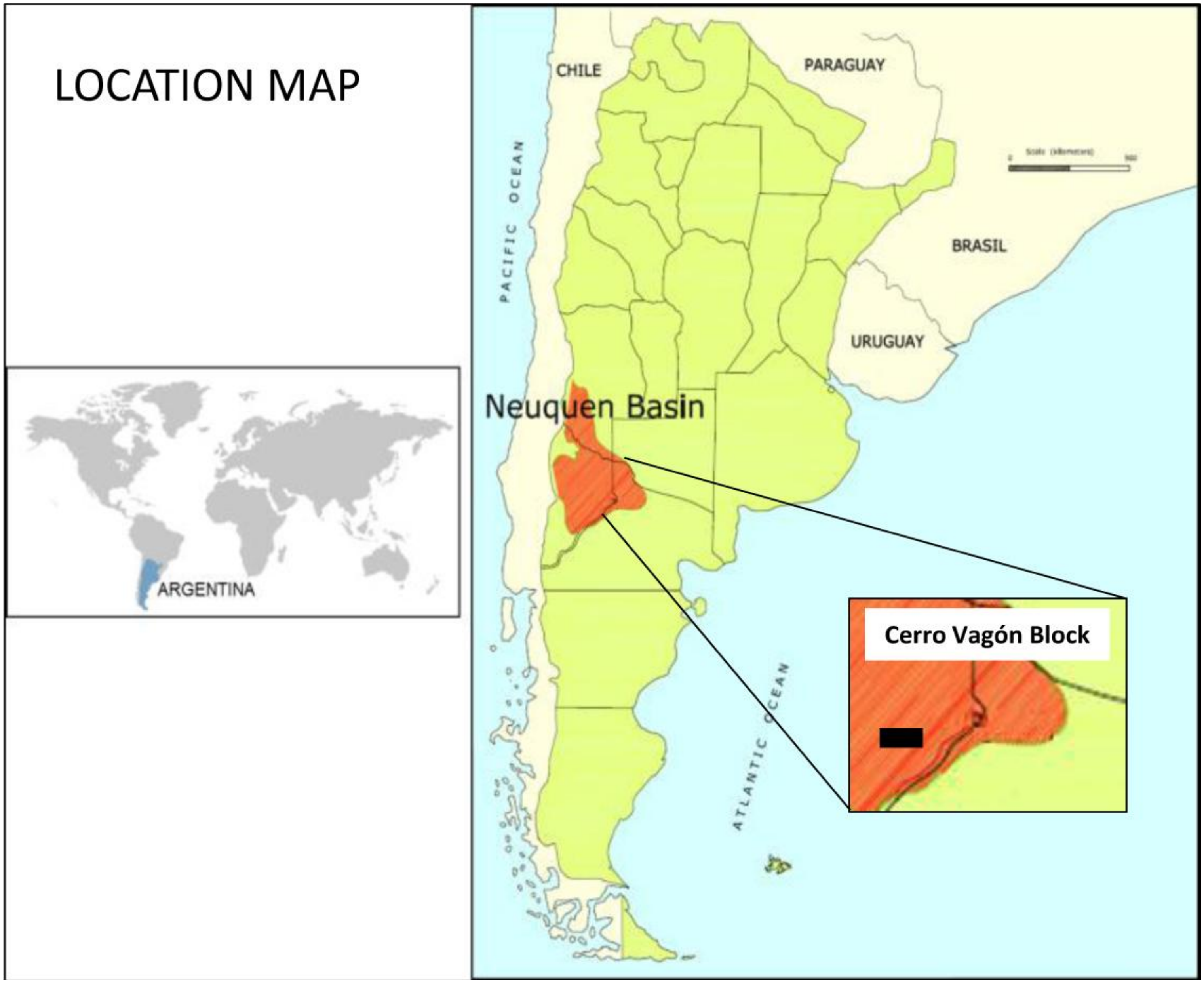

Figure 1. Neuquen Basin study are location map.

