The K/Rb Ratio and Its Geological and Petrophysical Implications: A Test Case of the San Jorge Gulf Basin, Argentina*

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Abstract

This article presents the conclusions of inorganic geochemical studies from cutting and cores belonging to wells located on the southern flank of the San Jorge Gulf Basin in Argentina. Chemical analysis was performed by nondestructive X-Ray fluorescence analysis with rapid hand-held equipment. Ten wells were studied and chemical analysis was performed on 2500 cutting samples and 27 m of core, with readings separated 10 cm from each other.

The San Jorge Gulf Basin is an extensional basin developed in Upper Jurassic sedimentary-volcanic complex rocks. Basin fill began during rifting stages from Late Jurassic to Early Cretaceous and successive sag stages during Middle to Late Cretaceous. Basin fill is predominantly of lacustrine (D129 Formation, the source rock) and fluvial origin (Mina del Carmen, Cañadon Seco and Meseta espinosa formations, the reservoirs) where the main petroleum system is developed.

Geochemical logs were built with major and trace elements and they were compared with core lithology, petrophysical and oil saturation logs. The most important observation was the correlation between the K/Rb ratio and oil saturation. Moreover, the source rock interval of the D129 Formation matched with an increasing K/Rb ratio. The D-129 Formation was developed as stacked lacustrine systems with an organic matter content of I/II to II/III kerogen type, while TOC values ranges from 0.5-3%. This indicates a lacustrine environment with contribution of plant material belonging to vascular plants.

Paleobotany indicates that the paleoenvironment corresponds to a tropical-subtropical forest ecosystem. Since Potassium (K) is an essential macro nutrient for higher plants, its presence in large quantities suggests the transport via fluvial system to the lakes. As observed by several authors, organic raw material such as oil has a high K/Rb ratio with values greater than 600 units, while for clastic rocks this relationship is

about 100 units. Here, values over 200 units were observed matching with source rock intervals and reservoir beds with oil shows and production.

As a result, we show the importance of the K/Rb ratio for the evaluation of organic matter thickness in continental source rocks such as the D129 Formation. Moreover, the K/Rb high ratio values in reservoirs with oil saturation allow discriminating between oil and water bearing sands.

Introduction

This article examines the K/Rb ratio related to paleoenvironmental conditions and its consequence in the identification of source rock intervals and reservoir quality evaluation, by inorganic geochemical analysis of rock samples from cutting and cores. Cutting and core samples belong to wells of the Cañadón León Block on the southern flank of San Jorge Gulf Basin in Argentina, and operated by Sinopec Argentina (Figure 1).

Geological Setting

The Golfo San Jorge Basin is located in the Patagonia region (44º to 47º S latitude) in southern Argentina. This basin is the second most important hydrocarbon producer of Argentina after the Neuquén Basin in northern Patagonia. It is an intracratonic extensional basin developed in an east-west direction, from the Andean range to the Atlantic Ocean. The basin economic basement consists of a sedimentary-volcanic complex, the Middle to Upper Jurassic Bahia Laura Group. The sedimentary history began with Neocomian sedimentary cycle under late rift conditions, graben and half graben filling, mostly continental but in some places showing marine Pacific transgressions.

After a regional tilt of the basin, the sedimentation of Chubut Group starts with the Pozo D-129 Formation (Barremian-Aptian). This formation is mainly of lacustrine origin, with low to moderate organic content, and it is the most important source rock of the basin. Legarreta and Villar (2011) stated that the D-129 Formation has TOC values ranging from 0.5 to 3% and organic matter with I/II to II/III kerogen type. The stratigraphic column continues upwards with the Mina El Carmen, Cañadón Seco and Meseta Espinosa formations (Upper Cretaceous), a group of fluvial-shallow lacustrine units deposited under late sag conditions. These units contain the main hydrocarbon reservoirs of the basin. During the Tertiary the basin shows an interbedding of marine and continental deposits. The stratigraphic column is completed with quaternary marine and continental beds. One main characteristic of the Chubut Group is the evidence of intense volcanic activity throughout the history, expressed by the high tuffaceous content of the entire column, sometimes affecting the reservoir quality. The petroleum system is characterized by hydrocarbon migration through a network of faults and pathways. Hydrocarbon generation and expulsion began at 50-80 My and oil was trapped in both extensional and compressional structures (Figure 1).

Biogeochemical Model of Potassium Occurrence: Potassium in Plants and Algae

Potassium is an essential macronutrient for vascular plants and aquatic macrophytes. Present in the cationic form K^+, it has a key role in vascular plant growth such as osmotic regulation and enzyme activation related to photosynthesis and respiration (Taiz and Zeiger, 2002). Since potassium is a plant nutrient and rubidium is not, the K/Rb ratio in biological debris is typically higher than in soils and rocks. It is therefore possible, as recently suggested, that a considerable portion of K carried by rivers has circulated via biota, and been leached into water bodies during litter decay (Peltola et al., 2008). These authors provide detailed information on the development of the K/Rb ratio during long-term decay of litter from typical plants in the boreal zone. These data show that it is indeed possible for decaying litter to deliver degradation products strongly enriched in K over Rb. Also, McIntire et al. (2014) states that "based upon assumptions regarding average chemistry of smectites and illites, the average shale requires 13.4% potassium feldspar to provide the necessary K+ (Totten and Blatt, 1996). As the average shale only contains 5% feldspar (Blatt, 1992), an additional source for potassium is required". In the present research, this feature appears in the D-129 Formation, where shale is K+ enriched. In the case of aquatic macrophytes like the charophytes, Talling (2010) observed that the uptake and high percentage of this nutrient in the dry weight of Charophytes, was related to the seasonal depletion of K ions of the surrounding environment.

