Unraveling the evolution, dynamics and time-scales of magmatic processes below the volcano, West-Java, Indonesia

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**UNRAVELING THE EVOLUTION, DYNAMICS, AND TIME-
SCALES OF MAGMATIC PROCESSES BELOW GEDE
VOLCANO, WEST-JAVA, INDONESIA**

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SUMMARY

Gede is the closest active stratovolcano to the capital of Indonesia, thus it is a potential hazard to millions of people around the volcano and in Jakarta. It is currently being monitored by various geophysical methods in a collaborative project between CVGHM and EOS. However, interpretation of new unrest is fraught with uncertainty unless its geological and petrological history is well understood. I present here a detailed petrochemical study to untangle Gede's past history since about the last 45 kyr to present that sheds light on its magmatic evolution and reservoir dynamics, and the time-scales of these processes. A key finding is that Gede's evolutionary path changed in the Holocene: the main magma dynamics has shifted from a deep mafic reservoir (about 24 km below its summit) to a shallow one (at about 4 km) made of silica-rich melts. Mingling and mixing of volatile-rich basaltic and crystal-rich rhyolitic magmas is one of the most important processes that lead to the main erupted compositions (andesites) and which also may lead to eruption. Three-dimensional numerical simulation of diffusion of chemically zoned minerals reveals that these shallow reservoir processes start probably only a month before eruption. These results should guide interpretations of monitoring signals and improve hazard mitigation efforts in a future unrest event.

INTRODUCTION

Subduction-zone volcanoes are among the most active and produce the most explosive eruptions worldwide. They are located along the convergent margins of oceanic and continental crusts, a place where landscape variability and therefore biodiversity is among the highest on the globe and thus are heavily populated. Along and across the subduction-zones volcanoes produce a large compositional variety of magmas through time and space (e.g. Ishikawa & Nakamura, 1994; Patino *et al.*, 2000; Plank & Langmuir, 1988), which manifests in different eruption styles. These volcanoes, therefore, often pose a great threat of human life (e.g. Merapi, 2010) and can lead to remarkable economical loss (e.g. Mount St. Helens, 1980). Magma compositions and eruption style may result from both the composition of the primary magma and the evolution paths and processes that it experiences. Fractional crystallization (e.g. Alonso-Perez *et al.*, 2009; Cawthorn & Brown, 1976; Davidson *et al.*, 2007; Melekova *et al.*, 2015; Nandedkar *et al.*, 2014; Sisson & Grove, 1993a), magma mixing (e.g. Anderson, 1976; Clynnne, 1999; Coombs *et al.*, 2000; Feeley & Dungan, 1996; Kratzmann *et al.*, 2009; Murphy *et al.*, 1998; Sparks & Sigurdsson, 1977), and assimilation of crustal materials (e.g. Davidson *et al.*, 1987; Garcia *et al.*, 1998; Huppert & Sparks, 1985; Knesel & Davidson, 1996) are the processes of great importance in determining the complexity and evolution of arc magmas.

A detailed fieldwork study that serves as a basis for robust interpretations (Dungan *et al.*, 2001) is essential, however, it may be very difficult in many arc volcanoes because of the variety of deposits (domes, pyroclastic flows, lahars, tephra), their complex geometrical relationships, the large variation in time, and the poor rock exposures of in equatorial and/or subtropical climates. Examples of the difficulty of conducting field geology and volcano stratigraphic studies are the Indonesian volcanoes (e.g., Belousov *et al.*, in press, Fontinj *et al.*, in review). Thus, among the many studies done in the Indonesian arc (e.g. Belousov *et al.*, 2015; Foden & Varne, 1980; Handley *et al.*, 2008

and 2010; Jeffrey *et al.*, 2013; Mandeville *et al.*, 1996; Reubi & Nicholls, 2004; Reubi *et al.*, 2002; Vukadinovic & Nicholls, 1989; Wheller *et al.*, 1987), only few focused on detailed petrochemical analyses taking stratigraphic or chronological markers into account (e.g. Reubi & Nicholls, 2005). Even less of these studies use various types of trace elements to supply and clarify their findings with robust evidence, and to allow for transfer of such information into more detailed efforts.

The most active convergent tectonic plates are located around the Pacific Ocean, along its margins almost continuous volcanic chains found and make up the so-called ‘Ring of Fire’. The islands of Indonesia represent the western tropical part of this volcanic front where the Gede volcano is located on the island of Java. Gede is the closest active stratovolcano to Jakarta, the capital of Indonesia (about 60 km) and Bandung, one of the most populated Indonesian metropolises (about 70 km). The Gede Volcanic Complex (Handley *et al.*, 2010) comprises the volcanic remains of Gegerbentang, active days of which date back probably to the Pliocene (Effendi *et al.*, 1998), the extinct stratovolcano of Pangrango-Masigit, which was built mostly in the Pleistocene, and the recently active member, the Gede-Gumuruh volcano. The stratigraphic record of Gede shows that older deposits of pyroclastic density currents and lahars date back to the Pleistocene epoch (Belousov *et al.*, in press). A more well-preserved and detailed record from the Holocene counts five main deposits (10 kyr, 4 kyr, 1.2 kyr, 1 kyr). These rather voluminous deposits are associated with somewhat explosive eruptions of VEI 2-4 (e.g. Belousov *et al.*, 2015). In the historical record, however, shows that the last two and half centuries produced over 20 eruptions in Gede, of which two were more violent and caused significant perturbation in normal flow of life (at the end of the 18th century and 1832-40). Consequently, the Gede volcano is a potential hazard to its immediate surroundings as well as to the two neighboring metropolises, and at times of unrest information on its past behavior eases the proper interpretation of monitoring signals.

Probably the most important question at times of an unrest event at any given volcano is whether the signals would lead up to an eruption and if so, when it would occur. In recent practice, there is no method to surely anticipate when an eruption would happen, but thorough knowledge on the system's past activities and especially their time-scales significantly improves the efforts. Understanding the processes, the depths at which these occur, and the timing of the events are critical pieces of information for better interpretation of volcanic unrest. This is particularly important at volcanoes like Gede where there has not been a recent eruption and thus there is no background information about monitoring data that can be used to anticipate the evolution of events once unrest starts.

In the last two decades, there has been a marked improvement on the availability and reliability in situ analytical techniques (electron microprobe, electron backscattered diffraction, laser ablation inductively coupled plasma mass spectrometry) that allow to precisely measure the chemical compositions of a large number of minerals, at a large range of concentrations and spatial scales. This information combined with thermodynamic models allows unraveling the complex petrological puzzle that characterizes the evolution of many arc magmas (e.g Costa *et al.*, 2013). The textural and chemical relationship between the different minerals and phases shows that most magmas are chemical and mechanical mixtures from various sources from various ages. Only after the identification of the different components and correlation between them it is possible to quantitatively reconstruct the storage depths, the main processes and the time scales that are needed to provide a realistic scenario that allows the contribution of petrological studies to mitigation of volcano hazards (e.g Blundy and Cashman, 2008). A point in case that is critical for the evaluation of volcano hazards are the time scales of the processes that may lead to eruption. Time is a critical variable for preparedness and emergency plans that can get the populations out of the harm's way. Modeling chemical diffusion in

minerals has been increasingly used in the last decade to understand timing and duration of certain magmatic process recorded in volcanic crystal cargo (e.g. Costa *et al.*, 2003, 2008, and 2010). 1D diffusion models are commonly used among volcanologists dealing with active and actively monitored volcanoes to gain improved understanding, and this recently became a very practical and almost inescapable tool in interpreting monitoring signals, which is essential for forecasting volcanic behavior (e.g. Kahl *et al.*, 2011; Kligour *et al.*, 2014; Martí *et al.*, 2013; Oeser *et al.*, 2015; Saunders *et al.*, 2012). However, more detailed studies on diffusion modeling in minerals have shown that scatter on obtained time-scales for even a given volcanic eruption could be significant (Allan *et al.*, 2013; Saunders *et al.*, 2012). Factors that most significantly influence the obtained time-scales are temperature and three-dimensional effects on diffusion that difficult to account for in 1D diffusion models (e.g. Shea *et al.*, in press). Having no firm control on the latter factors might result in up to 5-fold variation in calculated time-scales (e.g. Shea *et al.*, in press). Such large scatter in the time-scales may lead to misinterpretations in monitoring signals and taking early or late measures.

This dissertation contains three chapters, each of them is written almost independently of each other and have the format of a research paper. In the first chapter, I report the bulk of the major and trace element data of the bulk-rock and minerals from the last 45 kyr history of Gede. I reveal the magmatic evolution of a two-level reservoir system, where at depth fractionation of the primitive magma occurs and upon its injection into a shallow level reservoir it further differentiates. I give details on the magmatic processes and dynamics of these reservoirs and support the results of the plumbing systems and processes recorded in the phenocrysts zoning patterns. These results are integrated with available monitoring data for the volcano and also highlight potential unrest signs that can be expected. In the second chapter, I focus on the systematic behavior of rare earth elements (REE) and Eu-anomaly. The geochemical behavior of

REE and the large amount of previous work on this subject make them potential indicators of the depths of magmatic processes. I discuss the deep fractionated minerals and the shallow level differentiation, and describe a model that allows distinguishing Eu-anomaly developed in clinopyroxene due to plagioclase withdrawal and other factors. I highlight that although plagioclase plays a significant role, crystal growth kinetics and oxygen fugacity are key players to interpret the REE and Eu systematics. In the final chapter, I present a new three dimensional (3D) numerical model of chemical diffusion in orthopyroxene and describe the effects of 3D diffusion, crystal habit, and other parameters on commonly used one dimensional (1D) and two dimensional (2D) diffusion models, I also show the results of diffusion modeling and time-scale estimation of magmatic processes under Gede and interpret them in terms of eruption forecasting at an upcoming unrest even at the volcano.

During my PhD I have also been involved in two projects that are closely related the work presented here and which have recently been published or are currently in press. One details the volcanological and stratigraphic history of Gede (Belousov, A., Beolusova, M., Krimer, D., Costa, F., Prambada, O. & Zeannudin, A. (2015). Volcanoclastic stratigraphy of Gede volcano, West Java, Indonesia: how it erupted and when. *Journal of Volcanology and Geothermal Research* **301**, 238-252.), and the other discusses the effects of three-dimensional diffusion in olivine (Shea, T., Costa, F., Krimer, D. & Hammer, J.E. (in press). Accuracy of time-scales retrieved from diffusion modeling in olivine: a 3D perspective. *American Mineralogist*).

CHAPTER

1

CRYSTALIZE, INTRUDE, MINGLE, ERUPT, REPEAT: MAGMATIC EVOLUTION OF GEDE VOLCANO, WEST- JAVA, INDONESIA

CRYSTALIZE, INTRUDE, MINGLE, ERUPT, REPEAT: MAGMATIC EVOLUTION OF GEDE VOLCANO, WEST-JAVA, INDONESIA

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ABSTRACT

Subduction-zone volcanoes produce a large variety of magma compositions and eruption styles, but silica-rich explosive eruptions from arc volcanoes pose the largest hazards to populations and air traffic. The poorly-known Gede volcano (West-Java) is a composite arc-volcano which has experienced recurrent silicic explosive eruptions, and it is a hazard to its 1 million residences settled on its flank, as well as to the two most populated neighboring metropolises: Jakarta (60 km to the north) and Bandung (70 km to the east). Here we present the results of a detailed petrological and geochemical study of deposits of Gede with the aims of untangling its magmatic evolution, pinpointing the key magma reservoir processes, and exploring how this information can be used to better interpret monitoring data during future unrest and eruptions at this volcano.

Fieldwork and dating revealed 5 major explosive eruptions (VEI 2 to 4), four of which occurred in the last 10,000 years. The pyroclastic and debris avalanche deposits range from high-silica basalt to dacite and most show macroscopic mingling/mixing textures. Bulk-rock major and trace element compositions can be explained by a combination of fractional crystallization and magma mixing/mingling. Early magma evolution occurred with a two-stage differentiation of deep and water-rich basaltic magmas (amphibole-bearing and plagioclase-free; 600 ± 200 MPa, 6 ± 2 wt % H_2O) followed by a drier and shallower differentiation (plagioclase and pyroxene-bearing; <

100 MPa; <3 wt% H₂O) and which lead to high-Si melts (rhyodacitic to rhyolitic). In the Holocene most magmas experienced varying degrees of mixing and hybridization between basaltic and rhyodacitic magma types or crystal-rich cumulates. Differentiation of the hybridized magmas at intermediate depths and water contents (plagioclase- and amphibole-bearing) may have also occurred.

Our database of core to rim electron-probe micro analyser (EPMA) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses (>6000 EPMA and >450 LA-ICP-MS) of the main phenocrysts (amphibole, plagioclase, ortho- and clinopyroxene) allow to uniquely identify the processes and fingerprint the crystal sources. Amphiboles from the early units have high Mg/Fe, Cr, and Ni contents, and are low in incompatible elements, and thus grew from basaltic liquids. Cores of ortho- and clinopyroxene crystals in the older Holocene units have low Mg/Fe, high incompatible trace element concentrations (e.g. Zr, Rb, Ba, Th) and grew from much more evolved melts (dacitic) than the bulk-rock. They are probably the crystal-rich part of an evolved and shallow mush. Pyroxene rims have high Mg/Fe and compatible elements (e.g. Cr, Ni), and low incompatible trace element concentrations (e.g. Zr, Rb, Ba, Th) that mark the intrusion of much more primitive melts. Some amphibole cores record magma hybridization and suggest complete mixing between portions of the mafic the silicic magmas. Amphibole rims also record the arrival of primitive magma with high Mg/Fe and compatible elements (Cr, Ni) similar to the pyroxene rims. The major and trace element zoning patterns of most phenocrysts from the younger units record the recurrent intrusion of mafic, volatile-rich, and crystal-poor magma into an evolved and extensively crystallized shallow magma reservoir. The chemical zoning in the crystals tends to be abrupt. Diffusion modelling of the zoning suggests that about a month passed since the last mafic intrusions and the eruption for many of the units.

These findings should guide the interpretation of monitoring data in Gede during a

future unrest event. It can be expected that deep seismicity related to mafic magma movement would be located at around 24 ± 8 km depth, probably close to the crust-mantle boundary. The arrival of volatile-rich mafic magma into shallower, evolved and crystal-rich reservoirs (about 4 km below the crater) would be associated with major degassing. This would produce significant changes in the gas flux and composition of the existing fumaroles close to the Gede crater. The time frame between the last magma recharge and eruption was about a month during eruptive events in the Holocene. Assuming similar future activity, it should be enough for preparation of hazard mitigation strategies for the more than one million people living close to Gede volcano.

KEYWORDS: magmatic evolution; fractional crystallization; mineral zoning pattern; magma mixing; trace element fingerprinting

1. INTRODUCTION

Along and across arc, subduction-zone volcanoes produce a large compositional variety of magmas through time and space (e.g. Ishikawa & Nakamura, 1994; Patino *et al.*, 2000; Plank & Langmuir, 1988). Arc magmas also produce a large spectrum of eruption styles, and often pose a great threat for those living on and around volcanoes. The diversity of magma composition and eruption style may result from both the composition of the primary magma, i.e. partial melting, contribution from subducting oceanic plate and overriding sediment including volatile components (e.g. Gertisser & Keller, 2003a; Handley *et al.* 2007; Morris *et al.*, 1990; Plank & Langmuir, 1993; Turner & Foden, 2001), and the paths and processes that it experiences on its way to the surface. Fractional crystallization (e.g. Alonso-Perez *et al.*, 2009; Cawthorn & Brown, 1976; Davidson *et al.*, 2007; Melekova *et al.*, 2015; Nandedkar *et al.*, 2014; Sisson & Grove, 1993a), magma mixing (e.g. Anderson, 1976; Clyne, 1999; Coombs *et al.*, 2000; Feeley & Dungan, 1996; Kratzmann *et al.*, 2009; Murphy *et al.*, 1998; Sparks & Sigurdsson, 1977), and assimilation of crustal materials (e.g. Davidson *et al.*, 1987; Garcia *et al.*, 1998; Huppert & Sparks, 1985; Knesel & Davidson, 1996) are the most important processes responsible for the complexity and evolution of arc magmas. Detailed petrological and geochemical studies are crucial to tell apart what process plays the key role in magma evolution and how its importance changes in time and/or space (e.g. Humphreys *et al.*, 2006; Newhall, 1979; Streck, 2008). The petrological and geochemical observations need to be based on detailed fieldwork studies to establish a proper stratigraphy and chronology of events that will serve as a basis for robust interpretations (Dungan *et al.*, 2001). This is however very difficult in many arc volcanoes given the large number and variety of deposits (domes, pyroclastic flows, lahars, tephra), the complex geometrical relationships between the different deposits, the large changes that

can occur through time, and the poor rock exposures of many volcanoes located in equatorial and/or subtropical climates.

Examples of the difficulty of conducting field geology and volcano stratigraphic studies are the Indonesian volcanoes (e.g., Fontinj *et al.*, in review). In addition to the high weathering rates, the large population living around many volcanoes quickly modifies the landscape and even recent deposits may be almost impossible to find. Thus, although many studies have been done in the Indonesian arc (e.g. Belousov *et al.*, in review; Foden & Varne, 1980; Handley *et al.*, 2008 and 2010; Jeffrey *et al.*, 2013; Mandeville *et al.*, 1996; Reubi & Nicholls, 2004; Reubi *et al.*, 2002; Vukadinovic & Nicholls, 1989; Wheller *et al.*, 1987), most of them concentrated in broad geochemical and petrological relations and insights on the dynamics of magmatic processes are obtained by applying petrologic-geochemical models on the entire dataset independently of stratigraphic or chronological markers. By doing so, these studies obtain a general picture of how the given volcanic system works, however they do not allow for transfer of such information into more detailed efforts related, for example, to anticipation of future eruption or hazard mitigation of arc volcanoes. Understanding these processes for a given volcanic system is key to properly interpret new unrest activity and make well-informed and process-based eruption forecasts (e.g. Kushendratno *et al.*, 2012; Newhall & Pallister, 2014).

Arc magmas are notoriously complex in terms of their petrology and geochemistry. Mixing of different melts, mingling of magmas, and mingling of melts and crystals from disparate sources and origins is becoming one of the most common findings of magma petrogenesis (e.g. to name just some recent ones: Dungan *et al.*, 2002; Reubi *et al.*, 2011; Costa *et al.*, 2013; Cassidy *et al.*, 2015). Untangling these petrological puzzles is however crucial for making progress in the proper identification of the processes and time scales that operate below active volcanoes, and these are very important for providing

conceptual models of the magma plumbing systems that guide the interpretation of monitoring data. A major problem to identify the different components and processes in any given batch of magma is that the major element compositions of the crystals and glasses are not diagnostic. In other words, different combinations of pressure, temperature, compositions, water content and oxygen fugacity can lead to the same major element composition. In contrast, zoning isotopes and trace element in minerals can provide unique constraints on the processes and sources of the crystals (e.g. Blundy & Shimizu, 1991; Davidson & Tepley, 1997; Singer *et al.*, 1995).

In this contribution, we report the results of a detailed petrological and geochemical study of the magmatic system of the Gede volcano (Handley *et al.*, 2008 and 2010), the closest active volcano to Jakarta (Indonesia). Our study is based on considering stratigraphy and ages of samples collected around the volcano (Belousov *et al.*, in review). We reveal the deep fractionation of the primitive magma, its intrusion into a more evolved shallow silica-rich reservoir where after a short mixing period it probably triggers the eruption. We support our results of the plumbing systems and processes recorded in the phenocrysts zoning patterns, including major and trace elements systematics.

2. GEOLOGICAL SETTING AND DEPOSITS OF GEDE VOLCANIC COMPLEX

2.1 The Gede Volcanic Complex

The Gede Volcanic Complex (GVC; Handley *et al.*, 2010) is part of the Quaternary volcanic front of the Sunda arc (Fig. 1), one of the most active volcanic regions on Earth (Hamilton, 1979). The volcanic arc is the western part of the Indonesian subduction zone, where the Indo-Australian Plate heads down beneath the Eurasian Plate, and stretches along Sumatra, Java, and the Lesser Sunda Islands (Fig. 1). The volcanic activity arises

from a fast (about 75 mm/yr; von Huene & Scholl, 1991) and steep (60°; Widiyantoro & van der Hilst, 1996) subducting oceanic plate beneath a relatively thick Mesozoic lithosphere along West-Java (Halldórsson *et al.*, 2012). The subduction and associated volcanism along the Sunda arc have been going on since the Cretaceous (Hamilton, 1979).

Fig. 1. Topographic map of Gede Volcanic Complex and locations of sample in this study. Inset map shows Gede in the broader geotectonic context, field of view is 5°N to 12°S and from 95°E to 120°E. The sample locations and their units are also shown. The most active volcanoes from the area are labeled.

The GVC lies in the volcanic front about 250 km NNE from the trench and about 60 km south of Jakarta (Fig. 1). The GVC consists of three composite volcanoes, Gegerbentang, Pangrango-Masigit, and Gede-Gumuruh. Gegerbentang is a series of volcanic remnants, comprises of early Quaternary (Pliocene) mafic igneous rocks (Effendi *et al.*, 1998; Situmorang & Hadisantono, 1992). The GVC is dominated by the twin stratovolcanoes of Pangrango (3019 m a.s.l.) to the north-northwest, a volcano with no historical eruptions (Seibert *et al.*, 2010), and Gede (2958 m a.s.l.), the currently active member of the complex (Handley *et al.*, 2010). Early stratigraphic, morphologic, and

Table 1. Summary of petrographical features and field observations of the units.

Unit/Age	Sample	Bulk-rock (SiO ₂ - MgO; wt%)	Bulk- rock type	Pheno- crysts ^s	Main textural features and field relations
>45ky	Ayam, G130	51.1-4.8 to 51.7- 4.3	high- silica basalt to basaltic andesite	Pl, Cpx, Amph, Mt, Ol, Ilm	Debris avalanche deposit; poikilitic- porphyritic texture with oscillatory zoned cpx oikocrysts surrounded by large vesicles (‘floating crystals’) and large amph and plag phenocrysts; matrix consists of mostly plag microlites and microcrystalline, moderately vesiculated groundmass.
10 ky	Cig, Cip, Gek	55.0-3.9 to 56.4- 2.2	basaltic andesite	Pl, Cpx, Opx, Mt	Black, voluminous pyroclastic flow deposit; scoria-like poikilitic-porphyritic texture, plag & two-pyroxenes show reverse zoning; matrix rich in plag microlites. No macroscopic evidence of magma mixing.
4ky	Cip, CPN	54.4-4.6 to 60.3- 3.0	basaltic andesite to andesite	Pl, Opx, Cpx, Amph, Ol, Mt, Ilm	Light color PF deposit distinguished by 3 different sub-units: standing charred trees in bottom sub-unit, fallen (overturned) tree trunks in middle unit, no tree in top sub- unit. Porphyritic texture with plag dominancy, macroscopic evidence of different degree of magma mixing (mingling), non-equilibrium mineral assemblages (opx rimmed by cpx and oli rimmed by opx). Reversely zoned mafic minerals, complex plag zoning with sieve cores. Microlite-rich mafic matrix, glassy felsic groundmass with large bubbles (pumiceous).
1.2ky	Pata, Tega	54.6-4.4 to 69.2- 1.1	basaltic andesite to dacite	Pl, Opx, Cpx, Amph, Ol, Mt, Ilm	Very light PF deposit with lithic materials. Porphyritic & seriate texture with glassy & pumiceous groundmass, respectively. Inequilibrium mineral assemblages, with textural evidences of magma mixing. Geochemically two different trends. Complex zoning patterns of minerals.
1ky	SMT	52.0-5.0 to 58.6- 3.1	low- silica basaltic andesite to andesite	Pl, Cpx, Opx, Ol, Mt, Ilm	Dark, small volume PF on & around caldera. Samples belong to two different trends (see Fig. 19). Primitive samples are similar to >45 unit, whereas more evolved similar to members of 10 ky unit.
recent (1840?, 1955- 57?)	G385, ALUN	58.4-60.7	andesite	Pl, Cpx, Opx, Ol, Amph, Mt, Ilm	Lava dome in crater (1840?): porphyritic texture with large Plag and Opx, glassy, moderately vesiculated, collapsed bubbles. Volcanic bomb around the caldera rim (1955- 57): porphyritic textures, no Amph, Ol is trace, vesiculated.

^s Pl=plagioclase; Ol=olivine; Cpx=clinopyroxene; Opx=orthopyroxene; Amph=amphibole;
Mt=magnetite; Ilm=ilmenite

geochronological studies divided the Gede activity into Old and Young Gede (Situmorang & Hadisantono, 1992).

The Old Gede or Gunung Gumuruh is late Pleistocene according to Situmorang & Hadisantono (1992). Belousov *et al.* (2015) has found that the deposits of this edifice are >45 kyr. The eruptive products of Gunung Gumuruh occur almost all around the slopes of Gede except the north-northeastern region. Several smaller craters on the northern part of the Gede crater mark Young Gede. According to Belousov *et al.* (2015) these craters are not older than approximately 10 kyr. We have sampled and studied several locations of these older deposits and compared them to the Holocene Gede. Deposits of Young Gede occupy the northeastern area of the edifice and fan out in a very narrow belt on the slope and on the alluvium (Fig. 2).

Fig. 2. Geological map of Gede Volcanic Complex redrawn after Belousov *et al.* (2015). Age of stratigraphic units is from Belousov *et al.* (2015); capital letters mark the major locations of charred-coals used for dating. Young Gede (Holocene) deposits are channelized towards the NNE from the crater.

2.2 Holocene eruptive units of Gede, field observations, and sampling strategy

Ages of the different units were determined by radiocarbon (^{14}C) dating using charcoal (Belousov *et al.*, 2015) found in the deposits (Fig. 2). Belousov *et al.* (2015) reported the field relations and stratigraphy of Gede deposits which we summarize here.

Young Gede deposits are Holocene and consist mainly of four pyroclastic flow (PF) units (Table 1). The oldest (10 kyr) unit is a voluminous dark basaltic andesite PF ($\text{SiO}_2 = 55\text{--}56.4$ wt%) that is homogenous at the field scale, lacks of macroscopic evidence of magma mixing or mingling, aside from a few light-grey, angular xenoliths. Bread-crusts bomb fragments and coarse sand matrix characterize this unit. At the deepest part of the largest quarry we found that the deposit exceeds 50 m in thickness and the base is not exposed. Bulk-rock analyses of bread-crusts bombs and matrix from different locations and or stratigraphic positions show no differences in composition. Stratigraphically above the 10 kyr unit sits a grey PF unit (4 kyr; Fig. 3a) of smaller volume but with a wider variation in chemical and mineralogical composition (basaltic andesite to andesite; $\text{SiO}_2 = 54.4\text{--}60.4$ wt%). It shows clear macroscopic and microscopic evidence for magma mixing and mingling (Figs. 3.c to f). This PF unit is weakly sorted, ungraded, and mostly dominated by pebble to coarse sand; however, cobbles and boulders (in form of volcanic bombs and lithics) are also present. The 4 kyr unit shows 3 deposition subunits that clearly marked by discontinuity surfaces (Fig. 3.a). The most eye-catching difference is the presence or absence of tree trunks preserved in the PF flow, otherwise the three subunits are similar. In the lowest subunit of about 3 m thickness we found broken standing tree trunks whose height coincides with the discontinuity surface between the lowest and middle subunits (Fig. 3.a). The middle subunit has approximately the same thickness, with charred treetops lying at the bottom. The top subunit is probably a lahar deposit (Belousov *et al.*, 2015). We sampled all subunits and collected volcanic bombs and matrix samples from several locations in the same quarry, and did not find any

systematic variation within the subunits. The subunits were probably deposited soon after each other with the second (and possibly the third) having higher energy, and may represent subsequent collapses of an eruption plume. Both the 10 kyr and 4 kyr units have been recognized on the north eastern slope of the volcano (Fig. 2). A younger (1.2 kyr) and voluminous light grey PF and lahar unit extends onto the alluvium topographically below, and to the northeast of the previous unit (Fig 3b). It shows the broadest variation in bulk composition (basaltic andesite to rhyodacite; $\text{SiO}_2 = 54.6\text{--}69.1$ wt%), and also contains the highest degree of lithics and accidental materials. This deposit is dense (maybe weakly welded) and dominated by coarse pebbles and sand. It also shows some macroscopic evidence for magma mixing/mingling although not as prominent as in the 4kyr unit. Some lightly charred standing tree trunks in the middle of the rice fields are also found in this unit (Fig. 3.b). The youngest dated unit is dark and homogenous, about 1 kyr old and the smallest of the PFs. It was found on the northern part of the crater and also occupies a small valley on the higher slope of the volcano as block and ash flow deposits. This unit has the most mafic end-member of all and shows a more restricted compositional variation ($\text{SiO}_2 = 52\text{--}58.6$ wt%). It is also unsorted and consists of pebble scoria with smaller volcanic bomb fragments.

We also studied two samples from the recent infilling lava dome of the crater and two volcanic bombs from the outer caldera. Although ages of these samples are uncertain, we believe they are products of the most recent activities, perhaps the 1840 violent eruption and the 1955-57 phreato-magmatic episodes, respectively (Belousov *et al.*, in review).

We collected and analyzed only samples without apparent evidence of low-temperature hydrothermal alteration or weathering. For thin section production and detailed mineral chemistry analyses we used large bombs taken directly from the deposits at each location.

Fig. 3. Field-scale pictures of selected units and macroscopic to microscopic evidences for magmatic interaction. a) Deposits of the 4 kyr unit. A, B, and C denote the 3 subunits, and boundary between deposits shown by the black-and-white arrows. Red and black diagonal arrows point to the imprint of a once-standing tree trunk and a charred lying tree trunk, respectively. Note that the height of the imprint of the standing tree trunk marks the end of the bottom subunit. b) Standing charred tree trunk of the 1.2 kyr unit in the middle of a rice field. Remnants of the pyroclastic flow material still can be found attached to the trunk. c) Banded scoria in the 4 kyr deposit. Field of view is approx. 65 x 40 cm. Note the bands with different colours corresponding to different magma types. d) Hand specimen banded scoria sample from the 4 kyr unit. Band edges are sharp, but fuzzy suggesting quick, chaotic and dynamic interaction of the distinct magmas. e) Electron microprobe X-Ray map of Al and f) Ca distribution at the contact of a light (most of the SW part of the image) and dark (NE corner of the image) bands in the 4 kyr units. Plagioclase crystals are the green-yellow-orange squares or parallelepipeds; the blue patchy and fuzzy crystal is clinopyroxene. Bubbles (now seen as voids) are black and surrounded with the light (or dark) blue silicic matrix glass. Small yellow-green (or blue on image f) needles on the top right are plagioclase microlites in the mafic band. Note the very narrow mixing boundary shown by diluted microlite contents. The white grains (in image f) are apatite crystals.

2.3. Historical eruptions and geophysical monitoring data of Gede

Gede volcano is currently being monitored with broadband seismometers, tiltmeters, and continuous GPS stations of the CVGHM (Center for Volcanology and Geological Hazard Mitigation, Indonesia) and the EOS (Earth Observatory of Singapore, Nanyang Technological University). The last series of eruptions on Gede were phreatic and occurred in 1955-77, but they were not monitored with modern devices. From the mid-eighteenth century several small eruptions with short durations occurred repeatedly, the most violent ones with VEI 3-4 (Volcano Explosivity Index; Newhall & Self, 1982) in 1832 and in 1840 (Seibert *et al.*, 2010) that generated small pyroclastic flows (Belousov *et al.*, in review). Products and ejecta of the recent phreatic-phreatomagmatic eruptions are difficult to identify on the edifice or around the caldera because of their small volume, effects of erosion, as well as the heavy vegetation coverage. Historical reports also mention cases when ash fall reached and covered Jakarta as thick as 5-10 cm (Situmorang & Hadisantono, 1992). Some of the youngest craters show hydrothermal (fumarolic and solfataric) activity. Cumulative earthquake energy in the last five decades shows seismic swarms, most recently in 2006, end of 2010, end of 2011, Jan-Febr 2012, March-Apr 2012 (Hidayat *et al.*, 2012). This may suggest that the volcano plumbing system is periodically recharged by new magma intrusions in the last half-century, however, estimates of depth of the magma reservoir(s) under Gede is uncertain at the moment.

3. ANALYTICAL METHODS

The samples were characterized by optical microscope, X-Ray Fluorescence (XRF), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and Electron Probe Microanalysis (EPMA). Bulk-rock major- and minor-element compositions were obtained by XRF, and trace elements (< 0.1 wt%) by ICP-MS methods. Analyses were carried out in two laboratories: 1) at the CODES-ARC Centre of Excellence in Ore

Deposits, University of Tasmania and 2) at the GeoAnalytical Lab, Washington States University at Pullman. Error associated with XRF major elements analyses is very similar from the two laboratories; it is about 0.5 % for SiO_2 , TiO_2 , Al_2O_3 , FeO^* , and CaO , and about 1.2-1.7 % for the MnO , MgO , Na_2O , K_2O , and P_2O_5 (2 sigma). Errors associated with the ICP-MS analyses of WSU GeoLab are less than 1.5 %, except for Pb (2.9 %) and Cs (3.8 %). Precision of CODES-ARC ICP-MS analyses is between 2 and 7 %. As the whole rock analyses were carried out in two different institutes (machine, calibration, fusing technique, etc), the dataset shows some discrepancies in the results, especially for the REE, thus we applied an inter-laboratory calibration in order to obtain an internally consistent dataset. For details on how the inter-laboratory calibration were made, see Appendix 1.

Area phase modes were obtained by point counting methods, where a thin section was investigated under the optical microscope and about 1500-3000 points were used for phase proportions.

The major element compositions of minerals were analyzed with a Jeol JXA-8530F Field Emission Gun microprobe at the Nanyang Technological University, Singapore (NTU). Electron microprobe analytical conditions for mineral analysis were set to 15kV acceleration voltage, 20 nA probe current, and counting time from 10 up to 40 s for major elements, and 100 s for Mg in plagioclase. Submicron (in diameter) electron beam was used for mineral analyses. Na and K were always analyzed first to minimize alkali loss, and ZAF correction procedure was also used. In order to overcome the possible Na migration, for melt inclusion and interstitial glass analyses we used 15 kV acceleration voltage and 10 nA probe current, and defocused electron beam typically as wide as 3 to 10 μm in diameter depending on the target size; counting times for Na were reduced to 3 to 5 s. We made individual spot analyses of cores and rims of amphibole, pyroxenes, olivine, FeTi-oxide, and plagioclase. We also carried out several traverses from the rim to

the center of crystals to capture the details of zoning patterns. Distance between analyses in the traverses varied between about 3 to 15 μm . We also made X-Ray maps using WDS (wavelength dispersion spectrometers) with 15kV acceleration voltage, 20-80 nA probe current, 0.5–5 μm pixel size, and 20-100 ms dwelling time. We obtained the back-scattered electron (BSE) images using the same instrument. Some images appear pixelated (low graphical resolution) due to the high contrast applied capturing the fine (small compositional difference) zoning in some crystals. For major elements with abundances above 1wt% the reproducibility (standard deviation, SD) is $<<1\%$, for minor elements with concentrations between 0.1wt% and 1wt% SD is $<5\%$, for trace elements with abundances below 0.1wt% SD is $>5\%$.

We have analyzed more than 300 crystals for composition in core rim relation with total number of point analyses are over 1500. We have additionally analyzed 15 amphibole, 35 pyroxenes, 20 plagioclase, 7 olivine grains by collecting detailed traverses (rim-rim, 2,3 or 4 μm spacing) in length up to 1500 μm per crystal; plus 40 plagioclase semi-detailed half-traverses (core-rim) with 15-25 μm spacing in length of 400-800 μm . About 300 backscattered-electron images (BSE) were taken. We have collected 7 overview maps of thin sections (or part of them) with a 5-by-5 μm spacing in about 48 hours acquisition time for each. They were used to confirm manual modal counting results. We also collected 5 maps of amphibole breakdown (rhönite) assemblage with 0.5-by-0.5 μm resolution, 10 pyroxene maps with 1-by-1 μm , 4 olivine maps 0.5-by-0.5 and 1-by-1 μm . For detailed maps we used 80-100 ms dwell time, 40-80 nA beam current, and 15kV voltage. We usually collected all the major elements (Al, Si, Ti, Fe, Mn, Mg, Na, Mg, K, Ca) for the maps, and additionally P for olivine. The smallest map collected is 100 μm^2 , the largest one is about 4.5-by-4.5 mm.

Trace elements in mineral phases were investigated in-situ using an Agilent 7500cs ICP-MS equipped with a quadrupole collector coupled with a 193 nm Resonetics M-50E

ArF-laser system at the Laboratoire Magmas et Volcans (LMV), Blaise Pascal University, Clermont-Ferrand, France. Laser was set to a constant repetition rate of 4 Hz at 70% laser energy and analyses were conducted for 80 s after a 20 s period of background measurements. For most analysis we used a 58 μm laser beam width; where sample size or other known condition (e.g. width zoning pattern) indicated spot sizes we adjusted it accordingly to smaller (33 or 44 μm) or higher (73 or 100 μm). Precision (1 sigma error) was between 3% and 6% for all elements. External calibration was performed after every 25-30 analyses using glass reference material NIST 612 as unknown samples and USGS BCR-2g as internal check. Calcium (^{43}Ca), determined by EPMA, was applied as internal standard (i.e. Fryer *et al.*, 1995). The LA-ICP-MS data were processed and data reduction was done using the GLITTER software (van Achterberg *et al.*, 2001). A total of 37 trace and minor elements were determined in 134 crystals (456 points) of amphibole, clino- and orthopyroxene, plagioclase, and olivine.

We have analyzed volatiles in several melt inclusions in pyroxenes and plagioclase by following the König-Kramer transformed reflected micro FT-IR technique (King & Larsen, 2013). The FT-IR data was collect on a top-of-the-line Bruker Vertex 80v vacuum FTIR spectrometer is equipped with a Hyperion 2000 infrared confocal microscope at the Division of Physics and Applied Physics, NTU. We collected data between 6000 and 600 cm^{-1} , each target was scanned 512 times with the largest possible aperture size determined by the melt inclusion geometry (roughly 10-by-15 μm). Before data collection we scanned a gold coated reference material to ensure 100% reflectance and we collected background at the same wavenumber interval. During analyses the surrounding of the sample was flushed with pure nitrogen to minimize analyzing atmospheric water vapor and carbon-di/monoxide. We used an experimental rhyolite glass (about 73 wt% silica) with 0, 2.42, 4.24, and 6.38 wt% dissolved water, confirmedly, to calibrate both the total (at 3600 cm^{-1}) and the molecular (1700-1600 cm^{-1})

H₂O signals (Fig. A3). Dissolved carbonate concentration of the glass was not known. The chosen method of baseline determination and its position can have a significant impact on the result implied (King & Larsen, 2013) especially when the data is ‘noisy’, therefore we consequently determined baseline following the same protocol both for standard calibration and natural samples to ensure consistency and accuracy as much as possible.

