

# **Reactions of sub-arc mantle melt with mantle wedge and lower crust**

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# Declaration

This thesis, as a whole or in parts, has not been submitted for a degree or diploma in any university or institution. This work has not been submitted for a higher degree before. I have referenced all sources and the extent to which I used them during the write-up of the thesis. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made in the thesis itself.

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No ethics approval was required for this project.

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This thesis is formatted as a manuscript for submission to Lithos, with some exceptions to meet the requirements of Macquarie University. This includes the requirement of an abstract of 200 words, 2 cm margins on all sides, 1.5x line spacing, and figures & tables embedded within the text.

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# Abstract

Most volcanic arc magmas form from the partial melting of mantle wedge above subducting oceanic plates. The melts must migrate through the mantle wedge to reach the arc crust. However, little is known about chemical changes along melt migration pathways. This gap is explored by conducting melt-rock reaction experiments at 1.5 GPa pressure (depth ~50 km), and 1200<sup>0</sup>C & 1150<sup>0</sup> C. We used the synthetic primary mantle melt derived from partially melting phlogopite-pyroxenite source rock.

The peridotite rock does not melt at 1200<sup>0</sup>C at 1.5 GPa, but partial melting occurs in phlogopite-pyroxenite components of the mantle. The experiments simulated the flow-through of the partial melts by using a three-layer setup, including a glassy carbon trap at the topmost portion of the capsule, the starting melt at the bottom, which reacts with the peridotite and/or gabbro above it and eventually accumulates within the vitreous carbon trap. This is a novel addition to past experimental designs, improving our ability to analyse the melt composition after reactions with the rock.

Our study aims: (I) to understand the key sub-arc melt-rock reactions, (II) to evaluate geochemical trends resulting from melt-rock interaction under volcanic arcs and determine changes in melt composition, and (II) to compare experimental results with volcanic glass compositions from primitive arcs.

Keywords: Volcanic arcs, phlogopite-pyroxenite, mantle wedge peridotite, lower crustal gabbro, melt-rock reactions.

# Chapter 1: Introduction

Volcanic arcs are initiated when the mantle wedge partially melts over the subducted oceanic slab. In order for melt to reach the crust of the arc, it must migrate through both the mantle wedge and the lower crust. However, the reactions and changes in the melt chemistry along the melt migration pathways are poorly understood. Several studies on the trace elements and isotopes suggest that magmas from the subduction zone boundaries have multiple source petrogenesis (Atherton and Tarney, 1979; Kay, 1980; Green, 1980; Gill, 1981; DePaolo, 1981;). Regardless, the details of the process among the most profound source and the eruption or emplacement of magma still need to be clarified (Hildreth, 1981). Therefore, it is crucial to take into account the interactions of the surrounding peridotite powder with phlogopite-pyroxenite melt to understand partial melting processes in heterogeneous mantle comprehensively. As a result, melt extraction dynamics may be affected, and pyroxenite signatures may be preserved at the surface of aggregated melts. A variety of physical and chemical factors influence the pyroxenite-peridotite interaction process, such as the pyroxenite body size (Kogiso et al., 2004b), the composition of the melts derived from the pyroxenite bodies (Morgan & Liang, 2005), and the nature of the flow mechanism of transportation, such as pervasive porous flow, or focused flows in the dunite channels. The transportation of magma within channels makes it difficult to replicate these processes in a laboratory setting.

The upper portion of the mantle is the potential site which holds a modest amount of pyroxenite of 2.5% (Hirschmann & Stolper, 1996) on the basis of the ratio of the massifs of orogenic peridotite. In the past few decades, petrological, geochemical, and experimental studies have concentrated on the justifications for continental growth as part of a plate tectonic framework, concentrating on high magma volumes generated in continental margins and in island arcs. The subduction of the oceanic crust in the arc environment causes igneous crust and sediments to melt, and those melts travel into the peridotite-rich mantle wedge overlying the subducting slab. The results of these reactions are well established as a hydrous pyroxenite can be obtained from it (Sorbadere et al., 2013). Yet, advance investigation of the next phase of the process is necessary, which is the partial melting of the hydrous pyroxenite and the interaction between the ensuing peridotite and melt further up in the mantle wedge and also in the lower crust.

For melts to reach the arc crust, they must travel through the mantle wedge on their way to the arc crust. On the other hand, the reactions and changes in melting chemistry associated with these melt migration paths need to be better understood. Most petrological models assume an average oceanic crust thickness (Langmuir et al., 1992). Kinzler &

Grove, (1992), predicted an average melting pressure of less than 1.5 GPa for the peridotitic mantle. However, very little is known about the melting behaviour of pyroxenites at  $P < 2$  GPa.

In order to investigate this gap, we conduct melt-rock reaction experiments at 1.5 GPa pressure at 1200<sup>o</sup> C and 1150<sup>o</sup> C using a rapid quench piston-cylinder apparatus to simulate hybridisation between metasomatized mantle wedge melt ascending from the subducting slab of oceanic crust into mantle wedge peridotite and lower crustal gabbro overlying the mantle wedge peridotite. A harzburgite peridotite and gabbro from the lower crust were selected for experimental reactions with the primary melt. In addition, a glassy carbon trap was placed at the topmost portion of the capsule to collect the experimentally generated melts with new compositions after they migrated and interacted with the overlying rocks. This is a novel addition to past experimental setups. Noble metal capsules (Au<sub>80</sub>Pd<sub>20</sub>) of about 2.3 mm in diameter and 6 mm in length contain the experiments' samples.

This research investigates the melt flow reactions that occur when melt derived from the partially molten phlogopite-pyroxenite flows through mantle wedge peridotite and lower crustal gabbro above it. Through this study, we define the key melt-rock reactions in the mantle wedge and the lower crust and analyse the chemistry of the newly produced melts. In addition, we observe and compare the geochemical trends associated with melting beneath the arc crust and in global volcanic arc settings. These experiments simulate the reactions between a hydrous siliceous magma into an overlying harzburgite peridotite and gabbro layer, representing the mantle wedge above the subducting slab and the lower crustal composition.



# Chapter 2: Literature Review

The pyroxene lithologies in oceanic basalts have been studied extensively through a combination of experimental (Kogiso et al., 2004a) and geochemical (Le Roux et al., 2002; Sobolev et al., 2007) investigations. However, even though pyroxenites make up a much smaller part of the upper mantle than peridotite, they are likely to account for a substantial amount of melt production since they have a low temperature of solidus and a high productivity of melt (e.g., Hirschmann & Stolper, 1996; Pertermann & Hirschmann, 2003; Lambart et al., 2009).

## ***2.1. The processes within the mantle wedge***

### *2.1.1. Fluid infiltration and partial melting of the mantle wedge*

Several studies in early and active subduction zones indicate that some fluids released from the subducting plates migrate upwards into the mantle wedge directly above the slab. This migration occurs during subduction. The serpentinite diapirs have been said to be the result of the hydration of the mantle wedge directly above the subducting plate during the subduction process. It has been observed that at the pressures between 5 to 10 kbar, melts derived from subducted sediments and basalts layers and the mantle wedge produce hydrous carbonates and hydrous silicates (Talc, Mg-amphibole, and Serpentine) in the Trinity thrust system (in Northern California), and Catalina Schist terrane (in Southern California). Aside from the dissolved chemical species carried by the infiltrating H<sub>2</sub>O-CO<sub>2</sub> fluids, the mantle wedge also absorbed SiO<sub>2</sub>, and CaO dissolved within it, thereby changing its bulk composition. Metasomatic effects in the mantle wedge regions are observed on the basis of the composition of island arc basalts, which reflect the mantle sources that generated those basalts. In comparison with the Mid Ocean Ridge Basalts (MORB), the arc-basalts have a depletion of high-field strength elements, such as Zr, Ti, and Nb, compared to the large ion lithophile elements LILE: K, Sr, Ba, and light rare earth LREE. The presence of such imprints is associated with the MORB-type mantle melting enriched in LILE relative to HFSE after equilibration with metasomatic agents escaping the subducting oceanic crust (e.g., Brenan et al., 1994; Kelemen et al., 1993).

### *2.1.2. Depths of fluid release*

It has been determined from geophysical data that the slab lies at depths of 100 to 150 kilometres beneath arc volcanoes, according to Gill 1980. During the late 1980s and early

1990s, a study of the dehydration of the subducting oceanic crust revealed the appearance of a significant fluid pulse at relatively constant depths between 70 and 80 kilometres, roughly coinciding with the depth of the decomposition of amphibole (e.g., Tatsumi, 1989; Davies & Bickle, 1991). Few early experimental studies have also demonstrated that other hydrous phases such as phengite, lawsonite, antigorite, chloritoid, zoisite-clinozoisite, and staurolite have the ability to carry water much greater depth than amphibole (Wunder & Schreyer, 1992; Schreyer, 1988; Pawley & Holloway, 1993; Ulmer & Trommsdorff, 1995; Poli & Schmidt, 1995; Schmidt, 1996; Schmidt & Poli, 1998).

## ***2.2. Formation of calc-alkaline igneous rocks at converging plate boundaries***

There is growing consent today that calc-alkaline igneous rocks originated at the convergent plate boundaries through complicated multisource processes that also involved additional fractionation effects (Atherton & Tarney, 1979; Green, 1980; Kay, 1980; Gill, 1981; DePaolo, 1981; Wyllie, 1981; Hildreth, 1981). Several studies have been conducted on the petrology of subduction zones, the formation of the calc-alkaline igneous rocks at the convergent plate boundaries, and mantle hybridisation. Mantle hybridisation is a phenomenon that occurs when a mixture of two melts or a solid combined with another melt is produced, thus producing a secondary composition (Durocher, 1857).

Several papers were published by Sekine and Wyllie on hybridisation in subduction zones; As an example, Sekine and Wyllie (1982a) studied the data present in the  $\text{KAlSi}_3\text{O}_8\text{-SiO}_2\text{-H}_2\text{O}$  system, including two types of eutectic liquids (1) fluids containing silica hydrates from subducted ocean crust and (2) forsterite and enstatite assemblages derived from oceanic crust overlying mantle in the system  $\text{Mg}_2\text{SiO}_4\text{-SiO}_2\text{-H}_2\text{O}$ .

Besides the experiments done by Sekine and Wyllie in 1973, Yoder conducted two experiments with granite and pounded basalt separated by a vertical interface at 1 kbar with excess  $\text{H}_2\text{O}$  at  $1200^\circ\text{C}$  and  $950^\circ\text{C}$ , respectively. It was observed that when the glass was heated to  $1200^\circ\text{C}$ , the colourless and brown glass had a sharp interface separating them. Additionally, it was observed that colourless glass separated from recrystallised basalt at a sharp interface at around  $950^\circ\text{C}$ , and the flow of granite liquid around the basalt cake's end. On an interface similar to this at  $1200^\circ\text{C}$  (with different materials), electron microprobe analyses revealed a zone of diffusion that spanned  $300\text{ }\mu\text{m}$ , with the majority of the modifications taking place within  $60\text{ }\mu\text{m}$  (Yoder, 1973).

In the past, there has been an increasing number of studies supporting the possibility of convergent plate boundary magmas generated by multisource petrogenesis (Atherton &

Tarney, 1979; Kay, 1980; Green, 1980; Gill, 1981; DePaolo, 1981; Hildreth, 1981). For instance, the Yunshan Fold & Thrust Belt in eastern China has been intruded by a series of alkaline igneous rocks which has a compositional ranges from granite to trachyte. Three rocks have been identified on the basis of mineralogical, geochemical composition and Sr-Nd-Hf isotopic characteristics. Most of the rocks are composed of iron oxides, which contain low amounts of MgO, Al<sub>2</sub>O<sub>3</sub>, CaO, Ba, Sr, and Eu, but high amounts of Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, K<sub>2</sub>O, Ga, Nb, Ta, and heavy rare earth elements (HREEs). Geochemical analysis of these rocks and their Nd, Sr, Zr and Hf-isotopic compositions strongly suggest that they originated from shallow dehydration melting of granitoid crustal rocks containing biotite or hornblende, followed by mixing with contemporary magma from the mantle or lower crust. The geochemical makeup of ferroan syenites differs from the alkaline granites and rhyolites, which are formed by the fractionation of mantle melt from an enriched source mixed with lower and upper crustal magmas (Yang, J. H. et al. 2008). However, details of the processes between the most profound origin and magma eruption or emplacement remain unknown. Therefore, the hybridisation hypothesis should be tested considering the attention dedicated to the simple forward and inverse approaches.

### ***2.3. Key steps in the generation of calc-alkali fractionation trends***

A long and complicated history has been associated with the term 'calc-alkaline' (Arculus, 2003). In 1909, Harker identified two types of volcanic rocks: the Pacific Branch (which contains a greater amount of magnesium oxide and calcium oxide) and the Atlantic Branch (which contains a greater amount of alkali). Holmes (1918) observed that at 62 wt% SiO<sub>2</sub> for Pacific Branch-type calc-alkaline igneous rocks, there is a cross-over between the SiO<sub>2</sub>-CaO and SiO<sub>2</sub>-alkalis (K<sub>2</sub>O+Na<sub>2</sub>O) trends. As a result of the intersection of both alkali and caustic trends, Peacock (1931) defined a 'calc-alkalic' group (intersection at 56-61 wt% SiO<sub>2</sub>) based on the value of SiO<sub>2</sub> at which the two trends intersected. This characterisation guides to the term "calc-alkaline", but it has shifted away from this concept. The magma produced in subduction zones exhibits several evolutionary trends, such as noticeable depletion in iron (Fenner, 1926, Rose & Chesner, 1984; Kay & Kay, 1985; Grove et al., 2003; Carr et al., 2003.). Also, the depletion in iron has been reported in ocean island basalts (OIB) (Munoz Garcia, 1969; Ibarrola Munoz, 1970; Thirlwall et al., 2000 ) and also in the continental rift magmas (Trua et al., 1999; Wang et al., 2002; Krienitz et al., 2007 ).

The calc-alkaline trends of Fe depletion can be generated in several ways, depending on the conditions. In consequence, low-content of water (Grove & Baker, 1984; Baker & Eggler,

1987; Kinzler & Grove, 1992; Sisson & Grove, 1993a; Grove et al., 2003 ) or reduced crystallisation pressure ( Gust & Perfit, 1987; Kinzler & Grove, 1992 ) decreases the possibility of plagioclase crystallisation in aqueous solutions (Grove & Baker, 1984). Some hypotheses of the origin of calc-alkaline trends involve calcification of Fe-rich phases, like magnetite (Osborn, 1959; Gill, 1981; Sisson & Grove, 1993a, 1993b), or calcification of amphibole (Cawthorn & O'Hara, 1976; Grove et al., 2003 ). It is also possible that calc-alkali trends can result from the assimilation and mixing of silicic melts with a low Fe content ( Grove & Baker, 1984; McBirney et al., 1987; George et al., 2004 ) or from mantle melt reactions (Kelemen, 1990). Generally, arc magma can be defined as a combination of mantle material with one or more additional materials added to it (e.g., Gill, 1984; Hawkesworth et al., 1991).

The calc-alkaline trend is stronger in the line of descent (LLD) when magnetite crystallises earlier, an effect that is not reproduced by *pMELTS* ( Ghiorso & Sack, 1995; Ghiorso et al., 2002 ), even though there is strong experimental evidence to the contrary. It is believed that water depolymerises silicates; the more complex the silicate structure, the greater the level of depolymerisation, thereby allowing oxide crystallisation to occur. Based on the experimental data, it has been shown by Sisson & Grove (1993a) that a phase of spinel may emerge on the basalt liquidus with 3.5 to 6.0% H<sub>2</sub>O at ~NNO (nickel-nickel oxide).