Early Cretaceous Paleobotanical and Micropaleontologial Evidence

During the Aptian, the Patagonian vegetation entered a climax stage maximizing their diversification, both generic and specific. Several conifers dominated such as *Cheirolepidiaceae*, along with *Araucariaceae*, *Podocarpaceae* and a few *Taxodiaceae*. *Benettitales,* cycads, several fern species were present along with the first appearance of angiosperm pollen. Also *Gingkoales*, *Karkeniaceae* and a few pteridosperms taxa were found. In this time, when the weather was humid and temperate to warm, the San Jorge Basin showed extensive river and deltaic systems ending in lacustrine systems. At this stage, vegetation was varied and held various ecological niches, favored by abundant rainfall and an extensive river network (Del Fueyo et al., 2007). The presence of charophytes such as *Flabellochara harrisi*, *Porochara mundula* and *Sphaerochara sp.*, characterized the Cerro Barcino and Pozo D-129 formations in the San Jorge Gulf Basin (Musacchio, 2000), adding evidence for the high potassium content of the organic debris of the shale.

Materials and Methods

The methodology is based on an important number of chemical analyses and data processing justified in the *soft inorganic geochemistry* concept (Larriestra, 2013). It 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 entire rock samples population available is analyzed, involving thousands of chemical analyses of cutting and core samples, their processing using geostatistical techniques and the integration with well log data, to produce geochemical logs.

Data Acquisition

The major, minor and trace elements analysis on cutting and core samples was performed by portable hand-held X-Ray fluorescence equipment (HHXRF) as shown in Figure 2. The analysis is performed without any destruction or sample modification. Such devices have a lower accuracy (ability to reproduce an exact concentration) 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, formation heterogeneity can be investigated with a non-destructive, simple and fast method.

Results

Core Chemostratigraphy Analysis

The HHXRF recording consisted of recording points, separated 10 cm from each other, for every core. After that, geochemical logs with trace elements were built and compared with core lithology, petrophysical logs and oil saturation (Figure 3). The most important observation was the inverse correlation between the K/Rb ratio and water saturation curve, as it is shown in the right-most track of the geochemical log. The K/Rb ratio is shown with a continuous squared curve, while water saturation is shown as a dashed curve. Moreover, it can be observed that the coincidence of the K/Rb ratio with oil shows (second track), NMR porosity curves (third track) and porosity/permeability plug curves (fourth track). Mc Intire et al. (2014) used the same relationship to analyze oil-to-source rock correlation and to differentiate organic matter or oil from inorganic materials. In this case, clean sandstone K/Rb ratio has a mean value of 90 units, while for oil-bearing sandstone this relationship is over 150 units. Other observation is the correlation of sulfur (green) and calcium (blue) in the sixth track, indicating the presence of calcium sulfate, probably related to a dry environment during Cañadón Seco Formation sedimentation. Decreasing calcium (as carbonate or sulfate) is related to increasing porosity and permeability values together with the K/Rb increase related to pore oil content.

Figure 4 displays the geochemical log of the core belonging to the Mina del Carmen Formation. As it is shown above, the inverse relationship between high K/Rb units with oil saturation values can be seen (right-most track). Moreover, porosity and permeability, either log or plug derived, are correlated with K/Rb ratio, and peak permeability is coincident with the greatest value of K/Rb ratio. In all three cores the K and Th participation is due to presence pyroclastic material.

Chemostratigraphy Analysis of Cutting Samples

In the case of chemostratigraphy using cutting samples, there are additional sources of uncertainty, and they may be originated by depth provenance, wellbore collapse and mud contamination. Moreover, the sampling frequency was irregular with intervals of 2 m to 5 m. However, similar geochemical relationships in cutting samples like those observed in cores were seen in the set of 10 wells analyzed.

Figure 5 shows the geochemical log of well A, where matching between the K/Rb curve (red, seventh track) with oil shows and gas chromatography is observed. On the bottom, calcium increase detects the presence of the D-129 Formation due to limestone, and the increasing K/Rb ratio confirms the existence of organic compounds, either oil or organic matter. In that level the correlation between sulfur and iron (sixth track) indicates pyrite, confirming the anoxic source levels for the D-129 Formation and its relationship with the K/Rb ratio.

The geochemical log of well B is shown in Figure 6. Again, the K/Rb ratio shows the relationship of oil shows and gas chromatography (center of mud logging track). As mentioned above, the top of the D-129 Formation is detected by calcium increase due to limestone presence in the stratigraphic column. In the base, interbedded with limestone, there are anoxic levels depicted by pyrite, as it is shown by sulfur/iron spatial correlation. Finally, well C (Figure 7) shows very irregular cutting sampling, but nevertheless the vertical correlation between the K/Rb ratio, oil shows and gas chromatography can be observed almost perfectly.

Discussion

Proposed K/Rb Model

The high K/Rb ratio in the oil bearing sequences and source rocks of the Chubut Group suggests that terrigenous plant debris (both terrestrial and aquatic) represent the contribution of the main potassium concentration present in the organic matter of the D129 shale deposits. The potassium is transferred to oil during the maturation process and the final result may be a huge increase of K/Rb ratio, reaching values from 877 to 2000 units, as it was pointed out by McIntire et al. (2014).

