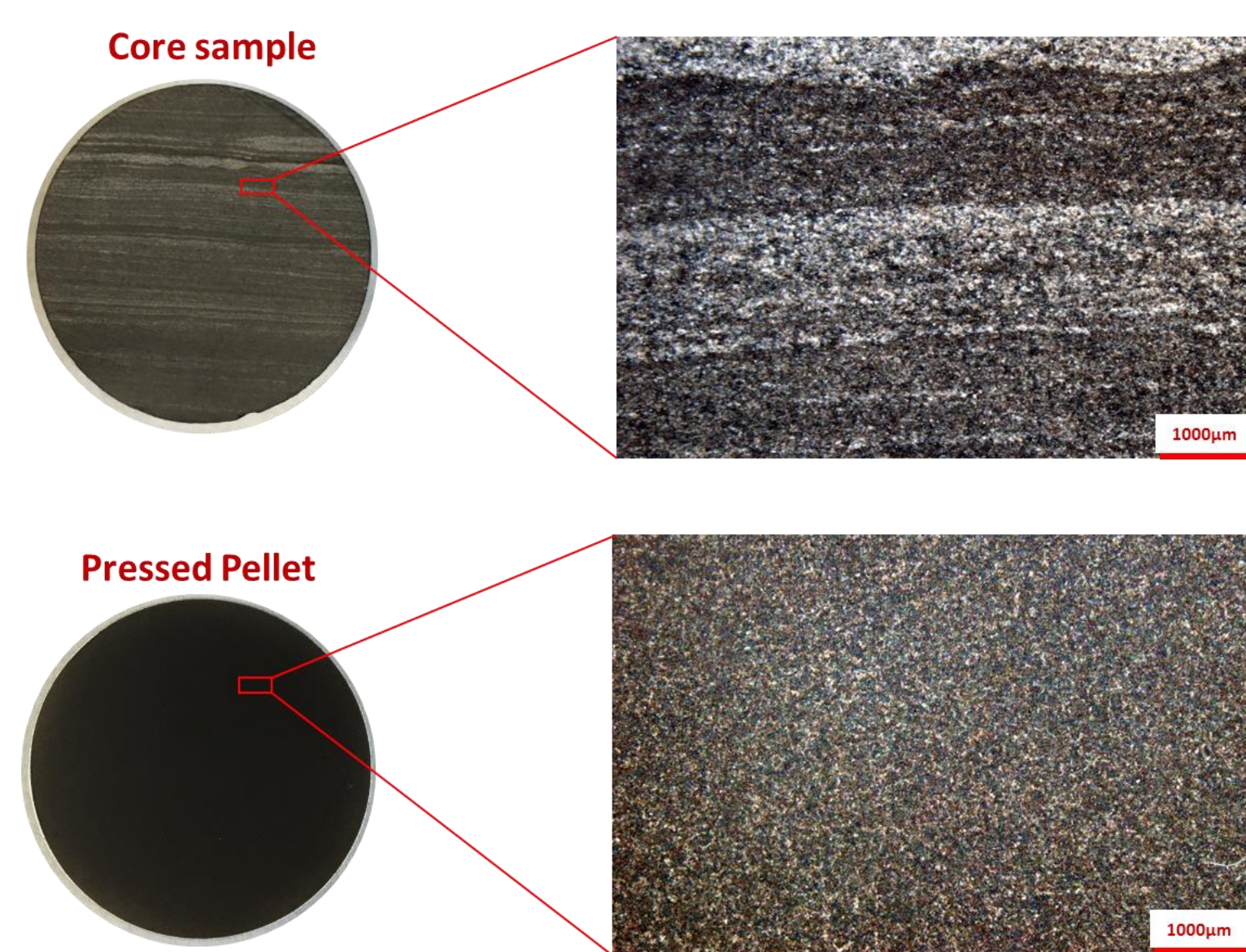


Introduction

X-ray fluorescence (XRF) spectroscopy is a common tool in inorganic geochemistry analysis for further chemo-stratigraphic study. Two main configurations of XRF include Energy Dispersive (ED) and Wavelength Dispersive (WD). WD-XRF is known for its lower detection limit and higher energy resolution compared with ED-XRF which is mainly used in the handheld instrument (hXRF) for rapid analysis. Therefore, WD-XRF produces more accurate results on elemental analysis in general (Fitton 1997). Although the specimens can be analyzed without any sample preparation on the drill core and flat rock surface for rapid analyses and further chemostratigraphic characterization using hXRF, results should be used with caution. hXRF potentially suffers from several limitations which can compromise its analytical accuracy. Inherent characteristics of this configuration can cause: (1) Improper sample analyzing depth for light elements (2) X-ray absorption under air environment and (3) low energy X-rays detection limits (Young et al. 2016). In addition the inadequate or the lack of sample preparation can cause: (4) heterogeneity of geological specimens, especially in the sedimentary rocks (5) non-uniform particle size and particle size greater than the analytical depth



Reliable result requires a proper sample preparation prior to the exposure of a sample to the X-rays due to heterogenic nature of geological samples regardless of any subsequent spectroscopic analysis method.