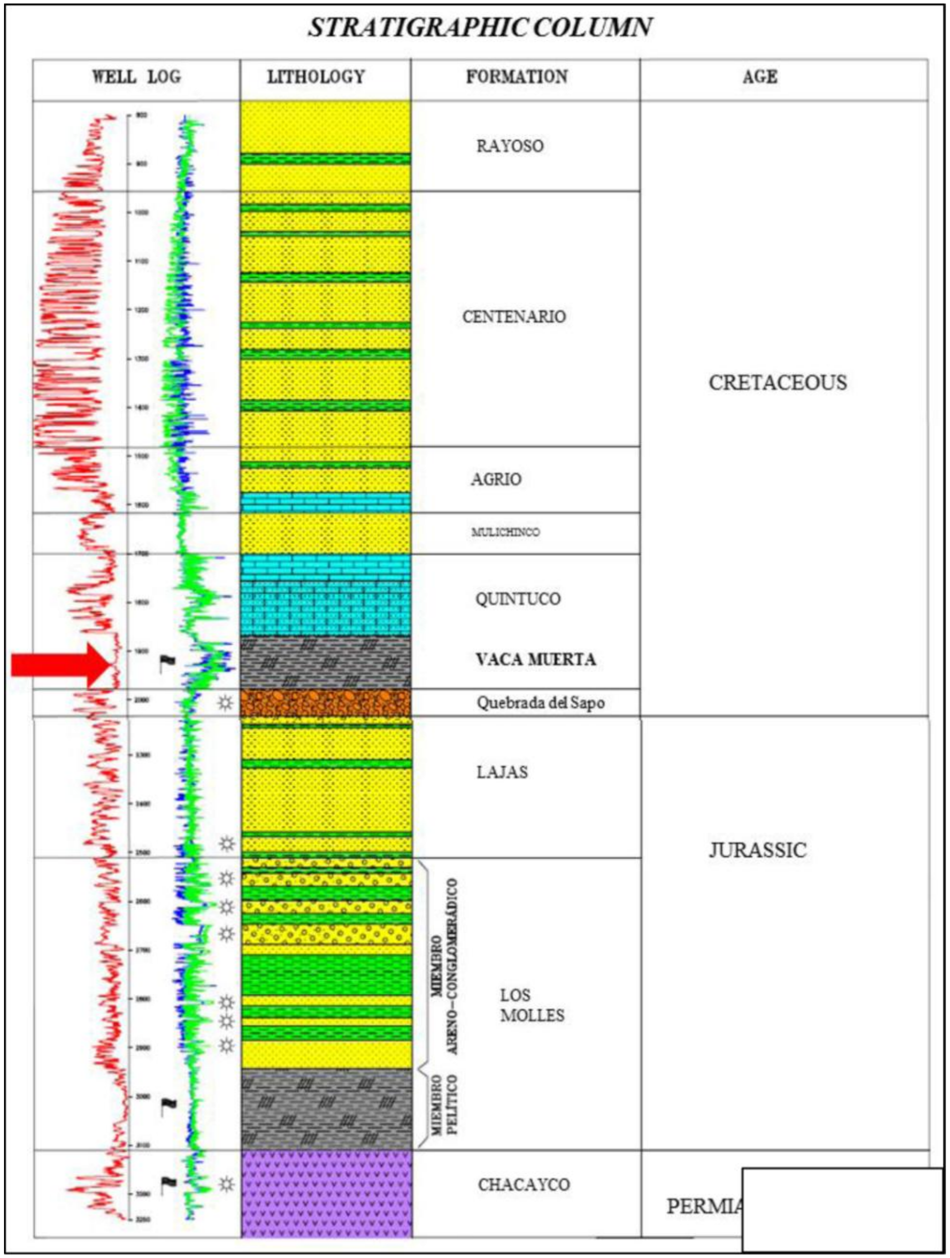

Figure 2. Study area stratigraphic column with type log.

