Effect of the Heat Input by Dolerite Intrusions and the Propensity for Spontaneous Combustion in the Highveld Coalfields, South Africa

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1 Introduction

Spontaneous combustion of coal has been a major problem for the industry (both coal producers and consumers), human health and the environment worldwide. Coal is a carbonaceous rock composed of combustible material of carbonized organic matter that may be oxidized at different conditions, especially when it comes into contact with the atmosphere and moisture (Avila et al. 2014; Pone et al. 2007; Sasaki and Sugai 2011). Put in simple terms, the combustible nature of coal arises from its formation processes in which, during the carboniferous period, the plant's biomass underwent burial metamorphism in anaerobic and aquatic environments (Speight 2005). Many authors believe that spontaneous combustion of coal is further elevated by the emplacement of igneous intrusions resulting in chemical and thermal alteration of the coal producing mainly methane, carbon dioxide and organic compounds (Golab 2003). The combined effects of the spontaneous combustion of coal and igneous intrusions are detrimental to coal mining affecting the quality of coal, atmospheric pollution by gaseous by-products, safety, productivity and economic feasibility (Avila et al. 2014; Golab 2003).

The burning of coal is a great concern globally as the by-products may cause major environmental problems. Analyses of gas from coal fires in India, USA, China, South Africa and other countries show that there are toxins harmful to human health in coal-fire gas that cause carcinogenic proprieties such as benzene,

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xylene and toluene (Finkelman 2004; Pone et al. 2007; Snyman and Barclay 1989). Moreover, the Intergovernmental Panel on Climate Change identified the uncontrollable spontaneous combustion of coal as a potential source emitting greenhouse gases (Pone et al. 2007). Having listed some of the detrimental effects caused by spontaneous combustion of coal, it is necessary to conduct more research to establish criteria necessary for future environmental impact assessment and regulations.

Usually, analyses and characterization of the metamorphic effects on coal are represented in terms of proximate and ultimate analyses, e.g. the in-house study by (Denisov and Metelitsa 1968; Emsbo-Mattingly and Stout 2011) and many others. The proximate analysis of coal is a measure of products determined from heating of the coal conveyed in four parameters: fixed carbon, volatile matter, moisture and ash content (Speight 2005). In contrast to the proximate analysis, there is ultimate analysis, which provides information on the elemental composition of coal. Thus, ultimate analysis includes the weight percentage determination of carbon, hydrogen, oxygen, nitrogen, sulphur and other trace elements that occur within coal (Speight 2005). However, the approach implemented in this study utilizes solely the volume of aromatic and aliphatic organic compounds on the coal surface to investigate their effect on the propensity of spontaneous combustion of coal.

This study investigates and documents the impact of the heat input (metamorphic effect) by the emplaced dolerite intrusions of the Karoo age in the 2 Secunda area Highveld coalfields, South Africa. The main aim of this research is to evaluate the chemistry of the organic compounds in the coal samples, thus tracing changes in chemistry within the coal material and consequently determining the propensity for spontaneous combustion triggered by the intrusive. To achieve this aim, analyses were performed on two samples of coal representative of the positions proximal and distal to the dolerite intrusion.

2   Research Approach

Principal objective of this study was to utilize chemistry data of the coal samples from a coal seam in the Highveld-Secunda coalfield in the vicinity of dolerite intrusions. The coal samples were collected from a coal seam located in the Secunda area. Sampling focused entirely on the C4 lower coal seam at the Ithembalethu shaft of Sasol Mining Secunda. The two coal samples collected represent the two proximal and distal positions in relation to their distance from the 3-m-wide dolerite sill. One coal sample represented a direct contact with the dolerite intrusion (0 m) and the other sample represented coal further away (20 m) from the dolerite intrusion contact.

The samples of this study were investigated using a combination of techniques. The collected coal samples were pulverized and homogenized through grinding to a powder of <1 mm size dimension. The coal powder then went through accelerated solvent extraction (ASE) with toluene as the extracting solvent in order to detect and extract all the organic compounds within the homogenized coal. The ASE allows a liquid concentrate composed of organic compounds to be created from

solid particles. The gas chromatographic analysis of the organic-rich extraction of the coal sample was then performed on Pegasus® 4D GC x GC-TOFMS in order to characterize and quantify the organic compounds in the coal sample. The data output of the results is in terms of excel spreadsheets that are utilized in this study for statistical analyses purposes.