## ***2.4. Experimental approaches to the subduction zone geochemistry***

At destructive plate boundaries, crustal recycling seems to be a rudimentary mechanism for maintaining the geochemical heterogeneity of the mantle (Armstrong, 1968; Chase, 1981; Hofmann & White, 1982; Allègre, 1982; Ringwood, 1982; Zindler & Hart, 1986; Hofmann, 1997; Stracke, 2012). Consequently, the radiogenic isotope and trace elemental composition in subduction zone magmas are determined mainly by the transfer of elements from the subducting crust to the overlying mantle wedge (e.g., McCulloch and Gamble, 1991; Woodhead et al., 1993; Tatsumi & Eggins, 1995; Turner & Hawkesworth, 1997; Stern, 2002; Spandler & Pirard, 2013; Kelemen et al., 2014; Zheng & Chen, 2016). Furthermore, several studies suggest that intraplate basalts can be utilised to study the geochemical signatures of subducting oceanic crust (Sun, 1980; Allègre, 1982; Zindler & Hart, 1986; Sun & McDonough, 1989; Hofmann, 1997; Stracke, 2012; Farmer, 2014; Zhao et al., 2015; Huang & Zheng, 2017; Xu & Zheng, 2017). In spite of the fact that the most important inputs during subduction can be traced through volcanic outputs, considerable uncertainty remains regarding the nature of element transfer from forearc depths of 60 to 80 km to sub-arc depths of 80 to 160 km to back-arc depths of > 200 km. In order to determine the dehydration behaviour of the

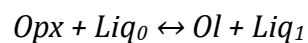
subducting crust and the elemental mobility at different depths, many geochemical investigations have been carried out. In general, these studies can largely diverge into two classifications: (a) The first class deals with igneous rocks of mafic composition (Elliott et al., 1997; Tatsumi & Kogiso, 1997; Churikova et al., 2001; Regelous et al., 2010; Cai et al., 2014; Kelemen et al., 2014; Ryan & Chauvel, 2014), (b) Other investigations have mostly focused on the high pressure (HP) or ultrahigh-pressure (UHP) metamorphic rocks (Zhao et al., Tribuzio et al., 1996; Becker et al., 2000; Zack et al., 2001; Spandler et al., 2003, 2004; Bebout et al., 2007, 2014; Gao et al., 2007; Miller et al., 2007).

Pyroxenite-peridotite interactions are influenced by a variety of physical and chemical parameters, for example, the body size of pyroxenites (e.g., Kogiso et al., 2004b), the composition of the melts obtained from a pyroxenite body (Morgan & Liang, 2005), and the transport mechanisms of the melt (such as porous pervasive flow and the focused flow within the dunite channels, and transport of magma in dikes). Hence, simulating these methods in the laboratory is difficult and takes a lot of time. Nonetheless, several experimental studies have been conducted to study how silicate melts interact with peridotites from a chemical point of view to understand the process better. The kinetic studies conducted by Morgan & Liang (2003, 2005) in different types of open reactors, where a large amount of matter is exchanged with the surroundings and which is responsible for the exchange of matter on interactions between basaltic melt and peridotite, demonstrate that the exchanges between the two substances are kinetic. As a function of the melt composition, it was observed that some modifications were made to the peridotite assemblage that was more or less significant.

Nevertheless, it is not easy to compute the interactions and their effect on the melt and the composition of peridotite in this kind of disequilibrium experiment. For example, in 'sandwich experiments', Yaxley & Green (1998) and Pilet et al. (2008) packed a layer of matter with a low-solidus temperature within the layers of the peridotite. As a comparison, Yaxley & Green (1998) employed a MORB-type eclogite and presented their experiments at the pressure of 3.5 GPa, whereas Pilet et al. (2008) utilised hornblendite at 1.5 GPa pressure. As opposed to experiments performed by Morgan & Liang (2003, 2005), most of the reaction experiments were done below the peridotite's solidus temperature, simulating a partially molten pyroxenite body in a sub-solidus host. There is an opposite conclusion to be drawn from the two studies of Yaxley and Pilet and Morgan and Liang, which conclude that melts from a source contribute to the formation of orthopyroxene (Opx), whereas melts from a source dissolve Opx from the neighbouring peridotite and precipitate olivine (Ol). The experimental studies of Yaxley & Green (1998) and Pilet et al. (2008) deal mainly with the

impact of melt-rock reaction on the melt composition. However, comparing their findings highlights the significance of the reaction's primary conditions, such as pressure and composition. Likewise, it demonstrates that the melt-rock reactions may greatly impact the mantle's lithological diversity. This study aimed to evaluate how melts from pyroxenite sources behave during their transportation through the mantle wedge peridotite as a function of their composition, P-T conditions, and the physical state (sub-solidus vs. partially molten) of the surrounding mantle during their transportation. This study examined three cases to assess how melt-rock interactions affect melt chemical composition, the surrounding peridotite's chemical and mineralogical compositions, and the melt's ability to penetrate the rocks.

For example, Garrido & Bodinier (1999) proposed that some pyroxenites of the Ronda Massif (SW Spain) originated as a consequence of an interaction between the melt of alkali basalt and peridotite. An important characteristic of the reaction between the pyroxenite derived melts, and host peridotite is the simultaneous dissolution of Opx and the precipitation of olivine that occurs. It is possible to describe this reaction by a simple equation such as:



When liquid, Olivine, and Opx are the only phases present in a simple system at constant pressure & temperature, the experimental (Daines & Kohlstedt, 1994) & thermodynamic (Kelemen, 1990) studies have indicated that the proportion of precipitated olivine to dissolved Opx,  $M_{Ol}/M_{Opx}$  is  $\sim 7$ . As a result, Opx dissolution and Olivine precipitation raise the proportion of melt in the system and accelerate its transport by enhancing the porosity and the permeability of mantle rocks. Alternatively, Opx crystallisation employing olivine dissolution may cause a decrease in porosity, which may slow down or even stop magma ascent through porous flows. In this case, interactions between basalt and peridotite may substantially influence the rate at which magma is transported from its source region to the surface.

Several petrological processes occur in the supra-subduction mantle, from dehydration in the subducted plate to partial melting and metasomatism in the wedge. In addition, these processes can significantly influence mantle peridotites' composition, rheology, and flow pattern. As an example, it has been demonstrated that melting fractions and water in the olivine can lower the strength of the mantle rocks (Blacic, 1972; Boudier, 1991; Demouchy et al., 2012; Hirth & Kohlstedt, 1995a; Hirth & Kohlstedt, 1995b; Mackwell et al., 1985; Karato et al., 1986; Mei & Kohlstedt, 2000a; Mei & Kohlstedt, 2000b; Mei). Furthermore, seismic anisotropy and mantle flow can be influenced by changes in plastic deformation mechanisms in olivine (Jung & Karato, 2001; Holtzman et al., 2003b). However, several experiments have found that melting. Percolation in peridotite massifs and xenoliths may be responsible for this effect, which enhances

pyroxene crystallisation and disturbs olivine crystal preferred orientations (CPO), reducing seismic anisotropy in peridotites (Le Roux et al., 2008; Soustelle et al., 2009; Soustelle & Tommasi, 2010; Soustelle, 2014).

## ***2.5. The review of past and current petrogenetic models***

Grove et al. proposed in 2003 that calc-alkali magma fractionates via dehydration of hydrous minerals and vapour-saturated anatexis (marked I, Figure 2.1) porous flow process (flux melting). This results in a melt traversing an inverted thermal gradient in a hotter shallower mantle. With a decrease in equilibration pressure, silicate minerals dissolving in the melt also lead to a reduction in the amount of water in the melt. Additionally, this process continues to shallow mantle depths (IV, Figure 2.1) as the hydrous melt is segregated (Grove et al., 2002; Grove & Gaetani, 2003). Grove and Gaetani (2003) found that the mantle was melted significantly (> 20 wt%) by this flux-melting model, causing a dilution of slab-contributed trace elements and fluids. Recently, studies have focused on the mechanisms explaining continental expansion within a plate tectonic framework, particularly in continental margins and island arc regions. As a result of geochemical studies on island arcs (Sakes and Gill, 1969; Gill, 1970; Jakes & White, 1971), the earlier view that andesite (~60% SiO<sub>2</sub>) dominates active orogenic areas has been replaced with three rock series (Sakes and Gill, 1969; Gill, 1970; Jakes & White, 1971):

- (a) Island arc tholeiitic series (dominant).
- (b) Calc-alkaline series.
- (c) Island arc alkaline (or shoshonitic) series (smallest abundant).

According to Middlemost (1985), determining the alkali-lime index of a standard suite of rocks containing orogenic andesites shows that some of the rocks are more likely to belong to the calcic series of Peacock rather than to the calc-alkalic series. Middlemost (p. 118) also noted that the basalt-Icelandic suite of rocks in the "tholeiitic" group usually falls within the "calc-alkaline" group.

To examine the hypothesis that calc-alkaline rocks of subduction zones are the result of the partial melting of hybrid rocks formed by the reactions between hydrous siliceous magma rising from subducted oceanic crust and adjacent peridotite, Sekine and Wyllie used granite and peridotite under pressures of 30 kbar. As a result of hybridisation, a pyroxenite without olivine is produced. The products obtained from the partial melting of this composition would be completely different from those made

from peridotite because there is no olivine present, and clinopyroxenes may contain up to 7% Na<sub>2</sub>O, whereas peridotite has little Na<sub>2</sub>O. Some scientists favour complex multi-source and fractionation processes, with multi-source processes being superimposed (Atherton and Tarney, 1979; Kay, 1980; Green, 1980; DePaolo, 1981; Hildreth, 1981; Gill, 1981; Wyllie, 1981) as Nicholls and Ringwood proposed (1973), the subducted crust and the overlying mantle are both involved in this process. Based on the results of this study, a hydrous siliceous melt of a similar composition to rhyodacite was formed in the oceanic crust and reacted with the peridotite overlying them. A second stage in the petrogenesis of andesites and other calc-alkaline magmas involving hybridisation was proposed by Nicholls and Ringwood in 1976, in comparison with the previous study conducted in 1973. They suggested that, in subducting oceanic crust, hydrous siliceous melts with solidification characteristics similar to rhyodacites formed, then reacted with mantle peridotite, forming olivine pyroxenite zones. In this zone, olivine pyroxenite accumulates episodically with subsequent partial melting and the formation of calc-alkaline magmas emanated from a variety of these wet, hybrid rocks.

The recent study of the internal structure of the mantle wedge, conducted by Turner et al. (2016), indicates that magma composition correlates with the depth of the Moho concentration zone under the arc. Alternatively, to the depth of the slab under the arc and the slab surface temperature, a slab 'thermal parameter' can be used to define the thermal structure of the down-going slab.



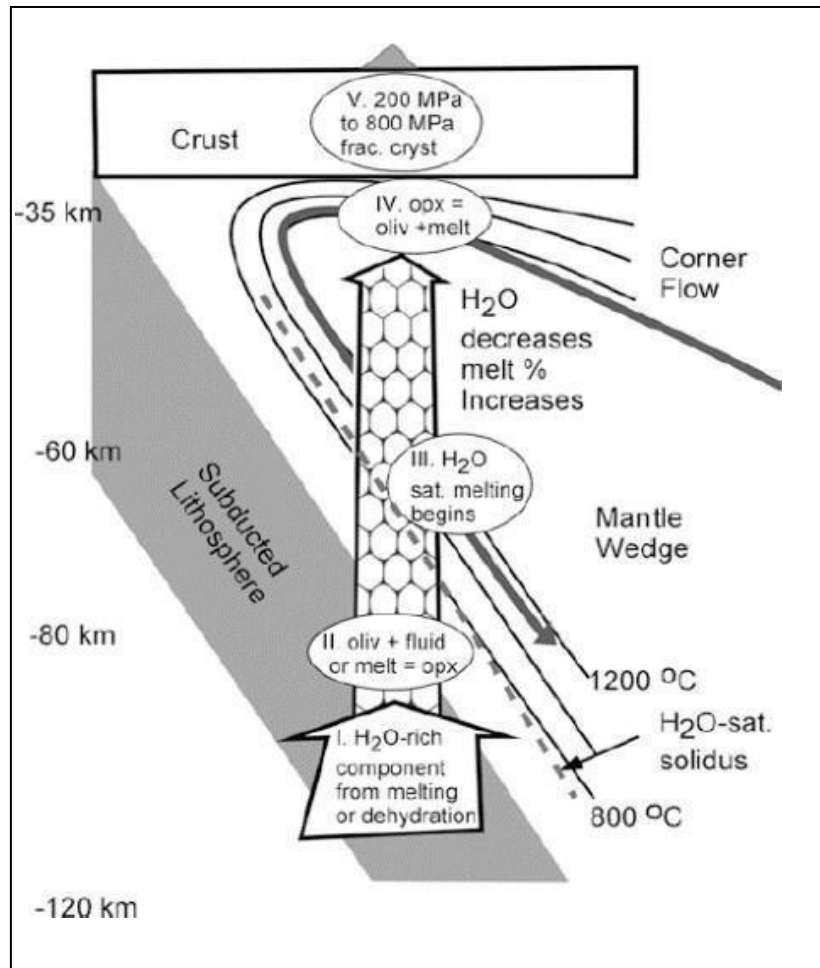


Figure 2.1: A multi-stage slab melting model was proposed by Grove et al., 2003 as an alternative to explaining the major and trace elements in these lava flows. As a consequence of flux melting, these magmas inherited the main element characteristics of a mantle wedge and progressed upward. Because of this, the melt is rich in  $\text{SiO}_2$ ,  $\text{MgO}$ , and  $\text{H}_2\text{O}$  and saturated with harzburgite. In fractional crystallisation under hydrous conditions, liquid derivatives rich in  $\text{SiO}_2$  followed calc-alkaline differentiation patterns. Moreover, a fluid component rich in  $\text{H}_2\text{O}$  and trace elements was released into the atmosphere during subduction. Upon melting, this component played a significant role (Grove et al., 2002).

In light of the new geochemical and experimental studies conducted in island arcs and continental margin areas, the petrogenetic models have been modified to make clear these geochemical and experimental results. In spite of the fact that most of the present models emphasise polygenetic origins for magma series, seawater from the subducted oceanic crust is released into the subducted lithosphere through dehydration and possibly melting reactions. However, there is an alternative explanation for the low  $\text{TiO}_2$  levels; early melting episodes may have depleted the mantle and resulted in a heterogeneous mantle (Ringwood, 1975; D.H. Green, 1973, 1976). The present models can be grouped into four large categories:

(A) Hydrous melting of peridotite above the Benioff Zone to form liquids at depths of 60 to 100 km, ranging in composition from olivine-tholeiite-quartz tholeiite, which produces basaltic andesite upon rising to the surface (e.g., Nicholls & Ringwood, 1973); and andesite-dacite (e.g., Kushiro, 1972).

(B) Melting of the subducted oceanic crust of eclogite mineralogy at depths of 100 to 200 km to produce (1) intermediate rocks belonging to the calc-alkaline series (i.e., primarily andesite) (e.g., T.H. Green and Ringwood, 1968; T.H. Green, 1972; Marsh & Carmichael, 1974); (2) very siliceous liquids (rhyodacite), which rise and "contaminate" and eventually lead to the melting of mantle peridotite (Ringwood, 1974, 1975; Nicholls, 1974),

(C) Hydrous fractionation of mantle derived mafic magma that ranges in composition from alkaline to tholeiitic (e.g., Cawthorn et al., 1973; Arculus, 1976) or both (e.g., Cawthorn & O'Hara, 1976), and

(D) A silicic volcanic and plutonic formation can be produced in mature island arcs and continental margins when thickened crust melts due to the advent of fluids from the Benioff Zone lowering the solidus and heating the crust due to underplating by lavas generated by mechanisms (A) and (B) (D.H. Green, 1972; Ringwood, 1974). Furthermore, magma mixing and contamination are also likely to play a crucial role in this type of environment (e.g., Wilcox, 1954; Anderson, 1976; Eichelberger, 1974).

