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Rubidium detected with X-ray fluorescence spectrometry: A new semi-quantitative assessment of clay content in sedimentary rocks

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Abstract: This paper deals with assessment of clay content in sedimentary rocks using portable X-ray fluorescence spectrometry. Whilst measuring trace metal content of sedimentary rocks, it was noted a positive, quasi-linear correlation existed between the rock's Rb concentration and both percentage of clay fraction, and also natural gamma ray radioactivity. Rb is relatively easy to measure with XRF and provides a semi-quantitative assessment of clay content. The measurement error of the tool is less than 10 %. Initial data indicate that the Rubidium content varies slightly in respect to clay mineral composition, given some samples deviate from others, by 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 or carbonate. For industrial limestone mining, the XRF tool could be used to estimate cleanness of carbonates, hence rock strength. It is believed that XRF Rubidium measurements could also be carried out in the subsurface.

Keywords: X-ray fluorescence spectrometry, rubidium, clay

INTRODUCTION

The greater Miri (NW Sarawak, Borneo island) area is essentially formed by three rock types: the Oligocene-Miocene Setap shale, the Mid-late Miocene sandy Belait Group (Miri and Lambir formations), and the semi-consolidated Tukai Formation of Late Miocene to Pliocene age (Figure 1). In view of only limited occurrences of age-significant fossils within the named formation, absolute age of the mentioned remain imprecise. Furthermore, there are only little geochemical data available. In 2011, Curtin Sarawak purchased a portable XRF device (Niton), with the objective to develop a chemo-stratigraphy of the sedimentary formations of NW Borneo. Used during several field campaigns, the XRF tool helped to gather basic geochemical data in sedimentary rocks, starting with the Tukai Formation.

Encouraging and widespread data regarding the presence of rubidium prompted further studies. The concentration of some elements may be increased as a result of its adsorption by clay minerals. The latter, an alkaline metal (Rb) with similar chemical characteristics to sodium and potassium, occurs as one of the trace elements present in most clay minerals, in which it substitutes

potassium. In the Earth's crust, Rb is relatively rare at about 110 ppm (Wedepohl, 1995) compared to K and Na.

The Rb⁺ readily substitutes for K⁺ in aluminosilicate minerals and its enrichment relative to K is greater in mica (muscovite) and to a lesser extent, in K-feldspar such as microcline and orthoclase (Ekweke, 1985), as well as rarer minerals, such as lepidolite, carnallite and pollucite, in which it replaces Cs. Rubidium used to be retained in weathering largely by those clays having a structural position for the ion, although adsorption plays an important part in both clays and shales (Horstman, 1957). Particularly during weathering, ion exchange and differential adsorption mechanisms tend to concentrate Rb relative to K (Heier & 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. In the oil industry, clay forms a sealing unit and can downgrade sandstone reservoir porosity or constitute baffles within