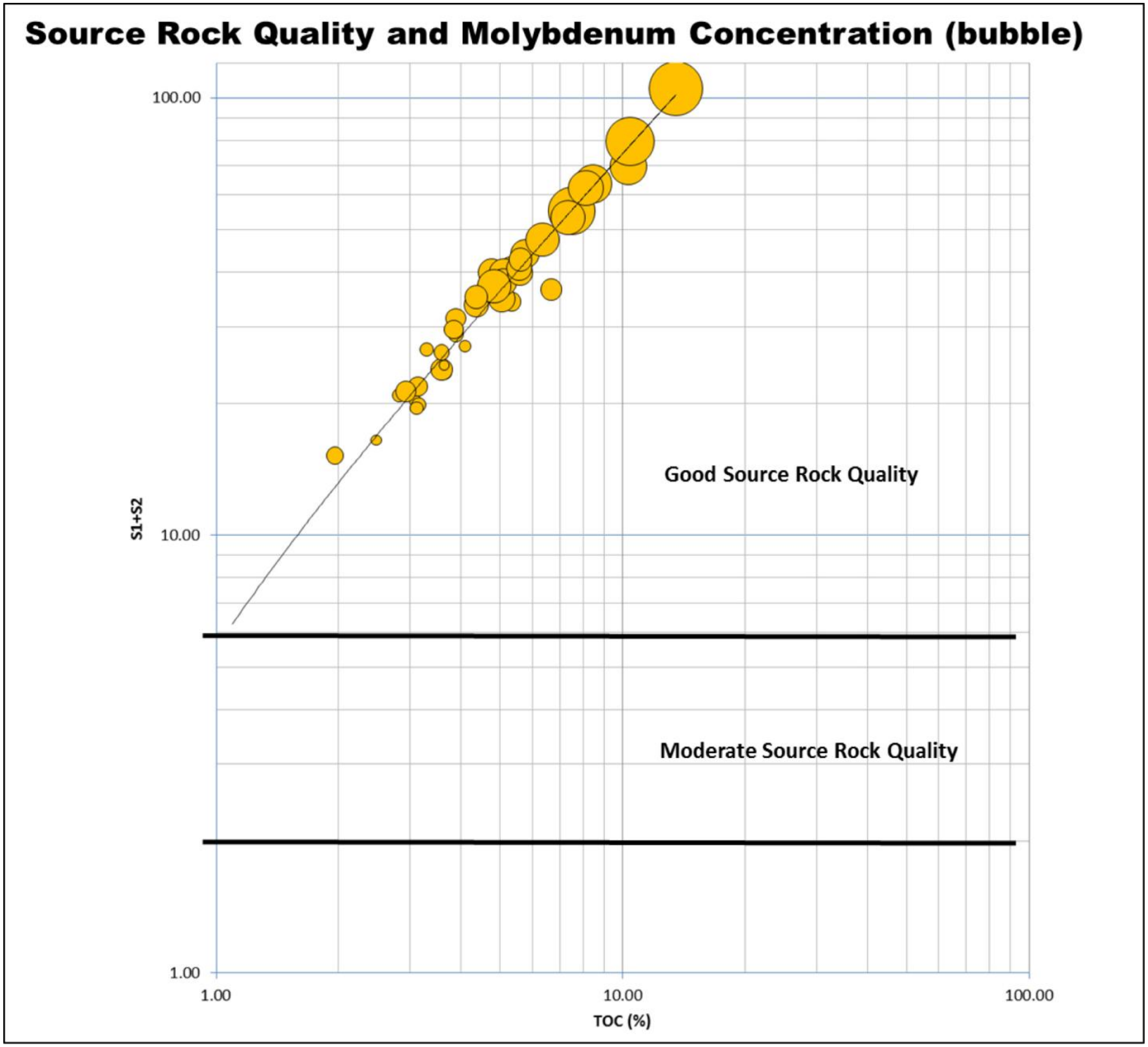

Figure 3. Bubble cross-plot of source rock quality vs. molybdenum concentration.