4. PETROGRAPHY AND MINERALOGY OF GEDE PYROCLASTIC FLOW UNITS

4.1. Nomenclature and symbols

Mineral names, structural formulae, and end-members of minerals were determined by following the methods of Morimoto *et al.* (1988) for pyroxenes; Leake *et al.* (1997) for amphiboles; Deer *et al.* (1992) for olivine, plagioclase, and apatite; and Stormer (1983) for ilmenite. We use the following abbreviations for mineral names: Ol for olivine, Cpx for clinopyroxene, Opx for orthopyroxene, Amph for amphibole, Ox for FeTi-oxide, Plag for plagioclase, and Apa for apatite. The Mg# (magnesium number) = $100 \times \text{MgO}/(\text{MgO} + \text{FeO}^*)$ in mols, (FeO* is total iron as ferrous iron). The plagioclase anorthite content is $\text{An} = 100 \times \text{CaO}/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$ in mols. Normal zoning refers to decreasing values of chemical indicators (e.g. Mg#) from core to rim, and reverse zoning refers to increasing values. Given the variety and complexity of crystal zoning patterns we have summarized them in a schematic diagram (Fig. 4). We show the BSE images or X-ray maps representative zoning patterns from all units (i.e. Figs. 5 to 10), and we report representative mineral compositions in Tables 2-7. We also distinguish crystals based on their size: megacryst is >3mm, phenocryst is between 3 and 0.3 mm, microphenocryst is from 300 to 50 μm , and microlite is <50 μm ; at the longest dimension of the crystal.

sample	>45 kyr	10 kyr	4 and 1.2 kyr	1 kyr	'recent'
whole rock	basalt	basaltic andesite	basaltic andesite - rhyodacite	basaltic andesite - andesite	andesite
SiO ₂ (wt%)	51.4±0.2	55.0-56.4	54.4-69.1	52.0-61.1	58.4-60.7
Plag					
Ol					
Cpx					
Opx					
Amph					
LEGEND unzoned reverse normal oscillatory sector observed zoning patterns					

Fig. 4. Schematic drawing showing a summary of the zoning and textural (for plagioclase only) types for the major phenocrysts (plagioclase, olivine, pyroxenes, amphibole) in all units. Not that the 4 kyr and the 1.2 kyr units are grouped together because they are mineralogically very similar. The two columns of the 1 kyr unit represent the low-silica basaltic andesitic samples (left), and the basaltic andesites (right) (see main text for details). The black and grey colors denote mafic (e.g. high Mg# or An) and evolved compositions, respectively, relative to each unit and crystals. The smaller symbol size of >45 kyr and 1kyr olivine represents that they are microphenocrysts.

4.2. The >45 kyr old PF unit

The juvenile blocks of the >45kyr unit are porphyritic evolved basalts (SiO2 = 51.4-53.6 wt%) with phenocrysts of Plag (< 20 vol%), Cpx (5-7 vol%), Amph (1-2 vol%), Ol (3-5 vol%), and Ox (2 vol%) sitting in a microlite-rich matrix (47-53 vol%) of which 15-21 vol.% are Plag microlites (Table 8). Cpx commonly forms mm-sized glomerocrysts and megacrysts of up to 6 mm.

Plagioclase is the most abundant phenocryst and microlite (Table 2 & 8). Most crystals are euhedral and normally zoned: high-An core (An₉₃₋₈₄) usually overgrown by a narrow, slightly less calcic rim (An₈₅₋₇₇; Figs. 4, 5.a & 11). In some grains a melt inclusion-rich zone separates the cores from their rims creating a sieve-like texture

Table 2. Representative plagioclase analyses

wt%	>45ky				10ky				4ky				1.2ky					
	A2P3c	A2P3r	A2P1c	A2P1r	A3P1c	A3P1r	C6P4c	C6P4m	C6P4r	C3P2c	C3P2r	C11P3c	C11P3r	C11P2c	C11P2r	P5P6c	P5P6r	P5P16c
SiO ₂	45.68	47.51	45.79	45.85	46.35	48.19	46.63	47.38	47.29	54.68	52.88	53.84	46.80	54.69	54.11	46.21	54.49	45.35
TiO ₂	0.01	0.01	0.01	0.02	0.01	0.00	0.00	0.00	0.02	0.03	0.03	0.02	0.01	0.03	0.01	0.02	0.13	0.01
Al ₂ O ₃	34.73	33.79	34.60	34.66	33.60	32.71	33.35	32.64	33.34	28.76	29.82	28.76	33.11	28.61	28.52	32.82	25.75	34.53
FeO*	0.39	0.44	0.54	0.45	0.46	0.54	0.58	0.63	0.57	0.60	0.58	0.49	0.54	0.49	0.52	0.58	0.95	0.52
MgO	0.04	0.05	0.047	0.04	0.061	0.071	0.058	0.05	0.06	0.055	0.053	0.044	0.089	0.052	0.045	0.050	0.186	0.046
CaO	18.53	17.15	18.36	18.47	17.61	16.42	17.44	16.88	17.20	11.76	12.91	12.38	17.35	12.09	12.06	17.27	11.41	18.76
Na ₂ O	0.89	1.69	0.97	1.10	1.18	1.79	1.32	1.64	1.47	4.40	3.91	4.21	1.34	4.16	4.49	1.55	3.39	0.82
K ₂ O	0.01	0.01	0.01	0.03	0.02	0.03	0.03	0.06	0.04	0.35	0.29	0.24	0.02	0.32	0.26	0.04	0.74	0.05
Total	100.27	100.65	100.32	100.62	99.27	99.74	99.40	99.27	99.99	100.62	100.48	99.99	99.25	100.45	100.01	98.54	97.03	100.08
An	92.0	84.8	91.2	90.1	89.1	83.4	87.8	84.7	86.4	58.4	63.5	61.0	87.6	60.4	58.9	85.8	61.9	92.4
Ab	8.0	15.1	8.7	9.7	10.8	16.4	12.0	14.9	13.3	39.6	34.8	37.6	12.3	37.7	39.6	14.0	33.3	7.3
Or	0.1	0.1	0.0	0.2	0.1	0.2	0.2	0.3	0.3	2.1	1.7	1.4	0.1	1.9	1.5	0.3	4.8	0.3
ppm																		
Sr	512	527	494	502	599	562	596	599	615	615	623	521	499	509	499			
Ba	18.3	19.4	13.1	13.5	20.9	18.4	27.6	25.5	27.0	132	139	108	24.5	108	117			
Pb	1.14	1.13	0.87	0.84	1.03	0.86	1.60	1.25	1.17	5.47	5.46	4.94	0.81	4.42	4.59			

FeO* = total Fe as FeO

An = percent anorthite, Ab = percent albite, Or = percent orthoclase; following the method of Deer *et al.* (1992)

c = core; m = middle; r = rim.

S4P4i is a potassic feldspar inclusion in calcic plagioclase (S4P4c)

Table 2. continued

	1ky										recent				
	P5P16r	P5P7c	P5P7r	S4P4c	S4P4i	S4P4r	S4P3c	S4P3r	S5P1c	S5P1r1	S5P1r2	G385P3c	G385P3r	G385P8c	G385P8r
wt%															
SiO ₂	45.48	55.21	56.81	47.25	66.61	54.80	47.66	48.08	46.20	52.52	48.92	47.04	54.97	53.87	48.80
TiO ₂	0.00	0.02	0.02	0.01	0.06	0.05	0.01	0.01	0.01	0.03	0.00	0.01	0.02	0.01	0.01
Al ₂ O ₃	34.19	28.00	26.24	34.02	18.34	27.83	33.16	32.70	33.43	29.65	32.03	33.46	27.47	28.86	32.24
FeO*	0.48	0.50	0.59	0.67	0.31	0.70	0.59	0.53	0.55	0.56	0.62	0.42	0.64	0.43	0.61
MgO	0.047	0.048	0.076	0.033	0.003	0.054	0.055	0.065	0.054	0.1	0.074	0.033	0.066	0.039	0.018
CaO	18.55	11.28	10.63	17.37	0.27	10.97	17.11	16.60	17.86	13.21	15.91	17.42	10.83	12.07	16.20
Na ₂ O	0.90	4.75	2.93	1.57	3.01	4.98	1.43	1.79	1.14	3.72	2.37	1.55	5.29	4.63	2.29
K ₂ O	0.04	0.31	0.54	0.07	11.8	0.38	0.04	0.08	0.03	0.17	0.05	0.06	0.28	0.25	0.09
Total	99.69	100.11	97.83	100.98	100.45	99.75	100.05	99.85	99.28	99.97	99.98	99.99	99.57	100.16	100.24
An	91.7	55.7	64.1	85.6	1.3	53.7	86.7	83.3	89.5	65.6	78.5	85.8	52.2	58.2	79.2
Ab	8.0	42.5	32.0	14.0	27.5	44.1	13.1	16.3	10.4	33.4	21.2	13.8	46.2	40.4	20.3
Or	0.2	1.8	3.9	0.4	71.2	2.2	0.2	0.5	0.2	1.0	0.3	0.4	1.6	1.5	0.5
ppm															
Sr		521	515				606	579	572						
Ba		111	67.7				24.9	27.0	24.0						
Pb	4.70	2.77				1.06	1.45	1.34		1.48					

‘dusty’ zone. Plag crystals are occasionally found as inclusions in Cpx outer (rim) zone, and have similar composition to those of phenocrysts. Plagioclase microlites exhibit a very wide range of composition and include some Na-rich compositions. (An₈₅₋₅₅).

Olivine appears almost exclusively as microphenocryst (Fig. 5.b, Table 3), is euhedral and tends to be homogenous or occasionally normally zoned (Fo₈₁₋₇₃; NiO and Cr₂O₃ are < 0.05 wt%). Some subhedral olivine is surrounded by Opx reaction rim. Open and hourglass inclusions are common in olivine. Some rare olivines show secondary alteration in the form of iddingsite or/and fine-grained oxides. (Fig. 5.c).

Pyroxene phenocrysts (up to 2 mm) and megacrysts (up to 4-6 mm in diameter) are clinopyroxene (Fig. 5.d, Table 4). Pigeonite and orthopyroxene occur occasionally as inclusions and rarely as microlites. Euhedral-subhedral clinopyroxene (augite) is the most abundant ferromagnesian mineral (5.4-6.7 vol%; Table 8). Cpx is rather mafic (about En₄₂₋₄₈Wo₃₇₋₄₅Fs₁₃₋₁₈; Mg# = 70-77; Figs. 12&13) with a wide range of Al₂O₃ content (2.2 to 6.5wt%, Fig. 13.a). Cpx shows strong sector and oscillatory zoning (Fig. 4 & 5.d), but no systematic reverse or normal zoning. It contains mineral (Fe-Ti oxides, Ol, Plag, Opx, and Amph) inclusions. Cpx also occurs as microlite, which tends to be slightly more Fe-rich (En₃₉₋₄₁Fs₁₉₋₃₂Wo₃₂₋₃₉) than the phenocrysts. Rare subhedral pigeonite (En₅₆₋₆₂Wo₈₋₁₂Fs₃₀₋₃₂) microlites occur in the matrix, often attached to other pyroxene microlites.

Orthopyroxene (En₆₉₋₇₁Wo₃Fs₂₆₋₂₈; Mg# of about 71-73) is also rare and occurs as small (up to 75 µm) inclusions in clinopyroxene megacrysts, or mantling olivine crystals in the matrix, and as microlite in the groundmass. Opx included in Cpx is more mafic than that in contact with the matrix glass (En₆₇Wo₃Fs₃₁). Rare xenocrystic orthopyroxene phenocrysts (based on textural observations) occur only in the basaltic andesite sample, suggesting participation of different crystal cargo, or slightly different conditions of crystallization.

Fig. 5. BSE images and X-ray map of selected minerals and electron microprobe traverses of the >45 kyr unit. (a) Oscillatory and normally zoned plagioclase. (b) Euhedral olivine microphenocryst. (c) Broken, fayalite-rich 'barred' olivine phenocrystals suggesting sudden change in oxidation state (J. Hammer pers. comm.). (d) Sector and oscillatory zoned clinopyroxene twin. Beside the sector zoning of the crystal, there is also low-Mg# (high-Al₂O₃) ring throughout the entire grain regardless of the sector. Electron microprobe analyses shows some anti-correlation between Mg# and Al content, and much more variable changes in concentration at the first 600 μm . Probably the crystal has also a twin plane along the main E-W crack. (e) Subhedral, chemically homogenous amphibole phenocryst (note the electron microprobe traverse) with very narrow breakdown rim (not seen in the image). Along the cracks (light grey) there is secondary mineral assemblage made of rhönite + clinopyroxene + oxides + plagioclase. (f) Disequilibrium texture of FeTi-oxide shows multiple generations of exsolution lamellae and thus a protracted cooling history.

Amphibole is pargasite with a $Mg\# = 74-77$ that tends to be higher than that of Cpx (Fig 12); it occurs as large subhedral phenocrysts (up to 1.5 mm) (Fig. 5.e, Table 6). Regardless of size, amphibole grains tend to be chemically homogenous with about 14 wt% Al_2O_3 and 12 wt % CaO (Figs. 12&13). Many amphibole grains are resorbed, having a breakdown reaction rim of up to hundreds of μm . Along cracks and cleavages a Plag + Cpx + Fe-Ti-oxide + rhönite mineral assemblage occasionally occurs in amphibole. According to Grapes *et al.* (2003) rhönite may reflect low pressure (<60MPa) alteration (and/or weathering) of Ti-rich amphibole species. Rhönite appearing along cracks suggests that it formed due to a secondary alteration process, and thus it is irrelevant for the discussion of magmatic processes.

Large Fe-Ti-oxides (about 500 μm) are accessory minerals in the groundmass and also occur as inclusions in clinopyroxene. Oxide grains are ulvöspinel (Table 7). Oxides in a reaction relation may be related to secondary alteration. They show several generations of exsolution lamellae and a complex textural pattern (Fig. 5.f) and include magnetite, ilmenite, and ferroan-spinel (Table 7). The multiple exsolution lamellae suggest a protracted cooling history.

We also identified two micro-xenoliths in the sample: (1) one is equigranular with microphenocrysts of Cpx + Opx + Ol + minor Amph (up to 5 μm) + Fe-Ti oxides. Cpx and Opx compositions are less MgO-rich than that of the phenocrysts. Interstitial glass is rarely present, the margin of the xenolith is somewhat rounded. (2) the other is inequigranular, with small orthopyroxene grains (30-80 μm) with quartz and glass inclusions, and glass pools (up to 25 μm). Very small biotite (3-5 μm) shards, and zircon grains are also present. However, plagioclase is inclusion free, 10-20 μm in diameter, and always normally zoned. The K_2O and FeO component of plagioclase is higher than those of the phenocrysts in the sample. A rounded quartz crystal (about 60 μm) is also present as individual grain. Interstitial glass is abundant. The margin of the xenolith is rounded,

Table 3. Representative olivine analyses

wt%	>45ky			4ky			1.2ky					
	A2OLm1c	A2OLm1r	A2OLm7c	A2OLm7r	C7OL2c	C7OL2r	C15OL1c	C15OL1m	C15OL1r	P5OL6c	P5OL6m	P5OL6r
SiO ₂	38.05	37.98	39.55	38.03	39.88	38.50	40.16	39.65	38.54	39.31	38.08	37.67
TiO ₂	0.00	0.00	0.00	0.02	0.00	0.00	0.01	0.01	0.01	0.02	0.00	0.00
Al ₂ O ₃	0.00	0.03	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr ₂ O ₃	0.00	0.00	0.02	0.00	0.01	0.01	0.02	0.01	0.00	0.01	0.00	0.00
FeO*	23.95	24.09	17.17	23.43	16.59	24.06	17.01	19.57	25.24	17.93	20.46	22.36
MnO	0.45	0.43	0.20	0.42	0.24	0.41	0.20	0.29	0.43	0.27	0.29	0.36
MgO	37.50	37.41	43.30	37.42	42.84	36.45	43.78	41.60	36.12	42.26	40.03	38.47
CaO	0.15	0.17	0.14	0.18	0.14	0.13	0.11	0.14	0.14	0.13	0.12	0.16
Total	100.10	100.12	100.37	99.53	99.70	99.55	101.31	101.27	100.47	99.93	98.97	99.03
Fo	73.6	73.5	81.8	74.0	82.2	73.0	82.1	79.1	71.8	80.8	77.7	75.4

FeO* = total Fe as FeO
Fo = Mg/(Mg+Fe)*100 in mols
c = core, m = middle, r = rim

Table 3. continued

wt%	1ky					Recent				
	P5OL3c	P5OL3m	P5OL3r	S5OLmle	S5OLmlr	S5OLm6c	S5OLm6r	G385OL1c	G385OL1r	ALUN_OL1 ALUN_OL3
SiO ₂	39.05	38.47	37.90	37.82	37.91	39.00	38.90	38.25	38.09	38.80 38.30
TiO ₂	0.00	0.01	0.00	0.02	0.04	0.01	0.02	0.01	0.00	0.01 0.00
Al ₂ O ₃	0.00	0.00	0.00	0.02	0.03	0.02	0.02	0.00	0.02	0.00 0.01
Cr ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00 0.00
FeO*	17.79	20.59	22.16	24.10	23.80	24.106	25.528	25.017	25.124	24.387 24.822
MnO	0.25	0.33	0.33	0.43	0.42	0.44	0.49	0.44	0.44	0.41 0.41
MgO	42.56	39.72	37.62	37.45	37.39	37.11	36.07	36.75	36.45	36.66 36.47
CaO	0.11	0.14	0.17	0.15	0.19	0.16	0.13	0.12	0.11	0.13 0.10
Total	99.77	99.26	98.18	99.99	99.77	100.86	101.16	100.59	100.23	100.39 100.10
Fe	81.0	77.5	75.2	73.5	73.7	73.3	71.6	72.4	72.1	72.8 72.4

but sharply distinct from the enclosing material. We believe these xenoliths may be fragments of a highly evolved crystal-rich part of the reservoir.

Textural relations between the different phases suggest early crystallization of mafic minerals Amph, spinel, and Cpx followed by high-An plagioclase. The olivine microphenocrysts apparently crystallized later since they are found in the matrix and are small, in accord with their melt inclusions compositions they are of a later crystallization episode (compared to Amph and Cpx, see later sections). The disequilibrium textures of Ol, and Ox, as well as the breakdown in Amph are attributed to weathering and oxidation rather than high temperature magmatic processes.

4.3. The 10 kyr old PF unit

The bread-crusts bombs of basaltic andesite composition ($\text{SiO}_2 = 55.0\text{-}56.4 \text{ wt}\%$) from the 10 kyr unit have similar porphyritic texture to that of the >45 kyr unit. The main phenocrysts are plagioclase (20-33 vol%), clinopyroxene (1-5 vol%), orthopyroxene (1-5 vol%), and FeTi-oxide (0.5-2 vol%) (Table 8). The matrix consists of microlites of Plag, Cpx, Opx, minor Ol, and glass. Although there is no macroscopic evidence for magma mixing/mingling; Cpx and Opx show a large variety of chemical zoning patterns emphasizing the importance of open-system processes in these magmas (Fig. 4). Glomerocrysts of two-pyroxenes, Fe-Ti oxide, and $\pm$ olivine also occur.

Euhedral plagioclase has similar size and composition to that of the >45 kyr unit (Figs. 6.a & 11, Table 2), but slightly less calcic (An_{90-78}). It also shows weak normal zoning with rims at about An_{80-70} , and fine-scale oscillatory zoning (Fig. 6.a). Plag phenocrysts commonly show a coarse sieved texture (Fig. 6.a), some have a small clear zone free of inclusions close to the edge. Plag shows minimal normal zoning pattern with unimodal An distribution (Fig. 11), and coarse sieved texture (Fig 6a), and probably indicates partial melting by decompression (Nelson & Montana, 1992).

Fig. 6. BSE images of selected minerals and some electron microprobe traverses from the 10 kyr unit. (a) Plagioclase phenocryst consists of a high An coarse sieve-textured core surrounded by a low-An rim with fine-scale oscillatory zoning. (b) Cpx-Opx-Ol glomerocryst. (c) Reversely zoned clinopyroxene phenocryst with a resorbed core surrounded by an oscillatory-zoned rim (d) Patchy zoning of Cpx-Opx-Pig glomerocryst. (e) Reversely zoned orthopyroxene phenocryst. Note that all reversely zoned pyroxene crystals are euhedral with strait margins, but the cores are subrounded, resorbed. (f) Apatite microphenocrysts grown together with evolved Opx and Cpx with apatite inclusions.

Anhedral olivine (Fo₇₀₋₇₂) occurs in Cpx-Opx glomerocrysts (Fig. 6.b) and rarely as subhedral microphenocryst/microlite in the matrix.

Clinopyroxene (about En₄₀₋₄₇Fs₁₃₋₂₀Wo₃₈₋₄₃) phenocrysts are euhedral, whereas Cpx in the glomerocrysts is anhedral and commonly shows patchy zoning (Figs. 6.b-d, Table 4). Cpx exhibits strong reverse zoning, with Mg# some times abruptly increasing from about 66 in the cores to about 75 in the rims, whereas Al₂O₃ (1.8 to 3.7 wt%) does not correspond to this clearly (Figs. 6.c, 12, 13). Cores can be subrounded and strongly resorbed; rims of reversely zoned Cpx phenocryst show fine oscillatory zoning. Cpx cores (Mg# is about 65-67) commonly contain small apatite and occasional zircon inclusions. The presence of these inclusions shows that these Cpx grew from a lower temperature and much more evolved magma than the rims, as it is also recorded in their trace element compositions (see below).

Pigeonite, with similar composition to that of >45 kyr, occurs in the glomerocrysts intergrowing with other pyroxenes (Fig. 6.d). Its (textural) appearance suggesting fast growth and slow cooling. Orthopyroxene (En₆₃₋₇₃Fs₂₅₋₃₄Wo_{2.6-3.3}) phenocrysts show similar textural features to Cpx (Fig. 6.e). Glomerocrystic Opx is subhedral-anhedral with patchy, oscillatory and sector zoning (Fig. 6.b,d). Phenocrysts are euhedral and reverse zoning in Mg # is common, with resorbed Fe-rich cores (Mg# = 64-69), mantled by high-Mg rim (Mg# = 73-75), with abrupt transition between them (Fig. 6e). Al₂O₃ in Opx varies from 1 wt% to 2.9 wt%, not always in a systematic manner with Mg# (Table 5). Opx in glomerocrysts displays a narrower compositional range (Mg# = 70-75) overlapping with those of phenocryst rims. Opx cores contain small oxides and apatite inclusions (Fig. 6.e). Opx microlites overlap in composition with that of phenocrysts.

Apatite is not abundant as phenocryst, however, inclusions are commonly found mostly in Cpx cores. One apatite crystal (Fig. 6.f) has fluorine and chlorine concentrations between 3.9 and 4.5 wt%, and 0.9 and 1 wt%, respectively.

Table 4. Representative clinopyroxene analyses

wt%	>45ky				10ky				4ky				1.2ky				
	A2C1	A2C3-lAl	A2C3-hAl	A2C6-lAl	A2C6-hAl	C6C1c	C6C1r	C6C2c	C6C2r	C3C8-lAl	C3C8-hAl	C7C1c	C7C1r	P5C2c	P5C2r	P5C3c	P5C3r
SiO ₂	50.93	51.74	50.59	51.02	48.98	49.42	49.94	49.88	51.15	51.54	50.82	51.34	49.44	50.25	49.20	52.11	51.89
TiO ₂	0.56	0.38	0.54	0.50	0.82	0.67	0.62	0.59	0.48	0.50	0.51	0.38	0.83	0.64	0.69	0.51	0.55
Al ₂ O ₃	2.66	1.79	2.81	2.77	4.68	2.80	3.07	2.47	2.20	2.78	3.22	1.64	4.21	2.91	5.40	2.22	2.35
FeO*	9.57	10.39	10.77	8.98	9.26	12.05	9.29	12.03	9.87	6.57	6.39	11.60	8.38	12.69	7.15	11.04	10.73
MnO	0.35	0.46	0.46	0.31	0.28	0.42	0.31	0.41	0.36	0.16	0.14	0.45	0.20	0.40	0.15	0.37	0.35
MgO	15.48	15.75	15.33	15.69	14.46	13.70	15.19	13.89	15.40	16.00	15.78	14.07	14.80	13.45	15.28	14.37	14.81
CaO	19.24	18.61	18.42	19.66	20.15	19.15	19.98	19.15	19.89	22.44	22.26	19.60	21.21	18.60	21.56	19.83	19.53
Na ₂ O	0.37	0.27	0.30	0.29	0.33	0.40	0.30	0.38	0.31	0.15	0.12	0.34	0.24	0.41	0.20	0.40	0.33
K ₂ O	0.00	0.00	0.00	0.01	0.00	0.00	0.02	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.17	99.38	99.22	99.22	98.97	98.61	98.71	98.81	99.65	100.15	99.23	99.42	99.29	99.35	99.63	100.84	100.53
En%	44.6	45.1	44.3	45.0	42.4	40.0	43.7	40.4	43.7	44.7	44.6	40.6	42.6	39.6	43.9	41.3	42.5
Fs%	15.5	16.7	17.5	14.4	15.2	19.8	15.0	19.6	15.7	10.3	10.1	18.8	13.5	21.0	11.5	17.8	17.3
Wo%	39.9	38.3	38.2	40.5	42.4	40.2	41.3	40.0	40.6	45.0	45.2	40.6	43.9	39.4	44.5	40.9	40.3
Mg#	74.2	73.0	71.7	75.7	73.6	67.0	74.5	67.3	73.6	81.3	81.5	68.4	75.9	65.4	79.2	69.9	71.1
ppm																	
Cr	5.14	1.45	1.90	3.55	8.61	13.2	12.6	10.0	11.5	634	374	16.4	43.9	34.4	164	8.44	10.3
Ni	10.6	6.30	6.28	9.05	13.5	17.7	29.1	16.7	24.8	26.2	29.5	18.4	13.4	51.4	46.0	49.9	50.4
Y	31.7	31.2	39.0	25.0	29.5	55.6	29.7	60.0	33.4	24.9	15.7	51.5	26.2	56.2	32.6	60.0	36.3
Zr	26.6	18.2	31.7	14.4	23.8	48.3	28.7	48.1	21.3	30.1	17.7	31.5	34.2	52.9	40.7	50.8	27.6

FeO* = total Fe as FeO

Mg# = [Mg/(Mg+Fe)]*100 in moles

En% = percent enstatite, Fs% = percent ferrosilite, Wo% = percent wollastonite; by the method of Papike *et al.* (1974)

c = core; m = middle; r = rim; hAl = high-Al sector; lAl = low-Al sector.

Table 4. continued

wt%	lky										recent				
	S5C4c	S5C4m	S5C4r	S5C6c	S5C6m	S5C6r	SMT4C3c	SMT4C3r	SMT4C5c	SMT4C5r	G385C1c	G385C1r	ALUN_C4c	ALUN_C4r	
SiO ₂	50.97	50.31	52.35	50.50	51.30	49.00	49.85	50.34	50.71	50.32	51.84	51.44	52.71	52.69	
TiO ₂	0.70	0.65	0.50	0.49	0.48	0.87	0.56	0.46	0.49	0.52	0.48	0.44	0.33	0.39	
Al ₂ O ₃	3.44	2.98	1.96	2.23	1.48	3.85	2.37	2.42	1.77	2.89	2.13	1.95	1.72	1.81	
FeO*	8.16	9.16	8.96	9.57	9.94	9.03	12.55	8.64	11.43	8.61	10.04	10.90	10.42	9.94	
MnO	0.24	0.32	0.34	0.36	0.37	0.26	0.45	0.30	0.45	0.28	0.33	0.40	0.37	0.41	
MgO	14.48	15.49	15.38	15.57	16.46	15.09	13.93	15.68	14.75	15.08	14.36	13.93	14.00	16.26	
CaO	20.88	20.09	19.33	19.85	18.83	20.47	19.24	20.65	19.26	21.00	20.25	19.93	20.56	18.35	
Na ₂ O	0.28	0.30	0.26	0.28	0.17	0.26	0.37	0.31	0.29	0.28	0.46	0.36	0.41	0.26	
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	
Total	99.15	99.30	99.08	98.85	99.03	98.82	99.30	98.80	99.15	98.98	99.89	99.34	100.53	100.10	
En%	42.5	44.2	44.8	44.2	46.3	43.3	40.0	44.3	42.1	43.1	41.6	40.5	40.4	46.4	
Fs%	13.4	14.6	14.7	15.3	15.7	14.5	20.2	13.7	18.3	13.8	16.3	17.8	16.9	15.9	
Wo%	44.1	41.2	40.5	40.5	38.0	42.2	39.7	42.0	39.5	43.1	42.1	41.7	42.7	37.7	
Mg#	76.0	75.1	75.4	74.4	74.7	74.9	66.4	76.4	69.7	75.8	71.8	69.5	70.6	74.5	
ppm															
Cr	372	317	284	368	311	409		15.4	15.3	24.4					
Ni	14.3	12.3	10.3	13.1	10.6	10.1		27.8	24.9	33.2					
Y	22.9	22.5	22.1	37.9	23.1	26.8		21.5	43.5	22.2					
Zr	20.3	16.9	14.2	35.1	18.3	26.2		15.5	28.8	18.2					

FeTi-oxide (micro)phenocrysts are typically ulvöspinel in composition ($\text{FeO}^* = \text{total iron as Fe}^{2+} = 74 \text{ to } 76\text{wt\%}$; TiO_2 is 10 to 14wt%; Cr_2O_3 is <0.1wt%) (Table 7). We did not find ilmenite. FeTi-oxides are also common constituents of the matrix.

Pyroxene glomerocrysts exhibit chaotic patchy zoning, Cpx and Opx display strongly resorbed cores and well-developed reverse zoning patterns. The complexity of zoning patterns and the large compositional differences between evolved cores and mafic rims of pyroxenes imply open-system processes (e.g. Streck, 2008), likely reflecting primitive magma recharge and associated mixing and mingling with pyroxene-rich cumulate. Apatite indicates an evolved, P_2O_5 -saturated liquid (e.g. Lee & Bachmann, 2014); tiny apatite inclusions found in pyroxene cores suggest low temperature crystallization of those cores (Fig 6e).

4.4. The 4 kyr old PF unit

Blocks of bread-crust bombs show macroscopic evidence of magma mingling, including scoria with grey and black bands that represent the different interacting magmas (Figs. 3.c-f). The porphyritic dark bands resemble in texture and mineralogy to a combination of the above-described mafic units (i.e. >45 kyr and 10 kyr), whereas the felsic bands have a vitrophyric-porphyric and more pumiceous texture (i.e. more vesicles; Fig 3), and a more evolved composition. Zoned minerals are common in all samples, even when matrix is compositionally and texturally homogenous. The mineral assemblage also indicates non-equilibrium conditions; plagioclase, clino-, and orthopyroxene, amphibole, olivine, FeTi-oxide, and minor apatite are present together in both the mafic and silicic bands. Normal, reverse, and oscillatory zoning often observed within the same crystal suggesting a dynamic, open-system behavior (e.g. Fig. 7). Compositions of the 4 kyr unit samples stretch from basaltic andesite to andesite ($\text{SiO}_2 = 54.4\text{-}60.4 \text{ wt\%}$).

Fig. 7. BSE images and electron microprobe traverses of the selected minerals of the 4 kyr unit. (a) and (b) Normally zoned, sieve-textured calcic plagioclase, and normally zoned, inclusion-free sodic plagioclase, respectively. (c) Normally zoned olivine shown two clear plateaus, suggesting the involvement of two mafic magmas before the reaction rim made of Opx grew. (d) Oscillatory and sector zoning in Cpx with a reacted and largely dissolved Opx in its interior. (g) Reverse zoning in euhedral Opx with many inclusions of apatite and oxides in the cores. (f) Reverse zoning in euhedral Amph, note the slightly more primitive rim. All mafic phenocrysts show reverse zoning (except for olivine) indicating mafic magma injection into evolved and crystal-rich reservoir.

Plagioclase phenocrysts tend to be euhedral and it is the most abundant mineral in both the mafic (10-18 vol%) and the silicic (22-28 vol%) bands (Table 8); it shows the largest compositional diversity from about An₄₉ to about An₈₇, and it is also bimodal at An₆₀ and An₈₅ (Fig. 11, Table 2). Plag phenocrysts display normal, reverse, and oscillatory zoning, and combinations of these patterns. Though sieve texture is very common in Plag, inclusion-free phenocrysts also occur (Fig. 7.a&b). Sieve-textured crystals show broader compositional range and higher maximum An-content. Less An-rich Plag contain inclusions of glass, Opx, Cpx, and occasionally olivine (Figs. 7.a).

Olivine (Fo₇₂₋₈₂) is an accessory mineral, found in both mafic and silicic bands as subhedral microphenocrysts (50-180 μ m), as microlite, and rarely as anhedral and resorbed phenocrysts (Fig. 7.c, Table 3). The most Mg-rich olivines are normally zoned, and are mantled by Opx reaction rims, and are believed to be xenocrysts in the mafic end-member magma (Fig. 7.c). Olivine inclusions are found in some Cpx and Plag.

Cpx phenocrysts (about En₃₉₋₄₆Fs₁₀₋₂₂Wo₃₉₋₄₈) show the largest range and most primitive (highest Mg# and Wo) composition of all units (Fig. 12). Mg# varies from about 60 to 82, and Al₂O₃ from about 1 to 8 wt% (Figs. 12&13, Table 4). Reverse zoning is the most common type, sector zoning is found in the grains with the highest compositional variety, but oscillatory zoning is only found in the sector zoned grains (Fig. 7.d). Fe-rich cores (Mg# is about 61-67) are subhedral, rounded, and often contain apatite and Fe-Ti oxide inclusions, whereas high-Mg# rims (75-82) are always euhedral and inclusion-free. Cpx microlites are rare and only found in the mafic bands with a composition similar to the phenocrysts. Rare pigeonite (about En₅₅₋₆₉Fs₂₅₋₂₈Wo₇₋₁₈) is found only as microlite.

Orthopyroxene (En₅₉₋₇₃Fs₂₄₋₃₆Wo₃₋₅) is the most abundant ferro-magnesian mineral, with Mg# variations of about 60 to 75 (showing mainly two modes at about 62 and 74; Fig 12), and Al₂O₃ from about 0.5 wt% to 2.5 wt% (Figs. 13; Table 5). Low alumina

Table 5. Representative orthopyroxene analyses

	4ky										1.2ky																						
	10ky		C6O1c		C6O1r		C6O2c*		C6O2r*		C6O10c		C6O10r		C3O10c		C3O10r		C3O11c		C3O11r		C11O7c		C11O7r ^a		P5O1r1 ^a		P5O1r2		P5O5		
wt%																																	
	SiO ₂	51.41	52.00	53.24	52.90	53.22	53.24	52.84	54.40	52.18	52.18	54.26	52.25	51.72	52.21	52.45	53.56	52.85															
	TiO ₂	0.27	0.27	0.23	0.27	0.31	0.25	0.26	0.19	0.17	0.17	0.15	0.17	0.44	0.25	0.40	0.24	0.20															
	Al ₂ O ₃	1.52	2.26	2.00	2.23	0.78	2.06	0.70	0.65	0.69	0.69	1.02	0.94	1.67	1.36	1.89	1.56	0.95															
	FeO*	21.51	17.13	16.67	16.77	19.87	16.40	22.36	16.92	22.76	22.36	16.36	22.48	9.98	23.60	8.23	17.39	22.55															
	MnO	0.63	0.49	0.47	0.45	0.69	0.50	0.74	0.52	0.79	0.46	0.77	0.35	0.74	0.29	0.54	0.82																
	MgO	22.25	25.65	25.89	26.07	23.06	25.58	22.39	26.74	21.54	26.87	21.79	15.56	19.86	1.60	20.81	1.36	21.83															
	CaO	1.61	1.57	1.38	1.37	1.82	1.61	1.73	1.44	1.44	1.54	1.45	1.45	0.33	0.02	0.19	0.02	1.43															
	Na ₂ O	0.04	0.02	0.04	0.01	0.02	0.00	0.04	0.03	0.04	0.03	0.03	0.03	0.33	0.02	0.19	0.02	0.02															
	K ₂ O	0.00	0.02	0.01	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	99.24	99.40	99.95	100.06	99.77	99.63	101.07	100.90	99.61	100.70	99.90	99.89	99.90	100.56	100.60	100.74	100.65															
	En%	62.7	70.5	71.5	71.5	64.9	71.2	61.9	71.8	61.0	72.3	61.5	43.9	59.1	45.5	70.8	61.5																
	Fs%	34.0	26.4	25.8	25.8	31.4	25.6	34.7	25.5	36.1	24.7	35.6	15.8	37.6	12.9	26.5	35.6																
	Wo%	3.3	3.1	2.7	2.7	3.7	3.2	3.4	2.8	2.9	3.0	2.9	40.3	3.3	41.7	2.7	2.9																
	Mg#	64.8	72.7	73.5	73.5	67.4	73.6	64.1	73.8	62.8	74.5	63.3	73.5	61.1	78.0	72.8	63.3																
ppm																																	
	Cr	6.43	8.82	15.7	16.0			2.00	4.56	4.05	22.1				5.41		12.6																
	Ni	30.5	43.6	47.0	51.1			21.5	30.2	20.7	51.9				86.2		86.1																
	Y	9.09	4.17	3.46	4.02			13.3	3.31	15.4	3.08				12.9		11.4																
	Zr	5.43	2.90	2.39	3.00			3.96	1.81	3.27	2.71				5.28		3.58																

FeO* = total Fe as FeO

Mg# = [Mg/(Mg+Fe)] * 100 in moles

En% = percent enstatite, Fs% = percent ferrosilite, Wo% = percent wollastonite; by the method of Papike *et al.* (1974)

c = core, m = middle, r = rim

^a Cpx rim on Opx

*from the glomerocryst in Fig. 6.d

Table 5. continued

	lky					recent										
	P303c	P303r	P309c	P309r1	P309r2	S406c	S406r	S408c	S408r	G385O4c	G385O4m	G385O4r	G385O2c	G385O2r	ALUN O6c	ALUN O6r
wt%																
SiO ₂	53.37	52.85	53.03	53.08	51.85	52.51	53.15	52.82	54.13	53.19	52.25	53.38	50.72	52.45	52.25	52.71
TiO ₂	0.25	0.16	0.24	0.28	0.35	0.28	0.23	0.29	0.19	0.17	0.22	0.16	0.25	0.17	0.24	0.31
Al ₂ O ₃	1.20	0.94	1.26	1.91	0.46	1.42	1.73	2.18	1.10	0.66	1.03	0.74	1.47	0.65	1.51	1.93
FeO*	18.20	22.34	19.94	17.59	23.83	17.53	16.43	16.83	16.36	18.17	20.46	16.64	24.00	19.89	22.22	17.75
MnO	0.49	0.60	0.50	0.50	0.73	0.55	0.46	0.46	0.48	0.57	0.66	0.52	0.64	0.64	0.57	0.55
MgO	24.13	21.36	22.36	24.25	19.28	25.12	26.28	25.50	26.14	24.80	22.86	25.81	19.38	23.29	21.09	24.23
CaO	1.63	1.43	1.62	1.51	1.96	1.68	1.46	1.65	1.57	1.49	1.28	1.55	2.28	1.60	1.66	1.69
Na ₂ O	0.04	0.02	0.00	0.02	0.06	0.03	0.03	0.04	0.00	0.00	0.02	0.05	0.04	0.01	0.05	0.03
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Total	99.31	99.70	98.96	99.13	98.51	99.11	99.77	99.77	99.96	99.04	98.79	98.85	98.78	98.68	99.60	99.22
En%	68.0	61.2	64.4	68.9	56.6	69.5	71.9	70.6	71.7	68.8	64.8	71.2	56.2	65.4	60.7	68.4
Fs%	28.7	35.9	32.2	28.0	39.2	27.2	25.2	26.1	25.2	28.3	32.6	25.7	39.0	31.3	35.9	28.1
Wo%	3.3	2.9	3.3	3.1	4.1	3.3	2.9	3.3	3.1	3.0	2.6	3.1	4.7	3.2	3.4	3.4
Mg#	70.3	63.0	66.7	71.1	59.1	71.9	74.0	73.0	74.0	70.9	66.6	73.4	59.0	67.6	62.9	70.9
ppm																
Cr						13.5		17.2	6.45							
Ni						52.8		63.7	42.0							
Y						4.68		4.26	4.32							
Zr						2.63		2.67	1.89							

usually corresponds to low-Mg#, however it does not systematically. Opx in glomerocrysts also tends to be less Mg-rich (Mg# up to 69). Opx phenocrysts are most commonly reversely zoned and the cores can be full of apatite and Fe-Ti oxide inclusions (Fig. 7.e). Cores may be rounded, while rims are always euhedral. Resorbed Opx is typically mantled by Cpx (Fig. 7.d). Opx inclusions in Plag tend to have low Mg# (about 64-67). Opx microlites are abundant in the mafic bands, and display a somewhat narrower compositional range than the phenocrysts.

