Core Analysis with the Tracer

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Key Points

Tables and Figures

Bruker Application Paper

Objective

The use of handheld XRF has seen growth in many applications, but a chief obstacle is the mass analysis of data. This requires a highly specific calibration as well as the ability to quickly generate data in a time series (e.g. line plot). The critical need is to generate clear trends that will assist in the identification of formation zones for petroleum as well as risks to the quality of petroleum, including contamination by Sulfur. The technology can also be important for environmental reclamation of former wells.

Exploration

Petroleum originates from the remains of plankton that falls to the bottom of the ea. Typically, the remains are consumed by bacteria and protists and the carbon is cycled back through the ecosystem. The calcium carbonate remains of the plankton are reworked into the seabed and over geologic time scales slowly crushed to form limestone deposits. However, this process requires oxygen for the organisms that consume the plankton to survive. In anaerobic conditions, the organisms all die, and the result is a large build up of carbon on the sea floor. Unusual sulfides tend to precipitate in these conditions, resulting in the deposition of Molybdenum, Vanadium, Sodium, Magnesium, and Iron. The presence of hydrocarbons will be indicated by sulfides formed with these elements.

Decision Making

Once hydrocarbon sources are found, they must be drilled with care. The act of drilling into the geologic formations overlying deposits presents risks for contamination. One chief threat can be sources of excess Sulfur such as Calcium Sulfate, more commonly known as Gypsum or Yeso. Should Sulfur enter the reservoir, there is a serious risk of poisoning the well. As such, rapid decision making is needed while drilling. Unfortunately, many companies now rely upon laboratories removed from wells to process samples to determine risk. This means that critical decisions can be delayed for some time.

Reclamation

Following the cessation of drilling activities, effort is required to remove contaminant metals and other undesired materials from the well sites. This requires the ability to see many different elements that are of concern, and not just heavy metals.

Tracer Solutions

As the Tracer can be used to measure concentrations of elements that range from Neon to Uranium, it is capable of fulfilling a significant need in each critical step of the process:

- For exploration, the Mudrock Calibration can be used to quantify concentrations of indicator elements for the anaerobic conditions that are critical to the formation of hydrocarbon reserves.
- In the course of decision making on site, the Tracer can be used to detect what the chemical composition of the formation is during drilling. It can be used to get early results on what concentrations of what elements are present, potential hazards, and perhaps most critically to determine when to begin horizontal drilling.
- As has been the case for years, the Tracer can be used to detect heavy metals and other potential contaminants in the course of recovering land that has been used for drilling.

Core Scanner

DeWitt Systems has developed a mobile core scanner compatible with the Bruker Tracer XRF system that can enable the sequential analysis of cores up to 1m in length. It operates using 100μm steps, resulting in a resolution of 10,000 measurements per 1m section of core. This high resolution data can be used to pinpoint the exact areas where conditions for hydrocarbon preservation are ideal. The unit is designed to provide the Tracer either a vacuum within the instrument or helium gas flow through the instrument. The latter is critical to accurate sodium analysis of the core.

CALIBRATIONS FOR QUANTITATIVE ANALYSIS

Mudrock Calibrations Set

The Mudrock calibration set was developed by Dr. Harry Rowe at the Bureau of Economic Geology. The set consists of 26 reference samples gathered from multiple drill cores based on elemental diversity (up to 96 reference samples are possible if a customer would like to work with Dr. Rowe). The calibration itself was published in the academic journal Chemical Geology (324-325). This calibration can handle a wide arrange of different matrices, from limestone to near pure silicates. Its principle aim is to quickly quantify the contents of drill cores.

As noted earlier, the critical needs are twofold:

1. Determine matrix of sediment being drilled through (principle elements: calcium, silica), along with the presence of potential threats to hydrocarbon reservoirs (sulfur).
2. Determine ppm concentrations of trace elements such as Molybdenum to identify paleoclimatic conditions that would have facilitated the preservation of hydrocarbons.

The combination of light and trace elemental analysis, in conjunction with a mobile handheld unit and core scanner, mean that this technology can be put into any field operation to determine elemental concentrations of cores in real time. Instead of having to send samples to distant laboratories and wait for results, all analysis can be done at the primary site location.