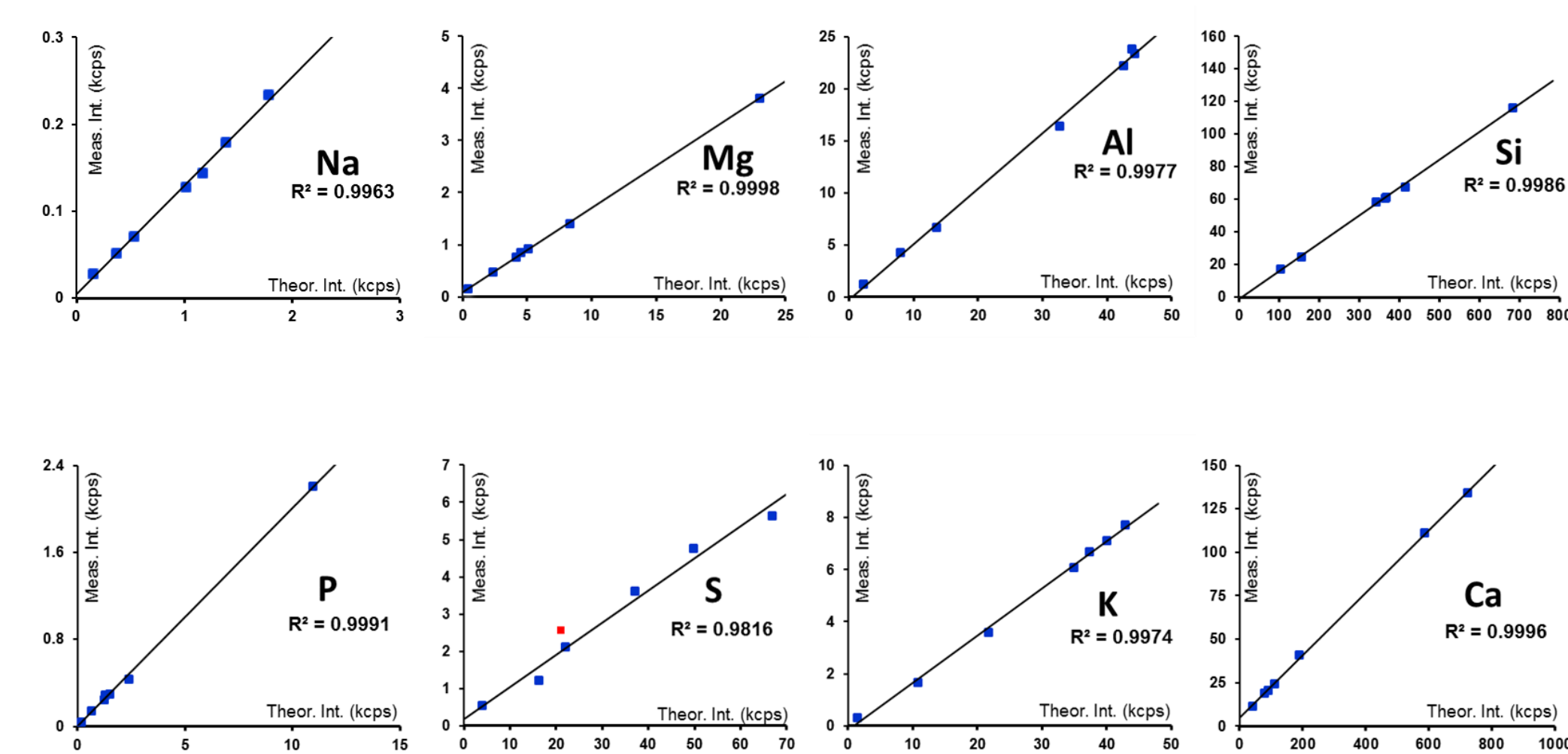


Two common methods of sample preparations for XRF are Fusion Bead (FB) and Pressed Pellet (PP) techniques. FB provides a complete homogenous glass for analysis and eliminates the mineralogical and particle size effects, providing the best accuracy and reproducibility. In the FB method, however, volatile constituents (such as F, S, Cl, Br) and trace elements can evaporate and escape from the sample to some extent due to the high fusion temperature (1000-1200°C). The PP method on the other hand is relatively simpler, sample preparation is minimal and it does not compromise the analysis of volatile elements. In addition, the detection limit of analysis is lower because little to no dilution is involved.