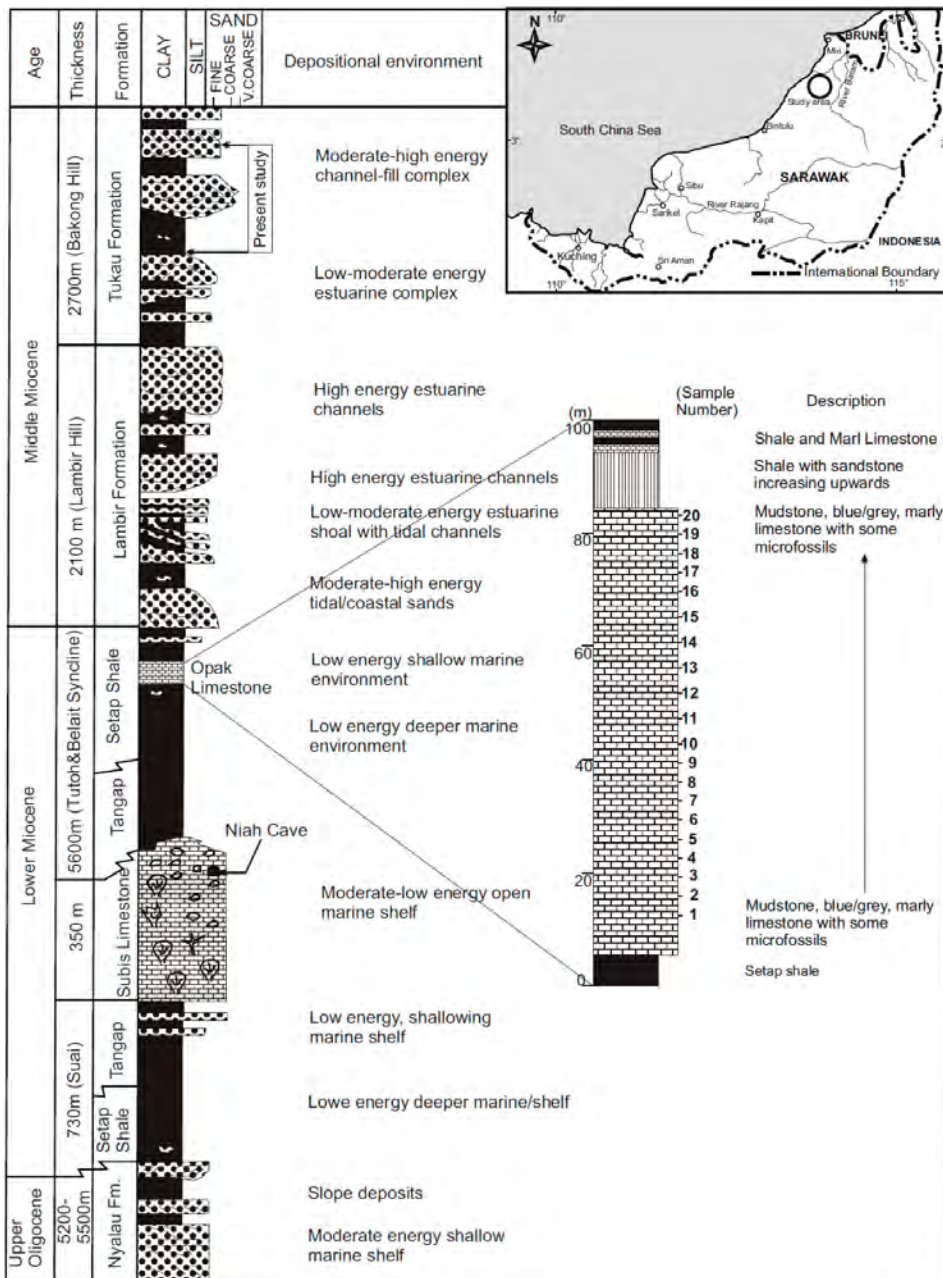


Figure 1: The stratigraphic profile of the molasses sediments as exposed along the Miri-Bintulu (inland) road. The principle sample locations (Tukau Formation and Opak limestone) for the XRF analysis are shown (modified after Hutchison 2005).

oil and gas reservoirs. In many parts of the world, hard limestones are used as construction material. The clay content in the limestone is often proportional to the strength of the material. Here, Rb can be used to quantify the clay content to estimate the rock strength. Rb/XRF detection for clay content does not suffer from cosmic radiation contamination, a problem encountered when using Gamma Ray in the field. Hence, determination of Rb with field portable XRF may form a handy tool to estimate limestone quality in quarries. The main aim of this study is that to assess the clay content by tracing Rb-concentration in sedimentary rocks using portable XRF as semiquantitative method.

STUDY AREA AND GEOLOGICAL SETTING

The geology of Sarawak has been divided into three distinct provinces: namely West Sarawak, Central Sarawak and North Sarawak. The North Sarawak region is occupied in North and East of the Rajang-Baram watershed. The adjacent offshore area is named the Luconia Block (Hutchison, 1989). This North Sarawak region is underlain by Neogene sediments of the NW Borneo Basin and the sediments are younging towards North and NNE with Oligocene base rocks. North Sarawak region is underlain by thick sequences of shallow and deep marine sediments, such as sand and shale formations respectively (Liechti et al., 1960). The formations which are: Nyalau, Setap,

Tanggap, Sibuti, Belait, Lambir, Miri and Tukai range in age from Oligocene to Pliocene. Based on the relative absence of planktic foraminifers Tukai Formation is considered to be formed under shallow marine to deltaic environments. The absence of foraminifers (except some brackish water forms), the presence of lignite layers and amber balls have lead Hutchison (2005) to conclude that the Tukai Formation was deposited in a coastal plain. The basal part of Tukai Formation conformably overlies the Lambir Formation near Sungai Liku in the eastern Lambir Hill where it is conformably overlain by the Liang Formation in Brunei.