Amphibole (pargasite) occurs as euhedral-subhedral phenocrysts (Fig. 7.f; Table 6) and as broken crystals in the mafic bands. The Mg# (69-76), Al₂O₃ (13-15wt%) and CaO (11-12 wt%) partly overlap with the Amph in the >45 kyr unit; the Mg# tends to be lower, with a mode at about 72 (Fig. 12). Amphibole phenocrysts show reverse zoning (unlike those in >45 kyr unit), with Mg# in cores of about 69 and in rims of about 74; in many cases multiple zones of Mg# changes are observed (Fig. 7.f). Mafic rim compositions are similar to the >45 kyr amphiboles (Figs. 12&13; Table 6). Amph in mafic bands may develop breakdown rims (few tens of μm thick). Amphibole is absent in the silicic bands except for one almost completely reacted grain. This almost entirely reacted amphibole is compositionally similar to those in the mafic bands, and consists of very fine grained Plag+Pyx+Ox assemblage. Amphibole cores rarely contain melt inclusions.

FeTi-oxides are commonly found as inclusions in Opx and Cpx, and also abundant in the matrix as microlites and as (micro)phenocrysts. Magnetite occurs abundantly, but ilmenite is also present.

The macroscopic-scale evidence for mingling, the reverse zoning of many phenocrysts, and the bimodal distribution of chemical indicators of pyroxenes and plagioclase (Figs. 11&12) are a record of open-system processes (e.g. Nakamura, 1995; Pallister et al., 1996; Streck, 2008 and references therein) and show that magma mixing and mingling played a key role in the evolution of this unit. The thin (up to 20 μm)

breakdown rims of amphibole in the mafic band shows that it was mostly stable, and only out of its stability for a relatively short time (e.g. Rutherford & Devine, 2003). On the other hand, the fully reacted amphibole found in the silicic band indicates that it was not stable in that environment. Thus, maybe the Mg-poor cores of Amph are newly formed grains from the mixtures rather than originated in the silicic melt. The textural and compositional zoning of the amphibole also suggest a complex history of crystal growth and dissolution.

4.5. The 1.2 kyr unit

This is a composite unit with the widest compositional ($\text{SiO}_2 = 54.6\text{-}69.1$ wt%) and textural range. It has similar mineralogical and petrological features both to the 10 kyr and the 4 kyr units. There is rare macroscopic (banded scoria or pumice), but abundant microscopic (at crystal-scale) evidence for the involvement of contrasting magmas in its evolution.

Euhedral plagioclase (An_{50-92}) is the most abundant phenocryst (14-19 vol%, Table 8), and shows a wide variety of textures, zoning patterns, and a mainly bimodal An distribution quite similar to the 4kyr old unit (Figs. 8&11; Table 2). Sieve-textured Plag is highly calcic (An_{78-92}) and typically normally zoned (Fig. 8.a). More sodic Plag (An_{50-67}) has similar sieve or 'dusty' texture and may contain Mg-rich Cpx, Opx and Ol inclusions (Fig. 8.b). Composite Plag crystals with a sort of haphazard mixture of the previous two types are also common. Abundant Plag microlites in the matrix have similar compositions (An_{57-68}) to those of the sodic phenocrysts.

Subhedral-anhedral olivine (Fo_{70-81}) is an accessory mineral (<0.6 vol%, Table 8). Olivine (micro)phenocrysts often show normal zoning and reaction textures with Opx at their rims. We found several grains with a three-stage normal zoning evolution: a Mg-rich

Table 6. Representative amphibole analyses

wt%	4ky										1.2ky					'recent'				
	>45ky										P5A6r					G385A				
	A2A1c	A2A1r	A2A2c	A2A2r	A3A1c	A3A1r	C11A3c	C11A3r	C7A3c	C7A3r	C7A1c	C7A1r	P5A6c	P5A6r1	P5A6r2	G385A1c	G385A1r	G385A2c	G385A2r	
SiO ₂	41.54	41.33	40.95	41.10	41.48	40.69	41.13	41.18	41.25	41.36	41.05	41.58	40.93	39.47	41.30	42.93	42.44	42.08	42.03	
TiO ₂	2.06	2.08	1.86	1.88	1.88	2.16	2.31	1.92	2.15	1.97	2.09	2.11	3.11	1.86	1.95	1.94	2.10	2.93	2.99	
Al ₂ O ₃	14.17	14.11	14.27	14.43	14.18	14.60	13.75	14.30	13.59	14.20	14.32	14.48	13.15	14.30	14.24	12.14	12.06	11.38	11.49	
Cr ₂ O ₃	0.09	0.13	0.03	0.16	0.18	0.01	0.01	0.03	0.01	0.04	0.00	0.03	0.00	0.02	0.04	0.01	0.00	0.00	0.00	
FeO*	8.71	8.80	9.07	9.33	8.55	9.32	10.73	8.95	10.76	9.47	11.00	9.79	12.27	9.33	9.39	10.51	10.19	11.70	11.62	
MnO	0.04	0.05	0.07	0.08	0.10	0.10	0.12	0.11	0.07	0.10	0.11	0.11	0.06	0.12	0.10	0.15	0.11	0.18	0.17	
MgO	15.57	15.45	15.25	15.10	15.90	15.13	14.75	15.58	14.11	15.35	14.29	15.17	13.53	14.59	15.10	15.41	15.23	14.17	14.01	
CaO	12.16	12.15	11.94	11.92	12.34	12.35	11.66	12.13	11.50	11.84	11.78	11.98	11.00	11.83	11.82	11.17	11.58	11.37	11.45	
Na ₂ O	2.53	2.50	2.50	2.50	2.42	2.37	2.34	2.39	2.31	2.20	2.26	2.26	2.43	2.30	2.31	2.48	2.67	2.84	2.78	
K ₂ O	0.55	0.51	0.52	0.51	0.55	0.53	0.61	0.51	0.49	0.56	0.58	0.59	0.65	0.51	0.54	0.38	0.38	0.53	0.54	
Total	97.40	97.12	96.46	97.02	97.58	97.27	97.42	97.09	96.23	97.09	97.47	98.09	97.13	94.30	96.81	97.12	96.76	97.16	97.07	
Mg#	76.1	75.8	75.0	74.3	76.8	74.3	71.0	75.6	70.0	74.3	69.8	73.4	66.3	73.6	74.1	72.3	72.7	68.4	68.2	
ppm																				
Cr	734	715	615	357	1150	129	84.0	217	27.8	378	37.0	93.8	172	84.0	751					
Ni	78.3	77.9	79.0	74.6	101	74.5	71.6	102	47.2	94.1	40.9	84.6	95.7	86.9	120					
Sr	147	147	187	185	178	188	151	160	161	173	178	175	165	155	155					
Rb	3.10	3.13	3.50	3.37	3.15	3.30	3.76	2.91	3.24	3.99	3.08	3.85	4.45	3.75	3.63					
Ba	46.8	46.4	44.7	45.0	38.8	46.1	48.3	45.0	51.2	59.9	51.4	62.4	82.8	48.3	51.3					
Y	15.6	15.4	14.1	14.1	12.9	14.6	22.5	15.8	22.8	21.5	19.6	23.2	34.5	16.5	19.0					
Zr	11.9	12.0	11.2	11.2	9.59	10.9	20.1	12.9	19.7	22.9	17.8	27.3	30.0	15.0	20.2					
Al/Si	0.402	0.402	0.411	0.414	0.403	0.423	0.394	0.409	0.388	0.405	0.411	0.410	0.379	0.427	0.406	0.333	0.335	0.319	0.322	

FeO* = total Fe as FeO

Mg# = [Mg/(Mg+Fe)]*100 in moles

c = core, m = middle, r = rim

core (Fo₈₀₋₈₁), surrounded by a well-developed intermediate zone (Fo₇₇₋₇₈), and a thin Fe-rich rim (Fo₇₀₋₇₂) (Fig. 7.c, Table 3). Microphenocrysts and microlites (Fo₇₂₋₇₇) also occur in the matrix and they are compositionally similar to the inclusions (Fo₇₂₋₇₆) in Plag.

Clinopyroxene (En₃₉₋₄₆Fs₁₂₋₂₁Wo₃₉₋₄₅) is the most abundant ferromagnesian mineral (3-5 vol%; Table 8), and is compositionally similar to those of the 4kyr unit and show a bimodal distribution (Mg# = 65-80, Al₂O₃ = 2.8-5.6 wt%) (Figs. 12&13; Table 4). Cpx phenocrysts are usually reversely zoned with a sharp compositional change between the core and the rim, just like those of the 4 and 10 kyr units. (Fig. 8.c). Cpx can occur mantling Opx, and has a similar composition to that of rims of reversely zoned Cpx. Cpx microlites are similar in composition to the phenocryst rims.

Opx is euhedral (En₆₀₋₇₄Fs₂₁₋₃₇Wo₃₋₅), and compositionally very similar to that of other Holocene units (10 kyr and 4 kyr units; Figs. 12&13, Table 5). Opx crystals are mostly reversely zoned, with Mg# as high as 75 in the rim and as low as 61 in the core, show also a bimodal distribution. Alumina in Opx is inversely correlated with Mg#, unlike in the 10 kyr and 4kyr units. Small Opx crystals included in Plag overlap in composition with the phenocrysts, except that they tend to have higher Al₂O₃. In one of the 1.2 kyr samples, intensely resorbed Opx (Mg# = 60) contains Cpx (Mg# = 63) and pigeonite lamellae (Fig. 8.e).

Euhedral phenocrysts of amphibole (pargasite) show multiple reversely zoned parts, and also the largest intracrystalline compositional range (Mg# = 66 in core, and 75 in rim; Fig. 8.f; Table 6). Compositional changes between cores and rims are abrupt. Al₂O₃ (12.5-14.6 wt%) and CaO (11-12 wt%) are similar to those of the 4 kyr unit (Figs. 12&13). No inclusions were found in Amph.

Fe-Ti-oxide is an important accessory phase (0.6-1.4vol%; Table 8), both as phenocryst and microlites. Ilmenite and magnetite appear commonly together (Table 7).

Fig. 8. BSE images and electron microprobe traverses of the selected 1.2 kyr unit phenocrysts. (a) and (b) Composite plagioclase with various mineral inclusions; fine-scale oscillatory zoning, sieve-texture and irregularly alternating calcic and sodic zones are common. (c) Reversely zoned Cpx phenocryst; note the abrupt change in composition at core-rim boundary. (d) Reversely zoned Opx twin; note the apatite and FeTi-oxide inclusions in the evolved core. (e) Evolved Opx crystal shows resorption (melting) around its edges. Due to extreme heat Pig (in immediate rim) and Cpx (farther from contact) lamellae appear indicating rapid rise in temperature. (f) Reversely zoned Amph phenocryst. Note that the reverse zoning in mafic minerals is similar to that of the 4 kyr crystals.

Although we did not observe extensive macroscopic-scale mixing/mingling in this unit, the reverse zoning patterns of mafic minerals and complex zoning patterns of plagioclase (dissolution zones and large intracrystalline variation of An), together with a bimodal distribution of chemical indicators (Mg# or An%) of phenocrysts shows that open-system processes involving magmas of contrasting compositions were important. The exsolution lamellae and resorption in Opx and the absence of reverse zoning all suggest reheating of previously existing and perhaps subsolidus magmas. The intruding mafic magma must have been hot, thus instead of crystallizing mafic rim on Opx, it melted it. Multiple reverse zones of Amph may indicate repeated magma recharges of primitive origin and/or magma convection in the reservoir (e.g. Costa et al., 2013).

4.6. The 1 kyr unit

This is also a composite unit, with some samples showing similar mineralogical and petrological features to those from the 10 kyr unit, and others share similarities with the >45 kyr unit samples, but they belong to the same eruptive unit. Samples of this unit are low-silica basaltic andesites to low-silica andesites ($\text{SiO}_2 = 52.0\text{--}61.1$ wt%).

Euhedral plagioclase ($\text{An}_{52\text{--}92}$) is the most abundant mineral in both rock types and typically has a sieved texture, and shows large variety of zoning patterns (Fig. 9.a, Table 2). Plag phenocrysts from the >45 kyr-like low-silica basaltic andesites are more calcic ($\text{An}_{80\text{--}92}$) contain partially devitrified glass inclusions, and display weak normal and oscillatory zoning. Plag from the 10 kyr-like basaltic andesites tends to be less calcic ($\text{An}_{77\text{--}87}$) and normal zoning extends to more Na-rich compositions ($\text{An}_{52\text{--}71}$). This latter plagioclase contains abundant inclusions of highly evolved glass, occasional low-Mg# Cpx, Fe-Ti oxides, quartz, and potassic feldspar ($\text{An}_{1\text{--}3}\text{Ab}_{28\text{--}33}\text{Or}_{65\text{--}71}$) (Fig. 9.b), and thus may indicate that thermal evolution allows crystallization of this low temperature mineral in these magma types (e.g. slow cooling or water loss in a crystal-mush system). The

Table 7: Representative FeTi-oxide analyses (touching ilmenite-magnetite pairs except for 10ky unit)

	>45ky	10ky	4ky	1.2ky			1ky			recent								
A3Ox1**	C6Ox1	C6Ox2	C7PX1	Ox1f	C7Ox4	m	P5Ox1	P5Ox2	S4C10Ox1	ALUN	O1Ox1							
wt%																		
SiO ₂	0.10	0.01	0.03	0.07	0.16	0.11	0.03	0.08	0.04	0.14	0.00	0.05	0.02	0.12	0.06	0.05	0.01	0.08
TiO ₂	44.23	14.43	0.81	1.05	13.13	10.21	38.45	14.24	42.01	14.25	45.10	14.11	41.61	10.97	41.49	4.63	44.90	13.12
Al ₂ O ₃	3.51	2.27	6.12	51.20	2.65	4.83	0.47	2.32	0.50	3.40	0.24	2.10	0.40	4.63	0.18	2.04	0.23	1.96
Cr ₂ O ₃	0.03	0.06	0.04	0.07	0.09	0.07	0.03	0.06	0.03	0.02	0.00	0.04	0.01	0.06	0.05	0.16	0.02	0.06
FeO*	42.82	72.84	80.53	24.50	74.23	75.63	54.09	74.30	49.40	72.51	48.56	75.75	49.77	74.55	50.91	84.33	50.67	77.06
MnO	0.105	0.137	0.954	0.544	0.528	0.342	0.339	0.478	0.368	0.439	0.561	0.547	0.310	0.363	0.573	0.278	0.590	0.520
MgO	2.87	1.29	3.56	18.80	3.22	3.56	2.34	2.17	4.24	3.55	3.18	2.09	4.83	3.42	3.55	1.39	2.29	1.55
log(Mg/Mn)							1.083	0.901	1.061	0.908	1.000	0.825	1.438	1.223	1.040	0.941	0.835	0.720
Recalculated analyses																		
FeO	34.7	41.2	25.9	10.9	37.8	35.5	30.1	40.2	29.9	38.6	34.3	40.4	28.5	36.1	30.5	32.9	35.7	40.3
Fe ₂ O ₃	9.0	35.2	60.7	15.1	40.4	44.6	26.7	37.9	21.7	37.7	15.8	39.3	23.6	42.7	22.7	57.1	16.6	40.9
total	94.54	94.61	98.12	97.74	97.97	99.23	99.53	98.35	99.84	99.01	100.17	99.46	100.72	99.59	100.15	99.49	101.18	99.21
X _{ilm}	90.1						72.9	77.5			84.0		75.5		76.8		83.6	
X _{mag}		54.1	97.7		61.9	68.9		57.4		57.7		58.7		66.2		86.3		61.0
X _{ulv}		46.0	2.4		38.1	31.1		42.6		42.3		41.3		33.8		13.7		39.0
T (°C)							1070		1050		958		994		734		941	
ΔNNO							0.86		0.83		0.34		1.03		1.36		0.42	

* raw EPMA data

** all the phases are found in the same grain showing exsolution pattern

ilm = ilmenite, mag = magnetite, ulv = ulvospinel; f = felsic band, m = mafic band of Cip-7

FeO and Fe₂O₃ values after Carmichael (1967)

oxide species are assessed after Stormer (1983)

log(Mg/Mn) equilibrium condition based on Mg-Mn test of Bacon & Hirschmann (1988)

wide compositional range suggests blending of chemically different magmas and crystal cargos. Plagioclase microlites in basalt are also more calcic (An_{69-85}) than those from the basaltic andesite (An_{39-61}), in accord with their respective phenocryst compositions and bulk-rocks.

Euhedral olivine (Fo_{68} to Fo_{74}) is relatively abundant (1.9 vol%; Table 8) in the low-silica basaltic andesite samples as microphenocrysts and in general shows normal zoning or weak reverse zoning (Fig. 9.c; Table 3). They also show an interesting skeletal growth pattern through P-content distribution (e.g. Welsch *et al.* 2013; Fig. 9.c). They rarely contain glass. Olivine is considered atypical in the 10 kyr-like basaltic andesites. We have found only one crystal (Fo_{69-70}) that is mantled by Opx (Mg# is about 68) reaction rim, a strong evidence for mixing of chemically different magmas (e.g. Coombs & Gardner, 2004).

Cpx is euhedral in both rock types, and the most abundant mafic phenocryst (6 vol% and 4 vol%, respectively; Table 8). Cpx ($En_{42-46}Fs_{13.6-17}Wo_{39-45}$; $Al_2O_3 = 1.3-5$ wt%) in the low-silica basaltic andesites shows fine-scale oscillatory zoning (Fig. 9.d) and a narrower compositional range than in the basaltic andesites ($En_{40-44}Fs_{14-20}Wo_{40-43}$; $Al_2O_3 = 1.4-3.6$ wt%) (Figs. 12&13, Table 4). Cpx phenocrysts from the basaltic andesites display a variety of complex zoning patterns (reverse, normal, and complex combinations of those), indicating complex mixing processes (Fig. 9.e). Cpx microlites are virtually absent in both samples. Cpx inclusions occur commonly in plagioclase in the basaltic andesites with compositions (Mg# = 66-71 and $Al_2O_3 = 0.9-1.9$ wt%) similar to the phenocryst cores indicating resorption of Cpx possibly due to interaction of different magmas.

Fig. 9. X-ray maps, BSE images and electron microprobe traverses of the 1 kyr unit phenocrysts. (a) Normally zoned coarse sieve-textured calcic plagioclase; white square notes area zoomed show in part (b) Recrystallized polyphase inclusion in plagioclase: evolved clinopyroxene, potassic feldspar, and quartz. This assemblage may represent a very evolved (rhyolitic) liquid that was slowly cooled, thus indicate interaction with compositionally completely different magmas suggested by host plagioclase composition (An_{82-87}). (c) X-ray maps of normally zoned euhedral olivine microphenocryst. From the top left clockwise they are P, Al, Fe, and Mg. Note the sector and oscillatory zoning shown by P, and the slight normal zoning in Mg and Fe. (d) Oscillatory zoning in a Cpx crystal with very limited core-rim compositional zoning. (e) Normally zoned Cpx phenocryst. Note that the change in core and rim composition is marginal. (f) Virtually unzoned Opx with olivine (Ol) and oxide (Ox) inclusions. Note the similarity between (c) & (d) and those minerals from the >45 kyr unit.

Orthopyroxene ($\text{En}_{64-72}\text{Fs}_{25-31}\text{Wo}_{3-4}$) occurs exclusively in the 10 kyr-like basaltic andesites, it is euhedral and less abundant than Cpx (3.1vol%; Table 8). Opx shows a relatively narrow range of Mg# (67 to 75) (Figs. 12&13; Table 5) and the characteristic reverse zoning seen in the older Holocene units is not always present, more commonly the crystals show complex zoning patterns (Fig. 9.f). Opx occasionally contains small olivine inclusions (about Fo_{71}) of similar composition to those in the basalt (Fig. 9.f). Opx microlites are common and compositionally similar to the phenocrysts.

Ilmenite and magnetite are accessory minerals (Table 7). They are more abundant in the basaltic andesites as microphenocrysts, but are atypical in the low-silica basaltic andesites, where they occur almost exclusively included in Cpx (Fig. 9.d). Fe-Ti oxides occur as microlites in the matrix.

The low-silica basaltic andesites show limited evidence (i.e. normally zoned olivine) for open-system processes and thus are more akin to the >45 kyr unit, except for the complete absence of amphibole. In contrast, the basaltic andesites show microscopic evidence for mixing and mingling (i.e zoning patterns of pyroxenes), however the characteristic reverse zoning of pyroxenes is much less predominant. Furthermore, it is worthy to note that we did not find evidences for mixing or mingling between the low-silica basaltic andesites and the 10 kyr-like basaltic andesite samples, no samples have been found with both olivine and orthopyroxene.

4.7. The 'recent' eruptions

We collected two samples from a recent lava dome emplaced in the inner crater of Gede, which is probably associated with the 1840 eruption (Belousov *et al.*, 2015). Two volcanic bombs from the older caldera were also collected and they are probably from the most recent activity, perhaps the 1955-57 eruption (Belousov *et al.*, 2015). Due to

compositional ($\text{SiO}_2 = 58.4\text{-}60.7 \text{ wt\%}$) and mineralogical similarities we discuss them together emphasizing only the most striking differences.

Fig. 10. Selected BSE images and electron microprobe traverses of minerals in 'Recent' eruptions (1840 and 1955-57). (a) Composite plagioclase with normally zoned rim and patchy zoned core, and melt inclusion zone in the middle. (b) Normally zoned anhedral olivine phenocryst coated with Opx corona. (c) Normally zoned Opx with Al_2O_3 zoning indicating abrupt compositional changes of melt. (d) Reversely zoned euhedral Opx phenocrysts, with more mafic overgrown rims. (e) Composite Cpx with alternating evolved (with apatite inclusions) and more mafic zones. (f) Amphibole crystal with breakdown corona of different grain size.

Fig. 11. Histograms of An content of plagioclase phenocrysts. Unimodal distributions in the mafic units (>45 kyr and 10 kyr, respectively) show gradually decreasing maxima at An_{87-90} and An_{85-87} . Note that the high-An maxima also occurs in the 4 kyr and 1.2 kyr units, but the overall distribution is strongly bimodal, which reflects the presence of multiple magmas and mingling. In the 1 kyr unit the high-An maxima is also present indicating the dominance of primitive magma. Note that the 1kyr unit consists of petrologically two different units (see main text) The 'recent' eruptions also shows a bimodal distribution, but the mafic maxima has shifted to a lower An of 75 reflects multiple magmas.

Euhedral Plagioclase is the most abundant phenocryst, it exhibits a wide range of composition (An_{45-94}), and zoning patterns (oscillatory, reverse, and normal) (Fig. 10.a, Table 2) and occurs in two main crystal sizes (500-1200 μm and >1800 μm). Low-An Plag ($An_{<65}$) is compositionally and texturally rather homogenous, contains various mineral (Cpx, Opx, Ol) and glass inclusions similar to those in 4 kyr and 1.2 kyr units. Plag microlites are also abundant, compositionally similar to the low-An phenocrysts.

Accessory olivine (For_{70-75}) phenocryst is resorbed and anhedral, and rimmed by Opx and/or occurs in glomerocrysts together with Plag, Opx, Cpx, and oxides (Fig. 10.b, Table 3). Ol in the 1955-57 samples is virtually homogenous (For_{72-73}). Olivine shows disequilibrium textures and indicates magma mixing (e.g. Coombs & Gardner, 2004).

Fig. 12. Histograms of Mg# values in mafic minerals (Cpx, Opx, Amph) unit by unit. Note the similar maxima of Cpx between >45 kyr unit and 1 kyr low-silica basaltic andesites sample (transparent bars), as well as the high-Mg# opx maxima among 10 kyr, 4 kyr, 1.2 kyr, and 1 kyr units. Amphibole maxima also show similar values among >45 kyr, 4 kyr, and 1.2 kyr.

Euhedral clinopyroxene ($\text{En}_{37-46}\text{Fs}_{13-21}\text{Wo}_{38-45}$) is the most abundant mafic mineral, occurs in two population sizes like Plag (Fig. 10.e, Table 4). Cpx displays broad compositional variation in major elements (e.g. $\text{Mg\#} = 62-77$, $\text{Al}_2\text{O}_3 = 0.8-4.1$ wt%, $\text{CaO} = 18.4-21.5$ wt%) (Table 4). Phenocrysts exhibit sector, oscillatory, normal and reverse zoning, commonly within the same crystal, suggesting disequilibrium crystallization and open-system processes. Cpx microlites are virtually absent in both samples. Anhedral, rounded Cpx inclusions occur commonly in

plagioclase.

Orthopyroxene ($\text{En}_{56-73}\text{Fs}_{25-41}\text{Wo}_{2-4}$) also occurs in two populations (large phenocrysts and microphenocrysts), and appears in all habits from euhedral to anhedral, and occasionally resorbed (Figs. 10.c&d). Resorbed Opx is sometimes mantled by Cpx.

Fig. 13. Selected major element distribution of pyroxene and amphibole phenocrysts. (a) & (b) are of Cpx, (c) & (d) are of Opx, and (e) & (f) are of Amph. Multiple analyses were done within individual crystals. Cpx compositions overlap and indicate a common source for the high-Mg# mafic Cpx. Whereas Opx compositions show three distinct groups: 1) <65, 2) 67-71, and 3) >73; the CaO and Al₂O₃ distributions are apparently independent of Mg#, and no overall trend can be observed. There are two distinct trends in Amph dataset, where CaO and Al₂O₃ increases with increasing Mg#, and the other where CaO and Al₂O₃ is constant/decreases with increasing Mg#. These trends may be interpreted related to plagioclase crystallization (see text).

Opx displays large compositional variations ($\text{Mg\#} = 57\text{-}74$, $\text{Al}_2\text{O}_3 = 0.5\text{-}1.9$ wt%), (Figs. 11&12, Table 5), commonly within a single crystal. Opx phenocrysts have complex zoning, but usually have a thin (about 50 μm) Mg-rich rim and an even thinner (<10 μm) Mg-poor zone (Figs. 10.c&d). Opx microphenocrysts show sector, reverse and normal zoning (last two commonly occur within a grain) and mostly euhedral. Opx is not found as microlite in the groundmass, but often occur included in Plag.

Amphibole is rare in the lava dome samples (1840), and is not present in the volcanic bomb samples (1955-57). Subhedral, resorbed amphibole (pargasite and tschermakite) is surrounded by reaction-rims and occurs as fragmental microphenocrysts indicating disequilibrium with surrounding liquid (Fig. 10.f). Amph composition ($\text{Mg\#} = 65\text{-}73$, $\text{Al}_2\text{O}_3 = 11\text{-}12$ wt%, $\text{CaO} = \text{about } 11$ wt%) is similar to those in older units (Fig. 12&14; Table 6). Individual amphibole grains show restricted chemical variation. Neither zoning nor any kind of inclusion is observed in the Amph grains.

FeTi-oxides microphenocrysts (<120 μm) occur in groundmass, and most abundantly included in Opx and Cpx phenocrysts. FeTi-oxides of the lava dome samples are exclusively magnetite, whereas those in the volcanic bomb samples are magnetite and ilmenite (Table 7).

Plag, and pyroxenes exhibit a wide range of compositional intracrystalline variation and textural features that are indicative for open-system processes (e.g. Streck, 2008). Plag, Cpx, and Opx often display composite grains (oscillatory, alternating reverse and normal zoning patterns in multiple cycles) also suggesting chaotic mixing processing and/or multiple magma recharges (e.g. Humphreys *et al.*, 2006).

5. TRACE ELEMENT GEOCHEMISTRY OF MINERALS

The previous textural and mineralogical description sets the background for interpretation on magmatic processes of the bulk-rock compositions and general evolution

of Gede. However, information of major elements in minerals does not necessarily lead to unique interpretations because different values of the thermodynamic variables and magmatic environment may lead to the same compositions. To better understand and fingerprint the magmatic processes in this section we describe the trace element compositions of the main minerals in the context of what we have already described above. We first address intracrystalline variations in different units to gain insights into the processes and later we compare trace element and ratios between units to better fingerprint changes in magma sources and crystal recycling.

5.1. Plagioclase

This mineral shows a large inter- and intracrystalline compositional and textural variation in most units (Fig. 11; Table 2). Trace and minor elements in plagioclase, in addition, reveal more detail on geochemical variation (e.g. $K_2O = 0.01-0.5$ wt %; $Ba = 10-160$ ppm, $Sr = 390-720$ ppm, $Pb = 0.8-7$ ppm; Table 2) and thus different magmatic processes. In general, high-An Plag exhibits lower incompatible element (e.g. K, Ba, Pb) concentrations (e.g. those of >45 kyr and 10 kyr units) than lower An Plag (e.g. the 4 kyr and 1.2 kyr units; Fig. 14) forming roughly linear relationships between An and some incompatible elements (e.g. K, Ba). This likely reflects an increase of incompatible elements in the liquid and perhaps an increase of the plagioclase/liquid partition coefficient (K_d) depending on temperature. In detail, at high An content between 75 and 90, the Ba content changes less than between 50 and 65 ppm, with a change in slope at about An_{70} . It is thus not clear if trace element content of the low-An plagioclase can be derived from differentiation of the magmas that grew the high-An crystals.

Comparison of plagioclase compositions from the different units does not show clear differences, with most data showing similar ranges. This could also partly be due to the impossibility of obtaining inclusion-free analyses of the 4 kyr and the 1.2 kyr plagioclase;

Fig. 14. Distribution of minor and trace elements in plagioclase. (a) Ba, (b) Pb, and (c) Sr versus anorthite (An); (d) Ba versus Sr; and (e) An versus An/K₂O. A permanent kink in between the low-An and high-An trends can be inferred at about An₇₀ shown on the Ba (a) and Pb (b) dataset. This may be due to a difference in source magma composition, or rather in crystal structure (i.e. low-, and high-plagioclase; Deer *et al*, 1992; R. Dohmen and J. Blundy, pers. comm.). Sr, however, shows no correlation with An, which probably due to the larger change of K_d. (d) Ba-Sr diagram shows that the 4 kyr and 1.2kyr (low-An) plagioclase is of a more evolved liquid than the rest. (e) An/K₂O ratio in plagioclase shows two different trends that do not overlap. MELTS models with >45 kyr starting composition do not yield high An (>70) plagioclase at high pressure (>6 kbar) runs, likely because under such pressure considerable amount of garnet crystallizes according to the MELTS model, and thus and Al/Si of liquid is not favorable for high-An plagioclase crystallization (i.e. Panjasawatwong *et al.*, 1995). Symbols are as in Figure 13.

because we almost completely lack trace element data from An-rich Plag from these units the low anorthite compositions are over-represented. This also means that >45 kyr and 10 kyr Plag cannot be compared to younger ones. However, An/K₂O ratios show two different trends when plotted against An (Fig. 14.e). The >45 kyr plagioclase contains higher An/K₂O ratio (and thus lower K₂O content) at a given An content than 4 kyr and 1.2 kyr plagioclase. This can be explained either by mixing between the silicic and calcic end-member forming magmas shown by the black line (Fig. 14.e) or different crystallization conditions (i.e. Pressure, H₂O content in the melt) (e.g. Panjasawatwong *et al.*, 1995; Prouteau & Scaillet, 2003). Closed-system fractionation modeling (MELTS; Ghiorso & Sack, 1995) revealed that the more potassic Plag at given An content cannot indeed be due to solely the differing depth of crystallization, a change in melt composition is required (Fig. 14.e).

5.2. Amphibole

Although amphibole crystals tend to show limited inter- and intracrystalline major element compositional variation, they have large ranges of trace elements concentrations, (e.g. Cr = 28-1149 ppm, Ni = 40-120 ppm, Zr = 9-35 ppm). The largest intracrystalline variation is found in >45 kyr crystals that show the most homogenous major element distribution, but strongly normally zoned in Cr and Ni and (Fig. 15, Table 6). This probably records the co-crystallization of Cr- and Ni-rich minerals like Cr-spinel and olivine. In reversely zoned crystals of the 4 kyr and 1.2 kyr units both Cr and Ni follow the major element trend: higher Cr and Ni content usually goes with higher Mg# likely reflecting the arrival of more primitive magma at a late stage (the crystal rims record this; Fig. 15). Other trace elements (e.g. Sr, Zr, Ba) show smaller variations. The Zr/Y values of amphibole of the >45 kyr unit and those of the 4 and 1.2 kyr mafic rims virtually show no overlap (Fig. 15.c). However, the Al/Si molar values of amphiboles of the >45 kyr unit

Fig. 15. Distribution of trace elements in amphibole. (a) Ba, (b) Cr, and (c) Zr/Y versus Mg#. The >45 kyr amphiboles are different from the 4 kyr and 1.2 kyr ones by having lower Ba and higher Cr concentration at given Mg#. Zr/Y shows two different groups of amphibole, but these are not separated by zoning relations (core-rim). Some Holocene amphibole cores (*filled symbols*) fall in the >45 kyr group. (d) On the Ni-Cr plot, the >45 kyr amphiboles are separated from the younger ones, implying the presence of both Ni- and Cr-rich phases (e.g. olivine and Cr-spinel, respectively) in >45 kyr magma. (e) Cr-Ba diagram also shows the two groups with >45 kyr amphibole contains less Ba at a given Cr content. Cr rapid decreases in both groups with slight or moderate increase in Ba, suggesting Cr-rich phase co-crystallization. (f) Molar Al/Si versus Cr plot shows that 4 kyr and 1.2 kyr amphibole cores (*filled symbols*) represent a more evolved liquid with lower Al/Si ratio and Cr than the rims and the >45 kyr ones. Also, the rims overlap with the >45 kyr compositions. Symbols are as in Figure 13.

overlaps with the crystal rims of the younger units (Fig. 15.f). This indicates that the mafic magmas of the >45 kyr unit are similar to the intrusions of mafic melt that occurred later on during the Holocene history of Gede and amphibole rims crystallized from.

Although trace element trends of Amph are similar among the units, the dataset shows two groups: the >45 kyr Apmh shows in general lower Ba concentrations for the

same Mg#, probably reflecting a slightly different magma source (e.g. more primitive) than the younger amphiboles. Also for a given Mg#, the amphiboles from the >45 kyr unit have higher Cr contents, lower Ni, and thus a higher Cr/Ni values than the younger amphiboles (Fig. 15). This could be explained by the delayed crystallization of Cr-spinel and thus more reducing conditions in the >45 kyr unit magmas compared to the younger ones.

5.3. Pyroxenes

5.3.1. Clinopyroxenes

Clinopyroxenes also exhibit a large inter- and intracrystalline compositional variation in trace elements (e.g. Cr = 1.1-785 ppm, Zr = 3.2-63 ppm, Ni = 5.1-88 ppm) (Table 4). Rims of reversely zoned crystals show more primitive origin (e.g. higher compatible and lower incompatible trace elements) and resemble to >45 kyr Cpx, whereas cores reflect an evolved liquid source as they are richer in incompatible elements (e.g. Zr). Difficulties emerge when comparing certain compatible trace elements: Cpx of a certain unit may corresponds to a group, regarding a certain trace element abundance, but overlaps with another unit's Cpx concerning another trace element. For instance, the 1 kyr low-silica basaltic andesite Cpx groups together with >45 kyr Cpx in terms of Ni abundance, (Fig. 16.b), however, it falls together with Cpx of the 4 kyr unit in terms of Cr concentration (Fig. 16.a). Moreover, on the Cr-Ni or Zr-Ni plots, Cpx appears to cluster in three groups, but the three classes do not have the same members (Figs. 16. d&e). For the sector-zoned crystals, we find that sectors with the higher Al content have higher concentration of highly charged incompatible trace elements like Zr^{4+} , Hf^{4+} than the low-Al sector. Other incompatible elements with smaller charges (e.g. Rb^{+}) are less affected. There is much less of an effect for compatible elements like Cr^{3+} and Ni^{2+} , partially because their

Fig. 16. Distribution of trace elements in clinopyroxene. (a) Cr, (b) Ni, and (c) Zr versus Mg#. Cr and Ni in the >45 kyr and 4 kyr Cpx rims (*open symbols*) exhibit positive correlation with Mg#, whereas Cpx in other units tend to correlate negatively. Zr correlates negatively with Mg#, most importantly defines one single continuous array suggesting direct relation between core and rims and the same magmatic evolution for all the units. (d) Cr-Ni diagram confirms that the >45 kyr and 4 kyr rims group together, the 4 kyr cores (*filled symbols*), the 1.2 kyr cores, the 10 kyr, and the 1 kyr basaltic andesites form an other group, the 1 kyr low-silica basaltic andesites represent an individual high-Cr and low-Ni group, and the 1.2 kyr Cpx show high-Ni with low-Cr concentration group (see main text). (e) Ni versus Zr show three definitive groups: >45 kyr and 1 kyr low-silica basaltic andesite Cpx, 1.2 kyr Cpx cores, and the rest of the dataset, (f) Zr versus Y shows the genetic relationship within and between units by defining one monotonous array. Note the low-Zr and low-Y 4 kyr rims having a slightly higher Zr at a given Y concentration. The excess Zr probably originates from the molten Cpx cores.

behavior also is controlled by the crystallization of other minerals (i.e. Cr-spinel and olivine, respectively).