# Chapter 3: Methodology

We conducted a series of reaction experiments to determine the key melt-rock reactions and to understand how the chemistry of melt changes during the melt migration through the mantle wedge and lower crust beneath the volcanic arc system. In these experiments, we used a rapid quench piston-cylinder instrument with a standard cell assembly, including MgO inner sleeves, graphite furnaces, and Pt-Rh thermocouple wires of type B. All experiments were conducted with a standard CaF<sub>2</sub> cell assembly, and no pressure corrections were required. Besides, a partial melt of homogeneous phlogopite-pyroxenite was synthesised in the laboratory for melt flux reaction experiments.

## ***3.1. Materials and method***

### *3.1.1. Sample preparations*

Each experiment comprised three layers: (1) melt, (2) rocks in powdered (harzburgite peridotite and dry gabbro) and core form (dry gabbro), and (3) a vitreous carbon melt trap.

- (1) Partial melt from a homogeneous phlogopite-pyroxenite was produced synthetically (details of the chemistry are presented in Table 3.2) using 16 major oxides and 21 trace elements. The synthetic melt was mixed and sintered at 950 °C in a furnace and stored in an oven to keep dry.
- (2) Two well-characterised rocks were powdered: (a) natural harzburgite peridotite rock from Kimberley, South Africa (sample and data are provided by Bill Griffin, Table 3.1) and (b) natural gabbro rock from Days Creek of the New England Orogen, NSW, Australia (sample provided by Nathan Daczko). Two experiments have been done with the initial melt and lower crustal gabbro. One experiment was between the melt and gabbro in the form of powder (crushed into the size of 15 – 20 µm), and another reaction experiment was run using a rock core drilled from the gabbro instead of powder. The core was cut down into 2.2 mm x 2.6 mm from the same gabbro.
- (3) 10–20 micrometre (µm) sized vitreous carbon beads were used to create porosity at one end of the experiment.

## ***3.2. Experimental design and analytical techniques***

### *3.2.1. Experimental setup*

A half-inch-diameter rapid quench piston-cylinder apparatus was used to react sealed samples

at 1.5 GPa pressure. To achieve the target temperature, a type B thermocouple was used for each experiment, with a positive leg made up of 70% of Pt and 30% of Rh and a negative leg made up of 94% of Pt and 6% of Rh.

In order to study melt-rock reactions, mantle wedge peridotite and lower crustal gabbro were selected for our study. We have begun our reaction experiments using a 1.5×6 mm Ag<sub>70</sub>Pd<sub>30</sub> metal capsule (Figures 1 & 2, Appendix) to minimise iron loss during high-pressure experiments. Subsequently, we employed a 2.3×5 mm Au<sub>80</sub>Pd<sub>20</sub> metal capsule (Figure 3.1A) to conduct the high-pressure experiments. As shown in Figure 3.1A, the melt was placed in the capsule on the bottom end, the peridotite in the middle, sandwiched between the vitreous carbon layer and the melt, and the vitreous carbon melt trap on top (Figure 3.1B). This same experimental design was applied to gabbro powder as well as to the gabbro core (Figure 3.1 C), in which melt migrated through both. After each experiment, all capsules were mounted in epoxy resin and polished with different grits of sandpaper to a diamond finish of 1/4 m.

Melt traps are primarily used to collect the new melt after each reaction with overlying rocks within the capsule; this is a novel addition to the previous experimental design to improve our ability to analyse the melt composition. The pore spaces within the carbon trap initially offers a lower pressure than elsewhere in the capsule. Melt movement had to occur against gravity as experiments were conducted with a melt trap at the top of the capsule. The proportion of vitreous carbon trap to silicate melt was kept low to allow complete filling of the pores with melt and subsequent melt equilibration. In this manner, the melt can reach equilibrium within a few hours, avoiding problems with achieving equilibrium, which can occur when the pore space of the trap is too large. In our study, all the experimental reactions happened for more than 24 hours. The capsules were heated at 110<sup>0</sup> C for more than 30 minutes to test for leaks after welding and reweighed. The details of the experiments are presented in Table 4.1 and discussed in the results chapter and table 1 in the appendix.

### *3.2.2. Analytical techniques*

The minerals and microstructures were identified with high resolution using backscattered electron images. An FEI Teneo Field Emission Scanning Electron Microscope (SEM) with NanoMin software (Figures 3 & 4, Appendix) was used for chemical field mapping, and a Zeiss EVO MA15 SEM with Aztec Software was used for microchemical data analyses at Macquarie Geo-Analytical, Macquarie University, to image polished, mounted and carbon coated sections of the samples. The SEM operating conditions were a high vacuum, 10 kV accelerating voltage, a dwell time of 5 ms and spot sizes between 30-50µm. For each sample, stitched images of

the thin sections were uploaded as layers to ImageMatrix. This software helps compile the individual major oxide's concentration map onto a BSE image (See [Au-Pd Zeiss SEM - Files - CloudStor \(aarnet.edu.au\)](#)). Additionally, they were used to identify different minerals and chemical phases and their distribution in the studied samples.

A laser ablation inductively coupled plasma mass spectrometry (La-ICP-MS) analysis was performed at the Macquarie Analytical & Fabrication Facility (MAFF) of Macquarie University to determine the trace elemental concentrations in melts. The instrument consists of an Agilent 7700 mass spectrometer coupled to a New-Wave Research UP213 Md- YAG (213 nm) laser. The analysis was conducted by ablating 30  $\mu\text{m}$  diameter spots at a rate of ten shots per second. The data reduction process was completed based on a standard methods (Longerich et al., 1996), utilising STD610 and STD612 glasses as the primary references and USGS BCR2g glass as a secondary reference. The details of the analyses are presented and discussed in the results chapter (Under section 4.4: Trace elemental analyses).

Oxides	KF 06-002
SiO <sub>2</sub>	46.07
TiO <sub>2</sub>	< 0.01
Al <sub>2</sub> O <sub>3</sub>	1.22
Fe <sub>2</sub> O <sub>3</sub> (TOTAL)	6.02
MnO	0.09
MgO	42.02
CaO	0.43
Na <sub>2</sub> O	<0.02
K <sub>2</sub> O	0.02
P <sub>2</sub> O <sub>5</sub>	<0.01
Cr <sub>2</sub> O <sub>3</sub>	0.37
LOI	4.22
Sum	100.46

*Table 3.1: Chemistry of natural harzburgite powder from Kimberley, South Africa (Sample and data provided by Bill Griffin).*

Chemicals	Melt	Normalised to 100	Added as	Calculated amount (1 g)
SiO <sub>2</sub>	38.00	40.58	The amount from Fe <sub>2</sub> SiO <sub>4</sub>	0.02840
			SiO <sub>2</sub>	0.37742
TiO <sub>2</sub>	3.29	3.51	TiO <sub>2</sub>	0.03514
Al <sub>2</sub> O <sub>3</sub>	7.48	7.99	Al(OH) <sub>3</sub>	0.12224
Cr <sub>2</sub> O <sub>3</sub>	0.09	0.10	Cr <sub>2</sub> O <sub>3</sub>	0.00096
FeO	6.36	6.79	Fe <sub>2</sub> SiO <sub>4</sub>	0.09633
MnO	0.10	0.11	MnO	0.00107
MgO	10.97	11.72	MgO	0.06514
			the amount from Mg(OH) <sub>2</sub>	0.05202
CaO	8.09	8.64	CaCO <sub>3</sub>	0.15420
BaO	0.50	0.53	BaCO <sub>3</sub>	0.00687
Na <sub>2</sub> O	1.34	1.43	Na <sub>2</sub> CO <sub>3</sub>	0.00690
			the molar Na from NaF	0.00033
K <sub>2</sub> O	10.58	11.30	K <sub>2</sub> CO <sub>3</sub>	0.16578
F	0.59	0.63	NaF	0.01393
H <sub>2</sub> O	5.50	5.50	Mg(OH) <sub>2</sub>	0.02168
			the amount from Al(OH) <sub>3</sub>	0.04236
Trace elements	1.17	1.17	Trace	0.01170
Sum	87.39	100.00	Total	1.20246

*Table 3.2: Calculation of synthetic melt of homogeneous phlogopite-pyroxenite as starting material.*

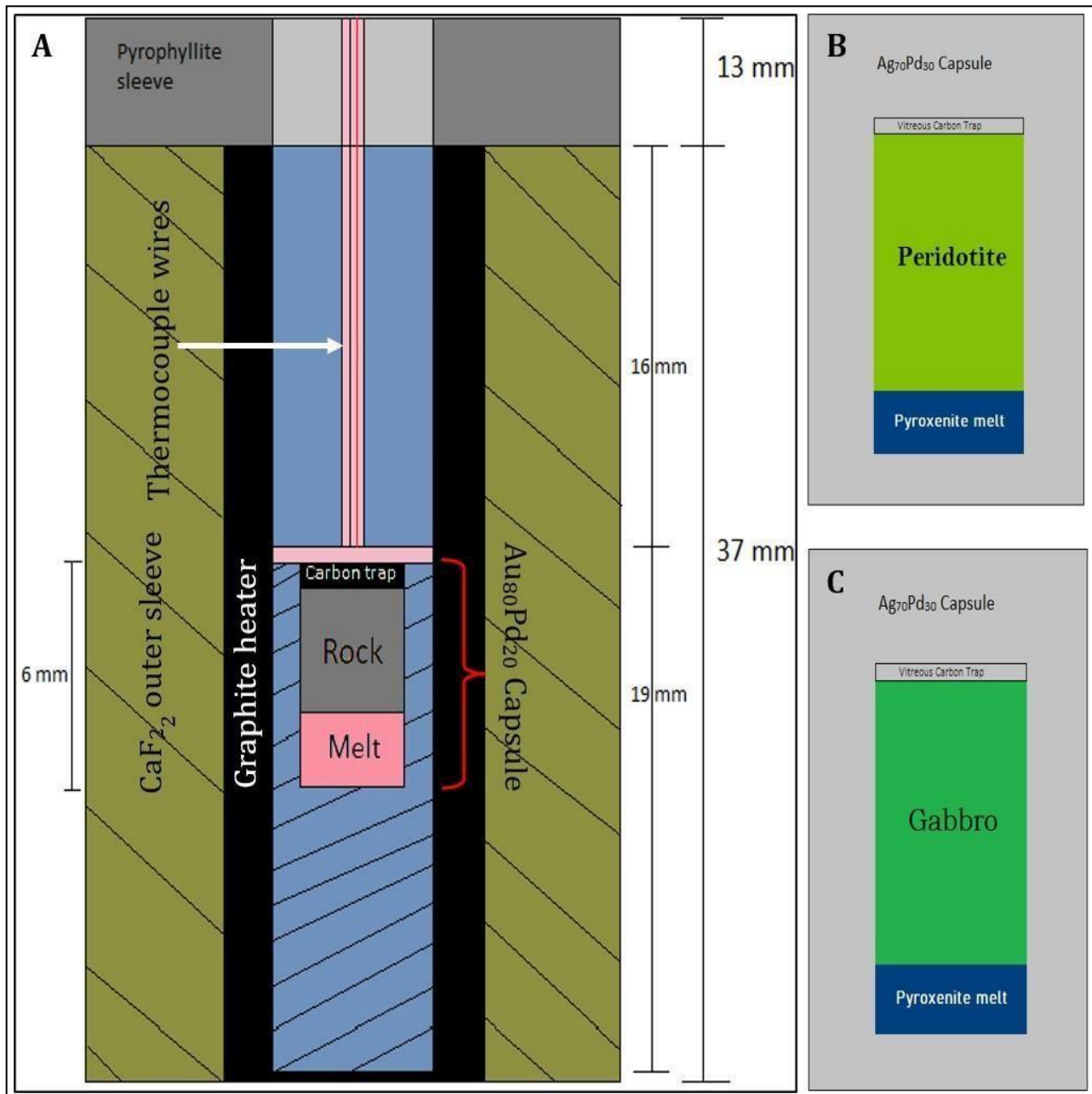


Figure 3.1: (A) The design of capsules ( $Au_{80}Pd_{20}$ ) used in the experiments. Dark lime is the  $CaF_2$  outer sleeve portion. Black coloured portion is the graphite heater sleeve. Pale blue is  $MgO$  inner sleeve. The capsule consists of three distinct layers. The top layer is composed of a vitreous carbon trap, the middle portion is composed of rock (powder as well as core), and the bottom part is composed of the synthetic partial melt of a phlogopite-pyroxenite. The vitreous carbon trap forms a low-pressure sink to draw the melt through the rock. (B) The design of capsules for experiments. Peridotite is packed below peridotite as separate layers, so the melt must flow against gravity, sucking through the vitreous carbon melt trap. (C) Design the design of capsules for experiments. Gabbro is packed below peridotite as separate layers, so the melt has to flow against gravity, sucking through the vitreous carbon melt trap.

# Chapter 4: Experimental Results

## ***4.1. Melt-rock reactions in the mantle wedge***

### ***4.1.1. Melt-Peridotite reaction***

At the pressure of 1.5 GPa and 1200<sup>o</sup> C (Table 4.1), we react the initial melt (Table 4., column 1) with the mantle wedge peridotite (Figure 4.1 a-c). As a consequence of the melt-rock reactions, forsterite olivine was produced (Figure 4.1b), with new orthopyroxene (Figure 4.1b & 4.2a), phlogopite (Figure 4.1c) and the composition of the initial melt modified into a new composition (Figure 4.1a, Table 4.2). This experimentally produced new melt is enriched in MgO, SiO<sub>2</sub>, MnO and Cr<sub>2</sub>O<sub>3</sub> and depleted in FeO, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O and Na<sub>2</sub>O (Table 4.2).

## ***4.2. Melt-rock reactions in the lower crust***

### ***4.2.1. Melt-Gabbro powder reactions***

During the melt-rock reaction experiments, the migration of the starting melt through the overlying gabbro powder layer forms new orthopyroxene minerals of second-generation as rims surrounding the first-generation clinopyroxene (Figure 4.1e, g and h, & figure 4.2c-f), second-generation labradorite plagioclase (Figure 4.1e-f, and Figure 4.2b), new garnet (Figure 4.1f & h, and Figure 4.2g-h), and a melt of new composition (Figure 4.1d & g). This new melt is enriched in Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and alkali oxides and depleted in MgO and FeO (Table 4.2).