The crossplot of Figure 8a illustrates the K-Rb relationship, with the K/Rb values shown in a color scale. The blue dots correspond to raw clastic material with no organic matter, while yellow and red dots show the influence of hydrocarbon in the case of reservoir and organic shale in the case of D-129 source rocks. The histogram of K/Rb values on Figure 8b, shows that most frequent K/Rb values range from 100 to 170 units, indicating that most intervals of the stratigraphic column are inorganic while those with more than 170 units represent the influence of organic materials.

The oil bearing sandstone has a lower K/Rb ratio than crude oil because the liquid hydrocarbon content is limited to pore space and oil saturation values. But, as it is demonstrated here (Figure 8a), the K/Rb ratio in an oil bearing sandstone is significantly greater than that of a clean sandstone. On the other hand, in the source rock levels of the D-129 Formation, the K/Rb and sulfur-iron spatial correlation (due to pyrite), indicates clearly the anoxic levels with I/II to II/III kerogen type presence (Legarreta and Villar, 2011). Finally, it can be concluded that K/Rb ratio is a valuable tool to determine net pay in oil-bearing sandstone and, when combined with pyrite, it gives a better approximation to source rock interval evaluation in continental source rocks.

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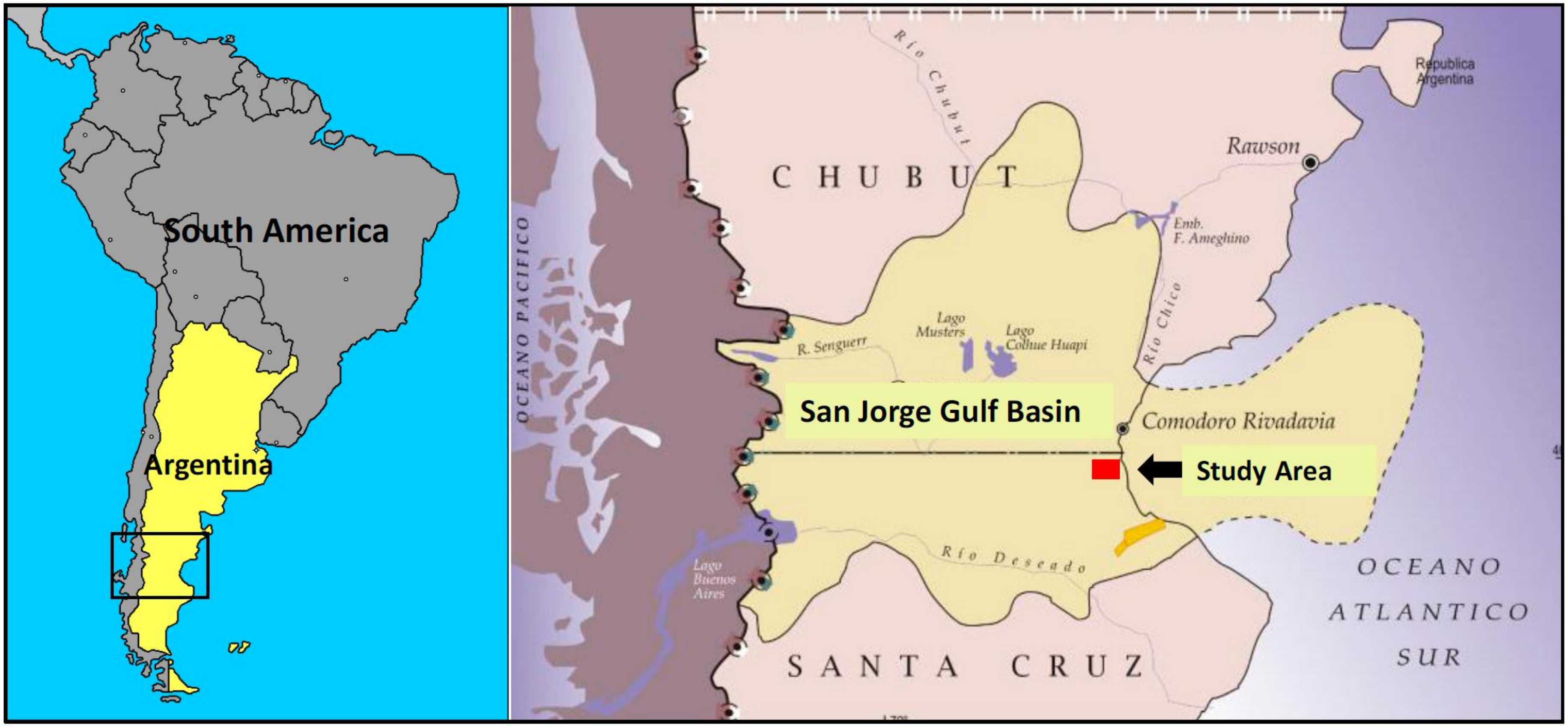

Figure 1. San Jorge Gulf Basin and study area location map.

