Mineral-Chemistry Quantification and Petrophysical Calibration for Multi-Mineral Evaluations*

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Abstract

There are a number of situations where modeling of mineral composition (as opposed to rock/lithology) adds real business value, for example; complex mineralogy leading to variable grain density means that more accurate estimation of porosity could be achieved through mineral volume analysis; in some reservoirs certain minerals may control permeability (e.g. diagenetic cements); the geomechanical properties of certain reservoirs may be controlled by abundance of key minerals; and mineral volume interpretations may help with well to well correlation. The mineralogical complexity of mudstone reservoirs has led to the increased usage of multi-mineral optimizing petrophysical models in recent times for estimating porosity, water and hydrocarbon volumes. A key uncertainty in these models is the log response parameter assigned for each log equation related to each volumetric variable. Default parameter values are commonly used and often need to be modified by taking into account subjective local knowledge or intuition in order to achieve a result that is considered acceptable. This paper describes the methods developed at Chevron for calibration of mineral log response parameters using core data (referred to as BestRock). Mineral log response parameters are controlled by the major and trace element chemistry of the individual minerals in the formation rock matrix. BestRock uses a non-linear approach to optimize whole rock chemistry with mineralogy to calculate individual mineral structural formulae and trace element associations from which log response parameters can be determined. Accurate quantitative phase analysis by X-ray diffraction (QXRD) and rigorous sample preparation are especially critical steps in the process. QXRD in combination with aliquot whole rock elemental analyses are processed using Chevron's BestRock optimization software to provide refined quantities of the mineral species present in the formation, their structural formulae, and their predicted wireline log responses. Calibrated petrophysical models are built from the information obtained from the QXRD and BestRock results. The method described herein provides an independent and robust method for determining petrophysical parameters that is independent of the interpreter, quick to implement, and is supported by real data. The application of this method leads to improved mineral volume predictions from petrophysical models.

Introduction

In recent years, induced gamma-ray spectroscopy tools have gained a higher degree of popularity (particularly in unconventional self-sourcing reservoirs) with the main objective of improving our ability to characterize the mineralogy and organic carbon content of the formation we are

investigating (Pemper et al, 2006, Galford et al, 2009, and Radtke et al 2012). There are a number of situations where modeling of mineral composition (as opposed to rock/lithology) can add business value to a petrophysical interpretation, for example, Claverie and Hansen (2009) describe the impact of mineralogy on permeability, water saturation and fluid sensitivity of two tight sandstones, while Skalinski and Sullivan (2001) show the importance of mineralogical assessment for the prediction of permeability in mixed lithology reservoirs.

The mineralogical complexity of unconventional reservoirs has led to the increased usage of multi-mineral optimizing petrophysical models in recent times for estimating porosity, water and hydrocarbon volumes. A key uncertainty in these models is the log response parameter assigned for each log equation related to each volumetric variable. Default parameter values are commonly used and often need to be modified by taking into account subjective local knowledge or intuition in order to achieve a result that is considered acceptable.

Methods and Data

Mineral log response parameters are controlled by the major and trace element chemistry of the individual minerals in the formation rock matrix. Many rock-forming minerals have a wide range of elemental compositions within the same mineral species, which result in significantly different physical properties such as density and other log responses. Major element variations from isomorphous substitution and solid solution are tied to each other to maintain charge balance and crystal chemical stability based on limitations of ionic size and valance. However, unlike Mg, Fe, and other major structural elements, those of low crustal abundances (such as the transitional metals and the rare earth elements [REE]) may occur in mineral structures in low parts per million (ppm) concentrations, where their exact mode of occurrence or ionic substitution is not certain.

The data presented in Figure 1 illustrates the impact of variable mineral chemistry on the total gamma-ray response (GR) values for a series of illite-smectite (I-S) minerals with variation in smectite layer content in the I-S structure and major and trace elements compositions. Inspection of this data reveals that the total GR response is not driven exclusively by the amount of potassium, but it is actually dominantly controlled by the concentration of trace elements U and Th in the I-S series. The exact crystallographic locations of U and Th in the silicate layer structure are not known, but they probably do not reside in cation exchange positions because the clay separates were thoroughly exchanged with calcium (McCarty et al., 2009). These trace elements must somehow be incorporated in the silicate layer structure or be in an auxiliary trace phase below x-ray diffraction (XRD) detection. This example highlights the importance of local calibration of mineral parameters and the potential impact that un-calibrated parameters assumed from major element composition alone could have on a log interpretation.