### ***4.2.2. Melt-Gabbro core reactions***

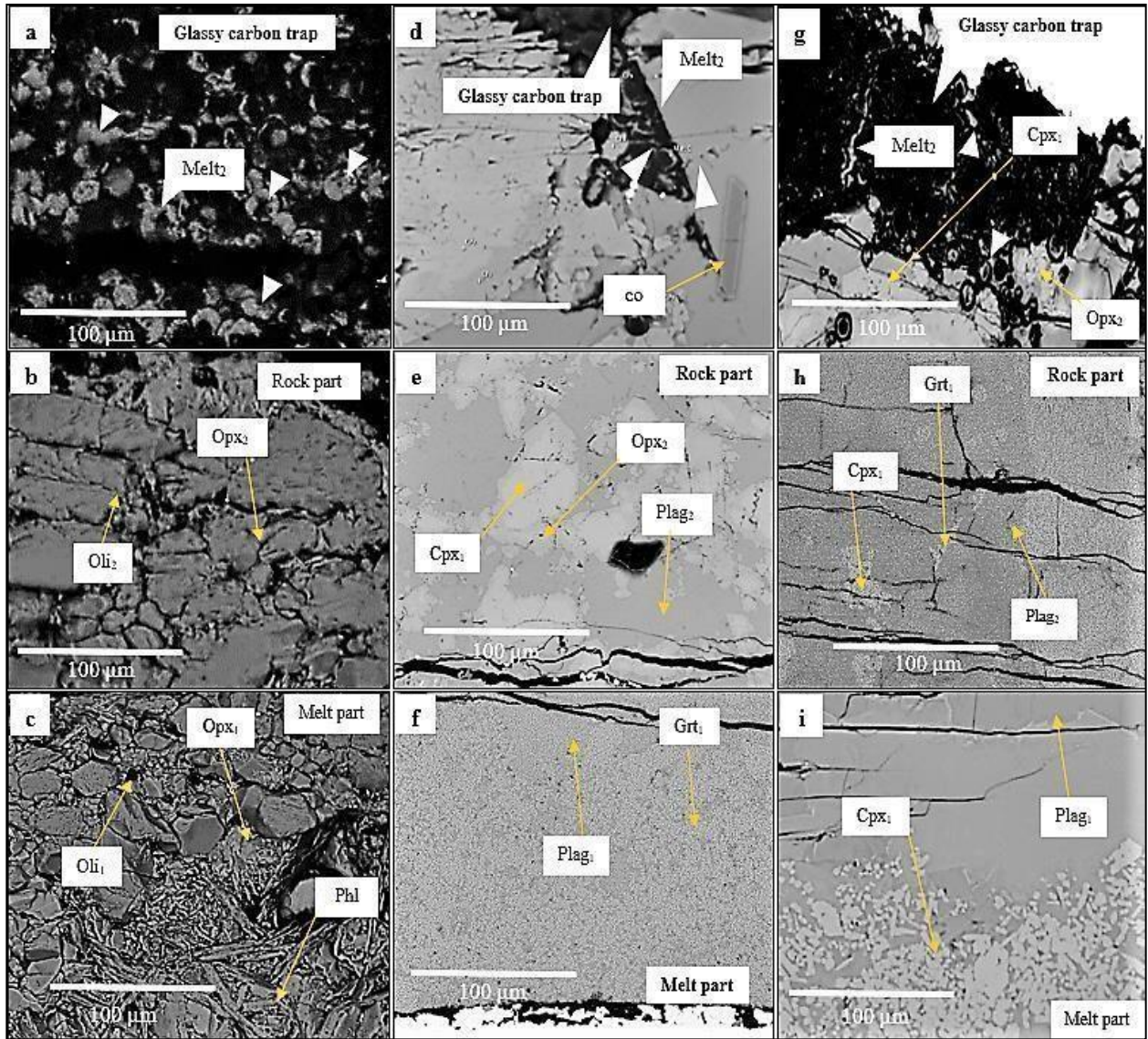
At 1.5 GPa pressure and 1150<sup>o</sup> C (Table 4.1), the initial melt reacted with lower crustal dry gabbro (in core form). The mineralogy of the sample (Figure 4.1, g- i) is diopside, enstatite, plagioclase and garnet and a melt with new chemical compositions (Table 4.2, column 4). This melt is very similar to the melt produced during the reaction with the gabbro powder. This melt is also enriched in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O and depleted in MgO, FeO, MnO, CaO, Cr<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O (Table 4.2, column 4). During the melt-rock reaction, the partial melt reacted with the gabbro and produced orthopyroxene (enstatite) (Figure 4.1 g & 4.2 B and Table 4.4) of the second-generation; on the other hand, clinopyroxene composition (diopside) (Figure 4.1 h & 4.2 A and Table 4.3) remained the same. Melt reacted with clinopyroxenes and formed rims of orthopyroxene surrounding the clinopyroxene cores of the first-generation, the same as the



melt-gabbro powder reaction. The melt also reacted and formed second-generation plagioclase feldspar of labradorite in composition (Figure 4.1 h, 4.2 C & Table 4.5). Garnet was produced (Figure 4.1. h & 4.2. D and Table 4.7) along the melt migration path during the melt-rock reactions.

Experimental ID	Material used	Pressure	Temp.	Run Length	Phases occurred
M-22-054	Capsule- Au <sub>80</sub> Pd <sub>20</sub> Pyroxenite+ peridotite+ vitreous carbon trap	1.5 GPa	1200° C	29 Hours	Rich in olivine, diopside, phlogopite and new melt. Rock minerals that have recrystallised include Mg-olivine (forsterite).
A-22-079	Capsule- Au <sub>80</sub> Pd <sub>20</sub> Pyroxenite+ gabbro (powder)+ vitreous carbon trap	1.5 GPa	1150° C	29 Hours	Rich in diopside, phlogopite ± garnet + melt. Rock minerals that have recrystallised include plagioclase and diopside.
A-22-080	Capsule- Au <sub>80</sub> Pd <sub>20</sub> Pyroxenite+ gabbro (core)+ vitreous carbon trap	1.5 GPa	1150° C	29 Hours	Plagioclase + Garnet + diopside + enstatite + melt. Rock minerals that have recrystallised include plagioclase and diopside.

*Table 4.1: Details of experimental run conditions for melt-rock and melt-rock reaction experiments.*



**Figure 4.1:** BSE Images of the mineralogical assemblage of melt-rock experimental reactions in  $Au_{80}Pd_{20}$  capsule at the pressure of 1.5 GPa and 1200<sup>o</sup> C for melt-peridotite and 1150<sup>o</sup> C for melt-gabbro reactions in the mantle wedge and lower crust, respectively. (a) Cross-sectional SEM image of minerals and experimental melts in carbon trap in the peridotite sample, white arrows showing the presence of experimental melts with new compositions within the carbon trap. (b) SEM image of the mineral assemblages in the capsule's middle part (rock part) for the same sample. The sample consists of oli and opx. (c) SEM image of mineralogical assemblages in the capsule's bottom part (melt part). The melt part consists of oli, opx and phl. (d) Cross-sectional SEM image of minerals and experimental melts in carbon trap in the gabbro (powder) sample. White arrows show the occurrence of experimental melt compositions within the carbon trap and the presence of crn mineral grain (e) SEM image of the mineral assemblages in the capsule's middle part (rock part) for the same sample. During the experiments, the melt of phlogopite-pyroxenite reacted with the first-generation cpx grains in the gabbro and produced opx minerals as rims surrounding the cpx core. (f) This is the capsule's bottom (melt) part consisting of cpx, plag and grt minerals. (g) Cross-sectional SEM image of the top part of the capsule with minerals in the gabbro (core) sample. This part comprises a cpx core and a rim of opx minerals. (h) the middle (rock) part of the capsule comprises grt, plag and cpx. (i) Bottom (melt) part of the capsule. This part consists of plag and cpx mineral assembly. Abbreviations or minerals, Phl: phlogopite, Cpx: clinopyroxene, Opx: orthopyroxene, Grt: Garnet, Oli: Olivine, Co: Corundum. The subscripts in the mineral's abbreviations denote the generation of the mineral, subscript 1: first-generation, 2: second-generation.

### ***4.3. Major oxides chemical analyses***

The major oxide compositions of Na<sub>2</sub>O, K<sub>2</sub>O, FeO, MgO, CaO, MnO, TiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> in two different melts produced by reacting the initial melt with both mantle wedge peridotite and the lower crustal gabbro were plotted on bivariate plots against SiO<sub>2</sub> (Figure 5.1). The trend of major oxide compositions of the experimentally produced melts has been compared with the chemical composition of some natural volcanic glasses. One of the reasons behind choosing these volcanic arcs is to see how compositionally this melt coincides with the natural volcanic glasses and whether it could describe the origin of rock suits found in the volcanic arcs.

The first-order observation of the bivariate plots (Figure 5.1) shows that in each plot, the phonotephrite melt does not exhibit any compositional similarities with the major oxides composition of volcanic glasses. On the other hand, it is seen that the composition of the shoshonite melt in each plot indicates a chemical relationship with the volcanic glasses.

Calculations of the chemical formula from major oxides analyses on phenocrysts from three representative experimental samples (SiO<sub>2</sub> = 44 wt%—55 wt%) are given in Tables 4.3 to 4.7 and reviewed further in the following discussion chapter. All other detailed calculations can be found in the supplementary data – [SEM Major Oxides Elemental Analyses \(version 1\).xlsb.xlsx \(sharepoint.com\)](#).

<b>Oxides</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
<b>SiO<sub>2</sub></b>	40.58	49.80	53.81	54.46
<b>TiO<sub>2</sub></b>	3.51	2.76	0.22	1.20
<b>Al<sub>2</sub>O<sub>3</sub></b>	7.99	5.81	22.10	20.13
<b>FeO</b>	6.79	3.38	1.91	3.74
<b>MnO</b>	0.11	0.15	-	0.13
<b>MgO</b>	11.72	22.53	2.71	3.05
<b>CaO</b>	8.64	4.31	6.14	6.66
<b>BaO</b>	0.53	-	-	-
<b>NiO</b>	-	-	-	-
<b>Cr<sub>2</sub>O<sub>3</sub></b>	0.10	0.29	-	-
<b>Sc<sub>2</sub>O<sub>3</sub></b>	-	-	-	-
<b>Na<sub>2</sub>O</b>	1.43	0.59	4.37	4.36
<b>K<sub>2</sub>O</b>	11.30	9.03	4.14	3.10
<b>F</b>	0.63	-	-	-
<b>H<sub>2</sub>O</b>	5.50	-	-	-
<b>Trace elements</b>	1.17	1.31	2.61	0.09
<b>Total</b>	100	99.96	98.01	96.69

1. Initial melt, phlogopite-pyroxenite
2. Melt in the melt-peridotite reaction
3. Melt in the melt-gabbro powder reaction
4. Melt in the melt-gabbro core reaction

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*Table 4.2: Major oxides compositions of the initial melt and experimentally produced melts after the melt-rock reactions.*

<b>Oxides</b>	<b>I</b>	<b>II</b>
SiO <sub>2</sub>	41.12	41.52
TiO <sub>2</sub>	-	-
Al <sub>2</sub> O <sub>3</sub>	-	-
Cr <sub>2</sub> O <sub>3</sub>	-	0.14
FeO	5.99	5.81
MnO	0.21	0.20
MgO	52.61	53.18
NiO	0.30	0.28
CaO	0.08	-
<b>Sum</b>	100.31	101.13
<i>Numbers of ions on the basis of 4 O</i>		
<b>Oxides</b>	<b>I</b>	<b>II</b>
Si	0.990	0.990
Ti	-	-
Al	-	-
Cr	-	0.002
Fe (ii)	0.120	0.116
Mn	0.004	0.004
Mg	1.888	1.891
Ni	0.006	0.005
Ca	0.001	-
<b>Sum</b>	3.009	3.009

*Table 4.3: Selected olivine analysis calculations from each melt-peridotite reaction experimental sample.*

Oxides	Gabbro powder	Gabbro core
SiO <sub>2</sub>	51.42	51.85
TiO <sub>2</sub>	0.24	0.72
Al <sub>2</sub> O <sub>3</sub>	8.94	1.63
FeO	5.27	7.90
MnO	0.14	0.22
MgO	13.65	14.59
Na <sub>2</sub> O	1.45	-
CaO	19.02	22.10
<b>Sum</b>	100.14	99.02
<i>Numbers of ions on the basis of 6 O</i>		
Si	1.8626	1.946
Ti	0.0065	0.020
Al	0.3816	0.072
Fe (ii)	0.1596	0.248
Mn	0.0043	0.008
Mg	0.7371	0.816
Na	0.1001	-
Ca	0.7381	0.889
<b>Sum</b>	3.9901	3.927

Table 4.4: Selected clinopyroxene analysis calculations from each experimental sample.

Oxides	Peridotite reaction	Gabbro powder	Gabbro core
SiO <sub>2</sub>	56.55	54.18	52.99
TiO <sub>2</sub>	-	0.29	0.32
Al <sub>2</sub> O <sub>3</sub>	2.57	0.76	0.85
Cr <sub>2</sub> O <sub>3</sub>	0.86	-	-
FeO	4.27	18.87	18.99
MnO	0.12	0.39	0.44
MgO	35.26	24.78	24.05
CaO	0.64	1.09	1.08
<b>Sum</b>	100.27	100.36	98.72
<i>Numbers of ions on the basis of 6 O</i>			
Si	1.933	1.978	1.972
Ti	-	0.008	0.009
Al	0.067	0.022	0.025
Al	0.037	0.011	0.012
Cr	0.023	-	-
Fe <sup>3+</sup>	0.009	0.033	0.037
Fe <sup>2+</sup>	0.113	0.543	0.554
Mn	0.004	0.012	0.014
Mg	1.797	1.349	1.334
Ca	0.023	0.043	0.043
<b>Sum</b>	4.007	3.998	4.000

Table 4.5: Selected orthopyroxene analysis calculations from each experimental sample.

<b>Oxides</b>	<b>I</b>	<b>II</b>
<b>SiO<sub>2</sub></b>	44.12	51.97
<b>TiO<sub>2</sub></b>	2.56	2.51
<b>Al<sub>2</sub>O<sub>3</sub></b>	11.72	6.61
<b>Cr<sub>2</sub>O<sub>3</sub></b>	0.98	0.33
<b>FeO</b>	1.88	2.80
<b>MgO</b>	26.76	26.18
<b>CaO</b>	-	1.52
<b>Na<sub>2</sub>O</b>	-	0.79
<b>K<sub>2</sub>O</b>	10.42	8.92
<b>Sum</b>	98.44	101.30
<i>Numbers of ions on the basis of 22 O</i>		
<b>Oxides</b>	<b>I</b>	<b>II</b>
<b>Si</b>	5.989	6.755
<b>Ti</b>	0.261	0.245
<b>Al</b>	1.875	1.013
<b>Al</b>	0.000	0.000
<b>Cr</b>	0.021	0.034
<b>Fe<sup>2+</sup></b>	0.213	0.304
<b>Mg</b>	5.415	5.073
<b>Ca</b>	-	0.094
<b>Na</b>	-	0.003
<b>K</b>	1.804	1.479
<b>Sum</b>	15.578	15.001

*Table 4.6: Selected phlogopite analysis calculations from melt-peridotite reaction sample.*



<b>Oxides</b>	<b>Gabbro powder</b>	<b>Gabbro core</b>
<b>SiO<sub>2</sub></b>	44.88	41.04
<b>TiO<sub>2</sub></b>	0.19	0.62
<b>Al<sub>2</sub>O<sub>3</sub></b>	24.89	22.28
<b>FeO</b>	9.10	11.24
<b>MnO</b>	0.27	0.67
<b>MgO</b>	17.15	15.50
<b>CaO</b>	4.63	8.68
<b>Sum</b>	101.11	100.03
<i>Numbers of ions on the basis of 22 O</i>		
<b>Oxides</b>	<b>Gabbro powder</b>	<b>Gabbro core</b>
<b>Si</b>	6.251	5.978
<b>Al</b>	4.086	0.022
<b>Al</b>		3.803
<b>Ti</b>	0.020	0.068
<b>FeO</b>	1.060	1.369
<b>MgO</b>	3.561	3.366
<b>MnO</b>	0.017	0.083
<b>Cao</b>	0.691	1.354
<b>Sum</b>	15.686	16.042

*Table 4.7: Selected garnet mineral analysis calculations from each experimental sample.*