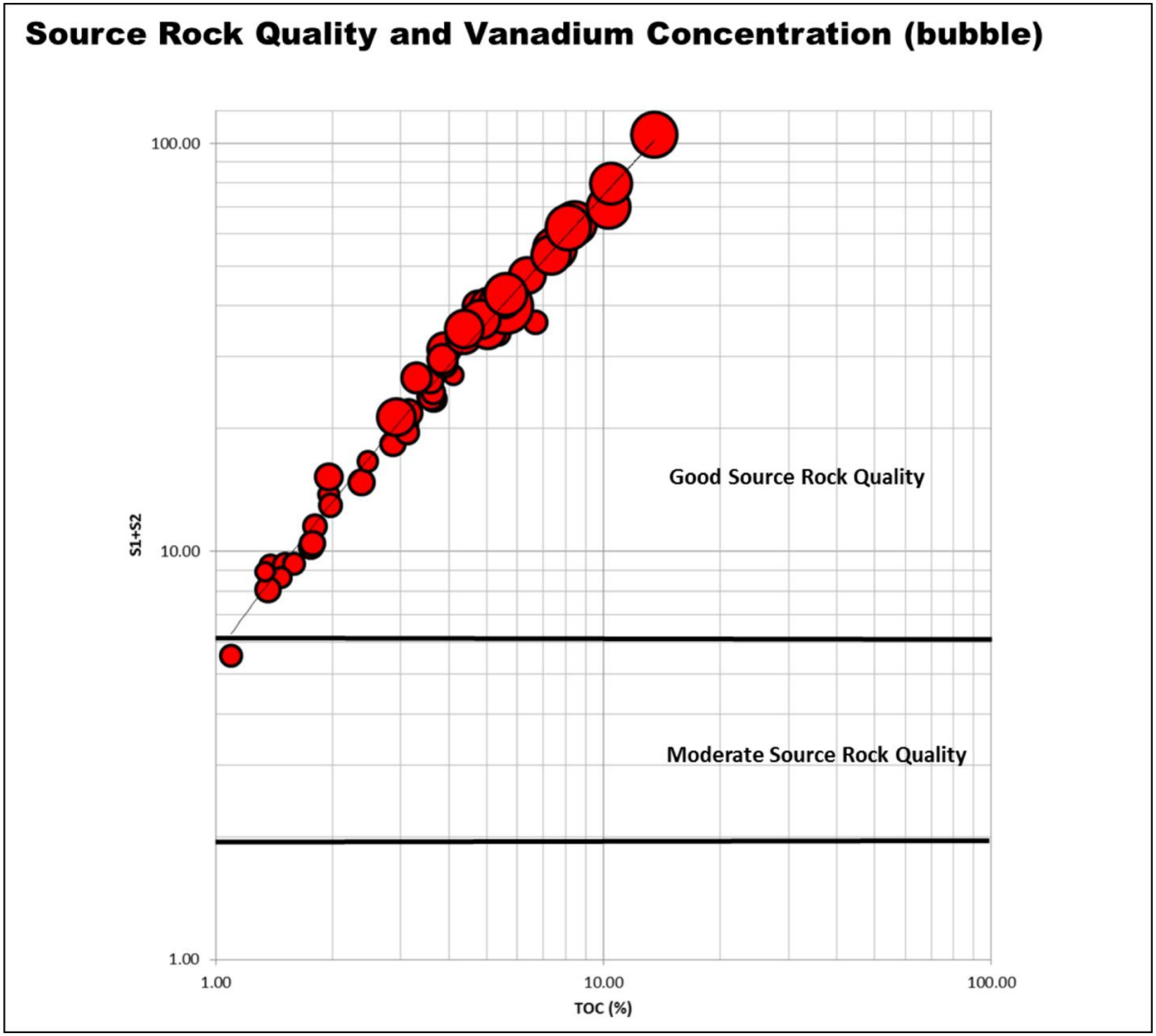

Figure 4. Bubble cross-plot of source rock quality vs. vanadium concentration.