Discussion

In an optimizing petrophysical interpretation, assumptions about the log parameters often come from software defaults, local knowledge or other technical references (e.g. Schlumberger, 2000). Herron and Matteson (1993) present elemental analyses, mineral end-point computations, and formation properties. Herron and Herron (1997) describe an effective approach to compute specific log response including sigma, HI and thermal neutron porosity from chemical data specific to a well or field. Given the potential variability of mineral composition beyond the field scale, relying on data from varied and unrelated sources is not ideal, especially considering the natural complexity of geological environments.

Core-log calibration. If accurate quantitative mineralogy and chemistry are available from core data, a reliable estimate of the parameters of the mineral volumes can be made from a well that also has good quality log measurements. In that case, measured core mineral volumes and log measurements can be used to solve for the optimum set of mineral parameters with the core-log combined local parameter calibration method (Quirean et al., 1986). In this type of parameter calibration, the optimum set of log parameters is solved for such that it provides the best possible match to the measured log data. A key advantage is that the actual log measurements from a particular vendor are used, and that any measurement with a near linear response equation can be solved for including sonic logs (DT) and neutron logs (NPHI). However, this method also has several potential disadvantages including:

- Borehole conditions - Logging tools are sensitive to the borehole conditions in which the logs were measured. If borehole effects are not corrected then calibrated values can be biased from well to well and not reflect the actual solid mineral matrix.
- Measurement scale differences - The core sample size used for QXRD analysis is different from the log's vertical resolution interval and can lead to a discrepancy between the mineralogy measured in the core sample and the "average" mineralogy sampled for the log measurement. This problem can be minimized by homogenizing a greater vertical interval of conventional core as opposed to sampling a single point such as would be obtained from a standard core plug.
- Depth shift - If core samples are located near sharp bed boundaries, a small error in the core-log depth shift could result in significant difference in the associated log response, which can be minimized by avoiding sampling near bed boundaries.
- Fluid and invasion effects - To back out the properties of the minerals in the solid rock matrix, the effects of fluids must be correctly accounted for. Unless fluids are accurately measured in core this may be difficult to achieve.
- Non-geological constraints - Volumetric relationships between minerals can be implemented along with the upper and lower limits of optimized parameters, but detailed geochemical constraints are not possible with this method as all the inverted log response parameters are statistically derived. Therefore, results from the inversion may not follow known geochemical and structure compositional relationships for particular minerals.

Core-core calibration. The log response parameters for properties such as spectral gamma-ray (K, Th, U), matrix density (ρma), intrinsic macroscopic absorption cross section (Σi), photoelectric absorption factor (Pe), and elemental dry weights (Fe, Ca, Si, etc.) can be derived directly from the chemical composition of each mineral itself (McCarty et al, 2015). The hydrogen index (HI) can also be calculated. However, the apparent neutron porosity (NPHI) measured during thermal and epithermal neutron logging is complex and tool dependent and must be modeled using empirically derived computer codes such as SNUPAR (McKeon and Scott, 1988). In the BestRock calibration method described here, quantitative mineral analysis and whole rock chemistry from aliquot core samples are optimized to obtain the chemical composition of the individual minerals present. The chemical composition of each mineral is then used to calculate the theoretical log parameters. Solid organic matter (OM) represented by kerogen or solid bitumen is considered as a part of the mineral matrix and treated like a mineral, while the volatile hydrocarbons are removed during sample pretreatment (Kuila et al., 2014). The limitations of this method are that not all log responses can be calculated from a chemical formula such as texture-dependent sonic travel time and mineral porosity response. For mineral log responses that can be calculated directly from chemical formula, the method is vendor independent and not tool specific. Thus, this completely core-based method offers several advantages, which include:

- There are no scale issues as the chemistry and the mineral volumes are from the same sample and the log properties are calculated.
- The calculated log responses are independent of fluid volumes and properties.
- Geochemical rules and known structural composition relationships are incorporated into the assignment of major elements into individual structural positions to maintain charge balance, so that all calculated responses are geologically and mineralogically reasonable.
- Calculated responses are independent of log measurements themselves, so they do not depend on good borehole conditions or the acquisition of certain log suites in the cored interval of the calibration well.