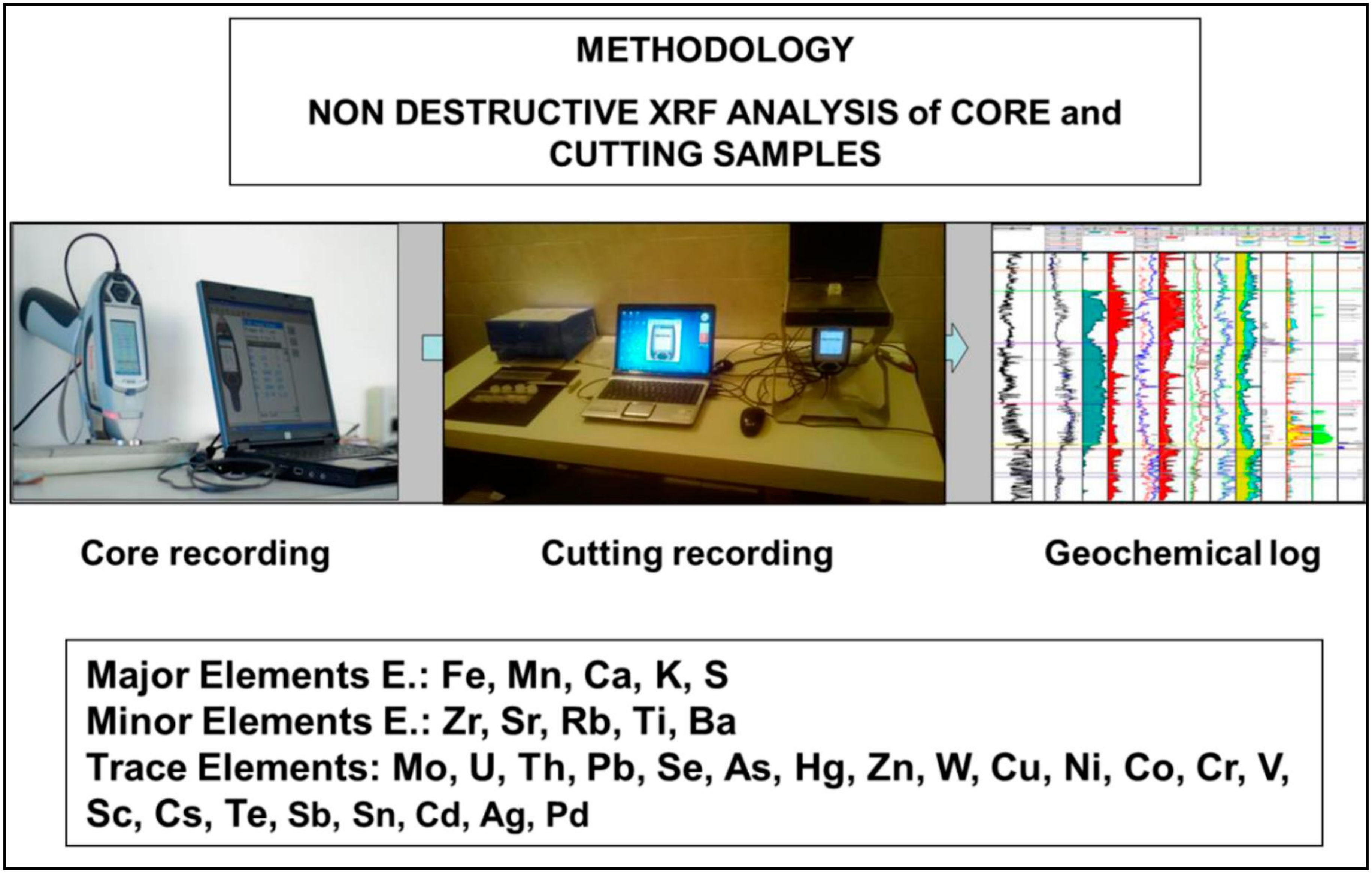

Figure 2. Rapid Hand-Held X-Ray Fluorescence equipment.