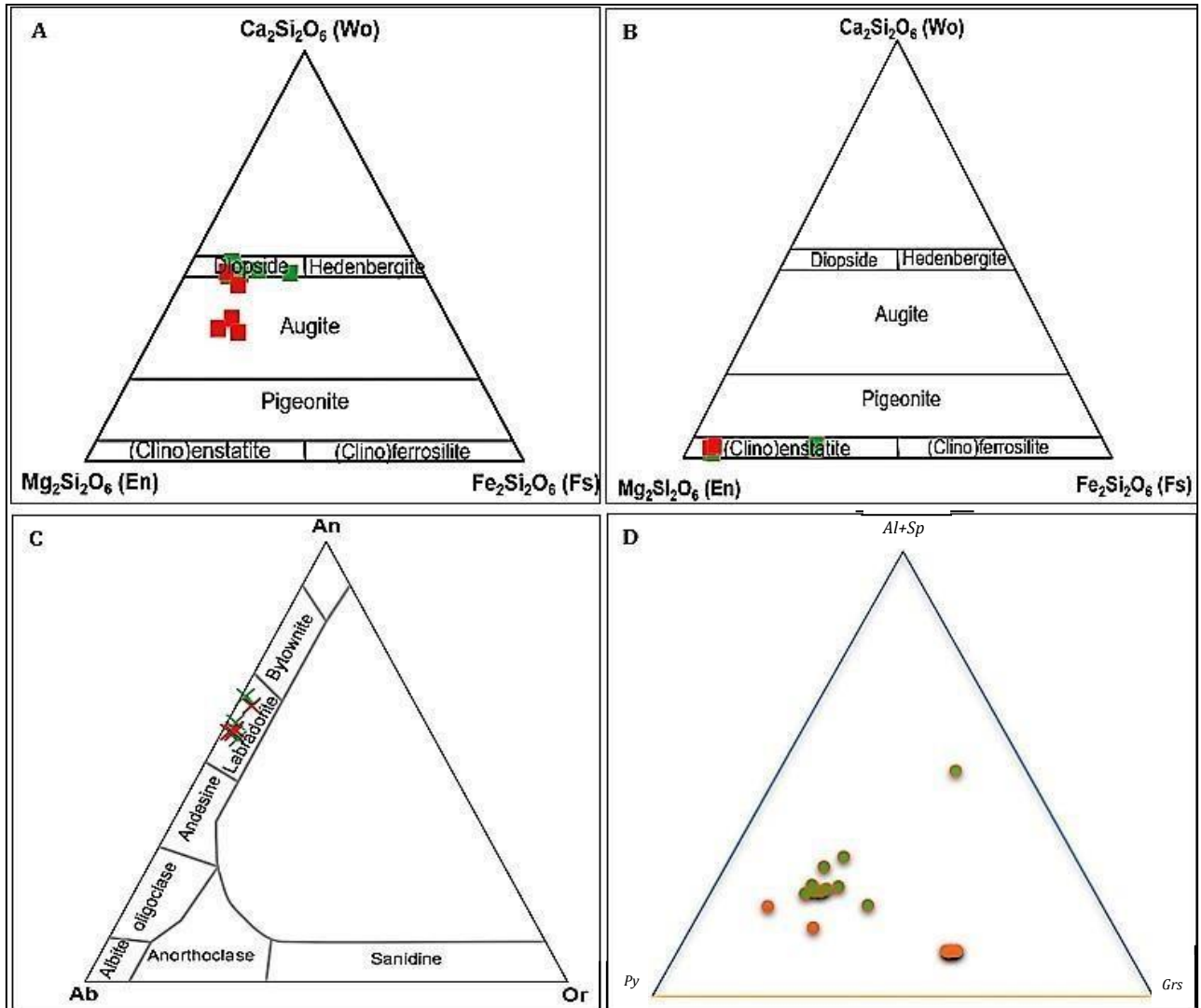


Figure 4.2: (A) Clinopyroxene triangular plots in gabbro powder (Green squares) and gabbro core (Red squares) reaction experiment. The end-members in this ternary diagram are Wo = Wollastonite, En = Enstatite & Fs = Ferrosilite, (B) Orthopyroxenes plots in pyroxene triangular diagram in the melt-peridotite (Green Squares) and melt-gabbro (Red squares) reactions, (C) Reaction of starting melt with gabbro (both powder and core) producing plagioclase in the lower crust, essential labradorite in compositions. Red crosses represent labradorite plagioclases formed in the gabbro powder samples, and the green crosses denote plagioclases from the gabbro core sample. The end-members in this ternary diagram are Ab = Albite, Or = Orthoclase & An = Anorthoclase, (D) Garnet compositions in melt-gabbro powder sample (Green circles) and melt-gabbro core sample (Red circles) reactions. The end-members on each vertex are Al+Sp = Almandine + Spessartine garnet, Py = Pyrope garnet & Grs = Grossular garnet.

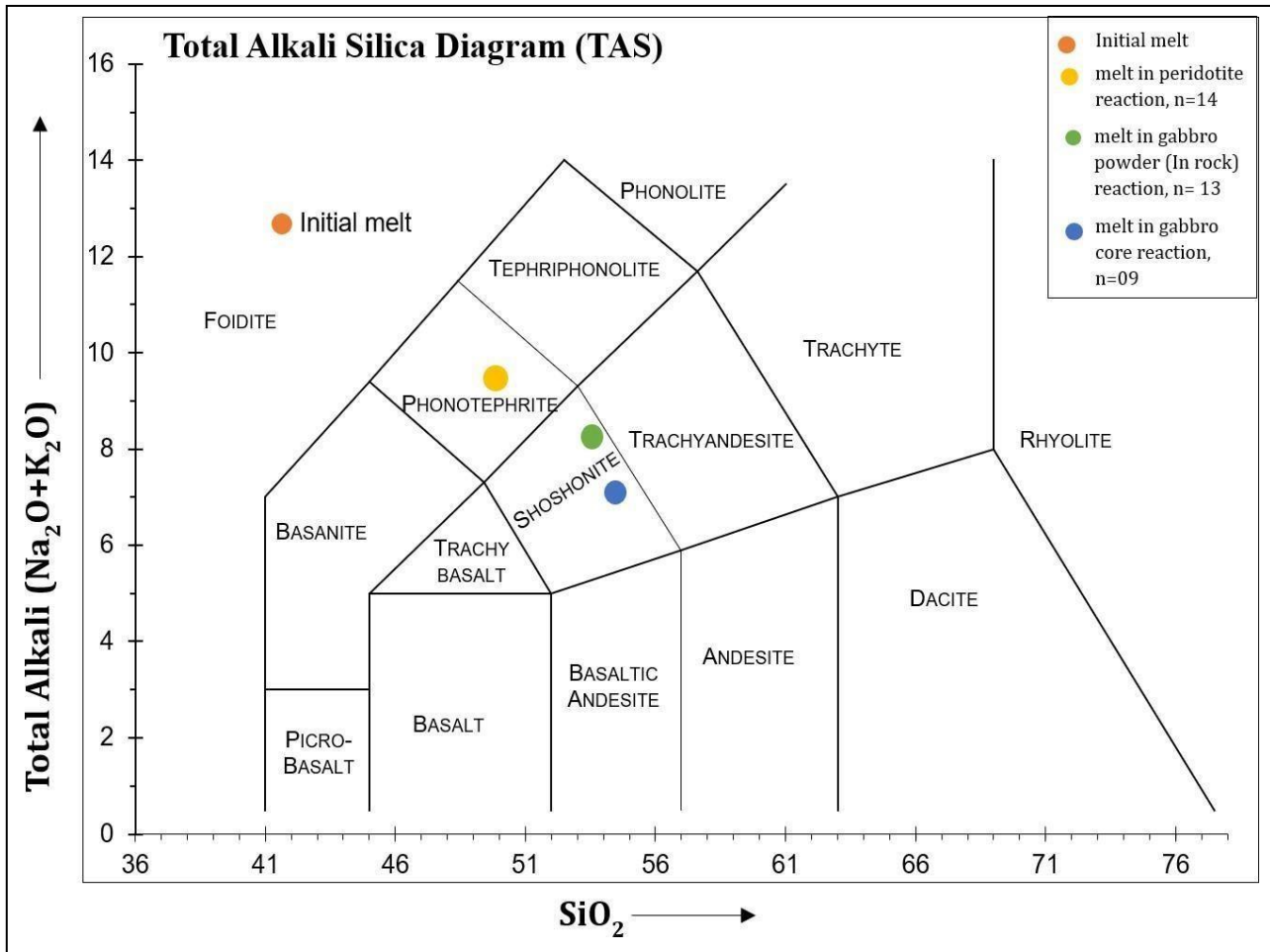


Figure 4.3: Total Alkali-Silica (TAS) diagram for magma series after Le Bas et al., 1986. The 'RED' solid circle in the foidite field in the TAS diagram represents the initial homogeneous partial melt of phlogopite-pyroxenite. The 'Orange' solid circle represents the experimentally produced phonotephrite melt in the peridotite sample (M-22-054) during the reaction of the initial melt with mantle wedge peridotite melt-peridotite reaction. The 'Green' & 'Dark Blue' solid circles representing melts of shoshonitic compositions were produced experimentally during the reaction of the initial melt with gabbro powder (A-22-079) and gabbro core (A-22-080). The upper right box is the legend, and 'n' is the number of data points averaged to get to each coloured point on the graph.

## 4.4 Trace elemental analyses

Before conducting the reaction experiments, a crucial step was to dope the initial melt with twenty-one trace elements, including lithophile elements like Rb, Cs, Ba and  $\text{Eu}^{2+}$ , and also the light & heavy REEs with high concentrations (Table 4.8). Due to high-pressure melt-rock reactions, the concentrations of trace elements in the experimentally produced melts are significant to the starting partial melt from hydrous pyroxenite.

Figure 4.5 illustrates Ba concentration plots showing the variations in Ba concentration in the shoshonitic melt within the carbon trap for the melt-gabbro powder sample (Sample ID: A-22-079). As the depth of the melt increases transversely within the capsule, the concentration of Ba in the melt increases with the time of spot analysis. It is interesting to note that there is a sudden drop in the Ba concentration in the analysis. This sudden decline in Ba could be due to the laser beam analysis intersecting more carbon beads relative to melt in the carbon trap. Since the carbon beads do not contain Ba within them, fluctuation in the Ba concentrations can be used as a proxy for the proportion of melt and carbon beads in each time slice of the laser ablation signal.

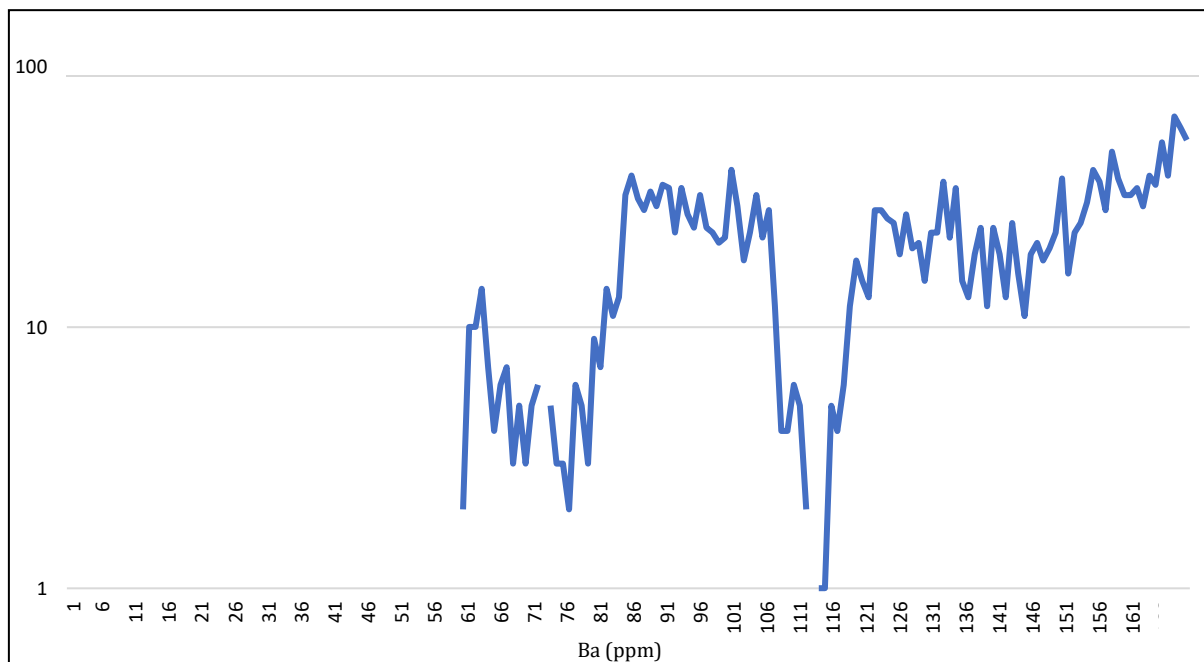
Figure 4.6a represents the bivariate plot for Ba/La, which has a positive slope in the plot. This line comprises two ending members; the carbon trap is placed in the lower left corner, and the experimental melt is placed in the upper right corner of the line. Based on the bivariate plot, it can be seen that the melt has a high Ba/La ratio, which is indicative of the melt. On the other hand, figure 4.6b illustrates a different bivariate plot with Ba and Co as the variables. Based on the slope of this plot, the carbon beads in the melt trap may contain a significant amount of cobalt, which is why there is a negative slope on the plot. Consequently, during the laser ablation analysis, cobalt marked a high signal; this was evident by the high enrichment for cobalt in the experimental melts.

Figure 4.7 compares enrichment and depletion factors between phonotephrite melt and shoshonite melt produced during melt-rock reactions. In phonotephrite melt, there are a few LILEs that are enriched, whereas the REEs are strongly depleted (Figure 4.7a). Conversely, shoshonite melt is strongly enriched in some LILE elements (Figure 4.7b), while some heavy rare earth elements (HREEs) are slightly depleted. It is interesting to note that both phonotephrite and shoshonite melts are enriched in Hf and are significantly depleted in U and Th; this is contrary to the behaviour of these three elements in most island arcs, in which Hf

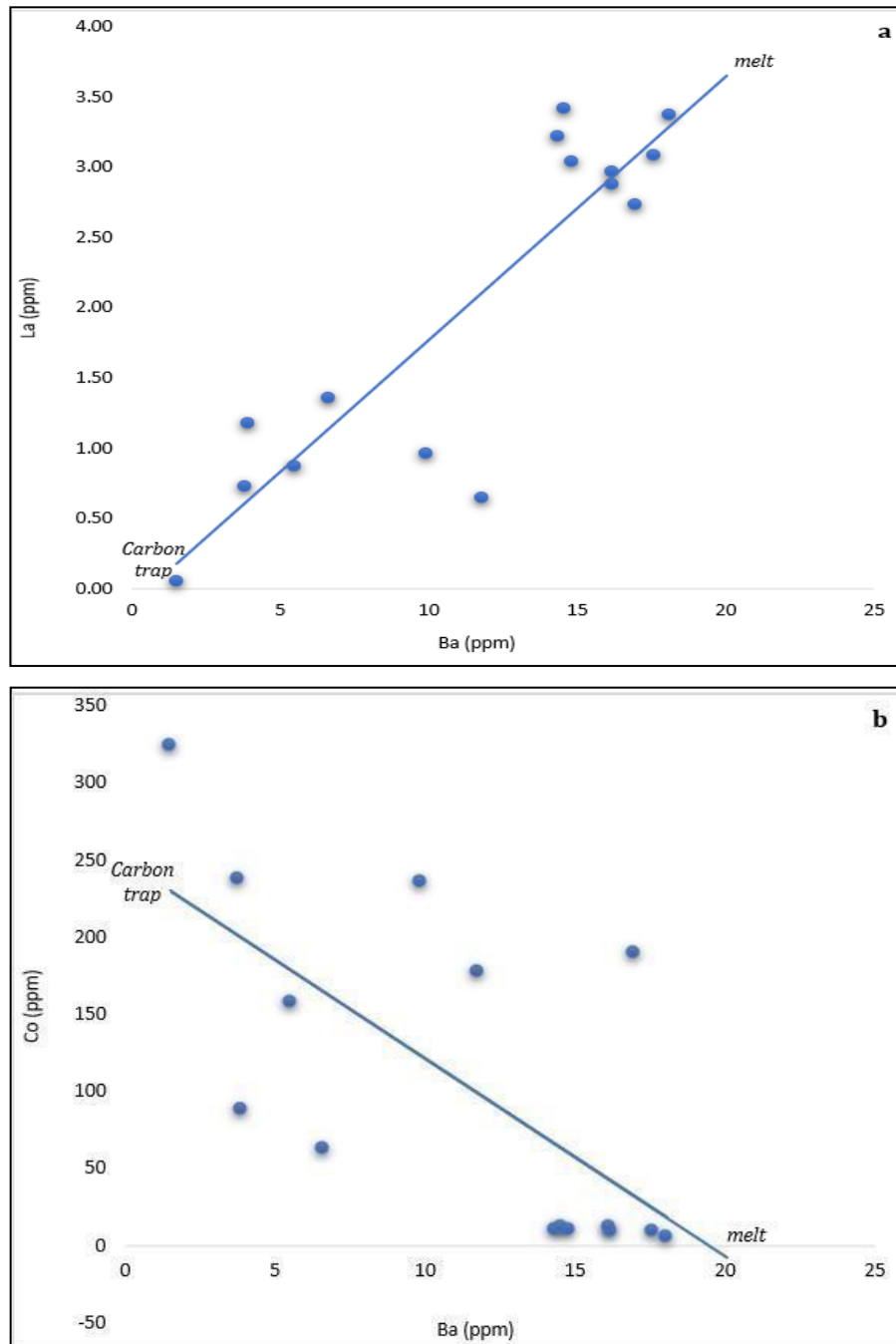
behaves similarly to U and Th.