On the other hand, incompatible elements (e.g. Zr, Y) plotted against a compatible general indicator of magma evolution (e.g. Mg#), or against each other, convincingly

show that the entire dataset follows one differentiation trend (Figs. 16.c&f). It suggests that the liquids, from which the Cpx crystallized, experienced slightly different evolution in terms of early crystallization of a Ni-rich and a Cr-rich phase. Based on these observations a crystallization sequence can be inferred involving first crystallization of a Ni-rich phase (olivine), followed by Cr-rich phase (Cr-spinel), while Cpx might also have co-crystallized from the liquid. Assuming the same parent magma source, thus, it seems the >45 kyr unit Cpx formation was preceded by extensive formation of both olivine and spinel, whereas crystallization of the Cpx rims from the 4 kyr unit occurred before extensive olivine and spinel formation. The high Ni and low Cr concentration of the 1.2 kyr unit Cpx suggests it was formed after spinel, but before major olivine precipitation. The 1 kyr low-silica basaltic andesite liquid, which Cpx formed from, however, seems to have experienced early olivine crystallization, but not affected by the onset of an extensive Cr-spinel formation. The Cpx in 1 kyr basaltic andesites is depleted in both Ni and Cr, and richer in Zr, hence, indicating a more evolved parent liquid, similarly to 10 kyr Cpx. The relative orders of crystallization of olivine, Cr-spinel and clinopyroxene probably reflect the variable amounts of water abundance in the melt and oxygen fugacity of the magmas from Gede volcano. These are discussed later on in the context of phase equilibria experiments from the literature.

5.3.2. Orthopyroxenes

Orthopyroxenes have also a broad variety of intra- and intercrystalline trace element concentrations (e.g. Cr = 2-216 ppm, Ni = 8-210 ppm, Zr = 1.2-54.3 ppm) (Table 5). As in the case of Cpx, the trace element abundances in the rims of Opx have more primitive characteristics than those of the cores (Fig. 17). The Opx composition – depending on trace elements of choice – splits into two (e.g. Ni-Cr) or three different groups (e.g. Ni-Zr) (Fig. 17). On the Ni-Zr diagram Opx rims of 1 kyr & 10 kyr units form a mutual group,

the 1.2 kyr cores group separately, and the 4 kyr Opx cores form another distinguished scatter. On the Ni-Cr plot, however, the 1 kyr, the 4 kyr, & the 10 kyr Opx align together and the 1.2 kyr ones plot separately (Fig. 17). The two apparent groups are probably reflecting sample bias; there is a gap in the dataset for crystals $66 < \text{Mg\#} < 71$. Likewise Cpx, Opx of 1.2 kyr unit show the largest Ni and Zr concentration. Pyroxenes of 1 kyr and 10 kyr cluster together independently what trace element is considered.

Fig. 17. Distribution of trace elements in orthopyroxene. (a) Cr, (b) Ni, and (c) Zr versus Mg#. Samples with $\text{Mg\#} > 70$ are the rims on reversely zoned Opx. Cr and Zr plots define two groups, whereas Ni shows three different groups; the rims group together independently of choice of trace elements. (d) Ni versus Cr plot shows that cores (*filled symbols*) and rims (*open symbols*) in all units are petrogenetically related, except for 1.2 kyr. (e) Zr-Ni plot also three different groups (c.f. Ni-Mg#). (f) Zr-Y diagram shows positive correlation between Zr and Y suggesting that Opx of the different units are related.

Table 8. Whole rock compositions (anhydrous, normalized)

wt%	>45 ky					10 ky		
	Ayam-1	Ayam-2	Ayam-3	Ayam-5	G130	Gek-1	Cig-2	Cig-3
SiO ₂	51.36	51.15	51.32	51.75	53.65	55.01	55.06	56.37
TiO ₂	1.04	1.04	1.01	1.03	0.80	0.89	0.74	0.70
Al ₂ O ₃	19.64	19.41	20.09	19.74	22.96	18.93	21.45	21.37
FeO*	9.21	9.33	9.18	8.89	6.65	7.92	6.24	5.67
MnO	0.174	0.180	0.176	0.177	0.135	0.160	0.135	0.127
MgO	4.73	4.81	4.28	4.54	2.38	3.78	2.55	2.17
CaO	10.00	10.31	10.15	10.01	8.95	8.93	9.23	8.67
Na ₂ O	2.93	2.84	2.89	2.92	3.28	3.09	3.18	3.31
K ₂ O	0.77	0.78	0.74	0.75	1.01	1.12	1.23	1.43
P ₂ O ₅	0.160	0.158	0.156	0.190	0.177	0.173	0.174	0.192
Total**	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
initial total	100.16	100.06	99.70	99.35	97.98	100.27	99.71	100.14
LOI	-0.26	0.05	0.56	0.25	1.96	-0.19	0.41	0.49
<i>ppm</i>								
Rb	23.6	26.1	24.2	25.2	36.6	40.3	46.1	54.2
Cs		1.88	1.82	2.02	3.40	1.73	3.28	3.95
Sr	330	327	343	350	370	318	373	361
Ba	128	140	136	148	269	219	259	290
Sc	31.5	31.5	25.6	24.2	16.9	25.1	16.1	14.1
V	279	269	253	253	145	219	138	117
Cr	7.10	10.9	8.42	11.7	4.17	9.91	1.66	2.02
Ni	8.10	6.74	6.20	6.81	5.92	5.27	2.45	2.95
Zn	82.3	81.7	81.4	86.3	73.4	76.9	69.8	67.8
Y	20.4	20.6	20.4	23.2	30.9	22.7	22.2	24.3
Zr	66.9	67.8	63.7	71.6	117	94.9	104	121
Nb	2.87	2.68	2.72	3.37	4.23	3.47	4.14	4.38
Ta		0.15	0.34	0.40	0.28	0.20	0.42	0.53
Hf		1.84	1.88	2.09	3.03	2.48	2.89	3.31
Pb	6.2	6.7	5.5	7.4	9.6	8.8	11.8	12.8
Th	4.10	2.65	2.43	2.73	5.77	4.21	4.85	5.80
U	<2	0.59	0.60	0.65	1.15	0.94	1.12	1.33
La	8.9	8.3	8.0	10.0	18.9	12.0	14.0	16.5
Ce	19.6	19.5	19.1	22.3	34.0	27.0	30.2	34.9
Pr		2.7	2.6	3.1	4.5	3.5	3.9	4.5
Nd	9.1	12.2	12.0	14.2	19.5	15.2	16.4	18.5
Sm		3.4	3.3	3.8	4.9	3.9	4.0	4.5
Eu		1.09	1.09	1.23	1.36	1.19	1.20	1.29
Gd		3.6	3.4	3.9	4.8	3.9	3.9	4.3
Tb		0.61	0.60	0.67	0.78	0.66	0.65	0.71
Dy		3.7	3.6	4.0	4.7	4.0	3.9	4.3
Ho		0.77	0.74	0.83	0.95	0.81	0.79	0.86
Er		2.2	2.2	2.4	2.9	2.4	2.4	2.6
Tm		0.32	0.31	0.34	0.40	0.35	0.34	0.37
Yb		2.0	2.0	2.2	2.6	2.2	2.2	2.4
Lu		0.30	0.29	0.33	0.38	0.34	0.34	0.37
<i>Modes (vol%; phenocrysts >0.3 mm; vesicle-free)</i>								
Plagioclase		18.1		19.7		30.5	32.5	32.85
Plagioclase [§]		15.0		21		7.9	9	5.5
Olivine		2.7		4.7		0.1	0.1	0.15
Clinopyroxene		6.7		5.35		5.1	1.3	1.05
Orthopyroxene		tr.		<0.1		4.5	1.5	1.35
Amphibole		2.3		1.1		-	-	-
FeTi-oxide		2.2		1.45		2.3	1.5	0.45
Glass		53.0		46.7		49.6	54.1	59.1

* total iron is given as Fe²⁺

** total is normalized to 100 wt% on anhydrous basis

§ microlites

Table 8. continued

	10 ky			4 ky				
wt%	Cip-1	Cip-5	Cip-6	Cip-2	Cip-3B	Cip-4	Cip-4A	Cip-4B
SiO ₂	56.08	55.67	55.78	56.29	60.01	59.77	57.35	57.58
TiO ₂	0.86	0.80	0.79	0.83	0.70	0.72	0.81	0.80
Al ₂ O ₃	18.60	20.28	20.48	18.40	17.93	17.91	18.32	18.12
FeO*	7.67	6.86	6.86	7.44	6.22	6.34	7.02	7.07
MnO	0.164	0.150	0.151	0.153	0.138	0.138	0.148	0.149
MgO	3.87	3.10	3.06	4.01	3.07	3.11	3.67	3.68
CaO	8.14	8.54	8.19	8.31	6.90	7.03	7.95	7.87
Na ₂ O	3.07	3.19	3.22	3.01	3.16	3.12	3.08	3.06
K ₂ O	1.38	1.22	1.26	1.41	1.72	1.72	1.50	1.53
P ₂ O ₅	0.183	0.195	0.198	0.151	0.145	0.152	0.151	0.148
Total**	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
initial total	99.72	99.81	98.69	100.04	99.23	98.60	99.72	99.63
LOI	0.11	0.54	0.92	-0.04	1.04	0.92	0.20	0.31
<i>ppm</i>								
Rb	55.4	49.0	49.1	56.2	69.2	69.4	61.1	62.3
Cs	3.74	3.21	3.29	3.64	4.39	4.39	3.93	4.01
Sr	315	345	341	290	285	293	296	292
Ba	253	226	230	269	311	306	276	282
Sc	21.2	17.4	17.0	24.0	18.3	18.4	22.3	22.5
V	158	124	125	192	135	139	175	178
Cr	15.9	12.9	8.79	10.4	17.0	14.5	13.7	13.6
Ni	9.10	5.58	5.74	7.96	6.71	6.95	7.43	7.41
Zn	70.3	63.5	66.2	73.5	65.8	69.6	71.3	73.3
Y	25.0	23.8	24.4	23.4	22.8	23.8	23.9	24.1
Zr	129	119	122	115	134	142	129	126
Nb	3.96	4.02	4.16	3.76	4.62	4.01	4.36	4.35
Ta	0.26	0.20	0.31	0.41	0.30	0.31	0.23	0.32
Hf	3.33	3.05	3.11	3.28	3.56	3.60	3.31	3.54
Pb	10.4	9.4	9.7	11.4	13.2	13.2	12.0	12.2
Th	6.19	5.39	5.60	5.95	7.82	7.86	7.00	6.68
U	1.34	1.17	1.20	1.36	1.65	1.65	1.46	1.50
La	14.7	13.0	13.5	14.4	16.8	16.9	15.2	15.2
Ce	32.5	29.8	31.0	30.7	36.4	36.8	33.5	33.0
Pr	4.2	3.9	4.0	3.9	4.4	4.5	4.2	4.2
Nd	18.0	16.8	17.4	16.3	18.0	18.5	17.5	17.4
Sm	4.5	4.2	4.3	4.1	4.3	4.4	4.3	4.3
Eu	1.22	1.24	1.24	1.13	1.10	1.12	1.15	1.13
Gd	4.5	4.2	4.3	4.1	4.0	4.2	4.3	4.2
Tb	0.75	0.71	0.72	0.69	0.69	0.70	0.72	0.71
Dy	4.4	4.2	4.3	4.2	4.0	4.2	4.3	4.3
Ho	0.90	0.86	0.86	0.84	0.80	0.83	0.87	0.86
Er	2.6	2.5	2.6	2.5	2.4	2.5	2.5	2.6
Tm	0.39	0.37	0.37	0.36	0.35	0.36	0.38	0.37
Yb	2.4	2.3	2.4	2.3	2.2	2.3	2.3	2.4
Lu	0.38	0.36	0.37	0.35	0.35	0.36	0.36	0.36
<i>Modes (vol%; phenocrysts >0.3 mm; vesicle-free)</i>								
Plag	19.8							
Plag [§]	12.4							
Olivine	<0.1							
Cpx	4.6							
Opx	2.65							
Amph	-							
FeTi-oxide 1								
Glass	59.55							

Table 8. continued

	4 ky							
wt%	Cip-8	G3D	G3L	Cip-11	Cip-13	Cip-14	Cip-15	CPN-7
SiO ₂	59.84	55.69	60.39	54.44	56.83	59.63	58.94	58.58
TiO ₂	0.72	0.91	0.72	0.88	0.81	0.72	0.74	0.76
Al ₂ O ₃	17.75	18.65	17.60	18.85	18.21	17.91	17.95	17.89
FeO*	6.34	7.24	6.06	7.92	7.32	6.26	6.58	6.86
MnO	0.139	0.143	0.129	0.159	0.154	0.139	0.146	0.144
MgO	3.08	4.02	3.00	4.53	3.91	3.06	3.31	3.46
CaO	6.97	8.76	6.92	9.02	8.15	7.16	7.35	7.45
Na ₂ O	3.20	3.03	3.11	2.84	3.01	3.23	3.19	3.06
K ₂ O	1.80	1.42	1.96	1.23	1.46	1.74	1.64	1.64
P ₂ O ₅	0.160	0.146	0.121	0.142	0.147	0.157	0.154	0.152
Total**	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
initial total	99.21	98.89	98.34	99.86	99.81	99.12	99.54	98.09
LOI	0.79	0.60	1.40	0.24	0.24	0.61	0.55	1.14
<i>ppm</i>								
Rb	71.7		72.3	48.9	58.4	68.1	66.4	65.8
Cs	4.62		4.82	3.22	3.76	4.44	4.29	3.96
Sr	282		284	291	290	289	299	289
Ba	316		333	232	270	306	310	290
Sc	18.5		18.4	27.6	24.2	18.2	20.2	22.4
V	140		148	222	191	136	152	170
Cr	14.86		9.69	15.4	14.5	12.4	13.5	12.2
Ni	6.79		5.19	9.18	8.12	6.42	7.30	7.93
Zn	67.6		68.7	74.4	73.1	66.6	71.4	67.8
Y	24.6		22.9	23.0	24.0	23.7	23.8	24.2
Zr	149		148	103	124	143	137	129
Nb	4.66		4.94	3.66	3.88	4.67	4.20	3.98
Ta	0.24		0.26	0.31	0.35	0.20	0.31	0.28
Hf	3.81		3.87	2.91	3.31	3.60	3.61	3.47
Pb	13.3		14.2	10.1	11.5	12.9	13.4	6.3
Th	8.01		8.05	5.15	6.26	7.70	8.17	15.1
U	1.71		1.92	1.17	1.38	1.64	1.59	1.63
La	17.3		17.9	12.7	14.6	16.8	17.4	16.2
Ce	37.6		36.8	27.5	32.1	36.4	36.6	33.8
Pr	4.6		4.5	3.5	4.1	4.5	4.5	4.2
Nd	19.1		18.0	15.1	16.8	18.4	18.4	17.7
Sm	4.5		4.3	3.9	4.2	4.4	4.5	4.4
Eu	1.12		1.06	1.11	1.13	1.12	1.13	1.12
Gd	4.4		4.0	4.0	4.2	4.2	4.3	4.2
Tb	0.73		0.68	0.68	0.72	0.71	0.71	0.72
Dy	4.3		4.1	4.0	4.2	4.2	4.2	4.2
Ho	0.86		0.83	0.82	0.87	0.85	0.85	0.87
Er	2.6		2.4	2.5	2.6	2.5	2.5	2.6
Tm	0.38		0.36	0.35	0.38	0.36	0.37	0.37
Yb	2.4		2.3	2.2	2.3	2.3	2.3	2.5
Lu	0.37		0.36	0.34	0.36	0.36	0.36	0.35
<i>Modes (vol%; phenocrysts >0.3 mm; vesicle-free)</i>								
Plag							22.7	
Plag ^s							6.1	
Olivine							0.5	
Cpx							3.1	
Opx							4.2	
Amph							-	
FeTi-oxide							1.8	
Glass							61.6	

Table 8. continued

wt%	4 ky					1.2 ky		
	CPN-8A	CPN-8B	CPN-9	CPN-10A	CPN-10B	Pata-1	Pata-2	Pata-3
SiO ₂	55.46	60.32	55.28	55.35	58.33	56.14	59.11	55.46
TiO ₂	0.85	0.69	0.87	0.85	0.74	0.85	0.77	0.84
Al ₂ O ₃	18.17	17.41	18.07	18.33	17.77	18.69	17.77	19.43
FeO*	7.93	6.32	7.78	7.84	6.83	7.55	6.73	7.26
MnO	0.158	0.137	0.162	0.158	0.146	0.159	0.126	0.131
MgO	4.44	2.97	4.67	4.38	3.56	3.90	3.52	3.79
CaO	8.57	6.83	8.79	8.71	7.67	8.18	6.81	8.57
Na ₂ O	2.85	3.32	2.84	2.87	3.13	3.01	3.29	3.04
K ₂ O	1.41	1.85	1.39	1.37	1.68	1.34	1.71	1.33
P ₂ O ₅	0.154	0.158	0.151	0.151	0.154	0.181	0.165	0.141
Total**	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
initial total	99.07	98.99	99.03	99.67	98.32	100.00	98.38	99.42
LOI						0.05	1.21	0.38
<i>ppm</i>								
Rb	57.2	77.5	57.1	55.9	68.4	54.2	60.6	51.9
Cs	3.66	4.76	3.61	3.48	4.19	2.86	1.62	2.22
Sr	289	297	288	291	295	324	257	300
Ba	254	328	249	245	292	248	283	246
Sc	27.4	17.5	29.4	27.1	21.4	21.4	18.4	23.9
V	210	135	219	212	162	164	148	194
Cr	14.9	11.8	14.9	12.4	13.2	17.0	9.14	8.03
Ni	8.43	7.66	8.49	8.43	8.04	9.21	6.20	8.08
Zn	76.0	68.1	74.7	74.0	69.7	85.4	83.1	73.8
Y	24.6	25.1	24.5	24.0	24.2	25.0	27.7	23.3
Zr	117	145	113	113	129	128	144	116
Nb	3.68	4.44	3.61	3.59	4.01	4.33	4.03	3.85
Ta	0.25	0.32	0.24	0.24	0.28	0.16	0.32	0.32
Hf	3.10	3.83	2.99	3.02	3.43	3.41	3.70	3.12
Pb	5.3	7.5	5.0	5.0	6.3	8.7	9.1	9.7
Th	12.7	15.7	12.2	12.2	12.8	5.99	7.00	5.81
U	1.43	1.90	1.37	1.37	1.65	1.37	1.54	1.30
La	14.1	18.4	13.8	13.6	16.3	14.8	17.0	12.8
Ce	30.3	37.8	29.8	29.4	34.0	32.4	37.8	28.8
Pr	3.9	4.7	3.8	3.8	4.3	4.2	4.8	3.7
Nd	16.3	19.4	16.1	16.2	17.7	18.0	20.6	15.7
Sm	4.3	4.6	4.3	4.2	4.5	4.5	5.0	4.0
Eu	1.10	1.13	1.11	1.11	1.10	1.25	1.25	1.16
Gd	4.3	4.5	4.2	4.2	4.2	4.5	5.0	4.0
Tb	0.73	0.74	0.72	0.71	0.72	0.74	0.83	0.69
Dy	4.5	4.4	4.4	4.2	4.4	4.5	5.0	4.1
Ho	0.88	0.88	0.87	0.86	0.86	0.90	1.01	0.83
Er	2.7	2.6	2.6	2.5	2.6	2.7	3.0	2.5
Tm	0.38	0.37	0.37	0.37	0.37	0.39	0.45	0.36
Yb	2.4	2.4	2.4	2.4	2.4	2.4	2.8	2.3
Lu	0.36	0.35	0.35	0.35	0.36	0.38	0.44	0.35
<i>Modes (vol%; phenocrysts >0.3 mm; vesicle-free)</i>								
Plag	10.5	27.6			21.6	20.75		
Plag [§]	20.4	13.7			5.9	15.4		
Olivine	0.5	0.6			<0.1	<0.1		
Cpx	1.6	3.0			2.9	3.35		
Opx	3.5	5.4			3.3	3.25		
Amph	2.5	-			-	-		
FeTi-oxide	0.5	2.2			1.7	1.4		
Glass	60.4	47.4			64.25	55.85		

Table 8. continued

	1.2 ky							
wt%	Pata-4	Pata-5	Pata-6	Pata-7	SPata-1 [†]	Tega-1	Tega-2	GB1
SiO ₂	54.61	55.19	59.97	69.09	54.85	55.02	55.56	61.61
TiO ₂	0.92	0.89	0.72	0.41	0.86	0.91	0.79	0.65
Al ₂ O ₃	18.86	18.64	17.68	15.78	19.43	18.79	20.37	17.15
FeO*	7.57	7.84	6.11	3.15	7.61	7.43	6.80	5.67
MnO	0.148	0.159	0.131	0.080	0.156	0.147	0.148	0.124
MgO	4.41	4.31	3.09	1.13	3.84	4.31	3.15	2.68
CaO	9.15	8.70	7.13	3.77	8.83	8.93	8.60	6.40
Na ₂ O	2.88	2.90	3.11	3.56	2.95	2.98	3.17	3.31
K ₂ O	1.32	1.23	1.91	2.94	1.32	1.35	1.22	2.26
P ₂ O ₅	0.140	0.146	0.138	0.100	0.148	0.140	0.187	0.147
Total**	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
initial total	99.70	99.35	99.30	96.95	99.52	99.73	100.02	99.11
LOI	0.38	0.31	0.75	2.69	0.16	0.13	0.29	
<i>ppm</i>								
Rb	43.9	23.6	75.7	106.8	53.0	49.5	46.5	92.0
Cs	2.99		4.71	6.95	1.82	3.09	2.61	5.67
Sr	315	330	289	225	303	314	356	288
Ba	232	128	340	486	243	245	235	375
Sc	28.6	28.8	20.3	8.2	24.7	31.7	18.1	16.4
V	248	236	155	47	197	238	133	131
Cr	18.3	18.0	11.6	17.0	8.47	3.61	15.3	8.27
Ni	8.37	10.90	6.95	8.66	6.08	7.54	6.23	7.19
Zn	72.1	78.9	66.5	49.1	70.8	71.8	65.3	61.2
Y	21.1	24.2	23.5	20.7	23.4	21.1	23.8	25.9
Zr	103	111	143	164	113	105	119	160
Nb	3.39	3.50	3.60	3.83	3.91	3.69	4.16	4.62
Ta	0.47		0.23	2.82	0.17	0.16	0.33	0.37
Hf	2.82		3.78	4.47	2.93	2.72	3.14	4.23
Pb	10.3	7.7	13.7	18.6	8.6	9.8	8.6	8.8
Th	5.32	5.50	8.55	11.7	5.94	5.88	5.27	18.2
U	1.17	<2	1.87	2.81	1.29	1.18	1.15	2.18
La	12.5	12.4	17.6	22.9	13.5	13.7	13.3	20.7
Ce	27.7	27.9	37.6	44.6	30.1	29.1	29.5	41.9
Pr	3.6		4.6	5.2	3.8	3.6	4.0	5.2
Nd	15.1	12.6	18.5	19.3	16.3	15.3	17.1	21.0
Sm	3.8		4.4	4.1	4.1	3.8	4.4	4.9
Eu	1.07		1.08	0.90	1.12	1.07	1.26	1.11
Gd	3.8		4.1	3.6	4.1	3.8	4.3	4.7
Tb	0.64		0.70	0.61	0.70	0.63	0.72	0.77
Dy	3.8		4.1	3.5	4.2	3.8	4.3	4.6
Ho	0.77		0.83	0.70	0.84	0.75	0.85	0.92
Er	2.3		2.5	2.2	2.5	2.3	2.5	2.7
Tm	0.32		0.36	0.32	0.36	0.32	0.37	0.39
Yb	2.1		2.3	2.1	2.3	2.0	2.3	2.6
Lu	0.31		0.36	0.33	0.34	0.31	0.36	0.39
<i>Modes (vol%; phenocrysts >0.3 mm; vesicle-free)</i>								
Plag	13.6	19.2						
Plag ^s	9.4	20.5						
Olivine	0.35	0.6						
Cpx	5.2	3.1						
Opx	2.2	2.0						
Amph	-	1.0						
FeTi-oxide	0.6	1.0						
Glass	68.65	52.6						

Table 8. continued

wt%	1.2 ky						1 ky	
	GB2	GP1	PanPF2	PanPF2/2	GPF8	GPF10	SMT-1	SMT-2
SiO ₂	52.41	60.64	65.26	66.60	54.59	53.91	55.42	57.65
TiO ₂	0.91	0.72	0.60	0.52	0.83	0.89	0.91	0.76
Al ₂ O ₃	19.66	17.00	17.29	16.17	19.24	18.96	19.67	17.77
FeO*	8.21	6.16	4.89	4.16	7.52	7.73	7.06	6.99
MnO	0.167	0.133	0.100	0.098	0.163	0.160	0.155	0.147
MgO	4.98	3.08	1.44	1.50	4.03	4.50	4.14	3.69
CaO	10.04	6.79	4.03	4.27	9.16	9.48	8.44	8.05
Na ₂ O	2.59	3.23	3.59	3.72	3.19	3.11	3.01	3.16
K ₂ O	0.89	2.10	2.66	2.85	1.11	1.09	1.06	1.63
P ₂ O ₅	0.143	0.147	0.150	0.135	0.166	0.159	0.152	0.145
Total**	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
initial total	99.17	99.22	94.87	96.80	99.99	99.81	96.02	99.39
LOI	0.53	0.90	4.74	2.59	0.29	0.24	3.38	
<i>ppm</i>								
Rb	30.8	83.1	100.3	112.2	37.3	36.1	36.0	63.3
Cs	2.09	5.05	6.03	6.72	2.27	2.20	2.30	3.73
Sr	329	281	232	242	358	349	331	310
Ba	174	352	416	454	208	199	199	293
Sc	32.3	20.3	12.1	9.8	25.1	31.8	29.3	22.6
V	257	163	83	72	225	254	232	189
Cr	8.27	10.4	7.90	8.39	9.84	12.3	7.29	8.04
Ni	7.46	6.96	6.57	7.24	6.84	7.46	7.10	7.37
Zn	78.9	67.5	50.5	51.6	82.7	79.7	66.6	73.7
Y	17.7	24.5	22.5	21.9	17.6	17.6	16.4	21.0
Zr	76.1	144	170	166	93.2	89.7	88.4	119
Nb	2.93	4.36	5.07	4.94	3.30	3.23	3.20	3.82
Ta	0.17	0.33	0.43	0.45	0.19	0.20	0.19	0.26
Hf	1.94	3.89	4.53	4.45	2.27	2.26	2.31	3.10
Pb	2.1	7.8	11.1	18.5	2.9	2.7	3.0	5.9
Th	8.06	15.9	22.2	13.2	10.0	8.93	9.51	13.2
U	0.75	1.98	2.59	2.64	0.87	0.83	0.89	1.57
La	9.9	19.4	22.4	23.8	12.2	11.7	10.8	15.4
Ce	21.7	39.2	43.9	45.7	26.2	25.1	22.9	31.7
Pr	2.8	4.8	5.2	5.4	3.3	3.1	2.9	3.9
Nd	12.0	19.5	20.2	20.6	13.8	13.4	11.7	16.4
Sm	3.1	4.6	4.5	4.6	3.2	3.2	2.9	3.9
Eu	1.00	1.06	0.98	0.95	1.04	1.02	0.97	1.04
Gd	3.2	4.3	3.9	3.9	3.1	3.2	2.8	3.7
Tb	0.54	0.72	0.66	0.62	0.52	0.53	0.47	0.62
Dy	3.2	4.3	3.8	3.7	3.0	3.0	2.8	3.6
Ho	0.67	0.86	0.80	0.76	0.63	0.62	0.60	0.75
Er	1.9	2.7	2.3	2.3	1.9	1.9	1.8	2.2
Tm	0.28	0.37	0.35	0.33	0.27	0.28	0.28	0.33
Yb	1.6	2.4	2.2	2.2	1.7	1.6	1.7	2.1
Lu	0.28	0.37	0.34	0.33	0.26	0.26	0.28	0.31
<i>Modes (vol%; phenocrysts >0.3 mm; vesicle-free)</i>								
Plag								
Plag ^s								
Olivine								
Cpx								
Opx								
Amph								
FeTi-oxide								
Glass								

Table 8. continued

wt%	1 ky							
	SMT-3	SMT-4A	SMT-4B	SMT-5A	SMT-5B	SMT-7A	SMT-7B	SMT-12
SiO ₂	52.60	55.46	55.76	52.20	52.09	52.03	54.17	58.62
TiO ₂	0.89	0.78	0.79	0.91	0.91	0.91	0.80	0.76
Al ₂ O ₃	19.34	20.00	19.91	19.52	19.50	19.49	18.92	17.56
FeO*	8.24	7.07	7.05	8.36	8.45	8.43	7.95	6.91
MnO	0.165	0.149	0.147	0.168	0.167	0.167	0.174	0.145
MgO	4.88	3.15	3.14	4.99	4.99	4.98	4.43	3.40
CaO	10.09	8.67	8.47	10.11	10.14	10.21	9.35	7.46
Na ₂ O	2.72	3.28	3.24	2.71	2.73	2.74	3.13	3.23
K ₂ O	0.92	1.25	1.30	0.89	0.89	0.88	0.91	1.75
P ₂ O ₅	0.142	0.186	0.188	0.142	0.142	0.142	0.165	0.155
Total**	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
initial total	100.03	99.01	99.60	99.28	99.93	99.91	99.59	99.53
LOI					0.28			
<i>ppm</i>								
Rb	32.4	48.3	49.8	30.7	30.6	30.9	30.3	67.3
Cs	2.08	1.51	1.32	1.97	2.06	2.01	1.94	4.17
Sr	342	355	351	333	339	338	359	314
Ba	179	229	232	172	174	172	182	307
Sc	31.9	17.2	16.9	33.1	33.2	32.5	25.8	20.8
V	253	126	130	256	258	253	211	167
Cr	8.70	10.8	10.1	8.11	8.11	8.78	8.04	8.18
Ni	7.72	7.60	7.78	8.01	7.45	7.84	7.90	7.07
Zn	79.1	62.4	65.1	86.1	81.7	81.0	86.3	70.4
Y	17.6	25.0	31.3	17.4	17.5	17.4	17.2	22.5
Zr	76.8	119	121	75.1	75.3	75.1	83.3	127
Nb	2.97	3.81	3.83	2.91	2.98	2.92	2.99	4.17
Ta	0.17	0.24	0.24	0.17	0.17	0.17	0.17	0.30
Hf	1.95	3.12	3.21	1.95	1.93	1.89	2.11	3.36
Pb	2.4	4.5	4.5	2.1	2.1	2.1	2.2	6.1
Th	8.66	8.71	8.70	8.68	9.29	8.23	8.38	12.1
U	0.80	1.28	1.33	0.71	0.74	0.74	0.72	1.61
La	9.9	12.9	16.5	9.8	9.9	9.8	10.9	17.2
Ce	21.7	29.2	37.2	21.6	21.9	21.7	23.8	35.3
Pr	2.7	3.9	5.0	2.7	2.8	2.8	3.0	4.4
Nd	11.9	17.0	22.1	11.7	11.7	11.8	12.7	17.9
Sm	3.0	4.4	5.6	3.0	3.0	3.1	3.2	4.4
Eu	0.98	1.23	1.37	0.99	1.01	1.00	1.05	1.10
Gd	3.1	4.4	5.6	3.1	3.1	3.1	3.0	4.1
Tb	0.51	0.70	0.94	0.52	0.52	0.52	0.50	0.66
Dy	3.0	4.4	5.7	2.9	2.9	3.0	2.9	3.9
Ho	0.64	0.89	1.11	0.65	0.67	0.65	0.59	0.81
Er	1.9	2.6	3.3	1.8	1.9	1.8	1.8	2.3
Tm	0.28	0.38	0.45	0.27	0.27	0.27	0.27	0.34
Yb	1.6	2.4	2.9	1.6	1.6	1.6	1.7	2.2
Lu	0.25	0.35	0.41	0.26	0.27	0.26	0.26	0.33
<i>Modes (vol%; phenocrysts >0.3 mm; vesicle-free)</i>								
Plag								
Plag ^s								
Olivine								
Cpx								
Opx								
Amph								
FeTi-oxide								
Glass								

Table 8. continued

	1 ky	1840?	1955-57?		
wt%	G134	G385	G385/2	G384	ALUN
SiO ₂	61.05	58.64	59.92	60.74	58.37
TiO ₂	0.68	0.76	0.69	0.67	0.75
Al ₂ O ₃	17.13	17.53	17.21	17.22	17.51
FeO*	6.17	6.94	6.38	6.06	7.02
MnO	0.134	0.144	0.139	0.126	0.145
MgO	2.73	3.37	3.13	2.90	3.47
CaO	6.61	7.49	7.08	6.78	7.65
Na ₂ O	3.34	3.22	3.41	3.22	3.18
K ₂ O	1.98	1.75	1.88	2.15	1.74
P ₂ O ₅	0.167	0.156	0.150	0.146	0.151
Total**	100.00	100.00	100.00	100.00	100.00
initial total	99.15	100.48	99.94	99.34	99.43
LOI	0.52	-0.10	-0.10	0.70	-0.12
<i>ppm</i>					
Rb	76.0	68.0	71.1	87.0	66.6
Cs	1.80	4.07	4.32	5.45	3.99
Sr	283	312	294	287	311
Ba	339	307	329	358	304
Sc	15.8	20.8	19.0	18.5	21.3
V	132	167	156	133	170
Cr	9.13	7.87	8.61	7.65	7.28
Ni	6.54	6.80	6.57	6.71	6.51
Zn	76.1	72.0	68.7	65.1	69.7
Y	29.0	22.7	22.0	25.1	22.1
Zr	161	130	136	152	127
Nb	4.67	4.19	4.11	4.52	4.10
Ta	0.37	0.31	0.31	0.35	0.31
Hf	4.33	3.42	3.57	4.12	3.35
Pb	13.5	11.0	12.3	14.6	11.7
Th	8.94	7.78	8.09	10.0	7.62
U	1.84	1.62	1.70	2.06	1.58
La	21.4	17.2	17.5	20.0	16.9
Ce	45.9	35.2	35.7	40.5	34.7
Pr	5.8	4.4	4.3	5.0	4.3
Nd	24.5	18.2	17.7	20.4	17.8
Sm	6.0	4.4	4.3	4.8	4.2
Eu	1.27	1.10	1.06	1.08	1.06
Gd	5.6	4.0	3.9	4.5	3.9
Tb	0.87	0.65	0.64	0.73	0.66
Dy	5.3	4.0	3.7	4.4	3.8
Ho	1.02	0.80	0.77	0.89	0.79
Er	3.1	2.3	2.3	2.7	2.3
Tm	0.43	0.34	0.34	0.38	0.34
Yb	2.8	2.2	2.1	2.4	2.1
Lu	0.40	0.33	0.32	0.35	0.32
<i>Modes (vol%; phenocrysts >0.3 mm; vesicle-free)</i>					
Plag					
Plag ^s					
Olivine					
Cpx					
Opx					
Amph					
FeTi-oxide					
Glass					

6. WHOLE ROCK AND GLASS GEOCHEMISTRY: MAJOR, MINOR, AND TRACE ELEMENTS

Major and trace element compositions of whole-rock samples (Table 8) are all medium-K and fall in both the calc-alkaline and the tholeiitic series (Fig. 18). They span from basalts to rhyodacite. As we have shown in the previous petrological description, many samples show evidence for open-system processes involving mafic and evolved magmas, or interactions between crystal-rich systems and new magma arrival. Overall, the units show linear arrays of incompatible elements in Harker diagrams that reflect both magma differentiation and mingling between mafic and felsic magmas (e.g. Si, Rb, Zr, Ba; Figs. 19 & 20). Compatible elements like Sr, Cr show more complex or scattered distribution that reflect differentiation, magma mixing, and also differential entrainment of crystals with high concentrations of compatible elements. Other elements like Y are more difficult to understand because they might be compatible in some compositions but not in others (e.g. Y in apatite and amphibole). Below we describe the whole rock trends of the different units and point out the first order processes that might be responsible for their compositions. For analyses, fresh and visibly non-weathered samples were selected to avoid weathering caused aleatory chemical alteration.

6.1. >45 kyr unit

The deposits from >45 kyr unit are mostly high-silica and high-alumina basalts ($\text{SiO}_2 = 51.4 \pm 0.2$ wt%; $\text{Al}_2\text{O}_3 = 19.4\text{--}20.1$ wt%; $\text{MgO} = 4.3\text{--}4.8$ wt%) (Fig. 18; Table 8), and are the most primitive compositions we have sampled. A low-MgO basaltic andesite sample (G130) also occurs and forms a linear trend in major and trace elements with the primitive ones (Fig. 18.a,b,c,e). CaO (not shown), FeO, and especially MgO contents strongly decrease with small increases in SiO_2 . Al_2O_3 , in contrast, increases with increasing SiO_2 . Incompatible trace elements (e.g. Zr and Ba) increase moderately with

Fig. 18. Variation of selected major elements of Gede whole rock, glass, and melt inclusion. Analyses are normalized on a 100 % anhydrous basis. Nomenclature adopted from Rollinson (1993). Solid black lines denote the low-, medium-, and high-K domains on the K_2O - SiO_2 diagram (from bottom to top) following Le Maitre *et al.* (1989). Dashed black line marks calc-alkaline and tholeiitic series (from bottom to top) on FeO^*/MgO versus SiO_2 .

minor increase of SiO_2 or Rb; compatible elements such as Ni and Cr (6-8 and 4-12 ppm, respectively; Table 8) are much lower than those of primitive basalts from subduction zones (e.g., 75-150 ppm, 200-400 ppm respectively; Winter, 2001). Trace element

compositions and incompatible element ratios of the high-silica basalts show a limited variation, however, with the low-MgO basaltic andesite sample (G130) form a well-defined trend (Figs. 19 & 20). Trace element ratios also show that Zr/Y and Ba/Y increase with increasing Rb, and K/Rb ratio decreases (Fig. 20). Sr/Y ratio, however, decreases with increasing Rb, despite the increasing values of both Sr and Y. The basaltic samples of this unit are very similar in both their major and trace element compositions to Pangrango basalts (Handley *et al.*, 2010).