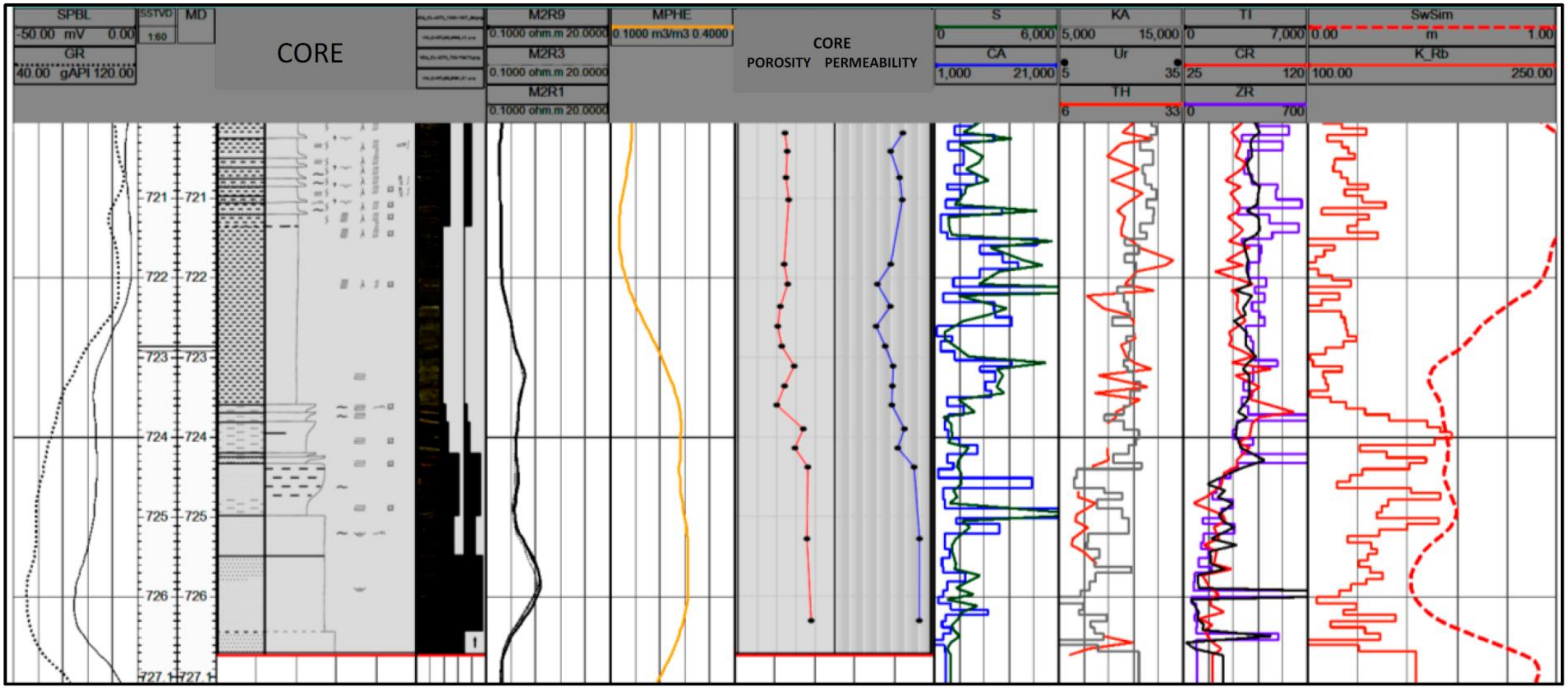

Figure 3. Core chemostratigraphy of Cañadón Seco Formation sandstone.

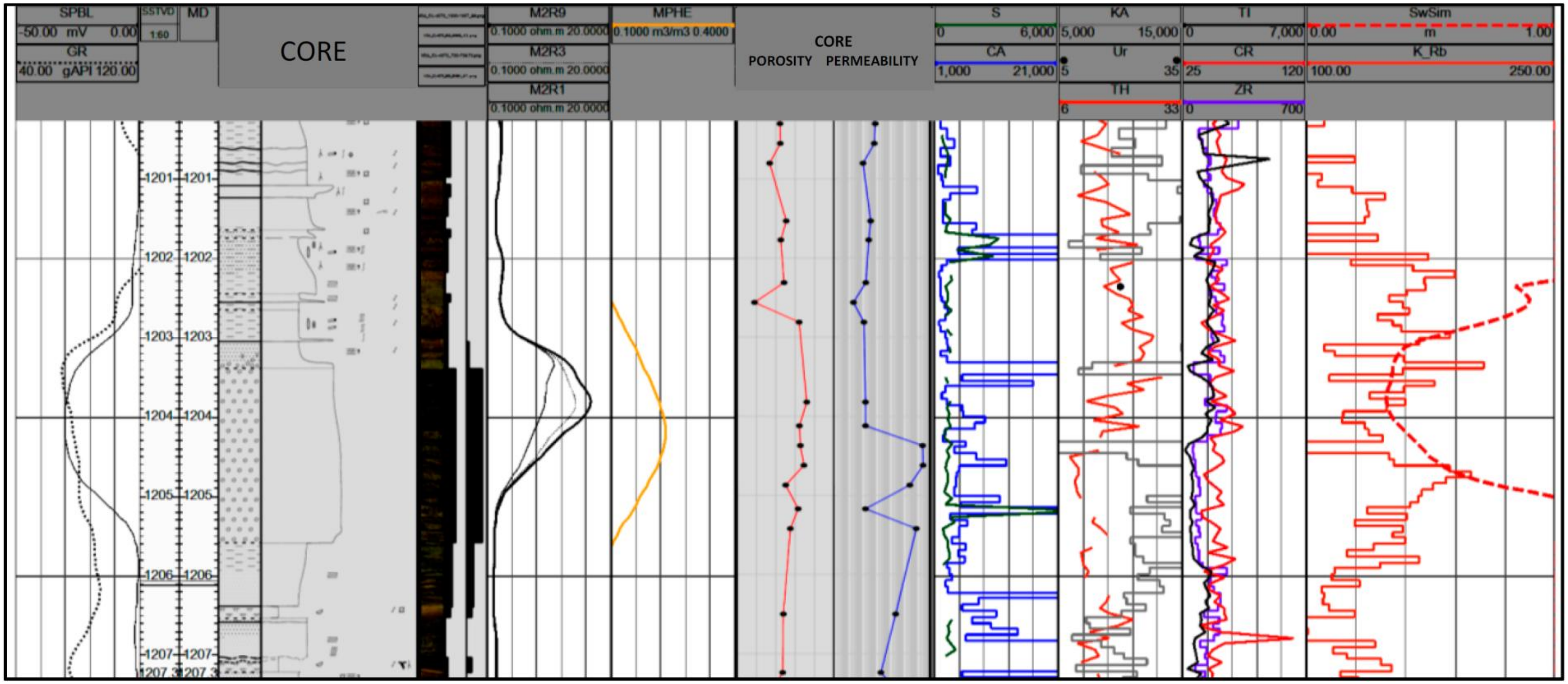

Figure 4. Core chemostratigraphy of Mina el Carmen Formation sandstone.