The Neogene sediments, measured with XRF in this article, belong to the Miri Zone, a term coined by Hutchison (2005) for molasse sediments in the Sarawak foreland. The sediments are largely derived from the metamorphic Rajang Group deepwater clastics that form a mountain belt in the interior of Sarawak, of which an estimated 6000 m have been eroded until today (Kessler unpublished). The molasses sequence, several kilometers thick, starts with anchi-metamorphic shales (Black Setap shale), silty claystones with turbidite deposits (grey setap shale), reefal carbonates (Subis Fm at Batu Niah), clastics and carbonates (Sibuti Formation, including Kpg. Opak limestone, Figure 1), and is concluded with the shallow marine and brackish clastics of the Lambir, Miri and Tukai (Figure 1) formations. Current XRF measurements have been confined to the upper part of the sequence, namely samples belonging to the Kpg. Opak (Sibuti Fm.), and Tukai formations (Figure 2).

METHODOLOGY

Totally 85 Fresh clastic and carbonate sediment samples were collected from the outcrops of Tukai Formation and Kpg. Opak quarry respectively (Figure 1). The outcrops of Tukai Formation are located 25 km South of Miri and Kpg. Opak quarry is located 45 km SW of Miri. The sediment samples were washed thoroughly in distilled water to remove any contamination. These sediments were air dried and then ground in an agate mortar. The lithology of the sediments was classified as claystone, (n=32), clay interbedded sandstone (n=6); sandstone (n=30), and marly limestone (n=17). The Rb concentration of these sediments was determined using a semiquantitative portable XRF spectrometer analysis.

Portable XRF spectrometers are a handy tool both in the field and under laboratory conditions. In many countries, XRF tools are strictly controlled given they constitute a source of ionizing radiation (X rays). In the field, rock is measured from a distance of several centimetres, and quality measurements require a minimum of one minute of X-ray exposure. In the laboratory, rock is powdered and radiated from a close distance. The tool detects heavy atoms, it's sensitivity (detection level) however is highly material-dependant. We used the hand held, high performance NITON XLt portable X-ray fluorescence (XRF) tool, and values were measured

in ppm. The measurement error of the tool is less than 10 % (current data are indicative for 6.75% mean). Clay percentage in the sediments was determined by the pipette method, in accordance with the procedure adopted by Krumbein & Pettijohn (1938). The Gamma ray gamma-ray radioactivity was determined by Geiger counter measurements.

RESULTS AND DISCUSSION

Rock samples (sandstone, clay inter-bedded sandstone, marl, marly limestone, limestone; number of samples n=85) were collected in NW Sarawak (Neogene age), from a siliciclastic unit known as the Tukai Formation. Rb concentrations were found to be higher in claystone, (42-141 ppm; average with standard deviation $avg.82.9 \pm 21.9$ ppm; n=32), compared to clayey inter-bedded sandstone (31-60 ppm; $avg.45.8 \pm 11.2$ ppm; n=6); sandstone (5-80 ppm; $avg.31.7 \pm 18.9$ ppm; n=30), and marly limestone (21-38 ppm; $avg.29.8 \pm 5.7$ ppm; n=17). For comparison, the measured clay content (by wet analysis) was found to be higher in claystone (55-98%; $avg.76.8 \pm 10\%$) than clay inter-bedded sandstone (29-94%; $avg.70.6 \pm 25.5\%$); sandstone (0-89%; $avg.26.5 \pm 26.2\%$), and marly limestone (11-31%; $avg.22.7 \pm 4.9\%$). The gamma ray count also recorded higher in claystone (23-31; $avg.24.4 \pm 2.4$) than the clay inter-bedded sandstone (18-26; $avg.21.5 \pm 2.6$) and sandstone (14-31; $avg.18.9 \pm 4$).

