

## Organic Geochemistry of Peat Deposits in southwest Rwanda

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### Abstract

Rwanda hosts million tons of peat deposits and that of western province is of great importance as it close to Kivu Lake. The discovery of methane gas in Kivu Lake has attracted investors in methane gas utilization as source of power supply and Compressed Natural Gas (CNG). Researchers identified Kivu Lake and adjacent area as an area of interest for hydrocarbon exploration. However, organic geochemical prospecting for hydrocarbon and energy content assessment is inadequate for the identified areas. The study aimed at determining the organic geochemistry of peat deposits in southwest, Rwanda. Forty (40) subsurface peat samples (1 to 10 m depth) were collected, air-dried and pulverized and screened. Five (5) samples with high organic matter content were subjected to biomarkers analysis using GC-GCMS. The *n*-alkanes distribution comprised mainly *n*-C<sub>11</sub> to *n*-C<sub>37</sub>. The Pr/Ph ratios (3.3-10.4, the waxiness index (0.09-0.87), CPI (3.6-7.8), OEP (3.5-6.0), C<sub>29</sub> steranes (63.0–100.0%), C<sub>28</sub> (0.0–28.0%), C<sub>27</sub> (0.0–18.0%) and C<sub>27</sub>/ C<sub>29</sub> sterane ratios (0.0-0.28). The  $\beta\beta/(\beta\beta + \alpha\alpha)$  and 20S/ (20S + 20R) are 0.5 and 0.46 respectively. The C<sub>30</sub> -moretane/ C<sub>30</sub> -hopane ratios ranged from 1.56 to 2.42, while the oleanane index ranged from 0.07 to 0.26. The Ts/ (Ts + Tm) ratios ranged from 0.13 to 1.05. The dominance of C-29 sterols and C<sub>29</sub>/C<sub>27</sub> sterane ratio which ranged from 3.5 to 100 indicating derivation from terrigenous higher plant material. The Pr/Ph ratio (>3) reflect the oxic to sub-oxic environmental condition during peat deposition. The peat deposits in Western Province, Rwanda are very rich in organic matter of mainly terrestrial precursor deposited in dry and cold climate.

**Keywords:** Biomarkers, depositional environment, *n*-alkanes, peat, steranes, terpanes

## 1. Introduction

Peatlands are the crucial environment for organic matter deposition. They offer a distinctive ecosystem services and cover 500 million hectares worldwide (Fatma and Sedattin 2015). Peat is formed in situ and rarely from transported materials, it is composed of organic constituents from plant growing in wetland where the environment is characterized by slow flow of water and presence of water near surface for whole year (Cohen *at al.*, 1987). However, change in temperatures, imply that the types of plant to accumulate change (Cohen *et al.*, 1987). The degree of decomposition may be studied using physical observation of peat column with reference to Von Post classification (Andriessse, 1988). Peat is generally considered as the first developmental stage in the coalification process, in which there is a gradual increase in the carbon content of fossil organic material and a concomitant reduction in oxygen (Myer Kurtz, 2006). It is also treated as a sub-category within brown coal and defined as a combustible soft, porous or compressed fossil sedimentary deposit of vegetal origin; which is easily cut, light to dark brown in color, and holds a high water content (up to 90% in the raw state) (IEA, 2007). Based on the fibre percentage; structure and appearance; presence and appearance of humus, amount and appearance of water, and elemental composition of organic matter of peat, it is classified into three categories namely Fibric (peat moss); hemic peat and sapric peat (MacDonald *et al.*, 1996).

Peat has been used by coal petrologist to study genesis, structures, petrology and biomarkers contents to establish the environment of deposition of peat that transformed into coal (Esterle and Ferm, 1990; Dehmer, 1995; Fatma & Sadettin, 2015). The detection of biomarkers in coal supports the geological, petrographic and chemical evidence that the coal is the result of progressive fossilization of plant debris (White *at al.*, 1977). As the biomarkers constitute intermediate components in coalification process, they have received increasing attention. Chaffe and Johns, 1983 stipulated that the significance changes in biomarkers distribution, increase the coal rank. The high preservation degree of peat deposits and their depositional regimes which are climate regulated (Strack *et al.*, 2008) makes them suitable for paleo-environmental reconstruction (Yu *et al.*, 2010; Fatma and Sedattin, 2015; Hans, 2015). The recognition of the depositional environments of peat have been studied in numerous researches using geochemical, sedimentology, palynology, trace fossils and macrobotanical remains proxies (e.g. Fielding, 1984a; Fielding, 1984b, Rahmani and Flores, 1984; McCabe, 1984; Esterle and Ferm, 1986;

