

The petrology and petrogenesis of lamprophyric dykes in the Bushveld Complex, and their possible role in causing gas outbursts

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fulfilment of the requirements for the degree of Master of Science.

I, Priyal Daya (604364), declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other University.



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13th day of August 2019 at the University of the Witwatersrand

Abstract

A suite of Jurassic-Cretaceous lamprophyric dykes cross-cuts the Bushveld Complex. The lamprophyric dykes, not observed at surface due to their friable nature, have frequently been documented underground in platinum mines due to their association with gas outbursts that have taken place in the Western Limb over the past decade. The dykes are steeply dipping, have a thickness of 0.5 to 3 m and occur in a dyke swarm consisting of irregular, subparallel segmented and anastomosing dyke sets. The dykes are composed of macrocrysts of olivine that have been serpentinised to variable degrees, phenocrysts of phlogopite and a groundmass composed of fine-grained phlogopite, pyroxene and apatite with interstitial calcite. Some dykes have voids and veins that cross-cut the dykes themselves and are infilled with secondary minerals.

Upon outburst in 2007, one dyke, composed of phlogopite and pyroxene phenocrysts and set in a glassy groundmass of halite and natrolite, contained a geode of halite and natrolite, indicating that voids (in excess of 10 cm size) were present within the lamprophyre dyke. Lamprophyric dykes associated with outbursts have no structural, textural or mineralogical differences to those that have not been involved in outbursts. The halite-natrolite geode sample contains fluid inclusions of three different types, three-phase liquid + vapour + solid, two-phase liquid + vapour and single-phase liquid-only inclusions, but shows very few phase-changes during microthermometry, preventing compositional characterisation by this method.

‘In-line’ gas chromatography shows that gases are trapped within the lamprophyric dykes within pore spaces or in the form of adsorbed gases, or fluid inclusions within secondary minerals. The dominant gases trapped in the dykes are $\text{CO}_2 + \text{CO}$, CH_4 and C_2H_6 and occur in average abundances of 5.05×10^{-9} mol/g, 1.66×10^{-8} mol/g and 6.86×10^{-10} mol/g, respectively. Four boreholes drilled underground through the face of the dykes were tested for gas by *in-situ* gas analysis. CH_4 , CO and H_2 were the prevalent gases detected by the gas sensor and these gases were found to be constantly streaming out of the dykes at maximum levels of 7500 ppm, 24 ppm and 135 ppm, respectively. Active gas emission from the dykes implies that there is a continuous source of gas originating, not from the dykes themselves, but elsewhere in the system. Therefore, the dykes are merely acting as a conduit through which these gases are passing.

The present mechanism of outbursts in platinum mines of the western Bushveld appears to be the over-pressurisation of the aforementioned gases (likely to be sourced externally from the dykes – e.g., deeper or laterally distal) within a conduit system, comprising lamprophyre dykes and possibly other permeable pathways (e.g. faults and fractures). Where present, voids of various sizes (but probably mostly micro-scale, although the geode would indicate that some decimetre scale examples exist) within the lamprophyre dykes also act to accumulate these gases, forming pressurised gas pockets. Upon rapid depressurisation due to mining activities such as blasting or drilling, outbursts (at a variety of scales and magnitudes) take place causing damage to underground equipment and injuries to mine workers.

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1 Introduction to the study

The Bushveld Complex (Fig. 1.1) is the largest platinum deposit globally, and contains a vast array of other metals (Cawthorn, 2010). The enormous volume of magma (10^6 km^3 ; Cawthorn & Walraven, 1998) that formed the Bushveld Complex was emplaced into the Kaapvaal Craton at 2055 Ma (Zeh et al., 2013). The Bushveld Complex is hosted in the Transvaal Supergroup and is divided into four limbs; the Northern, Southern, Eastern and Western Limbs (Cawthorn and Walraven, 1998; Kinnaird, 2005). In continuing pursuit of mineral resources, platinum mines in most portions of the Bushveld are growing deeper (with the exception of those in the Northern Limb), and therefore are facing increasing operational difficulties and costs of mining. One such impedance to development is the under-documented occurrence of underground gas outbursts in certain mines in the Western Limb of the Bushveld, especially within the past decade. Whilst there is uncertainty regarding the exact process for formation of these gas pockets, interviews with industry workers has led to suggestions that the outbursts are spatially associated with 177.2-131.8 Ma (Hughes et al., in prep) old lamprophyric dykes that cross-cut the Bushveld Complex.

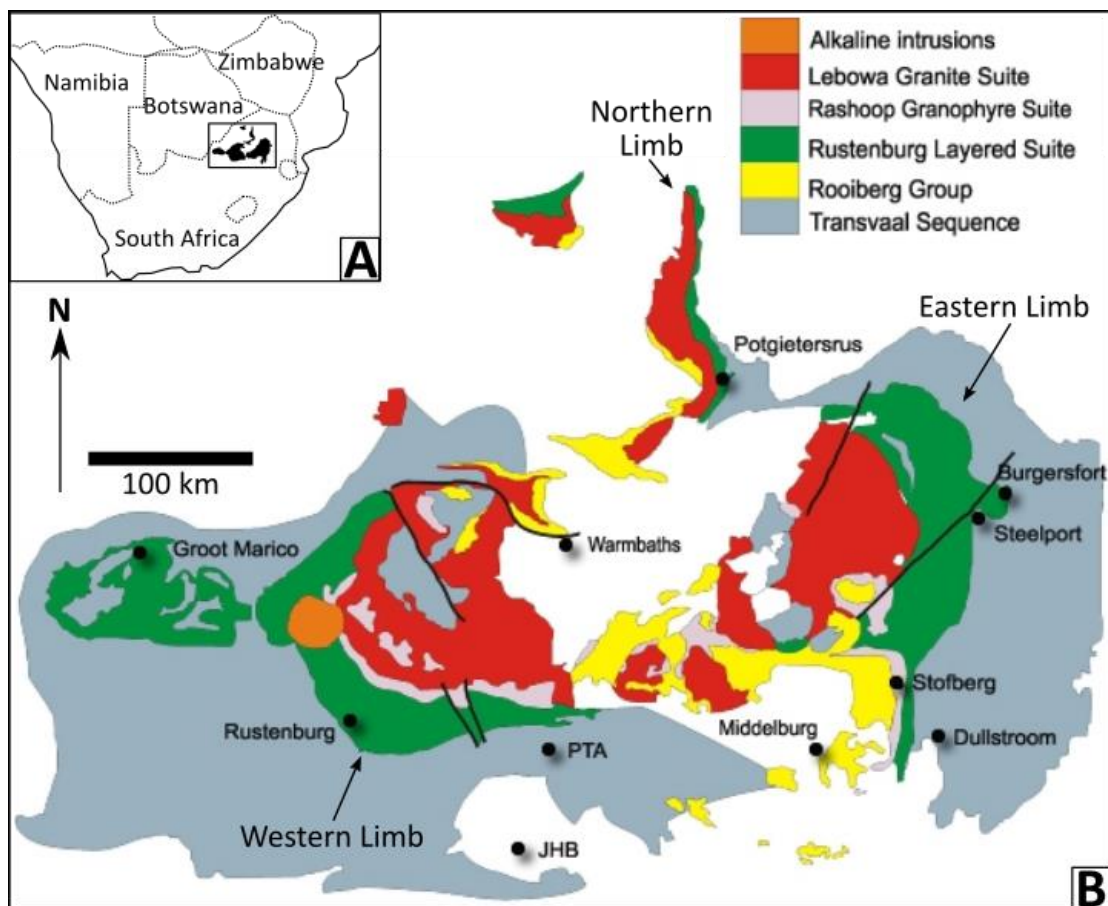


Figure 1.1. (A) A map of South Africa showing the location of the Bushveld Complex (adapted from Nex, 2004) and (B) a geological map of the Eastern, Western and Northern Limbs of the Bushveld Complex (adapted from Kinnaird, 2005).

Lamprophyric rocks are thought to be derived from volatile-rich, low degree partial melting of the subcontinental lithospheric mantle (SCLM; Rock, 1987). Thus, they provide information about the

composition of the SCLM and its evolutionary history (Becker and Le Roex, 2006; Mitchell, 1994). Currently lamprophyric rocks in South Africa are under-documented, but through an ongoing study initiated at the University of the Witwatersrand, lamprophyric dykes have been more openly documented in the Bushveld Complex and this recognition ultimately stems from the danger that such rocks pose to miners (ground falls and gas explosions; Hughes et al., 2016).

Falls of ground from lamprophyres are documented and explosive gas outbursts are particularly frequent in platinum mines in the Western Limb although other companies in the Western Limb of the Bushveld have reported similar problems (Hughes et al., 2016). Whilst such falls of ground are associated with the lamprophyres (that have been observed to rapidly ‘decay’, becoming very friable), the cause for the gas outbursts is yet uncertain. Indeed, there are varying ideas amongst the mining community as to whether these gas outbursts are truly related to the lamprophyric dykes, or if there is another underlying reason for their occurrence. This uncertainty stems from the complex geological features in outburst areas (e.g., presence of faults and iron replacement ultramafic pegmatites (IRUPs) and the observation that not all lamprophyres outburst. Therefore, a selection of these rocks will be studied in order to understand the types of lamprophyres that are prone to gas outbursts.

1.1 Aims, objectives and hypotheses

1.1.1 Aims

As lamprophyric rocks are typically volatile-rich, the alteration (either at the time of intrusion, or subsequently via percolating brines) associated with these intrusions may have significant implications for rock stability and explosive gas pockets, the formation of which is not currently understood (Mitchell, 1994 and Hughes et al., 2016). Thus preventative measures to ensure safe working environments of deepening mines cannot be enforced without an understanding of how and why such explosions occur.

This study documents a selection of lamprophyric dykes from the Western Limb of the Bushveld Complex, to investigate how (at a mineralogical scale) the dykes break down, and make predictions about the type of alteration and potential gases released during this process. **Via a combined mineralogical, geochemical and geotechnical approach, this investigation will establish the causes for the formation of explosive gas pockets facilitating direct remedial recommendations for mine safety.**

1.1.2 Objectives

In order to fully understand the various types of lamprophyres, predict how they decompose and identify volatile elements and gases that may be responsible for the explosive gas outburst, the objectives of this investigation are to:

1. Identify the major and accessory mineral assemblages, alteration, and textural features of the lamprophyric dykes using optical microscopy and scanning electron microscopy (SEM).

2. Analyse volatiles trapped within the dykes using traditional and Raman-based fluid inclusion studies.
3. Establish the bulk volatile content capable of being released from the dykes, using 'in-line' gas chromatography (GC).
4. Monitor gases emitted from dykes in real time using an *in-situ* gas detection system underground, adapted for the study.

1.1.3 Hypotheses

1. The mineral composition and textures of the lamprophyre dykes vary across the Western Limb of the Bushveld Complex. Therefore, there is not one, but multiple types of dykes in this area.
2. Fluid inclusions present in secondary minerals (halite, natrolite, calcite or barite) within the dykes are responsible for forming gas pockets, which are the cause for the gas outbursts.
3. Gases may be present in underground mines, in the Bushveld Complex, and could be responsible for the formation of gas pockets in the lamprophyric dykes.
4. The gas species associated with the outbursts, in the platinum mines, are similar to that of gases related to hazards in South African coal and gold mines.

2 Previous work on lamprophyres and gas outbursts

2.1 Definitions, classification, and mineralogical and geochemical properties of lamprophyres

Extensive research on the petrology and geochemistry of kimberlites and lamproites in South Africa has been carried out over the last 50 years. In comparison there are numerous publications on these rocks (e.g. Francis and Patterson, 2009; Janney, 2002; Jelsma et al., 2009) relative to the few papers published on lamprophyric rocks in this region (Anhaeusser, 1999; McNerney et al., 1992; Prevec et al., 2004; Shand, 1922). As lamprophyres have not been studied in detail, there is very little known about the types, ages and extent of lamprophyric dykes in southern Africa, and specifically, there is no published literature on lamprophyres that cross-cut the Bushveld Complex.

Lamprophyres commonly occur as dykes and are volatile-rich (Mitchell, 1994; Rock, 1987). Rock (1977; 1987) defines lamprophyres as alkaline rocks that contain lustrous plates of biotite or phlogopite, megacrysts of amphibole (often sodic), pyroxene or leucocratic ocelli, within an altered groundmass. Other key identifying minerals include ilmenites, spinels, halides, carbonates, sulphates/sulphides and zeolites (Rock, 1987). They are usually described as mesocratic (containing 30-60 % mafic minerals) to hypermelanocratic (containing 90-100 % mafic minerals), and are porphyritic in texture (Rock, 1987). According to Mitchell (1994), lamprophyres are characterised by containing euhedral-subhedral phenocrysts of phlogopite and/or amphibole, together with minor amounts of clinopyroxene and/or melilite, in a groundmass consisting of either plagioclase, alkali feldspar, feldspathoids, carbonates, monticellite, mica, amphibole, pyroxene, Fe-Ti oxide and glass, or in various combinations.

The nomenclature and classification of lamprophyres is not well defined and more than one classification scheme exists. A hierarchical system of classification for 'lamprophyric' rocks (including kimberlites) was first proposed by Rock (1987), consisting of five main 'branches': calc-alkaline lamprophyres, alkaline lamprophyres, ultramafic lamprophyres, lamproites and kimberlites (both groups I and II). 'Family' names (e.g., minette, camptonite, aillikite, etc.) were subsequently employed to differentiate specific lithologies. This attempt at justifying lamprophyric terminology greatly reduced the use of confusing regional or parochial terms (e.g., tjosite, baltorite, wesselite, etc.).

According to Rock (1987), the five branches of the lamprophyric clan are linked together by the presence of one or more of the following minerals: alkali or Ti-rich pyroxenes and amphiboles, Ba-Ti-phlogopites, Ba-K-feldspars, feldspathoids, melanitic garnet, melilite, monticellite, perovskite and silicates of alkalis with Fe, Ti, Zr, Nb etc. They contain combinations of feldspars such as the occurrence of K-feldspar coexisting with pure albite and alkali feldspars occurring with Mg-rich mafic minerals. Other striking features include high Mg and/or Mn ilmenites and high Zn-spinels (Rock, 1987).

The nomenclature of the lamprophyric clan is widely disputed, particularly by Mitchell (1994) and Woolley et al. (1996). It was argued by Mitchell (1994) that the "lamprophyric clan" merely unites rocks which have crystallised under volatile-rich conditions, and argues that the members of the clan are not

genetically related. He proposed that the term “lamprophyric” only be used to describe the observable characteristics of a set of rocks, that have been derived from a particular volatile-rich parent magma. The placement of kimberlites and lamproites under the lamprophyric clan has previously been considered inappropriate because the sub-classification of these rocks is unaccounted for (Woolley et al., 1996). Mitchell (1994) suggests the term ‘lamprophyric clan’ be replaced with ‘lamprophyric facies’ as the latter describes the common characteristics observed in a distinct group of rocks that disassociates them from other rocks. In contrast, the IUGS Subcommittee on the Systematics of Igneous Rocks does not validate the term ‘lamprophyric clan’. Alternatively, the IUGS classifies lamprophyres purely based on mineral contents and does not take into consideration any textural features, which makes the IUGS classification system limiting. Seifert (2008), however, has used both mineralogical and textural characteristics to classify lamprophyres.

Some attempt at diagnostic geochemical and mineralogical classifications has been made to distinguish lamprophyric rocks from each other. Lamproites are distinguished by their unique combination of K-silicate with rutile and either quartz or leucite. They can contain K-Ti-richterite and Fe-Ba-Ti-Zr silicates and have high K/Na and K/Al ratios (Bergman, 1987; Rock, 1987). Ultramafic lamprophyres (UML) have a high abundance of larnite (Ca_2SiO_4), soda-melilite, monticellite, Ti-Zr-garnet and are rich in Fe sulphides. They contain Mg-Mn-spinels and ferri-diopside which characterize them from other lamprophyres and are Si-poor and CO_2 -rich (Rock, 1987, 1986). Calc-alkaline (CAL) and alkaline lamprophyres (AL) have mineral assemblages of quartz and plagioclase, and nepheline and plagioclase, respectively, although neither contain any distinct mineral assemblage (Rock, 1987). Kimberlites are similar to UML and differ from lamproites by their lack of K-Fe-Ba-Ti-Zr silicates, low whole rock SiO_2 and high Mg, Cr and Ni contents, and are therefore also distinct from CAL and AL (Rock, 1987).

The first mention of lamprophyres in South Africa was by Shand (1922, p. 87), who classified two monchiquites (AL) in the Franspoort area in the Pretoria district. He described one of the dykes as “grey and fine-grained, with only a few phenocrysts of unfresh looking feldspar” and the other as “brick-red, and holds about 10 per cent of greenish feldspar phenocrysts”. A nearby area at Greenview was later described by McNerney et al. (1992), who provided supporting evidence. Based on the CaO, MgO, Sr and Ba concentration, the dykes were inferred to be alkaline lamprophyres (camptonites, AL).

First discovered by Anhaeusser (1999), and subsequently analysed geochemically by Prevec et al. (2004), the oldest lamprophyric dykes in the Kaapvaal Craton are found in the Nooitgedacht Migmatite Platform (Johannesburg Dome). These are calc-alkaline lamprophyres, dominantly formed of sericitised plagioclase, hornblende and biotite, and their lamprophyric character was identified due to their elevated abundances of K and Rb (Prevec et al., 2004). The dykes were recently age-dated and are 177.2-131.8 Ma (Hughes, in prep).

In comparison, kimberlites contain megacrysts of olivine/serpentine, ilmenite, mica, pyroxene and garnet, set in a groundmass of mica, spinel, perovskite, diopside and rarely monticellite. Like

lamprophyres, the constituents making up the groundmass occur in variable proportions (Dawson, 1980). Kimberlite dyke swarms, namely the Swartruggens and Star dyke swarms, located on the Kaapvaal craton have been well documented compared to that of lamprophyres. These dyke swarms are petrographically similar to each other (Coe et al., 2008). Both dyke swarms are dominated by anhedral to rounded olivine macrocrysts, with a lower proportion of phlogopite macrocrysts and is set in a fine-grained matrix comprising phenocrystic phlogopite, interstitial apatite, diopside, monticellite, serpentine and opaque minerals (Basson and Viola, 2003; Coe et al., 2008). The Swartruggens dykes are cross cut by the Muil dyke, which is identified as a lamprophyric dyke (Skinner & Scott, 1979 in Coe, 2004). The Muil dyke consists of euhedral to subhedral macrocrysts of olivine, phenocrysts of olivine, and lath-shaped phlogopite and diopside. The groundmass is dominated by acicular phlogopite with lesser calcite, serpentine, nepheline and sanadine (Basson and Viola, 2003; Coe, 2004). According to Coe (2004) the phlogopite phenocrysts, having a much darker red-brown colour and stronger pleochroism, are different to those of the Swartruggens kimberlites.

According to Mitchell (1994) and Woolley et al. (1996) Group I kimberlites lack phlogopite, pyroxene and amphibole phenocrysts, and are composed predominantly of second-generation olivine, calcite, serpentine and magnetite, together with minor phlogopite, apatite and perovskite. Group I kimberlites contain olivine macrocrysts which are the dominant constituent, set in a matrix composed of one or more of the following minerals; monticellite, phlogopite, perovskite, spinel, apatite, carbonate and serpentine. Accessory minerals include nickeliferous sulphides and rutile (Woolley et al., 1996).

Group II kimberlites are composed of phlogopite phenocrysts set in a groundmass composed of primary phases of diopside, titanian aegirine, Mg-bearing chromite to Ti-bearing magnetite spinels, perovskite, apatite, rutile and ilmenite. The primary phases are set in secondary minerals comprising calcite, dolomite, barite and serpentine (Woolley et al., 1996). The Group II kimberlite dyke swarms of Helam and Star Kimberlite are composed of variable proportions of olivine and phlogopite macrocrysts and phenocrysts set in a groundmass composed of apatite, diopside, monticellite, calcite, serpentine and opaque minerals (Mitchell, 1995).

2.1 Gas outbursts

2.1.1 Gas hazards in South African Mines

Through an ongoing regional study initiated at the University of the Witwatersrand, lamprophyric dykes have been recognised and documented in the Bushveld Complex (Hughes et al., 2016). This initial study miners highlighted the dangers posed by the lamprophyres in particular falls of grounds and explosions (“outbursts”). recognition ultimately stems from the danger that such rocks pose to miners (ground falls and gas explosions; Hughes et al., 2016). From this recognition of gases associated with lamprophyres a study has been conducted to assess the provenance of gases associated with lamprophyres and the mechanisms of outbursts with the aim of contributing to this safety problem. Most mines in South Africa are prone to gas outbursts and the number of flammable gas reports and accidents are steadily rising

(Abu-Mahfouz et al., 2014). In South Africa, methane is recognized as a hazard in gold and platinum mines (Abu-Mahfouz et al., 2014; Nivin et al., 2001). Volatiles, if present in varying lithologies, are sensitive to physical changes of the host rock (such as excavation and therefore depressurisation; Nivin et al., 2001). The release of volatiles contained in rocks is an important consequence of any mining or underground construction activity and must be understood in order to facilitate and implement appropriate health and safety criteria and mine operation regulations. The composition of gas(es) related to the lamprophyric dykes in the Western Bushveld is currently unknown, limiting the implementation of safety measures and prediction of gas outburst-prone areas.

2.1.2 Initial thoughts around lamprophyre-related hazards

Hughes et al. (2016) suggests that the decomposition of lamprophyre dykes is related to secondary salts (halite), carbonate or sulphate minerals. These salts and secondary carbonate/sulphate are seen in thin section of the dykes and sometimes can be seen leaching out of exposed lamprophyres underground. In particular, high amounts of halite are documented in a sample of lamprophyre that outburst during a large explosion underground in 2007 – this was analysed during the pilot study overleaf (Daya, 2016).

The linkage of the salt with the dyke, highlights the possibility that the mechanism of gas outbursts could be analogous to those in salt mines. For example, occurrences of outbursts have been investigated and mapped parallel to salt layers in the Cote Blanche salt mine in southern Louisiana, USA (Molinda, 1988; Warren, 2016). Other examples of gas outbursts have been documented in the USA, Canada and throughout northern Europe, where the salt domes contain zones of abundant fluid inclusions (Warren, 2016a). The literature documents simultaneous depressurisation of fluid inclusions as being responsible for these explosions (Nivin et al., 2001; Warren, 2016a). Fluid inclusions are liquids, solids and vapour that have been trapped during and/or after the growth of minerals (Shepherd et al., 1985), and can provide information about the petrogenetic processes of the host crystal. They are usually less than 100 µm in size and can occur in minerals such as halite, quartz, fluorite and calcite (Shepherd et al., 1985). According to Shepherd et al. (1985) the heating of a small sample of salt can cause individual crystals to explode. This is most likely due to a rapid build-up of fluid pressure in the inclusions, which causes them to decrepitate. Similarly, fluid inclusions formed at high pressures can undergo phase changes during decompression during mining activities (Warren, 2016a). A sudden phase change from liquid to gas can trigger abrupt expansion of the fluid inclusion. This results in fluid inclusions depressurising and thus decrepitating releasing gases. An outburst may occur when numerous fluid inclusions decrepitate at once (Shepherd et al., 1985; Warren, 2016).

Solid, liquid and vapour-phase changes can take place in fluid inclusions depending on their compositions (Shepherd et al., 1985). Whilst it is necessary to understand the composition of the fluid inclusions in this study, there are a vast number of techniques that are used to study fluid inclusions and analyse the gases within them. Fluid inclusion microthermometry is a process used to induce phase changes of fluid inclusions by heating or cooling the system (Shepherd et al., 1985). By measuring the

temperature at which these phase changes take place, it is possible to derive approximate values for the pressure, volume, temperature and composition of the fluids at the time of trapping (Shepherd et al., 1985). Microthermometry is usually coupled with Raman spectroscopy to understand the composition of a single fluid inclusion (Burke, 2001). Raman spectroscopy focuses a laser beam inside a single fluid inclusion. As different bonds between atoms of a compound vibrates at different frequencies, the frequency of the scattered light is measured. Information about the composition of fluid inclusions can thus be obtained (Shepherd et al., 1985; Burke, 2001).

Previous studies propose that the most abundant gases trapped in fluid inclusions in salt, carbonate or hydrothermal ore minerals are CO₂, CH₄, CO, N₂, SO₂ and H₂ (Kesler et al., 1986; Mulder et al., 2013; Salvi and Williams-Jones, 2003). Efforts were made by Kesler et al. (1986) and Mulder et al. (2013) to analyse gases in the fluid inclusions, trapped in minerals ranging from halite to jasperoid and quartz, by thermal decrepitation and step heating crushed samples in order for the gases to be released from the fluid inclusions within these minerals (via ‘desorption’). After desorption the sample was transferred to a gas chromatography system, which was used for the separation of hydrocarbons (Mulder et al., 2013). Kesler et al. (1986) and Mulder et al. (2013) observed a wide compositional variation (CO₂, CH₄, CO, N₂, SF₆, CF₄, CH₃Cl, CH₃Br and C₂H₅Cl) in gasses trapped in fluid inclusions as well as the release of CH₃Cl from halite. These variations can be correlated with the distribution of hydrothermal ore mineralisation in the system. It was also reported by Kesler et al. (1986) that the compositional and quantitative trends of gases observed are somewhat subtle and therefore gas analysis surveys would be most beneficial in conjunction with other geochemical surveys.

2.1.3 Pilot study on lamprophyres in the Bushveld Complex, South Africa

Daya (2016) used gas chromatography with thermal decrepitation to analyse the composition and relative volumes of gases produced from crushed lamprophyre samples. The samples were crushed to gravel-sized particles to preserve mineral associations but maximise reactive surface area. An experimental set up constructed in the School of Chemical and Metallurgical Engineering at University of the Witwatersrand, similar to Kesler et al. (1986) and Mulder et al. (2013), was used. Firstly N₂ gas was injected into the rubber tubing connecting all the components of the gas experiments and from one end of the experimental set-up (through the furnace tube) to the other. By decrepitating the samples under a nitrogen atmosphere in the furnace, the experiments prevented sample oxidation and formation of gases resulting from oxidation reactions, and were therefore representative of the gases primarily present within the rock sample itself. The crushed sample, placed in a silica-glass tube fitted within the tube furnace, was step heated at intervals of 100 °C. The reactions were timed at the target temperatures (1 minute reaction times), after which the gas was collected by simultaneously closing both sides of the outlets of the gas trap. The trapped gas was then transferred to the gas chromatography system (GC), based in the school of Chemistry at the University of the Witwatersrand, for analysis and identification of the gas species (molecular). The process was then repeated at the higher temperature step (ramp temperature 100 °C).

Three experiments were carried out on one lamprophyre sample, which had previously been associated with a major gas outburst (blowing out approximately 600 tonnes of rock). Gas experiment runs were carried out on dry samples. Headspace analyses were performed on the samples to record gases released at lower temperatures of 100 to 150 °C and were carried out directly on the gas chromatograph. For this the samples were incubated for 5 min at 100, 125, and 150 °C respectively.

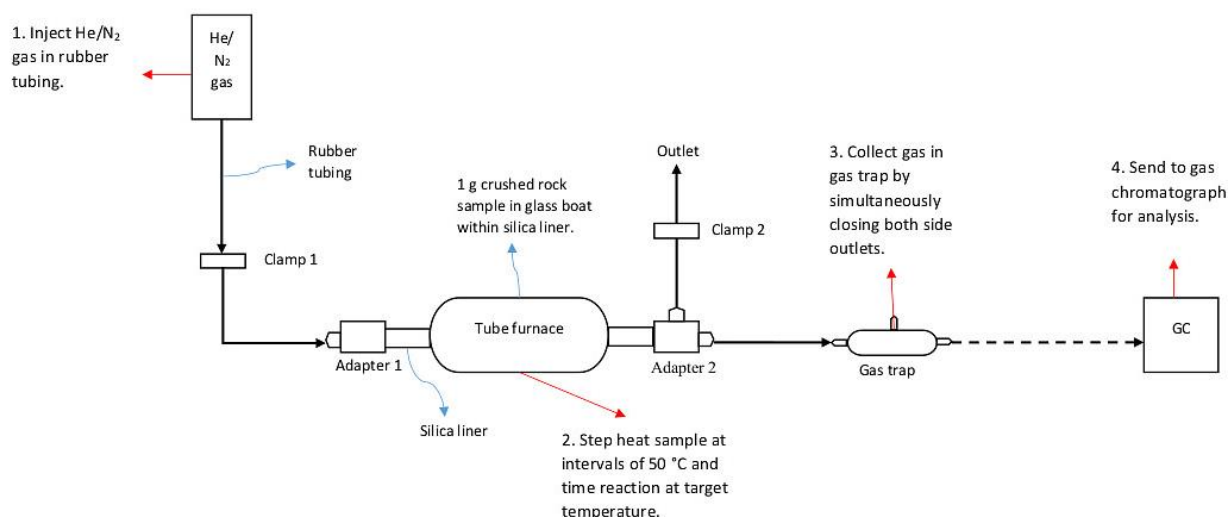


Figure 2.1. Schematic flow chart showing the process of gas extraction and analysis of crushed lamprophyre samples (Daya, 2016).

The GC Agilent© 7890B and MS Pegasus 4D GCXGC from Leco was used. The sample gas was measured at 0.5 mL and then injected into the injection port manually. The column type (BPX-5), length 29.851m of (30m), the internal diameter 250 μ m, and film thickness of 0.25 μ m with a maximum temperature of 350 °C was used. The carrier gas used was helium. The front inlet type was split with a split mode of 50:1. The flow rate was 1 ml/min at constant flow while the front inlet temperature was 200 °C. The initial oven temperature was 50 °C, maintained for 0.5 min, then ramped to 250 °C at 20 °C/min and held at 2500 °C for 1 min. The transfer line temperature was 225 °C. The data was then processed and a list of gases at each temperature was given.

Potter and Longstaffe (2007) assert that the gases trapped in fluid inclusions are most likely released during crushing of the rock which can be disadvantageous in most cases as only a sub-sample of the extracted volatiles is transferred to the gas chromatograph for analysis which limits detection levels. Furthermore extracting the gas by thermal decrepitation has proven to be the most problematic as the original gas compositions can be altered due to thermal decomposition and heat-induced chemical reactions (Salvi and Williams-Jones, 2003). A more efficient method of extracting gases trapped in fluid inclusions involves a setup whereby gases are released directly into the gas chromatograph by online crushing (Salvi and Williams-Jones, 1997) – i.e., using an inbuilt sealed crushing chamber to release gases directly into the GC system. The samples are crushed using a heat-treated stainless-steel crusher

adapted for immediate release of the fluid inclusion volatiles to the carrier gas which is directly injected into the gas chromatograph. The heat-treated stainless-steel crusher limits adsorption of gas onto newly created surfaces and the temperature is low enough to avoid chemical reactions between released gases. The online crushing technique maximises the amount of released volatiles injected into the gas chromatograph thereby increasing detection levels. Whilst this technique is excellent for fluid inclusion gas analysis, it does not cater for gas detection for volatiles chemically bound (crystallographically) within the minerals themselves that may be prevalent during higher temperature alteration (possibly by brines) of the rocks in nature. Therefore, both thermal decrepitation and the direct stainless-steel crusher method will be used for analysis during this study.

3 Methodology

3.1 Sample collection and preparation

A total of 51 lamprophyric dyke samples were collected from platinum mines in the Bushveld Complex, over a period of 4 years, commencing in 2015. Samples from historic outbursts, newer samples from recent outbursts and samples of lamprophyre dykes, not relating to outbursts, across the Rustenburg area were provided and collected from the mine. The sample suite studied included material from drillcore and hand samples.. Most of the core samples are from underground exploratory drilling and are 3.5 cm in diameter, and all the hand samples are from underground. Approximately 30 to 40 cm of core and hand samples were collected or provided for the study, and weighed between 1 to 5 kg. Core samples were split using the core splitter. One half of the core was used to make thin sections and the other half was crushed and used for gas chromatographic analysis. For the same reasons, hand samples were cut in half using a diamond saw. Information about each sample (core or hand sample) and what analyses were performed on each sample is summarised in Table 3.1.

3.2 Petrographic analyses

Fifty samples were made into polished thin sections for petrographic analysis. The thin sections were first examined by optical microscopy at the School of Geosciences (University of the Witwatersrand) using an Olympus BX41 petrographic microscope. Both transmitted and reflected light were used to identify and describe silicate, carbonate, sulphate, oxide and sulphide minerals present in the samples. After petrography was completed, the thin sections were then carbon coated at the Microscopy and Microanalysis Unit (MMU) at the University of the Witwatersrand and at the Camborne School of Mines, University of Exeter. Thereafter, scanning electron microscopy (SEM) and electron-probe microanalyses (EPMA) were conducted to document finer (20-200 μm) textural details of the lamprophyre dykes.

Fourteen dykes were studied using an SEM at Camborne School of Mines (University of Exeter, UK) in order to analyse dyke textures and further characterise mineral assemblages, particularly in the fine-grained groundmasses of the dykes. Analyses were conducted using the TESCAN VEGA3 GMU SEM, which is equipped with an X-ray Energy Dispersive Spectrometer (EDS) detector and a backscatter/secondary electron detector that are used simultaneously to evaluate a sample. The EDS detector measures X-rays to allow qualitative and semi-qualitative point-based chemical analysis (suitable to identify minerals and mineral compositions) and the secondary electron detector captures electrons scattered by a sample for visual detail. Samples were placed in a vacuum-sealed chamber on

Table 3.1. Sample information sheet containing a summary of the types of lamprophyric dyke samples, and analysis carried out on each sample.

Sample name	Dyke associated with outburst	Sample type	Petrography	SEM	EPMA	Fluid inclusion microthermometry	Raman spectroscopy	In-line GC
L-1F		Core	X					
L-2F/C		Core	X					X
L-4A		Core	X					X
L-4B		Core	X					X
L-7		Core	X					X
L-8B		Core	X					X
L-8C		Core	X					
L-9A		Core	X					X
L-9B		Core	X	X				
L-10A		Core	X					X
L-10C		Core	X					
L-11A	X	Hand sample	X	X	X			X
L-11B	X	Hand sample				X	X	X
L-12		Hand sample	X					
L-14		Hand sample	X					X
L-15		Hand sample	X	X	X			X
L-17		Core	X					X
L-19		Core	X					X
L-20		Core	X					X
L-23		Core	X					X
L-25		Core	X					X
L-40B			X	X	X			
L-62A			X		X			
L-76		Core	X					
L-88		Core	X					X
L-93		Core	X	X				
L-96		Core	X					X
L-97		Core	X					X
L-109		Hand sample	X					
L-111	X	Hand sample	X					X
L-112	X	Hand sample	X	X				X
L-113	X	Hand sample	X	X				X
L-114		Hand sample	X					X
L-115		Hand sample	X					X
L-116	X	Hand sample	X	X				X
L-125		Core	X					
L-131A		Core	X	X				
L-131B		Core	X	X				
L-PD1A		Core						X
L-PD1B		Core						
L-PD2		Hand sample	X	X				X
L-PD3		Core	X					
L-PD4A		Hand sample	X					X
L-PD4B		Hand sample	X					X
L-PD10*		Core						
L-PD11*		Core						
L-PD12*		Core						X
L-PD13*		Core	X	X				
L-PD14*		Core						X
L-PD15*		Core						X
L-PD16*		Core	X					
L-PD17*		Core						X
L-PD18*		Core						X
L-PD19*		Core		X				
L-PD20*		Core						X
L-PD21*		Core	X	X				
L-PD22*		Core						
L-PD23*		Core	X	X				X
L-AB1	X	Hand sample	X					X
L-AB2		Hand sample						X
L-AB3		Core						X
L-AB4		Core						X
41-166			X		X			
IRUP-001		Core		X				X

*Samples from boreholes drilled for underground in-situ gas analysis

high vacuum mode in the SEM. The chamber fits four polished thin sections. Operating conditions consisted of an accelerating voltage of 20 kV and a working distance ranging from 15 to 17 mm. AZtec software was used to navigate the sample, collect back-scattered electron images, and select a series of data points where EDS spectra were obtained for mineral identification.

Daya (2016) acquired mineral chemistry data for 5 lamprophyre samples (Table 5.1) using EPMA. Polished thin sections of these samples were carbon coated at the Microscopy and Microanalysis Unit (MMU) at the University of the Witwatersrand. Analysis was conducted at Rhodes University (South Africa) to measure the quantitative mineral chemistry of major rock-forming minerals (predominantly biotite-phlogopite, and pyroxenes). Four wavelength dispersive spectrometers on a JEOL JXA-8230 EPMA were used. The beam, generated by a tungsten cathode filament, had an accelerating potential of 15 kV, 15 nA beam current, and was 10 μm in size. Counts for all elements were measured on K-alpha peaks except for Ba, which was measured on L-alpha peaks. Counting times were 10 seconds on the peak, and 10 total on the background, for all elements. Commercial “SPI” standards were used, and included plagioclase (Si/Al/Ca/Na), orthoclase (K), willemite (Mn), crocoite (Cr), diopside (Mg), kaersutite (Fe), tugtupite (Cl), pentlandite (Ni), benitoite (Ba), SrTiO_3 (Ti), and MgF_2 (F). For pyroxenes, additional calibrations used were diopside (Si), kaersutite (Al/Mg) and biotite (Fe). Calibration acquisitions were peaked on the standards, while unknown acquisitions were peaked on the samples before each point analysis. The data were collected with JEOL software. An automated PRZ matrix algorithm was applied to correct for differential matrix effects between standards and analysed minerals, while ZAF was applied to everything else. Oxygen was calculated by stoichiometry per mineral species (Daya, 2016).

3.3 Fluid inclusion microthermometry

Fluid inclusion microthermometry was used to determine compositions of the volatiles trapped in fluid inclusions hosted in halite, within the lamprophyre dykes. A doubly polished thick section of a sample (L-11B) of halite and natrolite, was provided by Dr. Lynette Greyling from the University of Cape Town. The sample had previously been broken into smaller chips and used for fluid inclusion microthermometry by Dr. Greyling. This sample was re-analysed for this study at the School of Geosciences, University of the Witwatersrand.

Six of these chips were first examined using an Olympus BX41 petrographic microscope to locate and map fluid inclusions. Only three chips that were the most suitable (transparent and contained the most suitably sized inclusions) were analysed. The fluid inclusion microthermometry setup, at the School of Geosciences (University of the Witwatersrand), consists of a LINKAM 600 cooling and heating stage attached to an Olympus BX41 optical microscope, a liquid nitrogen tank and a water cooling pump. For analysis, a chip of the sample was placed in the cooling and heating stage. Using the Linksys 32 software the sample chip was first cooled to $-100\text{ }^{\circ}\text{C}$ to determine the freezing temperature of a single fluid inclusion, in order to obtain its composition. The stage was then heated to $230\text{ }^{\circ}\text{C}$ to acquire the melting

and homogenisation temperatures of the inclusion. The sample was held at this temperature for 5 minutes, to ensure that the phases in the fluid inclusion had homogenised. To avoid decrepitation of the inclusion, the sample was cooled down to room temperature (23-25 °C) before removing the sample from the cooling and heating stage. The samples were cooled and heated at a rate of 5 °C/min. The same process was repeated for every inclusion, and in total 10 inclusions were analysed. Images were taken, using the 50× objective and Stream Essentials software, for every phase change that took place.

3.4 Raman Spectroscopy

As fluid inclusion microthermometry only provides estimated results, Raman spectroscopy is needed to confirm the composition of volatiles inside the fluid inclusions. Raman spectroscopy was carried out at MMU at the University of the Witwatersrand, on the same doubly polished section used for fluid inclusion microthermometry. Raman spectra were acquired using the 514.5 nm line of a Lexcel Model 95 SHG argon ion laser and a Horiba LabRAM HR Raman spectrometer attached to an Olympus BX41 microscope. The incident beam was focused onto the sample through a 100× objective and the backscattered light was dispersed via a 600 lines/mm grating onto a liquid nitrogen cooled Charge Coupled Device (CCD) detector. The signal from the detector was acquired using LabSpec version 5 software. The laser spot diameter at the sample was approximately 1 micron.

A total of 19 inclusions were analysed and for every inclusion measurements were taken for every phase (liquid, solid and/or gas) present in the fluid inclusions. The sample hosting the fluid inclusions (where transparent enough) was also analysed using this equipment in order to confirm its composition. A once off analysis was performed to ascertain the Raman intensity of a single fluid inclusion compared to that of the host material. Measurements were taken at 15 points, every 2.5 microns, along a 35 micron line running through the liquid-phase of the fluid inclusion.

3.5 ‘In-line’ Gas chromatography

‘In-line’ gas chromatography (GC) was used to determine the bulk composition of volatiles trapped in fluid inclusions or pore spaces within lamprophyric dykes. Thirty-eight samples of lamprophyre dykes were analysed, 7 of which were from dykes associated with gas outbursts. One sample of an iron-rich ultramafic pegmatitic (IRUP) dyke was also analysed for comparison.

Collaboration of this work took place with Dr. Jacob Hanley at the Department of Geology at Saint Mary’s University (Halifax, Nova Scotia, Canada). Analysis was carried out using an Agilent 7890 series GC equipped with a micro-thermal conductivity detector (TCD) along with a H₂-burning flame ionization detectors (FID). Another FID is installed on a separate valve controlled assembly which enables this GC setup to have 2 distinct separation methods (Kerr, 2013). The first method of separation uses the TCD and both FIDs to detect and quantify inert and non-combustible compounds (i.e., CO₂, CO, H₂O) as well as hydrocarbons (i.e., CH₄, C₂H₆, etc.), respectively. CO₂ and CO are detected together and are not separated. Method 2 allows for only combustible compounds such as hydrocarbons to be

analysed and only employs one FID. The setup (Fig. 3.1A) consists of 4 stainless steel, hydraulically driven rock crushers (Fig. 3.1B). The crushers are attached to the GC by capillary tubes, through which the volatiles are directly injected into the GC after crushing of a sample. Hence 'in-line' GC is a more efficient technique that allows for maximum amount of volatiles to be transferred into the GC which improves detection levels, limits adsorption of gas on newly created surfaces and constrains chemical reactions taking place during crushing (Kerr, 2013). This technique has a lower detection limit of approximately 10^{-12} mol/g of crushed sample (Kerr et al., 2015).

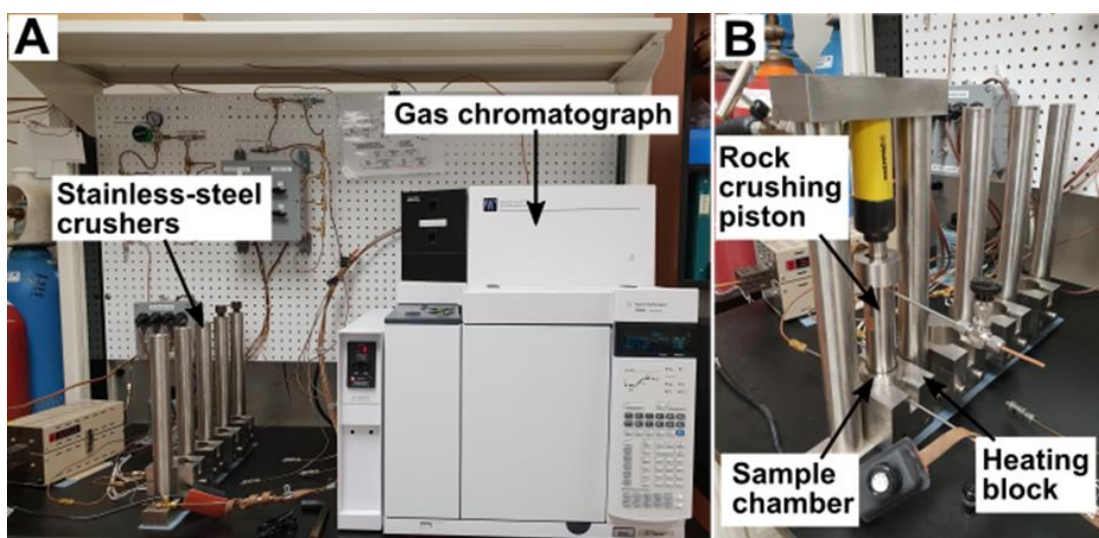


Figure 3.1. Photographs showing (A) the GC setup and (B) a close up of the four stainless-steel crushers connected to the GC.

Analysis of all 39 samples was performed using method 1 in order to identify the type of gases trapped in fluid inclusions within the dykes. Samples were prepared by first crushing 100 to 300 g of grab and core samples using a jaw crusher, which was cleaned in between each sample to avoid cross-contamination. Fragments, 1-3 mm in size, of crushed rock from each sample were handpicked using a pair of tweezers. This crushed material was picked until an aliquot of approximately 1.0 g was collected. The 1 g aliquot was placed in small sealed vials for storage. In preparation for analysis, each aliquot was washed in de-ionized water twice, sonicated and then re-washed in de-ionized water to ensure the removal of all adsorbed acids and organic solvents. A hot plate was then used to dry the aliquots at ~50-60 °C. These were then sieved and re-weighed, and baked in the oven overnight at ~50 °C prior to loading them in the pre-cleaned crushers connected to the aforementioned GC.

In preparation for aliquot loading, the rock crushers were cleaned using acetone for the sample chambers, isopropynol for the pistons and then dried with compressed air after solvent cleaning. A small amount of inert and volatile-free silicone grease was placed around crusher o-rings and the crushers were then sealed and heated overnight (~10-15 hours; ~100-110 °C) under dynamic He flow (≤ 2 ml/min) in order to remove any adsorbed compounds including water and cleaning solvents (Kerr, 2013).

A series of blank runs were performed using inclusion-free Brazilian quartz crystals to account for any volatiles released as a result of the mechanical action of the crusher (Kerr, 2013). The background information from the blank runs were then averaged and subtracted from the collected chromatograms (Kerr, 2013). After all 4 crushes were loaded, crushing of 1 sample at a time took place at elevated temperatures (~105-110 °C) to achieve instantaneous volatilisation of entrapped fluids (Kerr, 2013). Following analyses of all samples by method 1, the 4 samples that were most abundant in CH₄ were selected and analysed using method 2 to see what other hydrocarbons might be entrapped in the rocks.

3.6 Underground *in-situ* gas analysis

Unlike ‘in-line’ GC, which was used to analyse bulk volatiles trapped in fluid inclusions or pore spaces within the lamprophyre dykes, underground *in-situ* gas analysis was used to detect gases flowing through the dykes. This analysis was carried out on 4 lamprophyric dykes underground at a platinum mine in the Western Limb of the Bushveld Complex. A week prior to analysis 4 boreholes were drilled along strike and through the face of 4 different lamprophyric dykes (Fig. 3.2 and 3.3A). The boreholes were approximately 3 m in length and 3.5 cm in diameter (Fig. 5.3B). All 4 boreholes went out of the dyke and into Bushveld wall rock (Table 3.2) within the last 30 cm of the hole as a result of the bifurcating nature of the dykes. Two boreholes (BH1 and BH2) were drilled on the deepest level of the shaft, one (BH3) on an intermediate level and the fourth (BH4) on a shallower level (Table 3.2). The boreholes were drilled in the drives of the mine away from the working areas. The wall rocks of these dykes are anorthosite, mottled anorthosite and norite for boreholes 1, 2 and 4, and 3, respectively. Directly after these boreholes were drilled, they were plugged by cementing steel mechanical valves (Fig. 3.2) to allow for a build-up of gases over the preceding week. Core from each borehole was recovered. Thee cores were logged and photographed, and multiple samples of core from each borehole were collected for petrographical and gas chromatographic analyses so that comparison could be made between *in-situ* gas analysis and lab-based results.

Table 3.2. Summary of underground borehole information.

Borehole (BH) no.	Wall rock
BH1	Anorthosite
BH2	Mottled anorthosite
BH3	Norite
BH4	Mottled anorthosite



Figure 3.2. Photograph of a plugged borehole (BH1) in a lamprophyric dyke cross-cutting Bushveld anorthosite.