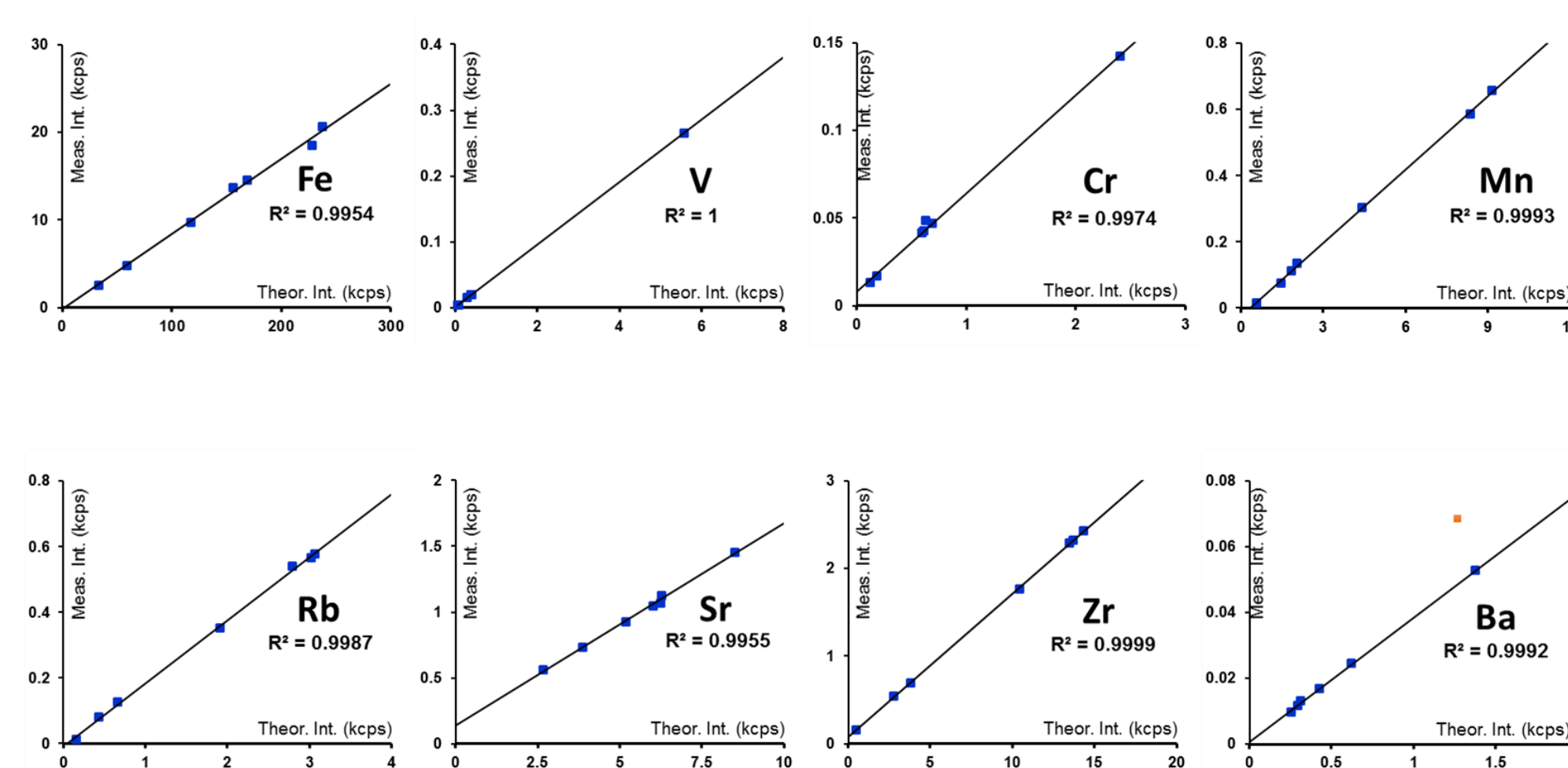
Pressed Pellet Method Development

Creation of calibration lines from PP samples of geological specimens where the mineralogy varies largely are not straightforward (e.g. clays). Mineralogy and particle size heterogeneity effects tend to cause several analytical errors in this case. Therefore, certified reference materials with different matrices do not necessarily fit in one desired calibration. Consequently, we used samples of the same geological formation to develop and validate the method. Core samples were pulverized with a Tungsten carbide grinding mill. The particle size range of pulverized samples was monitored and controlled using a Laser Diffraction Particle Size (LD-PSD) analyzer. Finally, pulverized samples were pressed with a hydraulic automatic press under optimized conditions. To generate the calibration lines