Fielding, 1987; Flores, 1988; Diessel, 1992; Staub and Esterle, 1992). It has been shown that n-alkanes from the same type of plant show a unique distribution model and abundance (Rao *et al.*, 2009) whereas n-alkanes from different biological origin have different abundance and distribution patterns (Schwark *et al.*, 2002; Lin *et al.*, 2009).

The Carbon Preference Index (CPI) can be calculated and used to interpret the paleo-environment. Xie *et al.*, (2004) suggested that CPI value can be preserved in cold and dry conditions because no diagenesis and microbial decomposition of organic matter occurs (Kuder and Kruege, 1998). However, under warm and wet conditions, CPI values decrease due to the diagenesis and microbial decomposition of organic matter (Zhou *et al.*, 2005). The hopanes content of peat is a good environmental proxy. Hunt, (1995) suggested that the presence of low carbon numbered homohopanes indicates suboxic depositional environment. In addition, the absence of C34 and C35 homohopanes can indicate oxic or suboxic conditions (Ramanampisoa *et al.*, 1990). Steranes composed by eukaryotic organisms are the bio-markers of steroids. Steroids are transformed into steranes under diagenesis (Waples, 1985). The dominance of C29 is an indicator of terrestrial origin of organic matter (Abrams *et al.*, 1999; Czochanska *et al.*, 1988; Huang and Meinschein, 1979; Robinson, 1987). On the other hand, the dominance of C30 steranes indicates a marine environment (Hunt, 1995; Mann *et al.*, 1998; Moldowan *et al.*, 1985).

The Peatlands in Rwanda are currently in critical condition and soon may extinct due to their use as source for fuel and for agricultural fields. The peats are distributed nationwide but are more abundant in the south and south west of Rwanda. Their thickness varies from 0.5 m to 12m. The objectives of this paper is to reconstruct paleo-environment and conditions during peat deposition; and to determine the source of the organic matters that contributed to the formation of the peat. This information will be useful for basin analysis in southwest of Rwanda.

## **2. Geological settings**

The regional geology, structural settings, stratigraphy, and metamorphism in the Kibaran orogen are well documented by Fernandez-Alonso *et al.* (2010). Kibaran Belt (KIB) and the Karagwe Ankole Belt (KAB) of East-Central Africa together (Kibaran Belt) evolved between three pre-Mesoproterozoic domains: The Archaean Tanzania Craton to the East, the Archean-Paleoproterozoic Congo Craton to the west and north, and Bangweulu block to the south. The Paleoproterozoic Rusizian-Ubendian Belt separates both sub-belts. They host two main granite

generations with the old granite dated at  $1375 \pm 10$  Ma and younger granite at  $986 \pm 10$  Ma (Tack, 2010). The latter is related to ore deposits of typical Nb-Ta-Sn-W metal association. Pegmatites can be found predominantly mineralised with Sn/Nb-Ta minerals namely cassiterite and columbite-tantalite while quartz veins are found to be mineralised with Sn/W minerals. The primary mineralisation are observed in quartz veins and pegmatites, and secondary mineralisation in alluvial/eluvial deposits. The KAB and KIB comprise meta-pelites and rare carbonates, minor volcanic rocks and dolerites, with some of them metamorphosed to amphibolite facies. Lithology of the study area is dominated with volcanic rocks of the Cyangugu (Figure 1).