In-situ gas analyses, down the holes, were carried out a week after the drilling of the boreholes using the Dräger X-am 5600 Multi-Gas Monitor attached to a pump and hose (Fig 3.3B). The gas monitor is battery operated, contains rechargeable batteries and has at least 6 hours of working time. All equipment fits in a small, lightweight carrycase. The hose is flexible, has a diameter of 3 mm and is up to 3 m in length. The gas detector was calibrated to detect six gases (CH_4 , CO_2 , CO , H_2 , H_2S and Cl_2) simultaneously. Calibration of the gas detector was performed by the Dräger supplier, at their laboratory, and the instrument undergoes an automatic fresh air calibration each time the device is switched on or is plugged into its charging cradle. A fresh air calibration is automatically carried out when the gas detector is placed in the charging cradle. The lower detection limits for CO_2 , CO , H_2 and H_2S are 0.01 vol.%, 3 ppm, 0.4 ppm and 1 ppm, respectively (Table C.1 in Appendix C). Background measurements were first taken, with the hose already attached to the pump and gas detector, over a 5 minute duration before analysing each borehole. The boreholes were opened via the cemented valves to allow for control when opening and closing the hole. The hose was then fed through the borehole with the instrument remaining switched on and actively detecting for gases. Measurements were taken every minute for a duration of 30 minutes. At 2 of the boreholes (BH3 and BH4), background measurements were repeated after the analysis of these boreholes. The valves were closed to allow gas to refill the boreholes over a period of 24 hours. The next day analysis took place following the same procedures for all 4 boreholes. However, this time around gas measurements were taken every minute for a duration of 15 minutes at each borehole. A second set of analyses served as a repeat for comparison to the previous day's dataset. The analysis could only be repeated once due to limited access underground in the working mine. Significant assistance was required, from mine personnel, to facilitate and carry out the analyses. The boreholes were finally unplugged to avoid a build-up of gas pressure.

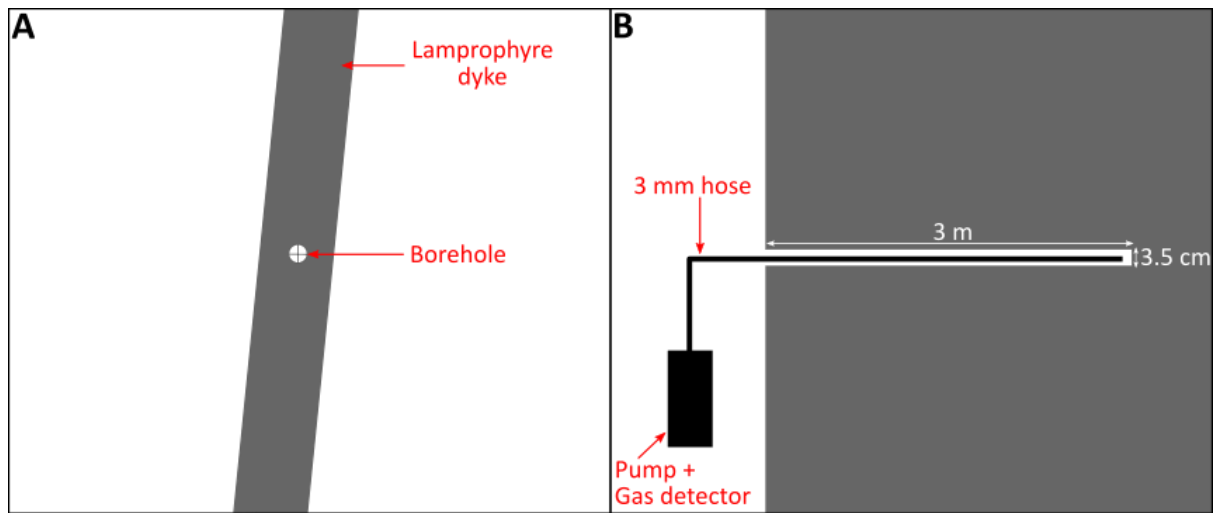


Figure 3.3. Schematic diagram of (A) a side view of the borehole drilled through the lamprophyre dyke and (B) a section view of the underground *in-situ* gas analysis setup showing the Dräger pump and gas detector attached to a hose which was fed into the borehole through the lamprophyre dyke.

4 Distribution and description of lamprophyric dykes

4.1 Distribution of lamprophyres

The lamprophyric dykes in the Western Limb of the Bushveld Complex occur as a swarm consisting of hundreds of sub-parallel dyke sets. The dykes are not exposed at surface but are easily observed in underground mining operations at depths between 1000 and 3000 m.

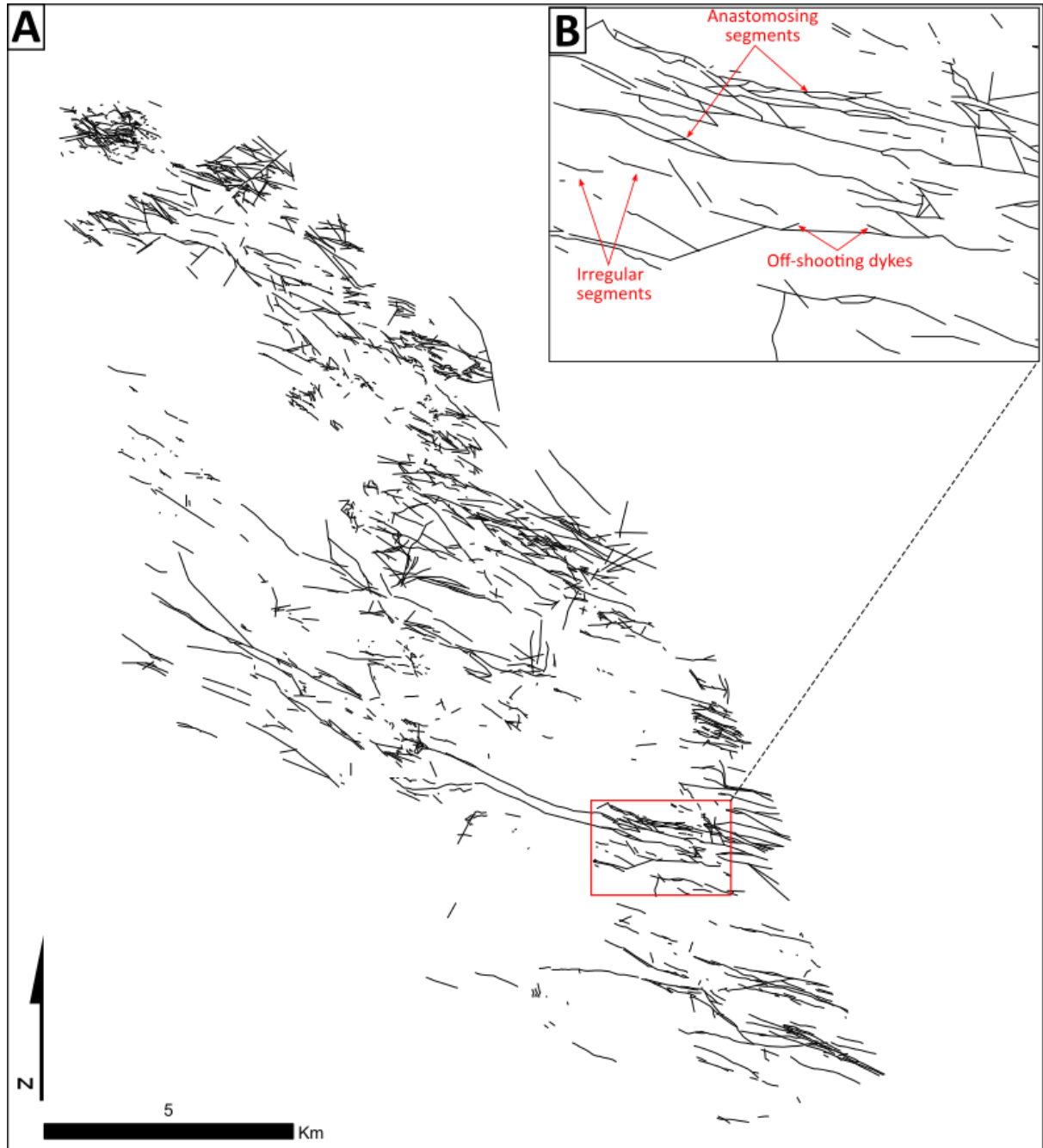


Figure 4.1. Map showing (A) the distribution of the lamprophyric dykes in the Western Limb of the Bushveld Complex and (B) a close up of the area in A (highlighted by the red square) illustrating the nature and trend of the dykes.

Figure 4.1A shows the nature and distribution of the dykes in the Western Limb of the Bushveld Complex. The dykes have a strike ranging between WNW and ESE and they can be traced along strike for approximately 50 km (Hughes et al., in prep.). The mean azimuth of the dykes are 112° (Hughes et al., in prep.). The dykes are sub-vertical and have a steep dip of greater than 80° . The width of the dykes ranges from ~ 0.1 to 20 m in apparent width but generally have a true width of between 0.5 to 3 m. They occur as irregular or anastomosing segments, or as continuous dykes that often bends away in another direction at the ends of the dykes (Fig. 4.1B). They are commonly seen to bifurcate and form networks of off-shooting millimetre-scale veinlets in their host rocks, which comprise norites, pyroxenites and anorthosites of the Bushveld Complex.

4.2 Description of dykes

The lamprophyric dykes are exposed underground in the mine, on the sidewalls and ‘back’ or roof (Fig. 4.2A and B). The colour of the lamprophyric dykes usually ranges from grey to brown (Fig. 4.2A and B) and they shimmer when light is shone on them because of the high abundance of mica present in them. Most dykes are friable and crumble, leaving loose lamprophyre on the floor of the mines. The bifurcating nature of the dykes is observed underground and veins of lamprophyre are seen to anastomose in their host rocks (Fig. 4.2C and 4.3B).

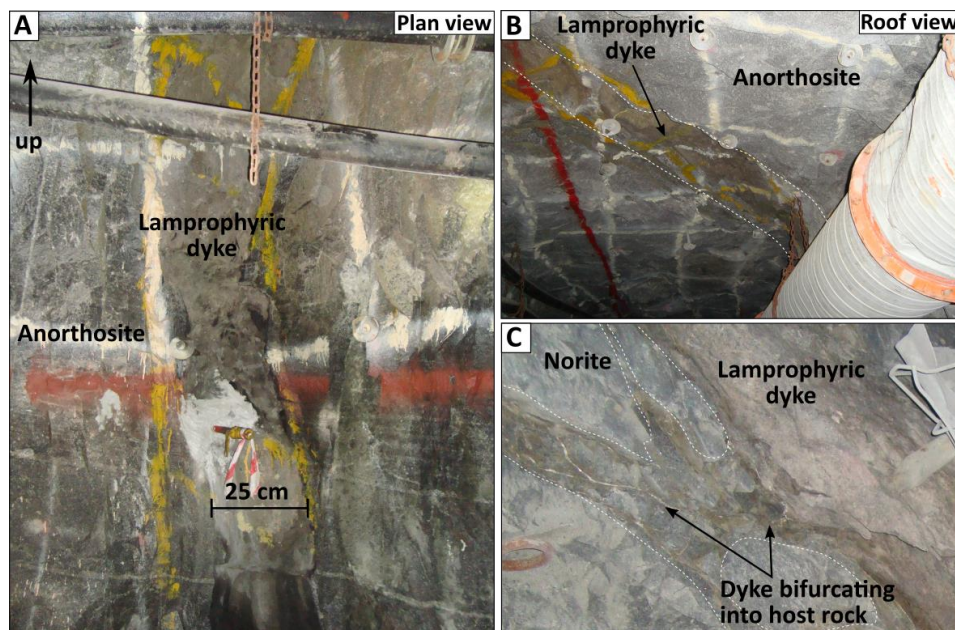


Figure 4.2. Photographs taken underground at a platinum mine in the Western Limb of the Bushveld Complex showing (A) a plan view of a lamprophyric dyke cross-cutting Bushveld anorthosite, (B) a roof view of the same lamprophyric dyke in (A) and (C) a bifurcating dyke, and veins anastomosing in Bushveld norite outlined by the dashed line.

The lamprophyric dykes vary in colour from light to dark grey and light to dark brown. They have sharp and straight contacts with their host rocks (Fig. 4.3C), and chilled margins, 0.1 to 0.3 cm in width, which

are observed by a darker colour and aphanitic texture. Crustal xenoliths from the Transvaal Supergroup and the Bushveld Complex are commonly contained within the lamprophyres (Fig. 4.3A). Several dykes contain olivine macrocrysts that are visible in hand/core sample. These macrocrysts are subhedral to rounded and are dark grey to black in colour (Fig. 4.3F). They range in size from 0.2 to 0.5 cm. One hand sample (L-AB1) contains euhedral to rounded phlogopite macrocrysts that are dark brown in colour and 0.2 to 1.5 cm in size (Fig. 4.3G). The rest of the dykes are either phenocrystic in texture with visible euhedral phlogopite phenocrysts (~ 0.1 cm; Fig. 4.3C) or fine-grained (<0.1 cm) with no visible grains. Flow features are commonly seen where the olivine macrocrysts and/or phlogopite phenocrysts are aligned. Figure 4.3D shows the vuggy-texture of the dykes, which contain voids that are 0.1 to 0.5 mm in size. Amygdales of secondary minerals such as calcite or barite, infill these voids and are white in colour (Fig. 4.3E). Veins (0.1-0.3 cm) filled with the same secondary material cross-cut the dykes. Banding is observed in some dykes, where abrupt changes in grain-size, colour and lithology occur. Figure 4.3E shows bands visible in a core sample. The bands are 0.5 to 1.5 cm thick and have both irregular and straight contacts with the host rock and in some cases can be seen to bifurcate. One particular dyke (L-11A) has a different texture and lithology from the rest of the lamprophyres. This sample contains green, prismatic pyroxene and brown, euhedral phlogopite crystals (0.1-0.4 cm in size), and is porous containing voids filled with secondary precipitates such as halite, calcite and/or barite (Fig. 4.3H). A large (20-30 cm) geode of secondary minerals from a void within sample L-11A is composed of a mixture of white to transparent acicular crystals of natrolite surrounded by pink halite (Fig. 4.3I). The natrolite crystals are 0.5 to 5 cm in length, 0.5 cm in width and are randomly oriented throughout the halite.

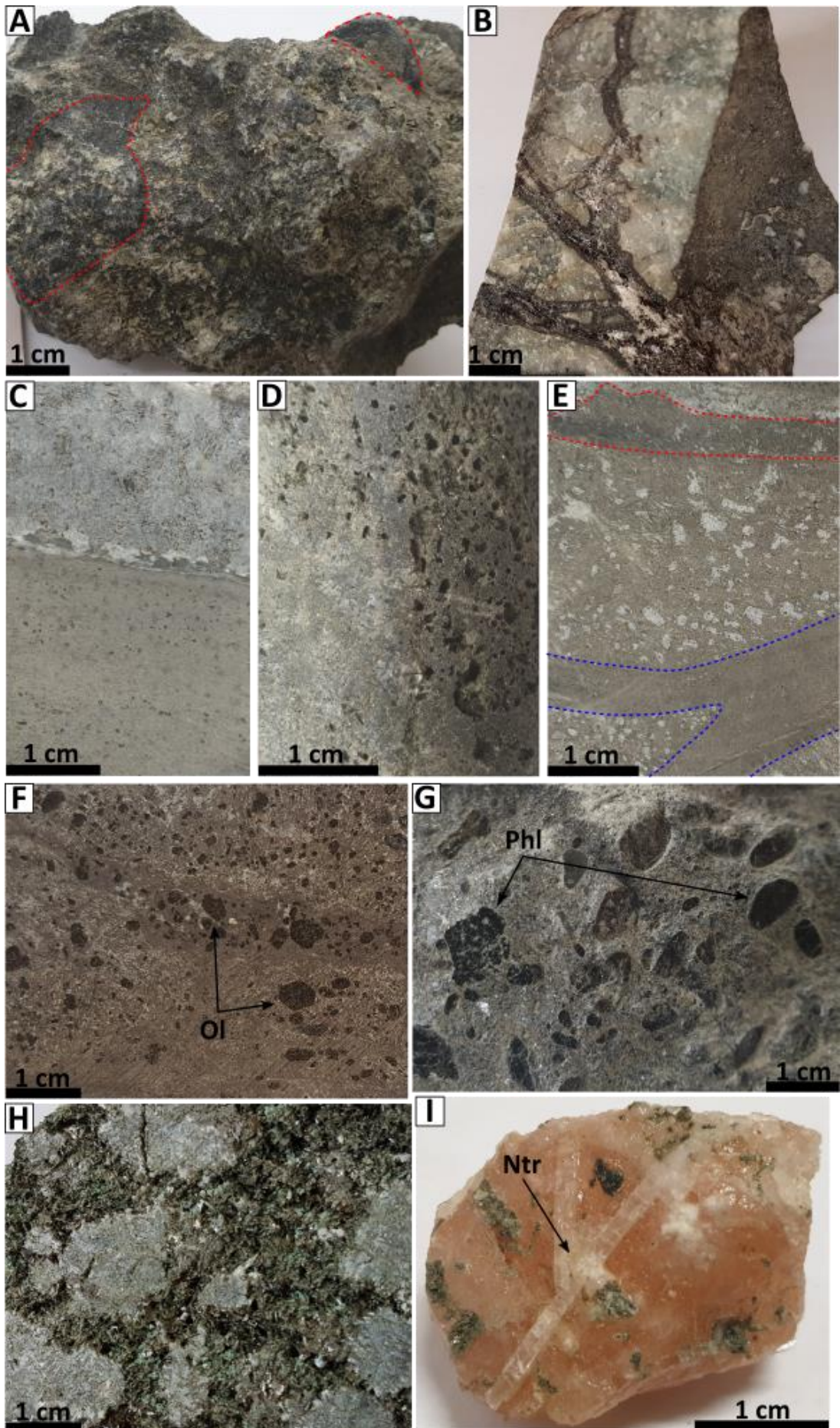


Figure 4.3. (overleaf). Photographs of hand and core samples showing (A) shale xenoliths from the Transvaal Supergroup in sample L-PD2, (B) lamprophyric veins in sample L-15 cross-cutting Bushveld anorthosite, (C) macrocrystic-free lamprophyre (sample L-9B) in contact with Bushveld norite, (D) sample L-2 containing unfilled voids, (E) bands of different lithologies in sample L-93, (F) olivine (Ol) macrocrysts in sample L-40B, (G) phlogopite (Phl) macrocrysts in sample L-AB1, (H) vuggy-textured, pyroxene-rich lamprophyre of sample L-11A and (I) a piece of sample L-11B, a halite-natrolite (Ntr) geode from a void within sample L-11A. Abbreviations of minerals were taken from Whitney and Evans (2010).

4.3 Description of underground borehole core samples

Four boreholes through the face of 4 different lamprophyric dykes were drilled in order to carry out underground *in-situ* gas analysis (see Section 3.6). The cores from these boreholes were recovered by mine personnel. The cores were logged to document textural and lithological features of the dykes. The core logs (Fig. 4.4A, B, C and D) represent the core from BH1, BH2, BH3 and BH4 (see Table 4.1), respectively. All 4 dykes are macrocrystic in texture and contain serpentinised olivine macrocrysts in a fine-grained (<0.1 cm) groundmass. The olivine macrocrysts are rounded, and range in size from 0.2 to 1 cm. Throughout the cores of boreholes 1, 2 and 4, calcite-bearing amygdales, ranging from 0.1 to 1 cm, are present. The core for borehole 3 contains thin calcite veins (0.1-0.5 cm in width) that occur in only some parts of the dyke. The core for all 4 boreholes starts in lamprophyre and ends in 40 to 80 cm of Bushveld wall rocks. Boreholes 1 (Fig. 4.4E), 2 and 4 (Fig. 4.4F) have 40, 80 and 50 cm of spotted anorthosite at the end of their cores, whilst borehole 3 contains 40 cm of norite. The contacts between the lamprophyric dykes and the Bushveld wall rocks are straight and sharp, with chilled margins (~2 cm) present in the cores of boreholes 1, 3 and 4. The lamprophyric dykes are mostly competent except at their contacts with Bushveld wall rocks, where they are friable. Xenoliths of a polycrystalline rock, of which the composition is unknown, and a brecciated-serpentinised olivine (Fig. 4.4F) is entrained in the core of borehole 4.

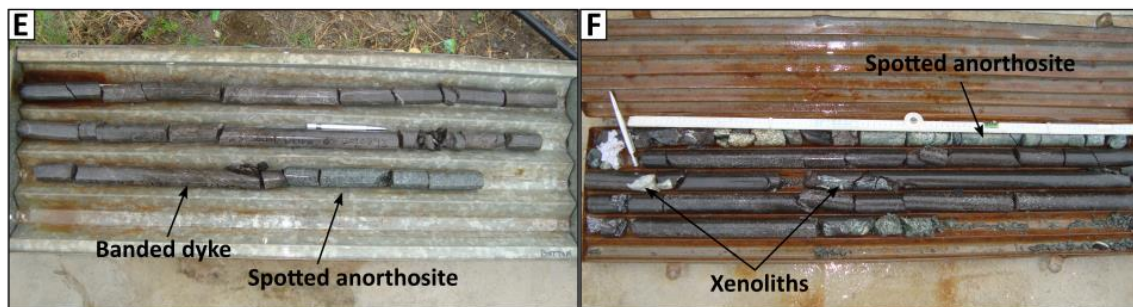
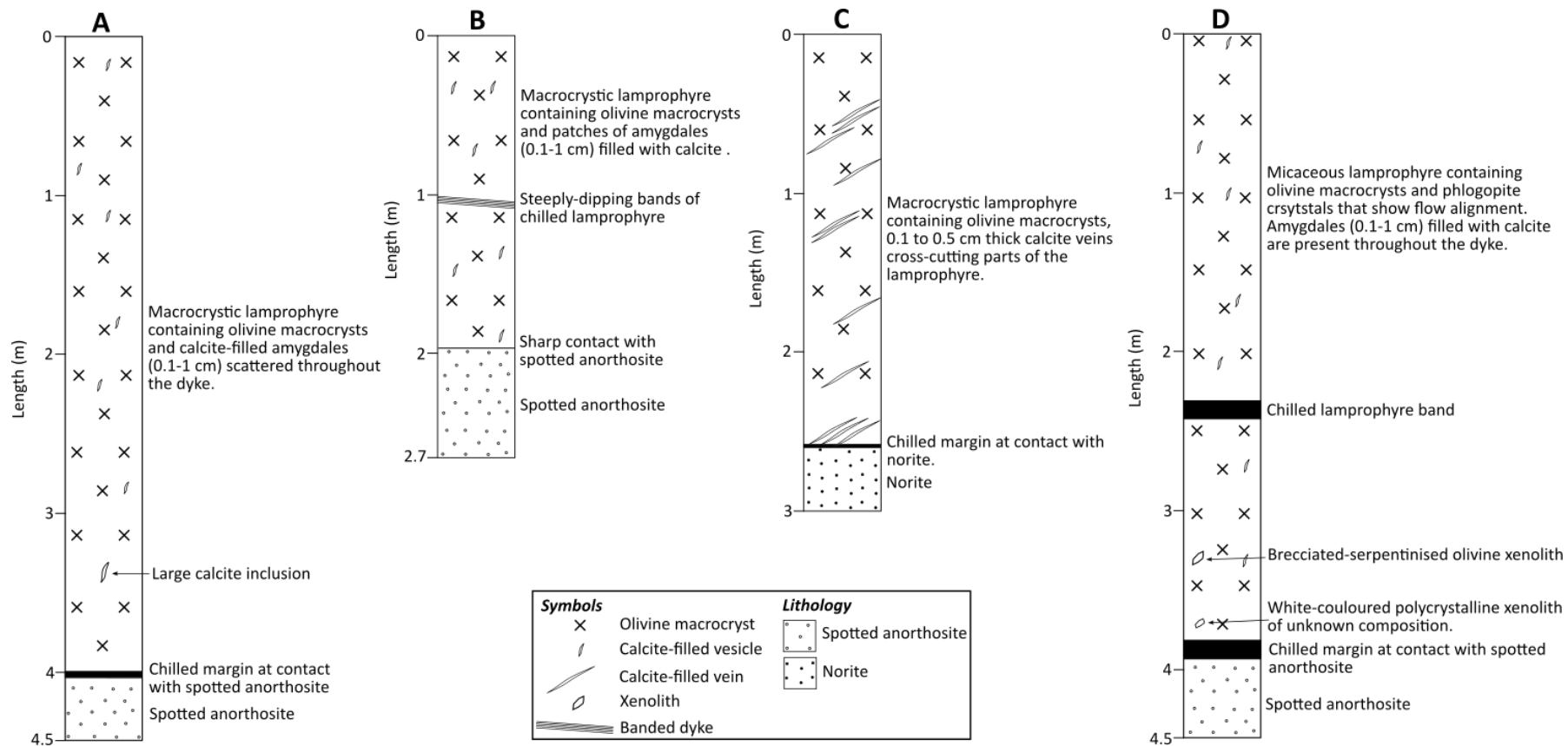


Figure 4.4. (overleaf). Core logs of core recovered from boreholes 1, 2, 3 and 4 of the underground gas analysis showing textural and lithological features of cores from (A) borehole 1, (B) borehole 2, (C) borehole 3 and (D) borehole 4. Photographs (E) and (F) show core from boreholes 1 and 4, respectively, illustrating banding in the lamprophyre and spotted anorthosite at the end of the core from borehole 1 and (F) xenoliths in the dyke and spotted anorthosite at the end of the dyke in core from borehole.

5 Results of laboratory-based analyses and underground *in-situ* analyses

5.1 Petrography

Petrography of the lamprophyric dykes was determined optically using transmitted and reflected light on 52 polished thin sections. Forty-four non-outburst samples, including core samples from the 4 underground boreholes, and 7 outburst samples were analysed. The petrography of 1 kimberlite sample (41-166), from the Marsfontein diamond mine, was determined and used as a reference sample. Polished thin sections from 11 non-outburst samples (including the 4 underground borehole samples; see section 4.5) and 4 outburst samples were also examined using SEM to document finer textural details and accessory mineral assemblages. The mineralogical and textural details of all 52 samples are summarised in Table 5.1.

5.1.1 Petrography of non-outburst dyke samples

The lamprophyric dykes are usually macrocrystic in texture. The abundance of macrocrysts and phenocrysts vary within individual dykes (Table 5.1), but can range from 1 to 40% macrocrysts and 5 to 70% phenocrysts. The majority of the samples (30 samples) contain both macrocrystic and phenocrystic phases and 1 sample contains only macrocrysts. Lamprophyres that contain only phenocrysts are referred to as macrocryst-free lamprophyres. There are 7 samples that are macrocryst-free and only contain phlogopite phenocrysts that have a modal abundance of 20-60%. The macrocrysts and phenocrysts are set in a groundmass that makes up the rest of the rock (~ 15 to 95% modal abundance). Some dykes are banded, which can be noted by abrupt changes in texture, grain size and colour, mineral assemblage and modal abundance (Fig. 5.1A and B). Veins, 0.1 to 0.3 cm in width, filled with calcite and/or barite commonly cross-cut the lamprophyres (Fig. 5.1B).

The macrocrystic suite comprises subhedral to rounded olivine that ranges from 2 to 10 mm in size. The olivine macrocrysts are variably altered to serpentine (Fig. 5.1B) and in some cases is further altered to chlorite. Five samples are unaltered, containing fresh olivine (Table 5.1). In sample L-9B, which contains fresh olivine, some of the olivine crystals are brecciated. The phenocrystic suite is composed dominantly of euhedral to subhedral laths of phlogopite ranging between 0.1 and 2 mm in size, with subordinate olivine. The phlogopite phenocrysts are compositionally zoned, as can be noted optically by variable intensity of brown colour from their cores to their rims. The rims of the phlogopites are typically a darker brown than the cores. Normal (Fig. 5.2A) and oscillatory (Fig. 5.2B) zoning are present in the phlogopite phenocrysts, but can only be observed using SEM. Resorption textures (Fig. 5.2A) are present in some phlogopite crystals marked by the rounded corners in compositionally zoned crystals. Chloritisation is evident by the jagged edges of the rims in some phlogopite phenocrysts.

Table 5.5.1. Table summarising the macrocrystic, phenocrystic and groundmass phases, modal abundances, and textural details for all non-outburst, underground borehole, outburst and kimberlite samples.

				Groundmass and accessory minerals		
	Sample name	Macrocrysts (2-10 mm)	Phenocrysts (0.1-2 mm)	Minerals present (listed in order of higher abundance)	Total modal abundance of groundmass	Textures
Non-outburst samples	L-1F	Olivine (20%)	Phlogopite (50%)	Calcite, sericite, opaques	30%	Contains euhedral zoned phlogopite phenocrysts set in a groundmass composed predominantly of interstitial calcite,
	L-2	Olivine (30%)	Phlogopite (10%)	Phlogopite, calcite, opaques	60%	Contains euhedral zoned phlogopite phenocrysts set in a groundmass composed predominantly of interstitial calcite, sericite and opaques.
	L-4a	Olivine (5%)	Phlogopite (30%)	Phlogopite, calcite, opaques	65%	Contains euhedral zoned phlogopite phenocrysts set in a groundmass composed predominantly of interstitial calcite, sericite and opaques.
	L-7	Olivine (30%)	Phlogopite (30%)	Phlogopite, calcite, opaques	40%	Rounded olivine macrocrysts and euhedral phlogopite set in a groundmass of phlogopite, interstitial calcite and opaques. Calcite veins (0.5-1mm thick) observed to be cross-cutting the dyke.
	L-8B	Olivine (10%)	Phlogopite (5%)	Phlogopite, opaques	85%	Rounded olivine macrocrysts and euhedral phlogopite set in a groundmass of phlogopite, interstitial calcite and opaques. Calcite veins (0.5-1mm thick) observed to be cross-cutting the dyke.
	L-8C	Olivine (10%)	Phlogopite (5%)	Phlogopite, opaques	85%	Phlogopite phenocrysts and groundmass phlogopite show flow alignment. There is a chilled margin present at the contact with the host rock and alteration of host rock minerals is seen only at contact (~2 mm).
	L-9A	Olivine (40%)	Phlogopite (20%)	Phlogopite, calcite, opaques	40%	Fresh olivine macrocrysts and euhedral phlogopite phenocrysts set in a groundmass of opaques and interstitial calcite.
	L-9B	Olivine (10%)	Phlogopite (15%)	Phlogopite, calcite, opaques, pyroxene, plagioclase	75%	Euhedral phlogopite phenocrysts showing flow alignment. There is a chilled margin present at the contact with the host rock which is anorthosite. There is alteration of the host rock and the thickness of the alteration zone is approximately 3 mm.
	L-10A	Olivine (40%)		Phlogopite, opaques	60%	Fresh olivine macrocrysts and euhedral phlogopite set in a groundmass of phlogopite, olivine and interstitial calcite. Some olivine macrocrysts are brecciated.
	L-10C	Olivine (30%)	Phlogopite (25%)	Phlogopite, olivine, opaques	45%	Fresh olivine macrocrysts and euhedral phlogopite set in a groundmass of phlogopite, olivine and interstitial calcite.
	L-12		Phlogopite (50%)	Calcite, sericite, opaques	50%	Macrocrystic-free lamprophyre with euhedral phlogopite phenocrysts set in a groundmass of interstitial calcite, sericite and opaques.
	L-14	Olivine (1%)		Phlogopite, calcite, garnet, opaques	99%	Lamprophyric veins in Bushveld anorthosite. The lamprophyric veins contain rounded olivine macrocrysts and interstitial calcite.
	L-15		Phlogopite (60%)	Calcite, opaques	40%	Lamprophyric veins in Bushveld anorthosite. The lamprophyric veins contain euhedral phlogopite phenocrysts and interstitial calcite.
	L-17	Olivine (25%)	Phlogopite (60%)	Phlogopite, calcite, opaques	15%	Fresh olivine macrocrysts and euhedral phlogopite phenocrysts set in a groundmass of opaques and interstitial calcite.
	L-19	Olivine (20%)	Phlogopite (70%)	Calcite, opaques	10%	Olivine macrocrysts and euhedral phlogopite phenocrysts set in a groundmass of opaques and interstitial calcite.
	L-20	Olivine (1%)	Phlogopite (2%)	Phlogopite, sericite	97%	Lamprophyre composed of phlogopite and sericite in contact with it's host rock.
	L-23	Olivine (10%)	Phlogopite (30%)	Phlogopite, calcite, garnet, opaques	60%	Olivine macrocrysts and euhedral phlogopite phenocrysts set in a groundmass of garnet, opaques and interstitial calcite.
	L-25	Olivine (30%)	n/d	n/d	n/d	Most of the sample was plucked out during polishing.
	LAMP-40B	Olivine (30%)	Phlogopite (50%)	Phlogopite, calcite, opaques	20%	Banded lamprophyric dyke. The sample contains rounded olivine macrocrysts and euhedral phenocrysts set in a groundmass composed of phlogopite, opaques and interstitial calcite. A band with the same mineral assemblage cross-cuts the sample. Less phlogopite phenocrysts are present in the band. The groundmass of the band is chilled compared to that of the host lamprophyre.
	LAMP-62A	Olivine (20%)	Phlogopite (40%)	Phlogopite, calcite, opaques	40%	Banded lamprophyre comprising 3 parts. The first part contains euhedral phlogopite phenocrysts in a groundmass of opaques and interstitial calcite. The second part contains rounded olivine macrocrysts and phlogopite phenocrysts with interstitial groundmass calcite. The 2 parts are separated by a third part comprising calcite with phlogopite crystals (<1 mm) at the margins.
	L-76	Olivine (25%)	Phlogopite (50%)	Phlogopite, calcite, opaques	25%	Olivine macrocrysts and euhedral phlogopite phenocrysts set in a groundmass of opaques and interstitial calcite.
	L-88	Olivine (15%)	Phlogopite (40%)	Phlogopite, calcite, opaques	45%	Olivine macrocrysts and euhedral phlogopite phenocrysts set in a groundmass of opaques and interstitial calcite.
	L-93		Phlogopite (40%)	Phlogopite, calcite, barite, opaques, pyroxene, apatite, titanite, monticellite, perovskite	60%	Macrocrystic-free lamprophyre with euhedral phlogopite phenocrysts set in a groundmass of interstitial calcite, sericite and opaques. Sample contains larger inclusions of calcite. A vein (most-likely composed of calcite) was plucked out during the making of the thin section.
	L-96	Olivine (30%)	Phlogopite (20%)	Phlogopite, calcite garnet, opaques	50%	Olivine macrocrysts and euhedral phlogopite phenocrysts set in a groundmass of garnet, opaques and interstitial calcite.

				Groundmass and accessory minerals		
	Sample name	Macrocrysts (2-10 mm)	Phenocrysts (0.1-2 mm)	Minerals present (listed in order of higher abundance)	Total modal abundance of groundmass	Textures
Non-outburst samples (cont.)	L-96	Olivine (30%)	Phlogopite (20%)	Phlogopite, garnet, calcite, opaques	50%	Olivine macrocrysts and euhedral phlogopite phenocrysts set in a groundmass of garnet, opaques and interstitial calcite.
	L-97		Phlogopite (60%)	Calcite, opaques	40%	Macrocrystic-free lamprophyre containing euhedral phlogopite phenocrysts set in a groundmass of opaques and interstitial calcite.
	L-109			Calcite, zeolite, phlog, opaques	40%	Lamprophyre containing phlogopite crystals set in a groundmass of interstitial calcite and zeolite. Multiple veins (1-1.5 mm thick) of serpentine are observed to be cross-cutting the lamprophyre.
	L-114	Olivine (20%)	Phlogopite (30%)	Phlogopite, opaques, calcite	50%	Euhedral phlog, rounded ol, some alignment of phlog flowing around ol. Chilled margin at contact with Bushveld rock. Alteration of host rock and alteration of phlog to chlorite.
	L-115	Olivine (10%)	Phlogopite (30%)	Phlogopite, calcite, sericite, opaques	60%	Olivine macrocrysts and euhedral phlogopite phenocrysts set in a groundmass of opaques and interstitial calcite.
	L-125	Olivine (10%)	Phlogopite (30%)	Phlogopite, calcite, sericite, opaques	60%	Olivine macrocrysts and euhedral phlogopite phenocrysts set in a groundmass of opaques and interstitial calcite.
	L-131A		Phlogopite (50%)	Phlogopite, calcite, sericite, opaques, barite, titanite, apatite, gypsum, halite	50%	Macrocrystic-free lamprophyre containing euhedral phlogopite phenocrysts set in a groundmass of sericite, opaques and interstitial calcite.
	L-131B	Olivine (1%)	Phlogopite (30%)	Phlogopite, garnet, calcite, opaques, plagioclase, apatite	69%	Lamprophyric dyke containing phlogopite phenocrysts, displaying flow alignment, set in a groundmass composed of phlogopite, garnet, opaques and interstitial calcite.
	L-PD1B	Olivine (1%)	Phlogopite (40%)	Phlogopite, calcite, sericite, opaques	59%	Olivine macrocrysts and euhedral phlogopite phenocrysts set in a groundmass of sericite, opaques and interstitial calcite.
	L-PD2	Olivine (25%)	Phlogopite (5%)	Phlogopite	70%	Olivine macrocrysts and euhedral phlogopite phenocrysts set in a groundmass of sericite, opaques and interstitial calcite.
	L-PD3		Phlogopite (50%)	Phlogopite, calcite, sericite, opaques	50%	Macrocrystic-free lamprophyre containing euhedral phlogopite phenocrysts set in a groundmass of sericite, opaques and interstitial calcite. Calcite veins (0.5 mm) cross-cut the lamprophyre.
	L-PD4A	Olivine (1%)	Phlogopite (5%)	Calcite, sericite, opaques	94%	Olivine macrocrysts and euhedral phlogopite phenocrysts set in a groundmass of sericite, opaques and interstitial calcite.
	L-PD4B		Phlogopite (5%)	Phlogopite, calcite, opaques	95%	Macrocrystic-free lamprophyre containing euhedral phlogopite phenocrysts set in a groundmass of phlogopite opaques and interstitial calcite.
Undergroud borehole samples	L-PD13		Phlogopite (50%)	Phlogopite, calcite, plagioclase	50%	Macrocrystic-free lamprophyre containing euhedral phlogopite phenocrysts set in a groundmass of phlogopite and interstitial calcite.
	L-PD16	Olivine (10%)	Phlogopite (30%)	Phlogopite, sericite, calcite, pyroxene, barite, monticellite	60%	Subhedral to rounded serpentinitised olivine macrocrysts and euhedral phlogopite phenocrysts set in a groundmass of phlogopite which is a darker red-brown colour compared to the phenocrysts. Calcite and sericite are interstitial to phlogopite and the pyroxene which can only be noted in SEM.
	L-PD19	Olivine (25%)	Phlogopite (15%)	Phlogopite, calcite, sericite, opaques	60%	Olivine macrocrysts and euhedral phlogopite phenocrysts set in a groundmass of phlogopite, sericite, opaques and interstitial calcite.
	L-PD21	Olivine (40%)	Phlogopite (25%)	Phlogopite, garnet, calcite, barite, titanite, gypsum, apatite	30%	Euhedral phlogopite and subhedral to rounded serpentinitised olivine-bearing lamprophyre.
	L-PD23	Olivine (30%)	Phlogopite (5%)	Phlogopite, garnet, calcite, natrolite, muscovite, plagioclase, titanite, leucite, melilite	65%	Euhedral phlogopite and subhedral to rounded serpentinitised olivine-bearing lamprophyre.
Outburst samples	L-11A		Phlogopite (20%), Clinopyroxene (30%)	Natrolite, calcite, halite	50%	Macrocrystic-free lamprophyre comprising prismatic pyroxene and euhedral phlogopite phenocrysts set in a groundmass of calcite, natrolite and halite. All groundmass minerals are interstitial to the phenocrysts.
	L-11B			Halite, natrolite, anhydrite	n/d	Large (0.5-10 cm) natrolite crystals surrounded with halite.
	L-111	Olivine (20%)	Phlogopite (30%)	Phlogopite, calcite, opaques	50%	Phlog seems to flow around ol
	L-112	Olivine (5%)	Phlogopite (20%)	Phlogopite, garnet, calcite, apatite, titanite	75%	Euhedral phlog and garnet, rounded olivine, calcite and phlo/sericite are interstitial to garnet.
	L-113			Phlogopite, garnet, olivine, calcite, perovskite	100%	Macrocrystic-free lamprophyre containing groundmass phlogopite and olivine with garnet and interstitial calcite.
	L-116	Olivine (10%)	Phlogopite (15%)	phlogopite, sericite, calcite, garnet, titanite, apatite	75%	Olivine macrocrysts and euhedral phlogopite phenocrysts set in a groundmass of phlogopite, sericite, opaques and interstitial calcite.
	L-AB1	Olivine (5%) Phlogopite (10%)	Phlogopite (50%)	Phlogopite, sericite, calcite, opaques	35%	Subhedral to rounded serpentinitised olivine, euhedral to subhedral phlog macrocrysts, phlog phenocrysts are euhedral. Alignment of phlog macrocrysts and phenocrysts while groundmass phlog is randomly oriented. Calcite and sericite are interstitial to phlog.
Kimberlite sample	41-166	Olivine (20%)		Phlogopite, sericite, calcite	80%	Olivine macrocrysts and euhedral phlogopite phenocrysts set in a groundmass of phlogopite, sericite and interstitial calcite.

Some phlogopite crystals show strain features such as undulose extinction and kink banding. In some instances flow alignment of phlogopite phenocrysts is present in dykes, whereas in the majority of the dykes the phenocrysts are randomly oriented. In most cases the phlogopite phenocrysts bend around the olivine macrocrysts.

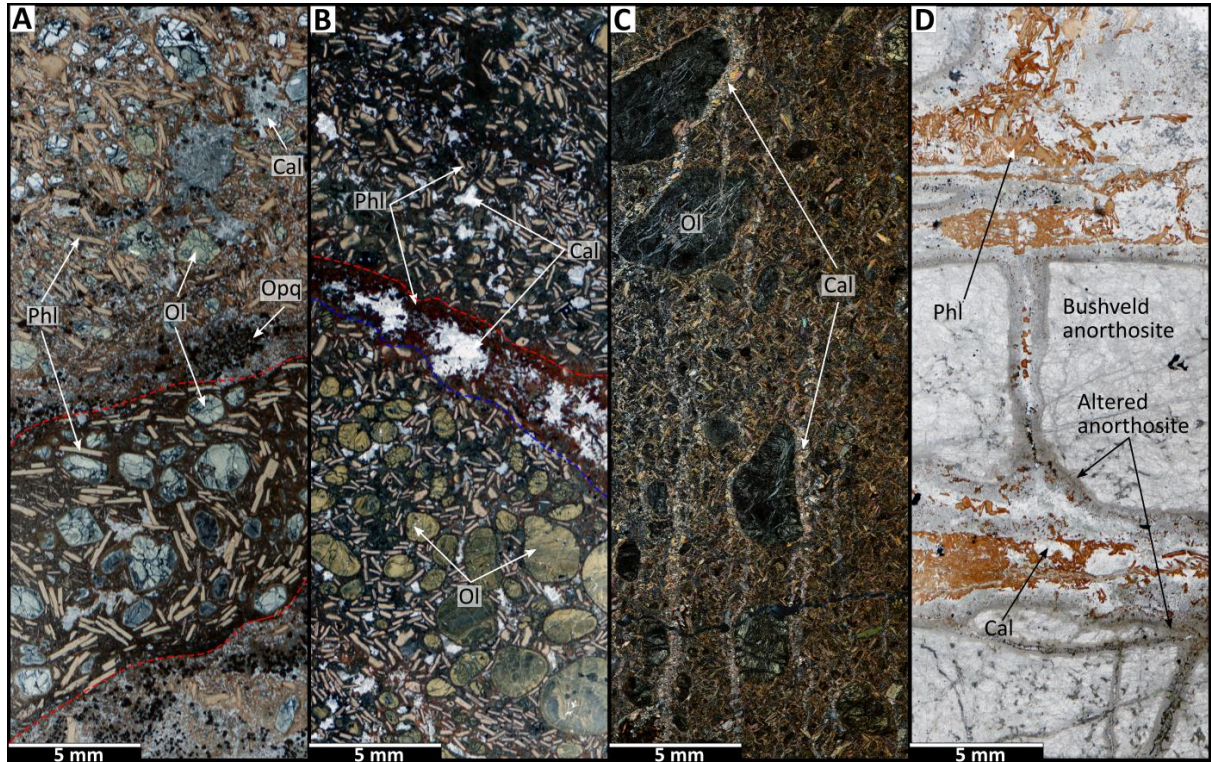


Figure 5.1. Photomicrographs showing (A) Banded lamprophyre L-40B, containing serpentinised olivine macrocrysts, phlogopite phenocrysts and opaque minerals set in a groundmass comprising calcite. A change in grain size and modal abundance is seen in the area between the 2 red lines. (B) Banded lamprophyre L-62A, containing 3 sections where there are differences in the lithology. Above the red line the dyke consists of phlogopite phenocrysts with interstitial calcite, below the blue line there is abundant serpentinised olivine macrocrysts and interstitial calcite and between the red and blue lines is a vein filled with calcite and phlogopite at the margins. (C) Lamprophyre L-7, containing serpentinised olivine macrocrysts (<2-5 mm) set in a groundmass of phlogopite, sericite and opaque minerals, and calcite veins cross-cutting the dyke and bending around the olivine. (D) Bushveld anorthosite containing veins of lamprophyre L-15, comprising zoned phlogopite phenocrysts and interstitial calcite. The darker-grey areas in the anorthosite is alteration (to sericite) from the intrusion of the lamprophyre. Phl- phlogopite, Ol- olivine, Cal- calcite and Opq- opaque minerals (Whitney and Evans, 2010).

The groundmass minerals range between <0.1 and 0.5 mm in size, and are dominantly composed of phlogopite, olivine and high-Ca pyroxene. The accessory minerals in the groundmass are garnet, amphibole, apatite, fluoro-apatite, titanite, monticellite, perovskite, melilite, celestine and opaque minerals namely: pyrite, chalcopyrite, chromite and/or magnesiochromite, and magnetite, which constitute the primary phases. The secondary accessory phases in the groundmass are halite, calcite, barite and gypsum. Apatite and garnet are typically euhedral. Garnet, in some dykes occurs in clusters in parts of the dyke. The pyroxene crystals are usually elongated and have a prismatic habit. Calcite mostly occurs as anhedral to irregularly-shaped crystals up to 0.2 mm in size, shows prominent cleavage, and is interstitial to the phenocryst phases. Halite is usually included within the calcite and is cubic in shape. The opaque minerals are mostly euhedral, less than 0.2 mm in size and are disseminated throughout the groundmass of all the lamprophyric dykes. The accessory and opaque minerals are interstitial to the phlogopite phenocrysts.

5.1.2 *Petrography of underground borehole samples*

Four boreholes were drilled through the face of 4 lamprophyric dykes (see Section 3.6) in an underground platinum mine in order to conduct underground *in-situ* gas analysis. The core from each borehole were recovered, logged and sampled (see Section 4.3). In total 5 thin sections were made of the core samples from the 4 boreholes (1 each from boreholes 1, 2 and 3, and 2 from borehole 4). The thin sections were examined using transmitted light and SEM.

The samples from the 4 boreholes (see Table 5.1) are similar to the rest of the lamprophyre samples in that they are macrocrystic in texture, containing olivine macrocrysts (10-40%) and phlogopite phenocrysts (5-50%), with the exception of L-PD13, which is macrocrystic-free. The olivine macrocrysts are subhedral to rounded and are partially serpentinised, and some are chloritized beyond. Phlogopite phenocrysts are euhedral and display normal zoning similarly to phlogopite phenocrysts in other lamprophyre samples. The macrocrysts and phenocrysts are set in a groundmass composed of predominantly phlogopite, calcite, and opaque minerals. Groundmass phlogopite is a darker-brown shade compared to the phenocrysts (e.g. L-PD16). Other groundmass minerals, only identified using SEM, include pyroxene, apatite, garnet, monticellite, titanite, barite, leucite, plagioclase and melilite (Fig. 5.2E). No significant differences, in the mineral assemblage and texture, of the dykes were observed between the samples from the 4 boreholes and between these samples and other lamprophyric dyke samples.

