



## **A Semi-Quantitative Assessment of Clay Content in Sedimentary Rocks Using Portable X-Ray Fluorescence Spectrometry**

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**Abstract:** This paper deals with assessment of clay content in sedimentary rocks using portable X-ray fluorescence spectrometry. Whilst measuring chemical properties of sedimentary rocks, it was noted a positive, quasi-linear correlation between the rock's Rb concentration and both percentage of clay fraction, and equally gamma ray emission. Rb is relatively easy to measure and provides a semi-quantitative assessment of a sedimentary rock's clay content. The measurement error of the tool is less than 10 %. Initial data indicate that the measurement is sensitive to clay mineral composition, given some samples deviate from others showing higher or lower-than-expected values. In clastic sediments, the Rb-XRF method can be used as an alternative to Gamma-Ray in determining clay content, such as to describe the cleanness of sand. Furthermore in carbonate rocks, the XRF measurements can be used to fairly accurately determine the content of clay. In such way, industrial carbonate hard rock's, clay content can be correlated with rock strength. By using XRF, it was demonstrated in the 'failed' Kpg. Opak quarry that the clay content some 20 % in the rock matrix. The high clay content is responsible here for a reduced industrial quality of the hard rock. With this method, limestone strength can be estimated on the spot. With proper calibration, the tool might also be used to detect clay mineral composition semi-quantitatively.

### **Introduction:**

Trace elements can be found in most rock types of the crust and in all the soil types of the diverse climatic regions of the globe. However the concentrations of those elements in rocks depend upon the rock type and the trace element considered. Rb is one of the trace elements present in several common minerals in which it substitutes for potassium. Rb is relatively rare with a crustal abundance of about 110 ppm (Wedepohl, 1995) compared to K and Na. The Rb readily substitutes for K in aluminosilicate minerals. However the enrichment of Rb relative to K is greater in mica (Muscovite) and, to a lesser extent, in K-feldspar such as microcline and orthoclase (Ekwere, 1985), as well as rarer minerals, such as lepidolite, carnallite and pollucite, in which it replaces Cs. Particularly during weathering, ion exchange and differential adsorption mechanisms tend to concentrate Rb relative to K (Heier and Billings 1970). Many types of shale and mudstone thus have high levels of Rb (160 ppm) mainly held in clay minerals, such as illite and montmorillonite, leading to lower K:Rb ratios than those of igneous rocks. The levels of Rb in shale, sandstone and carbonates 140, 60 and 3 ppm respectively (Horstman, 1957, Mielke, 1979) and impure limestone show higher Rb concentration than the pure limestones. Quantitative detection of clay minerals in materials has a good potential application

and it is very important in several industries. In the oil industry, clay forms sealing units and forms contamination in petroleum reservoirs. In many areas, hard limestones are used as construction material. The clay content in limestone is often proportional to the strength of the material. Since Rb readily substitutes for K in aluminosilicate minerals, it can be used to quantify the clay content in particular litho-type. The Rb detection by Field portable XRF forms an alternative detection method in respect to Gamma Ray. XRF results are also not affected by cosmic radiation (on surface) compared to gamma ray. Hence, determination of Rb with Field portable XRF may form a handy tool to survey in limestone quarries for selecting superior quality limestone for the use of construction material.

### **Results and Discussion:**

Field portable XRF was shown to be an effective tool for rapid assessment of trace metals in soils as well as sediments (Weindorf et al., 2012). Whilst measuring chemical properties of sedimentary rocks, in the NW Borneo, we noted a positive, quasi-linear correlation between Rb concentration, and both percentage of clay fraction, and equally gamma ray emission. This is particularly relevant given that gamma ray measurements on surface are often contaminated by radioactivity from other sources. Different rock samples (sandstone, clay inter-bedded sandstone, marl, marly limestone,