for elements, seven samples were used as in-house standards to develop a sufficiently broad range of major (Na, Mg, Al, Si, P, S, K, Ca, Ti, Fe) and trace elements (V, Cr, Mn, Fe, Rb, Sr, Zr, Ba) using PP sample preparation method.

Calibration plots



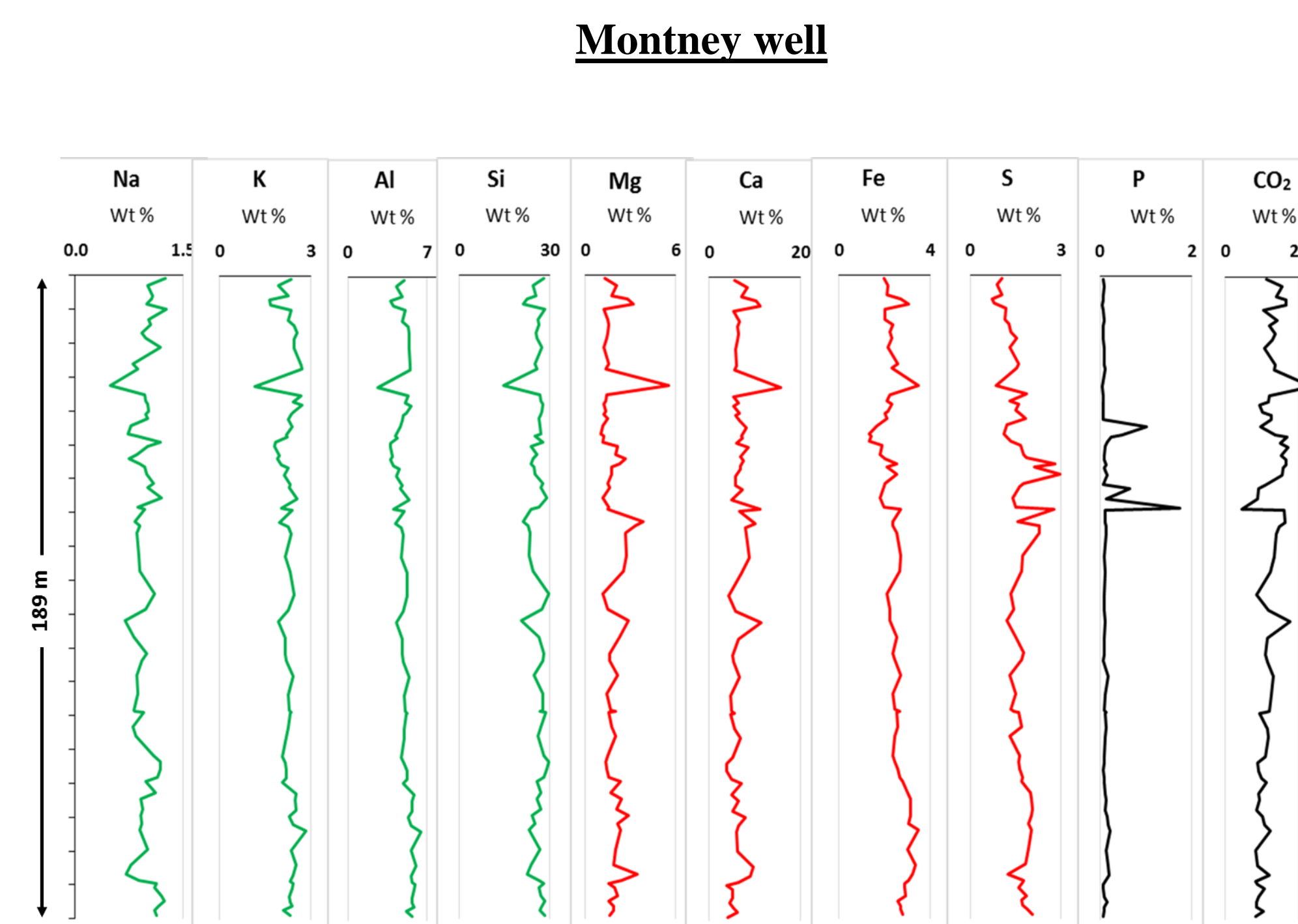
Linear calibration plots for major elements are shown in above illustration accompanied by the correlation coefficients (R^2). Very strong correlation with minimum 0.99 R^2 values (except for S with 0.98) is obtained for almost all the elements. This can only be achieved with (1) the excellent sample preparation technique, (2) reliable configuration of the benchtop WD-XRF, (3) advanced Fundamental Parameter algorithm (FP) of the instrument to correct the overlap and inter-element effects in matrix and (4) the proficiency of the analyst to generate accurate and precise results.