The chemical data obtained from the chromatographic analyses was further analysed and arranged in a simplistic manner. The data was presented in terms of bar graphs that revealed and compared concentrations (in area percentage) of different components. It should be pointed out that the 'area-%' of the organic compounds refers to the chemical identification of different peak series obtained from the chromatographic analyses. However, for the purpose of this study, although the different peaks do not represent the true concentrations of the different compounds on the coal surface, the measure of the peaks from the analyses should provide an estimate of the amount of the present compounds in the coal material. The data output of the proximal coal to the intrusion reported 1406 different organic compound peaks, whereas the distal coal to the intrusion reported 341 peaks.

The proximal and distal chemical data were treated separately and further subdivided into groups based on their functional groups and dominance. These components were further attributed into two major groups of importance, namely aliphatic and aromatic compounds, by assessing the chemical structures of each and every individual component based on the organic chemistry knowledge. The aliphatic and aromatic compounds resulted in a total of 16 and 41 subgroups, respectively. However, there was a presence of 27 unknown data points of organic compounds determined from the proximal coal. These unknown compounds were not allocated to any of the major groups.

3   Results of the Study

The organic compounds presented in the analysed coal samples consisted of a variety of functional groups that were classified into principal groups of aliphatic and aromatic compounds. The results of all analysed organic compounds in proximal and distal coal samples are presented in Figs. 1, 2, 3 and 4.

The analyses of the proximal coal sample (Fig. 1) show that the coal that is assumed to have received the maximum heat input is composed of more aromatic ($\sim$76 area-%) than aliphatic ($\sim$23 area-%) compounds and also a low concentration of unclassified unknown compounds ($\sim$0.2 area-%). In contrast, the distal coal sample analyses (Fig. 2) indicate that the composition of the organic compound is dominated by aliphatic compounds at $\sim$65 area-% and the remaining concentration of $\sim$35 area-% is made up of aromatic compounds. The distal coal sample contributes 73.4%, and the proximal coal sample contributes 26.6% of the overall aliphatic compounds. In addition, the contributions of proximal and distal coal samples to the overall aromatic compounds composition are 68.3% by the former and 31.7% by the latter.
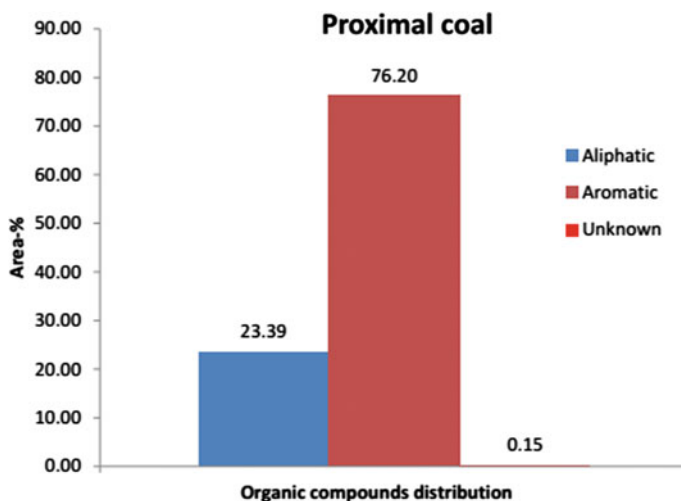
Fig. 1 Concentrations (in area-%) of organic compounds in proximal coal (direct contact) to the intrusion
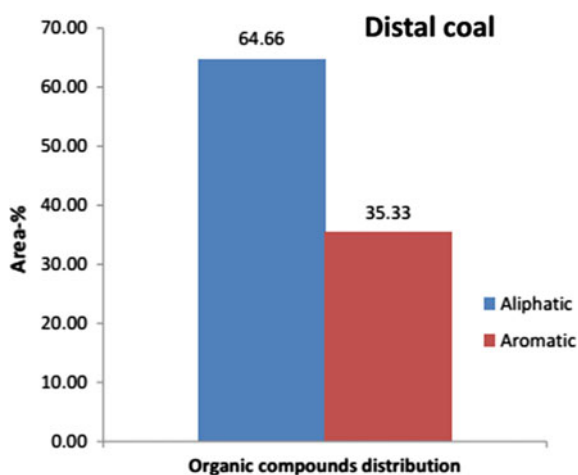

Fig. 2 Concentrations (in area-%) of organic compounds in distal coal (20 m away) to the intrusion