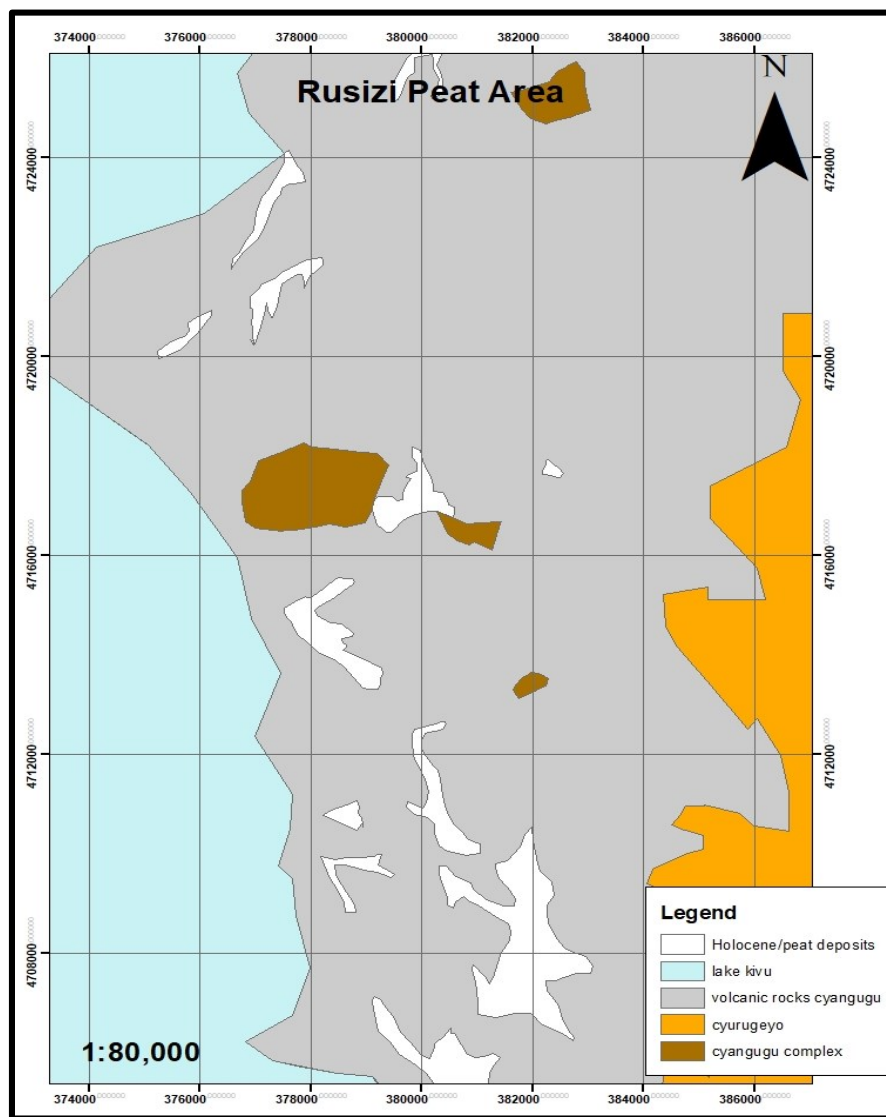


Figure 1. Study area map depicting rocks and peat deposits distribution in Rusizi District

### **3. Materials and Method**

#### **3.1 Sampling procedures**

Russian peat corer was used to collect core samples down to 10 m depth. At each location, the corer was pressed into layers by hand and the sampling interval was 100 m. The sampling geologists recorded sampling point coordinates. Samples were labelled before shipping to the laboratory. Initially 40 sub-samples were collected and through a series screening process, 5 samples were selected for biomarkers analysis.

#### **3.2 Analytical method**

##### **3.2.1 Soxhlet extraction**

The samples were air-dried and then crushed with mortar and powdered to less than 120 mesh sizes prior to extraction. 50 g of each of the powdered sample was weighed and sonicated with 50 mL methanol (three times), 50 mL methanol and dichloromethane (v/v) (three times) and 50mL dichloromethane (three times) for 20 minutes each respectively to extract the Extractable organic matter (EOM). Copper tunings was added to the extract to remove elemental sulphur. The desulphurized extract was deasphalted using excess n-hexane to get Maltene. Maltene was concentrated using rotary evaporator. Activated silica gel and alumina were used to pack the column with silica gel on top in the ratio of 3:1. 25mL of n-hexane was introduced in order to remove any hydrocarbon associated with them as a foreign body. A drop of the extracted sample (maltene) was introduced on the surface of the column and eluted with n-hexane, dichloromethane and n-hexane in the ratio of 3:2 and methanol to separate into saturate, aromatics and NSO (polar) fraction respectively. The solvent in the three fractions were concentrated to 2mL using rotary evaporator to remove excess solvent and then transferred into a weighed clean vial and kept for GC-MS analysis.