WDXRF also detects Na, which is undetectable by hXRF analyzers due to the low X-ray power limitations. Identifying Na is important in sedimentary rocks as it indicates the presence of Na-feldspar, certain clays (Na-Montmorillonite) and halite. Furthermore, this method gives reliable results for S which hXRF is incapable due to matrix effects (Rowe et al. 2012) or FB method due to the volatility of S at high temperatures. Calibration plots of Na and S are shown in above figure.

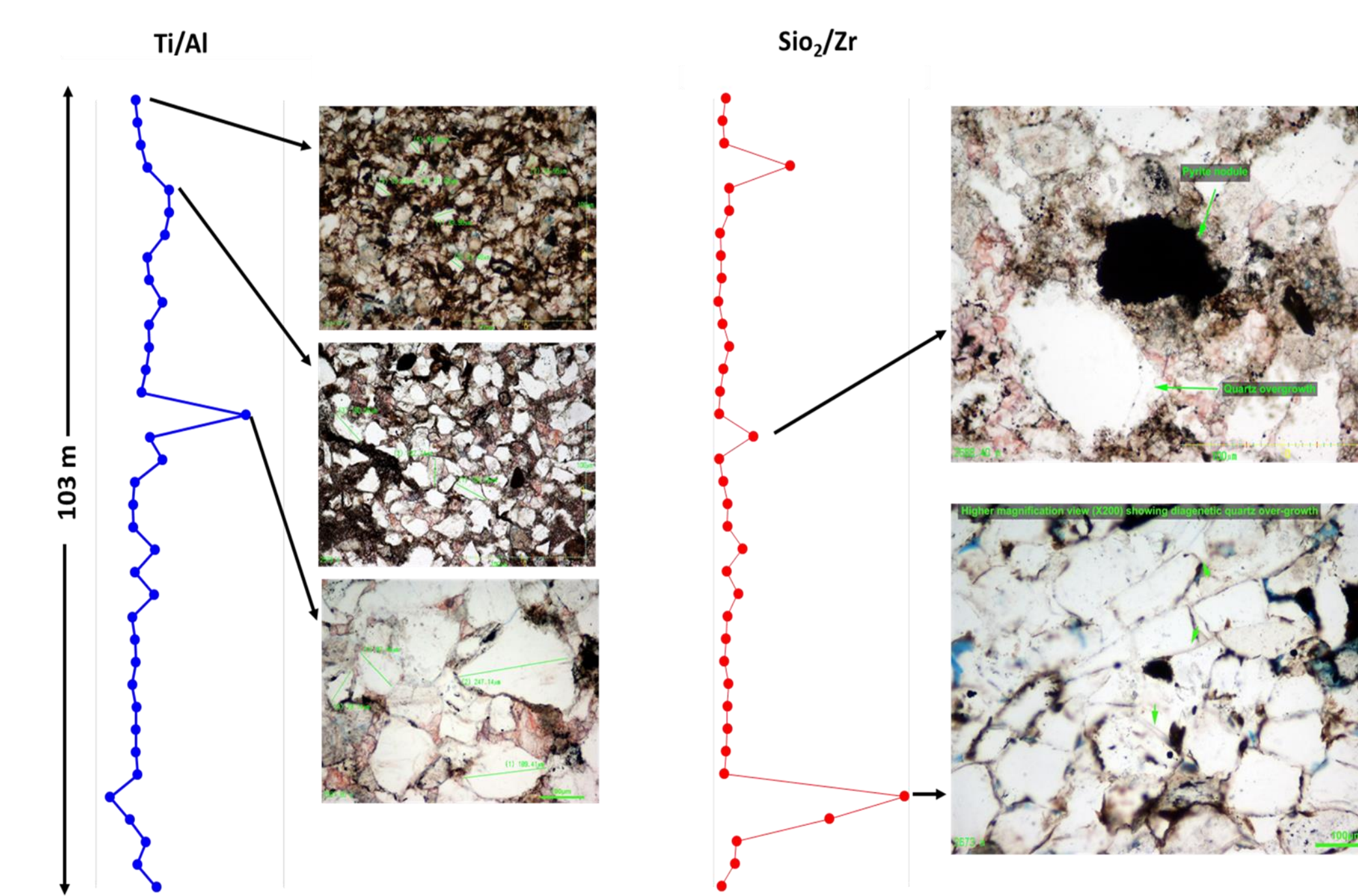
XRF Data Interpretation

The purpose of this study was to quantify commonly occurring major and trace elements in sedimentary environments by the PP method, thereby reducing the mineralogical and particle size effects. Elemental data of a Montney well is shown below.



Elemental results provide valuable information about stratigraphy, depositional environment, mineralogy, diagenesis, etc. For example Ti/Al ratio gives information about sediment transportation and grain size variation. Following Ti/Al ratio and grain size measurements taken with petrographic microscope are in good agreement, where higher Ti/Al ratio indicating relatively larger grain sizes. SiO_2/Zr ratio is an indicator of quartz cementation or biogenic silica precipitation.