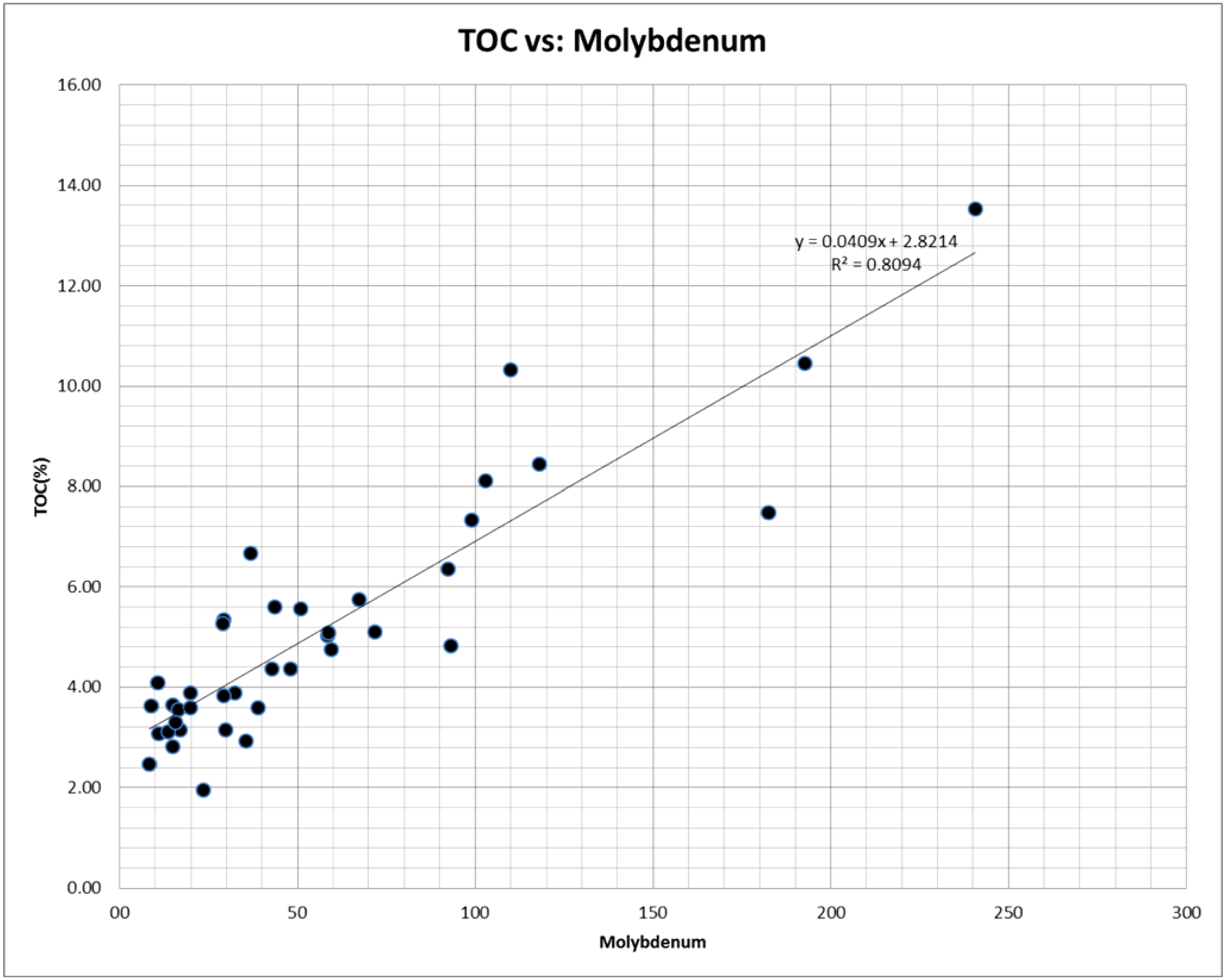

Figure 5. Cross-plot of TOC % vs. molybdenum concentration.