BestRock™ uses a non-linear approach to optimize whole rock chemistry with mineralogy to calculate individual mineral structural formulae and trace element associations from which log response parameters can be determined (Figure 2). Accurate quantitative phase analysis by X-ray diffraction (QXRD) and rigorous sample preparation are especially critical steps in the process. QXRD in combination with aliquot whole rock elemental analyses are processed using Chevron's BestRock optimization software to provide refined quantities of the mineral species present in the formation, their structural formulae, and their predicted wireline log responses. Calibrated petrophysical models are built from the information obtained from the QXRD and BestRock results. The component of the BestRock workflow that sets it apart from previous work are the detailed elemental relationships and subsequent assignments of the chemical analyses used to constrain the results and maintain charge balance in the structural formulas. BestRock has three types of elemental variables (Figure 3): (1) fixed in mineral structure with little or no natural variation; (2) variable (genes, in the genetic algorithm sense), which are optimized based on the constraints that are known from the natural variations in the species; and (3) calculated, which are derived from their relationship to structural formulas of the species (McCarty et al 2015). Trace elements that do not exist in mineral structures in specific crystallographic sites (such as U, Th, Sm, Eu, Gd, Li, B, Cl, and other elements that are not fitted during the formulas' calculation) are distributed in a similar way to the major elements but without hard constraints.

BestRock-derived log response parameters for individual minerals from different basins and different locations within the same basin can vary significantly from each other, as well as from other published and default values used in modeling programs. Two graphical examples illustrating the variability in log response parameters are presented for quartz and illite + smectite (Figure 4). These data are compiled from 38 conventional cored wells from around the world. Each BestRock well analysis optimized QXRD mineral and whole-rock elemental data with a minimum of 40 samples and up to 150 samples that were determined to be in the same geochemical system. For many of the mineral species, this wide variation is not a surprise considering the natural elemental variation in mineral species and the variable distribution of trace elements in different geological environments, which will alter the mineral's physical properties. However, minerals with stable chemistry such as quartz (Figure 4A) also have significant variation in log response because of variations in the associated trace elements.

The sensitivity of trace element variation in log response parameters to model calculations in obtaining mineral and fluid volumes is significant. This sensitivity is illustrated in Figure 5, where mineral volume estimations are compared using both vendor default and BestRock derived values, along with the QXRD mineralogy from 50 core points along a stratigraphic interval of 70 m (229 ft). The main differences between the BestRock and default log response parameters are the clay and calcite density, Pe of the clay, and the thorium and potassium responses of the orthoclase (see Table 1). Although it may not be obvious what is driving the model solution, it is likely that the total clay content was being

driven in part by thorium, where the BestRock increase in orthoclase thorium (with no change in orthoclase calculated volume) left less thorium to be apportioned to total clay, which resulted in the lower clay volume. At the same time, the lower clay volume along with the lower BestRock clay Pe value allowed more model calcite prediction. Such complex interactions are commonly observed in Multimineral analysis; they are relatively easy to understand in retrospect but difficult to predict in advance.

Summary

Significant global variation exists in individual mineral wireline log response parameters because of the natural variation in the chemical composition of minerals. At the field scale, usually the individual mineral composition is approximately constant for a given stratigraphic unit and only the concentration will change, which can be accurately measured by modern QPA methods such as XRD and FT-IR. BestRock is a nonlinear optimization model that combines multiple core measurements from a geochemically uniform section to produce a field- or formation-specific mineral-based geochemical model that defines the major and trace element composition of each mineral species present. This strategy provides the section-specific wireline petrophysical log responses of the rock matrix from which to build a multimineral-type petrophysical model to account for the total solid and fluid volumes over the logging interval.