Ratio correlations

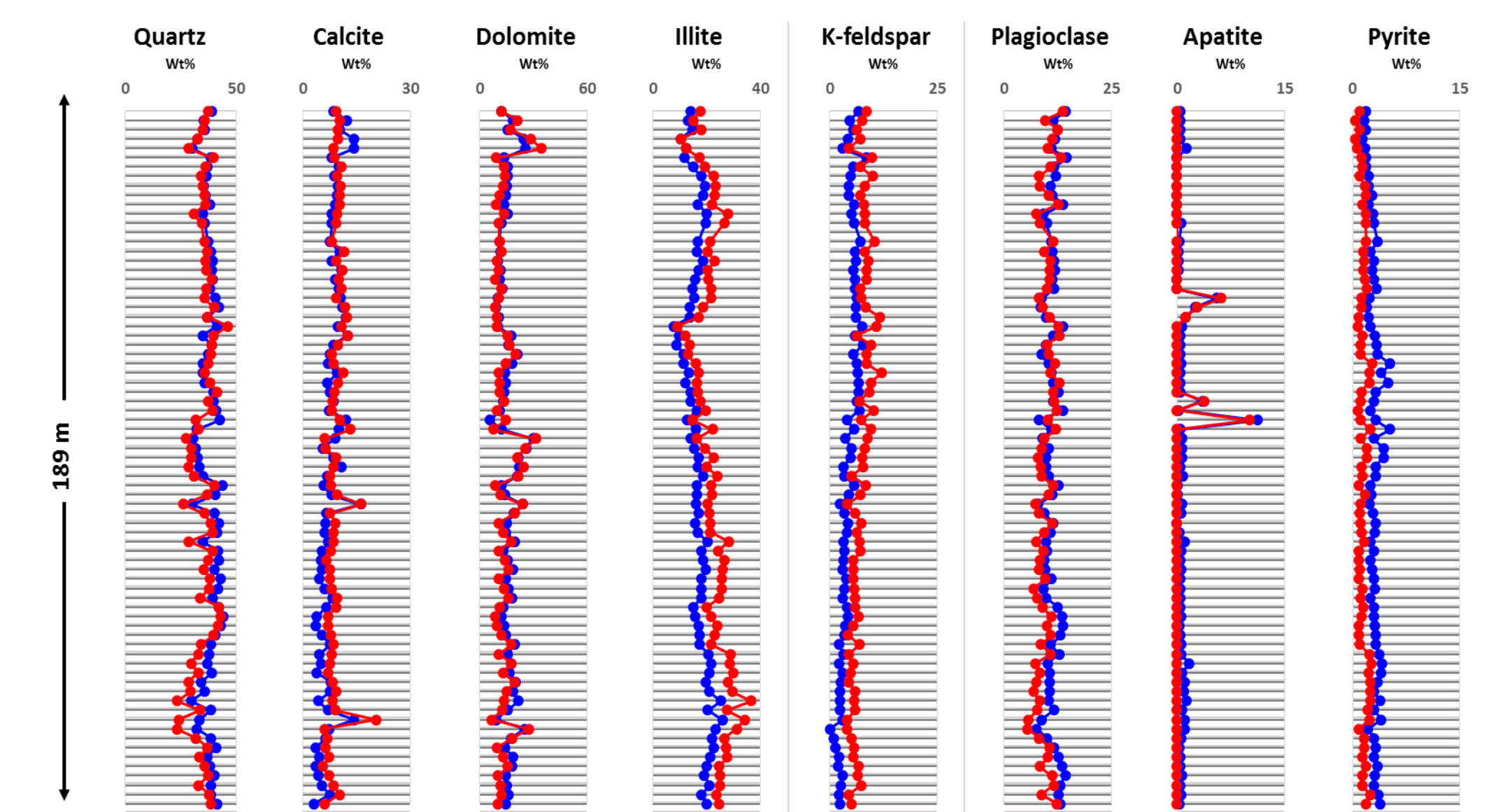


Mineralogy

XRF analysis provides chemical composition of the rock sample in the form of element or oxide. Interpretation of these chemical logs can offer valuable information, for example higher amount of Al_2O_3 in a sedimentary rock indicates higher clays or feldspars contents, high SiO_2 shows quartz percentage, and amount of phosphorus is an indication of apatite