Measurement Conditions:
Light Elements: 15 keV, 25 µA, No Filter, Vacuum Conditions
Trace Elements: 40 keV, 11 µA, Ti/Al Filter, Dry Air Conditions

Citations:
Rowe H, Hughes N, Robinson K. 2012. The quantification and application of handheld energy-dispersive x-ray fluorescence (ED-XRF) in mudrock chemostratigraphy and geochemistry. Chemical Geology 324-325: 122-131

DIFFERENTIATION

Other Handheld Units

The Tracer approach to data analysis is completely different than that of industrial handheld units with regard to cores. Rather than take a data point and save the results to an excel file, the Tracer does continuous analysis. The product PDZ files are then brought into a calibration spreadsheet and quantified all at once. These results can then be used to provide time-series analysis (visible in Figure 1). The idea isn't to say that "this core has 100 ppm of Molybdenum, let's focus here", it is to say that "based on the overall trends we are seeing, there seems to be a consistently high concentration of Molybdenum in this area in the context of the whole core, let's focus here". The Tracer is aimed at producing trendlines, not points. Rather than handling 10,000 small spreadsheets, the Tracer's goal is to produce a history of each element in the core, and to let the geochemistry speak for itself. High Sulfur? That means you will need to cap that section of the core. High Molybdenum, perhaps it is time to consider a horizontal drilling of that region. Hi Silicon? Keep moving as you are.

In general, every measurement parameter of the Tracer can be modified (Energy, Current, Filter, and Atmosphere). Calibrations can be customized toward different samples, and new reference standards can be added at any time and applied retroactively to all previously collected data.

Laboratory Systems

The accuracy of the Tracer is better suited to comparison with traditional laboratory systems, such as benchtop ED-XRF, WD-XRF, and ICP systems. Each of these systems has considerable advantages over the Tracer but they all have one critical limitation - they are in the lab. The Tracer can be placed in the field to reduce wait time and transportation risks and costs. The information from the Tracer system can be used to inform decision making on-site quickly. For many of the elements critical to the analysis of cores, including Silicon, Calcium, Sulfur, Vanadium, Iron, Molybdenum, etc., the Tracer's detection limits are sufficient to answer necessary questions.

MOLYBDENUM (MO)

CALCIUM (CA)

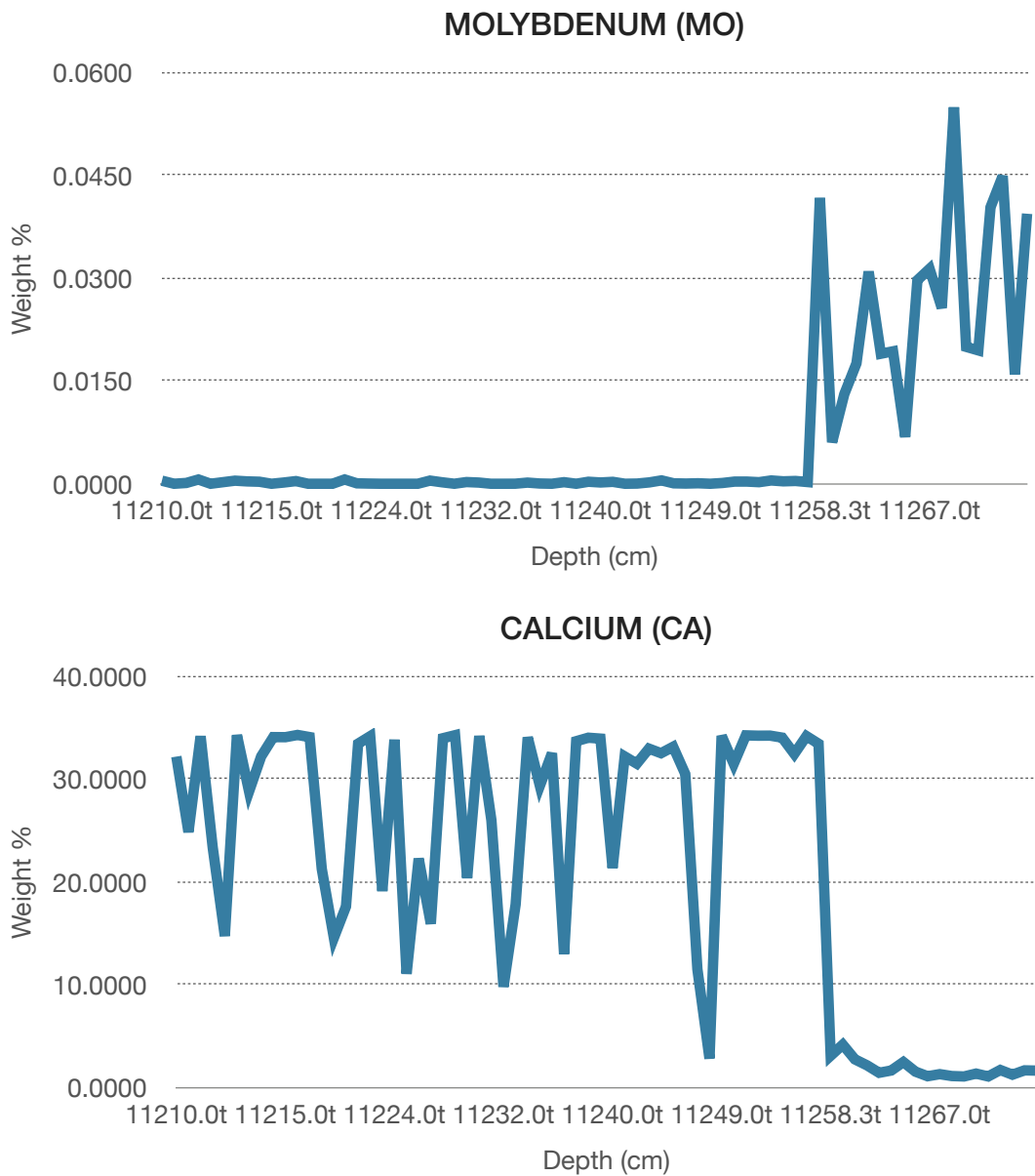
Figure 1: Example of time-series analysis of elemental data from a core.