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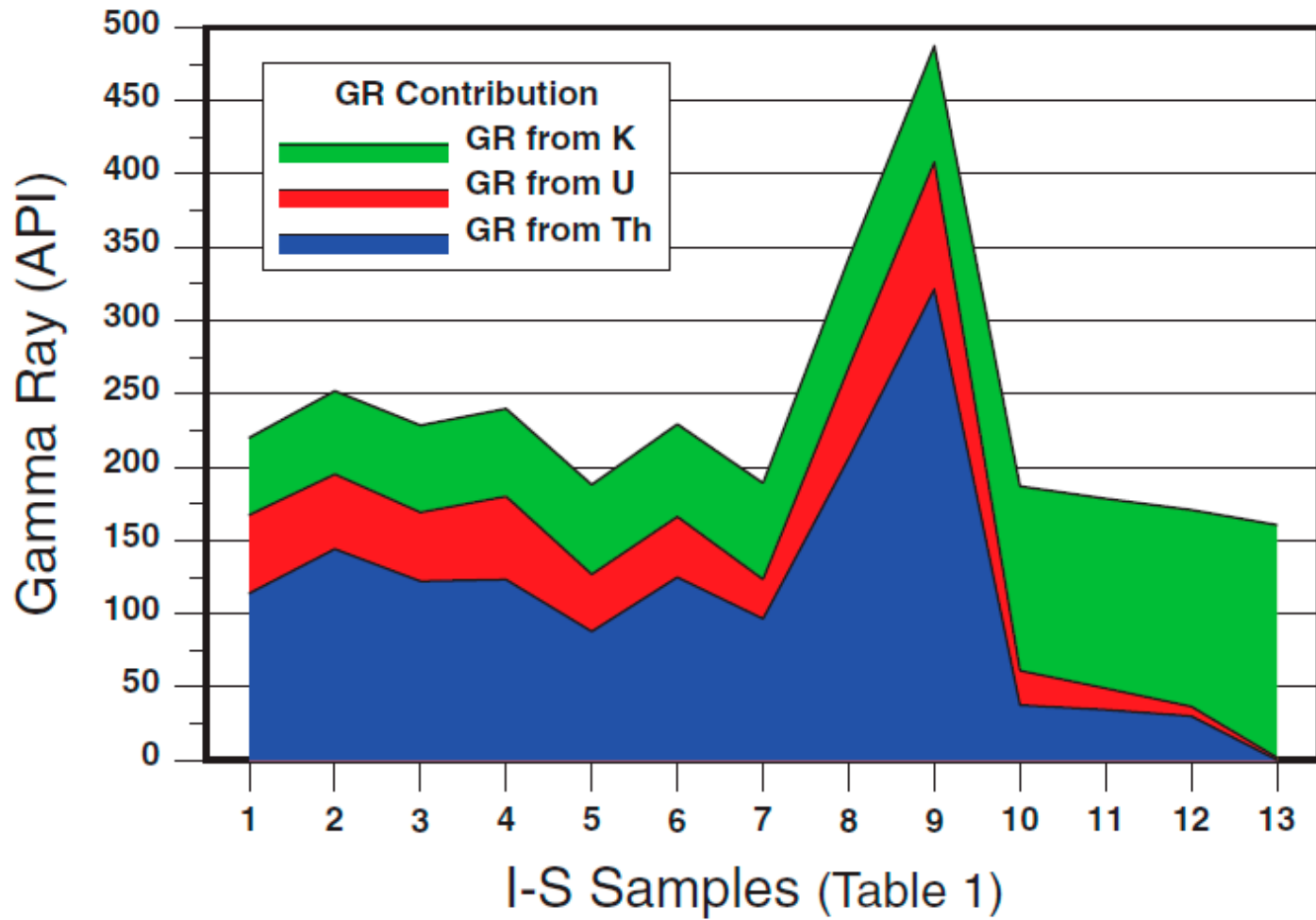
Figure 1. Comparison of measured spectral gamma-ray contributions in a mixed-layer illite-smectite (I-S) series selection of samples (McCarty el at, 2015).
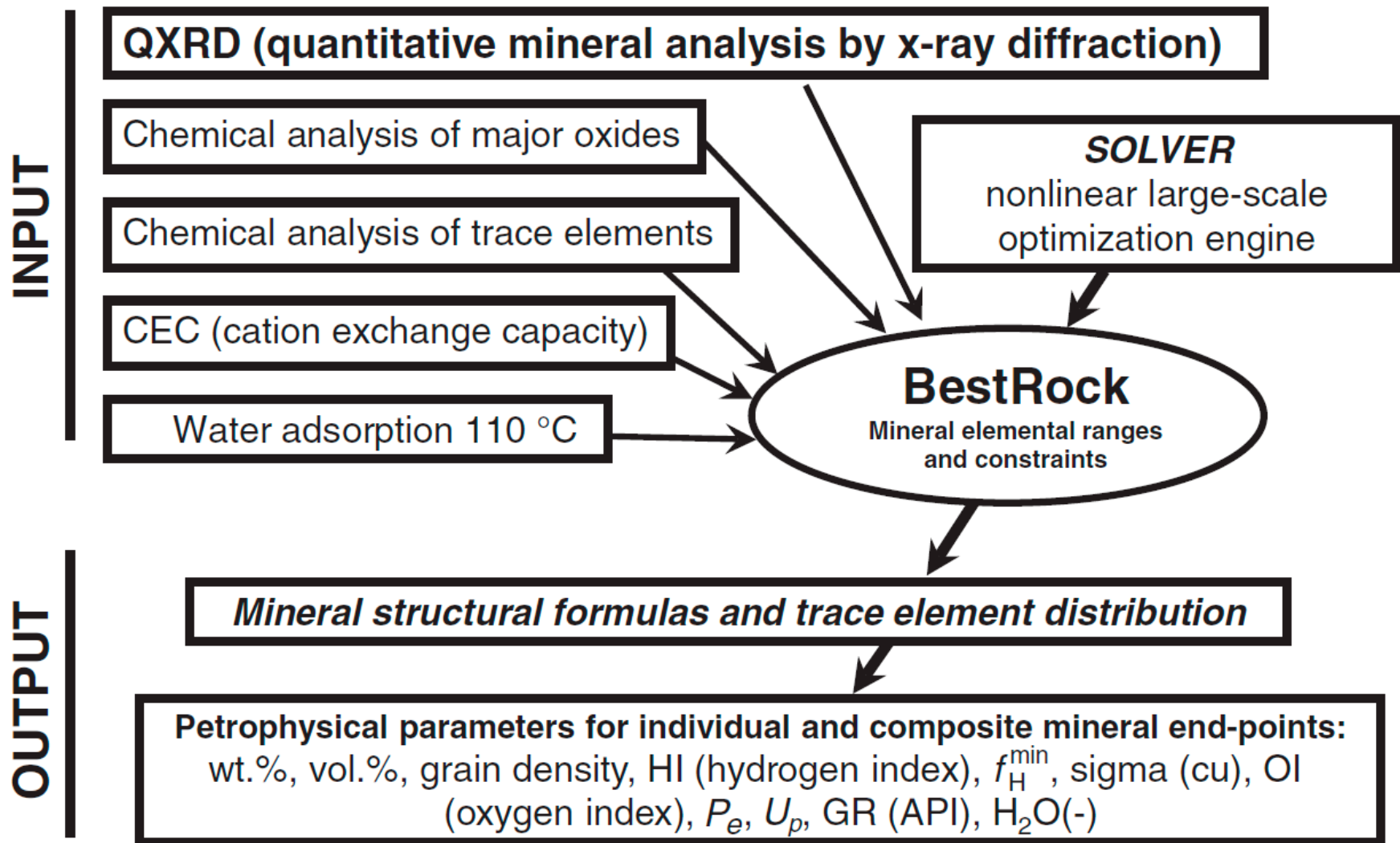
Figure 2. BestRock workflow and optimization scheme to adjust mineral formulas and minimize the difference between measured and theoretical whole-rock elemental content based on quantitative phase analysis mineral data (McCarty el at, 2015).