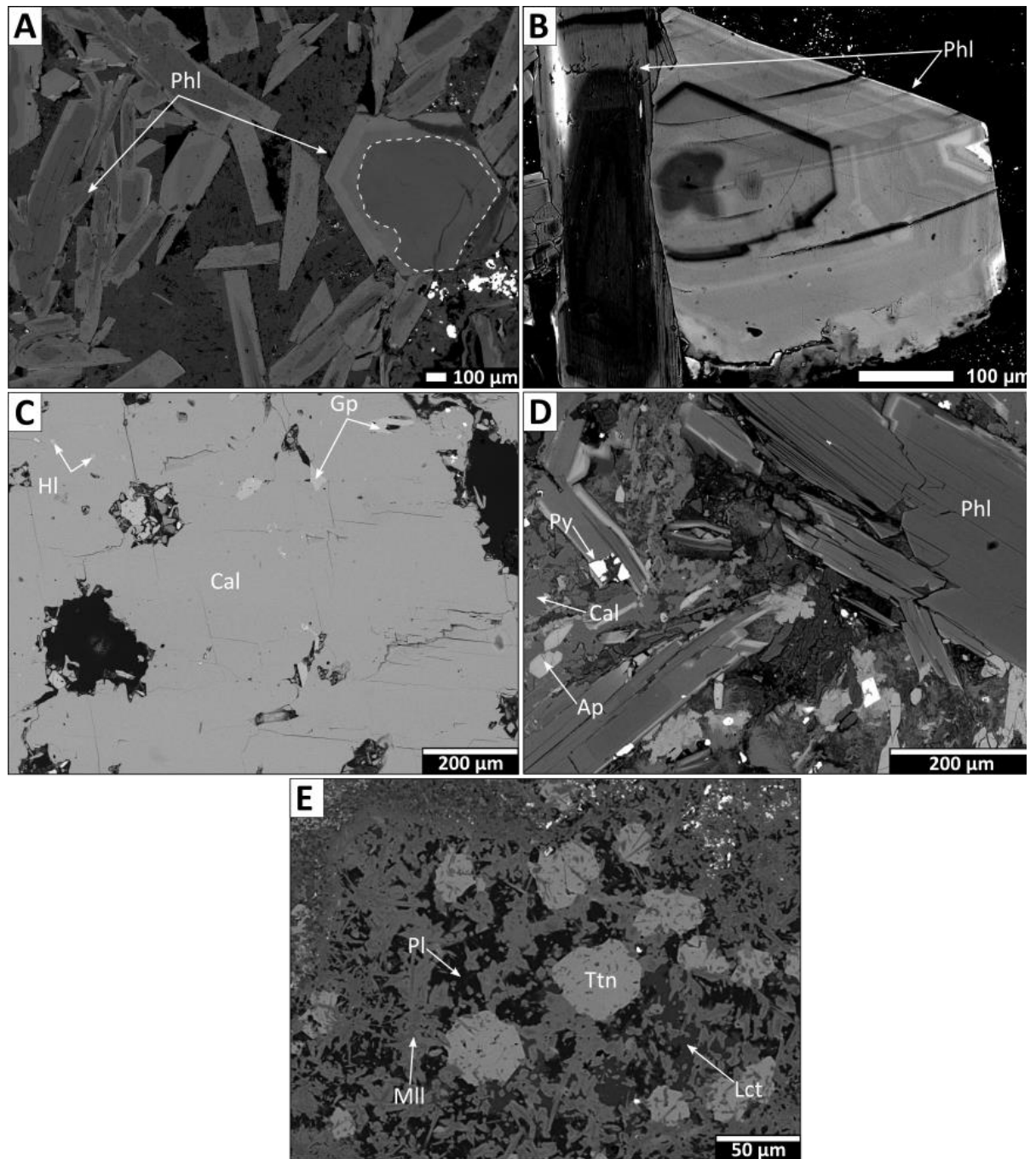


Figure 5.2. Backscattered electron images showing (A) normal zoning and resorption textures (outline in white dotted line) in phlogopite crystals in L-15, (B) oscillatory zoning in a euhedral phlogopite crystal in L-15, (C) groundmass of sample L-131A composed of secondary calcite containing included halite and gypsum, (D) L-131A comprising euhedral phlogopite phenocrysts set in a groundmass composed of apatite, pyrite and interstitial calcite and (E) groundmass of L-PD23 containing titanite, melilite, leucite and plagioclase. Phl- phlogopite, Cal- calcite, Hl- halite, Gp- gypsum, Ttn- titanite, Mll- melilite, Lct- leucite and Pl- plagioclase (Whitney and Evans, 2010).

5.1.3 Petrography of outburst dyke samples

From the 7 outburst samples analysed, 5 samples have the same or similar mineral assemblage to samples that are not associated with outbursts (Table 6.1). The other 2 samples (L-11A and L-11B) have a distinct mineralogical composition to the rest of the dykes. Both these samples are from the same dyke and therefore were associated with the same outburst (see section 2.2). The textural and mineralogical details of these samples are described below.

Sample L-11A (Fig. 5.3) is phenocrystic in texture and comprises phenocrysts (0.2-1.5 mm) of high-Ca pyroxene (30%) and phlogopite (20%) set in a white-coloured matrix (50%). The pyroxene crystals are euhedral to acicular in shape and range in size from 0.1 to 4 mm. Most of the crystals show normal zoning, which can be noted by the darker shade of green in the rims and a lighter shade of green in the cores in PPL (Fig. 5.3A). Details of zoning and more complex zoning such as sector zoning (Fig. 5.3C) can only be seen using SEM. Phlogopite crystals are euhedral, range in size from 0.5 to 5 mm and display normal zoning (Fig. 5.3B) as can be seen by the difference in the intensity of brown (in PPL) from their cores (lighter brown) to their rims (darker brown; Fig. 5.3A). Effects of dissolution of the dyke can be seen from the jagged edges and missing material at the rims of the phlogopite phenocrysts. A white-coloured groundmass surrounds the pyroxene and phlogopite crystals and is composed predominantly of intergrown secondary natrolite (Na-zeolite), calcite and halite. Natrolite occurs as fibrous crystals radiating outward from a single point or as blebs (Fig. 5.3D). The accessory minerals present in the groundmass are muscovite, barite, titanite, ilmenite, rutile, and pyrite. This sample lacks garnet and olivine macrocrysts, distinguishing it from the other lamprophyres.

Sample L-11B, a geode found within voids of the dyke from which sample L-11A came, is composed of elongated, acicular crystals of natrolite (0.5 to 10 cm in length) in a groundmass mixed of halite and anhydrite. The natrolite crystals are randomly oriented and fibrous in texture. In transmitted light the natrolite crystals are transparent whereas the mixture of halite and anhydrite is transparent to cloudy-white. Blebs of hematite are present in fractures within the sample. Fluid inclusions are contained within the natrolite crystals and groundmass minerals of this sample (see section 5.3).

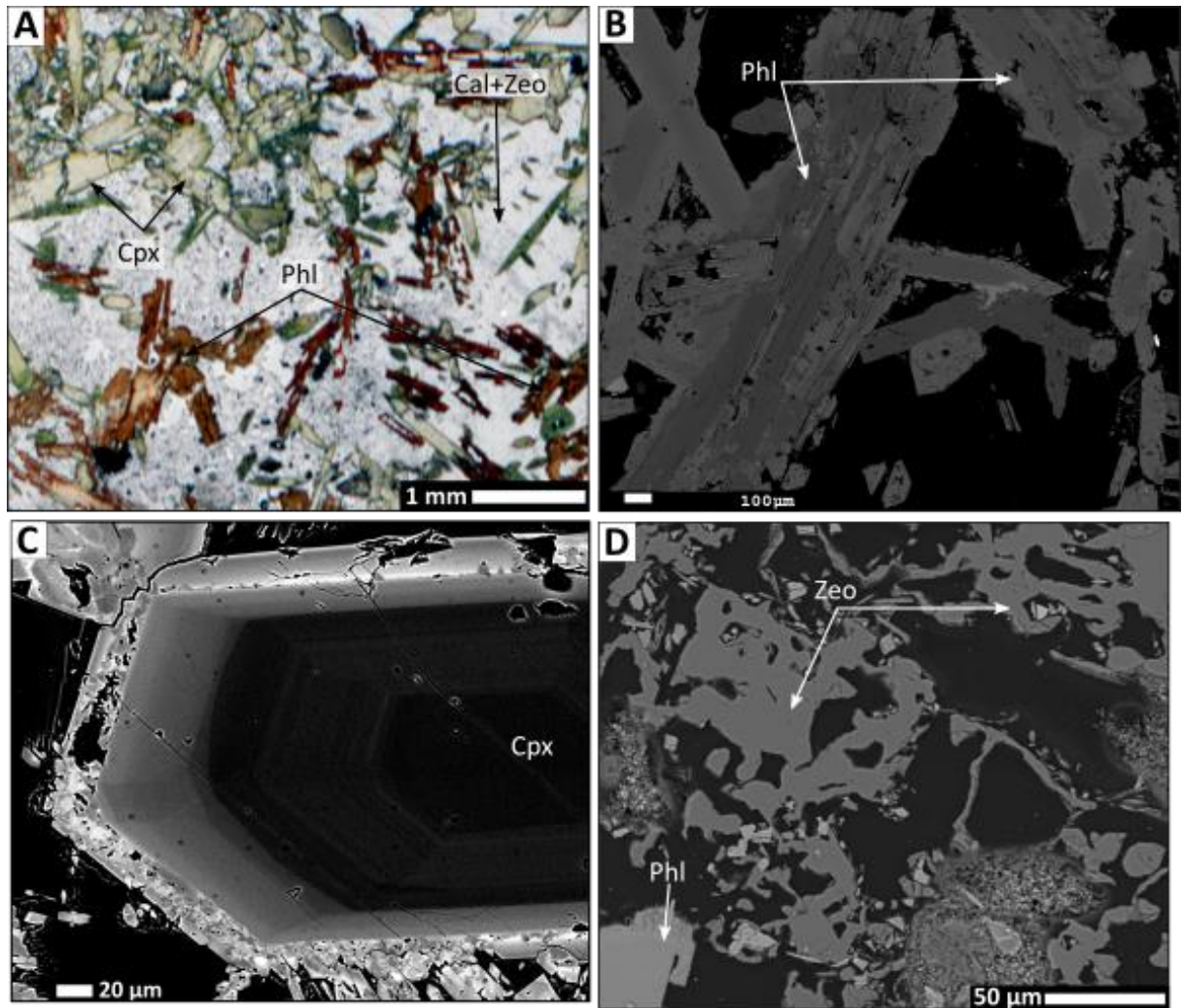


Figure 5.3. A photomicrograph showing (A) L-11A comprising phlogopite and clinopyroxene phenocrysts set in a groundmass composed of calcite and zeolite (natrolite). Backscattered electron images showing (B) euhedral phlogopite phenocrysts, in L-11A, displaying normal zoning, (C) oscillatory and sector zoning in a prismatic clinopyroxene crystal in L-11A and (D) a close-up of the groundmass in L-11A composed blebs of zeolite which is interstitial to the phlogopite phenocrysts. Phl- phlogopite, Cpx- clinopyroxene, Cal- calcite and Zeo- zeolite (Whitney and Evans, 2010).

5.1.4 Petrography of kimberlite dyke – sample 41-166

The Marsfontein kimberlite dyke is macrocrystic in texture (Fig. 5.4), comprising 20% olivine macrocrysts. The olivine macrocrysts are subhedral to rounded in shape and range from 1 to 4.5 mm in size. All the olivine macrocrysts are variably altered to serpentine. This kimberlite sample differs from the lamprophyric dyke samples as it lacks phlogopite and/or pyroxene phenocrysts. The olivine macrocrysts are set in a fine-grained (0.1-0.2 mm) groundmass composed of mainly phlogopite (Table 6.1). The phlogopite crystals in the groundmass are randomly oriented, euhedral to subhedral in shape and display normal zoning. Accessory minerals present in the groundmass are dominantly calcite and opaque minerals.



Figure 5.4. A photomicrograph scan of sample 41-166 showing serpentinised olivine macrocrysts set in groundmass composed of fine-grained (<1 mm) phlogopite and interstitial calcite. Ol- olivine, Phl- phlogopite and Cal- calcite (Whitney and Evans, 2010).

5.1.5 Bushveld Complex host rocks to lamprophyres

The rocks that host the studied lamprophyre dykes are composed predominantly of plagioclase, pyroxene and olivine. Lamprophyric dykes have sharp contacts with their host rocks and have chilled margins (Fig. 5.1D) that are 1 to 2 mm thick, composed dominantly of fine-grained (<0.1 mm) phlogopite and in some cases olivine macrocrysts and/or phlogopite phenocrysts. Most dykes have thin veins with a width of 0.1 to 1 mm which tend to anastomose into their host rocks. These veins are composed of the same lithology as their dykes from which they off-shoot. They continue to flow for approximately 1 to 20 mm into the host rocks. The extent of the alteration varies from dyke to dyke. In some samples little or no alteration of the host rocks is seen from the lamprophyric dykes. In other samples the alteration is pervasive, extending for approximately 2-5 mm into the host rock, and leads to the formation of clay, sericite and serpentine minerals making the contacts between the dykes and the host rocks friable.

5.2 Mineral chemistry

Major and minor element composition of pyroxene and phlogopite crystals from the lamprophyric dykes were analysed by EPMA. All EPMA data were collected during an Honours project (Daya, 2016) which represents a pilot study on the lamprophyric dykes in the Bushveld Complex. Four lamprophyric dyke samples were analysed namely, L-11A, L-15, L-40B, and L-62A, and one kimberlite dyke sample (41-166) was analysed in order to compare the mineral chemistry of lamprophyres to kimberlites. Mean chemical compositions of pyroxene and phlogopite crystals of all samples are reported in Table 5.2 and Table 5.3. The dataset containing chemical compositions for all pyroxene and phlogopite crystals are presented in Appendix A.

5.2.1 Pyroxene

Core and rim data for pyroxene crystals from sample L-11A were analysed. All pyroxene crystals are poor in TiO_2 (0.15-1.30 wt.%), Al_2O_3 (0.16-1.07 wt.%) and Cr_2O_3 (0-0.70 wt.%). Figure 5.5 which is a ternary classification diagram for pyroxene shows that the majority of the pyroxene is Fe-poor and exhibits a solid solution between diopside and augite. Most pyroxenes are zoned, showing compositional variations from their cores to their rims. Figure 5.6 illustrates the compositional variations, for the following cations: Al, Na, Fe, Ti, Mg and Ca, from the cores to the rims of 3 pyroxene crystals (Fig. 5.6D). In the case of all 3 crystals, similar trends are observed where Al, Na, Mg and Ca decrease and Fe increases from core to rim. These trends are not linear, as can be seen by the intermediate zones of the crystals. In crystal A (Fig. 5.6A) Na, Fe and Mg are seen to oscillate from the core to the rim. Overall, Ti only shows a slight difference in composition from core to rim in crystals A, B and C. Sodium increases significantly, from ~ 0.05 to 1 (cations), from core to rim in crystals A and C (Fig. 5.6C). Iron increases drastically, from ~ 0.1 to ~ 1.16 (cations) in crystal B (Fig. 5.3B).

Table 5.2. Mean chemical compositions for cores, rims and intermediate zones of pyroxene crystals from sample L-11A, where S.D. is the standard deviation.

L-11A						
	Cores (n=11)		Rims (n=10)		Intermediate zones (n=7)	
	Mean	S.D.	Mean	S.D.	Mean	S.D.
SiO ₂	55.26	0.77	54.70	0.81	55.09	0.78
TiO ₂	0.72	0.27	0.65	0.26	0.89	0.21
Al ₂ O ₃	0.56	0.21	0.47	0.16	0.79	0.19
Cr ₂ O ₃	0.15	0.17	0.32	0.22	0.07	0.09
FeO	5.85	3.55	9.86	4.36	5.68	3.07
MnO	0.13	0.07	0.19	0.06	0.14	0.05
NiO	0.04	0.04	0.04	0.05	0.02	0.03
MgO	14.97	2.44	12.21	3.04	15.21	2.10
CaO	23.48	2.36	20.46	3.12	23.86	2.10
Na ₂ O	1.03	1.22	2.63	1.64	0.88	1.08
ZrO ₂	0.00	0.00	0.00	0.00	0.00	0.00
Total	102.28	0.62	101.62	0.76	102.75	0.63
Si	1.99	0.02	2.02	0.03	1.98	0.02
Ti	0.02	0.01	0.02	0.01	0.02	0.01
Al	0.02	0.01	0.02	0.01	0.03	0.01
Cr	0.00	0.00	0.01	0.01	0.00	0.00
Fe	0.18	0.11	0.31	0.13	0.17	0.10
Mn	0.00	0.00	0.01	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.80	0.12	0.67	0.14	0.81	0.10
Ca	0.91	0.08	0.81	0.10	0.92	0.07
Na	0.07	0.09	0.19	0.12	0.06	0.08
Zr	0.00	0.00	0.00	0.00	0.00	0.00
Total	4.01	0.03	4.04	0.03	4.01	0.02

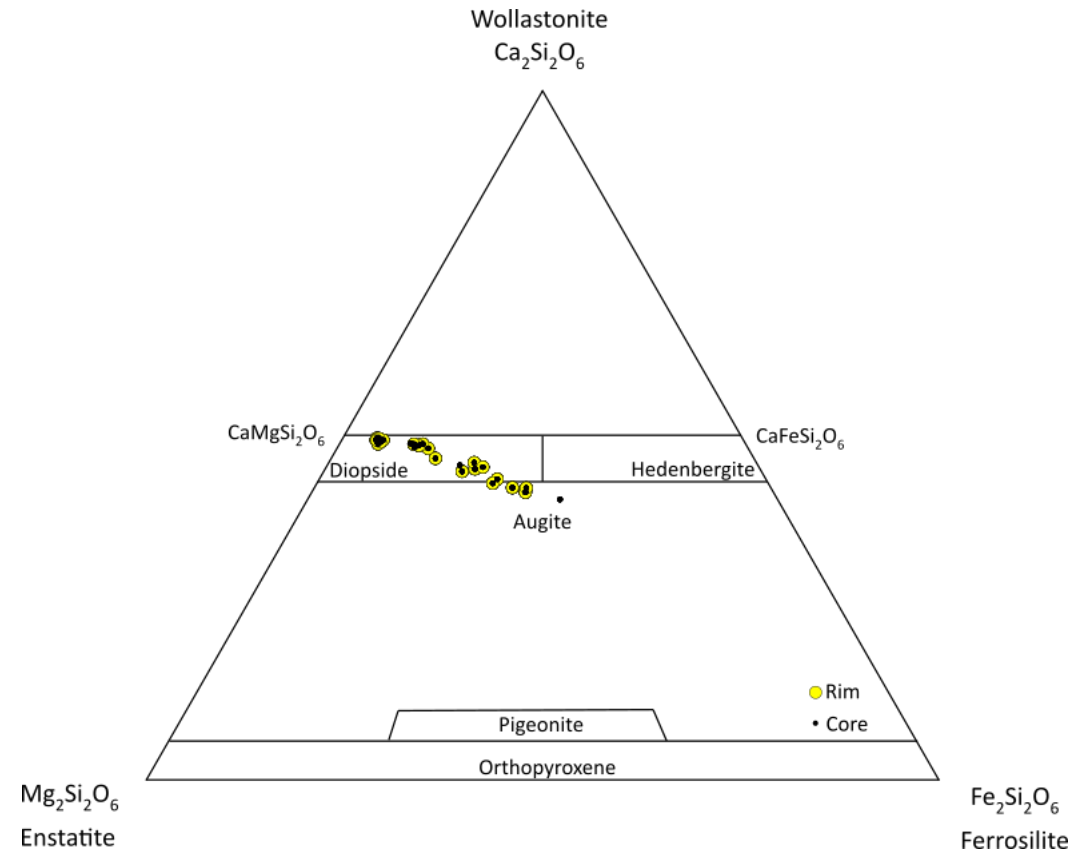


Figure 5.5. Pyroxene quadrilateral diagram showing compositions of cores and rims of pyroxene crystals from lamprophyre sample L-11A.

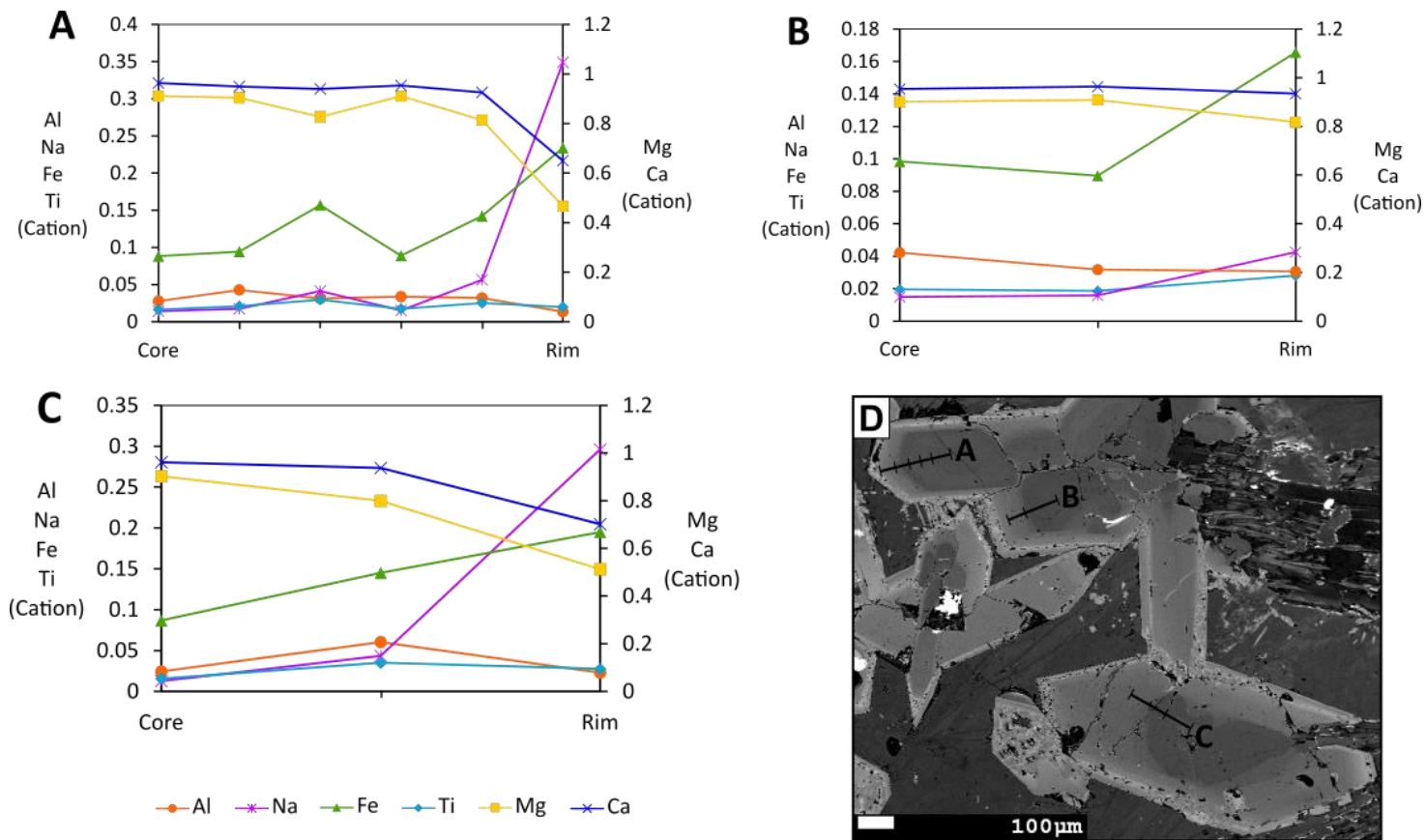


Figure 5.6. Major element compositions of 3 zoned pyroxene crystals in sample L-11A. Aluminium, Na, Fe, Ti, Mg and Ca compositions (cations) are plotted for core, rim and intermediate zones for (A) crystal A, (B) crystal B and (C) crystal C, in (D) which is a backscattered electron image showing the 3 pyroxene crystals and points along which analysis took place.

Figure 5.7 shows the Mg#, which represents $Mg/(Mg + \text{total Fe})$, plotted against Na, Ca, total Fe and Ti (cations) for core and rim data for every pyroxene. The cores of the pyroxene crystals are higher in Mg# and low in Na whereas the rims have a wide spread of Na and Mg# values. Overall the pyroxene decreases in Na and increase in Mg#. In Figure 5.7B Ca compositions of cores and rims are plotted against Mg#. The majority of the cores are clustered at 1 Ca, 0.9 Mg# and the rims have a range of Ca and Mg#. There is a linear trend overall where Ca is increasing with an increase in Mg#. Figure 5.7C also shows a linear trend and is similar to that of Figure A. There is no particular trend that can be seen in Figure 5.7D only a cluster of cores between 0.015-0.02 Ti and 0.9 Mg#. The rims are distributed showing a wide range of Ti and Mg# contents.

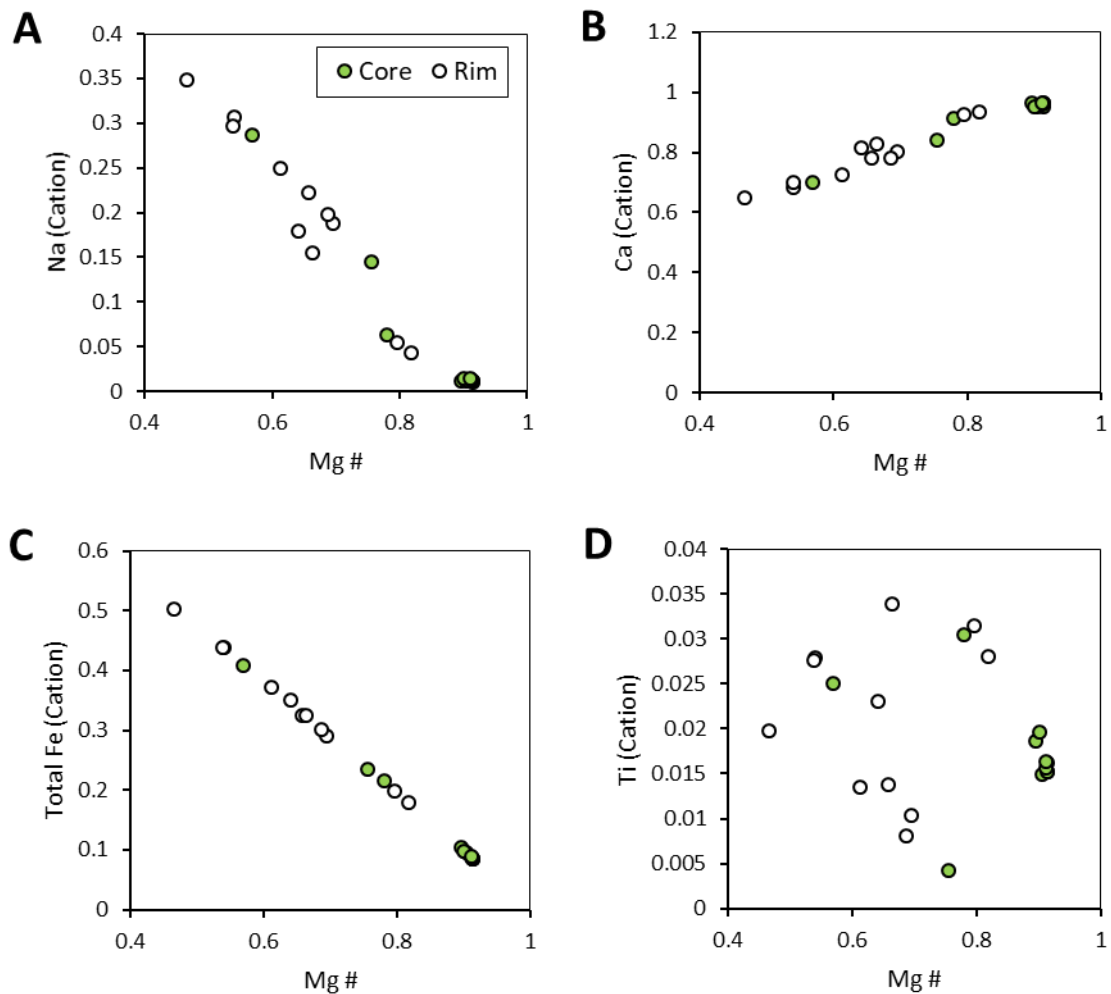


Figure 5.7. Major element composition diagram showing (A) Mg# vs Na, (B) Mg# vs Ca, (C) Mg# vs total Fe and (D) Mg# vs Ti plots for pyroxene cores and rims from sample L-11A.

5.2.2 *Micas*

Core and rim data for mica crystals (Table 5.3) in samples L-11A, L-15, L-40B, L-62A and 41-166 were analysed. Figure 5.8A shows that all mica crystals from each of these samples plot in the phlogopite field in the Al-Mg# classification diagram. From Figure 5.8 it can be seen that the cores of the phlogopite from samples L-11A, L-15 and L-40B are higher in Al and Mg# (cations) than their rims. Overall, a linear trend is seen where the Al content decrease with Mg# from core to rim.

Phlogopite data from South African Group II kimberlite dykes namely Helam and Star kimberlites are plotted for reference. Data for Helam and Star kimberlite dykes were obtained from Coe (2004). Figure 5.9A shows that the lamprophyric dykes are high in Al_2O_3 and low in TiO_2 (0-4.89 wt.%) and Figure 5.9B shows that the lamprophyric dykes are high in Al_2O_3 (5.14-34.34 wt.%) and low in FeO (1.56-35.16 wt.%). The Marsfontein kimberlite phlogopite is similar in that they are high in Al_2O_3 (9.99-11.32 wt%) and low in FeO (5.45-7.81 wt.%) and TiO (1.37-2.13 wt.%). Majority of the phlogopite from all lamprophyre samples and sample 41-166 plot in the Orangeite fields along with phlogopite from the Helam and Star kimberlite dykes.

Table 5.3. Mean chemical compositions for cores, rims and intermediate zones of pyroxene crystals from lamprophyre samples L-11A, L-15, L-40B and L-62A, and kimberlite sample 41-166, where S.D. is the standard deviation.

	L-11A						L-15						L-40B						L-62A						41-166	
	Cores (n=11)		Rims (n=4)		Intermediate zones (n=5)		Cores (n=20)		Rims (n=12)		Intermediate zones (n=16)		Cores (n=18)		Rims (n=16)		Intermediate zones (n=7)		Cores (n=11)		Rims (n=1)		Intermediate zones (n=16)		Cores (n=8)	
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
SiO ₂	40.11	0.88	40.03	0.28	42.57	1.80	39.47	0.78	38.57	1.61	39.69	2.51	40.33	0.37	40.32	0.37	39.87	1.58	39.16	1.19	40.51	0.00	39.46	0.96	39.84	0.28
TiO ₂	1.60	0.79	1.39	1.07	0.91	0.73	2.25	0.45	2.82	0.65	2.56	0.96	2.51	0.75	2.29	0.75	2.34	0.69	2.38	0.67	1.59	0.00	1.72	0.51	1.70	0.26
Al ₂ O ₃	11.07	1.91	9.81	1.59	16.49	3.88	10.33	1.46	8.67	1.65	10.77	6.19	12.17	1.88	9.73	1.88	11.85	2.47	9.11	3.65	11.44	0.00	11.53	2.58	10.62	0.47
FeO	10.70	4.97	14.15	3.00	4.27	0.65	12.82	4.11	20.66	5.89	16.43	6.91	6.90	4.13	11.41	4.13	7.12	3.59	12.76	5.82	6.13	0.00	7.60	4.70	6.32	0.79
MnO	0.14	0.11	0.20	0.07	0.04	0.03	0.18	0.08	0.28	0.09	0.19	0.08	0.07	0.09	0.15	0.09	0.09	0.04	0.17	0.11	0.05	0.00	0.08	0.07	0.05	0.04
MgO	21.17	2.17	19.53	0.98	14.45	11.79	19.53	2.68	14.23	4.64	15.55	5.75	22.59	1.58	21.04	1.58	22.41	1.53	20.17	2.97	24.10	0.00	22.54	3.05	24.37	0.35
CaO	0.02	0.02	0.02	0.01	10.56	12.92	0.02	0.03	0.03	0.03	0.03	0.05	0.04	0.07	0.07	0.07	0.74	1.73	0.03	0.01	0.06	0.00	0.04	0.04	0.02	0.02
Na ₂ O	0.12	0.02	0.14	0.01	0.14	0.05	0.08	0.03	0.08	0.02	0.14	0.19	0.12	0.03	0.09	0.03	0.11	0.05	0.15	0.04	0.09	0.00	0.20	0.04	0.10	0.02
K ₂ O	10.35	0.62	10.36	0.09	6.56	5.35	10.26	0.55	10.19	0.29	10.22	0.29	10.69	0.17	10.52	0.17	10.31	0.82	10.24	0.28	10.44	0.00	10.45	0.36	10.65	0.17
BaO	0.36	0.32	0.28	0.33	0.19	0.16	0.68	0.36	0.30	0.11	0.37	0.27	0.41	0.25	0.51	0.25	0.43	0.18	0.65	0.20	0.42	0.00	0.52	0.16	0.95	0.26
F	0.37	0.23	0.21	0.18	0.26	0.20	0.19	0.08	0.10	0.08	0.15	0.09	0.36	0.12	0.36	0.12	0.35	0.11	0.24	0.11	0.52	0.00	0.30	0.12	0.40	0.06
Cl	0.01	0.01	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00
Total	96.01	1.08	96.12	0.83	96.45	0.41	95.82	0.79	95.93	0.51	96.11	0.44	96.21	0.64	96.47	0.64	95.62	2.04	95.08	0.52	95.36	0.00	94.46	0.87	95.04	0.51
Si	5.88	0.16	5.96	0.20	5.97	0.20	5.88	0.10	5.96	5.96	5.96	0.13	5.79	0.09	5.92	0.12	5.78	0.02	5.89	0.13	5.84	0.00	5.81	0.13	5.82	0.03
Ti	0.17	0.08	0.15	0.08	0.10	0.08	0.25	0.05	0.33	0.33	0.29	0.12	0.27	0.02	0.25	0.08	0.25	0.07	0.27	0.09	0.17	0.00	0.19	0.06	0.19	0.03
Al	1.90	0.28	1.72	0.61	2.72	0.61	1.81	0.23	1.58	1.58	1.88	0.92	2.06	0.24	1.68	0.29	2.01	0.37	1.60	0.59	1.94	0.00	1.99	0.43	1.83	0.08
Fe	1.33	0.65	1.77	0.08	0.50	0.08	1.61	0.54	2.70	2.70	2.11	0.97	0.83	0.33	1.41	0.54	0.88	0.51	1.64	0.78	0.74	0.00	0.95	0.62	0.77	0.10
Mn	0.02	0.01	0.03	0.00	0.00	0.00	0.02	0.01	0.04	0.04	0.02	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.02	0.01	0.01	0.00	0.01	0.01	0.01	0.01
Mg	4.61	0.34	4.33	2.48	3.04	2.48	4.32	0.51	3.25	3.25	3.48	1.26	4.83	0.18	4.60	0.25	4.83	0.15	4.51	0.52	5.18	0.00	4.93	0.58	5.31	0.07
Ca	0.00	0.00	0.00	1.92	1.57	1.92	0.00	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.13	0.30	0.00	0.00	0.01	0.00	0.01	0.01	0.00	0.00
Na	0.03	0.00	0.04	0.01	0.04	0.01	0.02	0.01	0.02	0.02	0.04	0.05	0.03	0.02	0.02	0.01	0.03	0.01	0.05	0.01	0.03	0.00	0.06	0.01	0.03	0.01
K	1.93	0.09	1.97	0.96	1.18	0.96	1.95	0.11	2.01	2.01	1.96	0.09	1.96	0.03	1.97	0.03	1.90	0.08	1.97	0.05	1.92	0.00	1.96	0.04	1.98	0.03
BaO	0.02	0.02	0.02	0.01	0.01	0.01	0.04	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.03	0.01	0.02	0.01	0.04	0.01	0.02	0.00	0.03	0.01	0.05	0.01
F	0.17	0.10	0.10	0.09	0.12	0.09	0.09	0.04	0.05	0.05	0.07	0.04	0.17	0.04	0.17	0.06	0.16	0.05	0.12	0.05	0.24	0.00	0.14	0.05	0.19	0.03
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	15.90	0.11	15.98	0.86	15.13	0.86	15.91	0.04	15.91	15.91	15.77	0.43	15.82	0.05	15.91	0.10	15.85	0.18	15.98	0.15	15.87	0.00	15.94	0.09	15.99	0.02

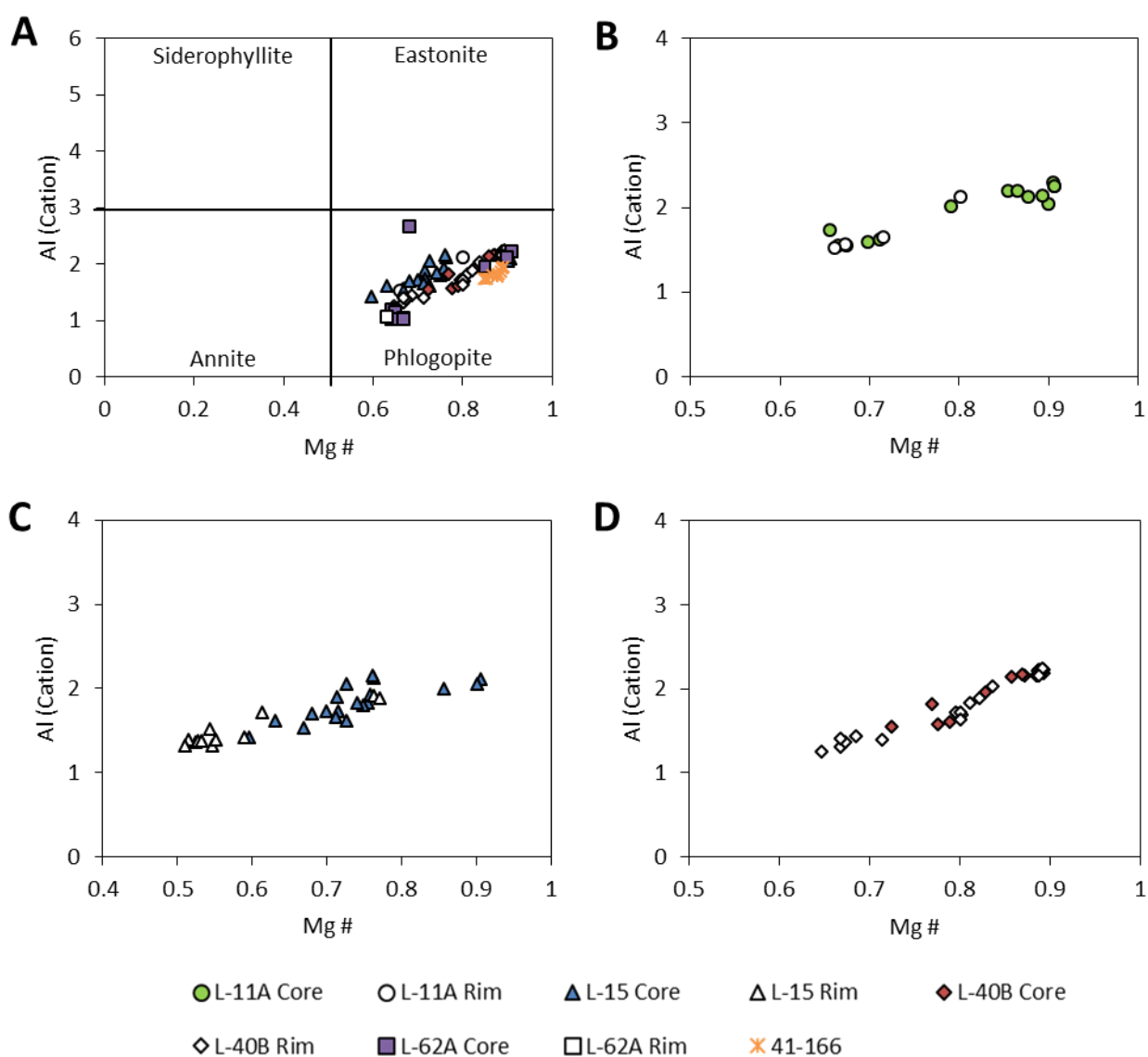


Figure 5.8. Mg# vs Al composition plots showing (A) classification of micas from lamprophyre samples and a kimberlite sample, (B) core and rim data for phlogopite from sample L-11A, (C) core and rim data for phlogopite from sample L-15 and (D) core and rim data for phlogopite from sample L-40B.

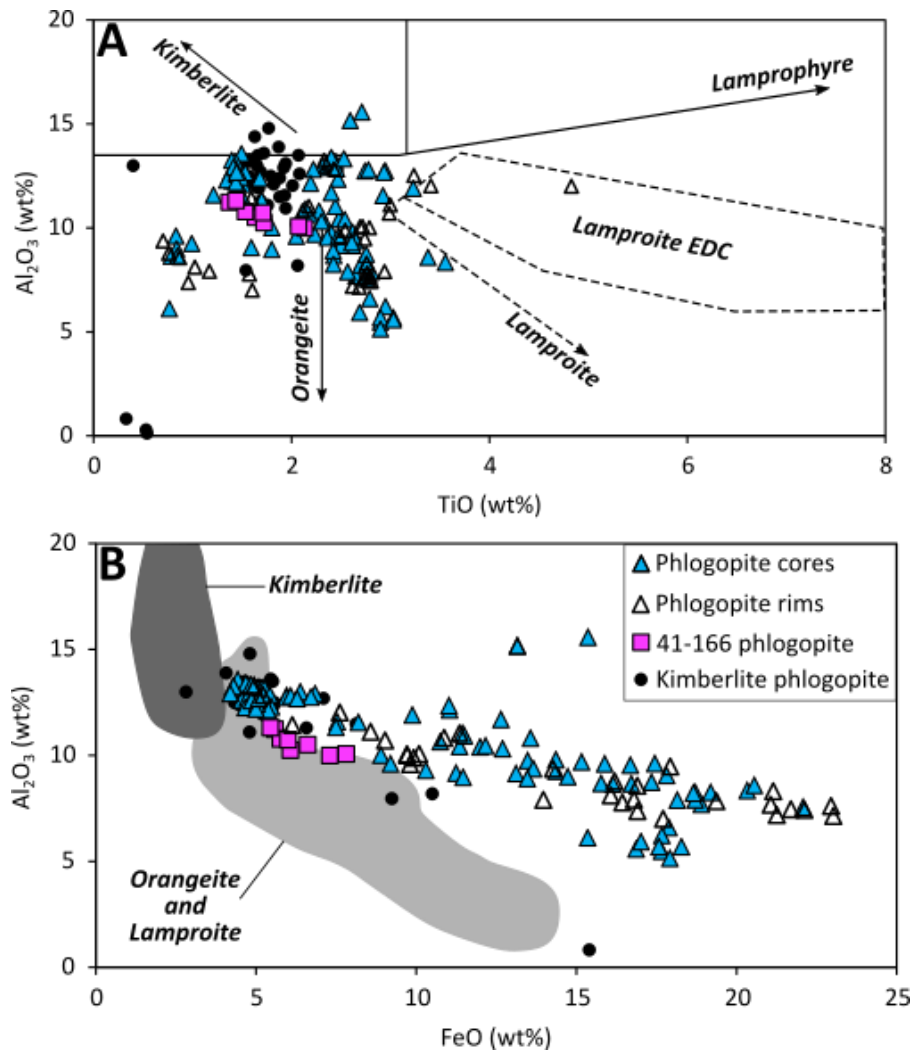


Figure 5.9. Compositional variation diagrams showing (A) Al_2O_3 vs TiO and (B) Al_2O_3 vs FeO for phlogopite core and rim data from lamprophyric dykes, sample 41-166 phlogopite data and South African Group II kimberlite phlogopite data obtained from Coe (2004). Kimberlite and orangeite fields adapted from (Dongre et al., 2017).

5.3 Fluid inclusions

Fluid inclusion microthermometry was only performed on the halite-natrolite sample (L-11B), as this is the most transparent and suitable sample for this analysis. Doubly polished wafer chips of the halite-natrolite sample (L-11A) were first examined petrographically in order to determine the types and population distribution of the fluid inclusions, and then by microthermometric analysis. Fluid inclusions, at room temperature (23-25 °C), were classified as either 1, 2 or 3-phase inclusions according to the criteria in Shepherd et al. (1985). Raman spectroscopy analysis was performed on the same chips of the doubly polished wafer to the composition of volatiles trapped in the fluid inclusions.

5.3.1 Petrography and microthermometry

Fluid inclusions mainly occur in trails along fractures (Fig. 5.10A, B and C) or in well-defined clusters within the halite and natrolite crystals of sample L-11B. Three types of fluid inclusions are observed at 23 to 25 °C namely, three-phase inclusions containing liquid (L), vapour (V) and solid (S) phases, two-phase inclusions comprising liquid and vapour phases, and single-phase inclusions consisting only of liquid. The three-phase inclusions range from 30 to 100 µm and are elongated to irregular in shape. Some inclusions are decrepitated showing signs of leaking. Phase ratios between the liquid and vapour phases are inconsistent and range from 5 to 85% liquid and 10 to 90% vapour. The daughter minerals, which are the solid-phases, typically take up 5% of the volume of the inclusions. The daughter minerals are translucent and have a cubic habit (Fig. 5.10D), with some having rounded edges. Three-phase fluid inclusions are dominantly found in fractures, although some are isolated. Two types of two-phase inclusions exist and these are liquid-rich two-phase and vapour-rich two-phase inclusions. Liquid-rich two-phase inclusions are identified by containing >50% liquid and vapour-rich two phase inclusions 50 to 80% vapour. The two-phase inclusions are usually <20 µm and have an oblong shape with a few between 20 and 30 µm and euhedral in shape. Two-phase fluid inclusions are mainly found along trails or in clusters, but the host mineral does not possess clear characteristics to be able to classify them as either primary or secondary origin. Single-phase, liquid-only, inclusions are small (<20 µm) and euhedral, and occur in trails along with other fluid inclusion assemblages but are not as common. Fluid inclusion trails along fractures contain either only three-phase inclusions or only two-phase inclusions but trails where no fractures are observed consist of a combination of all three types of fluid inclusions. Fluid inclusion trails cross-cut other trails, although there are no visible characteristics that allows us to determine if they are of a secondary or pseudo-secondary origin.