##### **3.2.2 Gas-Chromatography - Mass Spectrometry Analysis (GC-MS)**

Gas chromatography–mass spectrometric (GC–MS) analysis of saturate fraction was performed using an Agilent 7890A gas chromatograph coupled with Hewlett-Packard 5975C mass

spectrometer. The gas chromatography was equipped with a HP – 5 fused silica capillary column (30 m x 0.25 mm, i.d., 0.25 $\mu$ m) and Helium was used as the carrier gas with flow rate of 1ml/min.

The oven temperature was programmed from 80°C for 2 minutes to 280°C at the rate of 3°C per minute, followed by an isothermal phase for 20 minutes at 280°C. The samples were analyzed in the full scan and SIM modes respectively. The SIM modes; n – alkanes ( $m/z = 71$ ), triterpanes ( $m/z = 191$ ), and disasterances and regular steranes ( $m/z = 217, 218$ ) were detected and individual compound were identified by the relative retention times and comparison of mass spectra with literature and library data.

## **4. Results**

### **4.1 Field geology and observation**

The thickness of the peat deposits varies across locations. Gihitasi bog with thickness of less than 5 meters was found to be the shallowest compared to Mashya and Gishoma. The samples were brown to black color and some plant parts were visible to the unaided eye for samples with humification scale less than H3. Clays and sands were predominantly present at the bottom of the peat formations (Figure 2).

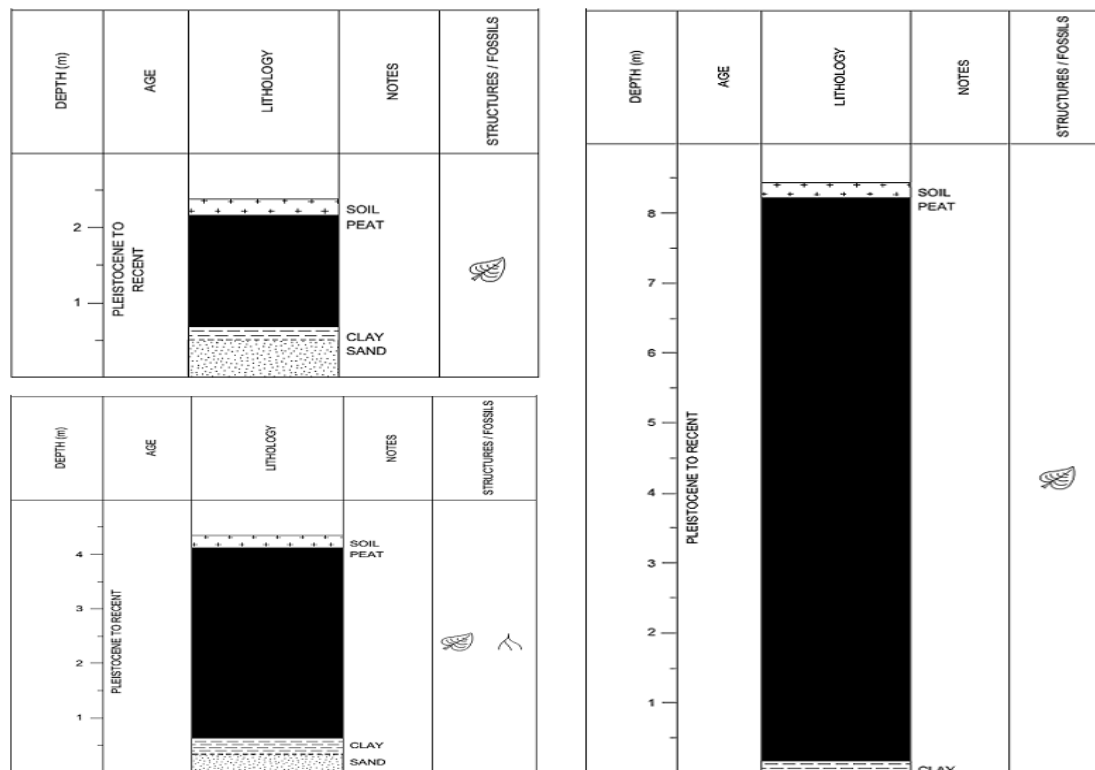


Figure 2. Auger logs showing stratigraphic sequence in Rusizi, southwest of Rwanda