Mineral	Structural formula
Quartz	SiO_2
K-feldspar	$(K,Na)AlSi_3O_8$
Plagioclase	$NaAlSi_3O_8 - CaAl_2Si_2O_8$
Excess-Ca Dolomite	$Ca(Ca,Mg,Fe)(CO_3)_2$
Mg-Calcite	$(Ca,Mg)CaCO_3$
Dolomite	$Ca(Mg,Fe)(CO_3)_2$
Siderite	$(Fe,Mg,Ca,Mn)CO_3$
Ankerite	$Ca(Mg,Fe)(CO_3)_2$
Chlorite	$(Mg,Al,Fe^{2+},Fe^{3+})_6(Si,Al)_4O_{10}(OH)_8$
Biotite	$(K,Na)(Al,Fe,Mg)_3(Si,Al)_4O_{10})(OH)_2$
Berthierine	$(Al_{0.75},Fe^{3+}_{0.25})_{x+2z}((Fe^{2+}_{0.67},Mg)_{0.33})_{3-x-3z}\square_z(Si_{2-x},Al_x)O_5(OH)_4$
Illite + Smectite (average)	$(K,Na,Ca)_{Fix+Exch}(Al,Fe,Mg)_2(Si,Al)_4O_{10}(OH)_2$
Trioctahedral Smectite	$(Na,Ca)(Al,Fe,Mg)_2(Si,Al)_4O_{10}(OH)_2$
Phillipsite	$K_2(Ca,Na)_4(Al_6Si_{10}O_{32})\cdot 12H_2O$
Mordenite	$(Ca,Na,K)_8(Al_8Si_{10}O_{96})\cdot 28H_2O$
Clinoptilolite	$(Na,K)_6(Al_6Si_{30}O_{72})\cdot 20H_2O$
Sepiolite	$Ca(Mg,Fe^{3+}, Al,\square)5(Si,Al)_8O_{20}(OH)_{10}\cdot 4H_2O$