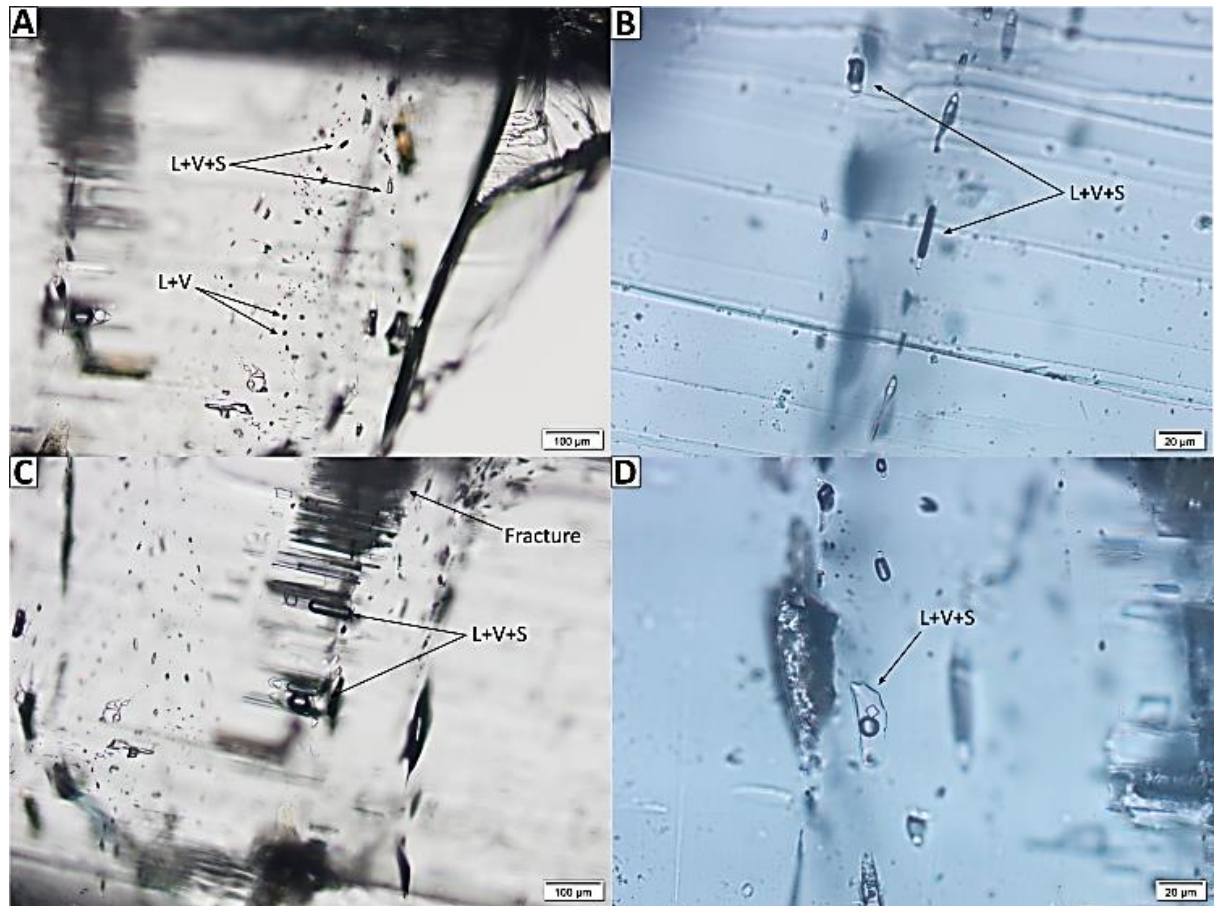


Figure 5.10. Photomicrographs of sample L-11B showing (A) trails of fluid inclusions containing L+V+S and L+V fluid inclusions, (B) close up of a fluid inclusion trail comprising L+V+S inclusions, (C) L+V+S fluid inclusions occurring in a trail in a fracture within the sample and (D) an isolated L+V+S inclusion.

Upon heating and cooling the samples to 300 and -100 °C, respectively, very few phase changes occurred. A two-phase, liquid-rich fluid inclusion was observed to freeze at a temperature of -69 °C (Fig. 6.10C). The inclusion homogenised to liquid at a temperature (T_{hV-L}) of 229 °C (Fig. 6.10E). In three-phase inclusions no freezing temperatures were observed. The vapour bubble of the three-phase inclusion in Figure 6.10F homogenised into the liquid-phase at 200 °C (Fig. 6.10G).

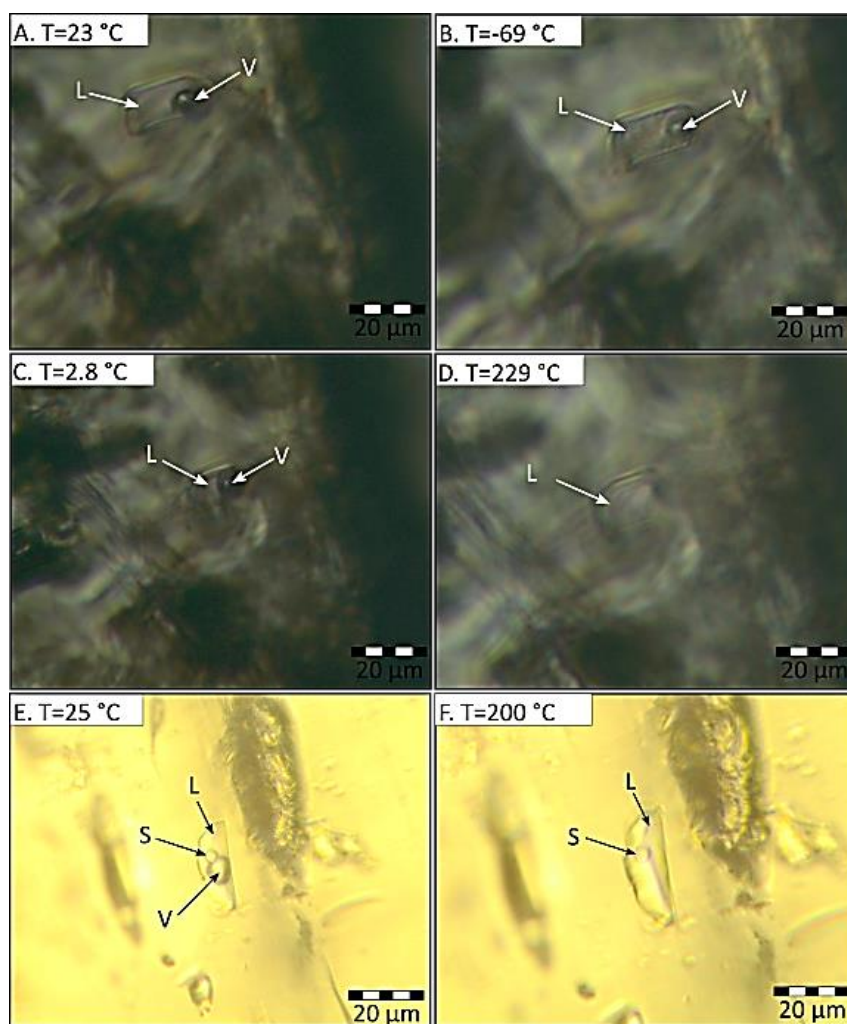


Figure 5.11. Photomicrographs of sample L-11B showing (A) trails of fluid inclusions containing L+V+S and L+V fluid inclusions, (B) close up of a fluid inclusion trail comprising L+V+S inclusions, (C) L+V+S fluid inclusions occurring in a trail in a fracture within the sample and (D) an isolated L+V+S inclusion.

5.3.2 *Raman spectroscopy*

Nineteen fluid inclusions in sample L-11B were analysed using Raman spectroscopy to acquire the composition of their volatiles. No Raman signals were observed for any of the fluid inclusions with the exception of one. This may be due to one or more of the following possible reasons: the sample is too thick and cloudy making it unsuitable for Raman spectroscopy, or the fluid inclusions are too small and/or too deep, making it difficult for the beam to acquire a signal. A Raman signal was obtained for one fluid inclusion, which was identified to be ethanol (Fig. 5.12A). This was confirmed by mapping a horizontal line through the inclusion to measure its intensity distribution. The photomicrograph in Figure 5.12B shows the mapping line that started in the groundmass of the sample, cut through the inclusion and ended again in the groundmass. Measurements were taken at a total of 15 points along the line with a spacing of 2.5 μm . Figure 5.12B shows the intensity peak of ethanol in the inclusion. As the line moves out of the inclusion the intensity drops and no ethanol is present in the groundmass of the sample.

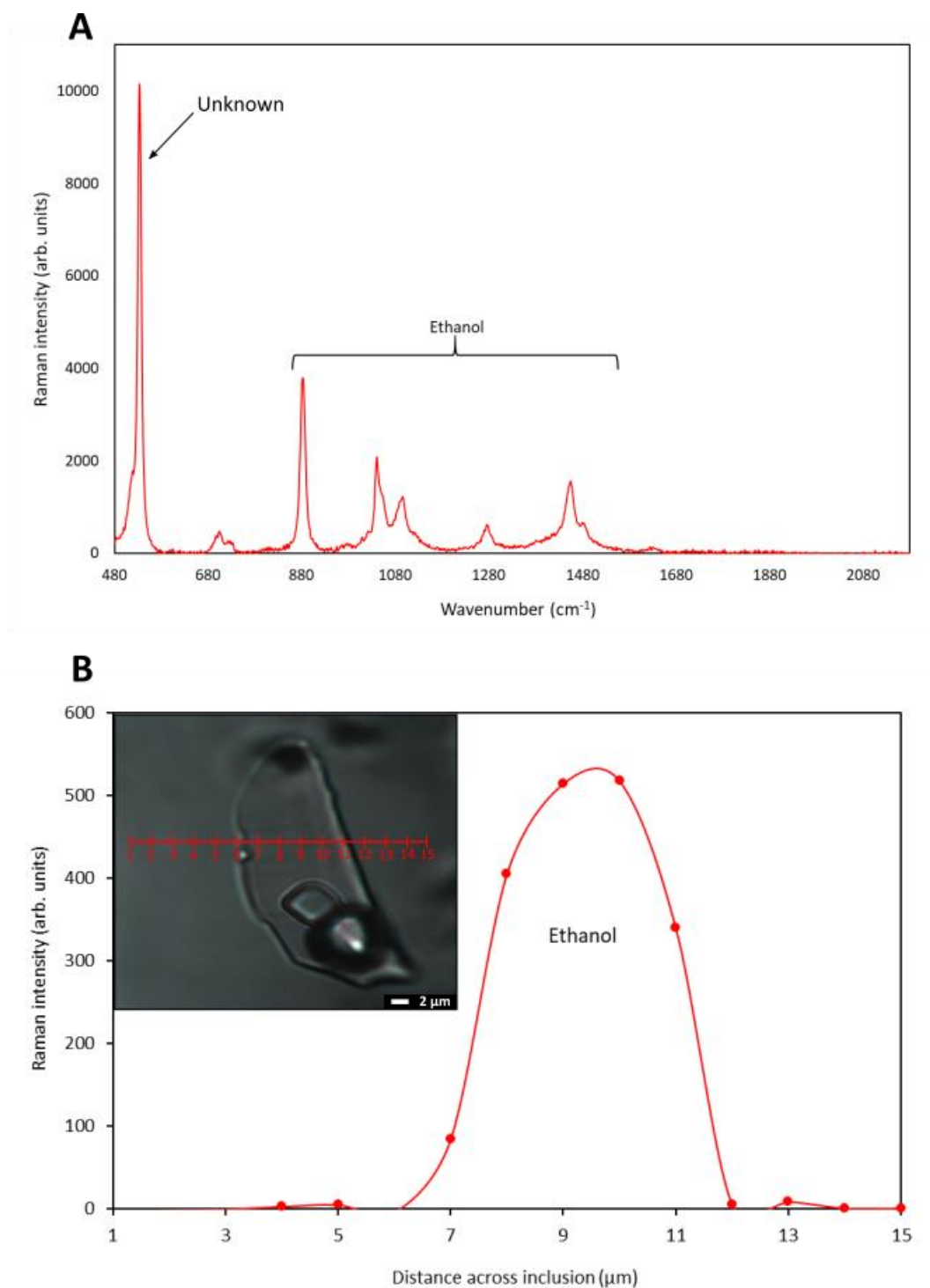


Figure 5.12. Raman intensity plots showing (A) the Raman signal and peaks of ethanol in the fluid inclusion and (B) the distribution of the intensity of ethanol across a series of points in fluid inclusion and in its host groundmass.

5.4 'In-line' gas chromatography

'In-line' gas chromatography (GC) was used to detect and quantify the composition of bulk volatiles trapped within pore spaces or in the form of adsorbed gases or fluid inclusions within rock-forming minerals in the lamprophyric dykes. A total of 38 lamprophyric dyke samples (31 non-outburst samples and 7 outburst samples) were analysed. The samples were crushed (to ~3 mm sized-grains), cleaned and inserted in stainless-steel crushes where they were heated and crushed further (see Section 3.5). The volatiles released from the samples were then directly injected into the GC where they were analysed. Data for methods 1 and 2 (see Section 3.5) of GC quantification are presented here.

5.4.1 Method 1

The gases detected by method 1 of GC quantification are H₂O, CO₂+CO, CH₄, C₂H₆, C₃H₈ and C₃H₁₀. All lamprophyric dykes contain detectable amounts of H₂O, CH₄ and C₂H₆. Nineteen samples contain C₃H₈. Seven samples contain CO₂+CO and 7 samples contain C₄H₁₀. The gas species focused on in this study are CH₄, CO₂+CO, C₂H₆, C₃H₈ and C₃H₁₀. These gases are present in variable amounts. Mean values for each gas species in non-outburst samples, outburst samples and the total number of samples were calculated and are summarised in Table 5.4. A comparison is made between the average abundances of CH₄ and CO₂+CO (between outburst and non-outburst samples) as they are the dominant gases contained in the dykes. It can be seen from Figure 5.13A that CH₄ is more abundant than CO₂+CO, with averages of 3.66×10⁻⁸ mol/g for outburst samples and 1.21×10⁻⁸ mol/g for non-outburst samples. The averages for CO₂+CO are 2.55×10⁻⁹ mol/g and 5.61×10⁻⁹ mol/g for outburst and non-outburst samples, respectively.

Table 5.4. Mean values for CO₂+CO, CH₄, C₂H₆, C₃H₈ and C₄H₁₀ in non-outburst, outburst and total number of samples. Where S.D. refers to the standard deviation.

	CO ₂ +CO (mol/g)	S.D.	CH ₄ (mol/g)	S.D.	C ₂ H ₆ (mol/g)	S.D.	C ₃ H ₈ (mol/g)	S.D.	C ₄ H ₁₀ (mol/g)	S.D.
Non-outburst samples	5.61×10 ⁻⁹	2.44×10 ⁻⁸	1.21×10 ⁻⁸	1.20×10 ⁻⁸	5.02×10 ⁻¹⁰	6.01×10 ⁻¹⁰	5.66×10 ⁻¹¹	8.76×10 ⁻¹¹	8.22×10 ⁻¹²	2.00×10 ⁻¹¹
Outburst samples	2.55×10 ⁻⁹	4.62×10 ⁻⁹	3.66×10 ⁻⁸	7.77×10 ⁻⁸	1.50×10 ⁻⁹	3.29×10 ⁻⁹	9.81×10 ⁻¹¹	1.95×10 ⁻¹⁰	2.65×10 ⁻¹¹	6.49×10 ⁻¹¹
Total number of samples	5.05×10 ⁻⁹	2.21×10 ⁻⁸	1.66×10 ⁻⁸	3.63×10 ⁻⁸	6.86×10 ⁻¹⁰	1.56×10 ⁻⁹	6.42×10 ⁻¹¹	1.16×10 ⁻¹⁰	1.16×10 ⁻¹¹	3.40×10 ⁻¹¹

Figure 5.13B shows CH₄ and CO₂+CO abundances for all outburst samples (n=7). All outburst samples contain CH₄ but only two samples (L-11A and L-11B) contain both CH₄ and CO₂+CO. Sample L-11A contains the most CH₄ (2.27×10⁻⁷ mol/g) and the most CO₂+CO (1.32×10⁻⁸) from all other outburst samples. Sample L-11B contains more CO₂+CO (4.72×10⁻⁹ mol/g) than CH₄ (2.12×10⁻⁹ mol/g). Samples L-111, L-112, L-113, L-116 and L-AB1 only contain CH₄ at abundances of 7.08×10⁻⁹ mol/g, 2.67×10⁻⁹ mol/g, 3.94×10⁻⁹ mol/g, 7.10×10⁻⁹ mol/g and 6.45×10⁻⁹ mol/g, respectively. Figure 5.13C shows CH₄ and CO₂+CO abundances for non-outburst samples (n=31). All non-outburst samples contain CH₄ but only 5 contain both CH₄ and CO₂+CO. Sample L-PD4 contains the most CO₂+CO (1.34×10⁻⁷ mol/g)

which is more abundant than CH₄ (2.68×10^{-8} mol/g). Sample L-PD12 contains the most CH₄ (5.19×10^{-8} mol/g) but does not contain any CO₂+CO. Samples L-PD12, L-PD14, L-PD15, L-PD17, L-PD18, L-PD20 and L-PD23 are samples collected from the 4 boreholes drilled through lamprophyric dykes underground for the *in-situ* gas analysis (see Section 5.5). All these samples contain CH₄ of varying abundances (5.19×10^{-8} mol/g to 2.80×10^{-9} mol/g).

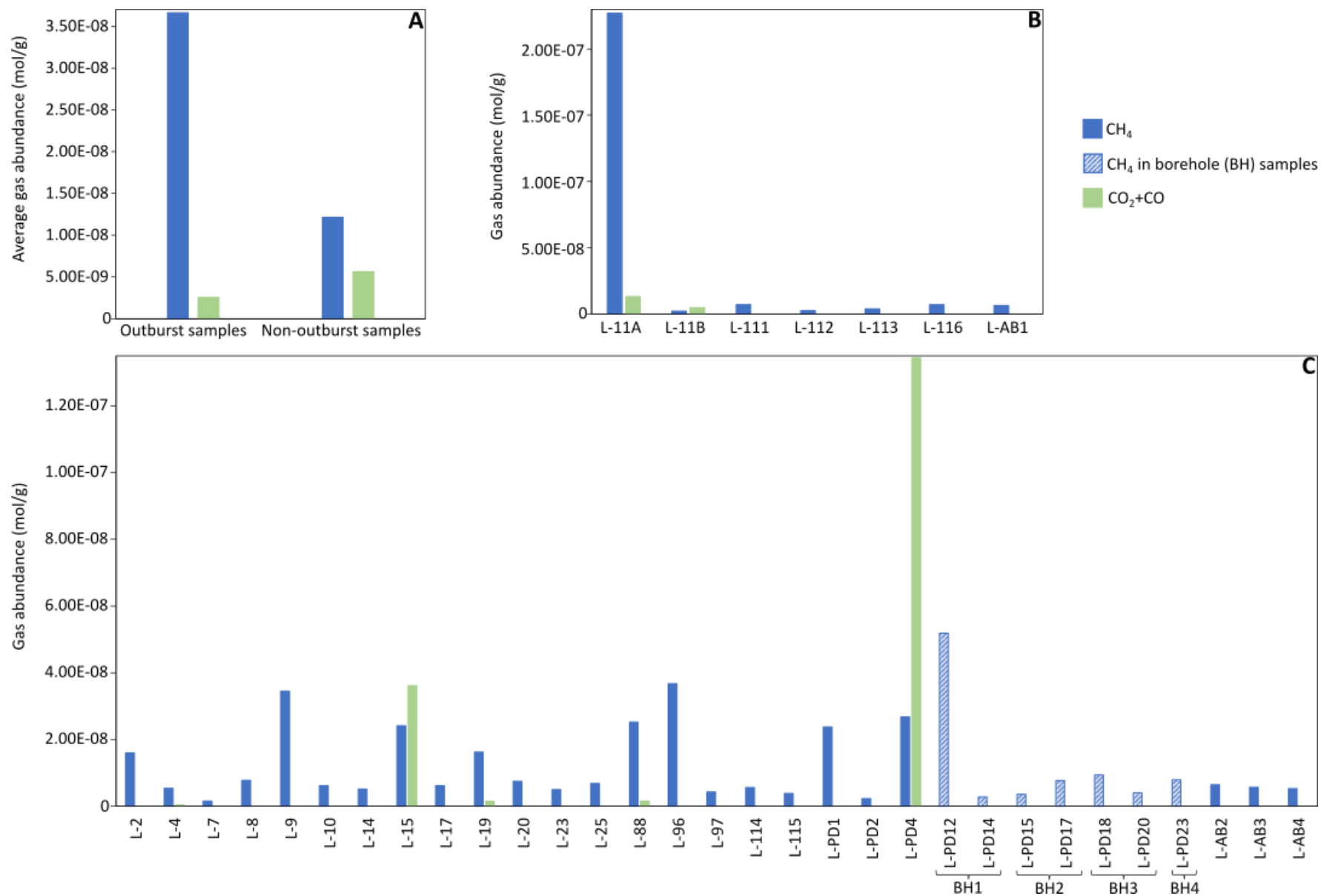


Figure 5.13. Bar graphs showing (A) the average abundances of CH₄ and CO₂ + CO in outburst samples and non-outburst samples, (B) the abundance of methane (CH₄) and carbon dioxide + carbon monoxide (CO₂+CO) in outburst samples and (C) the abundance of methane (CH₄) and carbon dioxide + carbon monoxide (CO₂+CO) in non-outburst samples using ‘in-line’ GC.

Figure 5.14 shows the abundances for the saturated hydrocarbons (C1-C4) in outburst samples and non-outburst samples. Methane is the most abundant hydrocarbon in the lamprophyric dykes. The abundances of CH₄, C₂H₆, C₃H₈ and C₄H₁₀ are higher in non-outburst samples than outburst samples (2.12×10^{-9} - 2.27×10^{-7} mol/g). The minimum and maximum values for the hydrocarbons in non-outburst samples are 1.56×10^{-9} to 5.19×10^{-8} mol/g (CH₄), 8.41×10^{-10} to 2.57×10^{-8} mol/g (C₂H₆), 0 to 2.76×10^{-9} mol/g (C₃H₈) and 0 to 7.91×10^{-9} mol/g (C₄H₁₀). The minimum and maximum values for the hydrocarbons in outburst samples are 2.12×10^{-9} to 2.27×10^{-7} mol/g (CH₄), 7.86×10^{-10} to 9.56×10^{-8} mol/g (C₂H₆), 0 to 5.72×10^{-9} mol/g (C₃H₈) and 0 to 1.86×10^{-8} mol/g (C₄H₁₀).

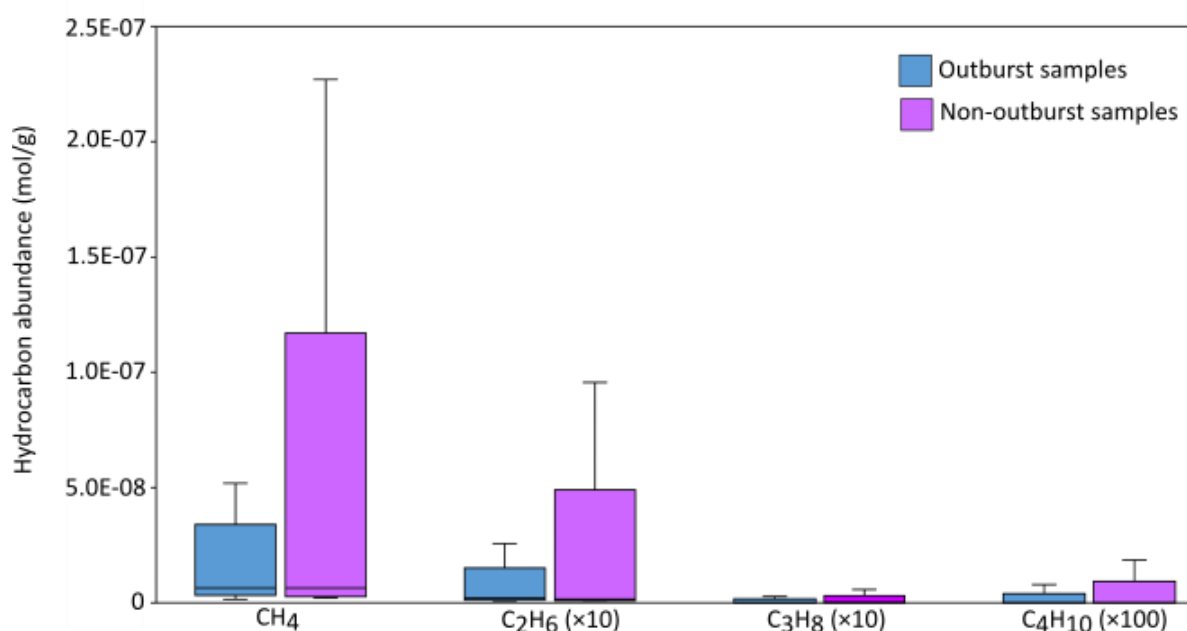


Figure 5.14. Box and Whisker plot showing saturated (C1-C4) hydrocarbon abundances for outburst and non-outburst samples.

5.4.2 Method 2

The 4 lamprophyric dyke samples (L-11A, L-9, L-96 and L-PD12) that contained the most CH₄ in Method 1 were re-analysed by Method 2 in order to get their detailed hydrocarbon signature. Molar abundances for saturated hydrocarbons (C1-C5) contained in all 4 samples were plotted on a Schulz-Flory distribution (Fig. 5.15) to see where they plot relative to the biogenic and thermogenic environments. All samples show a linear trend that decreases from CH₄ to C₅H₁₂. Molar abundances for the hydrocarbons are the highest in sample L-9 (9.40×10^{-1} - 8.83×10^{-5} mole%), followed by L-PD12 (9.10×10^{-1} - 1.40×10^{-4} mole%), L-11A (9.27×10^{-1} - 8.58×10^{-5} mole %) and L-96 (8.81×10^{-1} - 2.68×10^{-4} mole%). All the samples fall below the biogenic and thermogenic environments (see section 6.3.2).

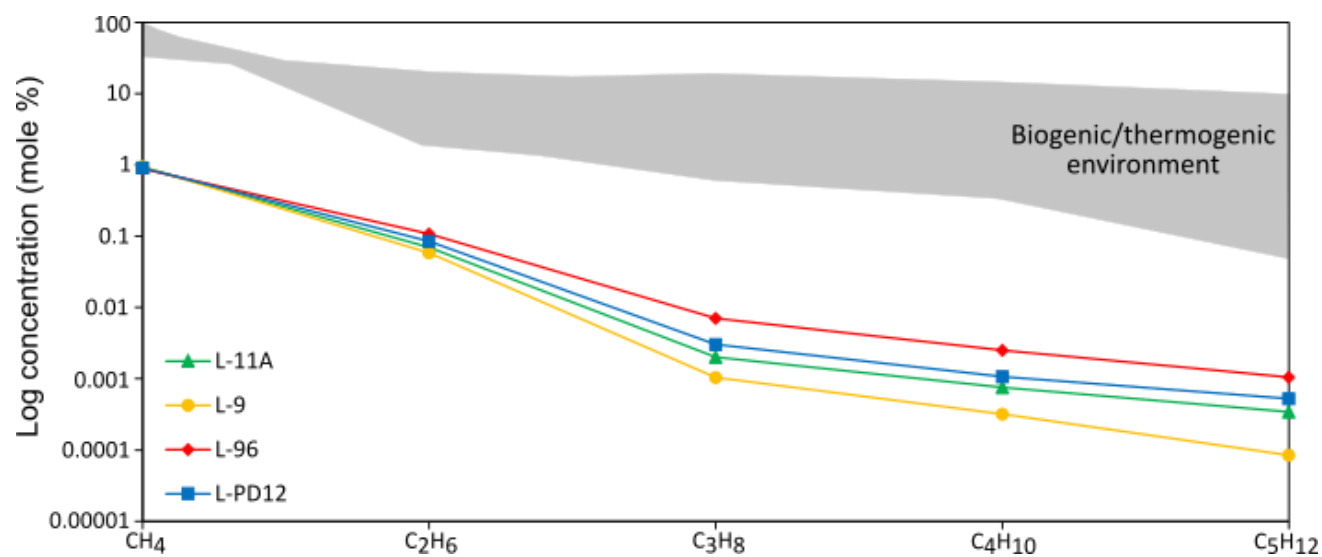


Figure 5.15. Schulz-Flory distribution showing saturated (C1-C5) hydrocarbon values in mole % of the 4 lamprophyre samples analysed by Method 2 of CG quantification. Biogenic and thermogenic fields adapted from Potter and Konnerup-Madsen (2003).

5.5 Underground *in-situ* gas detection

Gases were detected in boreholes that were drilled through the face of 4 lamprophyric dykes underground, at different levels of the mine (see Section 3.6). The Dräger X-am 5600 handheld gas detector attached to a pump and a hose were used to measure accumulated gas in boreholes in the lamprophyres as opposed to the ‘in-line’ GC (see Section 6.4), which analyses gas trapped within the rock itself. The gas species analysed by the Dräger X-am 5600 were CH₄, CO₂, CO, H₂, H₂S and Cl₂ (see Appendices (Table D.8) for lower detection limits and measuring standards). Two sets of analyses took place on each borehole. Analysis 1 was carried out at each borehole a week after they were drilled and plugged. The second set of analyses (analysis 2) took place after 24 hours. At each borehole, underground ambient air measurements (Fig. 5.17A) were first taken before opening the valve on the plugs. Thereafter the valves were opened and the hose was immediately fed through the borehole, measuring gas that had accumulated for a duration of a week (analysis 1) and for a period of 24 hours (analysis 2). This resulted in a peak flow of gas from each borehole (Fig. 5.16). After the peaks drop gas is observed to be constantly streaming out the boreholes. Gas measurements for analysis 1 are shown in Figures 5.17A, C, E and G and for analysis 2 in Figures 5.17B, D, F and H. Gas measurements for analysis 1 and 2 for all 4 boreholes are presented here.

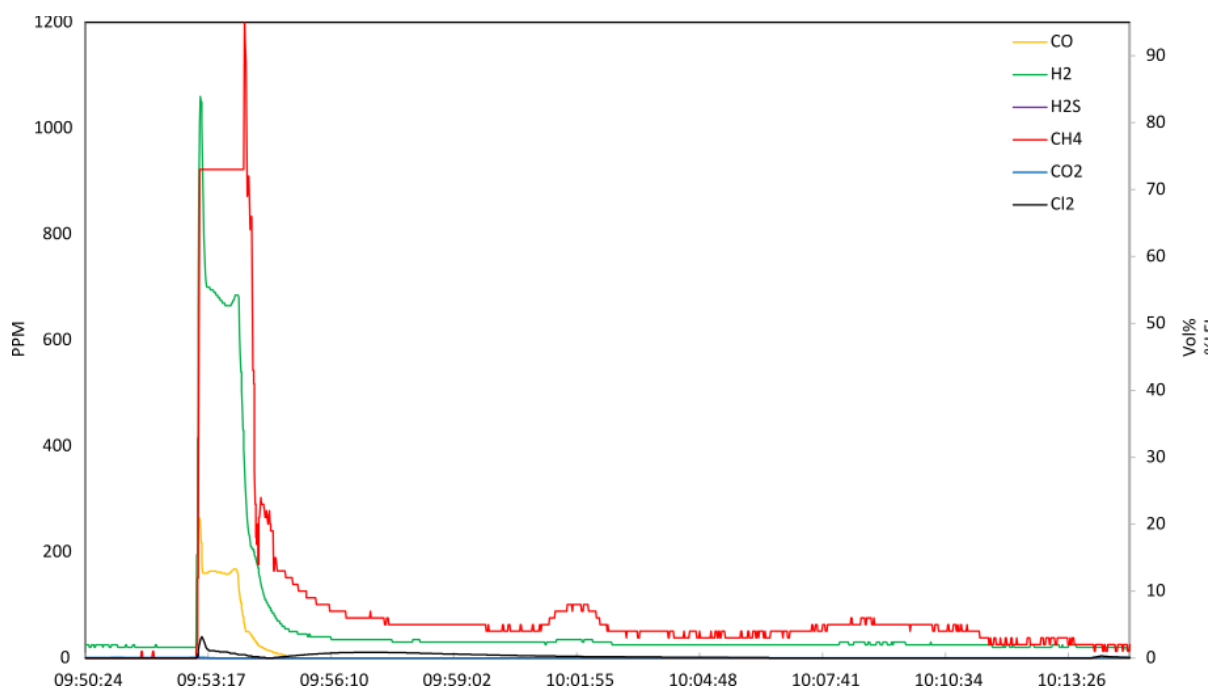


Figure 5.16. Line graph demonstrating the extent of the peak flow for methane (CH₄), carbon dioxide (CO₂), carbon monoxide (CO), hydrogen (H₂), chlorine (Cl₂) and hydrogen sulphide (H₂S) in borehole 1 from the underground *in-situ* gas analysis.

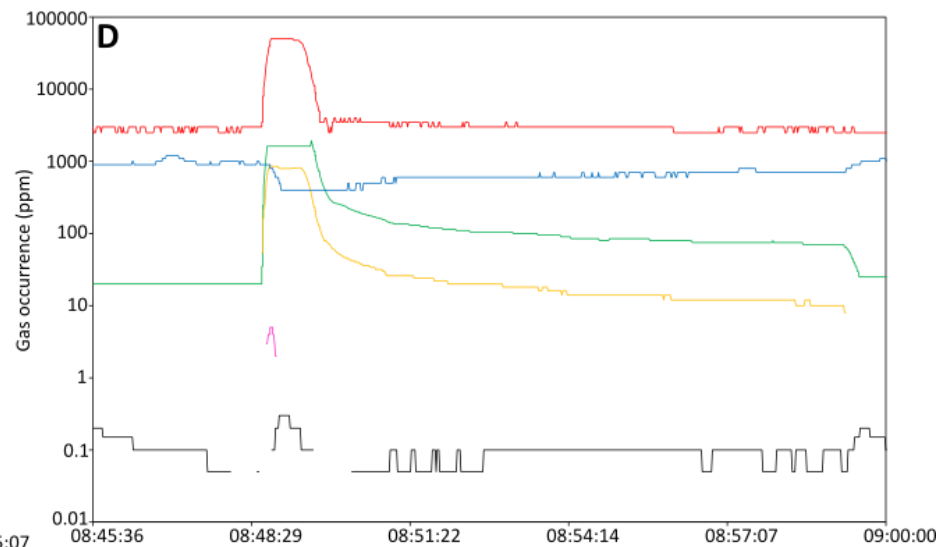
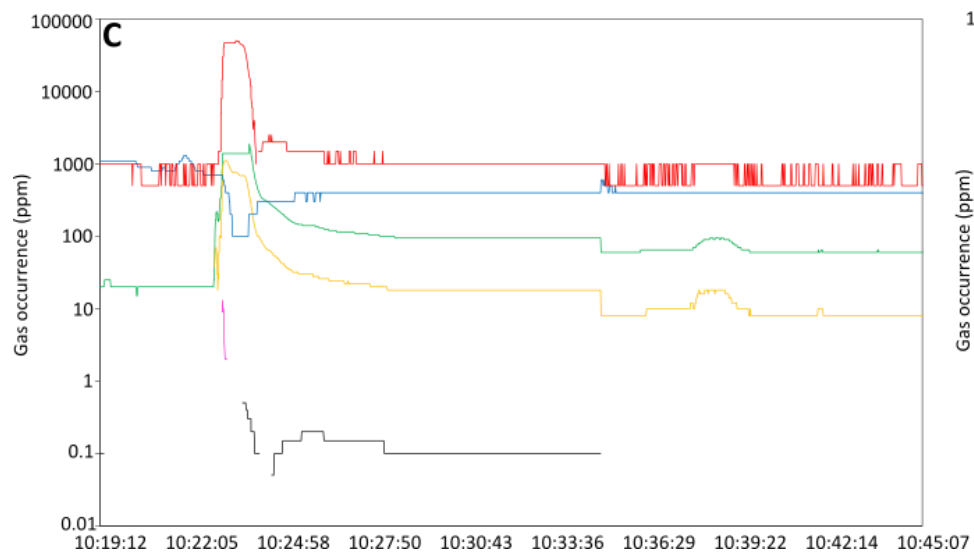
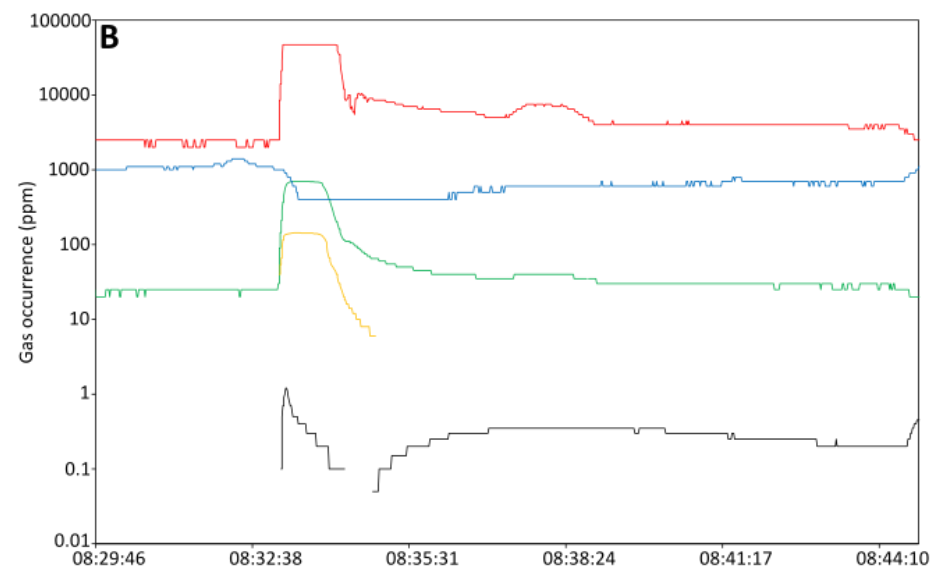
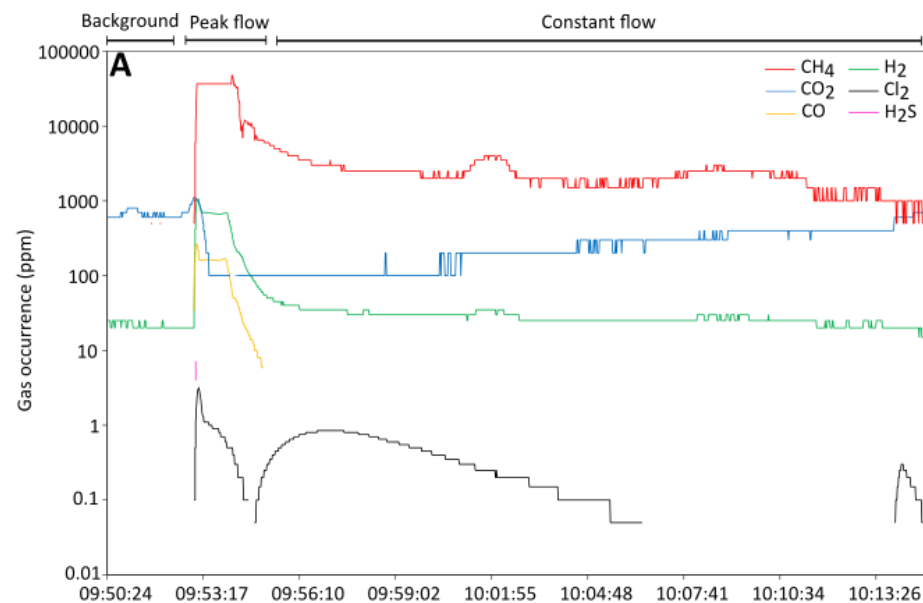
5.5.1 Analysis 1

CH₄, CO₂, CO, H₂ and Cl₂ were detected in all 4 boreholes while H₂S was only detected in boreholes 1 and 2 and only during the peak flow. No H₂S gas was detected to be constantly streaming out any of the dykes. Carbon monoxide appears only at the peak flow in boreholes 1, 3 and 4, and only in borehole 2 it is observed to constantly stream out the dyke. The amount of gas constantly flowing out of the boreholes and the peak flow of gases detected by the gas sensor are variable in each borehole. Peak values and ranges for constant flow of gas out of the boreholes for the first set of analyses are summarised in Table 5.5.

Table 5.5. Peak values and ranges (in ppm) for constant streaming of CH₄, CO₂, CO, H₂, H₂S and Cl₂ out of boreholes 1-4, obtained from analysis 1 of the underground *in-situ* gas detection.

	Borehole 1		Borehole 2		Borehole 3		Borehole 4	
	Peak value (ppm)	Constant flow (ppm)	Peak value (ppm)	Constant flow (ppm)	Peak value (ppm)	Constant flow (ppm)	Peak value (ppm)	Constant flow (ppm)
CH ₄	48000	500-4000	50000	0-1000	35500	0-1500	23000	0-1500
CO ₂	1200	100-700	1300	400-800	1300	700-1200	1100	600-800
CO	264	0	1110	0-18	20	0	64	0
H ₂	1060	15-35	1880	25-95	75	20-25	190	15-25
H ₂ S	7	0	13	0	0	0	0	0
Cl ₂	3.2	0-0.85	0.5	0-0.15	0.1	0-0.1	0.15	0-0.15

In borehole 1 (Fig. 5.17A) all 6 six gases were detected. The peak values for CH₄, CO₂, CO, H₂, H₂S and Cl₂ are 48000 ppm, 1200 ppm, 264 ppm, 1060 ppm, 7 ppm and 3 ppm, respectively. Borehole 1 had gas constantly streaming out in amounts ranging from 500 to 4000 ppm (CH₄), 100 to 700 ppm (CO₂), 15 to 35 ppm (H₂) and 0 to 0.85 ppm (Cl₂). Similarly, all 6 gases were detected in borehole 2 (Fig. 5.17C). Peak values for borehole 2 are 50000 ppm, 1300 ppm, 1110 ppm, 1880 ppm, 13 ppm and 1 ppm for CH₄, CO₂, CO, H₂, H₂S and Cl₂, respectively. The amount of gas constantly flowing out of the dyke range from 0 to 1000 ppm for CH₄, 400 to 800 ppm for CO₂, 0 to 18 ppm for CO, 25 to 95 ppm for H₂ and 0 to 0.15 ppm for Cl₂. Unlike the first 2 boreholes no H₂S was detected in borehole 3 (Fig. 5.17E). The gases peak at 35500 ppm, 1300 ppm, 20 ppm, 75 ppm and 0.1 ppm for CH₄, CO₂, CO, H₂ and Cl₂, respectively. The gases streaming out of borehole 3 was at amounts between 0 and 1500 ppm (CH₄), 700 and 1200 ppm, 20 and 25 ppm (H₂), and 0 and 0.1 ppm (Cl₂). Borehole 4 (Fig. G) is similar to borehole 3 in that it contains peak values of 23000 ppm for CH₄, 1100 ppm for CO₂, 64 ppm for CO, 190 ppm for H₂ and 0.15 ppm for Cl₂. Once again Cl₂ only occurs as a peak and was not detected to be streaming out of the borehole. The amount of CH₄, CO₂, H₂ and Cl₂ observed to constantly be streaming out of the dykes is 0 to 1500 ppm, 600 to 800 ppm, 15 to 25 ppm and 0 to 0.15 ppm, respectively.



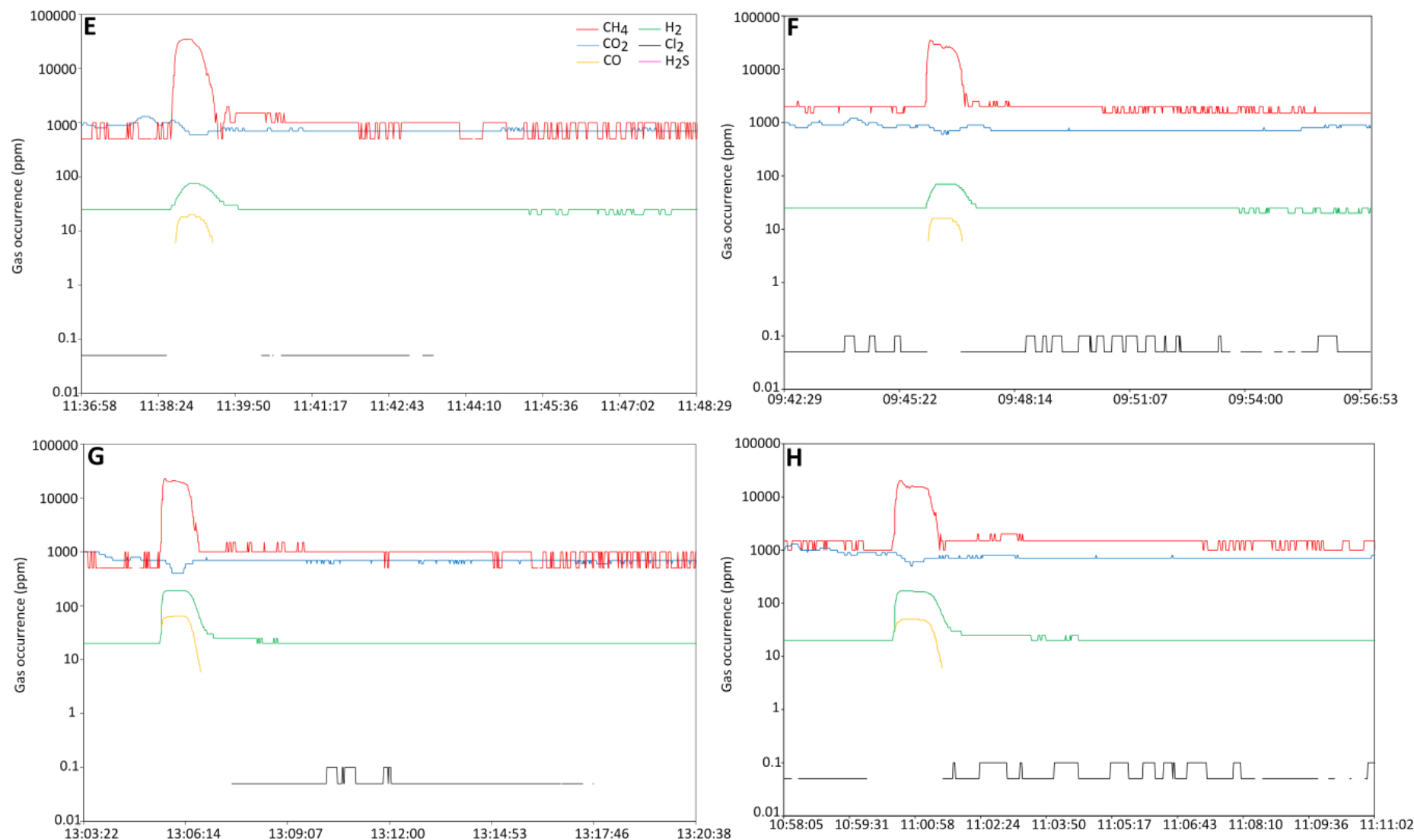


Figure 5.17. Line graphs showing the abundance of methane (CH_4), carbon dioxide (CO_2), carbon monoxide (CO), hydrogen (H_2), chlorine (Cl_2) and hydrogen sulphide (H_2S) in (A) borehole 1, (C) borehole 2, (E) borehole 3 and (H) borehole 4 from analysis 1 and (B) borehole 1, (D) borehole 2, (F) borehole 3 and (H) borehole 4 from analysis 2 of the underground *in-situ* gas analysis.

5.5.2 Analysis 2

Similar to analysis 1, CH₄, CO₂, CO, H₂ and Cl₂ were detected in all 4 boreholes, although H₂S is only observed in borehole 2 at peak flow. Carbon monoxide occurs only in the peak flow in all boreholes except for borehole 2, which is similar to results from analysis 1. The gas peaks from analysis 2 are generally smaller to that of analysis 1. The amount of gas seen constantly streaming out of each borehole appears to be similar to that of analysis 1. The peak values and amount of gas constantly streaming out the boreholes are summarised in Table 5.6.

Table 5.6. Peak values and ranges (in ppm) for constant streaming of CH₄, CO₂, CO, H₂, H₂S and Cl₂ out of boreholes 1-4, obtained from analysis 2 of the underground *in-situ* gas detection.