6.2. 10 kyr unit

Samples of this unit are evolved basaltic andesite with a narrow range of SiO₂ (55.6 ± 0.6 wt%), but wide range in MgO (2.2–3.9 wt%) and Al₂O₃ (18.6–21.5 wt%) (Fig. 18; Table 8). The 10 kyr unit samples form a steep linear trend shown in the MgO or Al₂O₃ vs. SiO₂ diagram, i.e. with small change of SiO₂ (scatter is not higher than analytical error) large change of MgO and alumina occurs. Sr (320–370 ppm) concentrations are among the highest of all Gede samples (Fig. 19.e & f). This observation along with high Al₂O₃ and abundant plagioclase phenocrysts (20–33 vol%) could be interpreted as plagioclase accumulation (e.g. Vukadinovic, 1993). However, this is not the case because the results of mass balance calculation of addition of calcic plagioclase, and the lack of a positive Eu anomaly both support that the high-Al is the result of differentiation (see Chapter 2). Ni (not shown) shows the lowest values in all Gede samples implying extensive olivine fractionation. Incompatible elements (e.g. Rb, Ba, or Zr) show a rather restricted variation and fit in the middle of the linear trend defined by all Gede samples (Fig. 19). Likewise, Trace element ratios (e.g. K/Rb or Zr/Y) also show limited variation and they fit to the overall Gede trend (Fig. 20).

Fig. 19. Variation of selected trace elements of Gede whole rock. Symbols are as in Figure 18.

6.3. 4 kyr unit

The 4 kyr unit contains macroscopic evidence (e.g. banded scoria) for mingling between two compositionally different magmas (Figs. 3.c-f). We physically separated the mafic and felsic bands from samples where possible and performed individual bulk-rock analysis of each band (Table 8).

The MgO, FeO, Al₂O₃, and CaO (not shown) contents decrease with increasing silica and form collinear trends plotted against SiO₂ (Fig. 18). This decrease is much more gentle than in previous units. Sample CPN8A is basaltic andesite (SiO₂ = 55.5 wt%, MgO = 4.4 wt%, Rb = 57 ppm, Sr = 289 ppm, Zr = 117 ppm) and CPN8B is andesite (SiO₂ = 60.3 wt%, MgO = 3 wt%, Rb = 77 ppm, Sr = 297 ppm, Zr = 145 ppm); they are the most

mafic and felsic compositions of this unit, and were found in one banded scoria specimen (Figs. 3 & 18; Table 8). Incompatible elements (e.g. Ba, Rb, Y) increase with silica and form a linear trend that overlaps with other units (Fig. 19). However, Sr concentrations exhibit a horizontal trend plotted against SiO₂, (Fig. 19.e) which is different from other units and may imply the contribution of individual plagioclase crystals rather than only magma mingling (e.g. Eichelberger *et al.*, 2006). On plots of trace element ratios versus Rb (i.e. Sr/Y, Zr/Y, or K/Rb) the 4 kyr trend is virtually indistinguishable from 1.2kyr unit, but shows different evolution from the >45 kyr unit (Fig. 20). The only difference is that only one of the 1.2 kyr samples falls in the 4 kyr Rb range (about 50-75) (Fig. 20).

Given that even the mafic and silicic end-member bands show petrologic evidence (composite zoning patterns of minerals and disequilibrium mineral assemblage) of open-system processes, it is likely that their compositions are modified and the true end-member magmas were more mafic and silicic than what we have analyzed. The rims on Cpx and Opx xenocrysts are more primitive than in any of the other units, it most likely shows that the mafic end-member was more Mg-rich and Ca-rich than the analyzed magmas.

6.4. 1.2 kyr unit

This unit shows the largest compositional range, mostly from basaltic andesite to andesite but includes a rhyodacite (SiO₂ = 54.6 – 69.1 wt%, Al₂O₃ = 20.4 – 15.8 wt%, MgO = 4.4 – 1.1 wt%) (Fig. 18; Table 8). Samples define linear trends in many elements that overlap with both the 4 kyr, and the 10 kyr units (Fig. 18), and thus they may be recording similar processes to those units (e.g., mingling between felsic and mafic magmas, and selective incorporation of pyroxenes, respectively). Some incompatible

Fig. 20. Variation of selected trace element ratios of Gede whole rock. Symbols are as in Figure 18.

element concentrations (e.g. Rb, Ba) of the rhyodacite are one end of the linear array, but other elements like Zr need a more evolved end-member that underwent fractionation of zircon. Y shows a rather scattered distribution, and in general shows a better overlap with the 10 kyr samples (Fig. 19.d). Sr distribution also indicates a relationship with 10 kyr samples and not with the 4 kyr ones, however, the lowest Sr content in the basaltic andesites are very close to the 4 kyr samples. Trace element ratios (Zr/Y or Ba/Y) also overlap with both the 10 kyr and the 4 kyr values, and are not diagnostic in separating the different evolutionary paths (Fig. 20). Sr/Y ratio, however, divides the 1.2 kyr basaltic andesitic samples into two groups, so that some of them are like the 10 kyr samples, others fit to the 4 kyr samples (Fig. 20.c).

6.5. 1 kyr unit

The bulk-rock compositions range from low-silica basaltic andesite to low-silica andesite ($\text{SiO}_2 = 52.1\text{-}58.6 \text{ wt\%}$; $\text{Al}_2\text{O}_3 = 17.6\text{-}20 \text{ wt\%}$; $\text{MgO} = 3.2\text{-}5 \text{ wt\%}$) they overlap

with previously described units (Fig. 18). Major elements in general overlap with the 4 kyr trends, except for a couple of samples (Fig. 18). MgO, FeO, CaO, and Al₂O₃ decrease with increasing silica, whereas Na₂O and K₂O increase. A group of low-silica basaltic andesites overlaps with the >45 kyr unit and they also have similar mineral assemblage and textures.

Most incompatible trace elements (Rb, Ba, and Zr) overlap with the other units, Y (and heavy rare earth elements – see Chapter 2), however, show much lower concentrations for a given Rb (or SiO₂) content (Figs. 19.e), which may indicate a different melting source or early crystallization of Y-rich phase. Moreover, Sr defines an array similar to the >45 kyr unit, but with a gentler slope pointing towards the high-aluminium, high-Sr basaltic andesite composition (Fig. 19). Trace element ratios (e.g. Sr/Y or Ba/Y) indicates geochemical evolution similar to the >45 kyr units (Fig. 20). Such trace element trends are probably due to delayed plagioclase fractionation (c.f. >45 kyr unit), and a complex mixing history among the magmas differentiated along different paths.

6.6. The ‘recent’ eruptions

Lava dome and bread-crust bomb samples of the latest eruptions are andesites (SiO₂ = 58.4-60.8 wt%, Al₂O₃ = 17.2-17.5 wt%, and MgO = 2.90-3.47 wt%) (Fig. 18; Table 8). They overlap with the 4 kyr unit trend; MgO, FeO, Al₂O₃, and CaO decrease with increasing SiO₂. Trace elements show a limited compositional range; incompatible trace elements (e.g. Rb, Ba, and Zr) certainly increase with growing silica similarly to other units. Y, however, is slightly lower at a given silica concentration than the 4 kyr unit (Fig. 19).

Table 9. Compositions of matrix glass and melt inclusions (corrected for PEC)(normalized, anhydrous)

host unit (age)	matrix glass 4 kyr	Cip-7_gl_1	Cip-7_gl_2	Cip-7_gl_3	Cip-7_gl_4	Cip-7_gl_5	Cip-7_gl_6	Cip-7_gl_7	Cip-7_gl_8	Cip-7_gl_9	Cip-7_s_gl*
wt%											
SiO2	72.14	72.07	72.52	71.64	71.62	72.00	72.05	72.07	72.65	72.08	
TiO2	0.71	0.69	0.66	0.71	0.69	0.70	0.76	0.70	0.69	0.70	
Al2O3	12.97	13.12	12.97	12.97	13.30	12.96	12.74	13.24	12.82	13.01	
FeO	3.51	3.56	3.47	3.78	3.78	3.79	3.98	3.59	3.55	3.67	
MnO	0.08	0.08	0.08	0.11	0.06	0.07	0.08	0.06	0.07	0.08	
MgO	0.65	0.60	0.64	0.70	0.66	0.65	0.61	0.65	0.61	0.64	
CaO	2.38	2.58	2.15	2.37	2.36	2.28	2.25	2.24	2.17	2.31	
Na2O	2.72	2.74	2.73	2.88	2.95	2.68	2.69	2.70	2.62	2.75	
K2O	4.52	4.28	4.49	4.49	4.25	4.53	4.51	4.44	4.48	4.44	
P2O5	0.16	0.11	0.13	0.14	0.16	0.14	0.12	0.13	0.13	0.14	
total***	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	
initial total	97.10	96.96	97.92	97.74	97.84	98.21	98.68	98.17	98.02		
Teq (°C)											
PEC (wt%)											
Fo/An in eq											

Ol = olivine, Opx = orthopyroxene, Plag = plagioclase, Teq = equilibrium temperature, PEC = post entrapment crystallization, H2O = water content of melt

Teq, PEC is estimated using Petrolog3; for Ol and Plag Danyushevsky (2001), for Opx Ariskin et al. (1993) models were used

* average of Cip-7 glass analyses collected from silicic band (gl_1-gl_9)

** average of Cip-3 glass analyses collected from silicic band (gl_1-gl_13)

*** normalized to 100 wt%, anhydrous

Table 9. continued

host unit (age)	matrix glass 4 kyr									
wt%	Cip-3_gl_1	Cip-3_gl_2	Cip-3_gl_3	Cip-3_gl_4	Cip-3_gl_5	Cip-3_gl_6	Cip-3_gl_7	Cip-3_gl_8	Cip-3_gl_9	Cip-3_gl_10
SiO2	71.27	70.65	71.06	73.62	74.24	73.84	69.35	71.26	71.85	74.36
TiO2	0.88	0.88	0.93	0.64	0.61	0.66	1.10	0.85	0.88	0.60
Al2O3	13.38	13.20	13.35	12.96	12.43	12.88	13.61	13.34	13.44	12.85
FeO	4.23	4.51	4.42	3.41	2.59	3.22	4.98	3.75	3.87	2.64
MnO	0.12	0.12	0.12	0.09	0.05	0.07	0.11	0.12	0.09	0.08
MgO	0.93	1.34	0.65	0.70	0.47	0.49	0.72	0.65	0.68	0.51
CaO	2.58	2.66	2.60	2.28	1.98	2.01	2.93	2.50	2.58	1.86
Na2O	2.06	2.00	2.15	1.68	2.52	1.81	2.29	2.56	1.92	2.34
K2O	4.14	4.22	4.31	4.37	4.85	4.78	4.45	4.57	4.30	4.53
P2O5	0.23	0.24	0.25	0.08	0.06	0.09	0.27	0.23	0.21	0.08
total***	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
initial total	96.54	96.90	97.12	93.01	94.15	96.53	97.00	96.97	95.24	96.34
Teq (°C)										
PEC (wt%)										
Fo/An in eq										

Table 9. continued

host	matrix glass	Ol									
unit (age)	4 kyr	>45 kyr									
wt%	Cip-3_gl_11	Cip-3_gl_12	Cip-3_gl_13	Cip-3_gl**	A2OLm1_gl	A2OLm4_gl	C5OLm11_gl	C5OLm12_gl	C5OLm13_gl		
SiO2	73.61	73.50	73.81	72.49	66.41	57.68	59.56	64.01	59.02		
TiO2	0.61	0.62	0.62	0.76	1.50	0.80	0.63	2.28	2.24		
Al2O3	12.86	13.06	12.57	13.07	17.03	20.93	21.65	14.65	18.61		
FeO	2.91	2.91	2.79	3.56	3.28	4.60	3.74	3.84	4.26		
MnO	0.07	0.05	0.07	0.09	0.07	0.07	0.05	0.07	0.06		
MgO	0.55	0.54	0.52	0.67	1.26	2.08	1.75	1.69	1.54		
CaO	2.07	2.03	1.97	2.31	3.81	7.93	7.34	6.86	6.06		
Na2O	2.53	2.47	2.65	2.23	4.02	4.73	4.17	3.86	5.04		
K2O	4.54	4.58	4.77	4.49	1.77	0.95	0.91	1.99	2.81		
P2O5	0.09	0.06	0.07	0.15	0.84	0.23	0.19	0.74	0.36		
total***	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00		
initial total	96.50	96.90	97.18		97.19	99.57	96.10	96.14	100.55		
Teq (°C)					954	897	875	895	910		
PEC (wt%)					1.2	4.4	3.4	1.6	1.7		
Fo/An in eq					72.2	73.6	73.4	72.7	71.8		

Table 9. continued

host unit (age)	Opx		Plag									
	Ol	4 kyr	>45 kyr									
			C3Ol_g1	C3Ol4_g1_1	C3Ol4_g1_2	C3Ol4_g1_3	C3Ol4_g1_4	A2Pa_g11	A2Pa_g12	A2Pa_g13	C3Pa_g1_3	C3Pa_g1_4
wt%												
SiO2	57.12		69.88	70.97	70.78	70.88	54.91	56.42	52.89	74.33	73.34	
TiO2	1.06		0.51	0.47	0.47	0.68	0.78	0.86	0.72	0.73	0.88	
Al2O3	19.09		13.88	13.69	13.77	13.84	21.25	20.51	21.44	13.25	13.25	
FeO	5.89		4.48	4.15	4.41	4.35	6.72	6.29	8.08	2.82	2.97	
MnO	0.14		0.13	0.09	0.06	0.09	0.18	0.18	0.20	0.07	0.07	
MgO	3.56		0.88	0.89	0.87	0.84	2.39	2.47	2.57	0.57	0.52	
CaO	8.40		3.47	2.97	3.37	3.38	9.18	8.41	10.36	2.17	2.17	
Na2O	2.56		2.82	2.4	2.52	2.13	2.46	2.64	2.28	1.71	1.74	
K2O	1.98		3.74	3.92	3.58	3.49	2.13	2.23	1.46	4.22	4.96	
P2O5	0.20		0.16	0.12	0.12	0.27				0.11	0.11	
total***	100.00		99.95	99.67	99.95	99.95	100.00	100.00	100.00	100.00	100.00	
initial total	95.21		96.45	95.72	96.69	96.31	96.80	96.75	96.89	93.64	94.31	
Teq (°C)	965		1020	1025	1016	998	924	937	915	843	834	
PEC (wt%)	7.6		0.3	3.2	1.5	2.8	39.4	37.9	49.1	0.0	0.0	
Fo/An in eq	78.0		63.1	62.9	63.0	63.3	89.0	85.7	90.9	75.1	75.0	

Table 9. continued

host	Plag				
unit (age)	4 kyr				
	C3Pa_gl_5	C3Pb_gl_1	C3Pb_gl_2	C3Pb_gl_3	C3Pb_gl_4
wt%					
SiO2	73.35	70.87	72.14	71.26	70.95
TiO2	0.59	1.12	0.94	1.11	1.10
Al2O3	13.21	14.18	14.29	14.28	14.26
FeO	3.05	3.41	2.81	3.10	3.26
MnO	0.07	0.08	0.06	0.08	0.07
MgO	0.54	0.74	0.56	0.67	0.73
CaO	2.19	2.84	2.63	2.77	2.67
Na2O	2.13	2.10	1.98	2.17	2.17
K2O	4.78	4.33	4.36	4.26	4.45
P2O5	0.07	0.32	0.22	0.30	0.33
total***	100.00	100.00	100.00	100.00	100.00
initial total	95.25	94.19	94.49	94.54	94.45
Teq (°C)	839	852	829	844	864
PEC (wt%)	0.0	0.0	0.0	0.0	0.0
Fo/An in eq	70.0	73.8	75.7	73.4	73.5

6.7. Matrix glass and melt inclusions and their relation to mineral zonings and whole rocks

We analyzed matrix glasses in the pumiceous textures only, where glass is free of microlites and seems homogenous (judged by uniform greyness of BSE images). MI data was collected from olivines, pyroxenes, and plagioclases, where the inclusion lacked signs of being compromised (e.g. crack passing through them). MIs were corrected for post-entrapment crystallization (PEC) using the Petrolog3 software (Danyushevskiy & Plechov, 2011) and only those with less than 10wt% PEC were considered for discussion. Given the complex open-system processes recorded by the minerals and the bulk-rock dataset, glass and MI data should allow us to gain additional constraints on magmatic processes and volatile contents of crystallizing magmas.

MI in olivine microphenocrysts from the >45 kyr unit exhibit a wide range of silica content (57.7–66.5wt%) with a rather restricted variation in MgO (2.1–1.2 wt%), thus forming a liquid line of descent pointing from a low-Mg basaltic andesite bulk-rock towards the most evolved rhyodacitic whole rock composition (PATA-7) (Fig. 18; Table 9). Plagioclase MIs for this unit are high-alumina basaltic andesite and scatter around the lowest MgO and the highest Al₂O₃ bulk-rock compositions (Fig. 18; Table 9). The composition of pyroxene and plagioclase hosted MIs and matrix glasses of samples from the 4 kyr unit are rhyolitic, more silicic than the rhyodacite bulk-rock (PATA-7) (Fig. 18; Table 9).

The combined record of MI and bulk-rock compositions gives a more detailed picture of the magmatic processes that occurred in Gede. For example, the kink of P contents seen in P₂O₅ vs SiO₂ diagram (Fig. 18) shows that apatite crystallization occurred at about 67 wt% SiO₂. The MI compositions together with the most primitive and evolved rocks at Gede also record the best liquid line of descent to generate the evolved silicic liquids that are involved in mixing/mingling in younger units.

7. GEOTHERMOMETRY, OXYBAROMETRY, AND HYGROMETRY

7.1. Temperature and oxygen fugacity estimates

We employed various geothermo(baro)meters to estimate intensive variables (temperature (T), pressures (P), oxygen fugacity (f_{O_2}) and water content (X_{H_2O})) at which different minerals grew in the different units. It is a complex endeavour because there are many evidences for open-system processes and thus is not easy to unequivocally identify which phases are in equilibrium. Where possible we have used equilibrium based on two minerals, otherwise we have used mineral-melt formulation. For estimation of the melt compositions we used either the melt inclusion or the bulk-rocks and only calculated the intensive variables when their compositions passed the equilibrium test proposed by the authors of the different geothermobarometers. To determine the temperatures from the two-pyroxene model (Lindsley, 1983), we used the QUILF software (Andersen *et al.*, 1993; A93) and the calibration of Putirka (2008; equation 36 = P36, with a standard error of estimate, SEE, of 56°C). We also used the orthopyroxene-liquid and clinopyroxene-liquid empirical thermobarometers of Putirka (2008; equation 28a = P28a, with a SEE of 28°C for orthopyroxene; equation 34 = P34 for clinopyroxene, SEE = 45 °C). Blundy and Cashman (2008) noted that two-pyroxene temperatures obtained using A93 overestimate the temperature by 100-150 °C in particular below 1000 °C. The amphibole geothermobarometer (RR12) calibrated by Ridolfi & Renzulli (2012) and the amphibole-plagioclase thermometer (HB94) by Holland & Blundy (1994) were also used to obtain temperatures where possible. We also applied the revised Fe-Ti two-oxide geothermometer and oxygen-barometer (GE08) by Ghiorso & Evans (2008) using touching ilmenite-magnetite pairs where possible. In order to assess equilibrium in between ilmenite and magnetite we employed the Mg/Mn test (Bacon & Hirschmann, 1988). Finally, we also calculated the apatite and zircon saturation temperatures using the

changes of concentration of P and Zr seen in the bulk-rocks and melt inclusions, and the formulations of Bea *et al.*, (1992) and Watson & Harrison (1983). Harrison *et al.*, (2007) noted that the zircon saturation temperatures might be underestimated.

We also calculated pressure using the empirical amphibole geothermobarometer of Ridolfi & Renzulli (2012). Unfortunately we found very large pressure changes (>300 MPa) within single crystals that alternate between low and high pressures multiple times in very short intervals (50 μm), independently of composition of the amphibole. Such variations seem unrealistic and are difficult to explain. Similar changes were found in Merapi amphiboles (Costa *et al.*, 2013) and were attributed to fast growth or sector zoning. Moreover the reliability of the barometer has been recently questioned (e.g. Erdmann *et al.*, 2014; Kiss *et al.*, 2014; Shane & Smith, 2013). Pressure estimates by Putirka (2008) barometers have a SEE of about 200-400 MPa (about 8-16 km). This variation in pressure estimates for a shallow reservoir is overwhelmingly large. Thus, we decided not to calculate crystallization pressures.

Given the textural complexity of the samples we conducted thermometry on orthopyroxene-clinopyroxene pairs based on their textural relation and trace element abundances. Similarly, the pyroxene-melt pairs were determined through major (i.e. Putirka, 2008) and trace element equilibrium (see below). Evolved pyroxene cores and rims from ortho- and clinopyroxene were used, where possible touching grains were selected to ensure equilibrium. Pyroxene pairs from glomerocrysts were also selected where composition and relation could be clearly assessed (e.g. Fig. 6.d -10 kyr). For amphibole-plagioclase thermometry (Holland & Blundy, 1994) equilibrium was tested by the criteria given therein. Please note that the uncertainties in temperature of the Putirka (2008) geothermometers are about 30-55 $^{\circ}\text{C}$ but are not reported explicitly below.

Fig. 21. Results of thermometric calculations using different models. A93 is the two-pyroxene model by Lindsley (1983); P36 is the two-pyroxene model, P34 is the Cpx-melt model, and P28a is the Opx-melt model by Putirka (2008); RR12 is the single amphibole model by Ridolfi & Renzulli (2012); GE08 is the two-oxide model by Ghiorso & Evans (2008); Zr is zircon saturation temperature by Watson & Harrison (1983); P is the apatite saturation temperature by Bea *et al.* (1992). Where standard error of estimate (SEE) is given there is no error bar associated with individual estimates. The elongated symbols on RR12 reflect the average intracrystalline variation, whereas on GE08 they mark the variation of multiple oxide pairs analyses. Note the large error bar on the 10 kyr and 1 kyr estimates of A93; these probably represent disequilibrium pyroxene pairs. Filled symbols are cores and open symbols are rims.

7.1.1. The >45 kyr unit

The 45 kyr has rare Opx but one small grain attached to a non-sector zoned Cpx gives two-pyroxene temperatures of 1060 ± 15 °C (A93) and 970 °C (P36). Clinopyroxene-melt thermometer P34 ranges from 1155 ± 50 °C with 4 wt% H₂O to 1006 ± 50 °C with 8 wt% H₂O. Amph temperature averages at about 990 ± 45 °C using RR12. Phase equilibria studies reproduce such Ol + pargasitic Amph + Cpx assemblage from a high-

MgO basalt under water-rich conditions and moderate T of 1000-1100 °C at various pressures from 400 MPa to 2 GPa (e.g. Adam & Green, 1994; Adam *et al.*, 2007; Dalpé & Baker, 2000; Melekova *et al.*, 2015). Using MELTS (Ghiorso & Sack, 1995) we calculated the liquidus temperature and water content that matches our geothermometry

results (1000-1050 °C) using the most mafic bulk rock. The best fitting water content and P are 6 ± 2 wt % H₂O and 600 ± 200 MPa, however, the exact observed mineral assemblage has not been reproduced as amphibole has not been generated by any MELTS run. We consider these conditions as the most likely ones at which these HAB were generated.

As is apparent from variation diagrams, the maximum P₂O₅ content that we have measured is 0.84 wt% from MI at 66.6 wt% SiO₂. Using Bea *et al.* (1992) we obtain a temperature for apatite saturation of 910 °C. This is somewhat lower (25-35 °C) than the two-pyroxene equilibria, Cpx-melt and Opx- melt of Putirka (2008) but it agrees with the scenario that these Cpx crystal cores grew from evolved melts.

7.1.2. The 10 kyr unit

The 10 kyr unit evolved orthopyroxene cores appear to have grown at a moderate temperature of 955 to 990 °C depending on water content (3 wt% to anhydrous; this unit does not have Amph), whereas the higher Mg# rims higher T of 1055 to 1090 °C (3 wt% H₂O to anhydrous). Similarly the Cpx cores give a T of 965 to 1000 (3 wt% H₂O to anhydrous), and the rims 1075 to 1115 °C (3 wt% H₂O to anhydrous). Two pyroxene equilibria using Putirka (2008; P36) gives similar estimates for the cores (955 °C), but significantly lower for the rims (990 °C), whereas Andersen *et al.*, (1993; A93) gives similar T for cores to the anhydrous estimates (1015 ± 90 °C), but for the rims it is lower (1050 ± 75 °C) in agreement with the hydrous estimate. The error estimates given by A93 are high indicating that Cpx-Opx were not fully in equilibrium. The estimations of low-T cores are in accord with the presence of apatite and zircon inclusions and on the origin of these crystals from hi-Silica melts, as we discuss below using incompatible trace element concentrations (e.g. Zr contents). The high Ts from the rims of Cpx and Opx vary between 990 to 1115 °C, which are within the values calculated for the high Mg# pyroxenes of the >45 kyr unit. We do not have good barometric estimates for this magma,

but the absence of Amph suggest less than 3 wt% of water in the melts which corresponds to a water-saturated pressure of about 100 MPa as several phase equilibria studies suggest (e.g Costa *et al.*, 2004, and references therein).

7.1.3. The 4 kyr unit

Temperatures for the 4kyr unit are also bimodal. Using the low-Mg# pyroxene core pairs we obtained 945 °C (equation P36) and 1010 ± 20 °C (equation A93), and using the high-Mg# rim pairs we obtained 975 °C (equation P36) and 1055 ± 30 °C (equation A93). Opx-liquid and Cpx- liquid equilibria for the cores using 3 wt% H₂O gives 965-970 °C and the liquid equilibria for the rims gives 1070-1090 °C. The temperature estimates for the evolved cores and rims are consistent with those of the 10 kyr unit. Estimates of T (using RR12) for the 4 kyr Amph are 950 ± 30 °C, there is no significant difference in T between cores and rims although their composition is different and suggest compositionally different magmas and likely grew from different Ts (see below). Assuming that Plag (An₈₀₋₈₈) and mid-Mg# Amph cores are cotectic (see next section), temperature estimates from HB94 are 1035 ± 25 °C (at 400 MPa), which is in between those of the low-Mg# and high-Mg# pyroxenes. We obtained temperatures using the compositions of ilmenite and magnetite included in pyroxene and the calibration of GE08. Oxide pairs from the mafic band yield T of about 1050 °C and f_{O_2} of NNO+0.8 (0.8 log units above the Nickel-Nickel oxide oxygen buffer).

7.1.4. The 1.2 kyr unit

Temperature estimates using two-pyroxenes using the formulation of A93 yielded 1010 ± 10 °C and 1035 ± 30 °C for the 1.2 kyr pyroxene cores and rims, respectively, whereas the formulation of P36 gives lower Ts of 940 °C for the cores and 960 °C for the rims. Core and rim Ts from Opx-liquid (P28b) are 970 ± 5 °C and 1070 ± 5 °C, respectively,

Table 10. Summary of geothermometry and oxybarometry results.

model*	>45 kyr	10 kyr rim	10 kyr core	4 kyr rim	4 kyr core	1.2 kyr rim	1.2 kyr core	1ky LBA	1 kyr BA mafic zone	1 kyr BA evolved zone	recent mafic zone	recent evolved zone
A93 (2pyx) T (°C)	1060±15	1050±75	1015±90	1055±30	1010±20	1035±30	1010±10		1060±150	1100±150	1075±50	925±10
P36 (2pyx) T (°C)	970	990	955	975	945	960	940		975	965	965	895±10
P34 (Cpx-m) T (°C)	1155	1075	965	1090	970	1075	980	1085	1090	970		
P28a (Opx-m) T (°C)		1055	955	1070	965	1070	970		1030	950	1060	950
RR12 (Amph) T (°C)	990±45			950±30		950±45					990±15	
HB94 (Am-Pl) T (°C)												
GE08 (ox) T (°C)			1050	1070		960-995			750±15			940
ANNO			0.83	0.87		0.69±0.35			1.50±0.15			0.43

* model abbreviations are found in the main text

Rim and core in case of GE08 model denote that the source of oxide pairs were mafic and silicic bands, respectively.

hydrous estimate of P34 for the >45 kyr unit is with 4 wt% water.

LBA =low-silica basaltic andesite; BA = basaltic andesite.

with 3 wt% H₂O in the melt, and Cpx-liquid (P34) temperatures are very similar (980 for cores and 1075 °C for rims). Calculations for the 1.2 kyr amphiboles, using RR12, yield T of 950±45 °C, with no significant variation between core and rims. The 1.2 kyr Amph cores paired with high-An Plag (An₈₅₋₉₀) yield temperatures of 1100-1185 °C (at 200 MPa) and with An₆₀ gives 940 °C. The Amph rims and An₈₅ give 970 °C, whereas An₆₅ give 835 °C. The 1.2 kyr cores give T comparable to 4 kyr ones if paired with An₇₇. The 1.2 kyr FeTi-oxides show temperatures of 960-995 °C, and f_{O_2} of NNO+0.34 to NNO+1.04. These Fe-Ti oxide results probably record the mixing /mingling of the two magmas and are in good agreement with the two pyroxene temperatures formulation P36.

7.1.5. The 1 kyr unit

We used the two-pyroxene thermometer of A93 for the 1kyr andesite unit gave temperatures similar to those of 10kyr but the large errors (±150 °C) suggest incomplete equilibrium, and thus we have not used them. However, two-pyroxene formulation of P36 gives lower Ts for the cores and rims, about 970 °C for both. Temperature calculated using Opx-liquid (formulation of P28a) is 950±10 °C for the evolved cores and 1030±10 °C for the rims assuming 3 wt % water in the melt. P34 (clinopyroxene-melt) is the only applicable thermometer for the 1 kyr basaltic samples. It gives T estimates of 1085 °C when melt is considered to have 3 wt% water as this unit does not have Amph.

7.1.6. The 'recent' eruptions

For the two historical eruptions, temperature estimates are 925±10 °C and 895 °C for pyroxene evolved zones, and 1075±50 °C and 965 °C for the mafic zones using the A93 and P36 formulations, respectively. Opx-liquid (P28a) yields T of 950 °C (3 wt% water) for the evolved zones, and 1060±5 °C (3 wt% water) for the mafic zones. Temperature

obtained from amphibole (using RR12) is 980 ± 25 °C. Fe-Ti oxides equilibria give a T of 940 °C and an f_{O_2} of NNO+0.43.

Figure 21 and Table 10 summarize the estimated temperatures obtained from various geothermometers for Gede eruption units. Results calculated by QUILF (Andersen *et al.*, 1993) seem to overestimate T, at least at low crystallization T, as noted by Blundy & Cashman, (2008) and Putirka (2008). There is a large difference between two-pyroxene T estimates of QUILF (Andersen *et al.*, 1993) and Putirka (2008), the former constantly yields higher T by 60-80 °C. Mg# increases at hydrous and possibly more oxidizing conditions (e.g. Freise *et al.*, 2009), thus a thermometer calibrated on anhydrous experiments might overestimate temperatures. The clinopyroxene-melt and the orthopyroxene-melt equilibria models of Putirka (2008) give similar T estimates for both pyroxenes. However, the Opx-Cpx thermometer of Putirka (2008) yields similar Ts for pyroxene-melt of the cores, but significantly lower Ts for the rims (Fig. 21). This may be due to the fact that the cores may reflect equilibrium crystallization, whereas the rims that have commonly sector and oscillatory zoning may have experienced dynamic crystallization due to undercooling (e.g. Putirka, 2008). Our calculated overall T range (about 935-1005 °C) by equation 36 of Putirka (2008) is somewhat lower, but in good agreement with T (962-1046 °C) reported by Handley *et al.* (2010).

Table 11. Water content of plagioclase and pyroxene hosted melt inclusions by micro-reflectance FT-IR.

	4 kyr										
	C15PX1 MI2	C15PX1 MI1	C15PL1 MI1	C15Ca MI1	C3PL2 MI2	C3PL2 MI1	C3PL1 MI1	C3O1 4MI2	C3O1 4MI1	C3C20 MI	C3C4 MI
H ₂ O _{tot}	2.01	2.06	7.84	-	0.62	1.05	1.34	-	-	1.76	1.70
H ₂ O _{mol}	1.20	1.53	5.93							3.59	
host	Cpx	Cpx	Plag	Cpx	Plag	Plag	Plag	Opx	Opx	Cpx	Cpx
Mg#/An	65.9	65.8						63.6	63.7	66.1	65.8

water concentration is given in wt%.
Calculated from H₂O_{tot} = total water; H₂O_{mol} = molecular water.
C15 is the pumiceous andesite, C3 is the banded-scoria.

7.2. Volatiles in melt inclusions

Volatile content (especially water) of an ascending magma is of great importance, as it is one of the main controls on eruption style (e.g. Cashman, 2004; Wilson *et al.*, 1980). Volatile solubility in silicate melts greatly depends on pressure, therefore volatiles trapped in melt inclusions are used to infer the depth of crystallization (e.g. Holloway & Blank, 1994; Moore, 2008). Using the abundance of H₂O and CO₂ it is possible to calculate the pressure where melt inclusion was trapped assuming fluid saturation (e.g. Newman & Lowenstern, 2002). If the concentration of only one volatile species (usually H₂O) is known or estimated, the assumption that the melt was saturated with the fluid produces pressure underestimates. Fluid-saturated conditions may be demonstrated by the presence of bubbles in 4 kyr Plag hosted MIs. As CO₂ degasses early (i.e. at higher pressure) because of its low solubility (e.g. Blank & Brooker, 1994), bubbles in melt inclusions may indicate saturation of CO₂ rather than H₂O (e.g. Wallace, 2005; and references therein).

We only analyzed 12 Cpx and Plag hosted MIs by FT-IR from two samples of the 4 kyr unit. Pyroxenes hosting MIs are rather Fe-rich (Mg# = 63.5 to 66; Table 11) and inferred to be in equilibrium with evolved silicic liquid. Although we do not have e-probe analyses from the host Plag crystals, they are from the felsic bands of the banded scoria, and thus are likely to be low-An plagioclase. The limited number of studied MI partly reflects that there are only a small number of them that look reliable for volatile determination, and are at the same time large enough for the infrared beam. From the 12 MIs, 8 yielded quantifiable FT-IR spectra for their water content (CO₂ was not analyzed because of lack of standards needed in reflected FT-IR). We calculated the water concentration using two different bands, one at about 3600 cm⁻¹ (the so called total water content), and the other at about 1650 cm⁻¹ (the so-called molecular water). We found that the water concentration from the 1650 cm⁻¹ was systematically lower than for the 3600

cm^{-1} , and here we will report the higher water content because this can be better estimated from the spectra (higher signal). It is difficult to estimate the errors on these determinations, because the values depend significantly on how one determines the position of the baselines in the FTIR spectra (i.e. King & Larsen, 2013), but the limited scatter on the calibration lines suggest that errors are 0.5 wt% H_2O or less.

Two MIs from a Cpx crystal gave the same values of 2 wt % H_2O , and two other MI from two different crystals in the same sample also gave very similar concentrations at 1.7 and 1.8 wt % H_2O . Three MIs from two different plagioclase crystals from the same sample gave lower values with 0.6 to 1.3 wt% H_2O . These water contents are in accord with the observation that the host magma did not have amphibole and thus water content of the melt should be less than about 3 wt%. They probably represent a shallow storage level of the crystal-rich cumulate piles. A single MI from another plagioclase crystal gave 7.8 wt% H_2O . It is difficult for us to determine the validity of such water content and further analyses would be necessary to confirm the presence of such high water content.

8. SELECTING PARTITION COEFFICIENTS

Crystal-melt partition coefficients (K_d) of many elements vary depending on intensive variables (T , P , $X_{\text{H}_2\text{O}}$, X_{mineral}) but also with crystal growth rate (e.g. Aigner-Torres *et al.*, 2007; Bindeman *et al.*, 1998; Blundy & Wood, 1991, 1994, and 2003; Lofgren *et al.*, 2006; Mollo *et al.*, 2013; Wood & Blundy, 1997 and 2002). The relative role of these parameters varies from mineral to mineral, and from element to element (e.g. Green *et al.*, 2000; McDade *et al.*, 2003; Wood & Blundy, 1997, 2002). K_d of any given element in the most important minerals (i.e. Plag, Cpx, Amph) can be predicted using by the lattice-strain model (LSM; Blundy & Wood, 1994; Dalpé & Baker, 2000; Wood & Blundy, 1997, 2002), which requires appropriate knowledge of the different parameters (e.g. T , P , water content) in controlling the K_d , thus, predicting K_d values requires

caution. Below we describe the K_d values that we have used for the elements of interest and discuss some of the limitations.

Partition coefficients for olivine in basaltic liquid (e.g. Adam & Green, 2006; Beattie, 1994; Canil, 1999) show that incompatible elements (e.g. Zr and Y) have very low K_d s (0.0007-0.002 and 0.004-0.02, respectively; Adam & Green, 2006; Beattie, 1994). Chromium is compatible in olivine and shows a small variation in K_d of less than an order of magnitude (0.35-1.85; e.g. Adam & Green, 2006; Canil, 1999).

Incompatible trace element (e.g. Zr, Y, and Rb) partition coefficient data for Opx in evolved liquid are limited, and shows a small range of variation. Y is the most compatible (0.2-1.1) followed by Zr (0.033-0.18), and Rb (<0.02) (e.g. Bacon & Druitt, 1988; Ewart & Griffin, 1994; Fujimaki *et al.*, 1984). According to the model of Wood and Blundy (1997), the K_d^Y should match the K_d of heavy rare earth elements (HREE), which is 0.96 for Yb in equilibrium with rhyolite liquid (e.g. Bacon & Druitt, 1988). Therefore, we decided to use the value closest to this (Table A2).

Trace element partitioning in Cpx is sensitive to changes in P, T, water in the magma, the composition of it, and also some minor elements, in particular Al seems to play a key role through substitution (Lofgren *et al.*, 2006; Mollo *et al.*, 2013; Wood & Blundy, 1997). Moreover, Mollo *et al.* (2013) observed that during cooling experiments, Cpx can grow sector-zoned and the K_d increases with increasing cooling rate. The difference in K_d s between different sectors changes with cooling rate. Because sectors grow with different Al contents, a complex relationship arises between the effect of the fast growth during high cooling rate experiments and the Al content of different sectors. Transition metals (e.g. Cr) and high field strength elements (HFSE; e.g. Zr and Hf) are highly sensitive to variation of cooling rate, whereas large ion lithophile elements (LILE; e.g. Rb) are less affected and hardly sensitive (Mollo *et al.*, 2013). Y follows the behavior of HREE. These K_d relationships are reflected in sector zoned Cpx from Gede: high-Al

sectors have more abundant trace element concentration, especially Y and Zr, but transition metals (e.g. Cr) show less variations. Assuming homogenous melt composition around such sector-zoned pyroxene (e.g. Adam & Green, 1994; Lofgren *et al.*, 2006), tracer incorporation must be controlled by different partition coefficients in each sector. Recently available LSM (Wood & Blundy, 1997, 2002) does not account for this kinetic effect, thus applying it is fraught with uncertainties. For comparison, later in the discussion section we show liquid compositions calculated from tracer abundance in both sectors in Cpx. For clinopyroxenes in a basaltic bulk composition we use K_d from Mollo *et al.* (2013), and for evolved Cpx we use values reported in Bacon & Druitt (1988) and Ewart & Griffin (1994).