When comparing the Rb values with the percentage of clay fraction obtained by classic grain separation, it was found that a strong paired sample correlation is observed between Rb concentration and clay percentage ($r=0.82$ with 2 tailed significance of 0.06) (Figure 3). Particularly, claystone shows high levels of Rb (82.9 ± 21.9 ppm) which is mainly held in clay minerals, such as illite/smectite leading to lower K:Rb ratios. This is also supported by the higher Rb content and high Rb/K ratios recorded from Setap Shale formation and Belait Formation, located in the Northern part of the Borneo (Burgan et al., 2008). The clay mineral assemblages in N Borneo based on the sediments from two rivers (Trusan and Baram Rivers) show a dominance of illite (75–85%, average 77%), with minor amount of chlorite (average 10%) and kaolinite (average 12%). Illite chemistry index in this subprovince decreases to 0.20–0.28 (Liu et al., 2012). This is seen to be indicative that the measurement of Rb is relatively sensitive to clay mineral concentration. The correlation is also deviating from linear in samples of both very high and also very low clay content, potentially pointing to a Beta-Function correlation rather than a true linear correlation. There is a moderate correlation between Rb values and gamma-ray radioactivity ($r=0.72$ with 2 tailed significance of 0.000000016) (Figure 4). As widely known, clay content and gamma-ray radioactivity have a significant relationship among them, which is confirmed by a moderate positive correlation between them ($r=0.64$; Figure 5). The good correlation between Gamma counts and clay concentration recorded in the outcrops are located



Figure 2: Upper portion of the Tukai Formation (moderate energy intertidal channel sequences) outcrops in the Sg. Rait valley.

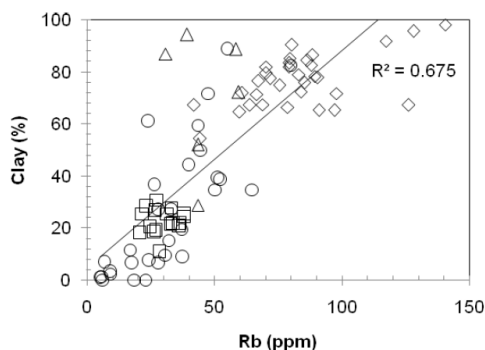


Figure 3: Rb vs. clay content (%) showing two clusters and show linear correlation between them for clastic and carbonate sediments (claystone - open diamond; clay interbedded sandstone - open triangle; marl limestone - open square; sandstone - open circle).

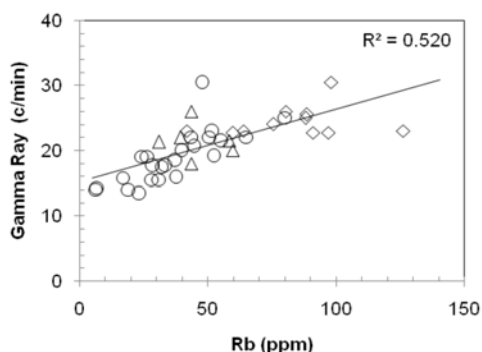


Figure 4: Rb (ppm) vs. gamma ray (c/min) showing a significant correlation for clastic and carbonate sediments (claystone - open diamond; clay interbedded sandstone - open triangle; marl limestone - open square; sandstone - open circle).

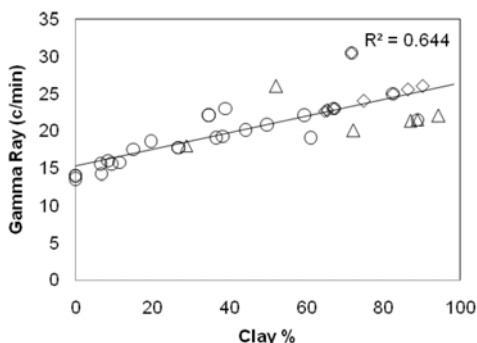


Figure 5: Clay (%) vs. gamma ray (c/min) showing a significant correlation for clastic and carbonate sediments (claystone - open diamond; clay interbedded sandstone - open triangle; marl limestone - open square; sandstone - open circle).

roughly at the same altitude, hence do not suffer from altitude-dependent cosmic gamma ray variation.

CONCLUSION

The analysed data suggests that XRF measurements of Rb concentration could semi-quantitatively determinate clay content in sedimentary rocks, both on surface and downhole applications. Further work should emphasize the correlation between Rb content and clay mineralogy. The improvement of accuracy of results must be developed further.

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