Elements	Concentrations in the mixture
B	1000
Cu	500
S	500
Nb	1000
Ce	500
Eu	500
Th	500
Dy	500
Er	500
Hf	500
Ho	500
Ho	500
La	700
Rb	500
U	500
Yb	500
Ba	500
Co	500
Lu	500
Y	500
Cs	500
Nd	500
<b>Sum</b>	<b>11700</b>

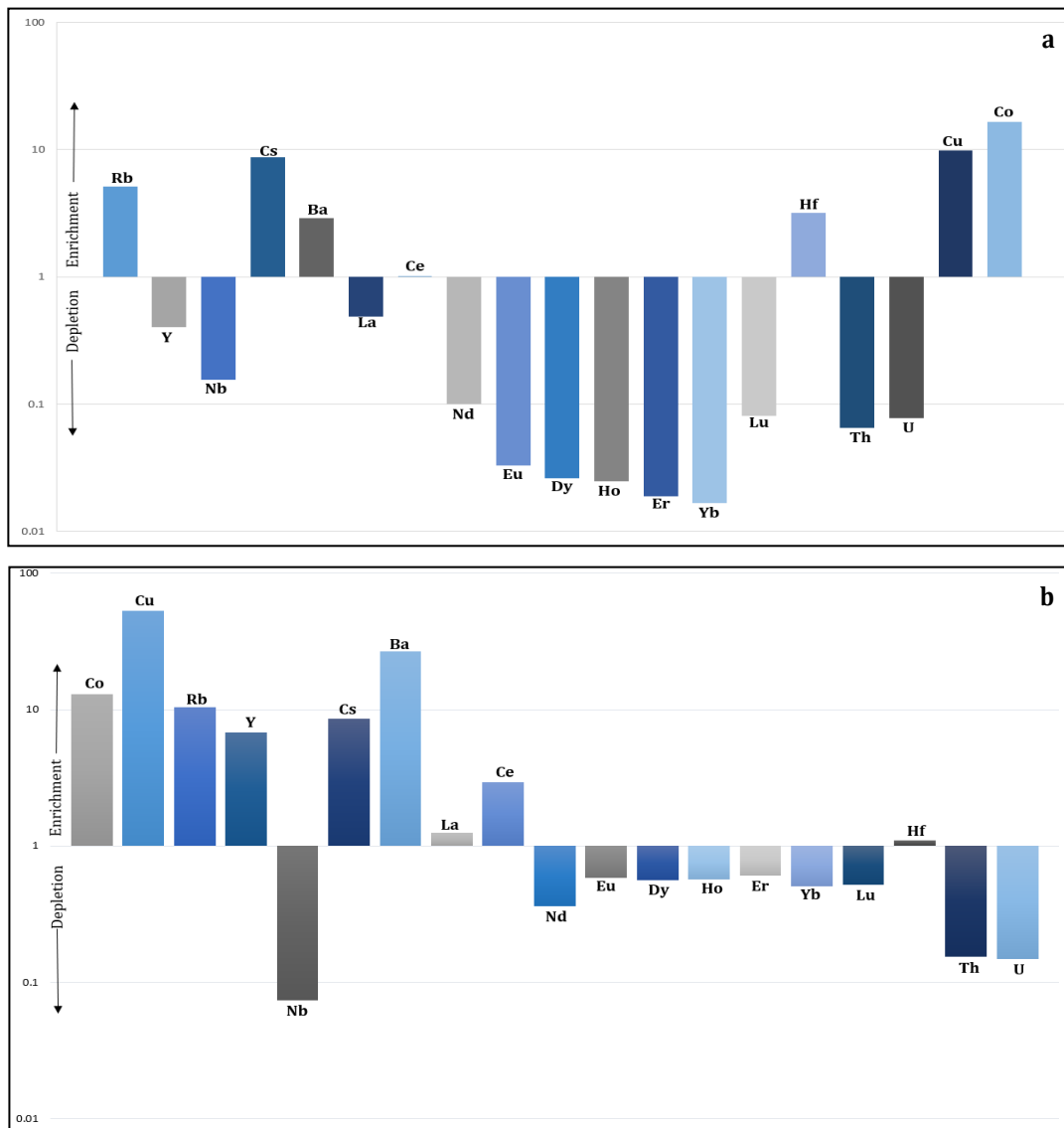
*Table 4.8: Trace elemental (in ppm) concentrations added to the initial melt.*



*Figure 4.5:  $Ba^{138}$  plots on a logarithm scale with factor 10. This plot shows the variations in Ba concentration in the shoshonitic melt within the carbon trap for the gabbro sample.*



*Figure 4.6:  $Ba^{138}$  vs  $La^{139}$  and  $Ba^{138}$  vs  $Co^{59}$  bivariate plots for shoshonite melt produced during the reaction between initial melt with the gabbro powder sample. (a) this bivariate plot has a positive slope in the plot. On the slop, there are two end-member, the carbon trap is placed on the lower left corner, and the experimental melt lies on the upper right corner of the line. This plot suggests that the shoshonite melt gives a high ratio of the Ba/La. (b) The plot shows a negative slope on the graph, which is opposite to the previous plot of Ba/La. This slope indicates that the carbon trap contains a considerable amount of cobalt compared to the experimental melt. That is why cobalt gives a high content during analysis.*



*Figure 4.7: Enrichment- Depletion diagrams showing the enrichment factor for 21 trace elements in experimentally produced melts. (a) Represents the enrichments of Rb, Cs, Ba, Ce, Hf, Cu and Co elements in experimentally produced phonotephrite melt in melt-peridotite reaction sample, (b) showing the enrichment of CO, Cu, Rb, Y, Cs, Ba, La, Ce and Hf in experimentally produced shoshonite melt in the melt-gabbro reaction sample.*

# Chapter 5: Discussion

## ***5.1. Understanding the key sub-arc melt-rock reactions***

### *5.1.1. Melt-rock reactions in the mantle wedge*

The time-series experiments had more starting melt proportions than the peridotite and a small proportion of carbon traps. The reaction experiments showed that the partial melt of phlogopite-pyroxenite reacted with peridotite and modified the initial melt to phonotephritic composition. The key melt-rock reaction in the mantle wedge is determined to be  $Ol_1 + Opx_1 + melt_1 = Ol_2 + Opx_2 + Phl + melt_2$ .

### *5.1.2. Melt-rock reactions in the lower crust*

In two different melt-rock reaction experiments, the melt-rock experiments had more starting melt proportions than dry gabbro powder and gabbro core and a small proportion of carbon traps. In both melt-rock reaction experiments, the reactions with the initial melt, the key melt-rock reaction in the lower crust are defined as  $Opx_1 + Cpx_1 + Plag_1 + Melt_1 = Opx_2 + Cpx_1 + Plag_2 + Grt_1 + Melt_2$ .

## ***5.2. Determining the changes in melt composition during melt-rock reactions***

### *5.2.1. Reaction between the mantle wedge peridotite and melt*

The reaction of the initial melt with the mantle wedge peridotite resulted in the formation of a melt of new composition. This reaction led to a significant increase in the percentage of  $SiO_2$  to 49.89 wt% in the experimentally produced melt compared to the initial melt. As compared to the initial melt, the new melt contains a higher percentage of  $MgO$ ,  $MnO$ , and  $Cr_2O_3$  and a lower percentage of  $TiO_2$ ,  $Al_2O_3$ ,  $FeO$ ,  $Na_2O$ , and  $K_2O$ . Olivine, on the other hand, exhibits an average magnesium number of 89.57 after chemical reactions. Furthermore, among all trace elements, the heavy rare earth elements (HREEs) are strongly depleted in this melt and have the highest enrichment in Co, Cu and Cs (Figure 4.7a).

### *5.2.2. Reaction between the lower crustal gabbro and melt*

As a result of the reaction between the lower crustal gabbro and the initial melt, the percentage of silica in the experimentally produced new melt increased significantly ( $SiO_2 > 52$  wt%). Comparing the new melt with the initial melt, the  $TiO_2$ ,  $MnO$ ,  $MgO$ , and  $CaO$



contents in the new melt decreased, and  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$  contents increased (Table 4.2, columns 3 & 4). Moreover, the chemical analysis shows that heavy rare earth elements (HREEs) in this melt are slightly depleted and enriched in Co, Cu and Ba (Figure 4.7b) in comparison to the original melt.

### ***5.3. Comparison between the compositions of experimental volcanic glass (melt) and natural volcanic arc glasses***

The lower crustal melt-rock reactions altered the composition of the initial melt to shoshonite (Figure 4.3) with an increased concentration of silicon, aluminium, and alkali oxides and a reduction in iron and magnesium oxides. Contrariwise, The melt-rock reactions in the mantle wedge on the other hand changed the composition of the starting melt to phonotephrite composition (Figure 4.3), with higher concentrations of silicon oxide, manganese oxide, and magnesium oxide and lower concentrations of aluminium, calcium, iron, and alkali oxides. One of the main reasons to choose some published data for comparison is to check whether the starting material with which we started our reactions could explain the formation of the rock suits found in volcanic arcs.

In relation to experimentally produced phonotephrite melt, the ankaramitic absarokite flows in Carmacks group in Yellowstone have MgO ranges up to 15 wt% and contains olivine phenocrysts with Mg compositions as high as  $\text{Fo}_{93}$ . Besides, the results of the melt-peridotite reaction show that the phonotephritic melt consists of an average amount of 18.53 wt% MgO. At the same time, the olivine phenocrysts in the melt-peridotite sample are compositionally similar to Carmacks absarokites (phonotephrite melt has Mg-rich olivine of  $\text{Fo}_{93.6}$ ). Besides, the experimentally generated phonotephritic melt suggests the presence of high concentrations of total alkali (>9 wt%) and moderate concentrations of  $\text{SiO}_2$  (44 – 51 wt%) and a very low amount of  $\text{Al}_2\text{O}_3$  (4.45 – 6.61 wt%). Furthermore, this phonotephrite melt has an average high Ca/Al ratio of 0.823, which is reasonably similar to some Carmacks group absarokite lava, which has low Ca contents in combination with a high Ca/Al ratio. Combined with the major oxide chemistry, the experimentally produced phonotephritic melt exhibits a periodic variation in LILE elements such as Rb/Ba (0.402-0.140) and K/Na (3.607 – 22.878) (Figure 4.7a). It is similar to the absarokite lavas of the Carmack group, which show systematic variation in the LILE proportions (e.g., Rb/Ba, K/Na).

Most of the Fiji volcanics show a high trend in MgO (>8.3 wt% MgO) absarokite composition. In contrast, the MgO content of phonotephrite melt is very high (with an

average of ~18.53 wt% MgO). On the other hand, shoshonite melts in the melt-gabbro reaction experiments contain more CaO (>5.8 wt% CaO) and less MgO (average ~2.88 wt% MgO), and the K<sub>2</sub>O/Na<sub>2</sub>O ratio varies between 0.94 – 1.4 with >3.1 wt% K<sub>2</sub>O at SiO<sub>2</sub> >50%, which chemically resembles the Viti Levu, Fiji shoshonites.

Most of the rocks found in the Zedong terrain in southern Tibet are absarokites in composition, with SiO<sub>2</sub> content between 45 wt% to 52 wt% with the increasing content of K<sub>2</sub>O. Some are more evolved into shoshonite and banakite rocks. Aside from K<sub>2</sub>O, the absarokites have similar concentrations of the major elements. Compared to the ocean island basalts, which are found in island arcs and tend to have higher concentrations of minor elements. The phonotephritic melt which has been produced during the reaction between the initial melt and peridotite (e.g., sample M-22-054, Figure 4.1a–c) show a high concentration of total alkali (>9 wt%) and moderate concentrations of SiO<sub>2</sub> (44 wt%– 51 wt%). The major oxides chemical analyses of the experimentally produced shoshonitic melts in gabbro samples (e.g., sample A- 22-079 & A-22-080, figure 4.1d & 4.1g) indicate that the melts contain 3.10 wt% to 4.14 wt% of K<sub>2</sub>O, and the K<sub>2</sub>O/Na<sub>2</sub>O ratios for these melts range between 0.94 and 0.71. However, shoshonite melts have high levels of SiO<sub>2</sub> (52 wt% – 55 wt%), tend to have a high amount of total alkalis ranging between 7 wt% – 8 wt% (Figure 4.3), and high aluminium oxide percentages (19.30 wt% to 22.10 wt%).

The reactions between the initial melt and gabbro show that the composition of the shoshonite melt is comparable to the natural volcanic glass compositions from a few volcanic arcs, which are rich in K<sub>2</sub>O. The shoshonites from the western Kunlun orogenic belt have high K<sub>2</sub>O content (2.54 wt% – 10.95 wt%, average 5.48 wt%), and high K<sub>2</sub>O/Na<sub>2</sub>O ratios (>0.6 for SiO<sub>2</sub> <55 wt% and >1 for SiO<sub>2</sub> >55 wt%). Moreover, these rocks also have high but variable Al<sub>2</sub>O<sub>3</sub> content (13.11 wt%–19.20 wt%), high Fe<sub>2</sub>O<sub>3</sub>/FeO ratio (0.85–1.51, with an average of wt%) and a low TiO<sub>2</sub> content (0.15 wt% – 1.12 wt%, with an average of 0.57 wt%). These chemical signatures are similar to the experimentally produced shoshonite melts, which evolved during the reactions between the initial melt and lower crustal gabbro. This experimentally generated shoshonites have K<sub>2</sub>O ranges from 2.55 wt%– 4.42 wt%, the average is 3.95 wt%, and high K<sub>2</sub>O/Na<sub>2</sub>O ratios of 0.94 – 0.71 for SiO<sub>2</sub> <55 wt%. The content of Al<sub>2</sub>O<sub>3</sub> is also high and varies between 18.11 wt% and 22.10 wt% and has an almost similar high ratio of Fe<sub>2</sub>O<sub>3</sub>/FeO (0.70 – 1.91) and low TiO<sub>2</sub> content range between 0.22 to 1.20 wt% as western Kunlun orogenic belt shoshonites. According to the chemical analysis of major oxides, all samples of western Kunlun shoshonitic plutons are potassium-rich and are predominantly lying within the shoshonite field as described by Peccerillo & Talyor 1976; further, SiO<sub>2</sub> generally ranges between 45 wt% to 75 wt% at high K<sub>2</sub>O (typically >3.5%). In spite of their high

content of  $K_2O$ , they are Not considered as ultra-potassic, maintaining a  $K_2O/Na_2O$  ratio between 0.5 and 2.0, likewise thin the Shoshonitic magma field. Additionally, post-collisional shoshonites from the Tibetan plateau display a variable Mg number  $[=MgO / (MgO \times 0.8 + FeO_{Total})]$  from 73 to 10, with increasing values of  $SiO_2$  and  $Al_2O_3$ . At the same time,  $Fe_2O_3$  and  $CaO$  (which have an inflexion at 5%  $MgO$  declined The decrease in magnesium oxide. Compared to these post-collisional Tibetan shoshonites, experimentally produced shoshonites show very similar chemical characteristics in terms of Mg number ranging between 73 to 44, with rising Si and Al oxide percentages and a decreasing amount of iron and calcium oxides with  $MgO$ . The experimentally produced shoshonites show very high enrichment of Rb, Cs, Ba, Ce, Hf, Cu & Co elements and depletion in Y, Nb, La, Nd, Dy, Eu, Ho, Er, Lu, Yb. It is also important to note that Hf shows the opposite trend to Th and U. While Hf is slightly enriched in the melt; on the other hand, U and Th are sharply depleted in the shoshonite melt. This result opposes the chemical characteristics of island arc magma, where these three elements behave similarly.