The comparisons among the 16 subgroups of the aliphatic compounds are shown in Fig. 3. *n*-Alkanes (straight-chain alkanes) are part of the organic compounds that make up most of the overall aliphatic compositions in both proximal and distal coal samples. These *n*-alkanes include octane, decane and higher alkanes (*n*C20–*n*-C31), all contributing $\sim$12.2 area-% in proximal coal and $\sim$26.1 area-% in distal coal.
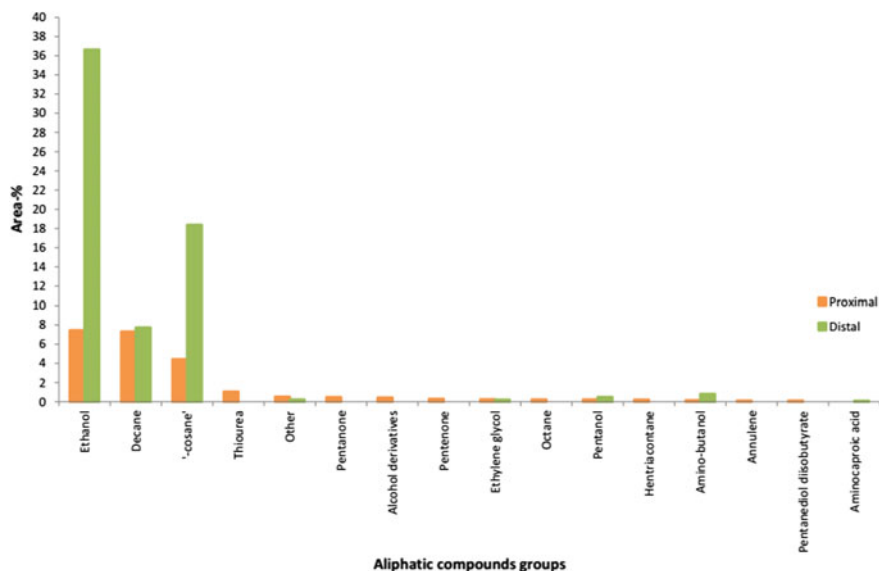
Fig. 3 Comparison of individual groups of aliphatic organic compounds concentrations (in area-%) in relation to the distance from the intrusion
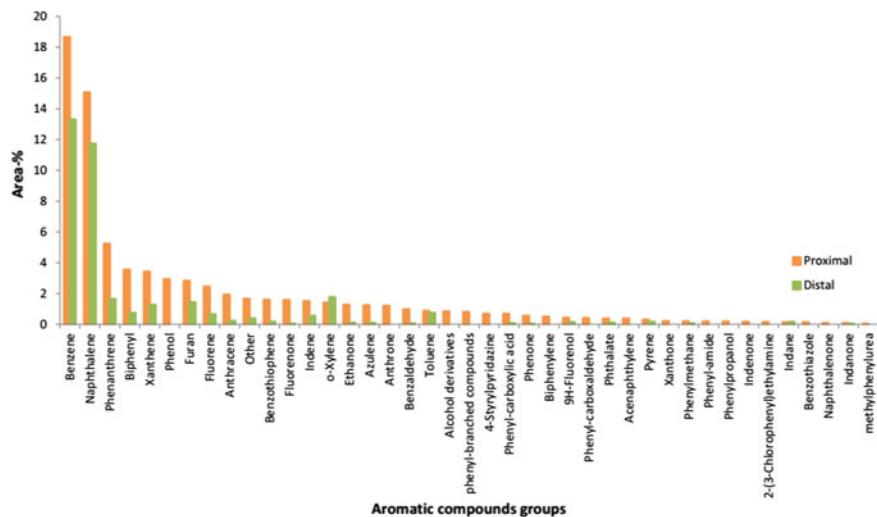

Fig. 4 Comparison of individual groups of aromatic organic compounds concentrations (in area-%) in relation to the distance from the intrusion

An aliphatic compound with the highest concentration evident in both coal samples is ethanol in which it contributes ∼7.4 and ∼36.6 area-% in proximal coal and distal coal, respectively. In addition, some of the aliphatic compounds such as

thiourea, pentanone, pentenone, octane, hentriacontane, annulene and pentanediol diisobutyrate occur in very low concentrations (<1.2 area-%) in the proximal coal and are absent in the distal coal.

The aromatic compounds that make up these coal samples are more varied and regular than the aliphatic compounds. The organic compounds identified 41 sub-groups composed of either entirely alkyl aromatic rings or a combination of both aromatic and aliphatic signatures. However, the organic compounds with both aromatic and aliphatic signatures (i.e. phenyl carboxylic acid) have the main functional group as aliphatic and the branches as aromatic (benzoic). Since the aromatic branches are significant, these compounds are classified into the 'aromatic compounds' group. Benzene, naphthalene, phenanthrene, biphenyl, xanthene, phenol, furan, fluorene and anthracene, inter alia, are the main aromatic compounds present in both coal samples in varying concentrations, especially in the proximal coal sample (Fig. 4). The proximal coal sample had the highest concentration for each aromatic compound compared to the distal coal with the exception being the concentration of o-xylene being more for the distal coal but with little variation. All these compounds consist of a variety of polycyclic and heterocyclic aromatic hydrocarbons.