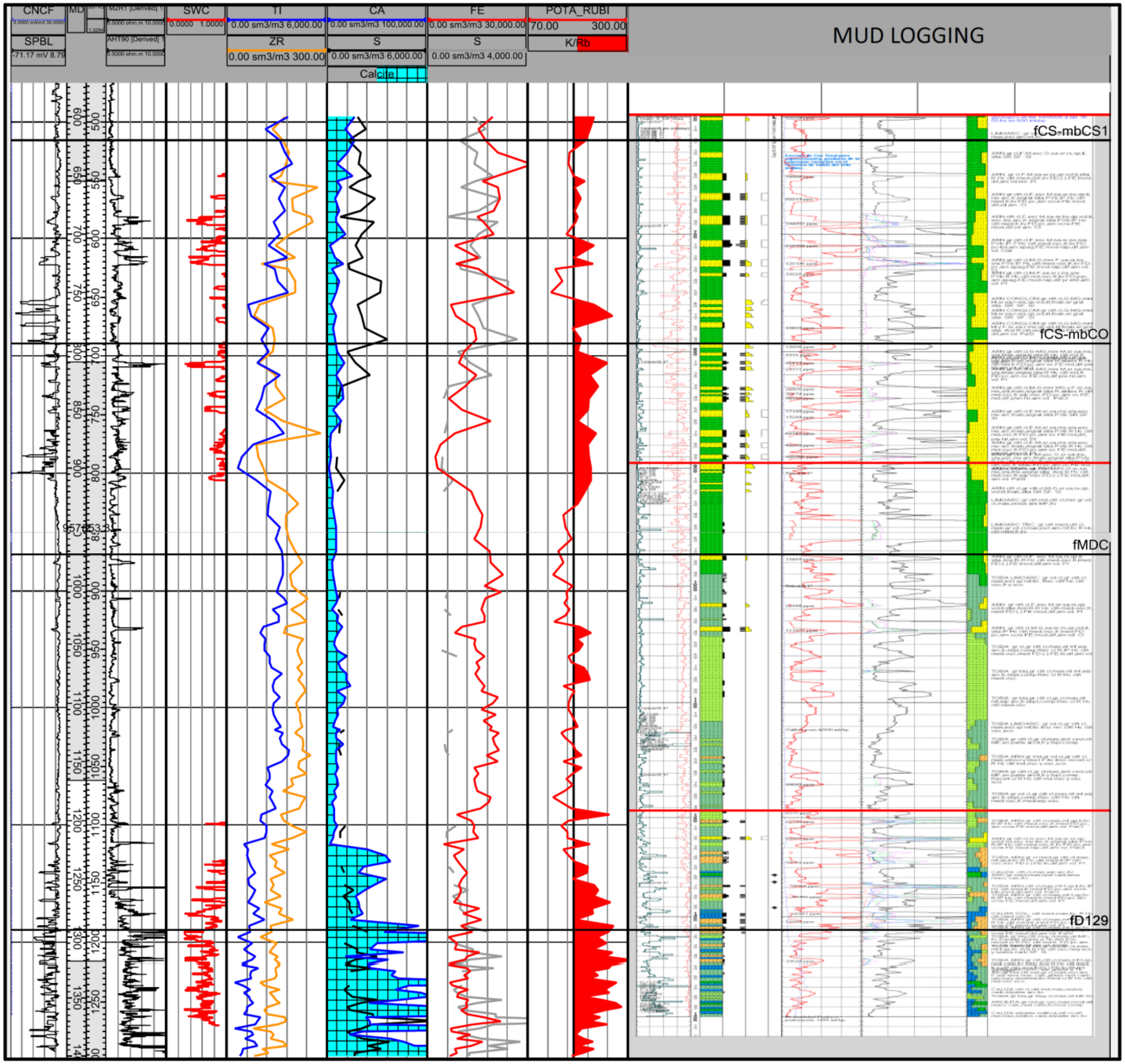

Figure 5. Geochemical log of well A.