	Borehole 1		Borehole 2		Borehole 3		Borehole 4	
	Peak value (ppm)	Constant flow (ppm)	Peak value (ppm)	Constant flow (ppm)	Peak value (ppm)	Constant flow (ppm)	Peak value (ppm)	Constant flow (ppm)
CH ₄	47000	2500-7500	50000	2500-3500	35000	1500-2500	1300	700-800
CO ₂	1400	500-1200	1300	600-1100	1200	700-900	20000	1000-2000
CO	144	0	860	0-24	16	0	50	0
H ₂	695	20-40	1940	25-130	70	20-25	170	15-25
H ₂ S	0	0	5	0	0	0	0	0
Cl ₂	1.2	0.2-0.45	0.4	0.05-0.2	0.1	0-0.1	0.1	0-0.1

Peak values for borehole 1 (Fig. 5.17B) are 47000 ppm for CH₄, 1400 ppm for CO₂, 144 ppm for CO, 695 ppm for H₂ and 1.2 ppm for Cl₂. Methane, CO₂, H₂ and Cl₂ are observed to be constantly flowing out the dykes at amounts ranging from 2500 to 7500 ppm, 500 to 1200 ppm, 20 to 40 ppm and 0.2 to 0.45 ppm, respectively. Borehole 2 (Fig. 5.17C) has peak values of 50000 ppm, 1300 ppm, 860 ppm, 1940 ppm, 5 ppm and 0.4 ppm for CH₄, CO₂, CO, H₂, H₂S and Cl₂, respectively. Gas that is constantly streaming out of borehole 2 occurs at amounts ranging between 2500 and 3500 ppm (CH₄), 600 and 1100 ppm (CO₂), 0 and 24 ppm (CO), 25 and 130 ppm (H₂), 0.05 and 0.2 ppm (Cl₂). In borehole 3 (Fig. E) the peak values for CH₄, CO₂, CO, H₂ and Cl₂ are 35000 ppm, 1200 ppm, 16 ppm, 70 ppm and 0.1 ppm, respectively. Borehole 3 has CH₄, CO₂, H₂ and Cl₂ constantly streaming out of it at amounts ranging from 1500 to 2500 ppm, 700 to 900 ppm, 20 and 25 ppm and 0 and 0.1 ppm, respectively. Peak values for borehole 4 are 1300 ppm (CH₄), 20000 ppm (CO₂), 50 ppm (CO), 170 ppm (H₂) and 0.1 ppm (Cl₂). The amount of CH₄, CO₂, H₂ and Cl₂ streaming out of borehole 4 at a constant rate ranges from 700 to 800 ppm, 1000 to 2000 ppm, 15 to 25 ppm and 0 to 0.1 ppm, respectively.

From the results in both analysis 1 and 2 it can be seen that CH₄, CO₂ and H₂ are the most common gases in all 4 boreholes. Methane is the most abundant gas, as can be noted by the high peak values and amount constantly streaming out of the dykes. Carbon dioxide is the second most abundant and H₂ the third. Carbon monoxide is commonly observed in all 4 boreholes but, with the exception of borehole 2,

it only occurs during the peak flow. Chlorine gas is frequently observed in all 4 dykes, but at lower quantities. Hydrogen sulphide occurs in boreholes 1 and 2 in analysis 1 but only borehole 2 in analysis 2. Whilst the abundance of gas clearly differs for each gas species and between the 4 boreholes, the amount of gas that is constantly streaming out the dyke does not vary much between analysis 1 and analysis 2.

5.5.3 Comparison of results from underground gas detection and 'in-line' gas chromatography

Methane and CO₂+CO were detected by both 'in-line' GC and underground *in-situ* gas analysis. In both cases CH₄ occurred in high abundances compared to other gas species. CO₂ + CO was detected in only 7 samples by 'in-line' GC and in the underground *in-situ* gas analysis both CO₂ and CO occur as trace gases. Ratios of CH₄/CO₂+CO were calculated for 'in-line' GC and the underground gas analysis. A comparison is made between these 2 data sets in Figure 5.18.

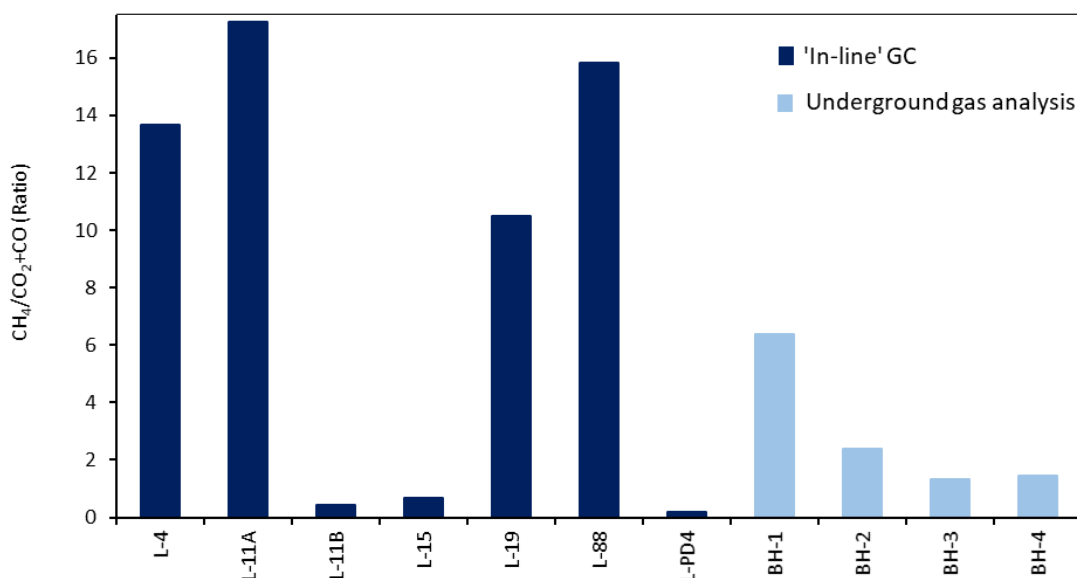


Figure 5.18. Bar graph showing the ratio of CH₄/CO₂+CO for samples analysed by 'in-line' GC and for gas detected by underground *in-situ* gas analysis.

6 Discussion

6.1 Lamprophyre paragenesis

Basson and Viola (2003) found that Group II kimberlite dykes in South Africa occur in small, en-echelon dyke-fracture arrays, with individual dykes showing variations in their dyke morphology. Dyke-fracture systems comprise either segmented fracture arrays or continuous fracture systems (Basson and Viola, 2003). Segmented fracture arrays appear as anastomosing segments, subparallel and irregularly spaced sets and/or as en-echelon arrays. Continuous fracture arrays display zig-zag patterns or they can show no pattern but have an overall trend (Basson and Viola, 2003). Lamprophyric dykes that cross-cut the Western Limb of the Bushveld Complex also occur in a dyke-fracture array. The lamprophyric dyke-fracture system trends WNW-ESE and comprises subparallel, irregular and anastomosing segmented dykes (see section 4.1). Continuous dykes that do not show any particular pattern also occur. Some dykes are ‘stepped’, resembling en-echelon fractures (see Section 4.1). Basson and Viola (2003) deduce that dyke-fracture systems were generated from a magma or fluid occupying a pre-existing fracture system. The dykes have straight terminations and minimal overlap with each other, similarly to Group II kimberlite dykes in South Africa, which indicates that there was a lack of magmatic overpressure during emplacement. According to Basson and Viola (2003), the kimberlite dyke-fracture system was formed from the rapid movement of low volume, low viscosity and highly volatile-rich fluid into a linear array of pre-existing joints and fractures. The features of the lamprophyric dyke-fracture array closely resembles that of the kimberlite dyke-arrays in South Africa. Therefore, the lamprophyric dykes most likely formed by the same mechanism whereby a highly volatile-rich magma of low viscosity and low in volume occupied a system of pre-existing fractures. The array of vertical to sub-vertical lamprophyric dykes acts as a network of conduits that allow gases to percolate through.

The lamprophyric dykes also contain micro-features that are visible in hand/core samples as well as in thin section. For example, some samples (e.g., L-40B, L-62A) are banded, with notable variations of megacryst (e.g., phlogopite) size, colour and pleochroism, and changes in the modal abundances of minerals present in these samples. These zones of variation suggests that there are several phases of intrusion into a single dyke. In sample L-40B (Fig. 5.1A) it is clear that a second generation of lamprophyre cross-cuts the first generation. This is suggested by the lower abundance of phlogopite phenocrysts, higher abundance of olivine macrocrysts and darker shade of brown of the groundmass in the second generation lamprophyre. In sample L-62A 3 generations of lamprophyre can be seen (Fig. 5.1B). The top half (above the red line) only contains phlogopite phenocrysts and the bottom half (below the blue line) contains both phlogopite phenocrysts and olivine macrocrysts. These zones are separated by a vein composed only of phlogopite and calcite (in between the red and blue lines). It is clear that the centre vein is the third generation as it cross-cuts the top and bottom halves. However, it is difficult to infer which dyke, top or bottom, intruded first.

The lamprophyric dykes are composed of predominantly olivine macrocrysts and phlogopite and pyroxene phenocrysts that are set in fine-grained groundmass. Olivine macrocrysts are round, partially or fully serpentinised and are sometimes further chloritized or replaced by calcite. The rest of the lithology in the lamprophyric dykes however remain unaltered. According to Mitchell (1995), olivine macrocrysts are not primary liquidus constituents but were rather entrained into the ultrapotassic magma when the magma infiltrated and disaggregated wall-rock containing olivine (Mitchell, 1995). During or after emplacement of the olivine-contaminated magma, reactions of residual magma and already crystallised minerals, specifically olivine, took place to form serpentine (Mitchell, 1995). Phlogopite and pyroxene phenocrystic and groundmass phases contained within the lamprophyric dykes are characteristically euhedral to subhedral and prismatic, respectively. Euhedral to subhedral habits of crystals are considered to be early-forming primary magmatic phases (Mitchell, 1995; Winter, 2010), which indicates that the phlogopite and pyroxene crystals are primary magmatic phases. However compositional zoning, is observed in pyroxene, phlogopite and apatite crystals within the lamprophyres. As a crystal grows its composition changes upon cooling (Winter, 2010). The different compositions can be noted by the difference in the intensity of the colour of the minerals between their cores and rims (see Section 5.1). Zoned pyroxene crystals display a lighter shade of green at their cores than their rims (Fig. 5.3A), and they decrease in Al, Mg and Ca contents and increase in Fe contents from core to rim (Table 5.2; Fig. 5.6). Similarly, zoned phlogopite crystals are light brown at their cores and darker brown at their rims. The chemical composition of phlogopite cores are higher in Al and Mg contents, and lower in Fe contents than their rims, showing a general trend of decreasing Al and Mg contents and increasing Fe contents from core to rim (Table 5.3; Fig. 5.8). The compositional trends of the pyroxene and phlogopite crystals from core to rim indicate that the magma from which they crystallised became depleted in Al and Mg contents and enriched in Fe contents as minerals were crystallising. This suggests that the magma differentiated during crystallisation of the lamprophyres (Winter, 2010). Resorption textures (Fig. 5.2) are also observed in phlogopite crystals within the lamprophyres, indicating dissolution of the early-crystallising phlogopite crystals back into the melt from which they formed (Winter, 2010). Oscillatory zoning and resorption textures also demonstrate that the phlogopite and pyroxene have not crystallised *in-situ* and therefore they do not represent primary liquid compositions (Mitchell 1994; Mitchell 1995). Mitchell (1994, 1995) suggests that disequilibrium, partial resorption and, crystal re-growth result from the mixing of multiple batches of magma during emplacement. Subsequent to emplacement and contemporaneous to the crystallisation of phenocrystic phlogopite and pyroxene, groundmass phases such as phlogopite, apatite, titanite, monticellite and perovskite also crystallised.

However, some portions of the groundmass consists variably of calcite, barite, gypsum, halite and natrolite (in the case of sample L-11A). Calcite is typically anhedral in shape and occurs interstitially to olivine, pyroxene and phlogopite. Calcite also occurs as thin veins cross-cutting the dykes. According to their textural setting, these minerals constitute secondary phases (Nesse, 2009; Rock, 1987; Woolley

et al., 1996) that most likely formed at lower (non-magmatic) temperatures at a later stage from the alteration of other minerals or by hydrothermal or meteoric fluids (Nesse, 2009).

6.1.1 Comparison to kimberlites

The lamprophyric dyke swarms in the Western Limb of the Bushveld Complex have similar structural, petrographical features to Group II kimberlite dykes (e.g. Star, Helam and Klipspringer kimberlites) in South Africa. Much like the lamprophyric dykes, Group II kimberlite dykes occur in small, dominantly en-echelon dyke-fracture arrays (Basson and Viola, 2003). They also have sub-parallel contacts between dykes and dyke segments that have sharp terminations and are joined to other segments in jogs (Basson and Viola, 2003). In South Africa, the Group II kimberlite dyke arrays usually trend E-W, which is similar to the WNW-ESE trend of the lamprophyric dykes (Basson & Viola, 2003; Hughes et al., in prep).

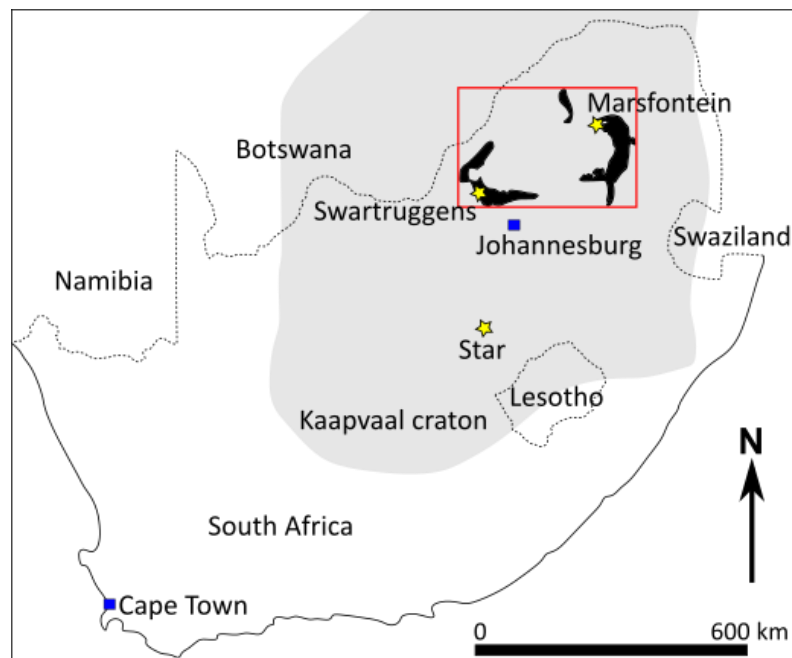


Figure 6.1. Map of South Africa showing the locations for the Marsfontein, Star and Helam (Swartruggens) kimberlites on the Kaapvaal Craton and relative to the Bushveld Complex (outlined in red box).

The macrocrystic and phenocrystic phases in the lamprophyric dykes comprise dominantly olivine and phlogopite, respectively. The groundmass is made up of phlogopite, olivine, calcite, barite, garnet, amphibole, apatite, titanite, monticellite, perovskite, melilite, celestine and opaque minerals namely: chalcopyrite, chromite and magnetite. Similarly Group II kimberlites contains olivine macrocrysts. Phlogopite is present as macrocrystic, phenocrystic and groundmass phases in the Star, Helam and Klipspringer kimberlite dykes. Other groundmass minerals contained in these dykes are diopside, calcite, apatite, monticellite, serpentine, perovskite and opaque minerals (Basson and Viola, 2003; Coe, 2004; Westerlund, 2000).

According to Mitchell (1994) the term “lamprophyric” should only be used to describe the observable characteristics of a set of rocks that have formed from a particular volatile-rich magma. Therefore lamprophyre would not be an appropriate term to classify the Bushveld dykes. There are, however, similarities in the structural features, mineral assemblages and geochemistry between the lamprophyric dykes and the Group II kimberlites, as noted by this comparison. Phlogopite crystals from the Marsfontein kimberlite (sample 41-166) plot in the same field as the phlogopite crystals from the lamprophyric dykes (Fig. 5.8), confirming that they are similar in composition. Similarly, as seen in Figure 5.9, most of the phlogopite crystals plot in the orangeite field along with the phlogopite crystals from the Marsfontein, Star and Helam kimberlites. Therefore, based on these similarities it can be said that the lamprophyric dykes are in actual fact Group II kimberlites or orangeites.

6.1.2 *Fluid inclusions*

Fluid inclusions are only present in the secondary minerals (e.g. halite, natrolite and calcite) of the lamprophyres. Fluid inclusions are rarely found isolated, with most inclusions found along fractures or well-defined clusters. According to Shepherd et al. (1985), fluid inclusions that are isolated and are euhedral-shaped are primary inclusions and formed during crystal growth. Primary fluid inclusions are clearly observed between crystal growth zones (Shepherd et al., 1985). However, in this case it is difficult to confirm that the isolated inclusions are definitely of primary origin, as crystal growth zones are not visible. Fluid inclusion trails that cross-cut crystal growth zones or occur in healed fractures are indicative of secondary fluid inclusions, according to Shepherd et al. (1985). Many of the fluid inclusions occur in trails within fractures in the halite-natrolite sample and are most likely secondary.

Three types of fluid inclusions occur; liquid-only inclusions, liquid and vapour inclusions and liquid + vapour + solid inclusions. Due the lack of data obtained from microthermometry, the composition of the fluid inclusions could not be determined. Also, Raman spectroscopy was unsuccessful and did not aid in obtaining the composition of the fluid inclusions analysed, with the exception of one (see Section 5.3.7). The composition of the liquid-phase in a three-phase inclusion was identified to be ethanol. The ethanol is most likely trapped within the fluid inclusion as no other ethanol peaks were identified in that sample. The daughter minerals present in the samples are cubic in shape and some are cubic with rounded edges, suggesting that the solid-phases in three-phase inclusions are either halite or sylvite, respectively. According to Shepherd et al. (1985), the daughter mineral precipitates from the liquid-phase as it reaches saturation after entrapment of the fluid inclusion. If the solid-phases in these fluid inclusions are halite or sylvite it is most likely that the liquid-phase, from which it precipitated, is a saline (NaCl or KCl) solution. It is still uncertain what volume % NaCl or % KCl is in the liquid phase, as no freezing temperatures were observed. Also the composition of the vapour phase in the three-phase inclusions as well as all phases in the two-phase inclusions remain unknown. The lack of phase changes observed upon cooling (to -100 °C) and heating (to 230 °C) of sample L-11B during microthermometry suggest that these inclusions formed at temperatures out of this range. It is possible then that the mineral (halite-natrolite-anhydrite) hosting these inclusions formed at temperatures higher than 230 °C.

6.1.3 *Comparison of outburst and non-outburst samples*

No major differences are observed between lamprophyric samples that are associated with outbursts and those that are not associated with outbursts. Almost all the samples are macrocrystic in texture containing serpentinised olivine macrocrysts and phlogopite phenocrysts set in a groundmass composed predominantly of phlogopite and calcite. The only signs of alteration in the dykes are shown by serpentinised olivine and sericitisation of wall rock minerals at their contacts with the lamprophyres. This alteration of the wall rock makes the contacts of the lamprophyres friable but there are no indications that the mineral assemblages of the dykes are what causes the dykes to outburst. Even though the modal abundance of sample L-11A is unique, in that it contains 30% pyroxene and 20% phlogopite phenocrysts, the mineral assemblage does not vary significantly from the rest of the dykes. However, the halite-natrolite-anhydrite contained in the voids of L-11A suggest that the dyke is more porous, enabling it to hold a greater amount of secondary minerals and therefore possibly has more space for gas to accumulate in the voids of the dyke.

The lamprophyric dyke swarm has many structural features that resemble dykes swarms of South African Group II kimberlites. The dykes have mineral assemblages essentially the same as the Group II kimberlites, specifically the Star and Helam kimberlites. Also, banding of the dykes and zonation of certain minerals is similar to the Group II kimberlites. There is no mineralogical difference between outburst and non-outburst dykes; neither is there a systematic difference in the level of alteration (serpentinisation and/or sericitic alteration), the texture, nor the structure (banded vs not) between outburst vs non-outburst dykes. Fluid inclusions were analysed by heating and cooling of the sample. However, very few phase changes occurred, and therefore the composition of the volatiles trapped in them could not be determined. However the habit of the daughter minerals suggest that they are either halite or sylvite. From this it can be inferred that the liquid is either a NaCl or KCl saline solution, as the daughter mineral precipitates from the liquid after entrapment.

6.2 **Understanding the cause of underground gas outbursts**

Data from salt, coal and gold mines (e.g. Ehgartner et al., 1998; Hyman, 1987; Mkhabela and Manzi, 2017; Molinda, 1988) show distinct relationships between the dynamic behaviour of gases and outbursts (Nivin, 2001). Gases can be held in rocks and minerals in either one or more of the following ways: (1) gas can be trapped in the form of vapour bubbles within fluid inclusions (Fig. 6.2) in rock-forming minerals (e.g quartz, calcite and halite), (2) gas molecules can be adsorbed on mineral surfaces and/or crystal boundaries (Fig. 6.2) and (3) accumulated gas can exist in fractures, voids and pore spaces within rocks (Fig. 6.2; Shepherd et al., 1985; Molinda, 1988; Ehgartner, Neal and Hinkebein, 1998). Gases in fluid inclusions are trapped either upon crystallisation of minerals (i.e. primary fluid inclusions) or they can be of hydrothermal-origin and form after the growth of a crystal (i.e. secondary fluid inclusions; Shepherd et al., 1985).

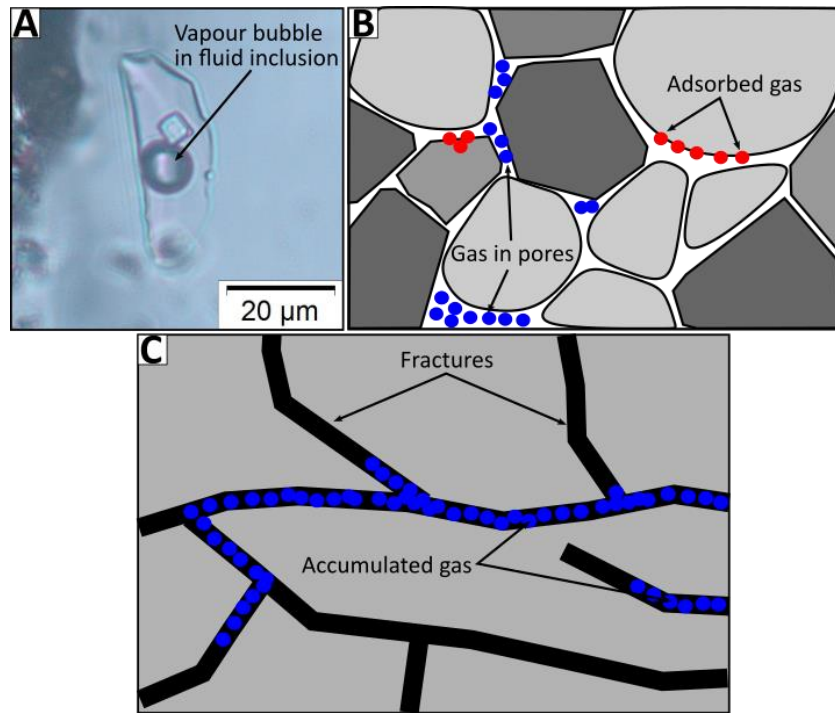


Figure 6.2. (A) A photomicrograph of a three-phase fluid inclusion comprising a liquid-, solid- and vapour-phase in which gas is held, (B and C) schematic diagrams of gas molecules adsorbed on mineral grain boundaries within a rock, gas trapped in pore spaces in a rock (shown in B) and accumulated gas in rock fractures (shown in C).

Gases in fluid inclusions are trapped under high confining pressure (Shepherd et al., 1985). Similarly, gases contained in voids or fractures in rocks that are beneath surface are also subjected to a high confining stress. Gases that are under high pressure are sensitive to physical changes of the host rock, whether due to a change in temperature or pressure (Nivin, 2001). When the host rock is subjected to changes in temperature or pressure, or both, phase changes of volatiles trapped within the rock take place, resulting in a change of volume (Shepherd et al., 1985). Figure 6.3 illustrates phase changes and the triple point of water as a function of temperature and pressure. However, other species (CO , CO_2) also undergo these phase changes. The specific temperatures and pressures at which these phase changes occur (including the triple point) is dependent upon each chemical species.

Mining or other underground construction activities can result in physical changes of the host rock and the volatiles trapped in them. When a liquid phase changes to a gaseous phase it causes abrupt expansion, which can lead to a gas outburst (Warren, 2016a). Outbursts occur in salt mines in the United States and Europe, and in coal and gold mines in South Africa. Although pressure and temperature changes are the underlying cause of these gas outbursts, factors such as how the gases are trapped, where the gases are sourced and what rock type the gases are held in (i.e. salt, coal vs hard rock), differ. In this thesis the mechanisms for the cause of the outburst includes these factors of each of the mines discussed below (see Sections 6.24-6.26) and does not just refer to pressure and temperature changes.

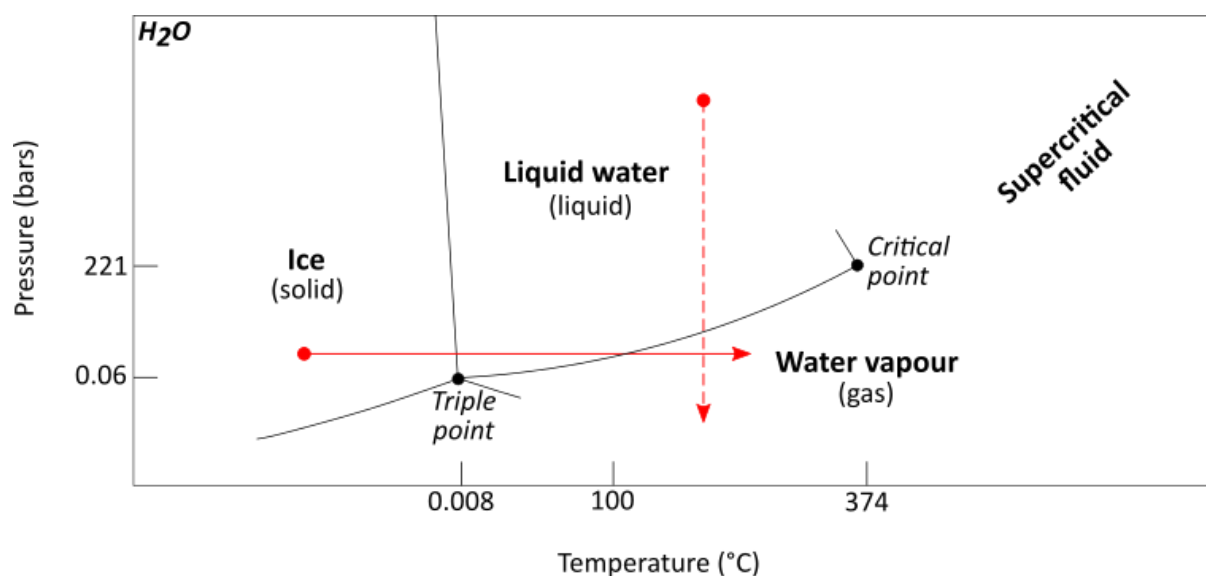


Figure 6.3. Pressure–temperature phase diagram (not to scale) for pure H₂O showing the occurrences of the three phases (solid/ice, liquid water, water vapour/gas) and the triple point, at which solid, liquid and vapour coexist. The solid red arrow indicates the phase change from solid to vapour and the dashed red arrow shows the phase change from liquid to vapour, after Robb (2005).

Fluid inclusions trapped in the lamprophyric dykes were subjected to temperature changes by cooling and heating their host minerals. However, very few phase changes were observed. Upon cooling the samples, no eutectic temperatures were recorded and therefore the composition of the fluid inclusions were not obtained. Daughter minerals, which are the solid phases in fluid inclusions, have crystallised after the entrapment of fluid that has reached saturation for that particular phase (Shepherd et al., 1985). The daughter minerals present in the three-phase inclusions are most likely halite and sylvite due to the cubic habit for halite and cubic habit with rounded edges for sylvite (Shepherd et al., 1985). Therefore halite and sylvite most likely crystallised from saline, NaCl and KCl-bearing, fluid trapped in the inclusions. It is suggested then that the three-phase inclusions are aqueous H₂O-NaCl-KCl systems.

Even though the composition of the fluid inclusions determined via *in-situ* methods are uncertain (see Section 6.1.3), the bulk compositions of volatiles trapped within in the lamprophyre dykes (in the form of fluid inclusions, adsorbed gas or gas contained in pore spaces) have been obtained using ‘in-line’ GC. Similarly, samples of crushed lamprophyre were induced to temperature and pressure changes upon crushing the samples in a heated crusher. The dominant gases in the dykes are H₂O, CH₄ and C₂H₆. Carbon dioxide and/or CO were only detected in 7 lamprophyres. Of these gases CH₄, C₂H₆ and CO are flammable. Saturated hydrocarbons (CH₄, C₂H₆, C₃H₈, C₄H₁₀ etc.) were also released in variable abundances from the 4 samples re-analysed using Method 2 (see Section 3.5) of ‘in-line’ GC.

Gases were detected, in varying quantities, in boreholes drilled through lamprophyric dykes underground (see Section 6.6). The results of the underground gas analysis show a peak flow of gas. The peak values of the gases detected by the boreholes are highest in analysis 1 compared to that of analysis 2. This is due to gas accumulating inside the borehole, which had been plugged for 7 days. The

peak flow of gas detected by analysis 2 had been from gas that accumulated only over 24 hours. After the gas peaks drop, in both analysis 1 and 2, a constant flow of gas is seen, suggesting that the boreholes were being replenished by new gas and therefore being detected by the gas sensor. The dominant gases observed to be actively streaming out of the dykes are CH₄ while CO₂, CO and H₂ are trace gases that are emitted out the dykes. Boreholes 1 and 2, situated in the deepest level of the mine, generally had the highest peak values for CH₄, CO₂, CO and H₂ and the most abundant gas constantly streaming out the dykes compared to boreholes 3 and 4, which are situated at shallower levels of the mine. Kupfer (1980) suggests that the size and abundance of gas pockets increase with depth. As the platinum mines grow deeper they are facing an increase in the number of outbursts. This indicates that depth may have an important factor on the control of the outbursts.

Methane gas, CO₂ and CO are common gases observed in both the ‘in-line’ GC results and the underground gas detection results. Ratios of CH₄ to CO₂+CO were calculated (see Section 5.5.3) from the ‘in-line’ GC results and for the underground gas detection results to compare the 2 datasets. Figure 5.18 shows that the ratio of CH₄ to CO₂+CO for lamprophyre samples analysed by ‘in-line’ GC are inconsistent. This is most likely because all samples analysed by ‘in-line’ GC contained CH₄ but only 7 samples contained CO₂+CO. However the ratio of CH₄ to CO₂+CO for the 4 underground boreholes are consistent with each other. When comparing the ratio of CH₄ to CO₂+CO for these 2 sets to one another, it is seen that they are not consistent, confirming that the gases detected by ‘in-line’ GC are from a different source to the gases observed underground. Considering that ‘in-line’ GC detects gases physically trapped in the rock (within fluid inclusions, pore spaces or adsorbed gases), it is possible that these gases are of primary magmatic or hydrothermal origin (Shepherd et al., 1985). In contrast, gases that are actively streaming out of the dykes underground are sourced from an open source which allows the gas to escape via permeable channels in rocks.

The outbursts of the platinum mines in the Bushveld Complex are compared to similar outbursts that take place in salt, coal and gold mines. Below, the mechanisms and gas types associated with outbursts in these other mines (both in South Africa and internationally) are explored and discussed, in order to place into context the outbursts that take place in platinum mines in the Bushveld Complex.

6.2.1 *Analogy to salt mines*

Outbursts in salt mines in the U.S. and northern parts of Europe occur due to the presence of gases trapped within discrete pockets of abundant fluid inclusions in salt. The gases trapped in these inclusions are under a high confining pressure. Advancing of the mine opening reduces the confining pressure at the salt face (Fig. 6.4) and this causes a phase change of the fluids in fluid inclusions within the salt (Ehgartner et al., 1998; Warren, 2016). As pressure drops, liquids trapped in fluid inclusions change to a gaseous phase, which causes the inclusions to expand (Shepherd et al., 1985; Warren, 2016a) This causes the fluid inclusions within the salt to decrepitate simultaneously, resulting in an outburst (Kupfer, 1980; Ehgartner et al., 1998; Warren, 2016a). Outbursts therefore only occur immediately around the

mined face when depressurisation takes place due to mining activities (e.g. blasting or drilling; (Kupfer, 1980; Ehgartner et al., 1998).

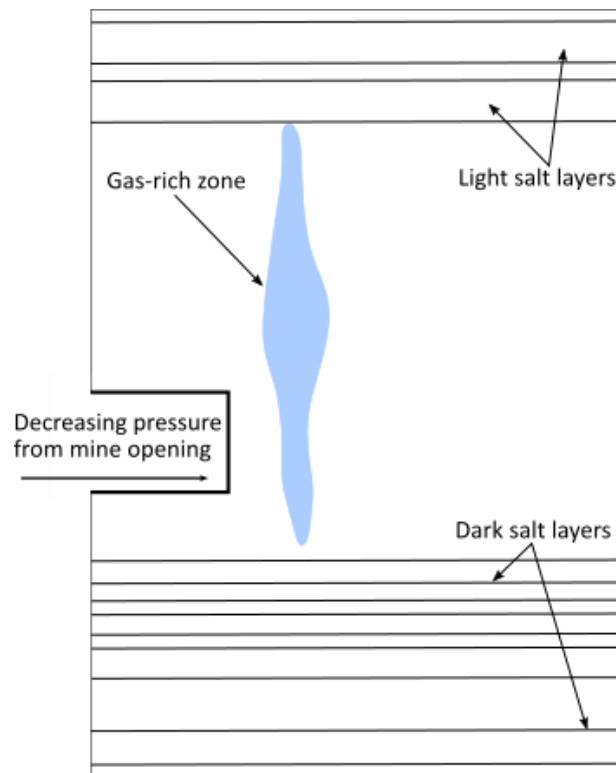


Figure 6.4. A schematic diagram showing a cross-section of a salt mine. The salt contains alternating light and coloured salt layers and a gas rich zone situated immediately after the mine opening. Upon encroachment of the mine opening, the confining pressure of the gas-rich salt zone decreases. When the gas zone is intersected the outburst occurs, after Ehgartner et al. (1998), Kupfer (1978) and Molinda (1988).

The effect of outbursts in salt mines is the expulsion of gas and rock salt from a mine production face, resulting in an open cavity in the salt. The size of the cavity ranges from one to tens of metres, can be conical, cylindrical or elongated in shape and decreases in diameter away from the opening (Warren, 2016a). Similarly Kupfer (1980) and Molinda (1988) infer (from historic outbursts) that gas rich zones are elongated, have tapered ends and occur within vertically layered beds of light and dark coloured salt (Fig. 6.4). The nature of the outbursts in the platinum mines are similar in that large blocks (0.5-1 m) of rock get thrown out of the face, forming cavities of similar shapes and sizes to those in salt mines. However, small-scale outbursts also occur during drilling, which causes the drill to kick-back onto the miner, resulting in injury. Cavities do not form from small-scale outbursts and only result from large-scale outbursts that happen during blasting.

The gases trapped in evaporates are usually mixtures of CH_4 , CO_2 and H_2 in varying abundances. Methane quantities of 2.03-8.78 cm^3 per 100 g NaCl have been documented in U.S. salt mines, hydrogen occurring between 1.1 and 32.6 vol.% has been reported in European salt mines and fluid inclusions in

salt mines in Europe have been reported to contain on average ~84 vol.% CO₂ (Molinda, 1988; Ehgartner et al., 1998; Warren, 2016b). Other gases in minor amounts include argon and short chain hydrocarbons (Molinda, 1988; Warren, 2016b). In comparison, ‘in-line’ GC data, which analyses gases trapped within lamprophyres (adsorbed gas or gas contained in fluid inclusions and pore spaces), show mixtures of varying proportions of CO₂+CO, CH₄, C₂H₆, C₃H₈ and C₄H₁₀. However, the presence of fluid inclusions are not as abundant in the lamprophyric dykes. Fluid inclusions are only present within halite, calcite and/or barite, which are interstitial minerals in the lamprophyre dykes, making it unlikely to cause an outburst. Additionally, the composition of these volatiles are from bulk volatiles trapped in the rocks. It is unknown whether these gases are from fluid inclusions contained within the secondary minerals in the lamprophyres due to the uncertainty of microthermometry and Raman spectroscopy data. However, it is certain, from *in-situ* gas analysis, that gas that is actively streaming out of the lamprophyric dykes underground. These gases are mixtures of CH₄, CO and H₂, which is similar to the composition of volatiles trapped in fluid inclusions and to the gases associated with outbursts in salt mines.

The *effects* of the outbursts and gases in salt mines appear similar to the outbursts in the Bushveld platinum mines, but there are significant discrepancies in the *causal mechanisms* between the two, namely: (1) Secondary minerals in the lamprophyric dykes contain a significantly lower abundance and volume of fluid inclusions than in salt mines, (2) Gases are actively emitted by lamprophyric dykes underground – a process that directly conflicts with the intermittent and sudden gas release in salt mines associated with simultaneous decrepitation of fluid inclusions during mining in salt mines (Shepherd et al., 1985; Warren, 2016a). Thus the gases emitted by the lamprophyre dykes (as detected using the Dräger X-am 5600) must be sourced from elsewhere and are likely unrelated to the small volume of gases hosted in fluid inclusions. Therefore, the mechanisms for outbursts in the Bushveld platinum mines are not analogous to that of salt mines, and other comparisons must be considered.

6.2.2 *Analogy to coal mines*

In South Africa, outbursts in coal mines are more common than in platinum mines, and have been well documented (Beamish and Crosdale, 1998; Hyman, 1987; Lama and Saghafi, 2002). Geological structures (strike-slip faults, reverse faults and shear zones) are often linked with gas outbursts in coal mines (Lama and Saghafi, 2002). Methane is the predominant gas associated with gas outbursts in coal mines, but CO₂ is also common (Beamish and Crosdale, 1998; Lama and Saghafi, 2002). Outbursts in coal mines occur when there is a high content of gas present in the coal and when these gases are under high pressure (Lama and Saghafi, 2002). Gas contained in coal can be in the form of gas pockets, whereby there are gas reservoirs within more fractured or ‘soft’ coal that is surrounded by more competent coal. Gas could also be stored in coal by adsorption on the surfaces of grain boundaries in the coal (Hyman, 1987). Like fluid inclusions that are under high confining pressure in salt mines, gases trapped in coal are also subjected to a high confining pressure. When mining of coal seams takes place, fractures are induced, which cause a rapid release of this confining pressure. The formation of fractures creates new surfaces and space such that the reactive surface area suddenly increases, and from which

adsorbed gases can be released (Hyman, 1987; Lama and Saghafi, 2002). Fast rates of fracture development and the formation of large new surfaces intensifies desorption of gas (Lama and Saghafi, 2002). Rapid release of high-pressure gas causes the coal face to fail, resulting in an outburst (Hyman, 1987; Lama and Saghafi, 2002). When gas outbursts occur, coal is pulverized into fine dust that intensifies the flow of gas and coal into the excavation and causes a gas haze which reduces visibility (Beamish and Crosdale, 1998; Hyman, 1987; Lama and Saghafi, 2002). Similar to salt mines, cavities form as a result of gas outbursts (Beamish and Crosdale, 1998; Hyman, 1987). However, the geometry of the cavities in coal mines are rectangular-shaped (Beamish and Crosdale, 1998). Furthermore, due to the porous nature of coal, and the increased number of fractures, gas can continue to be emitted out of the coal and without appropriate ventilation can accumulate in the newly-formed cavity (Hyman, 1987).

In the Bushveld platinum mines, faults, joints and fractures, together with the lamprophyric dykes are commonly reported as being associated with an outburst. Several gases detected by both ‘in-line’ GC and the *in-situ* underground gas analysis are of the same species as those in coal mines (e.g., CH₄ and CO₂). When performing the underground *in-situ* gas analysis, the valves on the 4 boreholes were sealed directly after analysis 1 (see Section 3.3). Analysis 2 took place after a 24-hour period, and just like analysis 1, detectable amounts of gas were present in the boreholes. This implies that the dykes are permeable (although their permeability may vary from dyke-to-dyke or along strike) and thus gases may also be following other permeable pathways such as faults, joints and fractures. Because the lamprophyres are porous (as observed in thin section), and apparently permeable, gases likely occur in pore spaces or voids within them, thus forming gas pockets in a similar fashion to coal. Although the peak values of gases detected in analysis 2 were slightly lower than the peak values from analysis 1, gas had still accumulated and replenished the boreholes after a short interval. This suggests that gas is flowing through the dykes (or other areas of discontinuity) and collecting in voids of the dyke at a fast rate.

Gas outbursts in coal mines and platinum mines are similar in that in both instances, they occur during mining or mining-related activities such as blasting and/or drilling. Furthermore, two factors make the mechanism for the cause of outbursts in platinum mines analogous to coal mines: (1) Methane is prevalent in both coal mines and the platinum mines in the Western Limb of the Bushveld Complex, and (2) More than 1 geological feature is associated with gas outbursts, suggesting that the gas is using these structures as pathways. The source of the gas is therefore unlikely to originate from the lamprophyric dykes and is supported by the active emission of CH₄ and other gases from the dykes (and other likely permeable pathways).

6.2.3 *Analogy to gold mines in the Witwatersrand Basin*

Methane gas (80-100 vol.%), with lesser amounts (0-5 vol.%) of other hydrocarbons (C₂H₆, C₃H₈ and C₄H₁₀) and hydrogen (0-20 vol.%), have been reported in South African gold mines (Abu-Mahfouz et al., 2014; Cook, 1998; Du Plessis and Van Greuning, 2011; Lippmann-pipke et al., 2011; Ward et al.,

2004). Methane is emitted in gold mines (~3000 m deep), particularly in the Witwatersrand basin, and is usually encountered when drilling into fractures, faults and dykes that extend beyond 7000 m deep (Cook, 1998; Du Plessis & Van Greuning, 2011; Manzi et al., 2012; Mkhabela and Manzi, 2017; Sherwood Lollar et al., 2006). Explosions have occurred in a number of gold mines in the Witwatersrand Basin when CH₄ was released during mining, resulting in a series of deaths and injuries (Mkhabela and Manzi, 2017).

There are several possibilities for where the methane is *sourced* and the *mechanisms* by which it is transported to the crustal levels being mined are still debated. Possible sources include: (1) Carbonaceous matter in the form of bitumen that is present in the gold-bearing quartz-pebble conglomerate reefs (England et al., 2002), (2) fluid inclusions, containing CH₄, C₂H₆, N₂, H₂ and H₂S that are present in the quartz pebbles of the reefs (Drennan et al., 1999; England et al., 2002; Frimmel et al., 1999), and (3) Several authors (England et al., 2002; Gray et al., 2007; Mkhabela and Manzi, 2017; Spangenberg and Frimmel, 2002; Wanger et al., 2012) consider shale units, underlying the gold-bearing reefs, to be the source rocks for hydrocarbons in the Witwatersrand Basin. Cook (1998) suggests that it is unlikely that the CH₄ originates from only one source, and it is most likely that the gases are from different origins. This is corroborated by ¹³C and ²H isotopic analyses of CH₄ collected from gold mines in the Witwatersrand Basin, which indicate that the gases are a mixture of biogenic methane derived from microbial processes (see section 6.6.2), and abiogenic methane produced by water-rock reactions (see section 6.6.1) (Sherwood Lollar et al., 2006; Ward et al., 2004). Faults, fractures and/or dykes may form channel-ways for the gases derived from either one or more of these sources (Cook, 1998; Manzi et al., 2012; Mkhabela and Manzi, 2017). Methane, as a gas or dissolved in groundwater, accumulates in voids or in fractures capped by overlying strata. When these structures are intersected by drilling, CH₄ is rapidly released causing an explosion (Cook, 1998; Manzi et al., 2012; Mkhabela and Manzi, 2017).

In comparison, the lamprophyric dykes contain CH₄, C₂H₆, C₃H₈ and C₄H₁₀ detected by ‘in-line’ GC (see Section 5.5). It is known that the hydrocarbons contained in the lamprophyric dykes are trapped as either adsorbed gases, gas in pore spaces, or as fluid inclusions similar to hydrocarbons trapped in fluid inclusions in the quartz-pebbles of the Witwatersrand reefs. However, it is unlikely that the fluid inclusions trapped inside the lamprophyric dykes are the source of the gas associated with the gas outbursts. This is substantiated by the results from the *in-situ* gas analysis performed in the 4 boreholes drilled through lamprophyric dykes underground (see Section 5.6). Methane and H₂, with minor amounts of H₂S, were detected during the underground *in-situ* gas analysis. The gases detected by the Dräger X-am 5600 are similar to some of the gases that have been reported in gold mines in the Witwatersrand Basin. However, the depths at which these gases are intersected in the platinum mines are ~4000 m shallower than depths that gases are intersected at in the gold mines. It is possible, however, that CH₄ is derived from one of the aforementioned sources (excluding fluid inclusions), or it could be that the CH₄

is derived from a mixture of microbial and abiogenic processes such as that of the findings in Sherwood Lollar et al. (2006) and Ward et al. (2004).

6.3 Proposed model for outbursts in platinum mines in the Bushveld Complex

The mechanism for the cause of outbursts in platinum mines is more similar to that of coal and gold mines than that of salt mines. Outbursts in platinum mines take place in a way that closely resembles a gas pipeline or a conduit (Fig. 6.5), where the lamprophyric dykes act as the pipe or conduit through which the gas flows, thus allowing the dykes to constantly emit gases underground (see Section 5.6). The gas then accumulates in voids (see Section 4.2) in the lamprophyric dykes forming gas pockets that are under a high confining pressure. During blasting, the high confining pressure drops, causing an outburst where the working face is blasted out with gas. This large-scale outburst results in the formation of a cavity, damage to underground ventilation and possibly injury or fatality to workers underground. Drilling of the mine working face would cause a smaller-scale outburst that would only be noted if the drill gets pushed back onto the miner, resulting in injury. Mixtures of CH_4 , CO_2 and H_2 that flow through lamprophyric dykes or faults, joints and fractures are therefore less likely to be from fluid inclusions. Mixtures of these gases are most likely from an external source, possibly beneath the Bushveld Complex or elsewhere. Methane can originate biogenically, through microbial processes or through thermal alteration of organic matter (thermogenic), and/or abiogenically through Fischer Tropsch-Type (FTT) reactions (Schoell, 1988). It is possible that CH_4 in the Bushveld Complex could originate from one or

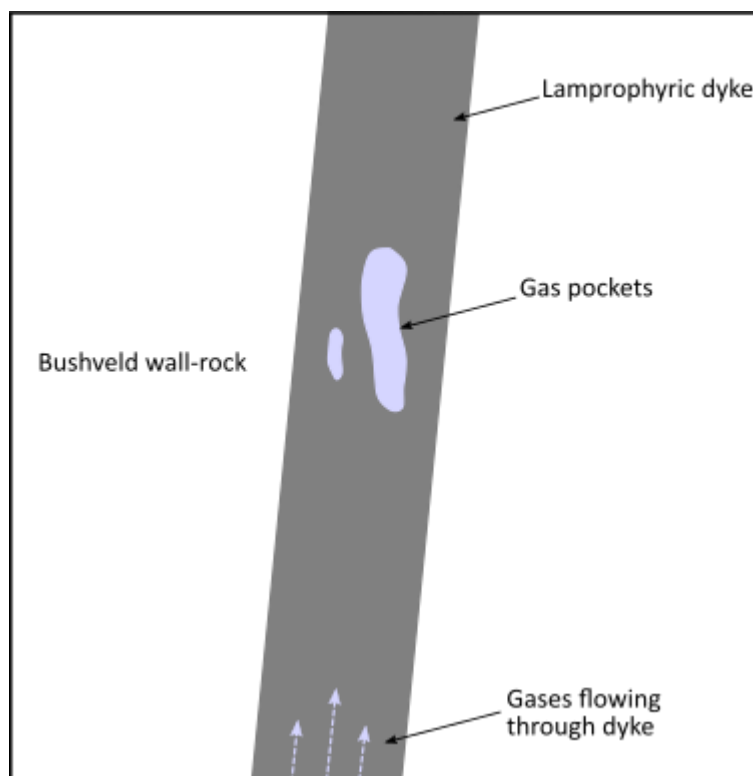
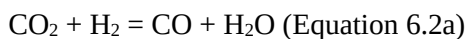
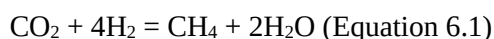


Figure 6.5. A schematic diagram showing a lamprophyric dyke acting as a conduit for gases to flow through. Gases collect to form gas pockets in voids within the lamprophyre.