Amphiboles have a large range of composition and a large stability field (e.g. Leake *et al.*, 1997). Here we focus on tracer partitioning in pargasitic amphibole. Amphibole composition changes with pressure (e.g. Adam & Green, 1994; Adam *et al.*, 2007). With increasing pressure trace elements K_d and Al content (in tetrahedral coordination) decreases. The opposite of this behavior has been observed in some phase equilibria experiments (e.g. Alonso-Perez *et al.*, 2009). Dalpé & Baker (2000) showed that increasing pressure affects K_d^{HFSE} negatively, but K_d^{LILE} positively; and oxygen fugacity has a rather unclear effect on K_d . Adam *et al.* (2007) reported K_d values for Amph-melt equilibrium pairs from experiments where crystallization conditions were similar to those assumed for the >45 kyr basalts of Gede. Amph in younger units (4 kyr and 1.2 kyr), are supposed to have formed at lower pressure, thus we use K_d from Sisson (1994).

Partition coefficients for plagioclase are more abundant and appear to be better understood (e.g. Aigner-Torres *et al.*, 2007; Bindeman *et al.*, 1998; Blundy & Wood, 1991). Trace element K_d in Plag positively correlates with T and negatively with anorthite content. K_d^{Ba} and K_d^{Sr} in Plag were calculated after the model of Blundy & Wood (1991).

In the following paragraphs we discuss magmatic processes underneath Gede using trace element partitioning to assess solid-melt equilibria. Partition coefficients that we have used for modeling are summarized in Table A2.

Fig. 22. Calculated liquid line of descent derived from fractional differentiation models, and result of magma mixing model. Models are explained in detail in main text. Hypothetical magma mixing indicates the silicic end-member is taken as the residual liquid of the two-stage differentiation of >45 kyr unit. Note that in all cases (i.e. Zr/Y , Sr/Y , Ba/Y , and K/Rb) the hypothetical mixing line gives closer results to the hybrid magma (CIP-8A) than the actual mixing line (PATA-7). Zr/Y and Ba/Y ratios are not diagnostic to differentiate between the different trends. Sr/Y and K/Rb , however, clearly shows difference between amphibole-bearing plagioclase-free and plagioclase-bearing fractionation.

9. DISCUSSION OF MAGMATIC PROCESSES: VARIABLE FRACTIONATION, MIXING, AND MINGLING

Gede rock suites show a wide range of major and trace element compositional variations. Major element diagrams (e.g. Fig. 18) show 3 distinct trends that herein we attempt to explain by integration of bulk-rock-mineral mass-balance, plus mixing and fractional crystallization modeling, together with the detailed zoning of major and trace elements in minerals. We do not have information on isotope compositions, but according to the work of Handley *et al.* (2010) Gede magmas share a very similar melt source and have been negligibly contaminated by continental crustal materials. On the other hand, a recent publication of Handley *et al.* (2014) discusses in detail the possibility of assimilation of crustal material or oceanic sediment revealed by Pb isotopes.

We first focus on the processes and source of the mafic magmas that are more abundant in the >45 and 4 kyr units. To understand the magma evolution and processes recorded in the different eruptive episodes it is necessary to have a good estimate of the most likely magma compositions that were involved. We calculated a mafic parent magma (PM) to be close to the >45 kyr and the 4 kyr mafic samples, lying at the low-Si and high-Mg intersection of the >45 kyr and 4 kyr trends (Fig. 22; Table 12). We added about 3.5 wt% of the mafic mineral assemblage of olivine, amphibole, clinopyroxene, and FeTi-oxide to the most mafic bulk composition (Ayam-2) and computed major and trace element compositions of the most probable mafic parent magma (Table 12), as it fits in the mixing trend shown by the Holocene units (Fig. 18). We have used this PM composition in fractional crystallization and mixing models in the following sections. Moreover, we will use the most evolved rhyodacitic bulk-rock from the 1.2 kyr old unit (sample PATA-7) as a proxy for a representative composition of evolved and silicic magmas at Gede volcano.

Table 12. Summary of modeling conditions and results

model	PM (by reverse crystallization)					>45ky stage 1 fractionation					>45ky stage 2 fractionation					4ky fractionation					'mixing-test' (4ky)**																								
sample	Ayam-1					PM					G130					G130					PATATA-7					CIP-8A					PATATA-7					CIP-8					'hybrid'				
wt%	P	C	M.A. (vol%)	P	D	C	R	M.S. (vol%)	P	D	C	R	M.S. (vol%)	P	D	C	R	M.S. (vol%)	P	D	C	R	M.S. (vol%)	H	C	R	M.S. (vol%)	H	C	R	M.S. (vol%)	H	C	R											
SiO ₂	51.36	50.89	Ol (Fo _{91.8})	1.0	50.89	53.65	52.98	0.68	Ol (Fo _{91.8})	4.0	53.65	69.09	69.19	-0.10	Plag (An ₆₀₋₉₀)	60	55.46	69.09	68.26	0.83	Plag (An ₆₀₋₈₀)	33	55.46	55.45	0.01	Plag (An ₆₀₋₈₀)	33	55.46	55.45	0.01	Plag (An ₆₀₋₈₀)	33	55.46	55.45	0.01										
TiO ₂	1.04	1.08	Cpx (Fo _{76.0})	1.3	1.08	0.80	0.88	-0.09	Cpx (Fo _{73.6})	6.4	0.80	0.41	0.43	-0.02	Ol (Fo _{71.2})	5	0.85	0.41	0.47	-0.06	Ol (Fo _{71.3})	3	0.85	0.91	-0.06	Ol (Fo _{71.3})	3	0.85	0.91	-0.06	Ol (Fo _{71.3})	3	0.85	0.91	-0.06										
Al ₂ O ₃	19.64	19.12	Amph (Fo _{76.6})	0.6	19.12	22.96	21.48	1.48	Amph (Fo _{76.6})	2.3	22.96	15.78	15.70	0.08	Ox	5	18.17	15.78	15.12	0.66	Cpx (Fo _{73.6})	5	18.17	18.28	-0.11	Cpx (Fo _{73.6})	5	18.17	18.28	-0.11	Cpx (Fo _{73.6})	5	18.17	18.28	-0.11										
FeO*	9.21	9.70	Ox	0.6	9.70	6.65	7.67	-1.02	Ox	2.2	6.65	3.15	3.17	-0.02	Zircon	tr	7.93	3.15	3.07	0.07	Opx (Fo _{71.9})	6	7.93	8.05	-0.13	Opx (Fo _{71.9})	6	7.93	8.05	-0.13	Opx (Fo _{71.9})	6	7.93	8.05	-0.13										
MnO	0.17	0.18			0.18	0.13	0.16	-0.03			0.13	0.080	0.292	-0.21	Apatite	0	0.16	0.080	0.18	-0.10	Amph (Fo _{71.4})	3	0.16	0.15	0.01	Amph (Fo _{71.4})	3	0.16	0.15	0.01	Amph (Fo _{71.4})	3	0.16	0.15	0.01										
MgO	4.73	5.30			5.30	2.38	2.60	-0.22			2.38	1.13	1.13	0.00		4.44	1.13	1.05	0.08	Apatite	0	4.44	4.25	0.19	Apatite	0	4.44	4.25	0.19	Apatite	0	4.44	4.25	0.19											
CaO	10.00	10.00			10.00	8.95	9.95	-1.00			8.95	3.77	3.58	0.19		8.57	3.77	4.56	-0.79	Ox	5	8.57	8.44	0.13	Ox	5	8.57	8.44	0.13	Ox	5	8.57	8.44	0.13											
Na ₂ O	2.93	2.84			2.84	3.28	3.23	0.05			3.28	3.56	3.43	0.13		2.85	3.56	4.19	-0.63			2.85	3.02	-0.17			2.85	3.02	-0.17			2.85	3.02	-0.17											
K ₂ O	0.77	0.74			0.74	1.01	0.85	0.15	F		14.9	1.01	2.94	0.00	F	70.7	1.41	2.94	2.98	-0.04	F	54.6	1.41	1.29	0.12	F	54.6	1.41	1.29	0.12	F	54.6	1.41	1.29	0.12										
P ₂ O ₅	0.16	0.15			0.15	0.18	0.18	0.00	R ²		2.18	0.18	0.100	0.150	-0.05	R ²	0.34	0.15	0.100	0.07	0.03	R ²	1.47	0.15	0.14	0.01	R ²	1.47	0.15	0.14	0.01	R ²	1.47	0.15	0.14	0.01									
ppm			bulk Kd						bulk Kd							bulk Kd							bulk Kd	R ²	0.36			bulk Kd					bulk Kd												
Rb	23.6	22.8	0.041		22.8	36.6	26.5		0.041		26.5	106.8	102.9		0.027	57.2	107	123.1		0.03		57.2	54.5	2.6			57.2	54.5	2.6			57.2	54.5	2.6											
K	6147	5996	0.297		5996	8359	6687		0.297		6687	24406	20972		0.070	11698	24406	26954		0.13		11698	-	-			11698	-	-			11698	-	-											
Sr	330	323	0.110		323	370	373		0.110		373	225	237		2.050	289	225	268		1.10		289	284	5			289	284	5			289	284	5											
Y	20.4	20.3	0.815		20.3	30.9	21.0		0.815		20.7	20.7	28.9		1.204	24.6	20.7	37.7		0.46		24.6	20.3	4.3			24.6	20.3	4.3			24.6	20.3	4.3											
Zr	66.9	64.8	0.393		64.8	117.4	72.2		0.393		74.5	164.5	183.6		0.709	116.8	164.5	233.7		0.12		116.8	102.5	14.3			116.8	102.5	14.3			116.8	102.5	14.3											

* total iron is given as Fe³⁺

** detailed calculations and method description is given in Appendix 3.

P, parent; D, daughter; C, calculated; M.A., minerals added; M.S., minerals subtracted; F, crystal fraction;

R, residual; R², sum of the square of the residuals; mineral abbreviation as in text.

9.1. Deep and shallow magma differentiation events recorded in the >45 kyr unit

The primitive basaltic magmas (>45 kyr unit; Table 8) appear to have undergone an early fractionation event given their low MgO (<5 wt%), Ni (6-8 ppm), and Cr (7-12 ppm) contents compared to primary mantle melts from subduction zones (i.e. Handley *et al.*, 2010; Winter, 2001) (Table 8). The >45 kyr unit compositions include whole-rock samples and melt inclusions and show two trends that can be attributed to two differentiation stages: the first one from a high-aluminium basalt to a low-MgO basaltic andesites, and the second from this low-MgO basaltic andesite to a rhyodacite, with a prominent kink (Figs. 18.a,b,e,g) between the two apparent in many variation diagrams.

9.1.1. Amphibole-bearing plagioclase-free mafic fractionation trend

This first fractionation (stage 1) can be reproduced by the subtraction of the observed modal mineral assemblage (Ol + Amph + Ox + Cpx; Ayam-2 sample, Table 12) from the calculated parent magma. An early and deep amphibole crystallization stage for the mafic Gede magmas was also proposed by Handley *et al.* (2010) and Davidson *et al.* (2007) using mainly geochemical arguments based on REE and $\delta^{18}\text{O}$ variations. This fractionation stage would produce a daughter liquid similar to the most evolved sample (G130) of the >45 kyr unit (Fig. 22; Table 12). Using the same mineral assemblage and modes, the Kd's noted in the previous section, and the Rayleigh fractionation equation, we find that the Sr concentrations of the >45 kyr series increases significantly with SiO_2 (or Rb) reflecting the absence of plagioclase in the fractionation assemblage (Fig. 22.e). For comparison, we tested the role of amphibole by calculating the liquids from amphibole-free mafic fractionation (also without plagioclase). The two trends are similar in major elements, but differ significantly in some trace element concentrations and ratios (Fig. 22). For instance, the K/Rb is only reproduced by the amphibole-bearing plagioclase-free differentiation trend (Fig. 22.f). Although some modeled trace element

concentrations and mostly their ratios match those of the G130 sample, others (i.e. Rb, Zr, and Y) are underestimated by about 30% (Table 12). This could be due to the K_d being too high and/or a limited amount of incorporation of a high-silica liquid (e.g. some sort of assimilation), similar to the most evolved rock at Gede. This latter possibility is supported by the presence of Opx in the G130 sample.

Additional constraints on the processes recorded by the >45 kyr unit can be obtained from the trace element concentrations in the minerals and using melt-crystal partition coefficients to recalculate the liquids. We found that the calculated liquids in equilibrium with amphibole cores have lower Zr and Y concentrations (about 36-48 ppm and <17 ppm, respectively), and higher Cr (about 100 ppm) and Sr (300-360 ppm) than the basaltic bulk-rock or PM composition. The calculated Cr is apparently even lower than the typical primitive arc basalt range (i.e. 200-400 ppm; Winter, 2001). On the other hand, the calculated Cr_{liq} in equilibrium with Amph rims is about 11 ppm, which matches the bulk-rock concentration (7-12 ppm; Fig. 23; Table 8). This implies – as the major elements show no zoning in the amphiboles – that Cr-spinel co-crystallized with amphibole in a mafic basaltic liquid at a moderate T and relatively high P (about 1000 °C at 600 MPa). The Ni-Cr relations of the amphiboles from the different units (Fig 16) suggest that the Cr-spinel grew somewhat later than olivine than in the other units, and thus these older mafic melts were probably more reduced than the younger ones (e.g. Canil, 1999). Experimental studies have proposed that the molar Al/Si of amphibole in equilibrium with Al/Si of the melt is about 0.94 independently of melt composition (Fig. 24; Sisson, 1994). The Al/Si of Amph in the >45kyr unit is about 0.4-0.42 and would be in equilibrium with a liquid of Al/Si of about 0.42-0.45. This value is between that of the >45kyr bulk composition (about 0.44-0.5) and that of the typical island-arc high-MgO basalt (about 0.38; Wilson, 1989), thus also suggesting a slightly more primitive origin for the amphibole than our calculated PM (0.44) (Fig. 24).

Calculated Cr concentration in liquid in equilibrium with olivine (Fo₈₁) is also about 100 ppm, suggesting early crystallization together with amphibole (Fig. 23). Incompatible trace element (e.g. Zr and Y) concentrations of the liquid calculated from olivine compositions (16-45 ppm and about 18 ppm, respectively) agree well with those calculated from Amph. Presence of few small olivine inclusions in Amph together with Ni concentration decreasing from core to rim in the amphibole also implies olivine co-crystallization with Amph (Table 6).

Given the presence of strongly sector zoned Cpx crystals with different trace element compositions between the sectors, it is possible that the Kd from equilibrium experiments or models are not applicable, and here we consider whether Kds from cooling rate experiments are more appropriate. In general, we found that using the model of Wood & Blundy (2002) to calculate the Kd from the low-Al sector of clinopyroxene is closer to those of equilibrium Cpx Kd's (see next chapter), therefore using calculated liquid concentrations from low-Al sector may reflect more realistic values. Using an equilibrium Kd, the Cpx apparently grew from a liquid with about 0.5-6 ppm Cr, or twice this amount (1-12 ppm Cr) if we use a Kd from cooling rate experiments at 50°C/h (e.g. Mollo *et al.*, 2013) (Fig. 23). These Cr_{liq} concentrations are lower than those obtained in equilibrium with olivine and amphibole, they partly overlap with the bulk-rock and extend to lower concentrations that might reflect the growth from the interstitial liquid. Thus, the Cpx grew after significant Cr-spinel crystallization. Calculated Sr in liquid in equilibrium with Cpx is 115-145 and 57-71 ppm depending if we use equilibrium or cooling rate partitioning coefficients, respectively, but they are about 50% lower than the bulk-rock. Zr calculated liquid compositions vary between 23-50 ppm, which is higher than those calculated in equilibrium with Amph and Ol, but between the bulk-rock and primitive arc magma. The calculated Y concentration in the liquid varies between 10-50 ppm, significantly higher than the bulk-rocks but close to those obtained from Ol and Amph.

Fig. 23. Calculated trace element (Cr, Zr, Sr, Y, and Rb) concentrations of liquids in equilibrium with different minerals and for different units. (a) >45 kyr, (b) 10 kyr, and (c) 4 kyr units. Symbol size indicates error associated with trace element measurement in both natural Gede samples and Kd experiments. Open symbols are crystal rims, filled ones are cores. In Cpx of >45 kyr unit, solid black arrows point from the liquid concentration calculated with Kd from equilibrium crystallization experiments to dynamic cooling experiments of Mollo *et al.* (2013). Horizontal lines (bands) are the whole rock compositions, of end-member compositions, and given for comparison. IAB denotes the average island arc basalt composition from Winter (2001) and Wilson (1989); PM marks our calculated 'parent' magma; 10WR is the average 10 kyr whole rock composition; PATA-7 is the rhyodacitic whole rock composition of PATA-7; HYBRID indicates the hybrid magma composition of CIP-8A (Table 8).

In fact, all calculated Y liquid concentration in equilibrium with Amph, Cpx, and Ol are consistently higher than that in primitive arc basalts or whole rock. This could be due to analytical problems related to the LA-ICP-MS analysis, presence of early formed apatite crystals (e.g. Adam *et al.*, 2002), or the $^{87}\text{Sr}/^{86}\text{Sr}$ for these phases are not yet well constrained.

As a summary, olivine and most of the amphibole grew first, and were closely followed by Cr-spinel, and Cpx was apparently later. This order of crystallization is also supported by the mineral inclusions (Amph, Ol) found in Cpx. It shows that Amph and Ol crystallized from a more primitive magma, which had lower incompatible element (i.e. Zr and Y) concentration and higher compatible (i.e. Cr and Ni) than PM (Fig. 23). Calculated liquid Sr concentration in equilibrium with Cpx is, however, much lower than basaltic whole rock concentrations and may indicate plagioclase formation along with Cpx, which is also supported by tiny Plag inclusions found in Cpx rims.

The crystal fractionation assemblage that we propose, where plagioclase crystallizes after the mafic minerals, has been experimentally reproduced in phase equilibria studies of arc magmas (e.g. Sisson & Grove, 1993a; Pichavant & Macdonald, 2007; Melekhova *et al.* (2013); Melekova *et al.*, 2015). Early crystallization of Al-rich pargasite (before Cpx) is rather uncommon, but is indicative of deep ($\geq$ mid-crust), ‘wet’ and soda-rich mafic differentiation, and implies having crystallized from a water-rich (>6wt%) liquid at rather moderate temperature (<1050 °C) (e.g. Sisson & Grove, 1993a,b; Adam & Green, 1994, Adam *et al.*, 2007). Melekova *et al.* (2015), found that high-alumina basalts (HAB) as daughter liquid of High-MgO Basalts (HMB) form only at moderate depth (0.4 GPa) and though Amph crystallizes, it does not precede Cpx. Blatter *et al.* (2013) reached the conclusions that in moderately hydrous arc basalt, higher pressure delays the formation of significant amount of Plag and, thus, increases alumina concentration more effectively. Foden & Varne (1980) and Wheller *et al.* (1987) demonstrated the existence of such HMBs and their relationship with HAB in natural rocks from the Eastern Sunda arc

volcanoes (i.e. Gunung Sangenges and Soromundi volcanoes). We used MELTS (Ghiorso & Sack, 1995) to try to reproduce the trend and mineral assemblage. The overall change in MgO and SiO₂ and Al₂O₃ can be approximately reproduced at about 600 MPa and water content >5 wt% (Fig 22; see also previous geothermobarometry section); however we found that at these conditions garnet is stable and Amph cannot be crystallized, and thus it is not clear how applicable the MELTS modeling results are to Gede Stage 1 evolution.

9.1.2. Amphibole-free plagioclase-bearing differentiation trend at shallow depth: the making of evolved magmas at Gede

The second geochemical trend (Stage 2) is shown mainly by MI compositions, those included in pyroxenes of the 4ky unit and the olivine-hosted glass inclusions from the >45 ky unit. The Stage 2 trend originates from basaltic andesite composition (SiO₂ ≈ 53wt%, MgO ≈ 2.5wt%, and Al₂O₃ ≈ 23wt%) and fractionates into an evolved, possibly rhyodacite magma. The glass inclusions in olivine microphenocrysts found in the matrix of the samples reflect in situ crystallization of the melt. This trend would have a parent that is the residual liquid of the first fractionation stage and may lead to the more silicic and evolved magmas erupted at Gede.

We did a mass-balance model using major elements and a representative mineral assemblage of Plag + Ol + Ox, as these are present in the >45kyr samples (Table 12). The starting composition is the high-alumina basaltic andesite sample (G130), the assumed daughter of the stage 1 mafic fractionation model. The stage 2 model yields a fractionation trend towards the rhyodacite end-member (PATA-7) suggesting that mainly Plag and olivine precipitation from a basaltic andesite could lead to the evolved magmas found in Gede (Fig. 23). It is to note that we do not need to include pyroxenes in the crystallizing assemblage (in accord with their absence in the >45 kyr unit), although

pyroxene crystallization clearly occurred at some point given that these minerals are very prominent in the Gede rocks. We cannot further test this stage 2 model using the glass inclusions because we do not have the trace element content due to their small size prevented analyzing them in-situ by the laser-ablation. Instead, we tried to reproduce the bulk-rock compositions. When we use Plag and Ol and we do a least squares model, we cannot match incompatible elements (e.g. Y, Zr) because they become too high. If we crystallize small amounts of zircon and apatite, Zr and Y concentration decrease significantly (Table 11) getting closer to the measured values. As a summary, the Stage 2 fractionation was dominated by plagioclase plus one or two mafic minerals (Ol $\pm$ pyroxenes) and was followed by apatite and zircon, when the liquid reached about 67 wt% SiO₂ (Figs. 18 & 19) evidenced by P in the olivine-hosted MIs. The evolved end-members do not have amphibole, and thus this second evolution stage was probably amphibole free. Given that the early fractionation was water-rich and with amphibole stable, the second stage would still be water-rich if it occurred by closed-system differentiation at the same pressure. The evidence for a drier (e.g. amphibole absent, plagioclase dominated) evolution for the more evolved stage 2 magmas likely reflects differentiation at a much shallower storage level where amphibole would not be stable even under water saturated conditions (e.g. < 3 wt% water in the melt at about 100 MPa; e.g. Costa *et al.*, 2004 and references therein). Trace element modeling yields a residual liquid of this Plag-rich Amph-free fractionation, which gives a close fit for the evolved end-member of Gede rock suites (i.e. PATA-7; Fig. 22, Table 12). Thus, the evolved magmas at Gede for which we consider the rhyodacitic whole rock composition (PATA-7) was likely generated at much shallower depths and thus under drier conditions. Movement of a mafic and volatile-rich magma from deep to shallow depth would generate a coexisting fluid phase that would either passively degas or accumulate as excess gas in the reservoir.

The onset of plagioclase crystallization at the second stage can also be tested using its Sr and Ba concentrations and calculating the liquids in equilibrium. Using the K_d of Bindeman *et al.* (1998) we found that An_{90} plagioclase could have grown from liquids with about 360 ppm Ba and about 440 ppm Sr. These are higher than those of the bulk-rock that we consider to be the starting composition for 2nd stage (i.e. G130; 270 ppm Ba and 370 ppm Sr), but still realistic if we consider that the trends are the correct ones. If, however, we use the K_d of Blundy and Wood (1991) we obtain similar Sr (about 390 ppm) to the bulk-rock but significantly lower Ba (about 150 ppm). Consequently, Plag most likely crystallized extensively from a source, which had not experienced a significant Plag fractionation event (stage 1).

Although the >45 kyr samples are free of evolved pyroxene crystals, they are abundant in the chronologically subsequent units (10 and 4 kyr) and melt inclusions from such evolved pyroxene cores show good agreement and define an array together with the >45 kyr olivine melt inclusions (Figs. 18.a,b,e,g).

The observations we have made based on mineral assemblages, and trace element abundances in bulk-rock and minerals have also been done by experimental phase equilibria studies (e.g. Melekova *et al.*, 2015, Sisson & Grove, 1993) and studies of natural rock suites (e.g. Tollan *et al.*, 2012). Sisson & Grove (1993a, b) among others, have extensively investigated the issue of delayed plagioclase crystallization of High-MgO Basalts (HMB) producing High-Alumina Basalts (HAB) as residual liquids and showed that a decrease in water content is necessary before the plagioclase formation can take place, or plagioclase saturation in liquidus phase. They also found that Plag crystallizes first from HABs so that the Mg# of the melt increases and promotes Ol and Cpx to form even from quite evolved liquids. This is consistent with our observations of olivine microphenocrysts in the matrix and the composition of evolved melt inclusions. It has also been shown that extensive plagioclase crystallization drives the residual melt

towards the calc-alkaline series (Blatter *et al.*, 2013; Nandedkar *et al.*, 2014; Melekova *et al.*, 2015). Melekova *et al.* (2015) observed differentiation trends where plagioclase formation is delayed and restricted only to lower T and P with fairly high water content in the magma – comparable to what we have illustrated above.

Fig. 24. Al/Si molar ratio in amphibole crystals and their calculated melt equilibrium Al/Si ($K_d^{Al/Si} \approx 0.94$; Sisson, 1994). Symbols are as in Fig. 18; filled symbols are cores, empty symbols are mafic rims. For comparison the most possible liquid sources are shown for each unit. It can be seen that over time the equilibrium melt composition becomes more silicic, but the rims stay primitive; except for the ‘recent’ amphiboles what exhibit strong disequilibrium textures at rims. Bottom panel shows the whole rock SiO_2 and Al_2O_3 compositions corresponding to the Al/Si ratios of liquids (black arrows). Dashed black arrows and symbols show the assumed equilibrium melt (and amphibole) based on the Al/Si ratio of the amphibole (and whole rock) Al/Si ratio. Note that PM seems less mafic than >45 kyr whole rock composition, it is due to its Plag-absent (tholeiitic) differentiation (see main text). Note the >45 kyr Amph cores corresponds to a melt composition close to HMB (high-magnesia basalt; Myers & Johnston, 1996) and IAB (island arc basalt; Wilson, 1989; Winter, 1993) whereas the rims represent an equilibrium HAB liquid (high-alumina basalt; Myers & Johnston, 1996).

Many arc volcanic rock suites (e.g. Freundt-Malecha *et al.*, 2001; Tollan *et al.*, 2012) show similar fractionation trends with a 1st stage of differentiation dominated by a wet mafic mineral formation, followed by the 2nd stage of mainly Plag precipitation from the

residual liquid. In St. Vincent, Tollan *et al.* (2012) found that a two-stage petrogenesis produced first Ol (Fo₈₁) + Sp + Cpx ± Amph at high pressure from a water-saturated primitive basalt, and upon decompression calcic Plag (An₉₀₋₉₄) + Ol (Fo_{~70}) crystallized at shallow crustal level. Their model requires an abrupt adiabatic change in pressure, which leads to water saturation and shifts the liquidus of the decompressing melt upon degassing, facilitating Ol formation from a rather MgO-poor liquid. It is very similar to what we have demonstrated.

Summarizing the petrologic evolution of the >45 kyr unit we need to highlight the contrasting conditions of the two-stage fractionation, where first by a rather deep and wet amphibole-bearing and plagioclase-free fractionation high-alumina basalt (HAB) forms, and from its daughter liquid, during the second stage, upon (most probably) decompression plagioclase-bearing and amphibole-free shallow fractionation occurs creating an evolved rhyolitic melt (Fig. 22).

9.2. Crystal-cumulate mafic magma replenishment and mingling/mixing of the 10 kyr unit

The bulk-rocks of the 10 kyr unit show a very limited variation in SiO₂ (i.e. 55.0-56.4 wt%), but quite a spread in MgO (i.e. 2.2-3.9 wt%) and Al₂O₃ (20-23 wt%). Reverse zoning patterns in the mafic minerals (Cpx, Opx) are characteristic of this unit, and reflect primitive magma injections and partial magma mingling/mixing with a pre-existing evolved crystal-rich cumulate zone. The low-Mg# pyroxene cores (Mg# = 60-65) are similar to those in the 4kyr and younger units (Figs. 12,13,16,17). The absence of amphibole implies a relatively dry magma (< 3 wt% H₂O; e.g. Costa *et al.*, 2003) since the temperatures or compositions should allow crystallizing amphibole. Two-pyroxene equilibrium shows that cores grew at significantly lower temperatures (950-1000 °C), than the mafic rims (1050-1090 °C) (Table 10). These observations and the 10 kyr whole

rock trends (Fig. 18) can be explained with a model where a magma similar to the daughter of the >45 kyr stage 1 (Table 12) entered into an evolved crystal-rich reservoir and interacted with evolved (Fe-rich) Cpx and Opx crystals which were perhaps lying at the bottom and/or the walls of the reservoir (e.g. Landi *et al.*, 1999) (Fig. 25).

Trace element contents (e.g. Zr, Y, Sr, and Cr) in evolved clinopyroxene cores and primitive rims are used to constrain the liquid composition from which they formed. For cores and rims different K_d values are used (see section 8; Table A2). We found that the evolved cores are in equilibrium with a liquid with 140-165 ppm Zr which is higher than the bulk-rocks and closer to the rhyodacite whole rock (165 ppm, PATA-7). The mafic rims are apparently in equilibrium with a liquid with 40-50 ppm Zr, which is even lower than our PM (Fig. 23.b). The calculated concentrations of Y in the liquid (16-20 ppm) are, however, similar for both the cores and rims, and within the bulk-rock values of both PM and PATA-7 compositions (about 20 ppm; Table 8), but apparently not in equilibrium with the 10 kyr whole rock (about 25 ppm, Table 8); It is not clear why Y does not seem to be really diagnostic of the different melt compositions. Calculated Cr concentrations in equilibrium with the cores and rims are similar and relatively low (about 15 ppm Cr) suggesting that the intruding mafic liquid had already fractionated a significant amount of Cr-spinel (Fig 23.b), similar to other mafic liquids in the Gede system. The calculated Sr in equilibrium with the cores (205-230 ppm) is similar to that of the rhyodacite bulk-rock (Sr = 225 ppm) whereas liquid in equilibrium with rims is more mafic, with about 120-140 ppm Sr (Fig. 23.b) much less than PM or IAB (Table 12). These detailed textural and geochemical observations show that the magma from this unit is the result of mingling and mixing between a rather mafic melt and an evolved crystal-rich system and interstitial liquid (e.g. rhyodacitic) and agrees with our inferences based on mass-balance between bulk-rock compositions and minerals (Fig. 22).

Rare clinopyroxene-rich glomerocrysts have an intermediate major element composition ($Mg\# = 70-71$) and are in equilibrium with liquid with about 140 ppm Zr and 150 ppm Sr. These crystals could have grown from the reaction of the interstitial melt and the incoming mafic liquid. This could reflect that the small amount of evolved liquid enriched in incompatible elements that dominated the Zr budget of these crystals, but poor in compatible elements.

Compared to the >45 kyr unit, the 10 kyr plagioclase crystals have slightly higher An/K₂O contents at a given An (Fig. 14). A mixing model using the end-member Plag composition (An₉₀ and An₅₀), may explain their composition as crystallization from a hybrid magma involving the daughter liquid of stage 1 (>45 kyr) and high-K evolved liquid that could be in the interstices of the evolved-crystal-rich cumulate. On the other hand, a change in pressure and/or water content may cause the same effect in the chemistry of crystallizing plagioclase (e.g. Prouteau & Scaillet, 2003). However, incorporation of 15-25% of the evolved end-member (PATA-7) to the daughter liquid yields comparable compositions to those of 10 kyr bulk compositions. Furthermore, this addition of evolved liquid explains the somewhat higher incompatible element abundance in Plag (e.g. Ba; compared to >45 kyr Plag) suggesting that it formed from the blended liquid.

9.3. Mafic-felsic magma mixing and mingling in the 4 kyr and younger units

The 4kyr unit, and some of the samples of the 1.2 kyr unit contain abundant macroscopic evidence for incomplete magma mixing and mingling (Figs. 3.c-f). At the thin-section scale, however, most samples of these units contain minerals with reverse and/or complex zoning patterns. Plagioclase histograms also show bimodal populations (Fig. 11). Zoning in olivine and in amphibole suggests that there were at least two major events in the magma mixing/mingling history. First, a hot mafic magma intruded into a

cooler silicic reservoir and produced a hybrid magma of intermediate composition ($\text{SiO}_2 = 54$ to 60 wt%). Later, shortly before eruption, an additional mingling occurred between this intermediate hybrid magma and the silicic end-member, which is manifested in macroscopic scale magma mingling (banded-scoria samples) in the 4 kyr and 1.2 kyr units. This sort of multi-step evolution during mafic and silicic magmas interactions has also been proposed in other systems (e.g. Costa & Singer, 2002 and references therein). Handley *et al* (2010) also proposed magma mixing and mingling as an important process for the evolution of some of Gede magmas.

9.3.1. Magma mixing and hybrid magma production

We tested the bulk mixing hypothesis (Fourcade & Allegre, 1981) assuming the PM and rhyodacite compositions as end-members before mixing, and we find that that the most mafic 4 kyr sample (Cip-8A; Table 8) is the product of hybridization, involving 75% of the PM and with 25% of the rhyodacite (Table 8, Appendix 3). Results show high correlation coefficients for both major and trace elements ($R^2 = 0.99$ and $R^2 = 0.98$, respectively). Some oxides and elements marginally deviate from the mixing line (e.g. FeO and CaO; Table A3), which may be the consequence of element mobility and diffusion (i.e. Morgavi *et al.*, 2013a,b) or the effect of selectively incorporating some minerals with particularly high concentrations of a given element (e.g. Sr in plagioclase or Ni in olivine: Costa and Singer, 2002). Modeling trace element ratios (e.g. Zr/Y or K/Rb), the calculated mixing line between the end-member magmas also shows a satisfactory fit to proposed hybrid magma (i.e. CIP-8A) (Fig. 22.; black line).

The compositional spread of most samples from the 1.2 kyr unit (e.g. PATA-4) can be explained by a bulk mixing using the same end-members as for the 4 kyr unit, although the model gives somewhat inferior correlation coefficients ($R^2 = 0.94$ for the majors, and $R^2 = 0.96$ for the tracers). Incompatible elements (e.g. Rb, Ba, and Zr if we account for

zircon crystallization) fit better the binary mixing models than compatible elements like Sr, Cr, Ni probably because these elements are also controlled by the fractionating minerals (e.g. plagioclase). In fact, we think that some samples also show a more selective mingling with mainly the incorporation of minerals as occurred in the 10 kyr unit (e.g. Fig. 19.e). Y is also complex and might show the variable roles of mixing, apatite and amphibole crystallization.

The mineral textures and zoning patterns of these two units are also a good record of mixing and partial hybridization. The trace element concentrations (e.g. Cr, Zr, Rb, and Y) of the Amph core and overgrowth rims record the change in magmatic evolution (Fig. 23.c). For example, Zr and Rb concentration in the core corresponds to a liquid with 125 and 45 ppm, respectively. These concentrations match the hybrid bulk-rock (Zr = 111 ppm and Rb = 44 ppm), and not those of the rhyodacite (Zr = 164 and Rb = 107 ppm), thus these amphibole cores grew from a hybrid liquid close to the interface of the mafic and felsic magmas (Figs. 23.c & 25). The amphibole rims apparently grew from a liquid with about 70 ppm Zr and about 35 ppm Rb, which also fits well to the PM composition and thus is a record of a more primitive magma arriving in the silicic crystal rich shallower reservoir (Fig. 23.c; Table 11). Amphibole rims are rich in Cr (up to 750 ppm) implying a similar melt source to those of >45 kyr amphiboles. The Al/Si values of the amphibole cores also suggest crystallization from a hybrid magma followed by crystallization from a more primitive one recorded by the rims (e.g. Pallister *et al.*, 1996). Amphiboles in equilibrium with rhyodacitic liquids, however, should have much lower Al/Si (e.g. about 0.27; Fig. 24). Additionally, a large relict Amph grain found in the silicic band also suggests disequilibrium between Amph and evolved liquid, probably due to variable water contents and/or chemical disequilibrium with host melt.

The major and trace element zoning patterns of Cpx and Opx also record the intrusion of a mafic melt into a more evolved magma reservoir. The Cpx cores apparently

grew in equilibrium with a melt similar to the rhyodacite, because their calculated Zr, Rb and Cr concentrations overlap with the rhyodacite (Fig. 23.c). The MI compositions from the evolved Cpx and Opx cores are also rhyodacitic to rhyolitic. In contrast, the liquids calculated in equilibrium with Opx and Cpx rims have trace element concentrations (Zr, Rb, Cr) close to primitive basaltic compositions (Fig. 23.c). Finally, the 4 kyr and 1.2 kyr units both show bimodal plagioclase populations, one that grew from the silica-rich and shallow reservoir (e.g. mode at about An₆₀), and another that grew from the incoming mafic liquid (e.g. mode at about An₈₅) (Fig. 11).

Mineralogical observations (oscillatory- and sector-zoned Cpx, absence of Opx, and presence of olivine microphenocrysts) of the 1 kyr primitive low-silica basaltic andesites (SiO₂ = 52-53 wt%) and trace element geochemistry of Cpx and Plag suggest a primitive origin as both minerals are compositionally similar to those of the >45kyr unit (Figs. 14&16). However, most major element bulk-rock data fits well to the ‘hybrid-mixing’ trend of the 4 kyr and the 1.2 kyr units and not to the >45 kyr unit (e.g. Fig. 18). These observations, along with the lack of characteristic reverse zoning and orthopyroxene, suggest that the mafic injection did not lead to mixing and hybrid magma formation. Instead, we propose an interaction between the mafic end-member (PM) and the evolved end-member (PATA-7) that ended in cooling and crystallization of the former. This rapid cooling of the mafic melt is shown by the skeletal distribution of phosphorus in olivine microphenocrysts and oscillatory and sector zoning of Cpx (Fig. 9). Thus, although the 1 kyr unit records some mafic-felsic magma interaction it is much less prominent than in the 4 kyr and 1.2 kyr units.

9.3.2. *Amphibole- and plagioclase-bearing differentiation trend?*

Bulk-rocks of the 4 kyr and younger units show a bulk-mixing trend between the virtual mafic end-member (PM) and the most evolved rhyodacite (Figs. 18&22). Because

of this, a Plag-rich mafic fractionation (plagioclase + amphibole $\pm$ olivine $\pm$ pyroxenes) from the hybrid basaltic andesite cannot be undoubtedly demonstrated as the bulk-rock compositions cannot be interpreted as liquid line of descent (Eichelberger *et al.*, 2006). However, the amphibole cores from the 4 kyr, 1.2 kyr, and 'recent' units have trace element characteristics and Al/Si value that indicate they grew directly from a hybrid basaltic andesite magma (Figs. 23 & 24). To test the hypothesis of Amph core crystallizing from the hybrid magma we use bulk-rock, instead of using glass composition, because Amph formed early and in small amount (<2 vol%), and therefore whole rock Al/Si ratio rather reflects equilibrium than matrix glass would. For instance, the Al/Si ratio of P5A6 amphibole core is 0.38, and in equilibrium with the hybrid liquid (PATA-5; Al/Si = 0.39), and the ratio (0.95) is within analytical error ($K_d = 0.94$; Sisson, 1994). These cores are undoubtedly out of equilibrium with the rhyodacite end-member indicated by the high Al/Si values (=1.41). Similarly, the Holocene overgrown amphibole mafic rim has Al/Si of 0.43, which is in equilibrium with PM composition (0.45) and thus indicating its primitive origin (Fig. 24).