#### 4.2 Normal alkanes (n-alkanes) distribution and isoprenoids

The results for n-alkanes and isoprenoids are presented in Table 1. Selected chromatogram of extractable organic matter from peats are shown in Figure 3. The n-alkanes in the peat samples ranged from the C<sub>11</sub>-C<sub>37</sub>, with abundance of C<sub>21</sub>, C<sub>23</sub> and C<sub>29</sub>. The n-alkanes in two samples show bimodal distribution patterns with a predominance of high molecular weight (>n-C<sub>20</sub>) varieties in most of the samples. Acyclic isoprenoids: Pristane (-C<sub>19</sub>) and Phytane (-C<sub>20</sub>) are present in all the analyzed samples. The Pr/Ph ratio for analyzed samples fall between 3.33 and 10.40, while the Pr/n-C<sub>17</sub> vs Ph/n-C<sub>18</sub> ratios in the samples are within 2.04 to 8.67 and 0.01 to 0.97, respectively. The CPI values of all analyzed samples in are 3.83, 8.39, 7.36, 6.95 and 8.32 (Table 1). The improved Odd-Even Predominance (OEP) were calculated using the formula of Scalan and Smith (1970) and with values ranging from 3.52 to 6.00.

Table 1. Molecular biomarker parameters

Sample ID	Pr/Ph	Pr/nC <sub>17</sub>	Ph/nC <sub>18</sub>	TAR	Paq	CPI	CPI(1)
DH42	4.37	2.04	0.97	0.37	0.34	4.94	3.83
DH43	3.68	7.76	0.16	0.03	0.16	7.75	8.39
DH44	10.4	3.4	0.01	0.04	0.22	7.63	7.36
DH54	3.33	8.67	0.15	0.81	0.93	3.6	6.95
DH55	4.58	2.18	0.03	0.74	0.94	4.0	8.3

Table 1 (Continued)

Sample ID	OEP(2)	OEP(1)	ACL	Pwax	C-range	Cmax	(C <sub>21</sub> +C <sub>22</sub> )/(C <sub>28</sub> +C <sub>29</sub> )
DH42	4.53	1.46	28.8	0.72	C <sub>11</sub> -C <sub>33</sub>	C <sub>29</sub>	0.69
DH43	5.72	2.26	29.2	0.87	C <sub>11</sub> -C <sub>35</sub>	C <sub>29</sub>	0.69
DH44	6.00	2.38	28.8	0.82	C <sub>11</sub> -C <sub>37</sub>	C <sub>31</sub>	0.69
DH54	3.52	2.38	28.8	0.82	C <sub>11</sub> -C <sub>37</sub>	C <sub>21</sub>	0.69
DH55	3.81	10.43	28.8	0.09	C <sub>11</sub> -C <sub>33</sub>	C <sub>33</sub>	0.69

The degree of waxiness in the studied samples is expressed by the formula  $C_{27}+C_{29}+C_{31}/C_{23}+C_{25}+C_{27}+C_{29}+C_{31}$  assuming that high molecular weight normal alkanes were thought to come from the terrigenous organic materials (Peters *at al.*, 2005). The waxiness index of peat samples from Southwest of Rwanda ranges from 0.09 to 0.87. The terrigenous/Aquatic ratio range from 0.03 to 0.81 for the analyzed samples.