Benzene as the main constituent of the aromatic compounds contributes ∼18.6 area-% in the proximal coal and ∼13.2 area-% in the distal coal. Benzene dominance is followed by naphthalene which composes ∼15.1 and 11.7 area-% of proximal and distal coal surfaces, respectively. In Fig. 4, the proximal coal shows a gradual trend of decreasing concentrations in organic compounds from left to right.

4 Discussion

The sampled coal can be assumed to have gone through the same initial coalification processes prior to modification by the dolerite intrusions since it is in the same coal seam. The analyses of the organic chemistry on the proximal and distal coal samples to the dolerite intrusion show significant variations in the aliphatic and aromatic compounds under investigation. One can safely suggest that these variations may have been caused by the emplacement of the dolerite intrusions. In addition, Snyman and Barclay (1989) reported that the metamorphic effects of the dolerite intrusions affected the South African coal, while the coal was still at the lignite stage of coalification. The heat input and interaction of the intrusions with the coal may have influenced the coal properties and driving different reactions resulting in the observed variations. Thus, the coal in the study area reached the bituminous coalification stage succeeding the effects already caused by the heat input of the intrusions. As a rule of thumb, the contact metamorphism of the dolerite intrusion effect on coal extends at variable distances, generally at 0.2–6 times the thickness of the intrusive (Snyman and Barclay 1989). Thus, one can postulate that the 3-m-wide dolerite sill in the study area affected coal at maximum distance of 18 m, excluding the position of the distal coal at 20 m away from the intrusive.

The differences in detected chemical identification peaks in gas chromatograms between the proximal (1406 compounds) and distal (341 compounds) coal samples indicate that the heat input breaks down heavy macromolecules of the coal into smaller constituents. Consequently, this results in formation of new compounds that are present in proximal coal and absent in the distal coal (i.e. anthrone and thiourea). It is evident from the present aromatic compounds in the proximal coal (Fig. 4) that the more complex their aromatic rings becomes, the lower their concentrations in the coal samples but with gradual variations. Benzene and naphthalene are the aromatic compounds that dominate both coal samples, and this can be due to these organic compounds having the simplest and more stable aromatic structures and containing at most two aromatic rings. The results indicated that the aromatic compounds are abundant in the proximal coal constituting approximately triple the concentration of the aliphatic compounds, and this suggests that aromaticity decreases with increasing distance from the intrusion. This signature exhibited by the burnt coal, which is slightly of lower rank relative to the distal unburnt coal, is contrasting with the general idea that aromaticity of coal increases with increasing coal rank. However, this can be explained by Puttmann et al. (1991) who reported that lower rank coals are generally characterized by a mixture of trapped alkylated aromatic and saturated hydrocarbons. The aliphatic compounds constitute most of the distal coal, and therefore, 'aliphaticity' increases with increasing distance from the intrusion. An uncommon substantial concentration of ethanol together with other hydroxyls is evident in the distal coal. This abundance possibly resulted from hydrothermal alteration on the coal through fluids generated by the intrusion rather than primary coalification processes. Literature does not support the existence of such large amounts of hydroxyls. In fact, hydroxyl functional groups should get progressively expelled as coalification progresses or get remobilized as pyrolytic residue by devolatilization processes (Avila et al. 2014; Denisov and Metelitsa 1968; Emsbo-Mattingly and Stout 2011; McMurry 1996; Pone et al. 2007; Sasaki and Sugai 2011; Snyman and Barclay 1989).

The spontaneous combustion in coal is driven by the oxidation reactions involving the organic matter of the coal (Emsbo-Mattingly and Stout 2011) Aromatic compounds are stable and should not oxidize at the temperatures commonly accepted for spontaneous combustion (i.e. at 60 °C) (Emsbo-Mattingly and Stout 2011). Generally, the chemical reactions involving aromatic compounds in nature occur at temperatures above 200 °C with the presence of catalytic fluids enriched in Cu and Fe ions (Emsbo-Mattingly and Stout 2011). In contrast, aliphatic hydrocarbons will readily oxidize at low temperatures (McMurry 1996). Avila et al. (Avila et al. 2014) reported that highly reactive coals, the distal coal in this case, produce unstable solid oxygenated complexes (oxycoal), which are readily decomposed by the liberation of heat at low temperatures, and low reactive coals (i.e. proximal coal) produce very stable solid complexes that react more slowly and break down at much higher temperatures.