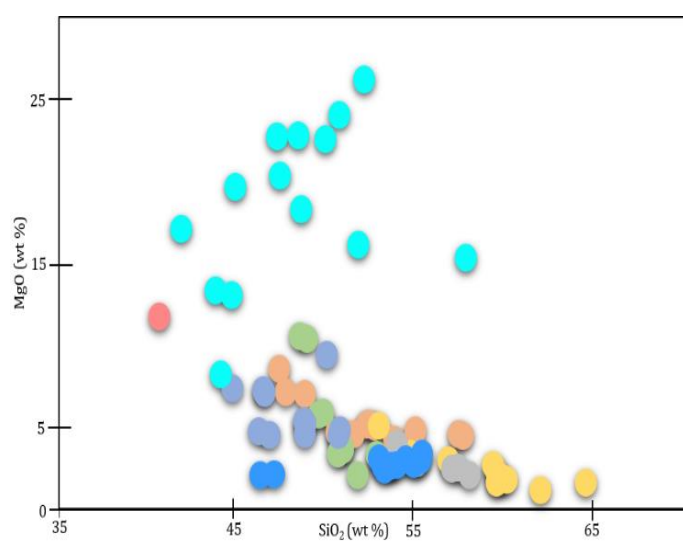
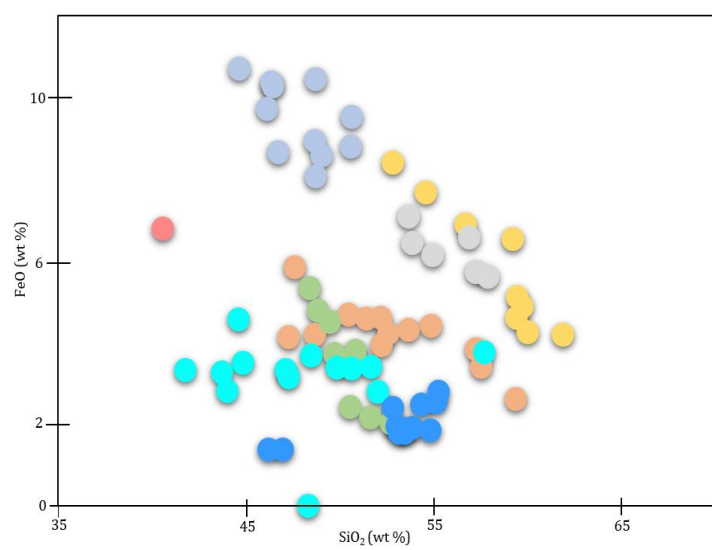
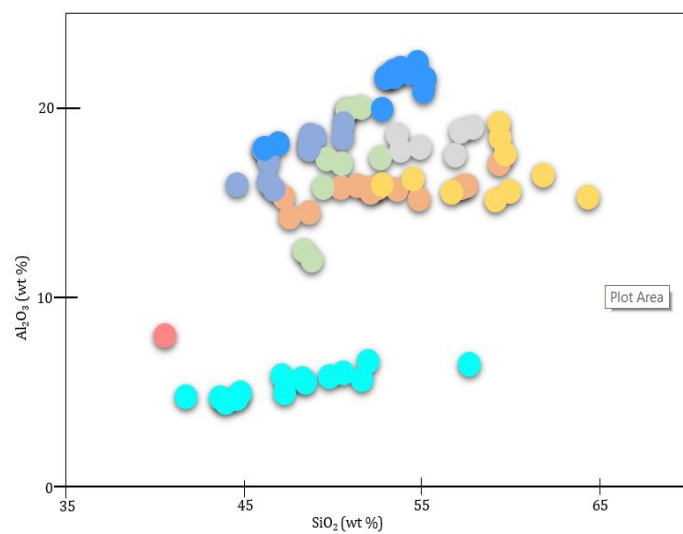
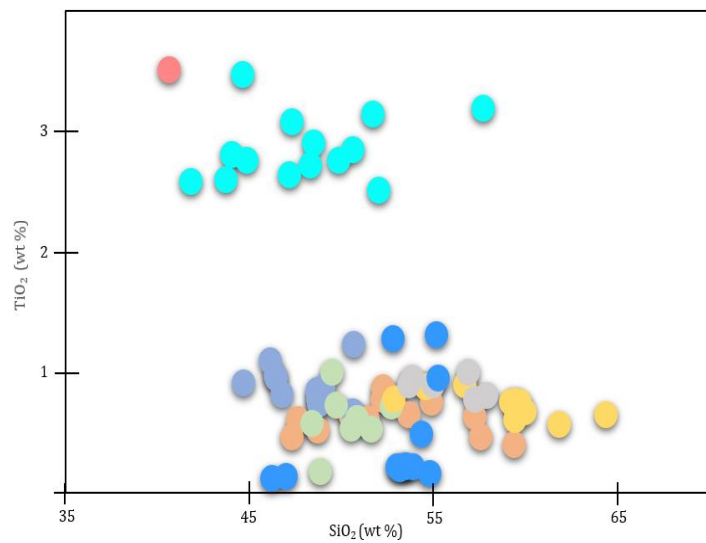
Furthermore, in the Tibetan plateau shoshonite, there is an inflected trend of  $TiO_2$ , with average excesses of 13 wt% to 15 wt% for  $Al_2O_3$  and 0 wt% to 5 wt% for  $TiO_2$ , respectively, and low absolute abundances of  $TiO_2$  and  $Al_2O_3$ . Likewise,  $Na_2O$  and  $K_2O$  have relatively continual surpluses, though  $K_2O$  is always slightly higher than the  $Na_2O$  ( $Na_2O/K_2O < 2$ ). In contrast to the Tibetan plateau shoshonites, the experimentally produced shoshonites have slightly lower  $K_2O$  than  $Na_2O$  content, with a  $K_2O/Na_2O$  ratio ranging between 0.94 and 0.71 (Table 4.2). Several other chemical signatures also intensify the idea that the experimentally generated shoshonite melt is chemically similar to the western Kunlun shoshonites and post-collisional Tibetan shoshonites. In addition to the Tibetan plateau shoshonite, experimentally produced shoshonite melt contains certain LILE elements and incompatible elements similar to the Tibetan plateau shoshonite. It is notable that La has a moderate but variable content in the melt, while Eu shows a predominantly negative anomaly (Figure 4.7b). Further, the melt also has a high degree of variation in the ratios; for example, the percentage of Ba/La varies from 2.297 to 42.424, that of La/Yb varies between 1.967 and 23.243, and that of La/Nb varies between 3.14 and 71.379.

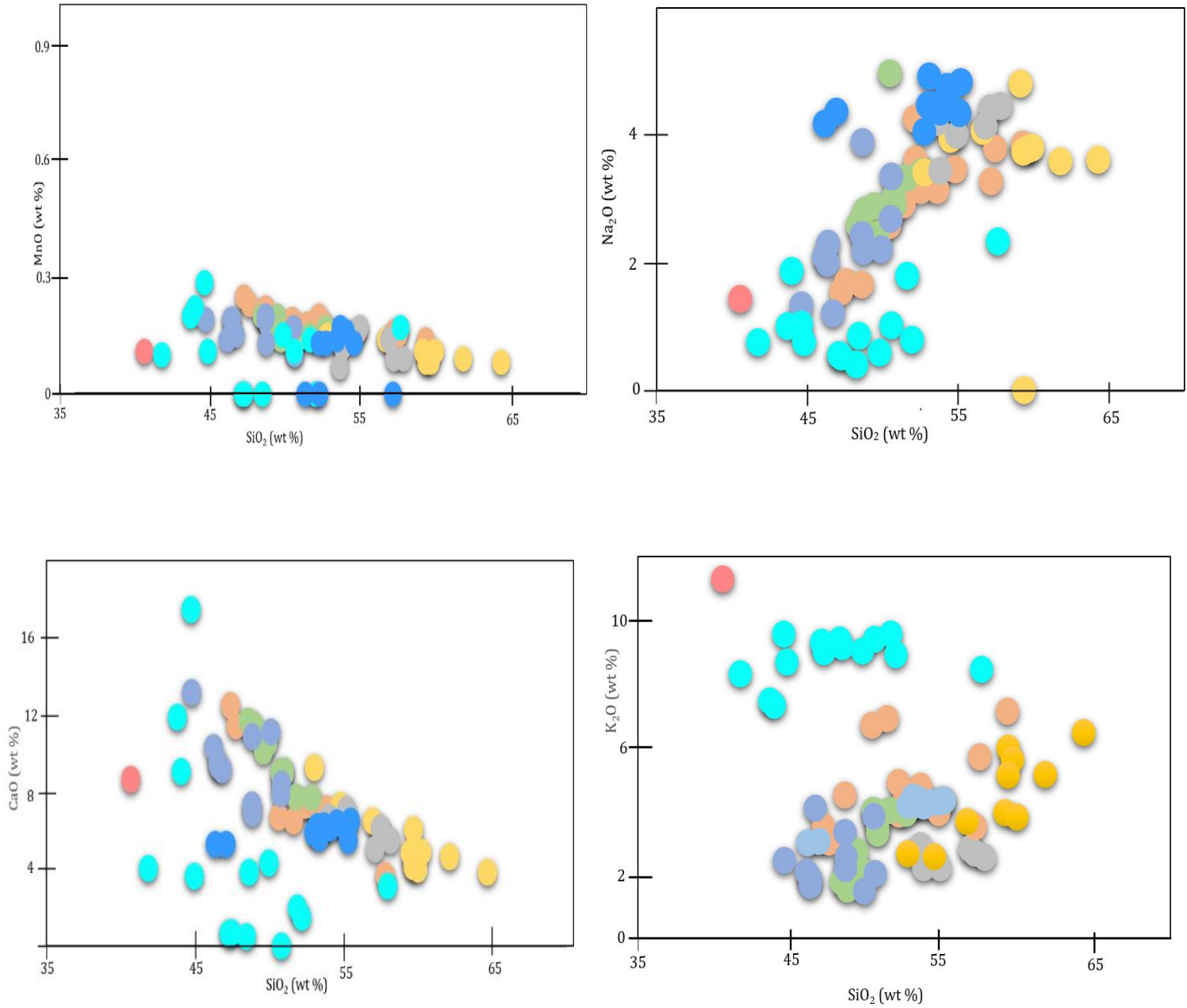
Additionally, in the Lavras do Sul shoshonitic association in southernmost Brazil, the basic volcanic rocks have higher values of  $K_2O$  than  $Na_2O$ , which are categorised as shoshonites and potassic trachybasalts (Le Maitre, 1989). They are generally composed of nearly saturated silica with normative olivine (9.75–23.25), hypersthene (8.19), and diopside (3.71–18.70). The aluminium content ranges from 11.43 wt% to 14.50 wt%, whereas the experimentally

produced shoshonite melt is slightly rich in aluminium (averagely~21.16 wt%); the lesser values are attributed to the accumulation of olivine and clinopyroxenes as indicated by the simultaneous rise in magnesium content from 8.20 wt% to 13.00 wt%. Gest and McBimey (1979) have suggested that shoshonites are obtained from more basic magmas through the fractionation of olivine and pyroxene.

An important observation from the bivariate plot for  $\text{SiO}_2$  vs  $\text{Al}_2\text{O}_3$  (Figure 5.1) is that the phonotephrite melt produced during the melt-peridotite reaction has a low aluminium content compared to shoshonite melt in gabbro. This is because gabbro is largely composed of plagioclase and clinopyroxene, whereas the plagioclase feldspar has a high percentage of aluminium. As a result, at the higher-pressure melt-rock reactions (>9 Kbar pressure) in the mid to lower crustal depth, a plagioclase breakdown reaction occurred in which calcic plagioclase breaks down to form corundum (Figure 4.1d) and a melt with high aluminium content (Wood, 1978).

All the regions of the island arcs that have been studied for the presence of shoshonites (e.g., New Guinea, Indonesia, Kamchatka, and Fiji) represent the latest volcanic events. This is because they are located the farthest from the trenches. As far as their mineralogy is concerned, they are similar to the alkali basalts of Japan and the Aleutians. However, they differ principally in their K/Na relationships and corresponding lithology. Similarly, an increase in potassium concentration in the western Aleutians was reported, with a transition from submarine assemblages to subaerial Assemblages and a decline in the enrichment of iron (Wilcox, 1959). Interestingly, out of all the areas investigated, only the Viti Levu the volcanic centre has a clear secular evolution from the tholeiitic to calc-alkaline and then to shoshonitic volcanism.





*Figure 5.1: Major oxides compositional bivariate comparison plots between the experimentally produced melts and natural volcanic glass compositions from a few volcanic arcs. Orange circle: Kamchatka arc; Green circles: Viti Levu, Fiji; Yellow circles: Kunlun Belt; Blue circles: Southern Tibet; Light grey circles: Southernmost Brazil; Light blue circle: Melt in Peridotite; Dark blue circles: Melt in Gabbro Powder; Red solid circle: Initial melt composition.*

# Chapter 6: Conclusion

The melt-rock reaction experimental study was focused on the volcanic arcs in subduction zone settings. The study began with a homogeneous partial melt of phlogopite-pyroxenite reacting with peridotite of the mantle wedge and lower crustal gabbro. This study explored the following questions (1) how does chemistry changes along sub-arc melt migration pathways during melt-rock reactions, (2) what are the main sub-arc melt-rock reactions that take place during melt ascent through mantle wedge and lower crust, and (3) could this melt explain the origin of the rock suites found in arc settings? In addition to these questions, the study has also explored the frequency of occurrence of this melt beneath the global volcanic arcs.