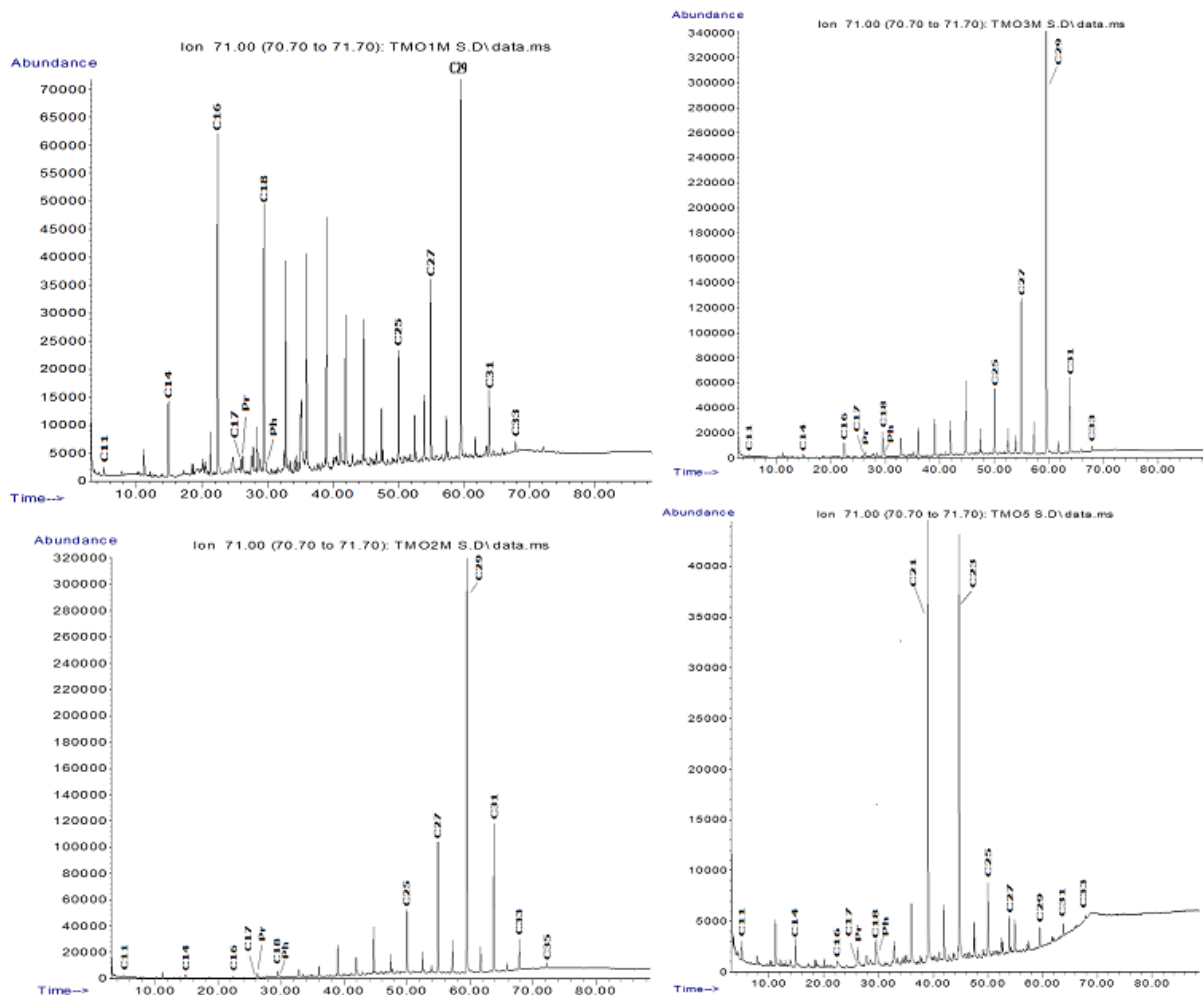


Figure 3. Chromatograms showing relative abundance of saturated hydrocarbon

### 4.3 Terpanes

The sterane and the hopanes distribution of analyzed samples from Southwest of Rwanda was obtained from  $m/z$  191 mass chromatograms (Figure 4). Based on retention time and published literature, the peaks fingerprint was recognized (Adegoke *et al.*, 2014; Adebayo *et al.*, 2018). The series of tricyclic terpanes ranging from C<sub>19</sub> to C<sub>26</sub> were observed in all samples. However, extended tricyclic terpanes were absent in all studied samples. C<sub>30</sub>-moretane/ C<sub>30</sub>-hopane ratios ranged from 1.56 to 2.42, while the oleanane index ranged from 0.07 to 0.26. The Ts/(Ts + Tm) ratios ranged from 0.13 to 1.05.