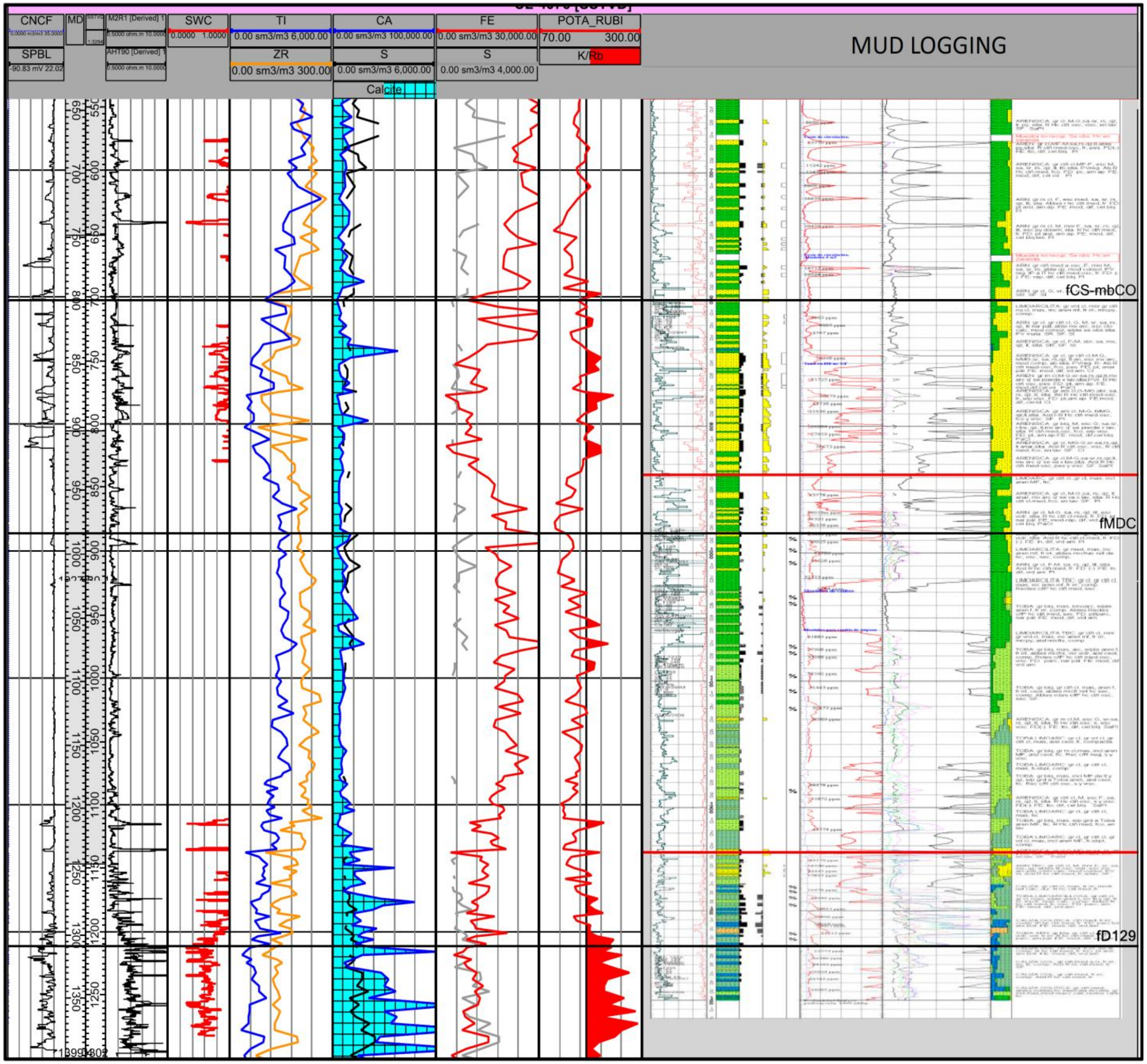

Figure 6. Geochemical log of well B.