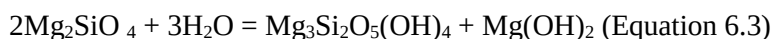
more of these processes. The 3 processes for the formation of methane are discussed in greater detail below.

6.3.1 Fischer Tropsch-Type reactions

One way of generating abiogenic CH₄ is through the FTT reaction (Eq. 6.1), a polymerisation reaction which generates higher hydrocarbons from CH₄ (Etiope and Sherwood Lollar, 2013; Potter and Konnerup-Madsen, 2003). The process is conducted through a series of reactions that usually take place at temperatures between 100 and 300 °C and at high pressures using Ni, Fe and Cr catalysts, which are abundant transition metals in ultramafic rocks (Potter and Konnerup-Madsen, 2003; Taran et al., 2007; Etiope and Sherwood Lollar, 2013). The FTT synthesis can either generate methane in a one-step reaction (Sabatier reaction; Eq. 6.1) or two-step reaction known as the water-gas shift (Eq. 6.2a and b; (Taran et al., 2007; Etiope and Sherwood Lollar, 2016)).



Fischer Tropsch-Type reactions may be dependent or independent of serpentinisation (Etiope and Sherwood Lollar, 2013). Serpentinisation (Eq. 6.3) is a hydrothermal process which alters minerals such as olivine and pyroxene to serpentine and brucite, respectively, at temperatures lower than 315 °C (Etiope and Sherwood Lollar, 2013; Holm et al., 2015; Moody, 1976).



forsterite

chrysotile

brucite

In the case where FTT reactions are dependent on serpentinisation, H₂ produced from serpentinisation may react with CO₂ or CO to produce CH₄. If either one of these C-gases are available, CH₄ may be generated through Equation 6.4 (Sherwood Lollar *et al.*, 1993).



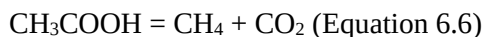
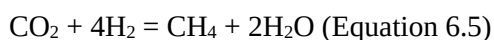
The Bushveld Complex contains many ultramafic rocks bearing olivine and pyroxene. If there are hydrothermal fluids percolating somewhere below the Bushveld Complex, conditions are favourable (100-300 °C; <3 km) and there is availability of Ni, Fe and Cr catalysts, then serpentinisation of olivine and pyroxene-bearing rocks is a possibility (Etiope and Sherwood Lollar, 2016; Potter and Konnerup-Madsen, 2003). Similarly the lamprophyric dykes themselves contain serpentinised olivine macrocrysts which constitutes 5 to 40% of the dykes. The olivine macrocrysts were subjected to volatiles during the emplacement of the lamprophyres which altered them to serpentine (Mitchell, 1995). It could be that CH₄ was formed by reacting with H₂ produced from the serpentinisation of olivine macrocrysts during

the emplacement of the lamprophyres. However it is not certain whether the serpentinisation of olivine at the time of emplacement of the lamprophyres is a potential source for the gases observed presently.

6.3.2 Biogenic methane

Biogenic CH₄ is derived from reactions, usually mediated by microbial organisms, involving organic matter (Whiticar et al., 1986; Schoell, 1988). Biogenic CH₄ is typically found in marine and freshwater sediments (Schoell, 1980; Whiticar et al., 1986). The process of the formation of biogenic CH₄ is called microbial methanogenesis and involves 2 primary pathways: 1) acetate fermentation and 2) CO₂ reduction (Schoell, 1980; Schoell, 1988; Lovley and Klug, 1986; Whiticar et al., 1986; Sherwood Lollar et al., 1993; Potter and Konnerup-Madsen, 2003; Ward et al., 2004; Strapoć, 2018). Archaea, specifically methanogens, are the microbial organisms responsible for the reactions that generate biogenic CH₄ (Balch et al., 1979; Whiticar et al., 1986; Strapoć, 2018).

The CO₂ reduction pathway (Eq. 6.5) uses hydrogen, from water or ongoing microbial reactions, as a reducing agent and produces methane and water (Schoell, 1980; Whiticar et al., 1986; Strapoć, 2018). In acetate fermentation (Eq. 6.6), methanogens break down an acetate molecule to form a CH₄ and a CO₂ molecule (Lovley and Klug, 1986; Whiticar et al., 1986; Strapoć, 2018). Biogenic CH₄ can be generated at temperature ranges of 60 and 80 °C and at depths of ~3 km (Rice and Claypool, 1981; Strapoć, 2018).



Thermogenic methane, another form of biogenic methane, is derived from organic matter that is thermally altered (Schoell, 1983; Whiticar et al. 1986; Sherwood Lollar et al., 1993; Potter and Konnerup-Madsen, 2003; Ward et al., 2004). As the temperature increases, lighter hydrocarbons are released from the organic matter (Rice and Claypool, 1981).

An isotope study was conducted on CH₄ gas found in millions of years-old fissure waters in gold mines in the Witwatersrand Basin, South Africa (Ward et al., 2004). Gas samples were collected from boreholes from several mines in the Witwatersrand Basin and tested for their δ¹³C and δ²H isotopic compositions (Ward et al., 2004). Ward et al (2004) found that the CH₄ gas in the Witwatersrand Basin are dominantly produced by microbial organisms, with some samples showing a mixture of microbially-produced and thermogenic CH₄ (Fig. 6.6). Microbial CH₄ differs from thermogenic CH₄ in that microbial CH₄ is more depleted in δ¹³C and δ²H values than thermogenic CH₄ (Fig.; Whiticar, 1999; Ward et al., 2004).

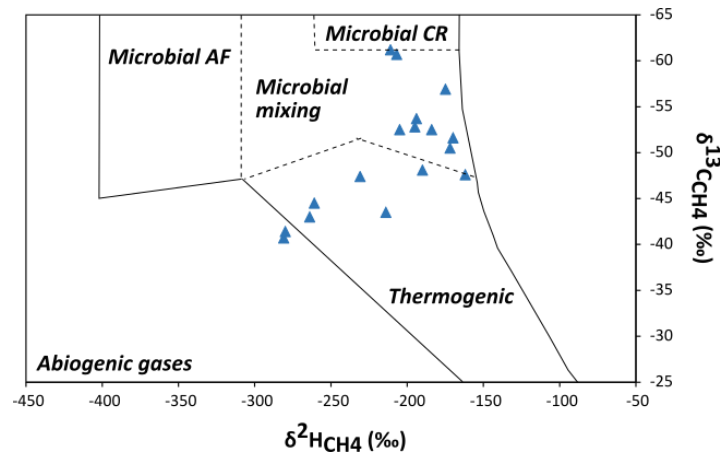


Figure 6.6. $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta^2\text{H}_{\text{CH}_4}$ values for CH_4 gas samples, collected from the Witwatersrand Basin, compared to empirically determined fields for thermogenic gas and microbial gas produced by CO_2 reduction (CR) and acetate fermentation (AF) after Whiticar (1999) in Ward et al. (2004). All samples plot in the microbial mixing and thermogenic fields (Ward et al., 2004).

6.3.3 Carbon from the Transvaal Supergroup

Organic matter, such as that of the bitumen nodules contained in the gold-bearing reefs of the Witwatersrand Basin, were most likely formed by connate fluids from the Transvaal Supergroup (Robb et al., 1997; Drennan et al., 1999; Frimmel et al., 1999). Robb et al. (1997) suggests that mobilisation of hydrocarbon-bearing fluids and the precipitation of organic matter is related to the onset of Transvaal Supergroup deposition.

6.4 Outburst risk mitigation and forecast

Gas outbursts in underground platinum mines are controlled by mechanisms similar to that of coal and gold mines. Outbursts are commonly associated with geological structures such as faults, joints and dykes (Hyman, 1987; Cook, 1998; Lama and Saghafe, 2002; Manzi et al., 2012; Mkhabela and Manzi, 2017). Stress and gases stored in rocks under high pressure are the main factors controlling gas outbursts (Lama and Saghafe, 2002). In platinum mines in the Bushveld Complex, gas outbursts are caused by gas being transported through lamprophyric dykes and faults that act as conduits, and by accumulation in fractures and voids in the lamprophyric dykes at mining levels (see Section 6.3). The source of these gases remains uncertain, but is most likely to be external from the lamprophyres (i.e., from the surrounding geology). To forecast areas prone to gas outbursts, the source of the gas must be determined, and geological structures associated with gas outbursts must be identified and mapped (Hyman, 1987; Lama and Saghafe, 2002). To mitigate the risks posed by outbursts or prevent outbursts, controls that minimise the chances of outbursts occurring must be put in place (Hyman, 1987; Lama and Saghafe, 2002).

In order to predict areas of the mine that are most likely or prone to gas outbursts, the gas source, amount of gas, and pathways for gases to migrate (e.g., faults, fractures and dykes) must be identified (Hyman,

1987; Lama and Saghafi, 2002). The scale of the gas outbursts in the platinum mines varies from large scale (where metres of rock get blasted out) to small scale (where the drill gets kicked back when in operation). Whilst this study has established that gases are constantly being emitted through the dykes, as tested by the underground *in-situ* gas analysis, the full variation of *rate* of gas emittance across the mine site remains untested (underground tests on four boreholes have already highlighted that there is significant variation in the *rate* of gas emittance, but this variation has yet to be quantified). Another consideration must be the likely existence (albeit, rare) of larger voids within the dykes (evidence for which has come from the geode in L11, as represented by the euhedral intergrowths of halite, anhydrite and natrolite in samples L11A) which may accumulate gases.

Geophysical methods such as seismic surveys can be used to identify geological structures (Lama and Saghafi, 2002; Manzi et al., 2012; Mkhabela and Manzi, 2017). For example, Manzi et al (2012) and Mkhabela and Manzi (2017) used 3D reflection seismics to map faults that transport water and methane to working areas in gold mines in the Witwatersrand Basin, and this has helped to mitigate the risks posed by water influxes and ignition of flammable gas. The gas source/s can be determined if the composition of the gas is known. In the case of carbon-bearing (e.g. CO₂, CO, CH₄ etc.) gases, such as those being emitted through the lamprophyre dykes in the platinum mines, carbon isotopes could be used to identify the source of the gas. Isotopic composition of C and H can be used to distinguish abiogenic CH₄ (see Section 6.3.7) from biogenic CH₄ (see Section 6.3.8; Etiope and Sherwood Lollar, 2016; Sherwood Lollar et al., 2006, Sherwood Lollar et al., 2002). According to Sherwood Lollar et al. (2006) and Sherwood Lollar et al. (2002) abiogenic methane decreases in ¹³C with increasing molecular weight (C1-C4), as opposed to thermogenic CH₄ which increases in ¹³C with increasing molecular weight. By knowing what the gas source is and where the geological structures are in proximity to working mine areas, a risk map or forecast could be developed which provides information as to which areas of the mine are at greater risk of facing outbursts.

On the other hand, forecasting mine working areas most prone to gas outbursts is only a step closer to solving the problem. Controls must then be put forward to prevent or minimise outbursts and their effects. Outburst control and prevention have been well documented for coal mines (e.g. Díaz Aguado and González Nicieza, 2007; Hyman, 1987; Lama and Saghafi, 2002), but have not been well documented for outbursts occurring in hard-rock mines. Some methods discussed in mitigating outbursts in coal mines can be applied in hard-rock mines, and specifically for the platinum mines in the Bushveld Complex. Since stress and gas pressure seem to be the main controls on causing gas outbursts (Hyman, 1987; Lama and Saghafi, 2002), changes on the stress and reduction of gas pressure need to be brought about in a way that will not cause an outburst but rather help to prevent it. These changes to stress and gas pressure need to be done ahead of the mine face (Hyman, 1987; Lama and Saghafi, 2002). Several methods to reduce stress are used in coal mines, such as mining of the overlying protective coal seam rather than the underlying coal seam (Hyman, 1987), or drilling 40 to 80 m long holes with a diameter of 30 cm ahead of the mining face (Lama and Saghafi, 2002). In the platinum mines the former method

cannot be applied, as mining methods of the Merensky Reef and UG2 chromitite differs from that of coal. However, drilling boreholes ahead of the mining face can be a useful way in reducing stress and reducing gas pressure. Similarly, preconditioning, a technique commonly used in deep mines, is used to increase the depth of a fracture zone in a working stope to decrease the occurrence of outbursts and reduce their violence (Tooper et al., 2006). Preconditioning involves setting off tailored blasts in the rock immediately ahead of the working face (Tooper et al., 2006). By inducing fractures in the rock ahead of the working face the stress of the rock in the working face is decreased (Tooper et al., 2006) allowing for gases (if present) to be released in a controlled fashion. Thus when drilling and blasting for production occurs, the stress profile is already lowered, decreasing the chances of an outburst. In the case where there is a gas pocket behind the working face, preconditioning will allow the gas to migrate through the induced fractures (Fig 6.7) which will cause a drop in gas pressure. This practice has successfully been employed at Northam Mine in the northern portion of the Western Bushveld, which had previously suffered from gas outbursts.

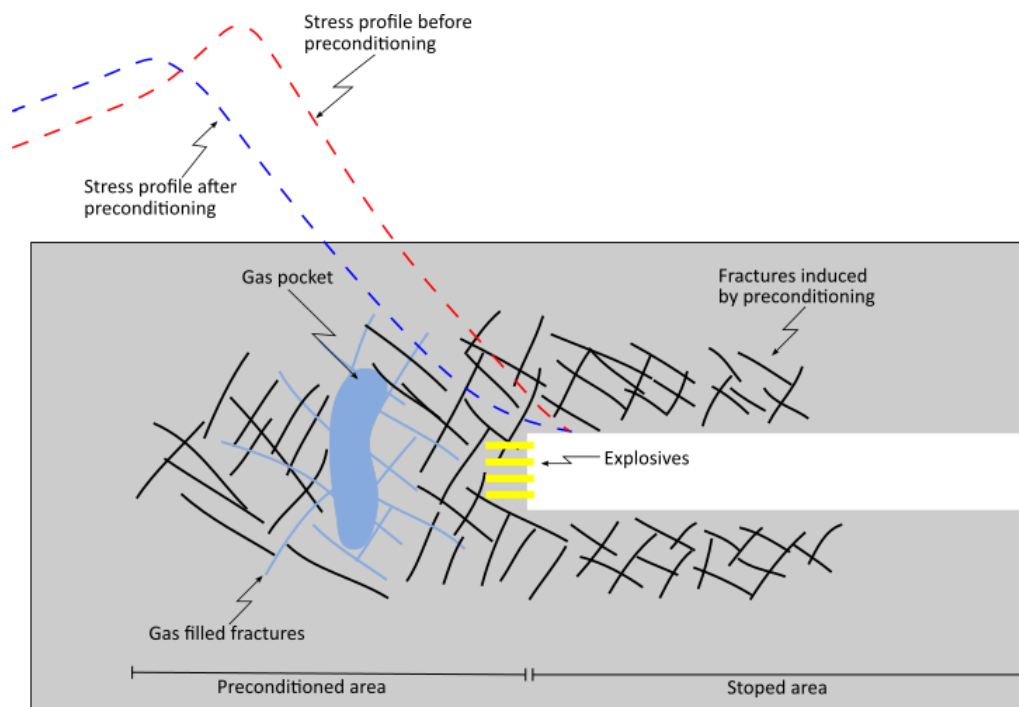


Figure 6.7. A schematic diagram illustrating the effect preconditioning has on the stress and gas pressure of a working face. The rock ahead of the working face is blasted with small explosives which causes fracturing of the surrounding rock. The stress profile (red line) decreases after preconditioning (blue line). Pressure of gas pockets in the working face is lowered as gas can move freely into the newly-created fractures, after Tooper et al (2000).

7 Conclusions, recommendations and future work

In continuing pursuit of mineral resources, platinum mines in most portions of the Bushveld are growing deeper (with the exception of the Northern Limb), and therefore are facing increasing practical difficulties and cost of mining. One such impediment to development is the under-documented occurrence of gas outbursts in certain parts of the Western Limb of the Bushveld, especially within the past decade. Whilst there was uncertainty regarding the exact process for mechanism of these gas outbursts, interviews with industry workers has led to suggestions that the outbursts are spatially associated with lamprophyric dykes that cross-cut the Bushveld rocks.

Lamprophyric dykes on the Western Limb are only exposed in underground mines, and occur as segmented and anastomosing dykes in a dyke swarm extending for ~ 50 km along strike. The dykes trend WNW-ESE, have a steep dip of greater than 80° and have a width of between 0.5 to 3 m. The majority of the lamprophyric dykes are macrocrystic in texture, containing macrocrysts of serpentinised olivine and phenocrysts of phlogopite. The macrocrysts and phenocrysts are set in a fine-grained groundmass comprising predominantly phlogopite, olivine and diopside-augite pyroxene, with accessory minerals such as halite, calcite, barite, gypsum, garnet, amphibole, apatite, fluoro-apatite, titanite, monticellite, perovskite, melilite, celestine and opaque minerals. When comparing outburst and non-outburst samples, no differences are seen in hand/core samples or in the mineral assemblages of the dykes. The lamprophyric dykes and South African Group II kimberlites both occur in dyke swarms, have similar structural features, are similar in texture and their mineral assemblages, and have similar major element compositions of phlogopite and pyroxene. Based on these similarities it can be said that the lamprophyric dykes in the Western Limb of the Bushveld Complex are truly Group II kimberlites. However, due to the sensitivity around the economic term “kimberlite”, the term “lamprophyre” is used throughout mine mapping and this thesis.

Gases are trapped in either one or all of the following ways within the lamprophyric dykes: (1) The crystal structure of rock-forming minerals, (2) In pore spaces, and (3) In fluid inclusions hosted in secondary minerals such as halite, natrolite, barite and/or calcite. Three types of fluid inclusions are found in the sample composed of halite and natrolite (L-11B) namely, three-phase liquid + vapour + solid, two-phase liquid + vapour and single-phase liquid-only inclusions, and mainly occur in trails or well-defined clusters. The composition of the volatiles trapped in fluid inclusions in the dykes remains uncertain due to the lack of phase changes observed upon heating and cooling of the halite-natrolite sample (L-11B) during traditional microthermometry. Using bulk analytical techniques such as ‘in-line’ gas chromatography (GC), the gases trapped in the lamprophyric dykes are composed dominantly of H₂O, CO₂+CO, CH₄ and C₂H₆. When performing underground *in-situ* gas analysis it was observed that gas is constantly being emitted out of the boreholes drilled through the face of four lamprophyric dykes (BH1-BH4), and that this seems to be inherently linked to the dykes and not the Bushveld wall rock. The predominant gases identified as being emitted from these boreholes are CH₄, CO and H₂. It is clear after repeating the underground analysis on a second day (by closing the valves after the first set of gas

analysis on the first day) that gas reaccumulates within a period of 24 hours – thus indicating a continuous source of the gases and that the dykes are acting as conduits for the gases (rather than producing the gases themselves).

The mechanisms for the cause of the outbursts in platinum mines in the Bushveld Complex were compared to those that occur in domal salt mines in the United States of America and Europe, and coal and gold mines in South Africa. The mechanisms for gas outbursts in the platinum mines are similar to those of outbursts that take place in coal and gold mines, whereby gases are accumulated within the rocks under a high confining pressure and are released when the pressure is decreased during mining. The proposed mechanism for gas outbursts in the platinum mines is that gas from an external source is using the lamprophyric dykes, and possibly joints, faults or other dykes, as conduits to escape to mining levels. The gases may also collect in void spaces in the lamprophyric dykes, forming pressurised gas pockets. As blasting or drilling take place, the stress of the working face and the confining pressure of the gas suddenly drops, causing an outburst. At the largest and most extreme scale, the result of these outbursts is chunks of rock (sometimes up to a few metres wide) and dust being blasted out of the working face. This leaves behind a cavity and the outburst material causes significant damage to underground ventilation and equipment. These largest events happen immediately after controlled production blasts (as a secondary blast). On a smaller scale, outbursts may happen during drilling of the working face – in these cases, dust and small fragments are outburst down the drill barrel and force the drill rig backwards out of the hole, causing injury to the operator and even fatalities of mine workers.

Three possible sources for CH₄ in the Bushveld Complex exist. Methane found in the Bushveld Complex could be (i) abiogenic, produced from Fischer-Tropsch reactions dependant on the serpentinisation of olivine or (ii) biogenic which is produced from chemical reactions involving organic matter and microbial organisms. Alternatively (iii) a possible source for CH₄ in the Bushveld Complex could be C-bearing gas from the underlying Transvaal Supergroup. In order to determine the source of the gas associated with the outbursts, C and H isotopic analysis must be carried out. Understanding what the gas source is will facilitate a better understanding of the source location of the gases, and thus knowing the location of dykes and faults that transport the gas, relative to mine working areas, can aid in forecasting of areas at greater risk of outburst. However, even with a forecast, steps must be taken to mitigate against the effects of these gas outbursts. Controls such as preconditioning and gas drainage could be implemented to reduce the ambient rock stress and gas pressure of the working face.

Recommendations and future work

1. Isotopic analysis of C and H isotopes of gas from platinum mines in the Bushveld must be carried out to determine the source of the gas.
2. More fluid inclusion work needs to be done on more samples and Raman spectroscopy used to find out the composition of the fluid inclusions, if present.
3. The isotopic composition of Transvaal xenoliths needs to be determined and compared to C isotope composition of the gases found in the Bushveld Complex.

4. The gases streaming out of the 4 boreholes underground need to be re-analysed by the same gas monitor (Dräger X-am 5600). This needs to be conducted a year later to see if mining activities have changed the ambient stress around the boreholes (i.e. increase the number of conduits for gases to pass through).
5. Underground *in-situ* gas detection must be conducted at other structures, such as joints, faults, and other dykes, to confirm if the gases presented in this study are also being emitted through these structures.

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Appendices

Appendix A: Petrology

Appendix B: Fluid inclusions (including Raman spectroscopy)

Appendix C: ‘In-line’ gas chromatography

Appendix D: Underground *in-situ* gas detection

Appendix A

Table A.1. Electron micro-probe data collected for mica, expressed as oxides (wt. %) and cations.

Sample	L-11A									
Mica	1	2	3	4	5	6	7	8	9	10
Description	Core	Rim	Core	Core	Core	Core	Rim	Core	Core	Core
SiO ₂	38.49	40.24	42.28	40.41	41.04	40.03	39.95	39.37	40.36	39.72
TiO ₂	0.83	0.70	1.68	0.99	1.47	1.49	0.76	2.34	0.84	2.32
Al ₂ O ₃	9.62	9.38	12.37	9.25	13.50	13.58	8.78	12.90	8.99	13.00
FeO	17.45	14.27	4.80	14.36	4.45	4.43	16.19	6.84	14.73	6.38
MnO	0.34	0.23	0.04	0.22	0.07	0.00	0.23	0.07	0.21	0.05
MgO	18.69	20.10	24.20	19.82	23.96	23.62	18.69	22.49	19.11	22.89
CaO	0.06	0.03	0.03	0.00	0.03	0.00	0.00	0.02	0.00	0.00
Na ₂ O	0.11	0.14	0.15	0.12	0.12	0.11	0.13	0.12	0.11	0.12
K ₂ O	8.61	10.23	10.93	10.40	10.82	10.89	10.44	10.63	10.50	10.60
BaO	0.06	0.09	0.24	0.14	0.34	0.33	0.09	0.67	0.07	0.57
F	0.16	0.07	0.52	0.24	0.46	0.63	0.07	0.52	0.16	0.73
Cl	0.00	0.00	0.00	0.03	0.02	0.01	0.01	0.00	0.00	0.00
Total	94.43	95.48	97.23	95.98	96.26	95.12	95.32	95.96	95.08	96.37
Si	5.88	6.02	5.92	6.02	5.80	5.74	6.06	5.68	6.08	5.69
Ti	0.10	0.08	0.18	0.11	0.16	0.16	0.09	0.25	0.10	0.25
Al	1.73	1.65	2.04	1.63	2.25	2.30	1.57	2.20	1.60	2.19
Fe	2.23	1.78	0.56	1.79	0.53	0.53	2.05	0.83	1.86	0.76
Mn	0.04	0.03	0.00	0.03	0.01	0.00	0.03	0.01	0.03	0.01
Mg	4.26	4.48	5.05	4.40	5.05	5.05	4.22	4.84	4.29	4.89
Ca	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.03	0.04	0.04	0.03	0.03	0.03	0.04	0.03	0.03	0.03
K	1.68	1.95	1.95	1.98	1.95	1.99	2.02	1.96	2.02	1.94
Ba	0.00	0.01	0.01	0.01	0.02	0.02	0.01	0.04	0.00	0.03
F	0.08	0.03	0.23	0.11	0.21	0.28	0.03	0.24	0.07	0.33
Cl	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Total	15.97	16.05	15.76	16.00	15.80	15.82	16.08	15.84	16.01	15.79
Sample	L-11A									
Mica	11	12	13	14	15	16	17	18	19	20
Description	Core	Rim	Core	Core	Core	Core	Core	Core	Core	Rim
SiO ₂	40.17	40.32	41.44	40.88	40.00	39.77	44.45	45.04	40.62	39.62
TiO ₂	0.79	0.87	1.59	1.45	0.85	3.23	0.00	0.02	2.22	3.24
Al ₂ O ₃	8.65	8.57	12.94	13.53	8.66	11.90	21.21	21.27	12.82	12.53
FeO	16.15	16.91	5.15	4.43	16.72	9.88	4.20	3.14	5.96	9.23
MnO	0.20	0.27	0.01	0.08	0.25	0.14	0.01	0.03	0.01	0.10
MgO	18.72	18.48	24.14	24.13	18.65	20.87	0.00	0.02	23.84	20.84
CaO	0.00	0.02	0.00	0.00	0.05	0.01	26.55	26.21	0.01	0.01
Na ₂ O	0.14	0.13	0.11	0.10	0.12	0.14	0.14	0.24	0.10	0.14
K ₂ O	9.98	10.45	11.15	10.81	10.10	10.34	0.02	0.02	10.85	10.33
BaO	0.12	0.10	0.33	0.27	0.11	1.11	0.00	0.00	0.58	0.86
F	0.03	0.16	0.29	0.49	0.08	0.52	0.07	0.00	0.48	0.52
Cl	0.00	0.00	0.01	0.00	0.01	0.01	0.01	0.04	0.00	0.00
Total	94.94	96.27	97.15	96.17	95.59	97.92	96.66	96.02	97.49	97.42
Si	6.10	6.07	5.83	5.78	6.05	5.72	6.16	6.24	5.74	5.70
Ti	0.09	0.10	0.17	0.15	0.10	0.35	0.00	0.00	0.24	0.35
Al	1.55	1.52	2.15	2.26	1.55	2.02	3.47	3.47	2.13	2.12
Fe	2.05	2.13	0.61	0.52	2.12	1.19	0.49	0.36	0.70	1.11
Mn	0.03	0.03	0.00	0.01	0.03	0.02	0.00	0.00	0.00	0.01
Mg	4.23	4.15	5.07	5.09	4.21	4.48	0.00	0.00	5.02	4.47
Ca	0.00	0.00	0.00	0.00	0.01	0.00	3.95	3.89	0.00	0.00
Na	0.04	0.04	0.03	0.03	0.03	0.04	0.04	0.06	0.03	0.04
K	1.93	2.01	2.00	1.95	1.95	1.90	0.00	0.00	1.95	1.89
Ba	0.01	0.01	0.02	0.02	0.01	0.06	0.00	0.00	0.03	0.05
F	0.01	0.08	0.13	0.22	0.04	0.24	0.03	0.00	0.21	0.24
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Total	16.02	16.05	15.88	15.81	16.05	15.77	14.11	14.05	15.85	15.74

Sample	L-15									
Mica	1	2	3	4	5	6	7	8	9	10
Description	Core	Interm	Rim	Core	Interm	Rim	Core	Rim	Core	Interm
SiO ₂	39.52	39.86	39.34	39.72	39.59	38.94	38.69	38.63	39.08	39.02
TiO ₂	2.48	2.57	2.62	2.54	2.81	2.81	2.65	2.73	2.44	2.43
Al ₂ O ₃	10.42	7.89	7.19	10.40	7.91	7.43	7.70	7.61	11.04	8.26
FeO	11.35	18.15	21.26	11.99	18.72	22.12	18.91	22.95	11.45	18.71
MnO	0.11	0.23	0.36	0.14	0.23	0.32	0.26	0.40	0.18	0.27
MgO	19.69	16.45	14.36	20.09	16.24	13.65	15.67	13.64	20.14	16.18
CaO	0.04	0.00	0.03	0.00	0.00	0.00	0.04	0.05	0.00	0.01
Na ₂ O	0.10	0.10	0.09	0.10	0.10	0.10	0.09	0.08	0.08	0.06
K ₂ O	10.26	10.29	10.14	10.51	10.07	10.37	10.28	10.14	10.42	10.21
BaO	0.79	0.24	0.17	0.92	0.27	0.36	0.19	0.33	0.81	0.21
F	0.22	0.22	0.03	0.26	0.12	0.20	0.06	0.00	0.27	0.11
Cl	0.00	0.01	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.00
Total	94.98	96.01	95.60	96.67	96.02	96.31	94.53	96.57	95.91	95.47
Si	5.90	6.07	6.12	5.85	6.04	6.05	6.03	6.01	5.79	6.00
Ti	0.28	0.29	0.31	0.28	0.32	0.33	0.31	0.32	0.27	0.28
Al	1.83	1.41	1.32	1.81	1.42	1.36	1.41	1.40	1.93	1.50
Fe	1.42	2.31	2.76	1.48	2.39	2.88	2.46	2.99	1.42	2.40
Mn	0.01	0.03	0.05	0.02	0.03	0.04	0.03	0.05	0.02	0.04
Mg	4.38	3.73	3.33	4.41	3.69	3.16	3.64	3.16	4.45	3.71
Ca	0.01	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.00	0.00
Na	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.02	0.02
K	1.95	2.00	2.01	1.97	1.96	2.06	2.04	2.01	1.97	2.00
Ba	0.05	0.01	0.01	0.05	0.02	0.02	0.01	0.02	0.05	0.01
F	0.10	0.10	0.01	0.12	0.06	0.10	0.03	0.00	0.13	0.05
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	15.85	15.89	15.93	15.90	15.89	15.93	15.98	15.99	15.91	15.96
Sample	L-15									
Mica	11	12	13	14	15	16	17	18	19	20
Description	Rim	Core	Interm	Rim	Core	Interm	Rim	Core	Core	Core
SiO ₂	38.52	41.43	39.30	38.90	41.42	39.24	39.16	38.56	39.51	38.61
TiO ₂	2.78	1.38	2.70	2.69	1.40	2.76	2.75	2.19	2.32	2.47
Al ₂ O ₃	7.46	12.62	8.23	7.15	12.27	8.25	7.56	12.15	10.46	12.35
FeO	21.70	4.55	18.65	23.02	4.80	19.19	22.08	11.05	12.17	11.02
MnO	0.38	0.06	0.28	0.35	0.06	0.19	0.33	0.16	0.22	0.16
MgO	13.62	24.74	16.03	13.46	24.71	15.90	14.13	19.88	19.54	19.70
CaO	0.03	0.04	0.01	0.05	0.00	0.05	0.04	0.01	0.00	0.02
Na ₂ O	0.06	0.07	0.10	0.09	0.11	0.07	0.08	0.03	0.06	0.08
K ₂ O	10.15	10.81	10.39	10.17	10.84	10.31	10.32	10.31	10.49	9.91
BaO	0.25	0.42	0.22	0.28	0.51	0.25	0.28	0.98	0.62	1.63
F	0.19	0.08	0.13	0.13	0.27	0.09	0.17	0.13	0.20	0.15
Cl	0.00	0.00	0.01	0.00	0.02	0.00	0.00	0.01	0.00	0.02
Total	95.14	96.21	96.05	96.27	96.40	96.30	96.89	95.44	95.56	96.11
Si	6.05	5.87	6.01	6.07	5.87	5.99	6.04	5.73	5.88	5.71
Ti	0.33	0.15	0.31	0.32	0.15	0.32	0.32	0.24	0.26	0.27
Al	1.38	2.11	1.48	1.31	2.05	1.49	1.37	2.13	1.83	2.15
Fe	2.85	0.54	2.38	3.00	0.57	2.45	2.85	1.37	1.51	1.36
Mn	0.05	0.01	0.04	0.05	0.01	0.02	0.04	0.02	0.03	0.02
Mg	3.19	5.22	3.65	3.13	5.22	3.62	3.25	4.40	4.34	4.34
Ca	0.00	0.01	0.00	0.01	0.00	0.01	0.01	0.00	0.00	0.00
Na	0.02	0.02	0.03	0.03	0.03	0.02	0.03	0.01	0.02	0.02
K	2.03	1.95	2.03	2.02	1.96	2.01	2.03	1.95	1.99	1.87
Ba	0.02	0.02	0.01	0.02	0.03	0.01	0.02	0.06	0.04	0.09
F	0.09	0.03	0.06	0.06	0.12	0.04	0.08	0.06	0.09	0.07
Cl	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Total	15.91	15.90	15.94	15.95	15.89	15.94	15.94	15.91	15.90	15.85

Sample	L-15									
Mica	21	22	23	24	25	26	27	28	29	30
Description	Core	Rim	Core	Core	Core	Rim	Core	Rim	Core	Interm
SiO ₂	39.17	39.31	38.77	38.97	39.19	39.88	39.22	39.85	39.95	40.18
TiO ₂	2.28	2.79	2.40	2.41	2.62	2.18	2.62	2.11	2.23	2.14
Al ₂ O ₃	10.82	7.68	11.70	9.75	9.14	11.05	9.80	10.83	9.70	10.92
FeO	13.57	21.07	12.64	13.48	13.12	11.35	14.36	10.87	15.16	11.51
MnO	0.16	0.25	0.16	0.14	0.22	0.19	0.22	0.18	0.19	0.15
MgO	19.03	14.53	18.89	19.01	19.46	20.42	18.76	20.44	18.14	20.33
CaO	0.00	0.01	0.02	0.00	0.04	0.00	0.08	0.11	0.01	0.04
Na ₂ O	0.05	0.11	0.07	0.06	0.09	0.10	0.05	0.07	0.08	0.10
K ₂ O	10.43	10.04	10.23	10.48	10.24	10.70	10.30	10.64	10.26	10.46
BaO	0.58	0.21	1.32	0.45	1.07	0.48	0.70	0.38	0.29	0.60
F	0.16	0.03	0.07	0.26	0.22	0.20	0.12	0.11	0.21	0.28
Cl	0.01	0.01	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.02
Total	96.26	96.02	96.26	95.02	95.41	96.54	96.23	95.60	96.21	96.72
Si	5.83	6.07	5.77	5.88	5.90	5.85	5.87	5.88	5.96	5.88
Ti	0.25	0.32	0.27	0.27	0.30	0.24	0.29	0.23	0.25	0.24
Al	1.90	1.40	2.05	1.73	1.62	1.91	1.73	1.88	1.71	1.88
Fe	1.69	2.72	1.57	1.70	1.65	1.39	1.80	1.34	1.89	1.41
Mn	0.02	0.03	0.02	0.02	0.03	0.02	0.03	0.02	0.02	0.02
Mg	4.22	3.34	4.19	4.27	4.37	4.46	4.18	4.50	4.04	4.43
Ca	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.02	0.00	0.01
Na	0.01	0.03	0.02	0.02	0.03	0.03	0.01	0.02	0.02	0.03
K	1.98	1.98	1.94	2.02	1.97	2.00	1.97	2.00	1.95	1.95
Ba	0.03	0.01	0.08	0.03	0.06	0.03	0.04	0.02	0.02	0.03
F	0.08	0.01	0.03	0.12	0.10	0.09	0.06	0.05	0.10	0.13
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	15.93	15.91	15.90	15.94	15.93	15.93	15.94	15.93	15.87	15.87
Sample	L-15									
Mica	31	32	33	34	35	36	37	38	39	40
Description	Interm	Rim	Core	Interm	Interm	Rim	Rim	Interm	Interm	Core
SiO ₂	39.63	38.84	39.43	41.87	38.81	33.47	33.49	38.03	42.06	40.36
TiO ₂	2.36	2.76	1.59	1.80	3.55	4.89	4.83	3.38	2.05	2.43
Al ₂ O ₃	9.54	8.32	9.06	10.01	8.35	11.82	12.01	8.59	9.61	8.69
FeO	16.69	21.15	17.82	8.90	20.34	34.79	35.16	20.56	9.20	15.78
MnO	0.14	0.34	0.37	0.09	0.35	0.17	0.13	0.26	0.09	0.27
MgO	17.44	14.11	17.03	22.25	14.46	0.98	0.99	14.32	21.91	17.87
CaO	0.06	0.07	0.01	0.00	0.00	0.00	0.05	0.01	0.00	0.00
Na ₂ O	0.11	0.08	0.08	0.08	0.10	0.00	0.02	0.12	0.11	0.08
K ₂ O	10.37	10.08	10.14	10.66	10.25	9.64	9.58	10.26	10.54	10.40
BaO	0.38	0.16	0.41	0.12	0.37	0.22	0.19	1.07	0.07	0.47
F	0.04	0.00	0.14	0.15	0.16	0.00	0.00	0.16	0.27	0.26
Cl	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.01	0.00
Total	96.77	95.91	96.09	95.91	96.76	95.99	96.45	96.76	95.91	96.59
Si	5.94	6.01	5.99	6.06	5.94	5.57	5.55	5.87	6.09	6.04
Ti	0.27	0.32	0.18	0.20	0.41	0.61	0.60	0.39	0.22	0.27
Al	1.69	1.52	1.62	1.71	1.51	2.32	2.35	1.56	1.64	1.53
Fe	2.09	2.74	2.26	1.08	2.61	4.84	4.87	2.66	1.11	1.97
Mn	0.02	0.04	0.05	0.01	0.05	0.02	0.02	0.03	0.01	0.03
Mg	3.90	3.25	3.86	4.80	3.30	0.24	0.24	3.30	4.73	3.98
Ca	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Na	0.03	0.02	0.02	0.02	0.03	0.00	0.01	0.04	0.03	0.02
K	1.98	1.99	1.97	1.97	2.00	2.05	2.03	2.02	1.95	1.98
Ba	0.02	0.01	0.02	0.01	0.02	0.01	0.01	0.06	0.00	0.03
F	0.02	0.00	0.07	0.07	0.08	0.00	0.00	0.08	0.13	0.12
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	15.95	15.92	15.98	15.85	15.87	15.68	15.69	15.94	15.79	15.87

Sample	L-15								L-40B	
Mica	41	42	43	44	45	46	47	48	1	2
Description	Core	Interm	Rim			Core	Interm	Rim	Interm	Interm
SiO ₂	46.47	39.49	38.98	39.05	39.16	39.13	39.42	38.06	40.44	40.52
TiO ₂	0.05	2.65	2.76	2.77	2.47	1.21	2.30	2.74	2.40	2.46
Al ₂ O ₃	34.34	9.38	8.74	7.85	9.60	11.60	10.32	9.48	13.39	13.43
FeO	1.56	13.66	17.34	19.37	15.89	7.53	12.69	17.93	4.69	4.75
MnO	0.03	0.21	0.19	0.28	0.21	0.05	0.14	0.20	0.09	0.08
MgO	2.40	18.92	16.58	15.59	16.94	25.14	20.39	15.93	22.97	23.19
CaO	0.21	0.00	0.04	0.00	0.01	0.08	0.00	0.01	0.01	0.05
Na ₂ O	0.88	0.07	0.10	0.07	0.05	0.19	0.12	0.06	0.20	0.15
K ₂ O	9.93	10.46	10.17	10.37	10.35	8.04	9.54	9.92	10.64	10.65
BaO	0.09	0.81	0.82	0.27	0.37	0.33	0.58	0.50	0.34	0.32
F	0.00	0.38	0.23	0.15	0.19	0.22	0.30	0.15	0.25	0.28
Cl	0.07	0.00	0.00	0.00	0.00	0.04	0.01	0.02	0.02	0.00
Total	96.02	96.04	95.93	95.77	95.24	93.57	95.82	94.99	95.43	95.88
Si	6.15	5.91	5.95	6.01	5.95	5.73	5.84	5.87	5.78	5.76
Ti	0.00	0.30	0.32	0.32	0.28	0.13	0.26	0.32	0.26	0.26
Al	5.36	1.65	1.57	1.42	1.72	2.00	1.80	1.72	2.26	2.25
Fe	0.17	1.71	2.21	2.50	2.02	0.92	1.57	2.31	0.56	0.56
Mn	0.00	0.03	0.02	0.04	0.03	0.01	0.02	0.03	0.01	0.01
Mg	0.47	4.22	3.77	3.58	3.83	5.48	4.50	3.66	4.89	4.92
Ca	0.03	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.01
Na	0.23	0.02	0.03	0.02	0.02	0.05	0.03	0.02	0.05	0.04
K	1.68	2.00	1.98	2.04	2.00	1.50	1.80	1.95	1.94	1.93
Ba	0.00	0.05	0.05	0.02	0.02	0.02	0.03	0.03	0.02	0.02
F	0.00	0.18	0.11	0.07	0.09	0.10	0.14	0.07	0.11	0.13
Cl	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.00
Total	14.11	15.88	15.90	15.94	15.87	15.86	15.85	15.90	15.77	15.77
Sample	L-40B									
Mica	3	4	5	6	7	8	9	10	11	12
Description	Interm	Rim	Core	Core	Rim	Core	Rim	Core	Interm	Rim
SiO ₂	40.20	40.17	40.55	40.46	39.85	41.38	40.72	40.37	40.66	40.34
TiO ₂	2.53	2.33	2.40	2.36	3.41	2.18	2.43	2.44	3.01	0.96
Al ₂ O ₃	13.33	13.26	13.30	13.03	12.03	10.65	12.85	13.07	10.98	7.37
FeO	4.84	4.93	4.94	5.03	7.62	10.75	5.22	5.00	8.54	16.90
MnO	0.04	0.03	0.01	0.04	0.04	0.09	0.02	0.08	0.10	0.30
MgO	23.11	22.90	23.02	23.16	21.95	20.11	23.28	23.40	22.58	19.11
CaO	0.02	0.03	0.01	0.01	0.00	0.05	0.02	0.02	0.01	0.01
Na ₂ O	0.15	0.16	0.17	0.09	0.08	0.35	0.12	0.15	0.04	0.07
K ₂ O	10.53	10.58	10.73	10.81	10.56	10.51	10.63	10.81	10.76	10.39
BaO	0.32	0.34	0.31	0.31	0.97	0.14	0.77	0.39	0.79	0.19
F	0.25	0.37	0.38	0.25	0.49	0.31	0.17	0.41	0.55	0.24
Cl	0.00	0.00	0.00	0.00	0.02	0.02	0.00	0.00	0.01	0.02
Total	95.30	95.09	95.81	95.54	97.02	96.52	96.24	96.13	98.03	95.90
Si	5.75	5.77	5.78	5.79	5.72	6.01	5.80	5.75	5.80	6.11
Ti	0.27	0.25	0.26	0.25	0.37	0.24	0.26	0.26	0.32	0.11
Al	2.25	2.24	2.23	2.20	2.04	1.82	2.16	2.19	1.85	1.32
Fe	0.58	0.59	0.59	0.60	0.91	1.30	0.62	0.59	1.02	2.14
Mn	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.01	0.04
Mg	4.93	4.90	4.89	4.94	4.70	4.35	4.95	4.97	4.80	4.32
Ca	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Na	0.04	0.04	0.05	0.02	0.02	0.10	0.03	0.04	0.01	0.02
K	1.92	1.94	1.95	1.97	1.93	1.95	1.93	1.96	1.96	2.01
Ba	0.02	0.02	0.02	0.02	0.05	0.01	0.04	0.02	0.04	0.01
F	0.11	0.17	0.17	0.11	0.22	0.14	0.08	0.19	0.25	0.11
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	15.77	15.77	15.76	15.80	15.76	15.79	15.80	15.80	15.81	16.08

Sample	L-40B									
Mica	13	14	15	16	17	18	19	20	21	22
Description	Core	Interm	Rim	Core	Rim	Core	Rim	Core	Rim	Core
SiO ₂	40.76	40.46	40.11	40.08	39.86	39.95	40.46	40.60	40.24	39.96
TiO ₂	2.27	2.93	1.03	2.92	1.60	2.41	1.58	2.44	1.17	2.74
Al ₂ O ₃	13.03	12.68	8.11	11.56	7.02	13.22	7.78	13.21	7.92	12.74
FeO	5.39	6.28	16.08	8.20	17.71	5.26	16.43	5.09	16.79	5.94
MnO	0.05	0.08	0.26	0.13	0.31	0.10	0.25	0.00	0.25	0.02
MgO	23.49	22.84	19.67	22.23	18.23	23.31	18.99	23.61	18.99	22.83
CaO	0.02	0.12	0.10	0.12	0.22	0.11	0.13	0.02	0.12	0.02
Na ₂ O	0.08	0.07	0.06	0.06	0.08	0.09	0.06	0.16	0.09	0.10
K ₂ O	10.71	10.58	10.08	10.57	10.45	11.00	10.54	10.40	10.32	10.79
BaO	0.40	0.59	0.19	0.65	0.23	0.39	0.28	0.26	0.20	0.56
F	0.32	0.46	0.15	0.61	0.31	0.30	0.38	0.28	0.38	0.35
Cl	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.01	0.00	0.01
Total	96.51	97.10	95.84	97.15	96.03	96.13	96.89	96.07	96.45	96.05
Si	5.78	5.74	6.04	5.75	6.08	5.71	6.06	5.76	6.05	5.73
Ti	0.24	0.31	0.12	0.32	0.18	0.26	0.18	0.26	0.13	0.30
Al	2.18	2.12	1.44	1.95	1.26	2.23	1.37	2.21	1.40	2.15
Fe	0.64	0.75	2.03	0.98	2.26	0.63	2.06	0.60	2.11	0.71
Mn	0.01	0.01	0.03	0.02	0.04	0.01	0.03	0.00	0.03	0.00
Mg	4.96	4.83	4.42	4.76	4.14	4.96	4.24	4.99	4.26	4.88
Ca	0.00	0.02	0.02	0.02	0.04	0.02	0.02	0.00	0.02	0.00
Na	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.04	0.02	0.03
K	1.94	1.92	1.94	1.94	2.03	2.01	2.01	1.88	1.98	1.97
Ba	0.02	0.03	0.01	0.04	0.01	0.02	0.02	0.01	0.01	0.03
F	0.14	0.21	0.07	0.28	0.15	0.14	0.18	0.13	0.18	0.16
Cl	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Total	15.79	15.75	16.06	15.79	16.06	15.87	16.00	15.77		15.82
Sample	L-40B									
Mica	23	24	25	26	27	28	29	30	31	32
Description	Rim	Core	Rim	Core	Rim	Core	Rim	Core	Rim	Core
SiO ₂	40.23	40.20	39.80	39.87	40.95	39.75	40.56	40.42	40.63	40.42
TiO ₂	2.54	2.39	2.99	2.40	2.79	2.78	2.72	2.41	2.69	2.43
Al ₂ O ₃	9.89	13.16	10.71	13.12	10.01	12.80	10.07	13.16	10.06	13.17
FeO	9.92	5.06	9.02	5.22	9.72	6.08	10.09	5.18	9.71	5.26
MnO	0.09	0.08	0.11	0.03	0.06	0.02	0.11	0.06	0.13	0.01
MgO	21.89	23.20	21.85	23.33	22.05	22.80	22.05	23.16	21.95	23.09
CaO	0.06	0.01	0.02	0.00	0.01	0.03	0.19	0.00	0.02	0.04
Na ₂ O	0.06	0.15	0.11	0.13	0.10	0.04	0.06	0.13	0.07	0.16
K ₂ O	10.54	10.87	10.68	10.80	10.77	10.45	10.40	10.64	10.70	10.54
BaO	0.73	0.39	0.69	0.41	0.55	0.57	0.58	0.38	0.52	0.37
F	0.36	0.43	0.62	0.38	0.45	0.43	0.37	0.40	0.50	0.33
Cl	0.02	0.01	0.00	0.00	0.01	0.02	0.00	0.01	0.00	0.00
Total	96.33	95.94	96.59	95.68	97.47	95.76	97.20	95.95	96.97	95.82
Si	5.88	5.74	5.78	5.72	5.90	5.71	5.87	5.76	5.88	5.77
Ti	0.28	0.26	0.33	0.26	0.30	0.30	0.30	0.26	0.29	0.26
Al	1.70	2.22	1.83	2.22	1.70	2.17	1.72	2.21	1.72	2.21
Fe	1.21	0.60	1.10	0.63	1.17	0.73	1.22	0.62	1.18	0.63
Mn	0.01	0.01	0.01	0.00	0.01	0.00	0.01	0.01	0.02	0.00
Mg	4.77	4.94	4.73	4.98	4.73	4.88	4.75	4.92	4.74	4.91
Ca	0.01	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.01
Na	0.02	0.04	0.03	0.04	0.03	0.01	0.02	0.04	0.02	0.04
K	1.97	1.98	1.98	1.97	1.98	1.92	1.92	1.94	1.98	1.92
Ba	0.04	0.02	0.04	0.02	0.03	0.03	0.03	0.02	0.03	0.02
F	0.17	0.19	0.29	0.17	0.20	0.19	0.17	0.18	0.23	0.15
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	15.89	15.81	15.83	15.84	15.85	15.77	15.86	15.77	15.85	15.77