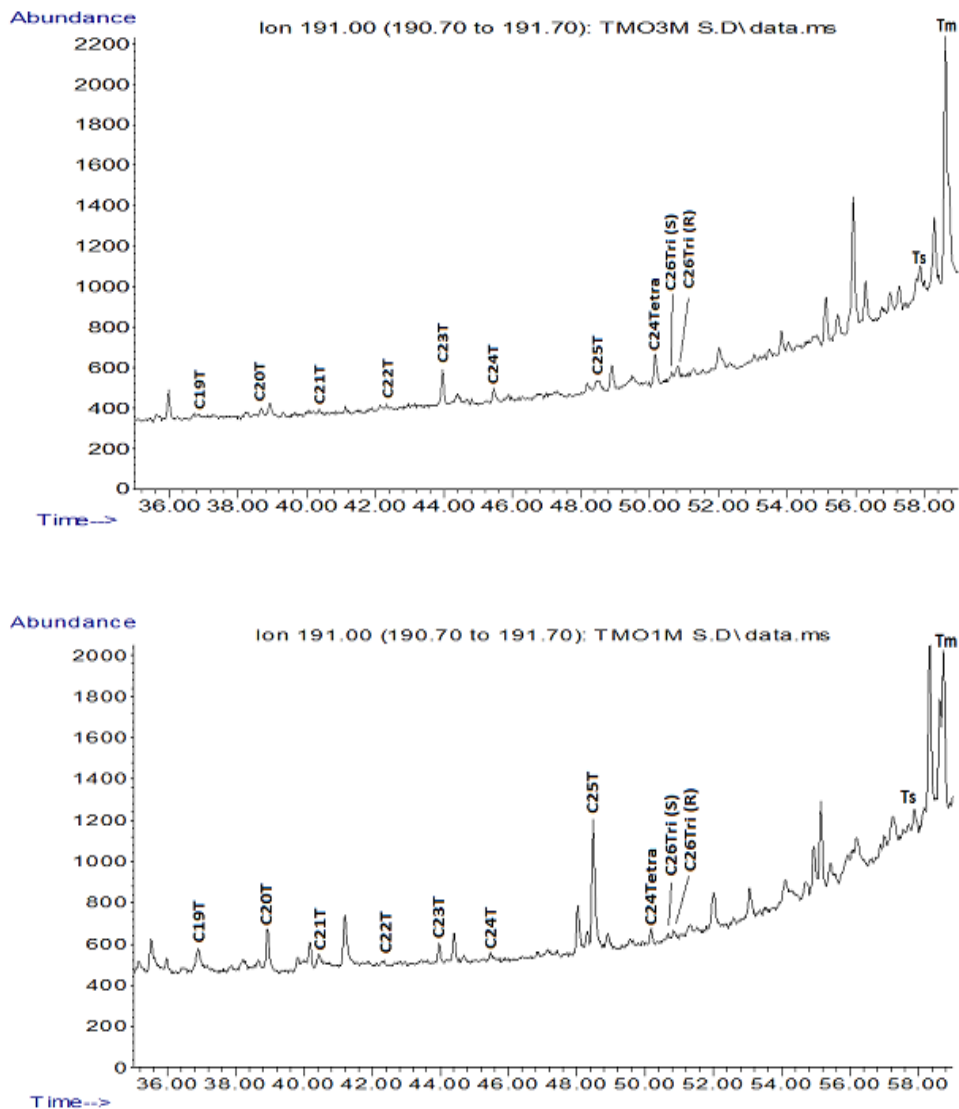


Figure 4.  $m/z$  191 chromatograms representing terpanes abundance of sediments from southwest of Rwanda.

#### 4.4 Steranes distribution

The  $C_{29}$  steranes (63.00–100.00%) are more abundant than the  $C_{28}$  (0.00–28.0%) and  $C_{27}$  (0.00–18.0%) steranes in the analyzed extracts (Table 2). Also, Mass chromatograms ( $m/z$  217) suggested that the peats samples are dominated by  $C_{29}$  regular steranes over  $C_{28}$  and  $C_{27}$  isomers. The  $C_{27}/C_{29}$  sterane ratios ranged from 0.00 to 0.28 in the samples. The values of  $\beta\beta/(\beta\beta + \alpha\alpha)$  and  $20S/(20S + 20R)$  regular steranes for the analyzed sediments are 0.5 and 0.46 respectively.