mineral. Geoscientists, petrophysicists and engineers rely more on the mineral framework of a rock in general as compared to the chemical constituents. Therefore, minerals can be calculated from elemental composition by using normative mineral algorithm.

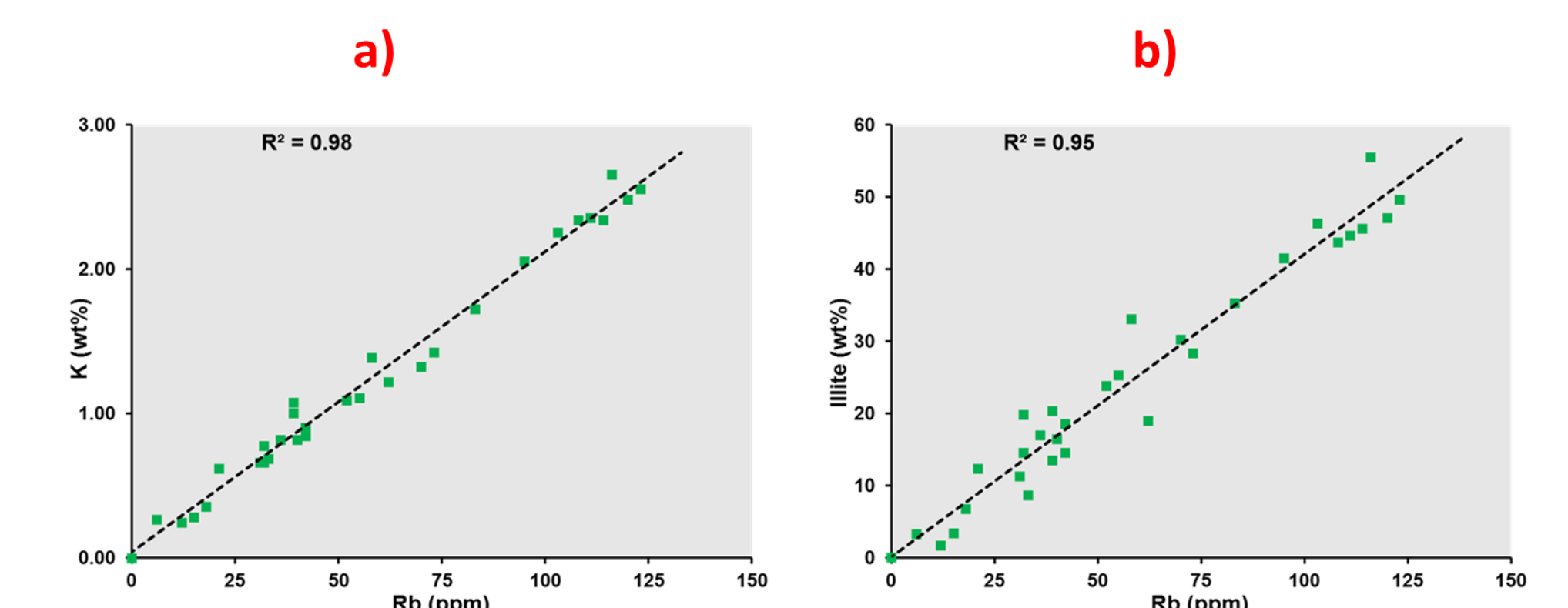
Normative Mineralogy

Comparison of calculated normative minerals (blue) and X-ray diffraction analysis (red) has been shown below for a Montney well.