Sample	L-40B									L-62A
Mica	33	34	35	36	37	38	39	40	41	1
Description	Rim	Core	Rim	Core	Core	Core	Rim	Core	Interm	Core
SiO ₂	41.00	40.51	40.25	40.55	40.41	40.20	39.88	40.32	36.02	40.77
TiO ₂	2.49	2.46	3.00	2.50	2.61	2.95	2.94	2.42	0.77	1.50
Al ₂ O ₃	9.59	12.84	11.12	9.17	9.30	12.75	7.90	8.90	6.12	12.73
FeO	9.81	5.43	8.57	11.24	10.30	6.71	13.97	13.47	15.35	4.72
MnO	0.10	0.04	0.09	0.16	0.13	0.06	0.18	0.19	0.19	0.02
MgO	22.12	23.45	22.11	21.77	21.67	22.67	19.54	19.87	18.71	23.99
CaO	0.04	0.01	0.01	0.05	0.03	0.05	0.06	0.25	4.97	0.02
Na ₂ O	0.11	0.13	0.10	0.09	0.07	0.10	0.04	0.03	0.08	0.18
K ₂ O	10.61	10.87	10.66	10.87	10.52	10.64	10.39	10.57	8.31	10.52
BaO	0.42	0.36	0.95	0.39	0.52	0.63	0.50	0.35	0.24	0.41
F	0.37	0.25	0.41	0.36	0.40	0.36	0.20	0.34	0.35	0.50
Cl	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.02	0.00
Total	96.67	96.35	97.27	97.15	95.96	97.12	95.59	96.73	91.12	95.36
Si	5.95	5.77	5.80	5.91	5.93	5.72	5.99	5.96	5.82	5.83
Ti	0.27	0.26	0.32	0.27	0.29	0.32	0.33	0.27	0.09	0.16
Al	1.64	2.15	1.89	1.58	1.61	2.14	1.40	1.55	1.16	2.14
Fe	1.19	0.65	1.03	1.37	1.27	0.80	1.76	1.67	2.07	0.56
Mn	0.01	0.01	0.01	0.02	0.02	0.01	0.02	0.02	0.03	0.00
Mg	4.78	4.98	4.75	4.73	4.74	4.81	4.38	4.38	4.50	5.11
Ca	0.01	0.00	0.00	0.01	0.00	0.01	0.01	0.04	0.86	0.00
Na	0.03	0.04	0.03	0.03	0.02	0.03	0.01	0.01	0.03	0.05
K	1.96	1.97	1.96	2.02	1.97	1.93	1.99	1.99	1.71	1.92
Ba	0.02	0.02	0.05	0.02	0.03	0.04	0.03	0.02	0.01	0.02
F	0.17	0.11	0.19	0.16	0.18	0.16	0.09	0.16	0.18	0.23
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	15.87	15.84	15.84	15.97	15.88	15.79	15.93	15.91	16.28	15.81
Sample	L-62A									
Mica	2	3	4	5	6	7	8	9	10	11
Description	Core	Core	Core	Interm	Interm	Rim	Interm	Core	Core	Rim
SiO ₂	41.00	41.00	37.73	36.15	39.45	40.51	40.33	39.66	38.70	38.35
TiO ₂	1.44	1.41	2.59	2.71	1.52	1.59	1.80	1.70	2.79	3.03
Al ₂ O ₃	13.22	12.53	15.17	15.58	11.37	11.44	8.97	11.33	6.60	5.70
FeO	4.27	4.82	13.16	15.36	5.46	6.13	11.46	7.49	17.89	18.28
MnO	0.02	0.02	0.09	0.15	0.06	0.05	0.18	0.14	0.33	0.29
MgO	23.98	23.95	15.83	13.47	23.44	24.10	21.74	23.67	17.94	17.52
CaO	0.05	0.01	0.05	0.06	0.04	0.06	0.12	0.02	0.03	0.01
Na ₂ O	0.18	0.14	0.21	0.24	0.19	0.09	0.07	0.07	0.15	0.14
K ₂ O	10.48	10.60	9.90	9.45	10.25	10.44	10.13	10.60	10.35	10.06
BaO	0.45	0.47	0.92	1.01	0.40	0.42	0.66	0.67	0.39	0.67
F	0.22	0.25	0.09	0.06	0.21	0.52	0.44	0.38	0.26	0.20
Cl	0.01	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.01	0.00
Total	95.31	95.20	95.74	94.25	92.39	95.36	95.91	95.74	95.44	94.26
Si	5.85	5.88	5.61	5.53	5.86	5.84	5.96	5.77	5.97	6.02
Ti	0.15	0.15	0.29	0.31	0.17	0.17	0.20	0.19	0.32	0.36
Al	2.22	2.12	2.66	2.81	1.99	1.94	1.56	1.94	1.20	1.05
Fe	0.51	0.58	1.64	1.97	0.68	0.74	1.42	0.91	2.31	2.40
Mn	0.00	0.00	0.01	0.02	0.01	0.01	0.02	0.02	0.04	0.04
Mg	5.10	5.12	3.51	3.07	5.19	5.18	4.79	5.13	4.13	4.10
Ca	0.01	0.00	0.01	0.01	0.01	0.01	0.02	0.00	0.01	0.00
Na	0.05	0.04	0.06	0.07	0.05	0.03	0.02	0.02	0.05	0.04
K	1.91	1.94	1.88	1.84	1.94	1.92	1.91	1.97	2.04	2.01
Ba	0.03	0.03	0.05	0.06	0.02	0.02	0.04	0.04	0.02	0.04
F	0.10	0.11	0.04	0.03	0.10	0.24	0.20	0.17	0.13	0.10
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	15.82	15.85	15.72	15.70	15.92	15.87	15.93	15.98	16.08	16.07

Sample	L-62A									
Mica	12	13	14	15	16	17	18	19	20	21
Description	Core	Core	Core	Interm	Core	Interm	Interm	Interm	Interm	Interm
SiO ₂	37.99	38.76	38.03	38.67	38.76	39.17	39.26	40.15	40.09	39.97
TiO ₂	2.95	2.90	2.90	2.90	3.03	2.69	1.49	1.51	1.40	1.41
Al ₂ O ₃	6.23	5.48	5.70	5.14	5.58	5.94	12.25	12.11	13.25	12.93
FeO	17.67	17.66	17.58	17.92	16.87	17.02	4.66	5.34	4.30	4.20
MnO	0.23	0.25	0.24	0.23	0.25	0.22	0.05	0.05	0.04	0.03
MgO	18.37	17.74	19.86	18.24	19.03	18.32	23.73	24.00	24.06	23.82
CaO	0.03	0.02	0.05	0.07	0.02	0.12	0.02	0.01	0.02	0.00
Na ₂ O	0.13	0.19	0.13	0.22	0.16	0.19	0.22	0.21	0.16	0.22
K ₂ O	10.16	10.11	9.76	10.11	10.05	10.04	10.79	10.85	10.71	10.52
BaO	1.04	0.75	0.77	0.78	0.64	0.52	0.40	0.48	0.40	0.36
F	0.12	0.24	0.19	0.00	0.24	0.26	0.35	0.34	0.35	0.24
Cl	0.00	0.01	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.01
Total	94.93	94.09	95.22	94.28	94.64	94.49	93.23	95.06	94.78	93.72
Si	5.93	6.08	5.89	6.07	6.01	6.07	5.78	5.81	5.77	5.81
Ti	0.35	0.34	0.34	0.34	0.35	0.31	0.16	0.16	0.15	0.15
Al	1.15	1.01	1.04	0.95	1.02	1.09	2.12	2.06	2.25	2.21
Fe	2.31	2.32	2.28	2.35	2.19	2.21	0.57	0.65	0.52	0.51
Mn	0.03	0.03	0.03	0.03	0.03	0.03	0.01	0.01	0.00	0.00
Mg	4.27	4.15	4.59	4.27	4.40	4.23	5.20	5.17	5.16	5.16
Ca	0.01	0.00	0.01	0.01	0.00	0.02	0.00	0.00	0.00	0.00
Na	0.04	0.06	0.04	0.07	0.05	0.06	0.06	0.06	0.04	0.06
K	2.02	2.02	1.93	2.02	1.99	1.98	2.02	2.00	1.97	1.95
Ba	0.06	0.05	0.05	0.05	0.04	0.03	0.02	0.03	0.02	0.02
F	0.06	0.12	0.09	0.00	0.12	0.13	0.16	0.16	0.16	0.11
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	16.16	16.05	16.19	16.16	16.08	16.03	15.96	15.95	15.88	15.88
Sample	L-62A							41-166		
Mica	22	23	24	25	26	27	28	1	2	3
Description	Interm	Interm	Interm	Interm	Interm	Interm	Interm	Core	Core	Core
SiO ₂	39.19	39.96	39.82	40.03	39.33	39.92	39.89	39.88	40.05	39.86
TiO ₂	1.35	1.46	1.45	1.53	1.49	1.44	1.45	1.37	1.64	1.72
Al ₂ O ₃	12.30	12.15	12.59	12.66	12.43	12.19	12.68	11.24	10.52	10.26
FeO	5.48	5.38	4.86	5.09	5.03	5.00	5.08	5.59	6.61	6.07
MnO	0.05	0.06	0.04	0.01	0.06	0.03	0.03	0.00	0.09	0.02
MgO	23.64	24.69	24.15	24.35	24.18	24.43	24.42	24.59	24.06	24.22
CaO	0.03	0.01	0.03	0.05	0.00	0.09	0.04	0.04	0.02	0.02
Na ₂ O	0.20	0.19	0.19	0.22	0.27	0.19	0.18	0.12	0.07	0.09
K ₂ O	10.50	10.78	10.71	10.49	10.52	10.63	10.70	10.50	10.89	10.65
BaO	0.48	0.39	0.45	0.53	0.45	0.47	0.49	1.14	0.72	0.93
F	0.39	0.38	0.31	0.30	0.37	0.42	0.32	0.40	0.44	0.44
Cl	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.01	0.00	0.00
Total	93.63	95.46	94.60	95.28	94.13	94.81	95.28	94.89	95.11	94.28
Si	5.76	5.75	5.77	5.76	5.73	5.78	5.74	5.81	5.85	5.86
Ti	0.15	0.16	0.16	0.17	0.16	0.16	0.16	0.15	0.18	0.19
Al	2.13	2.06	2.15	2.15	2.14	2.08	2.15	1.93	1.81	1.78
Fe	0.67	0.65	0.59	0.61	0.61	0.60	0.61	0.68	0.81	0.75
Mn	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00
Mg	5.18	5.30	5.21	5.22	5.25	5.27	5.24	5.34	5.24	5.31
Ca	0.01	0.00	0.00	0.01	0.00	0.01	0.01	0.01	0.00	0.00
Na	0.06	0.05	0.05	0.06	0.08	0.05	0.05	0.03	0.02	0.03
K	1.97	1.98	1.98	1.92	1.96	1.96	1.97	1.95	2.03	2.00
Ba	0.03	0.02	0.03	0.03	0.03	0.03	0.03	0.07	0.04	0.05
F	0.18	0.17	0.14	0.14	0.17	0.19	0.14	0.19	0.20	0.20
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	15.95	15.99	15.94	15.93	15.97	15.94	15.96	15.97	15.99	15.97

Sample	41-166				
Mica	4	5	6	7	8
Description	Core	Core	Core	Core	Core
SiO ₂	39.47	40.38	39.47	39.78	39.86
TiO ₂	1.53	1.71	1.44	2.13	2.07
Al ₂ O ₃	10.78	10.74	11.32	9.99	10.08
FeO	5.76	6.00	5.45	7.30	7.81
MnO	0.02	0.02	0.05	0.12	0.11
MgO	24.96	24.42	24.61	23.74	24.39
CaO	0.00	0.00	0.00	0.05	0.03
Na ₂ O	0.09	0.16	0.10	0.11	0.09
K ₂ O	10.46	10.70	10.68	10.87	10.42
BaO	1.10	1.30	1.23	0.59	0.62
F	0.46	0.42	0.43	0.28	0.34
Cl	0.00	0.00	0.00	0.00	0.00
Total	94.63	95.85	94.78	94.96	95.82
Si	5.78	5.85	5.77	5.84	5.80
Ti	0.17	0.19	0.16	0.24	0.23
Al	1.86	1.83	1.95	1.73	1.73
Fe	0.71	0.73	0.67	0.90	0.95
Mn	0.00	0.00	0.01	0.01	0.01
Mg	5.45	5.27	5.36	5.20	5.29
Ca	0.00	0.00	0.00	0.01	0.00
Na	0.03	0.04	0.03	0.03	0.02
K	1.95	1.98	1.99	2.04	1.93
Ba	0.06	0.07	0.07	0.03	0.04
F	0.21	0.19	0.20	0.13	0.16
Cl	0.00	0.00	0.00	0.00	0.00
Total	16.01	15.96	16.01	16.03	16.01

Table A.2. Electron micro-probe data collected for pyroxene, expressed as oxides (wt. %) an cations.

Sample	L-11A									
Pyroxene	1	2	3	4	5	6	7	8	9	10
Description	Rim		Core	Rim	Rim		Core	Core	Rim	Core
SiO ₂	55.51	56.21	54.79	54.29	54.83	55.88	54.56	53.53	54.24	54.71
TiO ₂	0.38	0.57	0.50	1.24	0.79	0.60	1.12	1.00	0.90	0.49
Al ₂ O ₃	0.30	0.55	0.33	0.43	0.46	0.61	0.49	0.57	0.39	0.34
Cr ₂ O ₃	0.47	0.06	0.27	0.06	0.07	0.20	0.07	0.34	0.29	0.70
Fe ₂ O ₃	4.30	0.00	5.73	3.80	6.03	0.00	0.74	8.78	7.23	6.34
FeO	5.72	2.82	5.47	7.24	6.93	2.81	6.47	6.22	6.72	6.45
MnO	0.22	0.09	0.15	0.27	0.21	0.09	0.17	0.24	0.24	0.19
NiO	0.01	0.09	0.00	0.09	0.05	0.00	0.02	0.06	0.00	0.00
MgO	12.27	16.93	11.42	11.82	10.56	16.81	14.20	9.30	9.80	10.77
CaO	20.69	25.28	19.91	21.23	18.87	24.84	23.51	17.22	17.70	18.51
Na ₂ O	2.67	0.18	3.13	2.19	3.47	0.15	0.90	4.26	4.00	3.52
ZrO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	102.54	102.78	101.70	102.66	102.27	101.99	102.24	101.52	101.52	102.01
Si	2.03	1.99	2.03	2.00	2.04	1.99	1.98	2.03	2.04	2.04
Ti	0.01	0.02	0.01	0.03	0.02	0.02	0.03	0.03	0.03	0.01
Al	0.01	0.02	0.01	0.02	0.02	0.03	0.02	0.03	0.02	0.01
Cr	0.01	0.00	0.01	0.00	0.00	0.01	0.00	0.01	0.01	0.02
Fe	0.29	0.08	0.33	0.33	0.38	0.08	0.22	0.45	0.42	0.38
Mn	0.01	0.00	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.01
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.67	0.89	0.63	0.65	0.58	0.89	0.77	0.52	0.55	0.60
Ca	0.81	0.96	0.79	0.84	0.75	0.95	0.92	0.70	0.71	0.74
Na	0.19	0.01	0.22	0.16	0.25	0.01	0.06	0.31	0.29	0.25
Zr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
total	4.04	3.99	4.05	4.04	4.06	3.98	4.01	4.08	4.07	4.06
Sample	L-11A									
Pyroxene	11	12	13	14	15	16	17	18	19	20
Description	Rim	Core	Core	Core	Rim	Core	Rim	Core	Interm	Rim
SiO ₂	56.22	55.38	54.67	55.78	53.88	55.66	55.96	53.87	53.53	55.17
TiO ₂	0.16	0.70	1.15	0.56	0.83	0.57	0.58	1.30	0.99	0.29
Al ₂ O ₃	0.16	0.79	0.62	0.68	0.36	0.58	0.58	1.07	0.53	0.31
Cr ₂ O ₃	0.61	0.00	0.04	0.00	0.00	0.14	0.08	0.02	0.31	0.69
Fe ₂ O ₃	2.37	0.00	0.00	0.00	5.47	0.00	0.00	1.77	8.74	4.44
FeO	5.65	3.48	6.54	3.21	6.47	2.83	2.92	4.82	6.30	5.87
MnO	0.17	0.04	0.13	0.09	0.25	0.11	0.08	0.17	0.26	0.21
NiO	0.01	0.04	0.12	0.06	0.00	0.15	0.07	0.01	0.02	0.00
MgO	13.49	16.78	14.30	17.08	11.41	16.97	17.03	14.90	9.28	12.11
CaO	21.76	25.28	23.78	24.95	20.66	25.24	25.22	24.30	17.69	19.94
Na ₂ O	2.07	0.18	0.78	0.17	2.51	0.17	0.18	0.62	4.12	2.81
ZrO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	102.67	102.67	102.13	102.58	101.84	102.42	102.71	102.85	101.76	101.84
Si	2.03	1.97	1.98	1.98	2.01	1.98	1.99	1.95	2.02	2.03
Ti	0.00	0.02	0.03	0.01	0.02	0.02	0.02	0.04	0.03	0.01
Al	0.01	0.03	0.03	0.03	0.02	0.02	0.02	0.05	0.02	0.01
Cr	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02
Fe	0.24	0.10	0.20	0.10	0.36	0.08	0.09	0.19	0.45	0.30
Mn	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.01	0.01
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.73	0.89	0.77	0.91	0.63	0.90	0.90	0.80	0.52	0.67
Ca	0.84	0.96	0.92	0.95	0.83	0.96	0.96	0.94	0.72	0.79
Na	0.15	0.01	0.05	0.01	0.18	0.01	0.01	0.04	0.30	0.20
Zr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
total	4.02	4.00	4.00	3.99	4.05	3.99	3.99	4.02	4.08	4.04

Sample	L-11A								
Pyroxene	21	22	23	24	25	26	27	28	29
Description	Rim	Core	Interm	Rim	Core	Interm	Interm	Interm	Interm
SiO ₂	55.33	56.22	54.58	55.58	55.48	54.58	56.02	54.65	53.78
TiO ₂	0.73	0.71	1.04	0.61	0.79	1.09	0.65	0.93	0.70
Al ₂ O ₃	1.01	0.77	0.72	0.66	1.02	0.74	0.81	0.66	0.30
Cr ₂ O ₃	0.19	0.18	0.12	0.08	0.25	0.00	0.00	0.00	0.19
Fe ₂ O ₃	0.00	0.00	0.50	0.00	0.00	0.50	0.00	1.54	9.58
FeO	3.31	3.05	5.49	2.96	3.16	5.20	2.99	4.72	7.48
MnO	0.08	0.08	0.13	0.07	0.08	0.19	0.11	0.17	0.27
NiO	0.04	0.08	0.10	0.06	0.00	0.00	0.02	0.00	0.00
MgO	16.87	17.04	14.97	17.07	16.73	15.14	17.10	15.03	7.89
CaO	25.03	25.57	24.18	25.27	24.85	24.32	25.12	24.01	16.23
Na ₂ O	0.22	0.23	0.61	0.21	0.25	0.59	0.22	0.81	4.81
ZrO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	102.80	103.91	102.43	102.56	102.60	102.34	103.03	102.53	101.25
Si	1.97	1.98	1.97	1.98	1.97	1.97	1.98	1.97	2.06
Ti	0.02	0.02	0.03	0.02	0.02	0.03	0.02	0.03	0.02
Al	0.04	0.03	0.03	0.03	0.04	0.03	0.03	0.03	0.01
Cr	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01
Fe	0.10	0.09	0.18	0.09	0.09	0.17	0.09	0.18	0.52
Mn	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.01
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.89	0.89	0.81	0.91	0.89	0.81	0.90	0.81	0.45
Ca	0.95	0.96	0.94	0.96	0.95	0.94	0.95	0.93	0.66
Na	0.01	0.02	0.04	0.01	0.02	0.04	0.02	0.06	0.36
Zr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
total	4.00	4.00	4.00	4.00	3.99	4.00	3.99	4.01	4.09

Appendix B

Table B.1. Raman intensity (arb. units) data for Figure 5.12A.

Wavenumber	Raman intensity	Wavenumber	Raman intensity	Wavenumber	Raman intensity	Wavenumber	Raman intensity	Wavenumber	Raman intensity	Wavenumber	Raman intensity	Wavenumber	Raman intensity
2224.58	54.79	2037.37	-23.21	1845.81	21.49	1649.75	61.39	1449.05	1346.85	1243.53	151.25	1033.05	832.20
2223.04	95.53	2035.80	-8.78	1844.20	-40.77	1648.10	34.06	1447.35	1272.01	1241.80	148.97	1031.27	635.90
2221.50	71.35	2034.22	-2.61	1842.58	7.22	1646.45	37.59	1445.66	1153.41	1240.07	132.57	1029.49	520.76
2219.95	20.80	2032.64	10.70	1840.97	1.15	1644.79	67.40	1443.97	1040.29	1238.33	118.57	1027.72	451.04
2218.41	32.55	2031.06	-26.45	1839.35	-1.13	1643.14	80.32	1442.27	917.89	1236.60	97.27	1025.94	458.85
2216.87	82.84	2029.48	6.09	1837.73	0.63	1641.48	52.02	1440.58	859.59	1234.86	94.47	1024.16	452.03
2215.32	33.06	2027.90	5.91	1836.12	27.94	1639.83	65.61	1438.89	732.59	1233.13	115.54	1022.39	476.45
2213.78	14.57	2026.32	-18.74	1834.50	7.85	1638.18	92.19	1437.19	660.98	1231.39	116.53	1020.61	456.66
2212.23	28.21	2024.74	-36.91	1832.88	34.22	1636.52	93.33	1435.50	601.20	1229.66	129.91	1018.83	414.09
2210.69	19.62	2023.16	-18.94	1831.27	13.98	1634.86	97.90	1433.80	551.93	1227.92	113.63	1017.06	335.78
2209.14	3.81	2021.58	2.52	1829.65	18.83	1633.21	100.00	1432.11	572.16	1226.18	102.80	1015.28	327.14
2207.60	33.91	2020.00	-1.66	1828.03	38.63	1631.55	115.96	1430.41	533.21	1224.45	119.94	1013.50	284.26
2206.05	50.38	2018.42	-4.84	1826.41	66.45	1629.90	122.59	1428.71	508.55	1222.71	94.64	1011.72	262.67
2204.51	43.56	2016.84	-13.57	1824.79	32.04	1628.24	106.52	1427.02	476.30	1220.97	91.20	1009.94	302.06
2202.96	23.01	2015.25	-59.69	1823.17	19.94	1626.58	57.79	1425.32	432.47	1219.24	87.13	1008.16	344.25
2201.41	4.08	2013.67	-19.79	1821.56	-17.57	1624.92	131.20	1423.62	425.37	1217.50	108.23	1006.38	282.22
2199.87	-7.67	2012.09	-19.18	1819.93	19.36	1623.26	119.60	1421.93	379.88	1215.76	119.96	1004.60	218.00
2198.32	11.38	2010.51	-48.41	1818.32	49.25	1621.61	110.45	1420.23	378.32	1214.02	72.54	1002.82	211.74
2196.77	3.18	2008.92	-12.63	1816.70	10.22	1619.95	59.07	1418.53	431.34	1212.28	73.83	1001.03	193.12
2195.22	33.15	2007.34	-81.83	1815.07	14.22	1618.29	79.96	1416.83	388.93	1210.54	77.83	999.25	187.02
2193.68	46.85	2005.75	-21.00	1813.45	4.27	1616.63	65.31	1415.13	384.46	1208.80	37.53	997.47	171.32
2192.13	35.85	2004.17	6.74	1811.83	9.45	1614.97	60.29	1413.43	416.72	1207.06	84.49	995.69	133.39
2190.58	7.36	2002.58	-24.81	1810.21	9.55	1613.31	78.53	1411.73	339.45	1205.32	57.87	993.91	113.72
2189.03	-0.20	2001.00	-41.95	1808.59	-7.62	1611.65	52.14	1410.03	327.50	1203.58	60.68	992.12	153.92
2187.48	4.70	1999.41	-29.53	1806.97	-23.14	1609.99	37.91	1408.33	306.40	1201.84	95.29	990.34	137.18
2185.93	45.83	1997.83	-2.56	1805.34	33.57	1608.33	54.96	1406.63	351.52	1200.10	90.13	988.55	167.02
2184.38	32.71	1996.24	1.53	1803.72	21.36	1606.67	82.11	1404.93	295.87	1198.35	55.80	986.77	102.87
2182.83	36.70	1994.66	-25.51	1802.10	-5.16	1605.01	45.44	1403.23	302.38	1196.61	65.17	984.98	172.45
2181.28	-0.01	1993.07	-12.51	1800.47	-17.73	1603.34	35.16	1401.53	351.01	1194.87	50.65	983.20	190.90
2179.73	15.29	1991.48	-24.22	1798.85	-3.45	1601.68	65.94	1399.83	301.52	1193.13	93.16	981.41	172.35
2178.18	-12.29	1989.90	-54.44	1797.23	15.21	1600.02	34.31	1398.12	260.84	1191.38	54.09	979.63	161.93
2176.63	-15.17	1988.31	-6.43	1795.60	15.85	1598.36	23.38	1396.42	300.19	1189.64	52.74	977.84	210.21
2175.08	-6.39	1986.72	-29.09	1793.98	10.12	1596.69	32.34	1394.72	272.92	1187.89	40.40	976.06	195.33
2173.53	-6.45	1985.14	-12.06	1792.35	-10.44	1595.03	41.41	1393.02	276.51	1186.15	99.35	974.27	180.15
2171.97	-0.18	1983.55	5.98	1790.73	1.36	1593.37	42.68	1391.31	218.91	1184.41	67.20	972.48	193.06
2170.42	-7.63	1981.96	-42.28	1789.10	-3.14	1591.70	52.05	1389.61	270.54	1182.66	93.95	970.69	135.23
2168.87	-2.78	1980.37	17.99	1787.47	22.56	1590.04	36.79	1387.90	249.29	1180.92	89.84	968.91	105.62
2167.31	-16.96	1978.78	-17.40	1785.85	26.04	1588.37	19.73	1386.20	256.04	1179.17	63.60	967.12	177.47
2165.76	-4.90	1977.19	-43.44	1784.22	12.85	1586.71	63.24	1384.49	254.85	1177.42	87.87	965.33	142.52
2164.21	8.39	1975.60	14.04	1782.60	77.37	1585.04	54.57	1382.79	259.42	1175.68	100.08	963.54	164.89
2162.65	-14.30	1974.01	-15.44	1780.97	9.18	1583.38	60.45	1381.08	257.03	1173.93	55.27	961.75	134.92
2161.10	14.46	1972.42	-11.87	1779.34	-10.19	1581.71	55.36	1379.38	272.46	1172.18	103.99	959.96	97.12
2159.55	-21.51	1970.83	-27.35	1777.71	49.30	1580.04	66.94	1377.67	229.04	1170.44	127.48	958.17	74.22
2157.99	-5.55	1969.24	-35.15	1776.08	6.12	1578.38	38.58	1375.96	208.46	1168.69	125.14	956.38	48.03
2156.44	-4.63	1967.65	-15.78	1774.46	12.74	1576.71	89.81	1374.26	201.69	1166.94	108.19	954.59	143.16
2154.88	-44.63	1966.06	1.79	1772.83	41.17	1575.04	58.57	1372.55	221.56	1165.19	75.69	952.80	50.98
2153.32	5.84	1964.46	6.85	1771.20	29.55	1573.37	60.38	1370.84	177.54	1163.44	96.78	951.01	71.02
2151.77	16.23	1962.87	-47.82	1769.57	5.62	1571.71	66.39	1369.13	201.38	1161.69	112.02	949.21	32.67
2150.21	26.52	1961.28	-27.16	1767.94	-0.81	1570.04	40.41	1367.43	185.96	1159.94	103.27	947.42	32.52
2148.65	33.49	1959.69	-20.07	1766.31	12.61	1568.37	39.23	1365.72	177.16	1158.19	115.95	945.63	48.06
2147.10	1.48	1958.10	-2.04	1764.68	26.32	1566.70	22.64	1364.01	139.95	1156.44	105.14	943.84	75.28
2145.54	5.28	1956.50	24.59	1763.05	33.18	1565.03	43.81	1362.30	152.49	1154.69	117.95	942.04	120.93
2143.98	9.52	1954.91	-13.33	1761.41	7.49	1563.36	71.84	1360.59	167.72	1152.94	125.57	940.25	73.03
2142.43	-6.57	1953.31	-0.07	1759.78	-6.51	1561.69	98.19	1358.88	132.93	1151.19	190.56	938.46	96.63
2140.87	-24.55	1951.72	-37.37	1758.15	-30.56	1560.02	80.37	1357.17	124.44	1149.44	136.13	936.66	63.29
2139.31	3.94	1950.13	-34.27	1756.52	52.59	1558.35	82.13	1355.46	107.63	1147.69	146.88	934.87	40.47
2137.75	3.77	1948.53	-9.43	1754.89	32.97	1556.68	103.67	1353.75	136.55	1145.93	162.98	933.07	106.25
2136.19	47.31	1946.93	6.55	1753.26	-21.99	1555.01	89.96	1352.04	155.93	1144.18	204.54	931.28	72.58
2134.63	7.51	1945.34	17.63	1751.62	58.87	1553.34	61.82	1350.32	158.71	1142.43	179.98	929.48	72.82
2133.07	-10.16	1943.74	5.43	1749.99	28.35	1551.66	135.27	1348.61	148.30	1140.67	212.95	927.68	32.00
2131.51	-14.74	1942.15	5.35	1748.36	54.64	1549.99	62.92	1346.90	171.09	1138.92	204.27	925.89	86.35
2129.95	-23.69	1940.55	-43.81	1746.72	-112.81	1548.32	87.42	1345.19	126.77	1137.17	234.57	924.09	70.03
2128.39	2.76	1938.95	2.95	1745.09	7.55	1546.65	74.09	1343.47	141.46	1135.41	245.30	922.29	101.41
2126.83	-3.73	1937.36	-10.63	1743.45	17.92	1544.97	116.63	1341.76	159.92	1133.66	289.38	920.49	67.58
2125.27	-27.24	1935.76	19.79	1741.82	17.14	1543.30	72.01	1340.05	126.68	1131.90	230.77	918.69	88.81
2123.71	-30.67	1934.16	20.76	1740.18	28.05	1541.62	125.99	1338.33	141.11	1130.15	298.70	916.90	98.41
2122.15	26.74	1932.56	-27.88	1738.55	13.81	1539.95	109.19	1336.62	113.94	1128.39	357.64	915.10	97.62
2120.59	3.96	1930.96	18.01	1736.91	-7.31	1538.28	130.27	1334.90	142.34	1126.64	340.47	913.30	178.33
2119.02	-6.24	1929.37	4.10	1735.27	63.20	1536.60	129.59	1333.19	173.25	1124.88	381.18	911.50	129.52
2117.46	-58.40	1927.77	17.82	1733.64	25.52	1534.92	115.61	1331.47	107.23	1123.12	401.93	909.70	221.46
2115.90	-3.52	1926.17	-27.48	1732.00	29.55	1533.25	93.29	1329.76	138.76	1121.36	442.85	907.90	189.90
2114.33	-52.05	1924.57	-23.18	1730.36	18.31	1531.57	138.03	1328.04	111.85	1119.61	443.37	906.10	225.25
2112.77	-39.40	1922.97	-14.49	1728.73	36.45	1529.90	138.03	1326.33	128.17	1117.85	401.64	904.30	253.96
2111.21	-27.75	1921.37	-25.58	1727.09	32.32	1528.22	142.37	1324.61	136.84	1116.09	463.09	902.50	313.34
2109.64	-2.76	1919.77	-29.39	1725.45	40.76	1526.54	143.11	1322.89	103.02	1114.33	450.48	900.70	307.53
2108.08	-55.40	1918.17	16.01	1723.81	-1.14	1524.87	121.66	1321.17	149.08	1112.57	475.18	898.89	340.89
2106													

Wavenumber	Raman intensity	Wavenumber	Raman intensity
817.42	56.86	596.47	58.53
815.60	114.73	594.60	21.68
813.78	94.12	592.74	29.32
811.96	46.42	590.87	36.97
810.14	128.51	589.01	16.12
808.32	93.68	587.14	-5.36
806.50	34.07	585.27	3.61
804.68	121.64	583.41	-3.85
802.85	65.94	581.54	35.38
801.03	92.54	579.67	7.82
799.21	41.99	577.81	68.44
797.39	77.85	575.94	13.93
795.56	87.97	574.07	70.58
793.74	40.37	572.20	0.82
791.92	29.35	570.33	55.23
790.09	61.43	568.46	111.19
788.27	49.31	566.59	85.83
786.44	25.53	564.72	141.04
784.62	0.07	562.85	141.50
782.79	44.21	560.98	164.93
780.97	-13.92	559.11	178.17
779.14	45.67	557.24	276.32
777.31	29.93	555.37	283.34
775.49	37.25	553.49	343.07
773.66	57.90	551.62	394.68
771.83	-17.72	549.75	548.84
770.00	22.28	547.87	622.68
768.17	-16.89	546.00	895.32
766.34	23.55	544.12	1233.76
764.52	47.45	542.25	1752.78
762.69	14.59	540.37	2535.42
760.86	41.04	538.50	4098.18
759.03	-12.72	536.62	6542.29
757.19	14.02	534.74	9110.68
755.36	17.34	532.87	10165.33
753.53	27.96	530.99	8860.93
751.70	-24.76	529.11	6066.44
749.87	25.63	527.23	3926.92
748.03	37.58	525.36	2751.98
746.20	32.88	523.48	2087.59
744.37	33.85	521.60	1843.62
742.53	-41.70	519.72	1715.01
740.70	65.02	517.84	1777.46
738.86	33.39	515.96	1622.10
737.03	52.42	514.08	1527.51
735.19	68.52	512.20	1383.57
733.36	198.69	510.32	1166.49
731.52	219.74	508.43	1023.78
729.69	185.93	506.55	852.80
727.85	255.90	504.67	788.40
726.01	211.20	502.79	598.88
724.17	241.36	500.90	502.68
722.34	270.03	499.02	555.87
720.50	216.19	497.14	424.25
718.66	222.78	495.25	413.74
716.82	214.69	493.37	403.04
714.98	194.29	491.48	331.03
713.14	216.00	489.59	321.94
711.30	239.94	487.71	330.43
709.46	295.47	485.82	306.06
707.62	391.11	483.93	309.99
705.78	414.29	482.05	347.23
703.94	471.84	480.16	216.88
702.09	448.05		
700.25	358.41		
698.41	337.98		
696.56	379.07		
694.72	309.99		
692.88	260.76		
691.03	205.53		
689.19	204.94		
687.34	127.47		
685.50	142.90		
683.65	78.61		
681.80	67.05		
679.96	65.09		
678.11	45.33		
676.26	34.19		
674.42	32.63		
672.57	7.57		
670.72	25.50		
668.87	-20.33		
667.02	-4.28		
665.17	14.22		
663.32	57.17		
661.47	-20.53		
659.62	-0.49		
657.77	18.55		
655.92	24.54		
654.07	-2.50		
652.21	-10.33		
650.36	24.81		
648.51	19.48		
646.65	-7.36		
644.80	-10.75		
642.95	19.63		
641.09	38.65		
639.24	6.86		
637.38	1.11		
635.52	17.29		
633.67	1.54		
631.81	-9.35		
629.95	14.83		
628.10	-12.91		
626.24	34.66		
624.38	-34.55		
622.52	-25.71		
620.66	29.66		
618.80	57.80		
616.95	15.76		
615.08	43.29		
613.23	5.66		
611.37	0.09		
609.50	4.86		
607.64	28.41		
605.78	38.10		
603.92	87.86		
602.05	39.58		
600.19	24.82		
598.33	61.09		

Table B.2. Raman spectroscopy data for Figure 5.12B.

Raman intensity (arb. units)	Distance across inclusion (µm)
-2.44	1
-1.12	2
-0.05	3
3.05	4
5.13	5
-3.85	6
84.48	7
405.01	8
513.83	9
517.18	10
339.53	11
5.50	12
8.89	13
1.11	14
1.13	15

Appendix C

Table C.1. Method 1 of GC quantification, expressed in mol/g.

Sample	mass (g)	water	carbon dioxide	methane (FID)	ethane (FID)	propane	butane
L-10	1.02	8.30E-06	0.00E+00	6.20E-09	1.81E-10	0.00E+00	0.00E+00
L-AB3	1.03	1.16E-04	0.00E+00	5.68E-09	2.59E-10	0.00E+00	0.00E+00
L-PD2	0.92	4.99E-07	0.00E+00	2.36E-09	9.20E-11	0.00E+00	0.00E+00
L-AB2	0.97	2.04E-05	0.00E+00	6.44E-09	1.64E-10	0.00E+00	0.00E+00
L-7	0.97	2.12E-06	0.00E+00	1.56E-09	8.41E-11	0.00E+00	0.00E+00
L-PD1	0.92	6.58E-06	0.00E+00	2.38E-08	7.00E-10	0.00E+00	0.00E+00
L-4	1.01	3.70E-06	3.95E-10	5.40E-09	2.52E-10	6.06E-11	0.00E+00
L-19	1.10	3.87E-05	1.54E-09	1.62E-08	1.23E-09	1.06E-10	2.61E-11
L-PD18	0.95	1.44E-05	0.00E+00	9.41E-09	3.90E-10	7.08E-11	0.00E+00
L-AB1	0.90	1.88E-06	0.00E+00	6.45E-09	2.69E-10	1.96E-11	0.00E+00
L-17	0.98	1.59E-07	0.00E+00	6.22E-09	1.66E-10	0.00E+00	0.00E+00
L-PD14	1.01	1.04E-05	0.00E+00	2.80E-09	2.01E-10	0.00E+00	0.00E+00
L-PD4	1.00	5.72E-06	1.34E-07	2.68E-08	3.59E-10	0.00E+00	0.00E+00
L-25	0.99	1.02E-05	0.00E+00	6.83E-09	1.52E-10	0.00E+00	0.00E+00
L-9	1.01	6.91E-06	0.00E+00	3.45E-08	8.66E-10	8.54E-11	0.00E+00
L-20	1.16	4.13E-06	0.00E+00	7.47E-09	2.07E-10	0.00E+00	0.00E+00
L-88	0.98	1.17E-06	1.59E-09	2.52E-08	1.10E-09	1.89E-10	1.96E-11
L-23	0.98	7.77E-06	0.00E+00	4.99E-09	1.94E-10	2.83E-11	0.00E+00
L-14	0.95	3.69E-06	0.00E+00	5.15E-09	1.89E-10	3.42E-11	0.00E+00
L-15	0.95	2.62E-05	3.61E-08	2.41E-08	1.51E-09	2.49E-10	6.60E-11
L-96	1.03	4.85E-06	0.00E+00	3.68E-08	2.57E-09	2.71E-10	7.91E-11
L-PD15	1.04	1.23E-05	0.00E+00	3.61E-09	2.47E-10	0.00E+00	0.00E+00
L-PD12	0.81	1.98E-05	0.00E+00	5.19E-08	2.17E-09	2.76E-10	5.19E-11
L-97	0.93	1.01E-05	0.00E+00	4.32E-09	1.36E-10	0.00E+00	0.00E+00
L-11A	0.99	1.20E-05	1.32E-08	2.27E-07	9.56E-09	5.72E-10	1.86E-10
L-115	1.05	2.33E-05	0.00E+00	3.86E-09	1.56E-10	4.00E-11	0.00E+00
L-111	0.87	1.93E-06	0.00E+00	7.08E-09	1.46E-10	3.44E-11	0.00E+00
L-11B	1.05	2.75E-06	4.72E-09	2.12E-09	7.86E-11	0.00E+00	0.00E+00
L-8	0.99	2.09E-05	0.00E+00	7.76E-09	3.96E-10	2.27E-10	0.00E+00
L-2	1.00	6.60E-06	0.00E+00	1.60E-08	4.91E-10	8.05E-11	1.21E-11
L-AB4	0.98	3.02E-05	0.00E+00	5.31E-09	1.35E-10	0.00E+00	0.00E+00
L-114	0.95	1.26E-05	0.00E+00	5.65E-09	2.02E-10	1.49E-11	0.00E+00
L-112	0.95	3.24E-05	0.00E+00	2.67E-09	8.26E-11	0.00E+00	0.00E+00
L-113	1.01	4.90E-06	0.00E+00	3.94E-09	1.57E-10	6.09E-11	0.00E+00
L-PD20	1.00	4.91E-05	0.00E+00	4.02E-09	1.27E-10	0.00E+00	0.00E+00
L-116	1.01	1.32E-05	0.00E+00	7.10E-09	2.10E-10	0.00E+00	0.00E+00
L-PD17	1.00	5.46E-05	0.00E+00	7.73E-09	4.17E-10	0.00E+00	0.00E+00
L-PD23	0.90	9.90E-06	0.00E+00	7.93E-09	2.21E-10	2.08E-11	0.00E+00

Table C.2. Method 2 of GC quantification, expressed in mol/g.

Sample	LAMP-11A	LAMP-9	LAMP-96	LAMP-PD12
mass (g)	1.03	1.04	1.00	1.10
methane	1.73E-07	2.78E-08	2.70E-08	1.55E-08
methane (adj)	1.72E-07	2.74E-08	2.68E-08	1.49E-08
ethane	1.29E-08	1.71E-09	3.29E-09	1.40E-09
ethylene	0.00E+00	0.00E+00	0.00E+00	0.00E+00
propane	3.74E-10	3.03E-11	2.14E-10	4.97E-11
propylene	8.78E-12	2.86E-12	4.57E-12	7.93E-12
acetylene	0.00E+00	0.00E+00	0.00E+00	0.00E+00
isobutane	4.45E-11	2.15E-12	2.51E-11	6.25E-12
butane	9.55E-11	7.19E-12	5.10E-11	1.13E-11
t-2-butene	8.42E-13	3.95E-13	2.52E-13	4.05E-13
1-butene	9.47E-13	6.01E-13	4.52E-13	0.00E+00
isobutylene	2.73E-12	1.11E-12	1.26E-12	1.51E-12
c-2-butene	5.31E-13	2.35E-13	0.00E+00	0.00E+00
2,2-dimethylpropane	2.32E-11	6.33E-13	1.16E-11	3.30E-12
2-methylbutane	3.31E-11	1.30E-12	1.54E-11	3.81E-12
pentane	7.24E-12	5.41E-13	5.07E-12	1.47E-12
1,3-butadiene	0.00E+00	0.00E+00	0.00E+00	0.00E+00
t-2-pentene	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1-pentene	5.26E-13	0.00E+00	2.51E-13	2.73E-13
c-2-pentene	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1-butyne	2.67E-11	7.28E-13	1.21E-11	3.59E-12
2,2-dimethylbutane	0.00E+00	0.00E+00	1.33E-12	3.73E-13
2-methylpentane	7.29E-12	1.71E-12	3.22E-12	7.43E-13
3-methylpentane	7.35E-12	8.67E-13	2.38E-12	7.35E-13
hexane	1.28E-12	0.00E+00	1.22E-12	4.48E-13
t-2-hexene	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1-hexene	0.00E+00	0.00E+00	0.00E+00	0.00E+00
c-2-hexene	0.00E+00	0.00E+00	0.00E+00	0.00E+00

Table C.3. Saturated hydrocarbon values (mol %) calculated using Method 2 of GC quantification.

Sample	LAMP-11A	LAMP-9	LAMP-96	LAMP-PD12
C1 sat	9.27E-01	9.40E-01	8.81E-01	9.10E-01
C2 sat.	6.97E-02	5.84E-02	1.08E-01	8.50E-02
C3 sat.	2.01E-03	1.04E-03	7.04E-03	3.03E-03
C4 sat.	7.55E-04	3.20E-04	2.50E-03	1.07E-03
C5 sat.	3.43E-04	8.47E-05	1.05E-03	5.23E-04
C6 sat.	8.58E-05	8.83E-05	2.68E-04	1.40E-04

Appendix D

Table D.1. Underground in-situ gas detection data for Analysis 1, Borehole 1.

[illegible]

	H ₂	Cl ₂	H ₂ S	CO	CO ₂	CH ₄	
10:14:17	20	0.25	0	0	0.06	2	
10:14:18	20	0.25	0	0	0.06	2	
10:14:19	20	0.25	0	0	0.06	1	
10:14:20	20	0.25	0	0	0.06	1	
10:14:21	20	0.25	0	0	0.06	1	
10:14:22	20	0.2	0	0	0.06	2	
10:14:23	20	0.2	0	0	0.06	2	
10:14:24	20	0.2	0	0	0.06	2	
10:14:25	20	0.2	0	0	0.06	2	
10:14:26	20	0.2	0	0	0.06	2	
10:14:27	20	0.2	0	0	0.06	2	
10:14:28	20	0.2	0	0	0.06	2	
10:14:29	20	0.15	0	0	0.06	2	
10:14:30	20	0.15	0	0	0.06	2	
10:14:31	20	0.15	0	0	0.06	2	
10:14:32	20	0.15	0	0	0.06	2	
10:14:33	20	0.15	0	0	0.06	1	
10:14:34	20	0.15	0	0	0.07	1	
10:14:35	20	0.15	0	0	0.07	1	
10:14:36	20	0.15	0	0	0.07	2	
10:14:37	20	0.15	0	0	0.07	2	
10:14:38	20	0.1	0	0	0.07	2	
10:14:39	20	0.1	0	0	0.07	2	
10:14:40	20	0.1	0	0	0.07	2	
10:14:41	20	0.1	0	0	0.07	2	
10:14:42	20	0.1	0	0	0.07	2	
10:14:43	20	0.1	0	0	0.07	1	
10:14:44	15	0.1	0	0	0.07	2	
10:14:45	20	0.1	0	0	0.07	2	
10:14:46	20	0.1	0	0	0.07	2	
10:14:47	20	0.1	0	0	0.07	2	
10:14:48	20	0.1	0	0	0.07	2	
10:14:49	15	0.05	0	0	0.07	2	
10:14:50	15	0.05	0	0	0.07	1	
10:14:51	15	0.05	0	0	0.07	1	
10:14:52	15	0.05	0	0	0.07	1	
10:14:53	15	0.05	0	0	0.07	2	
10:14:53	Instrument switch off						

Table D.2. Underground in-situ gas detection data for Analysis 1, Borehole 2.

[illegible]

Table D.3. Underground in-situ gas detection data for Analysis 1, Borehole 3.