Table 2. Sterane ratios

Sample ID	%C29S	%C28S	%C27S	C27/C29	S/H	C28/C29	C27/C27+C29	20S/20S+20R
DH42	0.67	0.28	0.04	0.06	0.070	0.420	0.058	0.46
DH43	0.98	0.01	0.01	0.01	0.150	0.012	0.011	0.46
DH44	1.00	0.00	0.00	0.00	0.420	0.002	0.001	0.46
DH54	0.63	0.19	0.18	0.28	0.076	0.307	0.217	0.46
DH55	0.62	0.18	0.20	0.32	0.070	0.290	0.243	0.46

## 5. Discussion

### 5.1 Source of organic matters

The parameter  $(C_{21}+C_{22}) / (C_{28}+C_{29})$  provides information regarding sources of organic matter. In general, terrestrial source materials give value  $<1.2$  whereas aquatic source materials give values  $>1.5$  (Steve, 1985). For the analyzed samples, the value is 0.69, which is less than 1.2, indicating organic matter of terrestrial origin. The CPI values for the studied samples are 3.83, 8.39, 7.36, 6.95 and 8.32. These values are greater than 1 which reflect the high level of alkanes associated to terrestrial organic matter input. The degree of waxiness in the studied samples is expressed by the formula  $C_{27}+C_{29}+C_{31} / C_{23}+C_{25}+C_{27}+C_{29}+C_{31}$  assuming that high molecular weight normal alkanes were thought to come from the terrigenous organic materials (Peters *et al.*, 2005). The waxiness index of peat samples ranged from 0.09 to 0.87. The terrigenous/Aquatic ratio ranged from 0.03 to 0.81 for the analyzed samples. The waxiness index reflects the amount of terrigenous organic materials. Of *aaa* C27-C29 steranes, C29 sterane (24-ethylcholestane) has the highest relative abundance generally accounting for about 82% of the total steranes. C28 sterane (24-methylcholestane), comes second as 6%. C27 however, is of the least abundance (12%). These relative abundances suggest that the analyzed samples originated mainly from terrestrial organic matter, that is, more from higher plants than from aquatic organisms. The C29/C27 sterane ratio ranges from 3.5 to 100. These molecular biomarkers suggest that the peat extracts are mainly derived from kerogen dominated by terrigenous higher plant material. Similarly, high Carbon Preference Index (CPI) is associated with organic matter from higher plant (Zhiguo *et al.*, 2009).

## 5.2 Paleocondition and paleoenvironment

The Pr/Ph ratio is universally used as an indicator of the redox potential of the depositional environment (Powell and McKirdy, 1973; Didyk *et al.*, 1978; Tissot and Welte, 1984). High Pr/Ph values ( $>3.0$ ) indicate oxic conditions, and values less than a unit indicate anoxic conditions. The calculated Pr/Ph ratio ( $>3$ ) reflect oxic to sub-oxic environmental condition during peat deposition.

According to Cadman (1985), Pristane/phytane ratio gives information regarding deposition environment such as relatively reducing depositional environment ( $<3.0$ ), reducing/oxidizing depositional environment (3.0-4.5) and oxidizing depositional environment ( $>4.5$ ). The samples under study were deposited in mixed reducing and oxidizing environment. Pristane/n-C<sub>17</sub>, which is calculated from the area of peaks representing these compounds and can give a clue about deposition environment and level of maturation of organic matters. For instance, immature crude oil has Pr/nC<sub>17</sub> ratio  $>1$ . In this study, the calculated Pr/nC<sub>17</sub> ratios are greater than 1.5 (Table 1). This reflects the peat-swamp depositional environment (Lijmbach, 1975). High CPI value indicated the dry and cold climate in southwest during peat deposition (Xie *et al.*, 2004; Zhou *et al.*, 2005; Fatma and Sadettin, 2015, Antonio *et al.*, 2020).

## 6. Conclusion

The organic geochemistry of peat is often used in the interpretation of past environment and the sources of organic matter which contributed to the formation of peats. This study aimed at analyzing the organic geochemistry of peat in the southwest Rwanda, and hence interpret the sources of organic matter and the past environment during peat deposition. Various biomarkers have been determined and revealed that the peats were formed as results of terrestrial inputs. Paleoenvironmental biomarkers showed that during the deposition of peat in southwestern part of Rwanda, the climate was dry and cold, and the environment was both reducing and oxidizing. The researchers recommend the use of multiproxy approaches in future researches to reconstruct the paleoclimate change over time.

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