The top graph shows small concentrations of Molybdenum (0 - 600 ppm), while the bottom shows Calcium (0 - 35%). An increase in Molybdenum and a decrease in Calcium at 11258 cm indicate the precipitation of Molybdenum sulfide, which forms in anaerobic conditions. This depth underground has a higher chance of hydrocarbons.
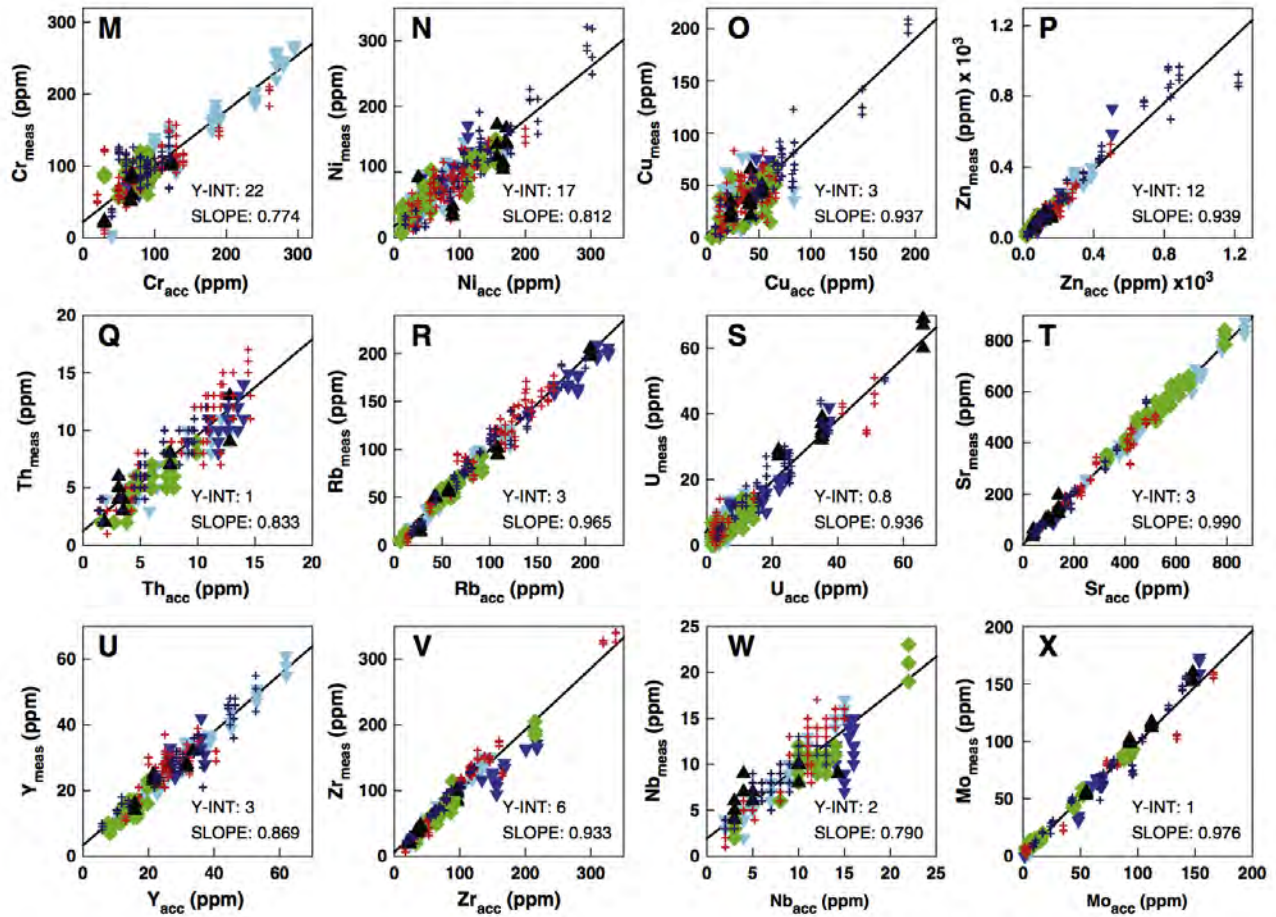
Fig. 2 (continued).