limestone; number of samples  $n = 85$ ) were collected from NW Sarawak (Neogene age). A hand held, high performance NITON XLt portable x-ray fluorescence (XRF) elemental analyzer was used for non-destructive chemical analysis of rocks, and values were measured in PPM. The measurement error of the tool is less than 10 % (current data are indicative for 6.75 % mean). The measured overall Rb concentration in this study is in the range of 5 to 150 ppm. However, a noticeable difference is observed in Rb concentration among the different rock types. Rb Concentration is recorded higher in claystone, (42-140.6 ppm; average with standard deviation  $avg. 82.9 \pm 21.9$  ppm;  $n=32$ ) than clay interbedded sandstone (30.9-59.6 ppm;  $avg. 45.8 \pm 11.2$  ppm;  $n=6$ ); sandstone (5.1-80 ppm;  $avg. 31.7 \pm 18.9$  ppm;  $n=30$ ), and marl limestone (20.6-38.3 ppm;  $avg. 29.8 \pm 5.7$  ppm;  $n=17$ ). The measured clay content (by wet analysis) also similar like Rb, recorded higher in claystone (54.5-98.3%;  $avg. 76.8 \pm 10\%$ ) than clay interbedded sandstone (28.8-94.4%;  $avg. 70.6 \pm 25.5\%$ ); sandstone (0-88.9%;  $avg. 26.5 \pm 26.2\%$ ), and marl limestone (10.7-30.8%;  $avg. 22.7 \pm 4.9\%$ ).

Comparing the Rb values with the percentage of clay fraction obtained by classic grain separation, it was found that a significant linear correlation between Rb concentration and clay percentage ( $R^2=0.675$ ), which indicates that the measurement of Rb is relatively sensitive to clay mineral composition. It is also noted that the correlation is deviating from linear in samples of both very high and also very low clay content. Equally, there is a moderate correlation between Rb values and gamma-ray radioactivity ( $R^2 = 0.520$ ). Likewise clay content and gamma-ray radioactivity have a significant relationship among them, which is confirmed by a strong positive correlation between them ( $R^2= 0.644$ ). The good positive correlation among the parameters indicates that Rb is adsorbed mainly on clay minerals and also indicating the presence of fine grained material in the particular sedimentary rocks. Because Rb is retained in weathered sediments, particularly in clays, having a structural position for the ion, thus, claystone shows higher concentration of Rb

than the other rock types. Rb can be used to fairly accurately determine the content of clay in limestone or dolomite rock; in industrial carbonate hard rock, clay content can be correlated with rock strength. In the 'failed' Kpg Opak quarry, for instance, we measured clay content of some 20 %. The high clay content is responsible here for a reduced industrial quality of the hardrock. With this method, limestone strength can be estimated on the spot. The analysed data suggests that XRF measurements could semi-quantitatively determine clay content in sedimentary rocks, both on surface and downhole applications. The improvement of accuracy of results is yet to be developed.

#### References:

- [1] [Ekwere, S. J. \(1985\), "Li, F and Rb contents and Ba/Rb and Rb/Sr ratios as indicators of postmagmatic alteration and mineralization in the granitic rocks of the Banke and Ririwai Younger Granite complexes, Northern Nigeria". \*Mineralium Deposita\*, 20 \(2\), 89-93.](#)
- [2] [Heier, K.S, and Billings, G.K. \(1970\), "Rubidium". In 'Handbook of geochemistry'. \(Ed. K.H. Wedepohl\) pp. 37-C-1-37-N-1. \(Springer-Verlag: Berlin and Heidelberg\)](#)
- [3] [Horstman, E.I.A. \(1957\), "The distribution of lithium, rubidium, and caesium in igneous and Sedimentary rocks". \*Geochimica et Cosmochimica Acta\*, 12, 1-28. Pergamon Press, London.](#)
- [4] [Mielke, J.E. \(1979\), "Composition of the Earth's crust and distribution of the elements". In: Siegel, F.R. \(Ed.\), \*Review of Research on Modern Problems in Geochemistry\*. UNESCO Report, Paris, pp. 13-37.](#)
- [5] [Wedepohl, K. H. \(1995\), "The composition of the continental crust". \*Geochimica et Cosmochimica Acta\*, 59, 1217-1232.](#)
- [6] [Weindorf, D. C, Zhu, Y, Chakraborty, S, Bakr, N. and Huang, B. \(2012\), "Use of portable X-ray fluorescence spectrometry for environmental quality assessment of peri-urban agriculture". \*Environmental Monitoring and Assessment\*, 184, \(1\), 217-227, DOI: 10.1007/s10661-011-1961-6.](#)