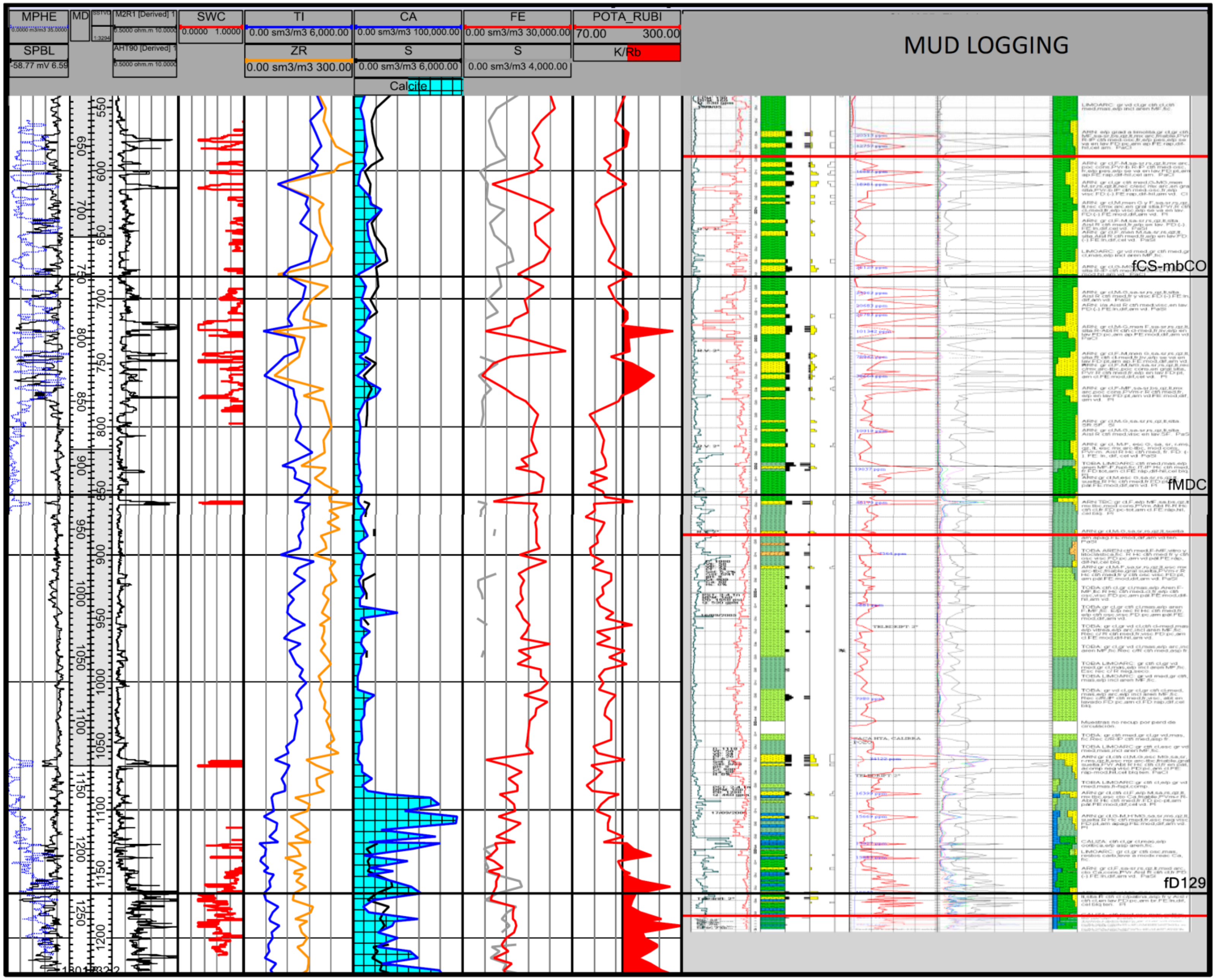

Figure 7. Geochemical log of well C.

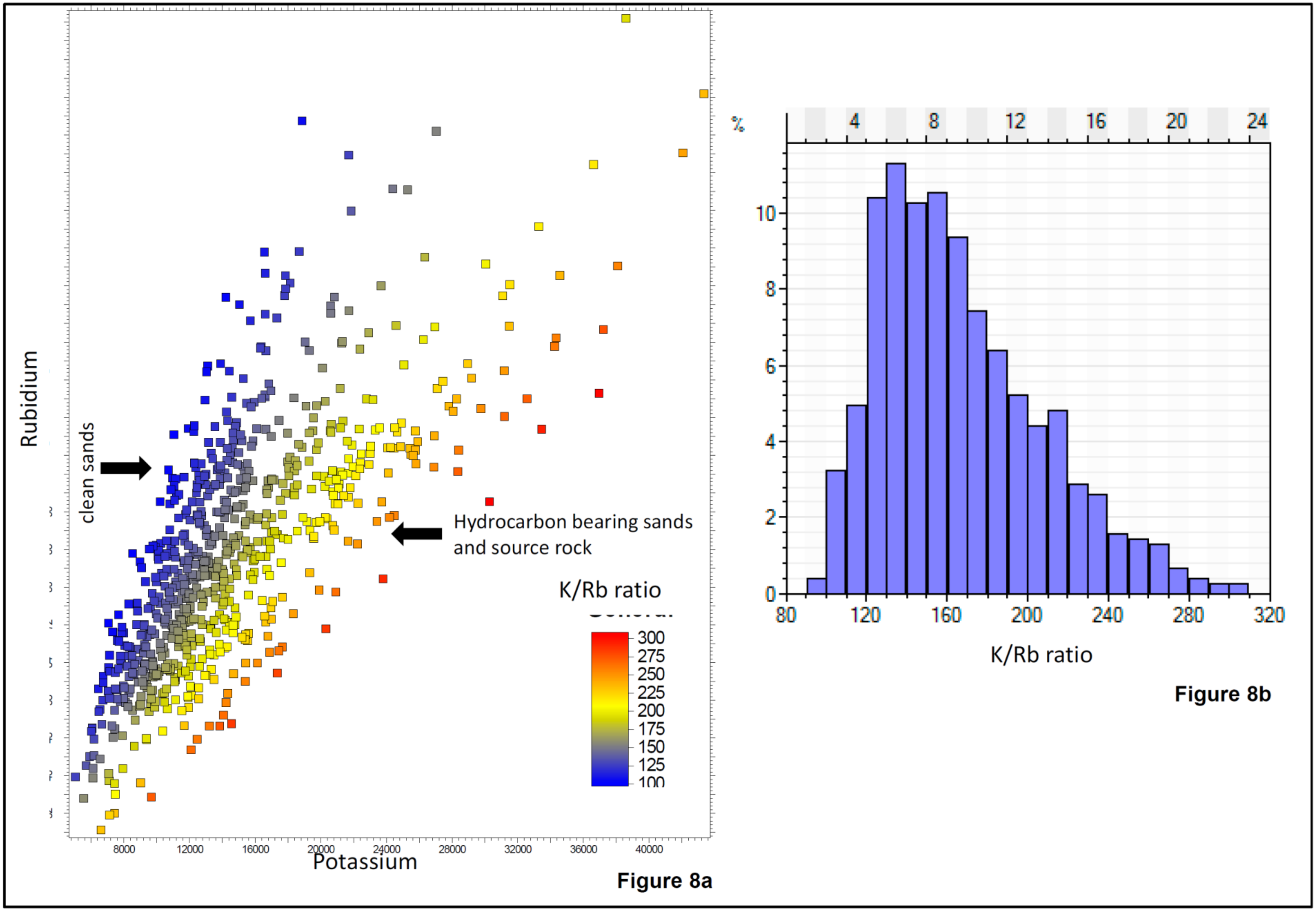

Figure 8. (a) Crossplot of K-Rb, and (b) histogram of K/Rb ratio values.