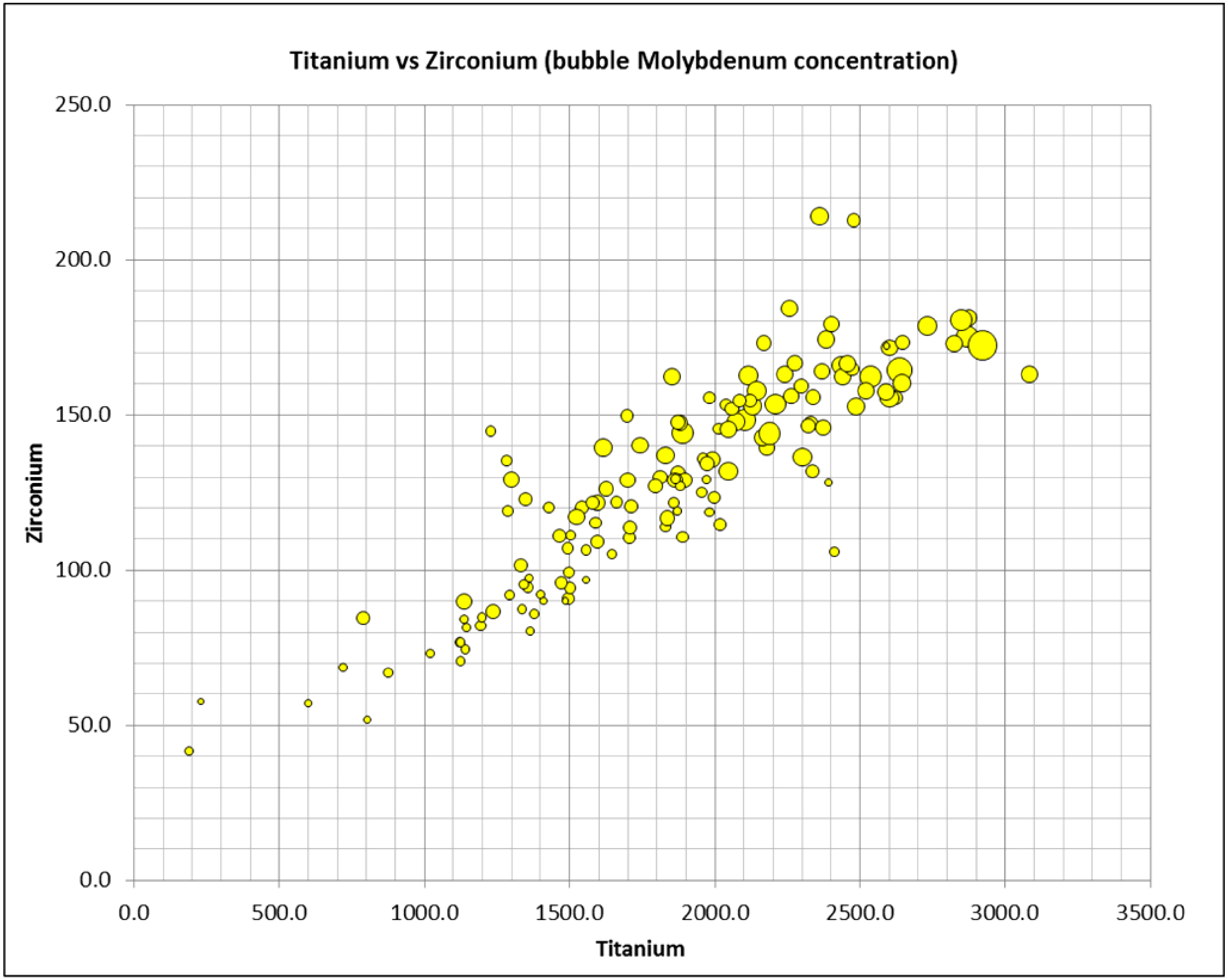

Figure 6. Bubble cross-plot of titanium concentration vs. molybdenum concentration.