H ₂										Cl ₂										H ₂ S										CO										CO ₂										CH ₄										H ₂										Cl ₂										H ₂ S										CO										CO ₂										CH ₄																																																																																																																																																															
200.00 ppm										0.50 ppm										5.00 ppm										30.00 ppm										0.50 Vol%										10.00 %LEL										11:36:31										25										0.05										0										0										0.08										1										11:38:42										30										0										0										0										0.11										24										11:40:55										25										0.05										0										0										0.07										2									
400.00 ppm										1.00 ppm										10.00 ppm										200.00 ppm										1.50 Vol%										20.00 %LEL										11:36:32										25										0.05										0										0										0.08										1										11:38:43										35										0										0										6										0.1										35										11:40:56										25										0.05										0										0										0.07										2									
11:34:34 Instrument switch on																																																												11:36:33										25										0.05										0										0										0.08										1										11:38:44										40										0										0										8										0.1										44										11:40:57										25										0.05										0										0										0.07										2									
11:34:36 any channel warning changed (Channel 5, ch4 : 00000001, 00000005)																																																												11:36:34										25										0.05										0										0										0.08										1										11:38:45										40										0										0										12										0.1										53										11:40:58										25										0.05										0										0										0.07										2									
11:34:36 INV INV INV INV OVR WUP																																																												11:36:35										25										0.05										0										0										0.08										1										11:38:46										45										0										0										14										0.1										58										11:40:59										25										0.05										0										0										0.07										2									
11:34:37 INV INV INV INV OVR WUP																																																												11:36:36										25										0.05										0										0										0.08										1										11:38:47										45										0										0										16										0.1										63										11:41:00										25										0.05										0										0										0.07										2									
11:34:38 any channel warning changed (Channel 4, CO2 : 00000001, 01000001)																																																												11:36:37										25										0.05										0										0										0.08										1										11:38:48										50										0										0										16										0.09										64										11:41:01										25										0.05										0										0										0.07										2									
11:34:38 any channel warning changed (Channel 5, ch4 : 00000005, 01000005)																																																												11:36:38										25										0.05										0										0										0.08										1										11:38:49										50										0										0										18										0.09										66										11:41:02										25										0.05										0										0										0.08										2									
11:34:38 INV INV INV INV OVR WUP																																																												11:36:39										25										0.05										0										0										0.08										1										11:38:50										55										0										0										18										0.09										67										11:41:03										25										0.05										0										0										0.08										2									
11:34:39 any channel warning changed (Channel 4, CO2 : 01000001, 00000005)																																																												11:36:40										25										0.05										0										0										0.08										1										11:38:51										60										0										0										18										0.08										68										11:41:04										25										0.05										0										0										0.08										2									
11:34:39 any channel warning changed (Channel 5, ch4 : 01000005, 00000001)																																																												11:36:41										25										0.05										0										0										0.08										1										11:38:52										60										0										0										18										0.08										69										11:41:05										25										0.05										0										0										0.08										2									
11:34:39 25 0 0 0 WUP OVR																																																												11:36:42										25										0.05										0										0										0.08										1										11:38:53										65										0										0										18										0.08										70										11:41:06										25										0.05										0										0										0.08										2									
11:34:40 any channel warning changed (Channel 4, CO2 : 00000005, 00000001)																																																												11:36:43										25										0.05										0										0										0.08										1										11:38:54										65										0										0										18										0.07										71										11:41:07										25										0.05										0										0										0.07										2									
11:34:40 25 0 0 0 WUP OVR																																																												11:36:44										25										0.05										0										0										0.08										1										11:38:55										70										0										0										18										0.07										68										11:41:08										25										0.05										0										0										0.07										2									
11:34:44 any channel warning changed (Channel 5, ch4 : 00000001, 00000005)																																																												11:36:45										25										0.05										0										0										0.08										1										11:38:56										70										0										0										18										0.07										70										11:41:09										25										0.05										0										0										0.07										2									
11:34:44 25 0 0 0 WUP WUP																																																												11:36:46										25										0.05										0										0										0.08										1										11:38:57										70										0										0										18										0.07										71										11:41:10										25										0.05										0										0										0.07										2									
11:34:45 25 0 0 0 WUP WUP																																																												11:36:47										25										0.05										0										0										0.09										1										11:38:58										75										0										0										20										0.07										69										11:41:11										25										0.05										0										0										0.07										2									
11:34:45 Unknown Event 49 : FF 00 0																																																																																																																																																																																																																																																																													

Table D.4. Underground in-situ gas detection data for Analysis 1, Borehole 4.

[illegible]

H ₂	Cl ₂	H ₂ S	CO	CO ₂	CH ₄		H ₂	Cl ₂	H ₂ S	CO	CO ₂	CH ₄		H ₂	Cl ₂	H ₂ S	CO	CO ₂	CH ₄		
13:19:27	20	0	0	0	0.07	1	13:21:42	20	0	0	0	0.07	2	13:23:57	20	0	0	0	0	0.07	1
13:19:28	20	0	0	0	0.07	2	13:21:43	20	0	0	0	0.07	1	13:23:58	20	0	0	0	0	0.08	1
13:19:29	20	0	0	0	0.07	2	13:21:44	20	0	0	0	0.07	1	13:23:59	20	0	0	0	0	0.08	1
13:19:30	20	0	0	0	0.07	2	13:21:45	20	0	0	0	0.07	1	13:23:59 alarm acknowledged							
13:19:31	20	0	0	0	0.07	1	13:21:46	20	0	0	0	0.07	2	13:24:00	20	0	0	0	0	0.08	1
13:19:32	20	0	0	0	0.07	1	13:21:47	20	0	0	0	0.07	1	13:24:01	20	0	0	0	0	0.07	1
13:19:33	20	0	0	0	0.07	1	13:21:48	20	0	0	0	0.07	1	13:24:02	20	0	0	0	0	0.07	1
13:19:34	20	0	0	0	0.07	1	13:21:49	20	0	0	0	0.07	2	13:24:02 instrument switch off							
13:19:35	20	0	0	0	0.07	1	13:21:50	20	0	0	0	0.07	2								
13:19:36	20	0	0	0	0.07	1	13:21:51	20	0	0	0	0.07	1								
13:19:37	20	0	0	0	0.07	1	13:21:52	20	0	0	0	0.07	1								
13:19:38	20	0	0	0	0.07	2	13:21:53	20	0	0	0	0.07	2								
13:19:39	20	0	0	0	0.07	2	13:21:54	20	0	0	0	0.07	2								
13:19:40	20	0	0	0	0.07	2	13:21:55	20	0	0	0	0.07	2								
13:19:41	20	0	0	0	0.07	2	13:21:56	20	0	0	0	0.07	2								
13:19:42	20	0	0	0	0.07	2	13:21:57	20	0	0	0	0.07	1								
13:19:43	20	0	0	0	0.07	2	13:21:58	20	0	0	0	0.06	2								
13:19:44	20	0	0	0	0.07	2	13:21:59	20	0	0	0	0.06	1								
13:19:45	20	0	0	0	0.07	2	13:22:00	20	0	0	0	0.07	1								
13:19:46	20	0	0	0	0.07	2	13:22:01	20	0	0	0	0.07	1								
13:19:47	20	0	0	0	0.07	2	13:22:02	20	0	0	0	0.07	1								
13:19:48	20	0	0	0	0.07	2	13:22:03	20	0	0	0	0.07	1								
13:19:49	20	0	0	0	0.07	1	13:22:04	20	0	0	0	0.07	1								
13:19:50	20	0	0	0	0.07	1	13:22:05	20	0	0	0	0.07	1								
13:19:51	20	0	0	0	0.06	1	13:22:06	20	0	0	0	0.06	1								
13:19:52	20	0	0	0	0.07	2	13:22:07	20	0	0	0	0.06	1								
13:19:53	20	0	0	0	0.07	2	13:22:08	20	0	0	0	0.06	1								
13:19:54	20	0	0	0	0.07	2	13:22:09	20	0	0	0	0.06	1								
13:19:55	20	0	0	0	0.07	2	13:22:10	20	0	0	0	0.07	1								
13:19:56	20	0	0	0	0.07	2	13:22:11	20	0	0	0	0.07	1								
13:19:57	20	0	0	0	0.06	1	13:22:12	20	0	0	0	0.07	2								
13:19:58	20	0	0	0	0.06	1	13:22:13	20	0	0	0	0.07	1								
13:19:59	20	0	0	0	0.07	1	13:22:14	20	0	0	0	0.06	1								
13:20:00	20	0	0	0	0.07	1	13:22:15	20	0	0	0	0.06	1								
13:20:01	20	0	0	0	0.07	1	13:22:16	20	0	0	0	0.07	1								
13:20:02	20	0	0	0	0.07	1	13:22:17	20	0	0	0	0.07	1								
13:20:03	20	0	0	0	0.07	1	13:22:18	20	0	0	0	0.07	1								
13:20:04	20	0	0	0	0.07	1	13:22:19	20	0	0	0	0.07	1								
13:20:05	20	0	0	0	0.07	1	13:22:20	20	0	0	0	0.07	1								
13:20:06	20	0	0	0	0.07	1	13:22:21	20	0	0	0	0.06	1								
13:20:07	20	0	0	0	0.07	1	13:22:22	20	0	0	0	0.06	1								
13:20:08	20	0	0	0	0.07	2	13:22:23	20	0	0	0	0.06	2								
13:20:09	20	0	0	0	0.07	1	13:22:24	20	0	0	0	0.07	2								
13:20:10	20	0	0	0	0.07	1	13:22:25	20	0	0	0	0.07	2								
13:20:11	20	0	0	0	0.07	1	13:22:26	20	0	0	0	0.07	2								
13:20:12	20	0	0	0	0.07	1	13:22:27	20	0	0	0	0.07	1								
13:20:13	20	0	0	0	0.07	1	13:22:28	20	0	0	0	0.07	1								
13:20:14	20	0	0	0	0.07	1	13:22:29	20	0	0	0	0.07	2								
13:20:15	20	0	0	0	0.07	1	13:22:30	20	0	0	0	0.07	2								
13:20:16	20	0	0	0	0.07	2	13:22:31	20	0	0	0	0.07	1								
13:20:17	20	0	0	0	0.07	2	13:22:32	20	0	0	0	0.07	1								
13:20:18	20	0	0	0	0.07	2	13:22:33	20	0	0	0	0.07	1								
13:20:19	20	0	0	0	0.07	1	13:22:34	20	0	0	0	0.07	1								
13:20:20	20	0	0	0	0.07	1	13:22:35	20	0	0	0	0.07	1								
13:20:21	20	0	0	0	0.07	2	13:22:36	20	0	0	0	0.07	1								
13:20:22	20	0	0	0	0.07	2	13:22:37	20	0	0	0	0.06	2								
13:20:23	20	0	0	0	0.07	2	13:22:38	20	0	0	0	0.06	2								
13:20:24	20	0	0	0	0.07	1	13:22:39	20	0	0	0	0.06	2								
13:20:25	20	0	0	0	0.07	1	13:22:40	20	0	0	0	0.07	2								
13:20:26	20	0	0	0	0.07	1	13:22:41	20	0	0	0	0.07	2								
13:20:27	20	0	0	0	0.07	1	13:22:42	20	0	0	0	0.07	2								
13:20:28	20	0	0	0	0.06	1	13:22:43	20	0	0	0	0.07	2								
13:20:29	20	0	0	0	0.06	1	13:22:44	20	0	0	0	0.07	2								
13:20:30	20	0	0	0	0.07	2	13:22:45	20	0	0	0	0.06	2								
13:20:31	20	0	0	0	0.07	2	13:22:46	20	0	0	0	0.06	2								
13:20:32	20	0	0	0	0.07	2	13:22:47	20	0	0	0	0.07	2								
13:20:33	20	0	0	0	0.07	2	13:22:48	20	0	0	0	0.07	2								
13:20:34	20	0	0	0	0.07	2	13:22:49	20	0	0	0	0.07	2								
13:20:35	20	0	0	0	0.07	1	13:22:50	20	0	0	0	0.07	2								
13:20:36	20	0	0	0	0.07	1	13:22:51	20	0	0	0	0.07	2								
13:20:37	20	0	0	0	0.07	1	13:22:52	20	0	0	0	0.07	2								
13:20:38	20	0	0	0	0.07	2	13:22:53	20	0	0	0	0.07	2								
13:20:39	20	0	0	0	0.07	2	13:22:54	20	0	0	0	0.07	2								
13:20:40	20	0	0	0	0.06	2	13:22:55	20	0	0	0	0.07	2								
13:20:41	20	0	0	0	0.07	2	13:22:56	20	0	0	0	0.07	1								
13:20:42	20	0	0	0	0.07	1	13:22:57	20	0	0	0	0.07	2								
13:20:43	20	0	0	0	0.07	2	13:22:58	20	0	0	0	0.07	2								
13:20:44	20	0	0	0	0.07	2	13:22:59	20	0	0	0	0.07	2								
13:20:45	20	0	0	0	0.07	2	13:23:00	20	0	0	0	0.07	2								
13:20:46	20	0	0	0	0.07	1	13:23:01	20	0	0	0	0.07	2								
13:20:47	20	0	0	0	0.07	1	13:23:02	20	0	0	0	0.07	2								
13:20:48	20	0	0	0	0.07	1	13:23:03	20	0	0	0	0.07	1								
13:20:49	20	0	0	0	0.07	1	13:23:04	20	0	0	0	0.07	1								
13:20:50	20	0	0	0	0.07	1	13:23:05	20	0.05	0	0	0.07	1								
13:20:51	20	0	0	0	0.07	1	13:23:06	20	0.05	0	0	0.07	1								
13:20:52	20	0	0	0	0.07	1	13:23:07	20	0.1	0	0	0.07	1								
13:20:53	20	0	0	0	0.07	1	13:23:08	20	0.1	0	0	0.07	1								
13:20:54	20	0	0	0	0.07	1	13:23:09	20	0.1	0	0	0.07	2								
13:20:55	20	0	0	0	0.07	2	13:23:10	20	0.1	0	0	0.07	1								
13:20:56	20	0	0	0	0.07	1	13:23:11	20	0.1	0	0	0.07	1								
13:20:57	20	0	0	0	0.06	1	13:23:12	20	0.1	0	0	0.07	1								
13:20:58	20	0	0	0	0.07	1	13:23:13	20	0.1	0	0	0.07	1								
13:20:59	20	0	0	0	0.07	1	13:23:14	20	0.15	0	0	0.07	1								
13:21:00	20	0	0	0	0.07	1	13:23:15	20	0.15	0	0	0.07	1								
13:21:01	20	0	0	0	0.07	1	13:23:16	20	0.15	0	0	0.07	1								
13:21:02	20	0	0	0	0.07	1	13:23:17	20	0.1	0	0	0.07	1								
13:21:03	20	0	0	0	0.07	1															

Table D.5. Underground in-situ gas detection data for Analysis 2, Boreholes 1 and 2.

	H ₂	Cl ₂	H ₂ S	CO	CO ₂	CH ₄		H ₂	Cl ₂	H ₂ S	CO	CO ₂	CH ₄		H ₂	Cl ₂	H ₂ S	CO	CO ₂	CH ₄		H ₂	Cl ₂	H ₂ S	CO	CO ₂	CH ₄		
	200.00 ppm	0.50 ppm	5.00 ppm	30.00 ppm	0.50 Vol%	10.00 %LEL	08:30:15	25	0	0	0	0	0.1	5	08:32:28	25	0	0	0	0.14	4	08:34:30	100	0	0	0	12	0.04	12
	400.00 ppm	1.00 ppm	10.00 ppm	200.00 ppm	1.50 Vol%	20.00 %LEL	08:30:16	25	0	0	0	0	0.1	5	08:32:29	25	0	0	0	0.14	4	08:34:31	100	0	0	0	12	0.04	11
08:28:16 Instrument switch on							08:30:17	25	0	0	0	0	0.1	5	08:32:30	25	0	0	0	0.13	4	08:34:32	95	0	0	0	12	0.04	18
08:28:17 INV INV INV INV WUP WUP							08:30:18	25	0	0	0	0	0.1	5	08:32:31	25	0	0	0	0.13	4	08:34:33	95	0	0	0	10	0.04	18
08:28:18 any channel warning changed (Channel 4, CO2 : 00000001, 01000001)							08:30:19	25	0	0	0	0	0.1	5	08:32:32	25	0	0	0	0.13	5	08:34:34 Alarm A2 on (Channel 5, ch4)							
08:28:18 any channel warning changed (Channel 5, ch4 : 00000001, 01000001)							08:30:20	25	0	0	0	0	0.11	5	08:32:33	25	0	0	0	0.13	5	08:34:34	90	0	0	0	10	0.04	20
08:28:18 INV INV INV INV WUP WUP							08:30:21	25	0	0	0	0	0.11	5	08:32:34	25	0	0	0	0.12	4	08:34:35	90	0	0	0	10	0.04	21
08:28:19 any channel warning changed (Channel 4, CO2 : 01000001, 00000001)							08:30:22	25	0	0	0	0	0.11	5	08:32:35	25	0	0	0	0.12	4	08:34:36	90	0	0	0	10	0.04	21
08:28:19 any channel warning changed (Channel 5, ch4 : 01000001, 00000005)							08:30:23	25	0	0	0	0	0.11	5	08:32:36	25	0	0	0	0.12	4	08:34:37	85	0	0	0	10	0.04	20
08:28:19 INV INV INV INV WUP WUP							08:30:24	25	0	0	0	0	0.11	5	08:32:37	25	0	0	0	0.12	4	08:34:38	85	0	0	0	8	0.04	20
08:28:20 30 0 0 0 WUP WUP							08:30:25	25	0	0	0	0	0.11	5	08:32:38	25	0	0	0	0.12	4	08:34:39	80	0	0	0	8	0.04	21
08:28:21 any channel warning changed (Channel 5, ch4 : 00000005, 00000001)							08:30:26	25	0	0	0	0	0.11	5	08:32:39	25	0	0	0	0.12	4	08:34:40	80	0	0	0	8	0.04	20
08:28:21 30 0 0 0 WUP WUP							08:30:27	25	0	0	0	0	0.11	5	08:32:40	25	0	0	0	0.12	5	08:34:41 Alarm A2 off (Channel 5, ch4)							
08:28:23 Unknown Event 49 : FF 00 00 00 00 00 00 00 00 00 00 00 00 00 00 00 00 00 00 00 00 00							08:30:28	25	0	0	0	0	0.11	5	08:32:41	25	0	0	0	0.12	5	08:34:41	80	0	0	0	8	0.04	18
08:28:24 Unknown Event 47 : FF 00 00 00 00 00 00 00 00 00 00 00 00 00 00 00 00 00 00 00 00 00							08:30:29	25	0	0	0	0	0.11	5	08:32:42	25	0	0	0	0.12	5	08:34:42	75	0	0	0	8	0.04	18
08:28:25 25 0 0 0 WUP OVR							08:30:30	25	0	0	0	0	0.11	5	08:32:43	25	0	0	0	0.11	5	08:34:43	75	0	0	0	8	0.04	19
08:28:26 25 0 0 0 WUP OVR							08:30:31	20	0	0	0	0	0.11	5	08:32:44	25	0	0	0	0.11	5	08:34:44	75	0	0	0	8	0.04	18
08:28:27 25 0 0 0 WUP OVR							08:30:32	20	0	0	0	0	0.11	5	08:32:45	25	0	0	0	0.11	5	08:34:45	70	0	0	0	8	0.04	16
08:28:28 25 0 0 0 WUP OVR							08:30:33	25	0	0	0	0	0.11	5	08:32:46	25	0	0	0	0.11	5	08:34:46	70	0	0	0	8	0.04	17
08:28:29 25 0 0 0 WUP OVR							08:30:34	25	0	0	0	0	0.11	5	08:32:47	25	0	0	0	0.11	5	08:34:47	70	0	0	0	8	0.04	18
08:28:30 25 0 0 0 WUP OVR							08:30:35	25	0	0	0	0	0.11	5	08:32:48	25	0	0	0	0.11	5	08:34:48	70	0	0	0	6	0.04	18
08:28:31 25 0 0 0 WUP OVR							08:30:36	25	0	0	0	0	0.11	5	08:32:49	25	0	0	0	0.11	5	08:34:49	65	0	0	0	6	0.04	18
08:28:32 25 0 0 0 WUP WUP							08:30:37	25	0	0	0	0	0.11	5	08:32:50	25	0	0	0	0.11	5	08:34:50	65	0	0	0	6	0.04	18
08:28:33 25 0 0 0 WUP WUP							08:30:38	25	0	0	0	0	0.11	5	08:32:51	25	0	0	0	0.11	5	08:34:51	65	0.05	0	0	6	0.04	18
08:28:34 25 0 0 0 WUP WUP							08:30:39	25	0	0	0	0	0.11	5	08:32:52	25	0	0	0	0.11	4	08:34:52	65	0.05	0	0	6	0.04	17
08:28:35 any channel warning changed (Channel 5, ch4 : 00000001, 00000005)							08:30:40	20	0	0	0	0	0.11	4	08:32:53	25	0	0	0	0.11	4	08:34:53	65	0.05	0	0	6	0.04	17
08:28:35 25 0 0 0 WUP WUP							08:30:41	25	0	0	0	0	0.11	5	08:32:54	25	0	0	0	0.11	5	08:34:54	65	0.05	0	0	6	0.04	17
08:28:36 25 0 0 0 WUP WUP							08:30:42	25	0	0	0	0	0.11	5	08:32:55	25	0	0	0	0.11	4	08:34:55	65	0.05	0	0	0.04	17	
08:28:37 25 0 0 0 WUP WUP							08:30:43	25	0	0	0	0	0.11	5	08:32:56	25	0	0	0	0.11	4	08:34:56	65	0.05	0	0	0.04	17	
08:28:38 25 0 0 0 WUP WUP							08:30:44	25	0	0	0	0	0.11	4	08:32:57	25	0	0	0	0.11	5	08:34:57	65	0.05	0	0	0.04	17	
08:28:39 25 0 0 0 WUP WUP							08:30:45	25	0	0	0	0	0.11	4	08:32:58	25	0	0	0	0.11	5	08:34:58	60	0.1	0	0	0.04	17	
08:28:40 25 0 0 0 WUP WUP							08:30:46	25	0	0	0	0	0.11	5	08:32:59	25	0	0	0	0.11	5	08:34:59	60	0.1	0	0	0.04	17	
08:28:41 25 0 0 0 WUP WUP							08:30:47	25	0	0	0	0	0.11	5	08:33:00	25	0	0	0	0.11	5	08:35:00	60	0.1	0	0	0.04	17	
08:28:42 25 0 0 0 WUP WUP							08:30:48	25	0	0	0	0	0.11	4	08:33:01	25	0	0	0	0.11	5	08:35:01	60	0.1	0	0	0.04	17	
08:28:43 25 0 0 0 WUP WUP							08:30:49	25	0	0	0	0	0.11	4	08:33:02	25	0	0	0	0.1	5	08:35:02	60	0.1	0	0	0.04	17	
08:28:44 25 0 0 0 WUP WUP							08:30:50	25	0	0	0	0	0.11	4	08:33:03	25	0	0	0	0.1	5	08:35:03	60	0.1	0	0	0.04	17	
08:28:45 any channel warning changed (Channel 5, ch4 : 00000005, 00000001)							08:30:51	25	0	0	0	0	0.11	4	08:33:04	25	0	0	0	0.1	5	08:35:04	60	0.1	0	0	0.04	17	
08:28:45 25 0 0 0 WUP WUP							08:30:52	25	0	0	0	0	0.11	5	08:33:05	25	0	0	0	0.1	5	08:35:05	60	0.1	0	0	0.04	17	
08:28:46 25 0 0 0 WUP WUP							08:30:53	25	0	0	0	0	0.11	5	08:33:06	25	0	0	0	0.1	5	08:35:06	55	0.1	0	0	0.04	16	
08:28:47 25 0 0 0 WUP WUP							08:30:54	25	0	0	0	0	0.11	5	08:33:07	30	0	0	0	0.1	5	08:35:07	55	0.1	0	0	0.04	16	
08:28:48 20 0 0 0 WUP WUP							08:30:55	25	0	0	0	0	0.11	5	08:33:08 Alarm A1 on (Channel 3, CO)						08:35:08	55	0.1	0	0	0.04	16		
08:28:49 20 0 0 0 WUP WUP							08:30:56	25	0	0	0	0	0.11	5	08:33:08 Alarm A1 on (Channel 5, ch4)						08:35:09	55	0.1	0	0	0.04	16		
08:28:50 20 0 0 0 WUP WUP							08:30:57	25	0	0	0	0	0.11	5	08:33:08	90	0	0	40	0.1	17	08:35:10	55	0.1	0	0	0.04	16	
08:28:51 20 0 0 0 WUP WUP							08:30:58	25	0	0	0	0	0.11	5	08:33:09 Alarm A2 on (Channel 5, ch4)						08:35:11	55	0.1	0	0	0.04	16		
08:28:52 20 0 0 0 WUP WUP							08:30:59	25	0	0	0	0	0.11	5	08:33:09	145	0	0	54	0.1	28	08:35:12	55	0.15	0	0	0.04	16	
08:28:53 20 0 0 0 WUP WUP							08:31:00	25	0	0	0	0	0.11	5	08:33:10 Alarm A1 on (Channel 0, H2)						08:35:13	55	0.15	0	0	0.04	16		
08:28:54 20 0 0 0 WUP WUP							08:31:01	25	0	0	0	0	0.1	5	08:33:10	210	-0.1	0	66	0.1	42	08:35:14	55	0.15	0	0	0.04	16	
08:28:55 20 0 0 0 WUP WUP							08:31:02	25	0	0	0	0	0.1	5	08:33:11 any channel warning changed (Channel 1, C12 : 00000000, 00000004)						08:35:15	55	0.15	0	0	0.04	16		
08:28:56 20 0 0 0 WUP WUP							08:31:03	25	0	0	0	0	0.1	5	08:33:11	290	-0.5	0	90	0.1	58	08:35:16	55	0.15	0	0	0.04	15	
08:28:57 20 0 0 0 WUP WUP							08:31:04	25	0	0	0	0	0.11	5	08:33:12	370	-0.7	0	116	0.1	94	08:35:17	50	0.15	0	0	0.04	15	
08:28:58 20 0 0 0 WUP WUP							08:31:05	25	0	0	0	0	0.11	5	08:33:13 Alarm A2 on (Channel 0, H2)						08:35:18	50	0.15	0	0	0.04	15		
08:28:59 20 0 0 0 WUP WUP							08:31:06	25	0	0	0	0	0.11	5	08:33:13	455	-0.9	0	130	0.1 OVR	08:35:19	50	0.15	0	0	0.04	15		
08:29:00 20 0 0 0 WUP WUP							08:31:07	25	0	0	0	0	0.1	5	08:33:14	540	-1	0	134	0.09 OVR	08:35:20	50	0.15	0	0	0.04	15		
08:29:01 20 0 0 0 WUP WUP																													

	H ₂	Cl ₂	H ₂ S	CO	CO ₂	CH ₄		H ₂	Cl ₂	H ₂ S	CO	CO ₂	CH ₄		H ₂	Cl ₂	H ₂ S	CO	CO ₂	CH ₄		H ₂	Cl ₂	H ₂ S	CO	CO ₂	CH ₄							
08:45:42	20	0.2	0	0	0.09	6	08:47:57	20	0.05	0	0	0.1	5	08:49:58	270	0	0	60	0.04	7	08:52:11	115	0.05	0	20	0.06	6	08:54:25	85	0.1	0	14	0.06	6
08:45:43	20	0.2	0	0	0.09	6	08:47:58	20	0.05	0	0	0.1	5	08:49:59	265	0	0	60	0.04	8	08:52:12	110	0.05	0	20	0.06	6							
08:45:44	20	0.2	0	0	0.09	6	08:47:59	20	0.05	0	0	0.1	5	08:50:00	265	0	0	58	0.04	8	08:52:13	110	0.1	0	20	0.06	6							
08:45:45	20	0.2	0	0	0.09	5	08:48:00	20	0.05	0	0	0.1	5	08:50:01	260	0	0	56	0.04	7	08:52:14	110	0.1	0	20	0.06	6							
08:45:46	20	0.2	0	0	0.09	6	08:48:01	20	0.05	0	0	0.1	5	08:50:02	260	0	0	54	0.04	7	08:52:15	110	0.1	0	20	0.06	6							
08:45:47	20	0.15	0	0	0.09	6	08:48:02	20	0.05	0	0	0.1	6	08:50:03	260	0	0	54	0.04	7	08:52:16	110	0.1	0	20	0.06	6							
08:45:48	20	0.15	0	0	0.09	6	08:48:03	20	0.05	0	0	0.1	5	08:50:04	255	0	0	52	0.04	7	08:52:17	110	0.05	0	20	0.06	6							
08:45:49	20	0.15	0	0	0.09	6	08:48:04	20	0.05	0	0	0.1	5	08:50:05	255	0	0	52	0.04	7	08:52:18	110	0.05	0	20	0.06	6							
08:45:50	20	0.15	0	0	0.09	6	08:48:05	20	0.05	0	0	0.1	5	08:50:06	250	0	0	50	0.04	8	08:52:19	110	0.05	0	20	0.06	7							
08:45:51	20	0.15	0	0	0.09	6	08:48:06	20	0.05	0	0	0.1	6	08:50:07	250	0	0	50	0.04	7	08:52:20	110	0.05	0	20	0.06	6							
08:45:52	20	0.15	0	0	0.09	6	08:48:07	20	0	0	0	0.1	6	08:50:08	245	0	0	48	0.04	7	08:52:21	110	0.05	0	20	0.06	6							
08:45:53	20	0.15	0	0	0.09	6	08:48:08	20	0	0	0	0.1	6	08:50:09	245	0	0	48	0.04	7	08:52:22	110	0.05	0	20	0.06	7							
08:45:54	20	0.15	0	0	0.09	6	08:48:09	20	0	0	0	0.1	5	08:50:10	240	0	0	46	0.04	8	08:52:23	110	0.05	0	20	0.06	7							
08:45:55	20	0.15	0	0	0.09	6	08:48:10	20	0	0	0	0.1	5	08:50:11	240	0	0	46	0.04	7	08:52:24	110	0.05	0	20	0.06	7							
08:45:56	20	0.15	0	0	0.09	6	08:48:11	20	0	0	0	0.1	5	08:50:12	235	0	0	46	0.04	7	08:52:25	110	0.05	0	20	0.06	7							
08:45:57	20	0.15	0	0	0.09	6	08:48:12	20	0	0	0	0.1	5	08:50:13	230	0	0	46	0.04	7	08:52:26	110	0.05	0	20	0.06	6							
08:45:58	20	0.15	0	0	0.09	6	08:48:13	20	0	0	0	0.1	6	08:50:14	225	0	0	44	0.05	7	08:52:27	105	0.05	0	20	0.06	6							
08:45:59	20	0.15	0	0	0.09	6	08:48:14	20	0	0	0	0.1	6	08:50:15	220	0	0	44	0.05	8	08:52:28	105	0.05	0	20	0.06	6							
08:46:00	20	0.15	0	0	0.09	6	08:48:15	20	0	0	0	0.1	5	08:50:16	220	0	0	44	0.04	8	08:52:29	105	0.05	0	20	0.06	6							
08:46:01	20	0.15	0	0	0.09	5	08:48:16	20	0	0	0	0.09	5	08:50:17	215	0	0	42	0.04	7	08:52:30	105	0.05	0	20	0.06	6							
08:46:02	20	0.15	0	0	0.09	5	08:48:17	20	0	0	0	0.1	5	08:50:18	215	0.05	0	42	0.04	7	08:52:31	105	0.05	0	20	0.06	6							
08:46:03	20	0.15	0	0	0.09	5	08:48:18	20	0	0	0	0.1	6	08:50:19	210	0.05	0	42	0.04	7	08:52:32	105	0.05	0	20	0.06	6							
08:46:04	20	0.15	0	0	0.09	6	08:48:19	20	0	0	0	0.1	6	08:50:20	210	0.05	0	42	0.04	7	08:52:33	105	0.05	0	20	0.06	6							
08:46:05	20	0.15	0	0	0.09	6	08:48:20	20	0	0	0	0.1	6	08:50:21	205	0.05	0	42	0.04	8	08:52:34	105	0.05	0	20	0.06	6							
08:46:06	20	0.15	0	0	0.09	6	08:48:21	20	0	0	0	0.09	6	08:50:22	205	0.05	0	40	0.04	8	08:52:35	105	0.05	0	20	0.06	6							
08:46:07	20	0.15	0	0	0.09	5	08:48:22	20	0	0	0	0.09	6	08:50:23	200	0.05	0	40	0.05	8	08:52:36	105	0.05	0	20	0.06	6							
08:46:08	20	0.15	0	0	0.09	5	08:48:23	20	0	0	0	0.09	6	08:50:24	200	0.05	0	40	0.05	7	08:52:37	105	0.05	0	20	0.06	6							
08:46:09	20	0.15	0	0	0.09	6	08:48:24	20	0	0	0	0.09	6	08:50:25	200	0.05	0	40	0.05	7	08:52:38	105	0.05	0	20	0.06	6							
08:46:10	20	0.15	0	0	0.09	5	08:48:25	20	0	0	0	0.09	6	08:50:26 Alarm A1 off (Channel 0, H2)							08:52:39	105	0.05	0	20	0.06	6							
08:46:11	20	0.15	0	0	0.09	5	08:48:26	20	0	0	0	0.09	6	08:50:26	195	0.05	0	40	0.05	7	08:52:40	105	0.05	0	20	0.06	6							
08:46:12	20	0.15	0	0	0.09	5	08:48:27	20	0	0	0	0.09	6	08:50:27	195	0.05	0	38	0.05	8	08:52:41	105	0.05	0	20	0.06	6							
08:46:13	20	0.15	0	0	0.09	5	08:48:28	20	0	0	0	0.09	6	08:50:28	190	0.05	0	38	0.04	7	08:52:42	105	0.1	0	20	0.06	6							
08:46:14	20	0.15	0	0	0.09	5	08:48:29	20	0	0	0	0.09	6	08:50:29	190	0.05	0	38	0.04	7	08:52:43	105	0.1	0	20	0.06	6							
08:46:15	20	0.15	0	0	0.09	6	08:48:30	20	0	0	0	0.09	6	08:50:30	185	0.05	0	36	0.04	7	08:52:44	105	0.1	0	20	0.06	6							
08:46:16	20	0.15	0	0	0.09	6	08:48:31	20	0	0	0	0.09	6	08:50:31	185	0.05	0	36	0.05	7	08:52:45	105	0.1	0	20	0.06	6							
08:46:17	20	0.15	0	0	0.09	6	08:48:32	20	0	0	0	0.09	6	08:50:32	185	0.05	0	36	0.05	7	08:52:46	105	0.1	0	20	0.06	6							
08:46:18	20	0.15	0	0	0.09	6	08:48:33	20	0	0	0	0.09	6	08:50:33	185	0.05	0	36	0.05	7	08:52:47	105	0.1	0	20	0.06	6							
08:46:19	20	0.15	0	0	0.1	6	08:48:34	20	0	0	0	0.09	6	08:50:34	180	0.05	0	36	0.05	7	08:52:48	105	0.1	0	20	0.06	6							
08:46:20	20	0.1	0	0	0.1	6	08:48:35	20	0.05	0	0	0.1	6	08:50:35	180	0.05	0	36	0.05	7	08:52:49	105	0.1	0	20	0.06	6							
08:46:21	20	0.1	0	0	0.09	6	08:48:36	20	0.05	0	0	0.1	6	08:50:36	180	0.05	0	36	0.05	7	08:52:50	105	0.1	0	20	0.06	6							
08:46:22	20	0.1	0	0	0.09	6	08:48:37	20	0.05	0	0	0.1	6	08:50:37	175	0.05	0	36	0.05	7	08:52:51	105	0.1	0	20	0.06	6							
08:46:23	20	0.1	0	0	0.09	6	08:48:38	20	0	0	0	0.09	6	08:50:38	175	0.05	0	34	0.05	7	08:52:52	105	0.1	0	20	0.06	6							
08:46:24	20	0.1	0	0	0.09	5	08:48:39	20	0	0	0	0.09	6	08:50:39	175	0.05	0	34	0.05	7	08:52:53	105	0.1	0	20	0.06	6							
08:46:25	20	0.1	0	0	0.09	5	08:48:40 Alarm A1 on (Channel 3, CO)							08:50:40	175	0.05	0	34	0.05	7	08:52:54	105	0.1	0	20	0.06	6							
08:46:26	20	0.1	0	0	0.09	5	08:48:40	35	0	0	54	0.09	7	08:50:41	170	0.05	0	34	0.05	7	08:52:55	105	0.1	0	20	0.06	6							
08:46:27	20	0.1	0	0	0.09	5	08:48:41 Alarm A1 on (Channel 0, H2)							08:50:42	170	0.05	0	34	0.05	7	08:52:56	105	0.1	0	20	0.06	6							
08:46:28	20	0.1	0	0	0.09	6	08:48:41 Alarm A1 on (Channel 5, ch4)							08:50:43	170	0.05	0	34	0.05	7	08:52:57	105	0.1	0	20	0.06	6							
08:46:29	20	0.1	0	0	0.09	6	08:48:41	245	0	0	160	0.09	16	08:50:44	170	0.05	0	32	0.05	7	08:52:58	105	0.1	0	20	0.06	6							

Table D.6. Underground in-situ gas detection data for Analysis 2, Borehole 3.

[illegible]

Table D.7. Underground in-situ gas detection data for Analysis 2, Borehole 4.

H ₂	Cl ₂	H ₂ S	CO	CO ₂	CH ₄		H ₂	Cl ₂	H ₂ S	CO	CO ₂	CH ₄		H ₂	Cl ₂	H ₂ S	CO	CO ₂	CH ₄		H ₂	Cl ₂	H ₂ S	CO	CO ₂	CH ₄	
	200.00 ppm	0.50 ppm	5.00 ppm	30.00 ppm	0.50 Vol%	10.00 %LEL	10:58:13	20	0.05	0	0	0.12	2	11:00:26	20	0	0	0	0.09	2	11:02:33	25	0.1	0	0	0.08	3
	400.00 ppm	1.00 ppm	10.00 ppm	200.00 ppm	1.50 Vol%	20.00 %LEL	10:58:14	20	0.05	0	0	0.12	2	11:00:27	20	0	0	0	0.09	2	11:02:34	25	0.1	0	0	0.08	3
10:56:16	25	0	0	0	0	0	10:58:15	20	0.05	0	0	0.13	2	11:00:28	20	0	0	0	0.09	3	11:02:35	25	0.1	0	0	0.08	3
10:56:16	25	0	0	0	0	0	10:58:16	20	0	0	0	0.13	3	11:00:29	25	0	0	0	0.09	3	11:02:36	25	0.1	0	0	0.08	3
10:56:17	25	0	0	0	0	0	10:58:17	20	0	0	0	0.13	3	11:00:30	30	0	0	0	0.09	4	11:02:37	25	0.1	0	0	0.08	4
10:56:17	25	0	0	0	0	0	10:58:18	20	0	0	0	0.13	3	11:00:31	30	0	0	0	0.09	4	11:02:38	25	0.1	0	0	0.08	4
10:56:17	25	0	0	0	0	0	10:58:19	20	0	0	0	0.13	3	11:00:31	30	0	0	0	0.09	4	11:02:39	25	0.1	0	0	0.08	3
10:56:18	25	0	0	0	0	0	10:58:20	20	0	0	0	0.13	3	11:00:31	85	0	0	32	0.09	12	11:02:40	25	0.1	0	0	0.08	3
10:56:18	25	0	0	0	0	0	10:58:21	20	0	0	0	0.13	3	11:00:32	115	0	0	38	0.09	18	11:02:41	25	0.1	0	0	0.08	3
10:56:18	25	0	0	0	0	0	10:58:22	20	0	0	0	0.13	3	11:00:33	115	0	0	38	0.09	18	11:02:42	25	0.1	0	0	0.08	4
10:56:19	25	0	0	0	0	0	10:58:23	20	0	0	0	0.13	3	11:00:33	135	0	0	42	0.09	24	11:02:43	25	0.1	0	0	0.08	4
10:56:20	25	0	0	0	0	0	10:58:24	20	0.05	0	0	0.12	3	11:00:34	145	0	0	42	0.08	29	11:02:44	25	0.1	0	0	0.08	3
10:56:23	25	0	0	0	0	0	10:58:25	20	0.05	0	0	0.11	3	11:00:35	155	0	0	44	0.08	34	11:02:45	25	0.1	0	0	0.08	3
10:56:23	25	0	0	0	0	0	10:58:26	20	0.05	0	0	0.11	3	11:00:36	160	0	0	44	0.08	36	11:02:46	25	0.1	0	0	0.08	3
10:56:24	25	0	0	0	0	0	10:58:27	20	0.05	0	0	0.1	3	11:00:37	165	0	0	46	0.08	40	11:02:47	25	0.1	0	0	0.08	3
10:56:24	25	0	0	0	0	0	10:58:28	20	0.05	0	0	0.1	2	11:00:38	170	0	0	46	0.08	40	11:02:48	25	0.1	0	0	0.08	3
10:56:24	25	0	0	0	0	0	10:58:29	20	0.05	0	0	0.1	2	11:00:39	170	0	0	48	0.08	40	11:02:49	25	0.1	0	0	0.08	3
10:56:25	25	0	0	0	0	0	10:58:30	20	0.05	0	0	0.1	3	11:00:40	170	0	0	48	0.07	40	11:02:50	25	0.1	0	0	0.08	3
10:56:26	25	0	0	0	0	0	10:58:31	20	0.05	0	0	0.1	3	11:00:41	170	0	0	50	0.07	38	11:02:51	25	0.1	0	0	0.08	4
10:56:27	25	0	0	0	0	0	10:58:32	20	0.05	0	0	0.1	3	11:00:42	170	0	0	50	0.07	36	11:02:52	25	0.1	0	0	0.08	4
10:56:28	25	0	0	0	0	0	10:58:33	20	0.05	0	0	0.1	3	11:00:43	170	0	0	50	0.07	34	11:02:53	25	0.1	0	0	0.08	4
10:56:29	25	0	0	0	0	0	10:58:34	20	0.05	0	0	0.1	3	11:00:44	170	0	0	50	0.07	34	11:02:54	25	0.1	0	0	0.08	4
10:56:30	25	0	0	0	0	0	10:58:35	20	0.05	0	0	0.1	3	11:00:45	170	0	0	50	0.06	32	11:02:55	25	0.1	0	0	0.08	4
10:56:31	25	0	0	0	0	0	10:58:36	20	0.05	0	0	0.09	2	11:00:46	170	0	0	50	0.06	30	11:02:56	25	0.1	0	0	0.08	4
10:56:31	25	0	0	0	0	0	10:58:37	20	0.05	0	0	0.1	2	11:00:47	170	0	0	50	0.06	31	11:02:57	25	0.1	0	0	0.08	4
10:56:32	25	0	0	0	0	0	10:58:38	20	0.05	0	0	0.1	3	11:00:48	170	0	0	50	0.06	32	11:02:58	25	0.1	0	0	0.08	4
10:56:33	25	0	0	0	0	0	10:58:39	20	0.05	0	0	0.1	3	11:00:49	170	0	0	50	0.06	31	11:02:59	25	0.05	0	0	0.08	4
10:56:34	25	0	0	0	0	0	10:58:40	20	0.05	0	0	0.1	3	11:00:50	170	0	0	50	0.06	29	11:03:00	25	0.05	0	0	0.08	4
10:56:35	25	0	0	0	0	0	10:58:41	20	0.05	0	0	0.1	3	11:00:51	170	0	0	50	0.06	30	11:03:01	25	0.05	0	0	0.08	4
10:56:36	25	0	0	0	0	0	10:58:42	20	0.05	0	0	0.1	3	11:00:52	170	0	0	50	0.05	31	11:03:02	25	0.05	0	0	0.08	4
10:56:37	25	0	0	0	0	0	10:58:43	20	0.05	0	0	0.1	2	11:00:53	170	0	0	50	0.05	32	11:03:03	25	0.05	0	0	0.08	4
10:56:38	25	0	0	0	0	0	10:58:44	20	0.05	0	0	0.1	2	11:00:54	170	0	0	50	0.05	32	11:03:04	25	0.05	0	0	0.08	4
10:56:39	25	0	0	0	0	0	10:58:45	20	0.05	0	0	0.1	3	11:00:55	170	0	0	50	0.06	32	11:03:05	25	0.05	0	0	0.08	4
10:56:40	25	0	0	0	0	0	10:58:46	20	0.05	0	0	0.1	2	11:00:56	165	0	0	50	0.06	31	11:03:06	25	0.05	0	0	0.08	4
10:56:41	20	0	0	0	0	0	10:58:47	20	0.05	0	0	0.1	2	11:00:57	165	0	0	50	0.06	31	11:03:07	25	0.05	0	0	0.08	4
10:56:42	20	0	0	0	0	0	10:58:48	20	0.05	0	0	0.1	3	11:00:58	165	0	0	50	0.06	31	11:03:08	25	0.05	0	0	0.08	4
10:56:43	20	0	0	0	0	0	10:58:49	20	0.05	0	0	0.1	3	11:00:59	165	0	0	50	0.06	31	11:03:09	25	0.05	0	0	0.08	4
10:56:44	20	0	0	0	0	0	10:58:50	20	0.05	0	0	0.1	3	11:01:00	165	0	0	50	0.06	31	11:03:10	25	0.05	0	0	0.07	4
10:56:44	20	0	0	0	0	0	10:58:51	20	0.05	0	0	0.1	3	11:01:01	165	0	0	50	0.06	31	11:03:11	25	0.05	0	0	0.07	4
10:56:45	20	0	0	0	0	0	10:58:52	20	0.05	0	0	0.1	3	11:01:02	165	0	0	50	0.06	31	11:03:12	25	0.05	0	0	0.08	4
10:56:46	20	0	0	0	0	0	10:58:53	20	0.05	0	0	0.11	3	11:01:03	165	0	0	50	0.06	31	11:03:13	25	0.05	0	0	0.08	3
10:56:47	20	0	0	0	0	0	10:58:54	20	0.05	0	0	0.11	3	11:01:04	165	0	0	48	0.06	31	11:03:14	25	0.05	0	0	0.07	3
10:56:48	20	0	0	0	0	0	10:58:55	20	0.05	0	0	0.11	3	11:01:05	165	0	0	48	0.06	31	11:03:15	25	0.05	0	0	0.07	4
10:56:49	20	0	0	0	0	0	10:58:56	20	0.05	0	0	0.11	3	11:01:06	165	0	0	48	0.06	31	11:03:16	25	0.1	0	0	0.07	4
10:56:50	20	0	0	0	0	0	10:58:57	20	0.05	0	0	0.11	3	11:01:07	165	0	0	48	0.06	31	11:03:17	25	0.1	0	0	0.07	3
10:56:51	20	0	0	0	0	0	10:58:58	20	0.05	0	0	0.11	2	11:01:08	165	0	0	48	0.06	31	11:03:18	25	0.1	0	0	0.07	3
10:56:52	20	0	0	0	0	0	10:58:59	20	0.05	0	0	0.11	3	11:01:09	165	0	0	48	0.06	30	11:03:19	25	0.05	0	0	0.07	4
10:56:53	20	0	0	0	0	0	10:59:00	20	0.05	0	0	0.11	3	11:01:10	165	0	0	48	0.07	30	11:03:20	25	0.05	0	0	0.07	3
10:56:54	20	0	0	0	0	0	10:59:01	20	0.05	0	0	0.11	2	11:01:11	160	0	0	46	0.07	30	11:03:21	25	0.05	0	0	0.07	3
10:56:55	20	0																									

Table D.8. Detection limits and measuring standards for underground in-situ gas detection.

	CH₄	CO₂	CO	H₂	H₂S	Cl₂
Lower detection limit	n/d	0.01 vol.%	3 ppm	0.4 ppm	1 ppm	n/d
Standards	n/d	EN 45544-1 EN 45544-2 EN 50271	EN 45544-1 EN 45544-2 EN 50271	EN 45544-1 EN 45544-2 EN 50271	EN 45544-1 EN 45544-2 EN 50271	n/d