From the observed effects due to heat input by the intrusives, one can deduce that since aromaticity increases with increasing heat input upon the coal, spontaneous combustion or rather coal oxidation will be inhibited. The distal coal with

substantial aliphatic compounds concentration is more prone to spontaneous combustion. However, if it occurs that both proximal and distal coal are subjected to oxidation (i.e. through ventilation), the more reactive distal coal will spontaneously combust earlier compared to the less reactive proximal coal which will take longer time to reach the self-heating temperature. As a result, the heat input by the dolerite intrusions has a positive impact on the organic matter of the proximal coal and a negative impact on the distal coal for the purpose of spontaneous combustion inhibition. However, this conclusion is only based on the chemical behaviour of the organic compounds among other intrinsic properties of coal that may behave differently to the metamorphic effects of the dolerite intrusions.

5   Conclusions

The spontaneous combustion of coal is a very complex process, and the processes still remain being not fully understood. The oxidation of coal is the principal mechanism leading to the initiation of the spontaneous combustion of coal. Among other factors affecting the spontaneous combustion, in the present study, the chemistry of the organic matter was utilized to evaluate the propensity of spontaneous combustion in the Highveld coalfields affected by dolerite intrusions. The functional groups detected from the chromatographic analyses are classified into aliphatic and aromatic compounds based on their reactivity when subjected to 19 oxidation processes, thus evaluating the concentration of these compounds within the proximal and distal coal. Aromatic compounds are stable and should not oxidize at the temperatures commonly accepted for spontaneous combustion, and in contrast, the aliphatic hydrocarbons will readily oxidize at low temperatures. The significant variations between the organic compounds' concentrations within the proximal coal and distal coal that underwent the same coalification processes suggest that the heat input by the dolerite intrusions had an effect on the coal. The proximal coal was subjected to maximum heat input and dominated by aromatic compounds. This observation thus suggests that the dolerite intrusion reduces the susceptibility of the spontaneous combustion in the proximal coal, however, based only on the chemical concentration of the organic compounds. The distal coal is more prone to spontaneously combust should the coal be exposed to ventilation.

References

Avila, C., Wu, T., Lester, E.: Estimating the spontaneous combustion potential of coals using thermogravimetric analysis. Energ. Fuels **28**(3), 1765–1773 (2014)

Denisov, E.T., Metelitsa, D.I.: Oxidation of Benzene. Russ. Chem. Rev. **37**(9), 656–665 (1968)

Emsbo-Mattingly, S.D., Stout, S.A.: Semi volatile hydrocarbon residues of coal and coal tar. In: Stracher, G.B., Sokol, E.V., Prakash, A. (eds.) Coal and Peat Fires: A Global Perspective, vol 1: Coal—Geology and Combustion, pp. 173–208. Elsevier (2011)

Finkelman, R.B.: Potential health impacts of burning coal beds and waste banks. Int. J. Coal Geol. **51**, 19–24 (2004)

Golab, A.: The impact of igneous intrusions on coal, cleat carbonate, and groundwater composition. PhD thesis, School of Geosciences, University of Wollongong (2003). Available from: http://ro.uow.edu.au/theses/164

McMurry, J.: Organic Chemistry, 4th edn. Brooks/ Cole Publishing Company. Pacific Grove, California (1996)

Pone, J.D.N., Hein, K.A., Stracher, G.B., Annegarn, H.J., Finkleman, R.B., Blake, D.R., Schroeder, P.: The spontaneous combustion of coal and its by-products in the Witbank and Sasolburg coalfields of South Africa. Int. J. Coal Geol. **72**(2), 124–140 (2007)

Puttmann, W., Steffens, K., Gobel, W.: Analysis of aromatic hydrocarbons in overburden from coal mines: assessment of the environmental impact. In: Peters, D.C. (ed.) Geology in Coal Resource Utilization, pp. 483–498. TechBooks, Fairfax, VA (1991)

Sasaki, K., Sugai, Y.: Equivalent Oxidation Exposure—Time for Low Temperature Spontaneous Combustion of Coal, Heat Analysis and Thermodynamic Effects. In Dr. Amimlu Ahsan (ed.). ISBN: 978–953-307-585-3 (2011)

Snyman, C.P., Barclay, J.: The coalification of South African coal. In: Lyons, P.C., Alpern, B (eds.) Coal: Classification, Coalification, Mineralogy, Trace-Element Chemistry, and Oil and Gas Potential. Int. J. Coal Geology, **13** 375–339 (1989)

Speight, J.G.: Handbook of coal analysis. In: Electronic Textbook. Wiley, New Jersey (2005)