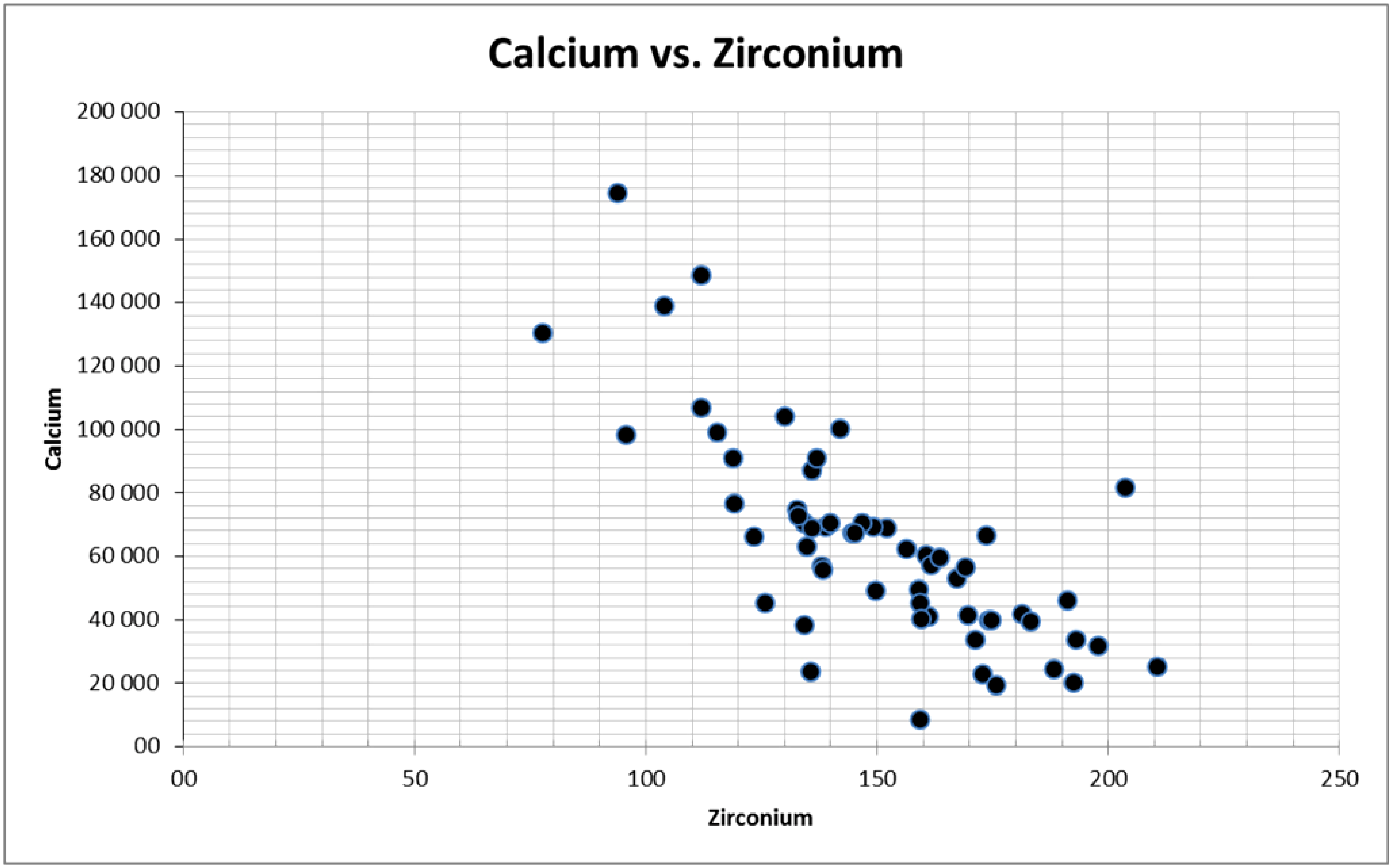

Figure 7. Cross-plot of calcium concentration vs. zirconium concentration.

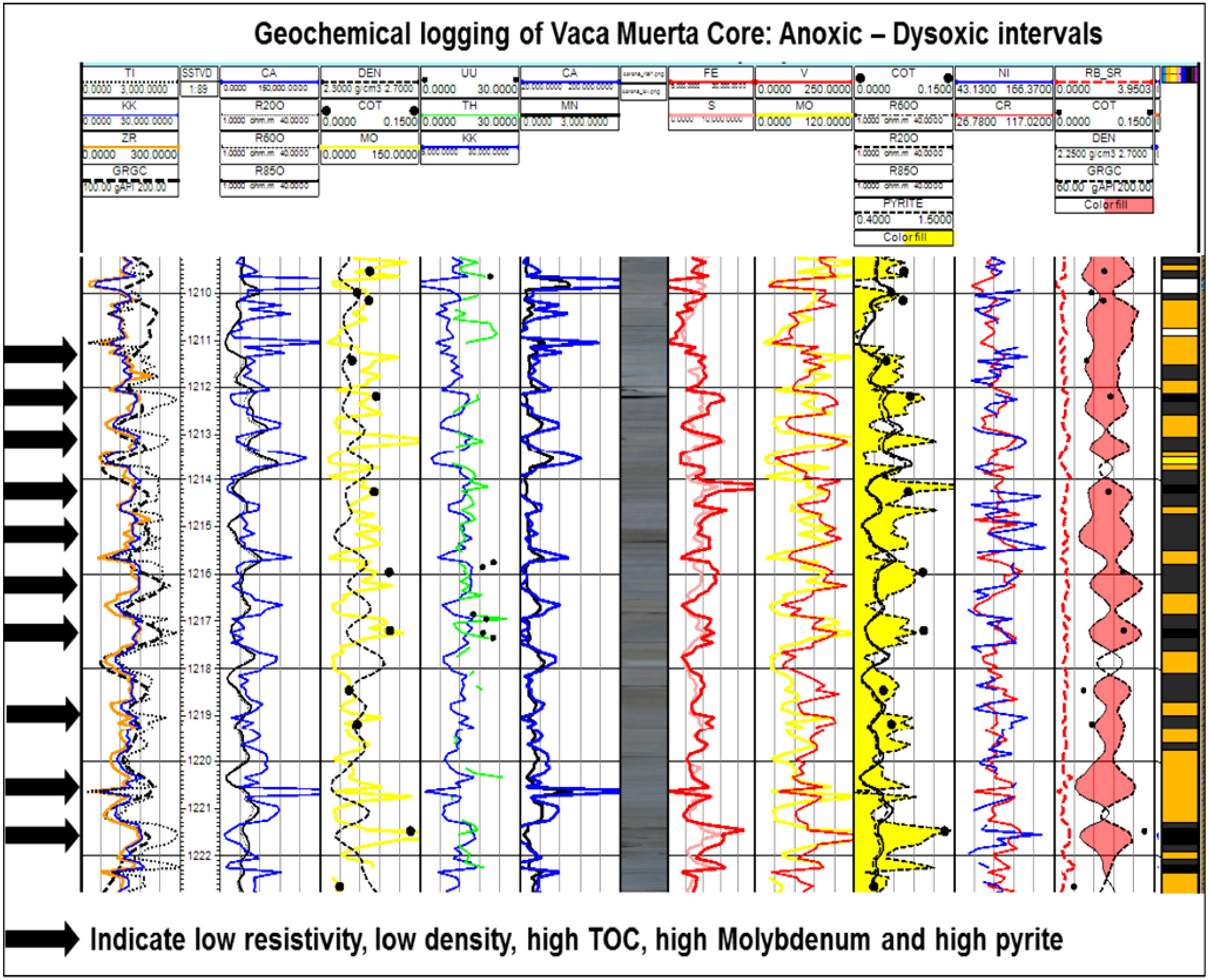

Figure 8. Geochemical log of Vaca Muerta core.