Figure 2: Validation of the Mudrock Calibration (from Rowe et al. 2012:126)

Element	Symbol	Minimum	Maximum
Arsenic	As	<1 ppm	69 ppm
Barium	Ba	30 ppm	1.5%
Calcium	Ca	786 ppm	34.66%
Cobalt	Co	1.4 ppm	46.8 ppm
Chrome	Cr	10 ppm	295 ppm
Copper	Cu	5 ppm	429 ppm
Iron	Fe	4267 ppm	6.53%
Manganese	Mn	77 ppm	1239 ppm
Molybedinum	Mo	<1 ppm	166 ppm
Niobium	Nb	2 ppm	16 ppm
Nickel	Ni	14 ppm	302 ppm
Lead	Pb	<1 ppm	28 ppm
Rubidium	Rb	6 ppm	224 ppm
Antimony	Sb	<1 ppm	47.1 ppm
Tin	Sn	<1 ppm	14 ppm
Stronium	Sr	39 ppm	869 ppm
Thorium	Th	2 ppm	14 ppm
Titanium	Ti	479 ppm	5336 ppm
Uranium	U	1 ppm	51 ppm
Yttrium	Y	6 ppm	62 ppm
Zinc	Zn	20 ppm	836 ppm
Zirconium	Zr	17 ppm	338 ppm

Table 1: Quantification limits for Mudrock Trace calibration

Element	Symbol	Minimum	Maximum
Aluminum	Al	9103 ppm	13.07%
Barium	Ba	30 ppm	1.5%
Calcium	Ca	786 ppm	34.66%
Cobalt	Co	1.4 ppm	46.8 ppm
Chrome	Cr	10 ppm	295 ppm
Copper	Cu	5 ppm	429 ppm
Iron	Fe	4267 ppm	6.53%
Potassium	K	1411 ppm	4.3%
Magnesium	Mg	2412 ppm	10.25%
Manganese	Mn	77 ppm	1239 ppm
Sodium	Na	964 ppm	8606 ppm
Nickel	Ni	14 ppm	302 ppm
Phosphorous	P	87 ppm	9819 ppm
Sulfur	S	200 ppm	5.35%
Silica	Si	3.75%	38.2%
Titanium	Ti	479 ppm	5336 ppm
Vanadium	V	22 ppm	1720 ppm
Zinc	Zn	20 ppm	836 ppm

Table 2: Quantification limits for Mudrock Major calibration

	Na	Mg	Al	Si	P	S	Cl
	0.5%	0.05%	150 ppm	100 ppm	100 ppm	100 ppm	75 ppm
K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Co**
75 ppm	75 ppm	75 ppm	60 ppm	30 ppm	15 ppm	15 ppm	8 ppm
Ni	**Cu**	**Zn**	**As**	**Se**	**Sr**	**Mo**	**Rh**
5 ppm	4 ppm	4 ppm	3 ppm	3 ppm	1 ppm	1 ppm	1 ppm
Ag	**Cd**	**Sn**	**Sb**	**Ba**	**Ta**	**W**	**Au**
1 ppm	1 ppm	1 ppm	1 ppm	60 ppm	1 ppm	3 ppm	3 ppm
Hg	**Tl**	**Pb**	**Th**	**U**			
3 ppm	1 ppm	3 ppm	3 ppm	3 ppm			

Table 3: Detection limits in a pure silicate