x = gene, y = calculated, z = fixed, $\square$ = site vacancy

Figure 3. Example of BestRock optimization strategy for some of the mineral phases hsowing elemental isomorphous substitutions that are (1) optimized (red), (2) calculated based on optimized site occupancy (blue), and (3) stoichiometric elements of stable content (black), McCarty el at, 2015.
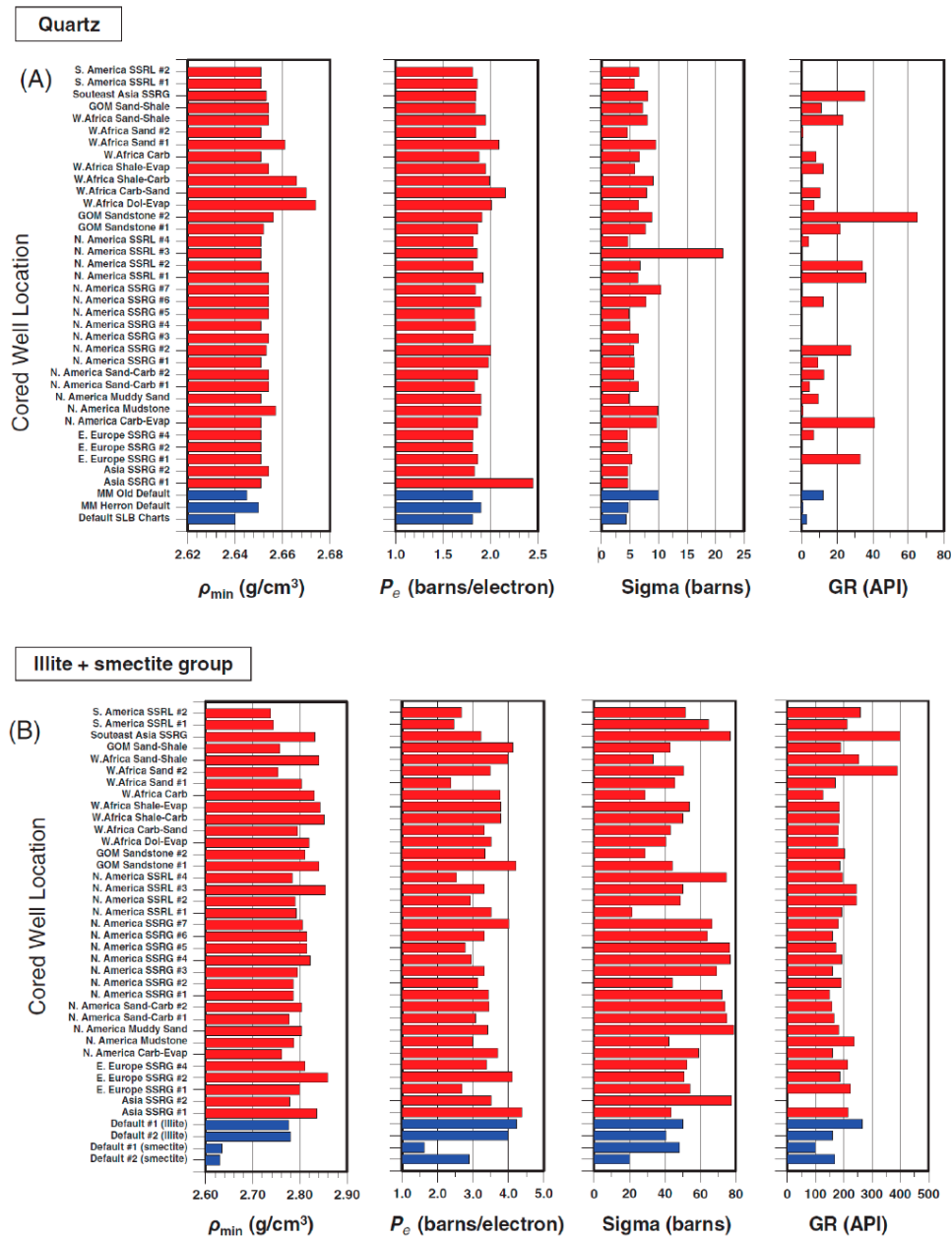
Figure 4. Example of mineral density, photoelectric effect, sigma capture cross section, and total gamma-ray (API) log responses for (A) the quartz and (B) the illite + smectite group from different locations, as determined by BestRock (red) and compared with a set of default values (blue). SSRL = self-sourcing reservoir liquid; SSRG = self-sourcing reservoir gas (McCarty el at, 2015).
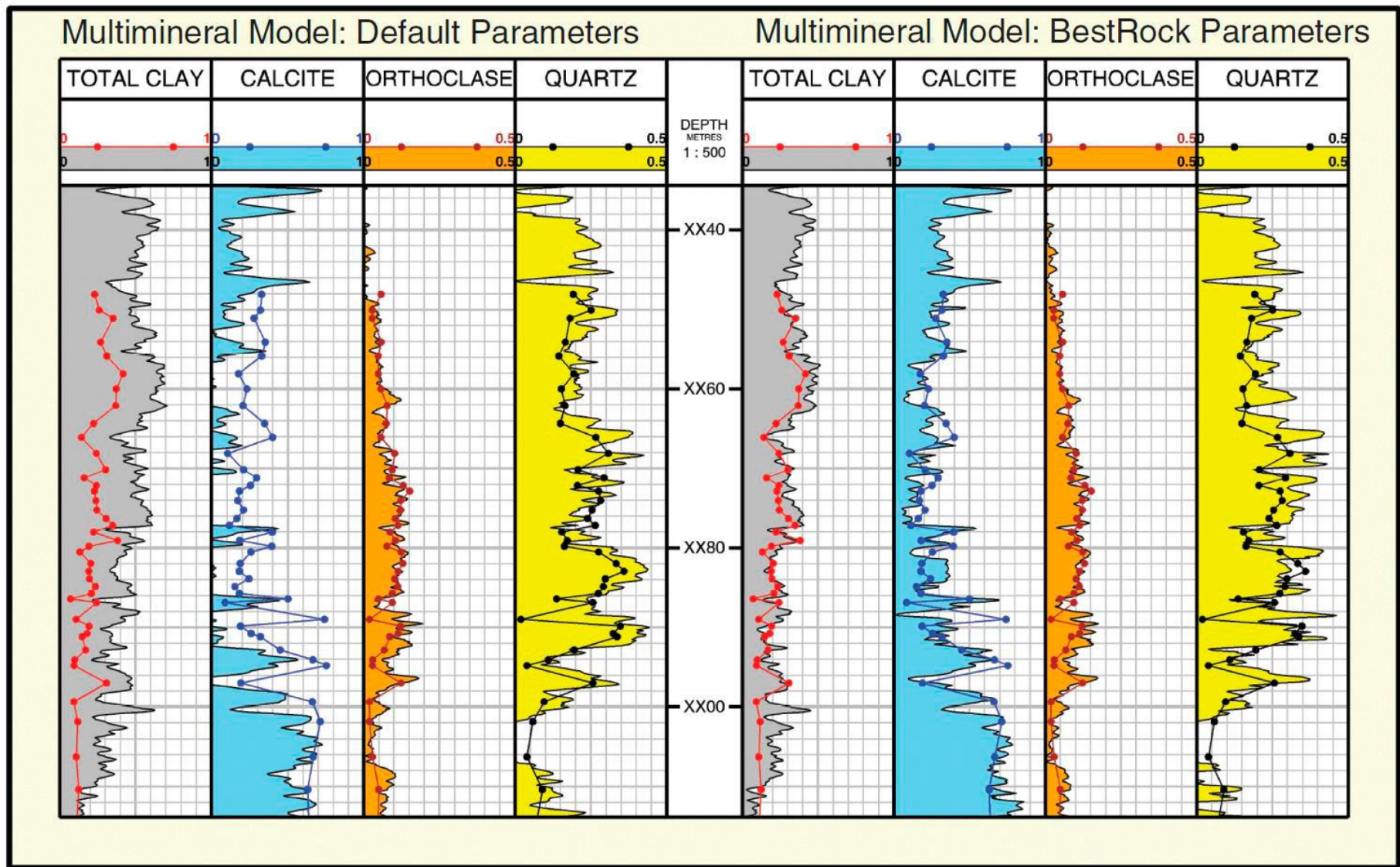
Figure 5. Mineral volume estimates from two Multimineral models, using vendor default log values (left) and BestRock values (right) compared with mineral fractions calculated from core samples using Chevron's quantitative phase analysis by x-ray diffraction (QXRD) method (dots), McCarty el at, 2015.