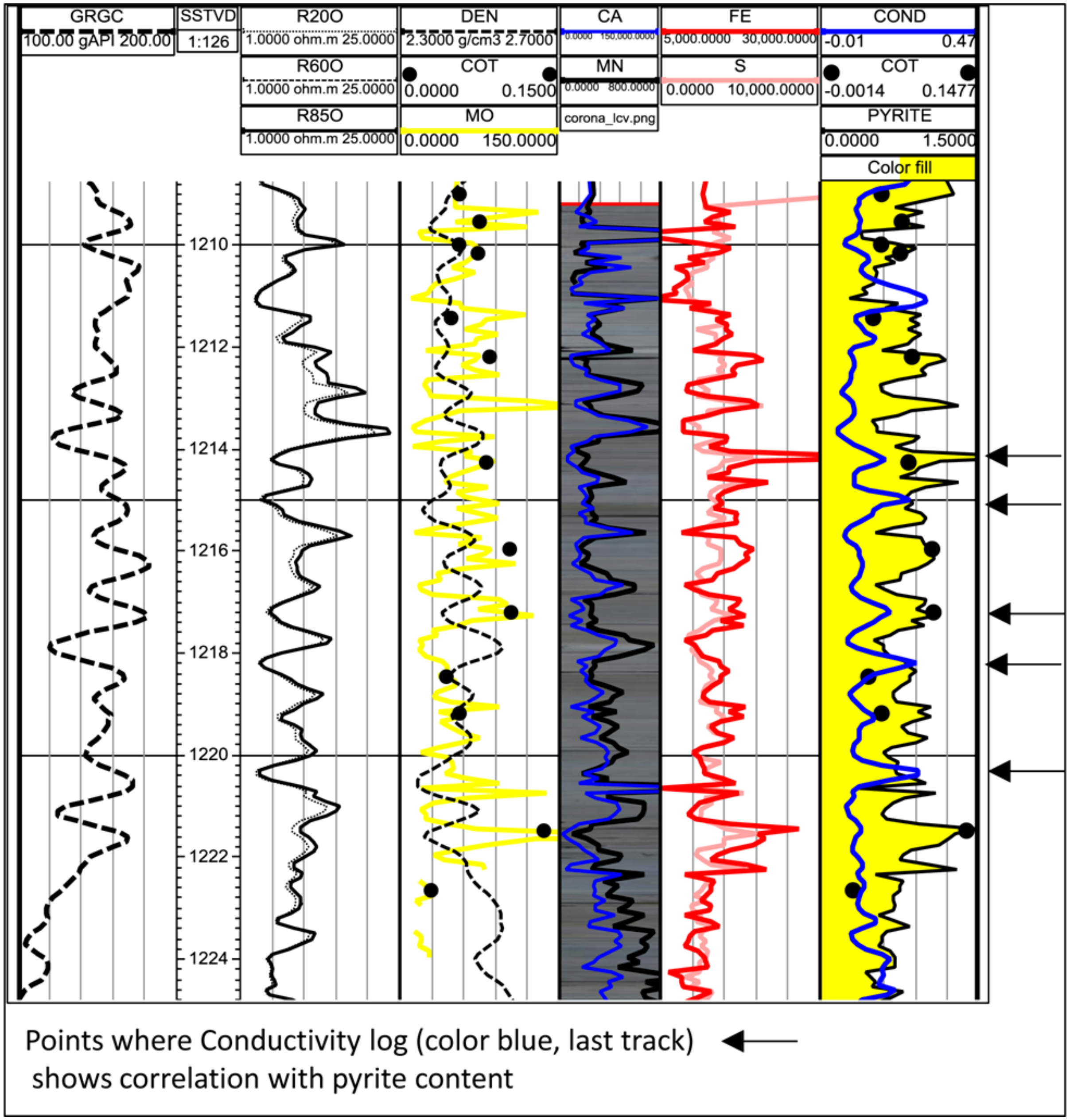

Figure 9. Portion of geochemical log of Vaca Muerta core, showing points where conductivity correlates to pyrite content.