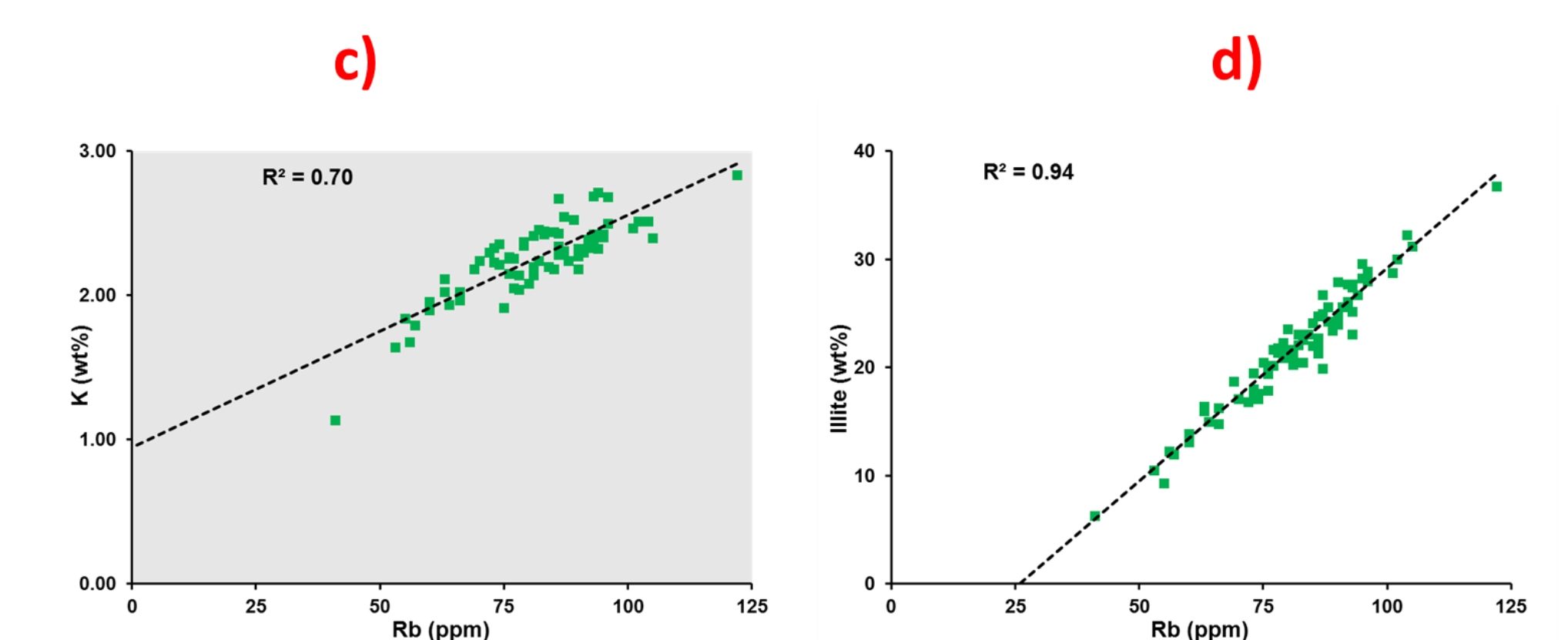


Most of the available algorithms use only major elements to calculate normative mineralogy. While in sedimentary system complex minerals like k-feldspar and illite consist of similar chemical composition (e.g. K, Al, Si). This similarity makes it difficult to calculate normative minerals. To overcome this, we are using the possible indicative trace elements to distinguish the presence of each mineral.

Nordeg well – k-feldspar not present



Montney well – k-feldspar present



For instance, Rb with effective positive surface charge adsorbs onto the illite resulting strong correlation between illite and Rb regardless of the presence of other k-minerals such as k-feldspar (Fig b and d). However, the correlation of the Rb and K can be used as an effective discriminator of the source of K-minerals. A strong correlation between Rb and K with a zero intercept means that illite is the only source of K (Fig a) whereas a weak correlation between the two and a positive intercept denote a mixed source of K constituent (illite and K-feldspar, Fig c).

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