Mineral	ρ_g (g/cm^3)			U_p (Barns/electron)			Th (ppm)			K (%)		
	D	BR	Delta	D	BR	Delta	D	BR	Delta	D	BR	Delta
Quartz	2.65	2.65	0.00	5.04	5.29	0.25	0.00	4.20	4.20	0.00	0.00	0.00
Calcite	2.71	2.75	0.04	14.13	14.22	0.09	0.00	0.00	0.00	0.00	0.00	0.00
Orthoclase	2.57	2.58	0.01	8.71	8.06	0.65	1.10	11.70	10.60	10.21	13.94	3.73
Illite	2.78	2.82	0.04	11.12	9.14	1.98	12.30	15.10	2.80	4.48	6.29	1.81
Pyrite	4.99	5.02	0.03	82.22	84.75	2.53	0.00	0.00	0.00	0.00	0.00	0.00

Note: Total clay content is modeled, but QXRD results show the clay content is dominantly the Illite + Smectite group (>90%) having low expandability (<10% smectite layers in I-S), with minor amounts of kaolinite and chlorite in the clay fraction. The vendor defaults chosen were that of Illite.
*ρ_g = mineral density; U_p = volumetric absorption index; Th = thorium; K = potassium; Delta = difference.

Table 1. Comparison of Default (D) and BestRock-Calibrated (BR) Log Response Parameters for the Mineral Estimations Shown in Figure 5 (McCarty el at, 2015).