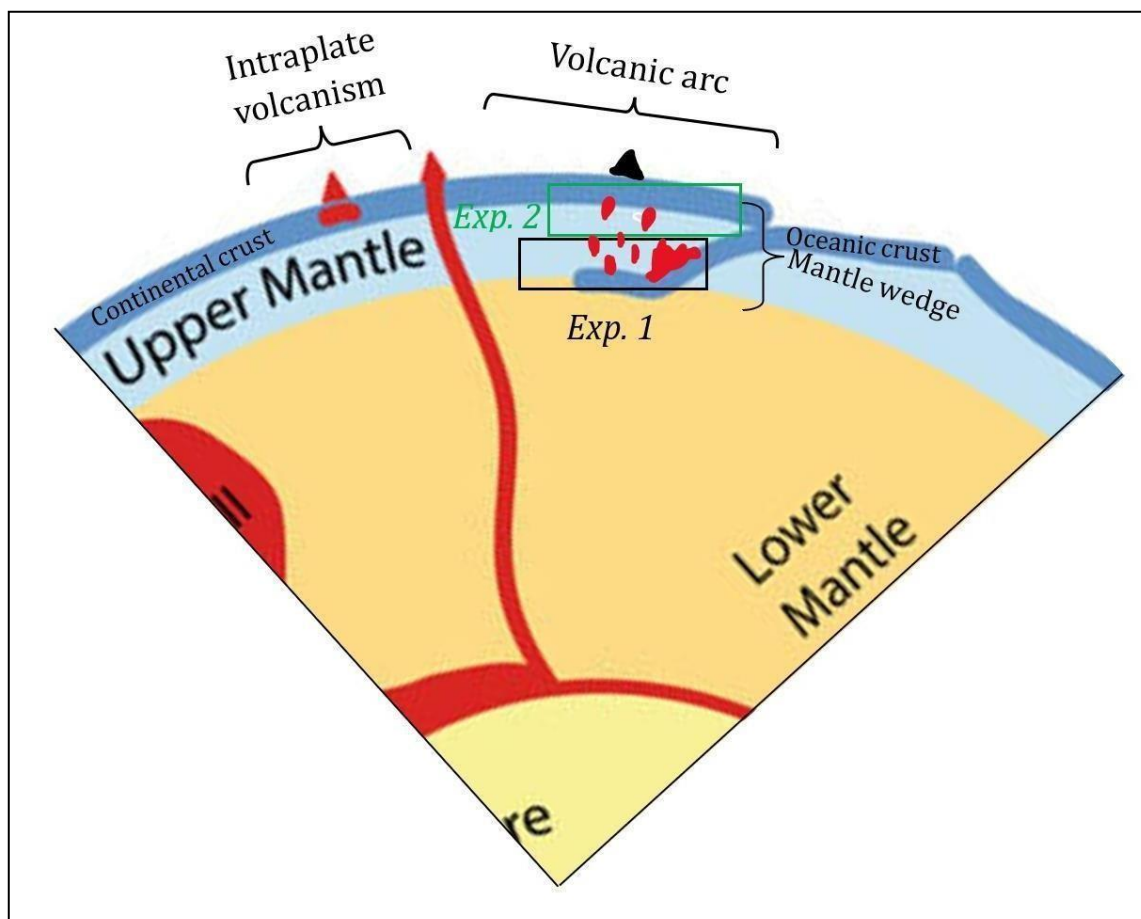
Interestingly, the major and trace elemental data obtained from phonotephrite melt does not clearly indicate any chemical relationships with the other natural volcanic arc settings. The bivariate plots of the major oxides (Figure 5.1) suggest that the chemical compositions of phonotephrite melt appear quite distant from other natural volcanic glass compositions, on the other hand, is more inconsistent with the rocks found in volcanic arc settings. Conversely, the shoshonite melts, on the other hand, show a similar geochemical trend to the other natural volcanic arc settings. Consequently, two possible explanations could be as follows:

(1) First, the initial melt used in the reaction experiments is uncommon beneath volcanic arc crust and found only in a few volcanic arc settings globally but is rather more common in intraplate volcanic settings (Figure 6.1).

(2) Second, since the occurrence of the initial melt is rare beneath the arc crust, reactions of harzburgite peridotite with this melt in the mantle wedge are also occasional in subduction zone settings. For this reason, it cannot explain the magma generation processes in subduction zone settings.

Taking into account the most recent studies and interpretations of the hybridisation of melt with the mantle and lower crust, some future melt-rock experimental studies at much higher pressure (from 4 to 4.5 GPa pressure, ~depth 120 – 135 km) and 1250<sup>0</sup> C temperature would enrich our current understanding through conducting repeated melt-rock reactions and comprehending how mantle hybridisation processes contribute to subduction zone magmatism. In future studies, we will conduct a series of reactions in three distinct ways. 1) In the first part, we will conduct a series of reactions between the mantle wedge peridotite and mica-pyroxenite partial melts at a pressure of 4 – 4.5 GPa and 1250<sup>0</sup> C temperature, 2) this

would be followed by reacting the new resulting melt from the first experiment with lower crustal gabbro, and 3) a different approach could be to mix the melt and rock components of the experiment so that there will be no separate layers of melt and rock powder in the capsule. Besides these crucial steps in reaction experiments. In addition, a further required piece of future work is to characterise the carbon beads better so that we know which trace elements are affected by the ablation of beads and the glass in the melt traps. As a result of these repeat reaction studies, we will be able to assess the melt-rock reaction studies in two ways: 1) understanding melt equilibration via the series of melt-rock reactions and 2) enriching our current interpretation of the fractionation trend of absarokite-shoshonite-banakite magma.



*Figure 6.1: An example of a schematic cross-sectional diagram of a subduction zone and intraplate volcanic setting. The phlogopite-pyroxenite melt (initial met) occurs (represented by red-coloured droplets) above the subducting oceanic crust beneath overriding continental lithosphere, which migrates upward into the mantle wedge where it reacts with harzburgite peridotite; the 'Black square' box shows the location of these reactions. The melt progressed further up and reacted with the lower crustal gabbro, represented by the 'Green square' on the diagram.*



# Supplementary Data

The links below contain the additional supplementary data set:

[Supplementary Data - OneDrive \(sharepoint.com\)](#)

ImageMatrix

<https://imagematrix.science.mq.edu.au/viewer/?mode=view&id=849>

<https://imagematrix.science.mq.edu.au/viewer/?mode=view&id=859>

<https://imagematrix.science.mq.edu.au/viewer/?mode=view&id=850>

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La-ICP-MS traceelemental analyses

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# Appendix

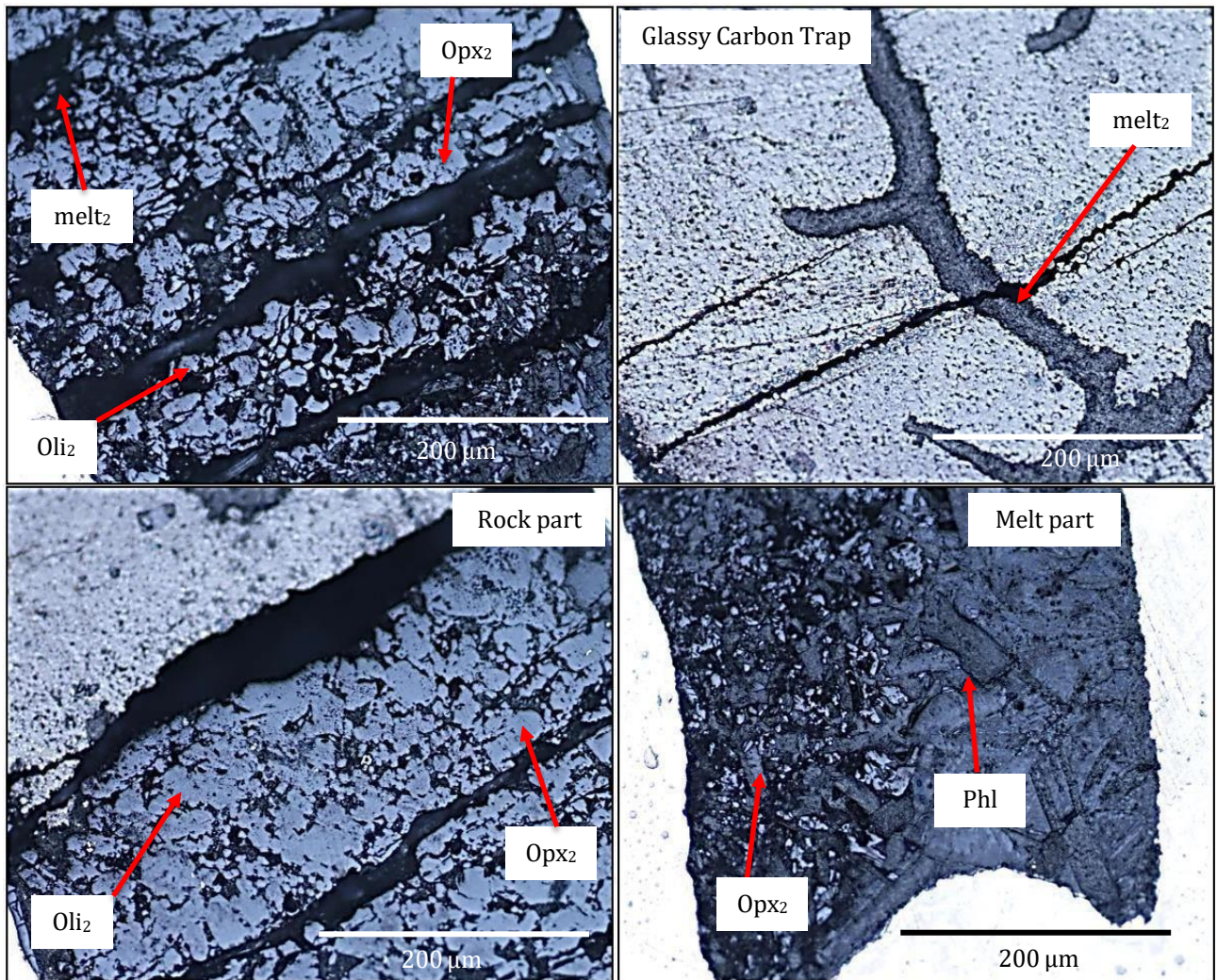
In the early stages of our study, we started the melt-rock reactions using noble metal capsules made of Ag<sub>70</sub>Pd<sub>30</sub> for high-pressure experiments. The samples were arranged in three layers, with the bottom layer being the initial melt and the top layer being the carbon trap. A layer of Peridotite and Gabbro rock was sandwiched between these two layers, allowing the initial melt to migrate through the rock layer and collect in the carbon trap.

The purpose of this section is to present the experimental details of the melt-rock reactions between the phlogopite-pyroxenite melt and mantle wedge peridotite and lower crustal gabbro using the Ag<sub>70</sub>Pd<sub>30</sub> noble metal capsule, together with some microscopic images, BSE images, along with a few mineralogical and chemical maps as well.

Experimental Run	Material used	Pressure	Temp.	Hours	Phases occurred
Melt-peridotite reaction	Capsule- Ag <sub>70</sub> Pd <sub>30</sub> Pyroxenite+ peridotite+ vitreous carbon trap	1.5 GPa	1200° C	28 Hours	Rich in diopside and phlogopite. Rock minerals that have recrystallised include forsterite.
Melt-gabbro powder reaction	Capsule- Ag <sub>70</sub> Pd <sub>30</sub> Pyroxenite+ gabbro (powder)+ vitreous carbon trap	1.5 GPa	1100° C	28 Hours	Rich in diopside, phlogopite ± garnet. Rock minerals that have recrystallised include plagioclase and diopside.
Melt-gabbro core reaction	Capsule- Au <sub>70</sub> Pd <sub>30</sub> Pyroxenite+ gabbro core+ vitreous carbon trap	1.5 GPa	1100° C	28Hours	Plagioclase, Garnet, diopside, enstatite. Rock minerals that have recrystallised include plagioclase and diopside.

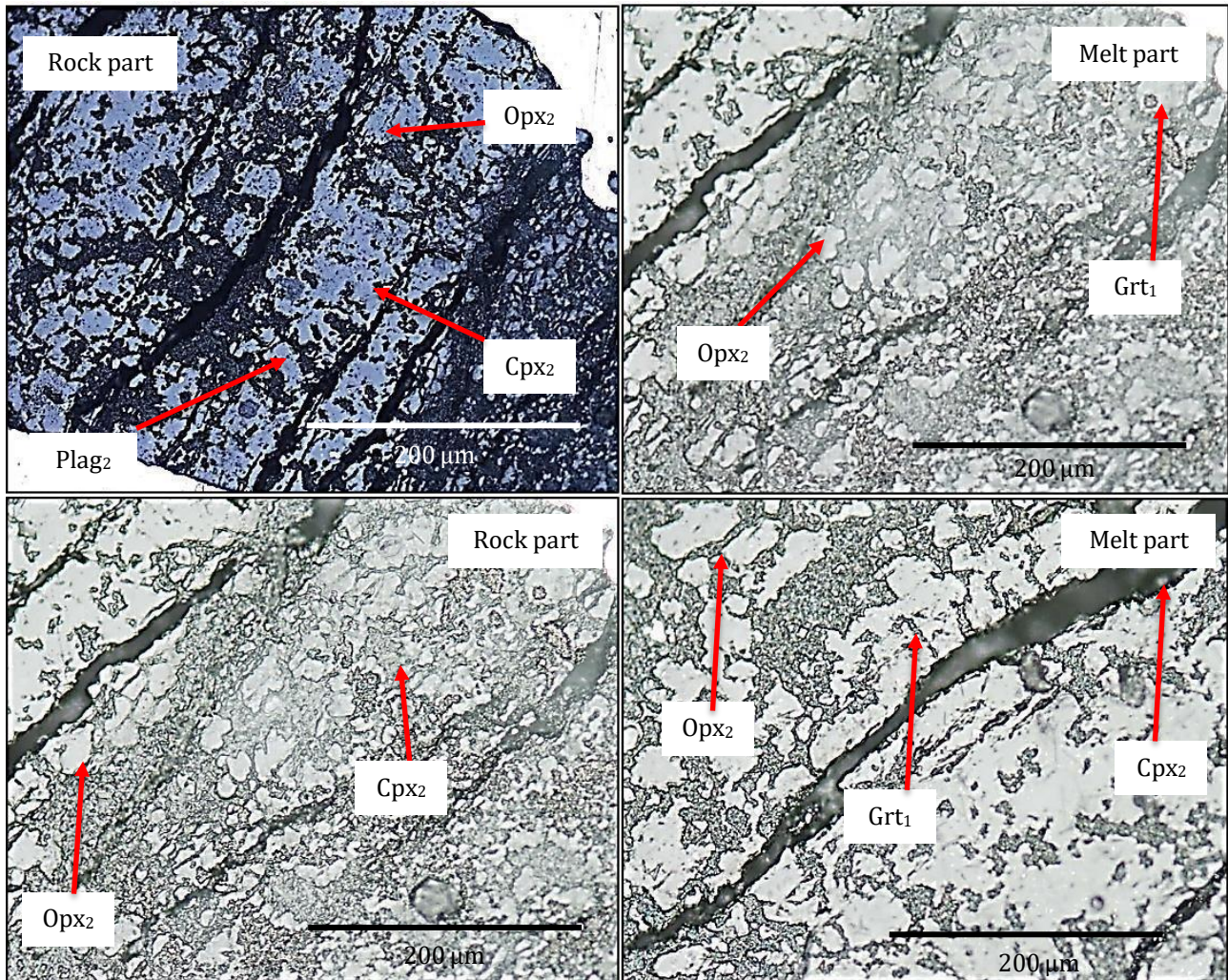
*Table 1: Details of experimental run conditions in Ag<sub>70</sub>Pd<sub>30</sub> capsule for melt-peridotite and melt-gabbro reaction experiments.*





*Figure 1: BSE Images of the melt-rock experimental reactions in  $\text{Au}_{70}\text{Pd}_{30}$  capsule at the pressure of 1.5 GPa and 1200°C for melt-peridotite reactions in the mantle wedge.*





*Figure 2: BSE Images of the melt-rock experimental reactions in  $\text{Au}_{70}\text{Pd}_{30}$  capsule at the pressure of 1.5 GPa and 1150°C for melt-gabbro reactions in the lower crust.*





*Figure 3: Mineralogical maps of melt-rock reactions obtained from an FEI Teneo Field Emission Scanning Electron Microscope (SEM) with the Nanomin software. (A) mineralogical maps of melt-peridotite reaction comprise annite (iron-rich end-member of biotite), phlogopite (magnesium-rich end-member of biotite), clinopyroxene, orthopyroxene and olivine, (B) mineralogical maps of melt-gabbro reaction comprise plagioclase, annite, phlogopite, clinopyroxene, orthopyroxene and garnet.*



*Figure 4: Chemical maps of melt-rock reactions obtained from an FEI Teneo Field Emission Scanning Electron Microscope (SEM) with the NanoMin software. (A) chemical maps of the melt-peridotite reaction including Mg, Al, Ca, K, and Fe oxides, (B) chemical maps of the melt-gabbro reaction including Si, K, Ca, and Fe oxides.*