Some of the spread in the An content of the plagioclase could also be the record of plagioclase crystallization from a basaltic andesite. The plagioclase composition of the 4 kyr (and younger) units shows substantial differences in minor (i.e. K) and trace element concentration compared to >45 kyr ones (Fig. 14). An/K₂O plotted against An shows two definite trends: >45 kyr (and 10 kyr) Plag contains less potassium at a given An-content, whereas 4 kyr (and younger) Plag units tend to be more potassium-rich (Fig. 14.e). It is to be noted that similar differences in K₂O content can be made by changes in H₂O content and/or pressure (Panjasawatwong *et al.*, 1995; Prouteau & Scaillet, 2003). MELTS modeling also reproduced the observed An/K₂O variation to some extent. However, good fits to the 4 kyr and 1.2 kyr plagioclase composition were obtained only when the hybrid magma composition was used as parent magma instead of the most mafic end-member

(PM) (Fig. 14.e). Unfortunately, the Plag trace element dataset is more difficult to interpret because it has a bias: the low anorthite compositions are over-represented in the 4 kyr and 1.2 kyr units (Fig. 14). Thus, these two trends cannot be distinguished in Plag trace element plots. We suggest that the 4 kyr and 1.2 kyr calcic Plag population is of the hybrid magma.

Such plagioclase- and amphibole-bearing differentiation trend has been produced experimentally at various pressures (0.2-1 GPa), moderate water-content (3 – 6 wt%) and moderate temperature (<1050 °C) (e.g. Freise *et al.*, 2009; Melekova *et al.*, 2015; Sisson & Grove, 1993b). Starting from high-MgO basalts the experiments produce residual melts that stretch from basaltic andesite to dacite. These differentiation trends show linear relationships in many major element Harker diagrams (e.g. MgO and Al₂O₃ vs. SiO₂) and thus overlap to a large extent with the linear trends shown by the Gede samples that are controlled by mixing. However, given the amphibole and plagioclase compositions that we have discussed above, it seems that fractionation of hybrid magmas of intermediate water contents could also be important at Gede volcano.

10. A MODEL FOR RESERVOIR DYNAMICS AND MAGMATIC EVOLUTION BENEATH GEDE VOLCANO

Here, we summarize our main observations and propose a model for reservoir dynamics and magmatic evolution under Gede volcano. Although there is not a clear evolution or change of these processes with time, some were more prevalent in some eruptions than others (Fig. 25).

The oldest unit contains the best record of the evolution of primitive melts below Gede. In particular the high Al/Si and Mg/Fe, high Cr and Ni concentrations of the amphiboles from the >45 kyr unit suggest that they crystallized from primitive arc magmas. MELTS calculations using the bulk-rock and temperature obtained from

Fig. 25. Idealized illustration of characteristic magmatic processes underneath Gede volcano in the Holocene. Note that the >45 kyr event is characterized by processes on the left panel (quiescence) only. The isolated magma reservoirs are to represent the characteristic magmatic processes; the existence of a continuous reservoir is not ruled out.

geothermometry indicate that such melt would be close to near liquidus conditions at about 600 ± 200 MPa, 6 ± 2 wt % H_2O , at about 1090 °C. This volatile-rich magma was a high-alumina basalt and did not grow plagioclase until it migrated to shallower depths and stalled around the stability field of amphibole (about 3 wt% of water in the melt; 100 MPa). Degassing occurred and was followed by crystallization of high An-plagioclase, minor olivine, and later by evolved pyroxenes. The interstitial melt differentiated towards the rhyodacitic and rhyolitic compositions that we have sampled as bulk-rock and as melt

inclusions in the >45 kyr olivine microphenocrysts and in the 4 kyr evolved pyroxenes. Such a two-stage crystallization history is supported by several studies of high-MgO basalts and high-Al basalts (e.g. Melekova *et al.*, 2015); it has also been reported in other studies of volcanic suites (e.g. Tollan *et al.*, 2012).

The other of the units record the same process, but with slightly different variations: the mafic magmas from the deep reservoir intruded a pre-existing evolved magma reservoir or a crystal-rich mush. Depending on the proportions of the liquids and crystal-rich zones, we find various degrees of hybridization. The upper silicic reservoir probably had a significant vertical extent crossing the stability field of amphibole, since in some units we find that interaction between the incoming mafic magma and the silicic reservoir amphibole is stable (e.g. 4 kyr and 1.2 kyr units), whereas in others it is not (e.g. 10 kyr unit). Thus, the vertical reservoir ranged from about the stability field of amphibole with about 3-4 wt % water in the melt (100-120 MPa assuming water saturation) to much shallower depths. Such a vertically elongated but shallow reservoir has been proposed at other arc volcanoes such as Mount St. Helens (Pallister *et al.*, 2008) and Merapi (Costa *et al.*, 2013). It seems that some hybrid basaltic andesite and andesite magmas differentiated by crystallizing amphibole and plagioclase, since amphibole core compositions have intermediate trace element concentrations. It is also possible that the mafic magmas that intruded the silicic reservoir before the 4kyr and 1.2 kyr eruptions were somewhat different from the 45 kyr unit. The Ni contents of these younger amphiboles tend to be higher, but the Cr contents are similar or lower than those of the 45 kyr. This could indicate that the mafic magmas that intruded the upper reservoir were perhaps more oxidized (e.g. earlier crystallization of Cr-spinel) or slightly different in T and H₂O values. Interactions between evolved and pyroxene-rich magmas or crystal cumulate piles are recorded as strongly zoned patterns in ortho- and clinopyroxenes. Pyroxene cores have systematically lower Mg/Fe and compatible elements (Ni, Cr) and higher

incompatible elements (Zr, Rb, Hf, Ba) than their rims, which have high Mg/Fe and compatible elements, and lower incompatibles. The bimodal plagioclase compositions of the 4 and 1.2 kyr samples also show the mafic-silicic magma interactions, but in this case the intruding magma would already carry a significant amount of plagioclase. Again, this suggests that the later mafic magmas were different in T and H₂O conditions than the 45 kyr ones, where we infer that they did not crystallize plagioclase until much shallower depths.

The 1 kyr and recent eruptions show more complex patterns that include differentiation and more complete hybridization, because we do not recognize petrological evidence of the mafic and silicic end-members, but rather more intermediate compositions. The abundant evidence for mafic silicic interactions in almost all of the Holocene deposits suggest that mafic magma intrusion is probably instrumental in triggering the eruptions at Gede.

11. RELATION OF GEDE PETROLOGY AND GEOCHEMISTRY TO VOLCANO HAZARDS AND MONITORING DATA

The data that we have gathered and the processes that we have unravelled having been involved in the Gede magmatic evolution should inform the interpretation of monitoring data in Gede and also be useful to interpreting unrest. For example, we find it very likely that the current magma plumbing system of Gede is a high-crystallinity system with evolved interstitial melt, which is being remobilized during mafic magma recharge and often records multiple recharge events (e.g. Cooper and Kent, 2014). The depth of such system probably straddles the amphibole stability field (e.g. 100 MPa). Assuming a crustal density of about 2600 kg/m³ (average andesite rock), we find that the crystal-rich zone would be at least at about 4 km below the summit, although it could extend to shallower depths where amphibole is not stable. Another likely depth for the

storage of the mafic magmas comes from the pressure estimates using MELTS calculations (600 ± 200 MPa). Assuming the same density as above, we find that it could be located at about 24 ± 8 km, which is similar to what was proposed by Handley *et al* (2010), this might be close to the crust-mantle boundary (e.g. Dahren *et al.*, 2012). Currently there are not enough determinations of seismic sources at Gede to be able to discuss any relation between the petrological and seismic depths, but the recurrent seismic crises at Gede do suggest magma replenishment (Hidayat *et al.*, 2012).

Another relevant finding of our study is that mafic magmas from depth are volatile rich and they will be saturated when they reach the upper and crystal-rich zone of the Gede reservoir. This means that there will be lots of fluids and gases that will be released from the mafic intrusions which will potentially leak to the surface and could be measured at the existing fumaroles below the volcano's crater. These fumaroles are not currently being monitored for their gas compositions, but it is likely that the clearest signal of renewed mafic intrusion from depth would be increases in CO₂ concentrations. Sulphur might also increase although given the presence of hot springs in Gede it might be partly dissolved into the hydrothermal system.

We also find that repetitive mafic intrusion in silicic magma has occurred multiple times in the past. This is what might reflect the repetitive seismic crises that have been recorded in Gede in the last decades (Hidayat *et al.*, 2012). It is difficult to estimate the amount of magma intrusion that might be involved in each seismic crisis. From our petrological study we can speculate that if the erupted magma is a basaltic andesite (about 55 wt% silica content; the most abundant composition in the Holocene history of Gede), the amount of intruded basaltic magma into the shallow silicic reservoir should be around 75% of the volume that would be erupted. In other words, if the next eruption at Gede were of 0.1 km^3 (mean volume of the last Holocene eruptions; Belousov *et al.*, 2015) we would expect a mafic intrusion of at least 0.075 km^3 . The movement and addition of such

an amount of magma would be probably seen in the deformation of the new GPS network that has been recently installed at Gede by CVGHM-EOS collaboration. A final piece of useful information for the hazards evaluation is the likely times between the new intrusions and the eruption. As it is reported in chapter 3, the zoning of Opx crystals records times of about one month between these two processes. This time frame should be long enough for preparation and making evacuation plans for future eruptions at Gede, although it is clear that not every intrusion leads to eruption.

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APPENDIX 1

As bulk-rock analyses were done in two laboratories, trace element compositions, especially REE, showed moderate differences. Thus, on three reference samples – covering a wide compositional range and calibrated at both laboratories – inter-laboratory calibration was necessary, because of the differences between reference samples. We conducted simple linear regression for all analyzed elements and obtained an linear equation ($y = a * x + b$) describing the correlation in between lab A and lab B results, and the correlation of determination (R^2). We used UTAS analyses as standard and re-calculated WSU to UTAS values. For example, the equation for La is $Ce^{UTAS} = 1.1007 * Ce^{WSU} - 2.6012$ ($R^2 = 1$) (Fig. A1), employing this we re-calculated all WSU samples. R^2 was usually higher than 0.99, except for Sr, transition metals, the heavy REE (Ho-Lu). Eu (0.613) shows the poorest correlation between UTAS and WSU analyzes. After recalculating the major elements, we normalized them to 100%; trace elements were not normalized. Equations used and R^2 values are in Table A1 below.

Table A1. Regression analyses of inter-laboratory calibration of bulk-rock compositions.

wt%	UTAS			WSU			regression parameters		
	AYAM-2	GEK-1	CIP-15	AYAM-2	GEK-1	CIP-15	a	b	R ²
SiO ₂	51.15	55.01	58.94	51.42	55.27	58.65	1.077	-4.293	0.998
TiO ₂	1.04	0.89	0.74	1.045	0.904	0.763	1.041	-0.050	1.000
Al ₂ O ₃	19.41	18.93	17.95	19.65	18.86	18.47	1.148	-3.047	0.856
FeO*	9.33	7.92	6.58	9.47	8.11	6.65	0.975	0.065	0.999
MnO	0.180	0.160	0.146	0.178	0.162	0.144	1.003	0.000	0.986
MgO	4.81	3.78	3.31	4.43	3.57	3.12	1.152	-0.306	0.999
CaO	10.31	8.93	7.35	9.95	8.73	7.38	1.152	-1.137	1.000
Na ₂ O	2.84	3.09	3.19	2.89	3.09	3.11	1.482	-1.451	0.954
K ₂ O	0.78	1.12	1.64	0.80	1.15	1.57	1.131	0.146	0.996
P ₂ O ₅	0.158	0.173	0.154	0.159	0.172	0.148	0.813	0.032	0.916
Total	100.00	100.00	100.00	100.00	100.00	100.00			
ppm									
Rb	26.1	40.3	66.4	26.2	39.0	60.5	1.179	-5.114	0.999
Cs	1.9	1.7	4.3	2.0	1.8	4.3	1.063	-0.249	1.000
Sr	327.1	317.6	298.6	337.2	316.8	312.4	0.938	12.209	0.730
Ba	140.3	219.1	309.7	138.2	209.3	286.6	1.141	-18.201	1.000
Sc	31.5	25.1	20.2	27.5	22.8	19.1	1.349	-5.593	1.000
V	268.7	219.4	152.4	274.4	218.9	156.9	0.992	1.359	0.997
Cr	10.9	9.9	13.5	8.2	4.5	12.4	0.455	7.632	0.952
Ni	6.7	5.3	7.3	8.0	5.8	8.9	0.640	1.590	1.000
Zn	81.7	76.9	71.4	89.4	81.1	75.0	0.705	18.976	0.986
Y	20.6	22.7	23.8	21.3	22.7	23.5	1.461	-10.477	1.000
Zr	67.8	94.9	136.8	68.3	92.7	137.2	0.995	0.914	0.998
Nb	2.7	3.5	4.2	2.8	3.5	4.7	0.787	0.577	0.976
Ta	0.2	0.2	0.3	0.2	0.3	0.4	0.909	-0.042	1.000
Hf	1.8	2.5	3.6	2.0	2.6	3.8	1.024	-0.242	1.000
Pb	6.7	8.8	13.4	7.2	9.6	13.1	1.143	1.721	0.989
Th	2.6	4.2	8.2	2.7	4.1	7.2	1.229	-0.708	0.999
U	0.6	0.9	1.6	0.6	1.0	1.6	1.079	-0.098	1.000
La	8.3	12.0	17.4	8.7	12.4	16.4	1.194	-2.374	0.995
Ce	19.5	27.0	36.6	20.1	26.9	35.6	1.101	-2.601	1.000
Pr	2.7	3.5	4.5	2.8	3.6	4.4	1.146	-0.569	0.999
Nd	12.2	15.2	18.4	12.8	15.5	18.0	1.203	-3.259	0.998
Sm	3.4	3.9	4.5	3.5	3.9	4.3	1.346	-1.349	0.999
Eu	1.1	1.2	1.1	1.2	1.2	1.2	1.070	-0.147	0.613
Gd	3.6	3.9	4.3	3.8	4.1	4.4	1.326	1.532	0.986
Tb	0.6	0.7	0.7	0.7	0.7	0.7	1.368	-0.284	0.996
Dy	3.7	4.0	4.2	4.1	4.3	4.4	1.521	-2.557	0.998
Ho	0.8	0.8	0.9	0.8	0.9	0.9	1.352	-0.382	0.916
Er	2.2	2.4	2.5	2.3	2.4	2.5	1.561	-1.350	0.955
Tm	0.3	0.3	0.4	0.3	0.3	0.4	1.328	-0.116	0.998
Yb	2.0	2.2	2.3	2.0	2.2	2.3	1.621	-1.346	0.984
Lu	0.3	0.3	0.4	0.3	0.4	0.4	1.176	-0.076	0.963

* Total iron is given as Fe²⁺

a and b are linear equation parameters obtained by regression analyses; R² is the correlation determination.

APPENDIX 2

Partition coefficients used in trace element modeling of magmatic fractionation are in Table A2.

Table A2: Partition coefficients (K_d) used in bulk-rock and mineral-melt trace element modeling

	olivine	clinopyroxene ^a	clino- pyroxene ^b	ortho- pyroxene	amphibole	plagioclase	magnetite	apatite	zircon
Cr	1	1.3/3.1	1	-	11.9	-	-	-	-
Rb	0.0098	0.004/0.007	0.0012	0.003	0.1	0.0080-0.0228	0.110	0.004	-
K	0.0068	0.038	0.037	0.002	0.88-1.76	0.0436-0.0848	0.045	0.0	-
Sr	2.5*10 ⁻⁴	0.28/0.14	0.08	0.009	0.50	1.1137-2.6985	0.011	2.0	-
Y	0.0049	0.8/2.0	3.0	1.0	0.91	0.0121-0.0441	0.2	162.0	71.4
Zr	0.0090	0.60/0.83	0.30	0.2	0.24	0.0001-0.0012	0.1	0.3	2000*

Kd for Ol are from Beattie (1994); for Cpx^a from Mollo et al. (2013); for Cpx^b from Bacon & Druitt (1998) and Ewart & Griffin (1994); Opx, K-fsp, magnetite, apatite, and zircon from Rollison (1993) and Bea et al. (1994); for Amph from Adam et al. (2007).

^aCpx in basaltic bulk composition, equilibrium/dynamic cooling (50°C/h) crystallization

^bCpx in rhyolitic melt

*estimated

APPENDIX 3

The collected spectra from Plag- and Cpx-hosted MIs using FT-IR micro-reflectance method (King & Larsen, 2013), and the calibration lines for total water (3600 cm⁻¹) and molecular H₂O (1650 cm⁻¹).

APPENDIX 4

The ‘mixing test’ (Fourcade & Allegre, 1981) was used in order to determine whether certain bulk-rock compositions can originate from mixing between the calculated mafic end-member magma (PM) and the most evolved bulk-rock composition observed (PATA-7). A brief summary of how to apply the method is given here.

The compositions of the assumed end-members and the assumed hybrid need to be known from what two parameters need to be calculated. These are the difference of the felsic end-member and the mafic end-member ($\Delta F - \Delta M$), and the difference of the assumed hybrid and the mafic end-member ($\Delta H - \Delta M$), for each major and trace elements (Table A4). Next, simple linear regression needs to be conducted on the dataset gained in previous set, separately on major and trace elements (Fig. A4). Intercept of y-axis can be set at zero, since the b-value is infinitely small if the mixing hypothesis is correct (in the linear equation of $y = a * x + b$). Once equation of regression obtained, the hybrid composition can be calculated for each major and trace elements by using the equation:

$$H^i = a * (F^i - M^i) + F^i \quad (A1)$$

where H^i is the calculated composition of element i , a is the slope of regression, F^i is the felsic composition of element i , and M^i is the mafic composition of element i . After it is done, the residuals (R) can be calculated to check whether the assumed hybrid is significantly different. Differences may not exclude the hybrid origin for the sample in question, but reflect certain aspects of magma mixing (i.e. Morgavi et al., 2013a,b).

Table A4. Mixing-test calculation after Fourcade & Allegre (1981)

sample	PATA-7							PATA-4								
	PM	mafic end-member	felsic end-member	assumed hybrid	$\Delta F-\Delta M$	$\Delta H-\Delta M$	calc. hybrid	R	PM	mafic end-member	felsic end-member	assumed hybrid	$\Delta F-\Delta M$	$\Delta H-\Delta M$	calc. hybrid	R
wt%																
SiO ₂	50.89	69.08	55.46	18.19	4.57	55.45	0.01	50.89	69.08	54.61	18.19	3.72	54.67	-0.06		
TiO ₂	1.08	0.41	0.85	-0.67	-0.23	0.91	-0.06	1.08	0.41	0.92	-0.67	-0.16	0.94	-0.02		
Al ₂ O ₃	19.12	15.77	18.17	-3.34	-0.95	18.28	-0.11	19.12	15.77	18.86	-3.34	-0.26	18.42	0.43		
FeO*	9.70	3.15	7.93	-6.55	-1.77	8.05	-0.13	9.70	3.15	7.57	-6.55	-2.13	8.34	-0.77		
MnO	0.18	0.08	0.16	-0.10	-0.02	0.15	0.01	0.18	0.08	0.15	-0.10	-0.03	0.16	-0.01		
MgO	5.30	1.13	4.44	-4.17	-0.85	4.25	0.19	5.30	1.13	4.41	-4.17	-0.88	4.43	-0.02		
CaO	10.00	3.77	8.57	-6.23	-1.43	8.44	0.13	10.00	3.77	9.15	-6.23	-0.85	8.71	0.44		
Na ₂ O	2.84	3.56	2.85	0.72	0.01	3.02	-0.17	2.84	3.56	2.88	0.72	0.04	2.99	-0.11		
K ₂ O	0.74	2.94	1.41	2.20	0.67	1.29	0.12	0.74	2.94	1.32	2.20	0.57	1.20	0.12		
P ₂ O ₅	0.15	0.10	0.15	-0.05	0.00	0.14	0.01	0.15	0.10	0.14	-0.05	-0.01	0.14	0.00		
ppm																
Rb	22.8	106.8	57.2	84.0	34.3	54.5	2.63	22.8	106.8	43.9	84.0	21.0	46.2	-2.34		
Sr	320	225	289	-95	-30	284	5	320	225	315	-95	-4	293	22.12		
Ba	124	486	254	362	130	261	-7	124	486	232	362	108	225	7.09		
Sc	32.3	8.2	27.4	-24.0	-4.8	23.2	4.23	32.3	8.2	28.6	-24.0	-3.7	25.6	2.98		
V	318	47	210	-271	-108	216	-6	318	47	248	-271	-70	243	5.30		
Cr	6.9	17.0	14.9	10.1	8.0	10.7	4.19	6.9	17.0	18.3	10.1	11.4	9.7	8.62		
Ni	7.8	8.7	8.4	0.8	0.6	8.1	0.29	7.8	8.7	8.4	0.8	0.6	8.1	0.32		
Zn	79.5	49.1	76.0	-30.3	-3.5	68.0	7.94	79.5	49.1	72.1	-30.3	-7.4	71.0	1.05		
Y	20.1	20.7	24.6	0.6	4.5	20.3	4.28	20.1	20.7	21.1	0.6	1.0	20.3	0.83		
Zr	64.9	164	117	99.6	51.9	102	14.31	64.9	164	103	99.6	38.4	92.6	10.72		
Nb	2.8	3.8	3.7	1.0	0.9	3.2	0.49	2.8	3.8	3.4	1.0	0.6	3.1	0.31		
Ta	0.0	2.8	0.2	2.8	0.2	1.1	-0.82	0.0	2.8	0.5	2.8	0.5	0.8	-0.31		
Hf	0.0	4.5	3.1	4.5	3.1	1.7	1.41	0.0	4.5	2.8	4.5	2.8	1.2	1.57		
Pb	6.0	18.6	5.3	12.5	-0.8	10.8	-5.49	6.0	18.6	10.3	12.5	4.3	9.5	0.77		
La	8.6	22.9	14.1	14.3	5.5	14.0	0.13	8.6	22.9	12.5	14.3	3.9	12.6	-0.06		
Ce	19.0	44.6	30.3	25.6	11.3	28.6	1.68	19.0	44.6	27.7	25.6	8.7	26.1	1.59		
Pr	0.0	5.2	3.9	5.2	3.9	1.9	1.91	0.0	5.2	3.6	5.2	3.6	1.4	2.13		
Nd	8.8	19.3	16.3	10.4	7.5	12.8	3.58	8.8	19.3	15.1	10.4	6.3	11.7	3.35		
Sm	3.3	4.1	4.3	0.8	1.0	3.6	0.70	3.3	4.1	3.8	0.8	0.5	3.5	0.25		
Eu	1.07	0.90	1.10	-0.17	0.04	1.00	0.10	1.07	0.90	1.07	-0.17	0.01	1.02	0.05		
Gd	3.5	3.6	4.3	0.1	0.8	3.5	0.78	3.5	3.6	3.8	0.1	0.3	3.5	0.23		
Tb	0.60	0.61	0.73	0.01	0.13	0.60	0.13	0.60	0.61	0.64	0.01	0.04	0.60	0.04		
Dy	3.6	3.5	4.5	-0.1	0.8	3.6	0.87	3.6	3.5	3.8	-0.1	0.2	3.6	0.20		
Ho	0.74	0.70	0.88	-0.04	0.14	0.73	0.16	0.74	0.70	0.77	-0.04	0.03	0.73	0.04		
Er	2.2	2.2	2.7	0.0	0.5	2.2	0.52	2.2	2.2	2.3	0.0	0.1	2.2	0.11		
Tm	0.30	0.32	0.38	0.02	0.08	0.31	0.07	0.30	0.32	0.32	0.02	0.02	0.31	0.01		
Yb	1.9	2.1	2.4	0.2	0.5	2.0	0.45	1.9	2.1	2.1	0.2	0.1	2.0	0.09		
Lu	0.29	0.33	0.36	0.04	0.07	0.31	0.06	0.29	0.33	0.31	0.04	0.02	0.30	0.01		

* Total iron is given as Fe²⁺

$\Delta F-\Delta M$, difference of the felsic and the mafic end-member; $\Delta H-\Delta M$, difference of the assumed hybrid and the mafic end-member; R, residuals

CHAPTER

2

EU-ANOMALY AND RARE EARTH ELEMENTS ZONING IN CRYSTALS FROM SUBDUCTION ZONE MAGMAS AS INDICATORS FOR PROCESSES AND VOLCANO PLUMBING SYSTEMS: A CASE STUDY OF THE GEDE VOLCANO, WEST-JAVA, INDONESIA

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ABSTRACT

The geochemical behavior of Rare Earth Elements (REE) has been used since a long time to interpret the generation of magmatic rocks and the processes of differentiation. In particular the presence of Eu-anomalies have been successfully used to infer changes in oxygen fugacity and the role of plagioclase crystallization due to its bivalent state in many natural magmas. Earlier works relied on mineral separate analyses and thus had limitations of interpretation due to the possible mineral and melt inclusions that could skew the results. Here we have performed a laser ablation ICP-MS study (more than 450 point analyses) that allows us to determine in situ the REE concentrations of coexisting plagioclase, clinopyroxene, and amphibole in a suite of magmatic rocks from Gede volcano. Our study spans a wide compositional range (basalt to rhyodacite) and also a range of processes (deep and shallow fractional crystallization and magma mixing). We collected the REE within a previous detailed compositional and textural study of the same rocks (Chapter 1) so that our inferences from REEs are supported by a robust petrological and geochemical context. The REE patterns and Eu-anomalies show that mafic magmas and minerals record evidence for early crystallization of amphibole and clinopyroxene that pre-dates plagioclase in many cases. In more evolved magmas and mineral compositions the role of plagioclase crystallization is very important in controlling their Eu-anomalies. However, the negative anomalies of early crystallized clinopyroxene is also controlled by the growth kinetics, and different REE patterns (e.g.

La/Lu) and Eu-anomalies in different sectors of clinopyroxene crystals are the result of fast growth rates related to large undercooling (e.g. > 50 °C/h) according to comparisons to available experimental data. Moreover, our data and review of the literature of REE partition coefficients also show that the effect of oxygen fugacity plays a key role in plagioclase but also probably in clinopyroxene. Decreasing oxygen fugacity leads to higher positive Eu-anomalies in plagioclase, but increasing negative anomalies in clinopyroxene. Eu- anomalies in evolved magmas and minerals are also not only affected by plagioclase crystallization but the crystallization of accessory minerals like apatite can play a significant role. Our detailed study highlights that care needs to be taken when interpreting the REE patterns and Eu-anomalies in minerals, and that plagioclase crystallization alone cannot always explain the presence and size of Eu-anomalies in magmatic crystals.

1. INTRODUCTION

The depth of magma storage and configuration of plumbing system of arc volcanoes are difficult to constrain, but critical for interpretation of monitoring data used in anticipating eruptions. Phase equilibria experimental results can provide some constraints (e.g. Costa *et al.*, 2004; Prouteau & Scaillet, 2003; Rutherford & Devine, 2003; Scaillet & Evans, 1999), also melt inclusion volatile saturation pressures (e.g. Roedder & Bodnar, 1980; Wallace, 2005), or inverse modeling of deformation (e.g. Mattioli *et al.*, 2010; Pritchard & Simons, 2002; Sparks, 2003). However, in magmas with complex magmatic histories involving mixing, mingling and open-system processes these constraints are difficult to apply, because their crystal cargo is a mixture of disparate sources (e.g. Jeffrey *et al.*, 2013; Pallister *et al.*, 1996; see Chapter 1). Geobarometrical calculation from mineral compositions or mineral-melt equilibria can provide some constraints (e.g. Kiss *et al.*, 2014; Putirka, 2008; Ridolfi & Renzulli, 2012; Shane & Smith, 2013), but

unfortunately the volume changes for most reactions involved in igneous system are small and thus not very well constrained (e.g. Adam *et al.*, 2007; Daplé & Baker, 2000; Holland & Blundy, 1994).

An additional source of information that is becoming increasingly available is the trace element compositions (e.g. Rare Earth Elements; REE) of minerals and melts that can be measured in situ via laser-ablation mass spectrometry. Several authors (e.g. Blundy *et al.*, 2008; Kent, 2015; Samaniego *et al.*, 2010; Vukadinovic, 1993) have proposed that the REE patterns and, in particular, the Eu-anomaly ($Eu/Eu^* = Eu_N / \sqrt{Sm_N \times Gd_N}$) (where subscript N stands for normalized with respect to chondrites) can be used to indirectly constrain the pressure and oxygen fugacity (f_{O_2}) of crystallization. This is because plagioclase crystallization is thought to be responsible for the creation of Eu-anomaly and its stability is strongly controlled by water pressure. Here we explore this possibility but also consider the roles of oxygen fugacity and crystal growth kinetics in producing the Eu-anomaly in plagioclase, clinopyroxene, and amphibole.

In this chapter we look at the REE systematics, and in particular the Eu-anomaly of the bulk-rocks, plagioclase, clinopyroxene and amphibole. We show that although the negative Eu-anomaly of some evolved clinopyroxene can be interpreted to be due to shallow crystallization of plagioclase, others are the results of fast growth and oxygen fugacity. Below we first give a summary of results from Chapter 1.

2. SAMPLES AND PREVIOUS WORK

The evolution of Gede volcano was shown to record two main processes: (1) crystallization at various depths and evolution from mafic to silicic liquids, and (2) interactions between the mafic liquids and evolved crystal-rich systems and liquids. Early mafic crystallization is best recorded in the >45 kyr high-alumina basalts where an olivine-amphibole-clinopyroxene phenocryst assemblage grew at high pressure and

water-rich conditions (about 600 MPa, and 6 wt% H₂O). This is a plagioclase absent crystallization that led to the creation of high-Al mafic liquids (stage 1). Additional fractionation of plagioclase, olivine and two pyroxenes from high Al basalts led to the creation of rhyodacitic evolved melts. This occurred at shallow and rather dry (<3 wt% H₂O, about 100 MPa) conditions (Stage 2). We have determined the REE concentrations in amphibole, plagioclase and clinopyroxene from these samples.

Mixing and mingling occurred between (1) mafic and evolved melts and (2) mafic melt and evolved crystal-cumulate as is recorded macroscopically by the textures, and also in the sharp compositional changes in pyroxenes and amphiboles. In addition, some amphibole compositions also record growth from blended melts, rather than directly from any of the two end-member magmas (Chapter 1).

3. ANALYTICAL METHODS

REE in minerals were analyzed in-situ using an Agilent 7500cs ICP-MS equipped with a quadrupole collector coupled with a 193 nm Resonetics M-50E ArF-laser system at the Laboratoire Magmas et Volcans (LMV), Blaise Pascal University, Clermont-Ferrand, France. Laser was set to a constant repetition rate of 4 Hz at 70% laser energy and analyses were conducted for 80 s after a 20 s period of background measurements. In general, a 58 µm (in diameter) laser beam width was employed, but in the cases where sample size or other known conditions (e.g. width zoning pattern) indicated it, spot sizes were adjusted accordingly to smaller (33 or 44 µm) or larger (73 or 100 µm). Precision (1 sigma error) on REE concentrations was between 3% and 6% in amphibole and clinopyroxene, and above 7% in plagioclase. Light REE (La to Nd) in plagioclase are below 10%, but medium REE (Sm to Ho) are between 10% and 20% and heavy REE (Er to Lu) climb above 20%. Precision achieved in the case of both Cpx and Plag from the >45 kyr unit represents the lower end of the range. External calibration was performed

after every 25-30 analyses using the NIST 612 glass reference material as an unknown and the USGS BCR-2g standard for cross-checking. Calcium (^{43}Ca), determined by EPMA, was applied as internal standard (i.e. Fryer *et al.*, 1995). The LA-ICP-MS data was processed and data reduction was done using the GLITTER software (van Achterberg *et al.*, 2001).

4. REVIEW OF EUROPIUM (RARE EARTH ELEMENTS) AND STRONTIUM PARTITIONING IN AMPHIBOLE, CLINOPYROXENE, AND PLAGIOCLASE

Equilibrium crystal-melt trace element partitioning (K_d ; particularly REE) is mainly governed by crystal chemistry and structure, but also pressure, temperature, and volatile fugacities (e.g. Onuma *et al.*, 1968; Blundy & Wood, 1994). In general, increasing pressure decreases the K_d for REE in amphibole (e.g. Adam & Green, 1994; Adam *et al.*, 2007), but increases it in pyroxenes (e.g. Wood & Blundy, 1997 and 2002); whereas increasing temperature and water content of the melt tend to decrease it (e.g. Adam & Green, 1994; Aigner-Torres *et al.*, 2007; Bindeman *et al.*, 1998; Wood & Blundy, 1997 and 2002, Blundy *et al.*, 1998). The crystal chemical effects on partitioning are more complex, REE K_d tend to increase with increasing concentration of the major or minor element in crystals for which it substitutes (e.g. Al^{3+} for REE^{3+}). However, the relation is not straightforward since, for example, in plagioclase the different elastic properties of the anorthite and albite end members have been shown to play a key role (Blundy & Wood, 1994).

The partitioning of Eu in crystals however, critically depends on the oxygen fugacity since Eu^{2+} and Eu^{3+} can co-exist in natural magmatic conditions. In particular, it has been known for quite some time that in a large range of oxygen fugacity ($f\text{O}_2$) Eu exists mainly as Eu^{2+} , and plagioclase incorporates much more Eu compared to other REE because of its different charge and likely substitution mechanism (e.g. Aigner-Torres *et al.*, 2007;

Drake & Weill, 1975; Sun *et al.*, 1974; Wilke & Behrens, 1999). Thus, although the liquid from which plagioclase grows might not have any Eu-anomaly, plagioclase will develop a positive Eu-anomaly. In the results of the Bindeman *et al.* (1998) plagioclase Kd experimental study, the crystals do not have a positive Eu-anomaly because the runs were done in extremely oxidizing conditions (atmospheric air) and thus it is likely that all Eu was present as Eu^{3+} , no different than the rest of the REE.

Eu partitioning in clinopyroxene has also been found to depend on $f\text{O}_2$, albeit to a lesser extent (i.e. Sun *et al.*, 1974). However, the dependence of the partitioning appears to be the opposite of that in plagioclase. Eu^{3+} is more compatible than Eu^{2+} , and thus a clinopyroxene growing from a liquid with no Eu-anomaly can develop a negative anomaly depending on the $f\text{O}_2$. For example, Lofgren *et al.* (2006) ran crystallization experiments under reducing conditions (1.2 log unit above iron-wustite, IW, buffer) and found that clinopyroxene grew with a negative Eu-anomaly. Experiments run at close to the quartz-fayalite-magnetite (QFM) buffer by Mollo *et al.* (2013) found no Eu-anomaly. Moreover, cooling rate experiments run at reducing conditions grew sector zoned Cpx crystals (Lofgren *et al.*, 2006) and found that increasing growth rates generate increasingly negative Eu-anomalies, with the anomaly changing depending on the sector in a systematic manner. The more oxidizing experiments of Mollo *et al.* (2013) did not find an effect on the Eu anomaly with cooling rate but there was an effect on the overall partitioning of REE and other highly charged elements.

The experimentally determined Kd's in amphibole from Dalpé & Baker (2000) do not show any systematic trend in Eu-anomaly, although the Kd compilation by Rollison (1993) does report that amphibole can develop a negative Eu-anomaly even if it grows from liquids without any anomaly. Unfortunately there is no clear evidence on the role of $f\text{O}_2$ or crystallization kinetics in REE partitioning, although one could expect similar

effects as for clinopyroxene if REE incorporation occurs by a similar, but probably more complex mechanism (e.g. substitution for Al^{3+}).

Fig. 1. REE and Eu-anomaly systematics in plagioclase. (a) La, (b) Eu, (c) La/Nd (d) Eu/Eu* versus anorthite (An); (e) spider diagram of REE; (f) Eu/Eu* versus La. Plagioclase shows two different groups based on REE abundance, which may be due to the differences in the crystal structure of the albite- and the anorthite-rich plagioclase. This is seen best in the LREE distribution in plagioclase.

5. TEXTURAL OBSERVATIONS, MAJOR ELEMENT ZONING IN MINERALS AND RELATION TO REE AND EU-ANOMALY

In chapter 1, we reported the textural relations, major, and some trace element systematics of many minerals from all Gede eruptions. Below we describe in some detail how the REE and Eu-anomalies follow the systematics of major element zoning in

minerals. In general, we found that Eu-anomalies become more negative in amphibole and clinopyroxene, whereas more positive in plagioclase with decreasing Mg# or An, respectively (Figs. 1-3). Incompatible elements show positive correlations with REE. In this section we show details of REE and Eu-anomaly behavior in each minerals.

5.1. Plagioclase

Eu-anomaly in plagioclase is always positive showing that Eu is much less incompatible (although K_d^{Eu} is still < 1) than other REE in the plagioclase lattice. REE (e.g. La, Nd and Eu) concentrations show an increase with decreasing An-content which likely reflects the combined effects of K_d increasing with decreasing An (Bindemann *et al*, 1998) and also the increasing amount of REE in progressively differentiated liquids. We also see a kink in the REE concentrations at about An₇₀ as we found for other incompatible elements (Chapter 1) suggesting two slightly different groups (Fig. 1). The plagioclase from the >45 kyr and 10 kyr units has the lowest Eu/Eu*, about 5, whereas plagioclase in the younger (4 and 1.2 kyr) units has twice as much, about 10 (Fig. 1). This means that potentially double amount of >45 kyr plagioclase segregation is needed for creating a given negative Eu-anomaly in the residual liquid compared to the 4 kyr and 1.2 kyr (low-An) plagioclase.

5.2. Amphibole

Amphibole REE patterns vary according to their order of crystallization and incompatible trace element abundances as discussed in Chapter 1. The early crystallized amphiboles from the 45kyr unit and some of the rims of the crystals from the 4 kyr and 1.2 kyr units have the lowest REE contents (e.g. La) and show no or small negative Eu-anomaly (1.05 to 0.9). Amphibole crystallization from a melt with no Eu-anomaly will show small negative anomalies given the existing data on K_d partitioning and the

Fig. 2. REE and Eu-anomaly systematics in amphibole. (a) La, (b) Yb, (c) La/Yb versus Y; (d) Eu/Eu* versus La; (e) Eu/Eu* versus Mg#; (f) spider diagram of REE. >45 kyr amphiboles have the lowest REE concentration and the least negative Eu-anomaly. Some of the overgrowth rims of the younger amphiboles overlap with the >45 kyr ones suggesting similar origin. Note the increasing Eu/Eu* with decreasing Mg# in the >45 kyr amphiboles, and the opposite in the younger ones, suggesting absence and presence of plagioclase, respectively (shown schematically by the arrows). Symbols are as in Fig. 1.

presence of variable concentrations of Eu^{2+} and Eu^{3+} in the liquid. With increasing concentrations of incompatible elements and REE the amphiboles show a progressively more negative Eu-anomaly, reflecting crystallization from more evolved liquids that had negative Eu-anomalies, probably the result of mixing between the mafic and evolved melts, rather than amphibole crystallization from evolved liquids (Chapter 1). The La/Yb

values show a limited variability overall, but they tend to increase with increasing incompatible elements. The variation of Sr vs Eu anomaly does not show a clear trend that could enable to differentiate between amphiboles that grew before or after plagioclase crystallization (Fig. 2.f). This could reflect the complex evolution of a liquid that would first grow amphibole and other mafic minerals and thus have increasing Sr and a rather constant Eu/Eu*, but once plagioclase starts to crystallize, Sr and Eu/Eu* would decrease. Amphiboles that grew from mixing of these liquids would fill the gap between the two trends and thus give a complex image of the processes. We believe that similar processes are recorded in the clinopyroxene, albeit in a clearer manner (see below).

5.3. Clinopyroxene

Clinopyroxene REE patterns and Eu-anomalies follow similar trends to those of the amphiboles, although the range of variation is more extreme. The lowest concentrations of REE and incompatible elements are also those having the smallest negative Eu-anomalies and are found in Cpx crystals from the >45 kyr, and rims of the 10 kyr, 4 kyr, 1.2 kyr ones. These are also the crystals with the highest Mg#. In detail, the >45 kyr Cpx are somewhat different from the rest. For instance, La concentration is somewhat lower at a given Mg# (or Y) than in the other units. La/Yb ratio correlates negatively with Mg# and positively with Y. The >45 kyr Cpx have somewhat lower La/Yb values at a given Mg# than the Holocene ones (Fig. 3). The small negative Eu-anomalies of these mafic pyroxenes reflect the various processes including plagioclase crystallization, the effect of oxygen fugacity on the Kd and also crystal kinetics (see discussion section).

The evolved low Mg# cores of the 4 kyr and 1.2 kyr units have larger negative Eu-anomalies (down to about 0.4) and the highest concentrations of incompatible elements, including REE. These evolved Cpx crystals grew after/during plagioclase crystallization. The distribution of Sr vs Eu/Eu* can potentially track the relative order of plagioclase

Fig. 3. REE and Eu-anomaly systematics in clinopyroxene. (a) La, (b) Yb, (c) La/Yb versus Mg#; (d) Eu/Eu* versus La; (e) Eu/Eu* versus Sr. Note that Cpx of the >45 kyr and rims of 4 and 1.2 kyr units show a more or less horizontal array that implies no or limited plagioclase crystallization, since we interpret it as increasing Sr with roughly constant Eu/Eu*. In contrast the decreasing trend of the more evolved Cpx starts at the highest Sr concentrations and reflects plagioclase crystallization (arrows show the likely evolution of the system). Mixing between the different liquids likely lead to the rest of the scatter of the data. (f) spider diagram of REE. Symbols are as in Fig. 1.

crystallization. However, we find a complex pattern that shows first an increase of Sr with limited change in Eu/Eu* due to crystallization of mafic minerals (e.g. > 45 kyr unit crystals), followed by a simultaneous decrease of Sr and Eu/Eu* once plagioclase starts to crystallize and liquids becomes more evolved as recorded by the lower Sr and Eu/Eu*

Fig. 4. REE and Eu-anomaly systematics in a >45 kyr sector zoned clinopyroxene. Note the different concentrations in the sectors being controlled by different Al³⁺ contents and how there are systematic changes between both sectors from core to rim.

values of the low-Mg# Cpx crystals. Mixing between the mafic and felsic liquids could give Cpx with intermediate compositions.

Many of the >45 kyr clinopyroxenes show strong sector zoning in major elements (e.g. Al, Ti, Mg) and also in their REE distribution.

We have done core to rim traverses in two different sectors of a large crystal and found that the high-Al sectors have significantly higher REE concentrations (Fig 4), as can be expected from crystal-site substitution effects (e.g. Blundy & Wood, 1994). Moreover, we found that the higher REE³⁺ sector has more negative Eu-anomaly than the sector with lower REE concentrations. It has been experimentally shown that Eu-

anomaly and REE concentration increases with increasing cooling rate (e.g. Lofgren *et al.*, 2006; Mollo *et al.*, 2013), which also promotes the appearance of sector- and oscillatory zoning patterns (e.g. Dowty, 1976) and probably reflects the differences of REE, Al and Eu/Eu* between sectors (see discussion).

Fig. 5. REE, their ratios, and Eu-anomaly in the whole rocks and calculated liquid line of descent. *Dashed lines* indicate boundaries between rock types (basalt, basaltic andesite, andesite, and dacite) inferred from Figure 18.a in chapter 1. Note that none of the models reproduces the exact observed whole rock REE ratio compositions, but truthfully returns the observed trends.

Table 1. Whole rock REE composition of samples from Gede eruption products.

wt%	>45 kyr					10 kyr		
	Ayam-1	Ayam-2	Ayam-3	Ayam-5	G130	Gek-1	Cig-2	Cig-3
SiO ₂	51.36	51.15	51.32	51.75	53.65	55.01	55.06	56.37
ppm								
La	8.9	8.3	8.0	10.0	18.9	12.0	14.0	16.5
Ce	19.6	19.5	19.1	22.3	34.0	27.0	30.2	34.9
Pr		2.7	2.6	3.1	4.5	3.5	3.9	4.5
Nd	9.1	12.2	12.0	14.2	19.5	15.2	16.4	18.5
Sm		3.4	3.3	3.8	4.9	3.9	4.0	4.5
Eu		1.09	1.09	1.23	1.36	1.19	1.20	1.29
Gd		3.6	3.4	3.9	4.8	3.9	3.9	4.3
Tb		0.61	0.60	0.67	0.78	0.66	0.65	0.71
Dy		3.7	3.6	4.0	4.7	4.0	3.9	4.3
Ho		0.77	0.74	0.83	0.95	0.81	0.79	0.86
Er		2.2	2.2	2.4	2.9	2.4	2.4	2.6
Tm		0.32	0.31	0.34	0.40	0.35	0.34	0.37
Yb		2.0	2.0	2.2	2.6	2.2	2.2	2.4
Lu		0.3	0.3	0.3	0.4	0.3	0.3	0.4
Eu/Eu*		0.96	0.99	0.98	0.85	0.93	0.92	0.90

Table 1. continued

wt%	4 kyr							
	Cip-1	Cip-5	Cip-6	Cip-2	Cip-3B	Cip-4	Cip-4A	Cip-4B
SiO ₂	56.08	55.67	55.78	56.29	60.01	59.77	57.35	57.58
ppm								
La	14.7	13.0	13.5	14.4	16.8	16.9	15.2	15.2
Ce	32.5	29.8	31.0	30.7	36.4	36.8	33.5	33.0
Pr	4.2	3.9	4.0	3.9	4.4	4.5	4.2	4.2
Nd	18.0	16.8	17.4	16.3	18.0	18.5	17.5	17.4
Sm	4.5	4.2	4.3	4.1	4.3	4.4	4.3	4.3
Eu	1.22	1.24	1.24	1.13	1.10	1.12	1.15	1.13
Gd	4.5	4.2	4.3	4.1	4.0	4.2	4.3	4.2
Tb	0.75	0.71	0.72	0.69	0.69	0.70	0.72	0.71
Dy	4.4	4.2	4.3	4.2	4.0	4.2	4.3	4.3
Ho	0.90	0.86	0.86	0.84	0.80	0.83	0.87	0.86
Er	2.6	2.5	2.6	2.5	2.4	2.5	2.5	2.6
Tm	0.39	0.37	0.37	0.36	0.35	0.36	0.38	0.37
Yb	2.4	2.3	2.4	2.3	2.2	2.3	2.3	2.4
Lu	0.38	0.36	0.37	0.35	0.35	0.36	0.36	0.36
Eu/Eu*	0.83	0.91	0.88	0.84	0.81	0.79	0.82	0.81

Table 1. continued

wt%	4 kyr							
	Cip-8	G3D	G3L	Cip-11	Cip-13	Cip-14	Cip-15	CPN-7
SiO ₂	59.84	55.69	60.39	54.44	56.83	59.63	58.94	58.58
<i>ppm</i>								
La	17.3		17.9	12.7	14.6	16.8	17.4	16.2
Ce	37.6		36.8	27.5	32.1	36.4	36.6	33.8
Pr	4.6		4.5	3.5	4.1	4.5	4.5	4.2
Nd	19.1		18.0	15.1	16.8	18.4	18.4	17.7
Sm	4.5		4.3	3.9	4.2	4.4	4.5	4.4
Eu	1.12		1.06	1.11	1.13	1.12	1.13	1.12
Gd	4.4		4.0	4.0	4.2	4.2	4.3	4.2
Tb	0.73		0.68	0.68	0.72	0.71	0.71	0.72
Dy	4.3		4.1	4.0	4.2	4.2	4.2	4.2
Ho	0.86		0.83	0.82	0.87	0.85	0.85	0.87
Er	2.6		2.4	2.5	2.6	2.5	2.5	2.6
Tm	0.38		0.36	0.35	0.38	0.36	0.37	0.37
Yb	2.4		2.3	2.2	2.3	2.3	2.3	2.5
Lu	0.4		0.4	0.3	0.4	0.4	0.4	0.4
Eu/Eu*	0.77		0.78	0.86	0.82	0.79	0.79	0.79

Table 1. continued

wt%	1.2 kyr							
	CPN-8A	CPN-8B	CPN-9	CPN-10A	CPN-10B	Pata-1	Pata-2	Pata-3
SiO ₂	55.46	60.32	55.28	55.35	58.33	56.14	59.11	55.46
<i>ppm</i>								
La	14.1	18.4	13.8	13.6	16.3	14.8	17.0	12.8
Ce	30.3	37.8	29.8	29.4	34.0	32.4	37.8	28.8
Pr	3.9	4.7	3.8	3.8	4.3	4.2	4.8	3.7
Nd	16.3	19.4	16.1	16.2	17.7	18.0	20.6	15.7
Sm	4.3	4.6	4.3	4.2	4.5	4.5	5.0	4.0
Eu	1.10	1.13	1.11	1.11	1.10	1.25	1.25	1.16
Gd	4.3	4.5	4.2	4.2	4.2	4.5	5.0	4.0
Tb	0.73	0.74	0.72	0.71	0.72	0.74	0.83	0.69
Dy	4.5	4.4	4.4	4.2	4.4	4.5	5.0	4.1
Ho	0.88	0.88	0.87	0.86	0.86	0.90	1.01	0.83
Er	2.7	2.6	2.6	2.5	2.6	2.7	3.0	2.5
Tm	0.38	0.37	0.37	0.37	0.37	0.39	0.45	0.36
Yb	2.4	2.4	2.4	2.4	2.4	2.4	2.8	2.3
Lu	0.36	0.35	0.35	0.35	0.36	0.38	0.44	0.35
Eu/Eu*	0.78	0.76	0.80	0.81	0.77	0.85	0.76	0.88

Table 1. continued

wt%	1.2 kyr							
	Pata-4	Pata-5	Pata-6	Pata-7	SPata-1 [†]	Tega-1	Tega-2	GB1
SiO ₂	54.61	55.19	59.97	69.09	54.85	55.02	55.56	61.61
ppm								
La	12.5	12.4	17.6	22.9	13.5	13.7	13.3	20.7
Ce	27.7	27.9	37.6	44.6	30.1	29.1	29.5	41.9
Pr	3.6		4.6	5.2	3.8	3.6	4.0	5.2
Nd	15.1	12.6	18.5	19.3	16.3	15.3	17.1	21.0
Sm	3.8		4.4	4.1	4.1	3.8	4.4	4.9
Eu	1.07		1.08	0.90	1.12	1.07	1.26	1.11
Gd	3.8		4.1	3.6	4.1	3.8	4.3	4.7
Tb	0.64		0.70	0.61	0.70	0.63	0.72	0.77
Dy	3.8		4.1	3.5	4.2	3.8	4.3	4.6
Ho	0.77		0.83	0.70	0.84	0.75	0.85	0.92
Er	2.3		2.5	2.2	2.5	2.3	2.5	2.7
Tm	0.32		0.36	0.32	0.36	0.32	0.37	0.39
Yb	2.1		2.3	2.1	2.3	2.0	2.3	2.6
Lu	0.3		0.4	0.3	0.3	0.3	0.4	0.4
Eu/Eu*	0.31		0.78	0.71	0.84	0.86	0.89	0.71

Table 1. continued

wt%	1 kyr							
	GP1	PanPF2	PanPF2/2	SMT-1	SMT-2	SMT-3	SMT-4A	SMT-4B
SiO ₂	60.64	65.26	66.60	55.42	57.65	52.60	55.46	55.76
ppm								
La	19.4	22.4	23.8	10.8	15.4	9.9	12.9	16.5
Ce	39.2	43.9	45.7	22.9	31.7	21.7	29.2	37.2
Pr	4.8	5.2	5.4	2.9	3.9	2.7	3.9	5.0
Nd	19.5	20.2	20.6	11.7	16.4	11.9	17.0	22.1
Sm	4.6	4.5	4.6	2.9	3.9	3.0	4.4	5.6
Eu	1.06	0.98	0.95	0.97	1.04	0.98	1.23	1.37
Gd	4.3	3.9	3.9	2.8	3.7	3.1	4.4	5.6
Tb	0.72	0.66	0.62	0.47	0.62	0.51	0.70	0.94
Dy	4.3	3.8	3.7	2.8	3.6	3.0	4.4	5.7
Ho	0.86	0.80	0.76	0.60	0.75	0.64	0.89	1.11
Er	2.7	2.3	2.3	1.8	2.2	1.9	2.6	3.3
Tm	0.37	0.35	0.33	0.28	0.33	0.28	0.38	0.45
Yb	2.4	2.2	2.2	1.7	2.1	1.6	2.4	2.9
Lu	0.37	0.34	0.33	0.28	0.31	0.25	0.35	0.41
Eu/Eu*	0.73	0.71	0.69	1.05	0.83	0.98	0.86	0.74

Table 1. continued

wt%	1 kyr							
	SMT-5A	SMT-5B	SMT-7A	SMT-7B	SMT-12	G134	GPF8	GPF10
SiO ₂	52.20	52.09	52.03	54.17	58.62	61.05	54.59	53.91
<i>ppm</i>								
La	9.8	9.9	9.8	10.9	17.2	21.4	12.2	11.7
Ce	21.6	21.9	21.7	23.8	35.3	45.9	26.2	25.1
Pr	2.7	2.8	2.8	3.0	4.4	5.8	3.3	3.1
Nd	11.7	11.7	11.8	12.7	17.9	24.5	13.8	13.4
Sm	3.0	3.0	3.1	3.2	4.4	6.0	3.2	3.2
Eu	0.99	1.01	1.00	1.05	1.10	1.27	1.04	1.02
Gd	3.1	3.1	3.1	3.0	4.1	5.6	3.1	3.2
Tb	0.52	0.52	0.52	0.50	0.66	0.87	0.52	0.53
Dy	2.9	2.9	3.0	2.9	3.9	5.3	3.0	3.0
Ho	0.65	0.67	0.65	0.59	0.81	1.02	0.63	0.62
Er	1.8	1.9	1.8	1.8	2.3	3.1	1.9	1.9
Tm	0.27	0.27	0.27	0.27	0.34	0.43	0.27	0.28
Yb	1.6	1.6	1.6	1.7	2.2	2.8	1.7	1.6
Lu	0.3	0.3	0.3	0.3	0.3	0.4	0.3	0.3
Eu/Eu*	0.99	1.02	0.98	1.05	0.80	0.68	1.00	0.97

Table 1. continued

wt%	1840?		1955-57?		
	GB2	G385	G385/2	G384	ALUN
SiO ₂	52.41	58.64	59.92	60.74	58.37
<i>ppm</i>					
La	9.9	17.2	17.5	20.0	16.9
Ce	21.7	35.2	35.7	40.5	34.7
Pr	2.8	4.4	4.3	5.0	4.3
Nd	12.0	18.2	17.7	20.4	17.8
Sm	3.1	4.4	4.3	4.8	4.2
Eu	1.00	1.10	1.06	1.08	1.06
Gd	3.2	4.0	3.9	4.5	3.9
Tb	0.54	0.65	0.64	0.73	0.66
Dy	3.2	4.0	3.7	4.4	3.8
Ho	0.67	0.80	0.77	0.89	0.79
Er	1.9	2.3	2.3	2.7	2.3
Tm	0.28	0.34	0.34	0.38	0.34
Yb	1.6	2.2	2.1	2.4	2.1
Lu	0.28	0.33	0.32	0.35	0.32
Eu/Eu*	0.97	0.80	0.80	0.71	0.80

6. WHOLE ROCK GEOCHEMISTRY: RARE EARTH ELEMENTS

Bulk-rocks of Gede show a slight negative Eu-anomaly in the basaltic magmas, but more evolved compositions show progressively increasing negative anomalies down to $\text{Eu}/\text{Eu}^* = 0.7$ in the rhyodacitic whole rocks (Fig. 5; Table 1). The negative Eu-anomaly increases with increasing concentrations of incompatible trace elements, including REE. La/Yb and La/Nd increase, whereas Dy/Yb decreases with increasing concentrations of incompatible elements. In general, we find that the LREE (e.g. La) form linear trends in whole rock compositions, whereas MREE and HREE (e.g. Eu and Yb) exhibit rather scattered distribution on diagrams plotted against Rb (Fig. 5). The high-Al rocks (>20 wt%) from the >45 kyr and 10 kyr units do not show a positive Eu anomaly, indicating again that their compositions are not due simply to plagioclase accumulation.

The mafic rocks from the 1 kyr unit stand out from most of the REE trends defined by the other units by their high La/Yb and La/Nd for a given concentration of incompatible elements. The high La/Yb (about 7) compared to the >45kyr rocks (La/Yb = about 4) is due to lower HREE concentrations in the 1 kyr unit and thus probably reflects a mantle source with larger amounts of residual garnet (e.g. Davidson *et al.*, 2007).

The changes in La/Yb and Eu anomaly with increasing incompatible elements reflect the two-stage differentiation that we proposed in Chapter 1. The first one (stage 1) was deep and water rich, and controlled by amphibole, olivine (plus or minus Cr-spinel) and clinopyroxene, but free of plagioclase. Crystallization of such an assemblage would produce liquids with increasing La/Yb and roughly constant Eu/Eu^* with increasing incompatible elements, and can explain some of the trends (Fig 5). A similar explanation was given by Davidson *et al.* (2007) although they did not have explicit evidence for the presence of amphibole in the Gede rocks. The second major crystallization environment (stage 2) was much shallower and dominated by plagioclase, pyroxenes (plus or minus olivine) and apatite (Chapter 1). Such a crystallizing mineral assemblage can lead to

evolved liquids, but the evolution is done at more or less constant La/Yb and strongly decreasing Eu/Eu* with increasing compatible elements (e.g. Rb). Mixing between these two end members could explain the rest of the bulk-rocks from Gede.

7. DISCUSSION

A negative Eu-anomaly in melt and/or in mafic minerals is traditionally attributed to plagioclase crystallization, which implies that water pressure is low enough for stabilizing plagioclase (e.g. Danyushevsky *et al.*, 2003; Bachmann & Bergantz, 2008). However, a literature review of partition coefficients for clinopyroxene and amphibole also shows that these minerals will grow with a negative Eu-anomaly within the natural ranges of fO_2 even if the liquid does not have a negative Eu-anomaly. Moreover, the size of the anomaly also seems dependent on the growth rates, at least for clinopyroxene. Below we discuss in some detail the evidence for clinopyroxene growth before plagioclase, the effects of crystallization kinetics, and the evidence for growth of clinopyroxene and amphibole after/during plagioclase crystallization.

7.1. What caused the moderate negative Eu-anomalies and REE patterns in mafic clinopyroxenes?

7.1.1. The 'plagioclase-effect' in Eu-anomalies of clinopyroxene

The Cpx crystals from the >45 kyr unit and some of the rims of the 4ky and 1.2 kyr units show moderate deficits in Eu compared to other REE ($Eu/Eu^* = 0.68-0.88$; Table 2, Fig. 3), whereas amphibole shows no or small negative Eu-anomalies (about 0.9 to 1; Fig. 2). High-Ca plagioclase (An_{90}) of the same unit shows a major positive anomaly (Eu/Eu^* is about 5.5; Table 2, Fig. 1). In Chapter 1 we presented evidence for amphibole crystallization before plagioclase in the > 45 kyr unit which is consistent with the lack of

Eu-anomaly. Here we test the extent to which plagioclase preceded Cpx crystallization by making a series of calculations for the Eu and Sr balance in Cpx, Plag and bulk-rocks (Table 2, Fig. 6).

The variables involved in this exercise are the Kds of Eu in plagioclase and clinopyroxene (which aside from major element composition depend also on fO_2), and the amount of plagioclase crystallized. We aimed at reproducing the measured REE concentrations and Eu anomalies of plagioclase and clinopyroxene of the >45 kyr unit. Although amphibole is also present we disregarded it, because it is a minor phase (about 2 wt%) and should have a limited effect on the Eu anomaly (if anything it would make the liquid with a slightly positive value). We tested three different scenarios: (A) first we aimed at reproducing the Eu anomaly and REE patterns in plagioclase by varying its ^{Eu}Kd and amount, and checking whether this explains the Eu anomaly in Cpx using ^{Eu}Kd after Blundy & Wood (1997, 2002). We determined the magma fO_2 during plagioclase crystallization using the equations of Wilke & Behrens (1999). (B) We then varied the ^{Eu}Kd in Cpx until we found a good match to the naturally observed REE pattern and we check if the implied fO_2 from Eu in Cpx was compatible with that of Eu in plag using the equations of Sun *et al.* (1974). (C) Finally, we tested if Cpx crystallization without Plag reproduces the observed REE pattern and abundance and at what fO_2 would it be possible (Table 2, Fig. 6). We have also used the Sr vs Eu^*/Eu relations shown by Cpx (Fig. 3) to obtain additional constraints.

We use REE partition coefficients for Plag (An_{90}) from Bindeman *et al.* (1998) except for Eu because the Bindeman *et al.* (1998) experiments were done in air so that most Eu was oxidized to 3+; Sr is from Blundy & Wood (1991). The REE Kd in Cpx are calculated after Wood & Blundy (1997, 2002) and Blundy & Wood (2003), Sr is from Wood & Trigila (2001). Kds of Wood & Blundy (1997, 2002) are not dependent on fO_2 , but such dependence has been experimentally calibrated (Sun *et al.* 1974).

Table 2. Selected REE and Eu/Eu* calculation in >45kyr Stage1 plagioclase and clinopyroxene

element	La	Ce	Sm	Eu	Gd	Eu/Eu*	Lu	Sr
CI chondrite			0.153	0.058	0.2055			
C ₀ PM	8	19	3.3	1.07	3.4	0.98	0.42	322
>45 kyr Plag	0.60-	1.28-	0.17-	0.27-0.4	0.16-	4.000-7.000	0.015-	490-600
	0.98	1.84	0.28		0.23		0.021	
>45 kyr Cpx	0.75-	3.55-	2.4-5.4	0.8-1.4	3.2-6.7	0.675-0.887	0.24-	16-22
	1.6	7.4					0.56	
C _d (G130)	18.9	34	4.9	1.36	4.8	0.857	0.38	369.9
apparent Kd Plag	0.04-	0.04-	0.035-	0.199-0.294	0.033-		0.074-	1.324-
	0.48	0.053	0.053		0.048		0.089	1.622
apparent Kd Cpx	0.04-	0.104-	0.49-	0.588-1.029	0.666-		0.632-	0.043-
	0.85	0.218	1.102		1.396		1.474	0.059
F = 10% plag								
Kd Plag	0.136	0.079	0.054	0.178	0.278	0.378	0.478	0.050
Kd 1 Cpx	0.106	0.171	0.567	0.647	0.647	0.647	0.647	0.713
Kd 2 Cpx	0.134	0.216	0.717	0.819	0.819	0.819	0.819	0.902
Kd 1 Cpx	0.106	0.171	0.567	0.547	0.447	0.347	0.247	0.713
Kd 2 Cpx	0.134	0.216	0.717	0.719	0.619	0.519	0.419	0.902
in Plag (ppm)	1.19	1.65	0.20	0.21	0.32	0.43	0.54	0.19
in liquid (ppm)	8.76	20.94	3.65	1.17	1.15	1.14	1.13	3.76
in Cpx 1 (ppm)	0.98	3.78	2.13	0.77	0.77	0.76	0.75	2.73
in Cpx 2 (ppm)	1.24	4.76	2.66	0.97	0.96	0.95	0.94	3.41
in liquid 1 (ppm)	9.31	22.14	3.75	1.18	1.18	1.18	1.18	3.83
in liquid 2 (ppm)	9.29	22.07	3.72	1.17	1.17	1.17	1.17	3.78
in Cpx 1 (ppm)	0.98	3.78	2.13	0.65	0.54	0.42	0.30	2.73
in Cpx 2 (ppm)	1.24	4.76	2.66	0.85	0.73	0.62	0.50	3.41
in liquid 1 (ppm)	9.31	22.14	3.75	1.19	1.20	1.21	1.21	3.83
in liquid 2 (ppm)	9.29	22.07	3.72	1.18	1.18	1.19	1.20	3.78

Kds are at 1060 °C; Cpx Kd¹ & Kd² is after Wood & Blundy (1997, 2002) at 1 GPa, 5wt% & 3wt% H₂O, respectively; C₀ is the parent magma. Scenario A is marked by grey color, Scenario B is by blue, and Scenario C (where Cpx formed a priori Plag) is by pink.

Table 2. continued

	La	Ce	Sm	Eu		Gd	Eu/Eu*		Lu	Sr
F = 20% plag										
Kd Plag	0.136	0.079	0.054	0.178	0.278	0.378	0.478	0.050	3.406	0.053
Kd 1 Cpx	0.106	0.171	0.567	0.647	0.647	0.647	0.647	0.713	1.018	1.364
Kd 2 Cpx	0.134	0.216	0.717	0.819	0.819	0.819	0.819	0.902	1.018	0.04
Kd 1 Cpx	0.106	0.171	0.567	0.547	0.447	0.347	0.247	0.713	0.861	0.05
Kd 2 Cpx	0.134	0.216	0.717	0.719	0.619	0.519	0.419	0.902	0.894	0.04
in Plag (ppm)	1.32	1.84	0.22	0.23	0.35	0.46	0.57	0.21	3.235	0.05
in liquid (ppm)	9.70	23.34	4.08	1.29	1.26	1.23	1.20	4.20	0.950	404.9
in Cpx 1 (ppm)	1.09	4.21	2.38	0.85	0.83	0.81	0.80	3.06	0.966	0.52
in Cpx 2 (ppm)	1.37	5.31	2.98	1.07	1.04	1.02	1.00	3.82	0.966	0.364
in liquid 1 (ppm)	10.30	24.67	4.20	1.32	1.29	1.26	1.23	4.28	0.949	12.667
in liquid 2 (ppm)	10.28	24.60	4.15	1.30	1.27	1.24	1.22	4.23	0.949	15.823
in Cpx 1 (ppm)	1.09	4.21	2.38	0.71	0.58	0.46	0.33	3.06	0.804	0.53
in Cpx 2 (ppm)	1.37	5.31	2.98	0.92	0.80	0.67	0.55	3.82	0.835	316.45
in liquid 1 (ppm)	10.30	24.67	4.20	1.30	1.30	1.31	1.32	4.28	0.934	0.53
in liquid 2 (ppm)	10.28	24.60	4.15	1.28	1.29	1.30	1.31	4.23	0.934	316.67
F = 30% plag										
Kd Plag	0.136	0.079	0.054	0.178	0.278	0.378	0.478	0.050	3.406	0.053
Kd 1 Cpx	0.106	0.171	0.567	0.647	0.647	0.647	0.647	0.713	1.018	1.364
Kd 2 Cpx	0.134	0.216	0.717	0.819	0.819	0.819	0.819	0.902	1.018	0.04
Kd 1 Cpx	0.106	0.171	0.567	0.547	0.447	0.347	0.247	0.713	0.861	0.05
Kd 2 Cpx	0.134	0.216	0.717	0.719	0.619	0.519	0.419	0.902	0.894	0.04
in Plag (ppm)	1.48	2.08	0.25	0.26	0.38	0.50	0.62	0.24	3.175	0.05
in liquid (ppm)	10.89	26.39	4.62	1.43	1.38	1.34	1.29	4.77	0.934	443.1
in Cpx 1 (ppm)	1.22	4.76	2.70	0.95	0.92	0.89	0.85	3.47	0.950	0.59
in Cpx 2 (ppm)	1.54	6.01	3.38	1.19	1.15	1.11	1.07	4.33	0.950	0.41
in liquid 1 (ppm)	11.56	27.90	4.76	1.47	1.42	1.37	1.32	4.86	0.933	0.49
in liquid 2 (ppm)	11.54	27.82	4.71	1.45	1.40	1.35	1.30	4.80	0.933	301.64
in Cpx 1 (ppm)	1.22	4.76	2.70	0.78	0.64	0.50	0.36	3.47	0.780	301.44
in Cpx 2 (ppm)	1.54	6.01	3.38	1.01	0.88	0.74	0.60	4.33	0.810	12.67
in liquid 1 (ppm)	11.56	27.90	4.76	1.43	1.44	1.45	1.46	4.86	0.907	15.82
in liquid 2 (ppm)	11.54	27.82	4.71	1.41	1.42	1.43	1.44	4.80	0.907	301.64

Table 2. continued

	La	Ce	Sm	Eu		Gd	Eu/Eu*		Lu	Sr				
F = 50% plag														
Kd Plag	0.136	0.079	0.054	0.178	0.278	0.378	0.478	0.050	3.406	5.321	7.236	9.153	0.053	1.364
Kd 1 Cpx	0.106	0.171	0.567	0.647	0.647	0.647	0.647	0.713	1.018	1.018	1.018	1.018	0.687	0.04
Kd 2 Cpx	0.134	0.216	0.717	0.819	0.819	0.819	0.819	0.902	1.018	1.018	1.018	1.018	0.817	0.05
Kd 1 Cpx	0.106	0.171	0.567	0.547	0.447	0.347	0.247	0.713	0.861	0.703	0.546	0.389	0.664	0.04
Kd 2 Cpx	0.134	0.216	0.717	0.719	0.619	0.519	0.419	0.902	0.894	0.769	0.645	0.521	0.525	0.05
in Plag (ppm)	1.98	2.84	0.35	0.34	0.49	0.62	0.73	0.33	3.049	4.444	5.639	6.654	0.043	341.268
<i>in liquid (ppm)</i>	14.56	35.98	6.36	1.89	1.77	1.65	1.54	6.57	0.895	0.835	0.779	0.727	0.81	250.20
<i>in Cpx 1 (ppm)</i>	1.63	6.49	3.71	1.25	1.17	1.09	1.02	4.78	0.911	0.850	0.793	0.740	0.568	10.675
<i>in Cpx 2 (ppm)</i>	2.06	8.19	4.64	1.57	1.46	1.36	1.27	5.96	0.911	0.850	0.793	0.740	0.670	13.335
<i>in liquid 1 (ppm)</i>	15.46	38.04	6.54	1.94	1.81	1.69	1.57	6.70	0.895	0.835	0.779	0.727	0.83	266.87
<i>in liquid 2 (ppm)</i>	15.43	37.92	6.48	1.91	1.79	1.67	1.56	6.61	0.895	0.835	0.779	0.727	0.82	266.69
<i>in Cpx 1 (ppm)</i>	1.63	6.49	3.71	1.00	0.82	0.64	0.46	4.78	0.723	0.595	0.465	0.333	0.550	10.675
<i>in Cpx 2 (ppm)</i>	2.06	8.19	4.64	1.29	1.12	0.95	0.77	5.96	0.751	0.651	0.549	0.446	0.439	13.335
<i>in liquid 1 (ppm)</i>	15.46	38.04	6.54	1.82	1.83	1.84	1.86	6.70	0.840	0.846	0.852	0.858	0.83	266.87
<i>in liquid 2 (ppm)</i>	15.43	37.92	6.48	1.80	1.81	1.82	1.84	6.61	0.840	0.846	0.852	0.857	0.84	266.69
no Plag														
Kd 1 Cpx	0.106	0.171	0.567	0.547	0.447	0.347	0.247	0.713	0.861	0.703	0.546	0.389	0.664	0.04
Kd 2 Cpx	0.134	0.216	0.717	0.719	0.619	0.519	0.419	0.902	0.894	0.769	0.645	0.521	0.525	0.05
Cpx 1 (ppm)	0.90	3.43	1.93	0.60	0.50	0.39	0.28	2.47	0.846	0.696	0.544	0.390	0.295	13.738
Cpx 2 (ppm)	1.13	4.32	2.41	0.78	0.68	0.57	0.47	3.09	0.878	0.761	0.642	0.522	0.348	17.161
<i>liquid 1 (ppm)</i>	8.50	20.09	3.40	1.10	1.11	1.12	1.13	3.47	0.983	0.989	0.996	1.003	0.429	343.460
<i>liquid 2 (ppm)</i>	8.48	20.03	3.36	1.09	1.10	1.11	1.11	3.42	0.983	0.989	0.996	1.003	0.425	343.230

As parent liquid, we chose the calculated PM composition in Chapter 1, which has a negligible Eu-anomaly ($\text{Eu}/\text{Eu}^* = 0.98$) (Table 1 & 2).

We found that the best match for Eu and Eu/Eu^* in Plag occurred with a $K_d = 0.28$ and crystallization of 20-30% of An_{90} plagioclase (Scenario A). This best estimate K_d^{Eu} in plagioclase (0.28) is also within the values that we obtain if we calculate the apparent K_d^{Eu} using the measured concentrations in the plagioclase and bulk-rocks (Table 2). Using the Wilke & Behrens (1999) formulation with parameter values for basaltic melt (at 1200 °C and atmospheric pressure; Weill & McKay, 1975) we found that this K_d implies a $\log f\text{O}_2 = -7.9$ bar for the >45 kyr Plag, which corresponds to 0.3 log units above the QFM buffer (QFM buffer according to Wones & Gilbert, 1969). Correcting for temperature and assuming the same temperature dependence, the buffer gives a $\log f\text{O}_2$ of about -9.8 bar. Using the equation of Sun *et al.* (1974) the calculated redox state is $f\text{O}_2 = -9.7$ bar, virtually within error of Wilke & Behrens (1999).

Using these conditions it becomes apparent that it is not possible to reproduce the observed Eu-anomaly in Cpx using a K_d calculated from Wood & Blundy (1997, 2002; using 3-5 wt% H_2O ; $K_d^{\text{Eu}} = 0.82\text{-}0.65$). In other words, the >45 kyr Cpx has a more negative Eu-anomaly than what we calculated in scenario A. The best match for Eu/Eu^* in Cpx needs about 50-80% of plagioclase crystallization. However, this results in very high REE concentrations in Plag (Fig. 6, Table 2) and would lead to major element concentrations in the residual liquid that are very different from the bulk-rocks. To match the data we need to decrease the K_d^{Eu} in Cpx (Scenario B) by 12-15% (from 0.82-0.65 to 0.72-0.55) and have 30% of Plag crystallization. In detail, the best match of K_d that also reproduces the absolute REE is in the high range of K_d s, about 0.72 (Table 2). The lower K_d^{Eu} , or rather the more negative Eu-anomaly, in the >45 kyr Cpx could be in part explained by a lower $f\text{O}_2$, although, as shown by Sun *et al.* (1974), K_d is less $f\text{O}_2$ dependent (a change of about a factor of two with a change of the $f\text{O}_2$ by 6 orders of

magnitude). Using the $\log f\text{O}_2$ value (-9.7 bar) calculated from Plag Eu Kd above we calculate a $\text{Kd}^{\text{Eu}} = 0.77$ for Cpx at 1060 °C. This is not very different from our best estimate (0.72) but would imply an $f\text{O}_2$ of 0.2 log units below the QFM buffer, thus 0.5 log units more reducing than the plagioclase estimate.

In our last setup (Scenario C), we find that to fit the Eu-anomaly in Cpx without plagioclase we need to lower the Kd^{Eu} in Cpx even more, and its crystallization could result in very similar REE pattern compared to Scenario B (Fig. 6). La, Ce, and Lu would be within the observed natural range. The Kd^{Eu} in Cpx = 0.62 would reproduce the observed mean Eu-anomaly when Cpx crystallizes before Plag (Fig. 6, Table 2). However, this Kd^{Eu} implies a significantly lower $\log f\text{O}_2 = -12.0$, which is about 2 log units below the QFM buffer, close to lunar conditions (e.g. Lofgren *et al.*, 2006), and thus is not realistic for mantle derived basalts from subduction zones (e.g. Gaillard & Scaillet, 2014). This shows that Eu-anomaly in Cpx cannot be explained simply either by the effect of $f\text{O}_2$ or Kd.

The above discussion shows that plagioclase crystallization may have played a role in producing the Eu-anomaly in Cpx, although other factors are needed as well. The Sr vs Eu/Eu* relation in Cpx shows that the >45 kyr crystals and the mafic crystal rims from the younger units show a range of Sr concentrations within a more or less constant Eu/Eu* values (Fig. 5.f). Such a trend can be interpreted as increasing Sr in the liquid with limited changes in the Eu/Eu*, although given the scatter of the data is difficult to reach definitive conclusions. In contrast, the evolved Cpx show a decreasing Sr and decreasing Eu/Eu* that clearly reflects plagioclase crystallization, a very different trend from that of the mafic Cpx. Unfortunately the Sr and Eu-anomaly do not show a clearly changing pattern in core-rim traverses from individual crystals, the tendency changes from crystal to crystal. Another factor that comes into play is the possibility of fast crystal growth rates on Kd partitioning of REE and this is discussed next.

Fig. 6. Modeled REE and Sr abundances in plagioclase and clinopyroxene at different percentages of plagioclase crystallization during Stage 1 differentiation. In scenario A Plag $EuKd$ is varied to find the best fit to observed REE pattern; in B, Cpx $EuKd$ is varied to find best fit of Cpx REE pattern. Note that in A and B scenarios Plag comes before Cpx. In scenario C, Cpx is the sole crystallizing phase. For details of modeling see main text.

7.1.2. Effects of crystal growth kinetics on the *Eu*-anomaly of clinopyroxene

Lofgren *et al.* (2006) and Mollo *et al.* (2013) showed that Kd^{REE} increases with increasing growth rates. Experimental Cpx of Mollo *et al.* (2013) has slightly positive

(>1) Eu/Eu^* at QFM and nickel–nickel-oxide (NNO) +1.5 oxygen fugacity buffers, but no sector zoning was reported for cooling rates of 2.5 to 50 °C/h. In contrast, Lofgren *et al.* (2006) produced sector-zoned Cpx and negative Eu-anomalies ($\text{Eu}/\text{Eu}^* < 1$) at 1.2 log units above the iron-wüstite (IW) oxygen fugacity buffer at all investigated cooling rates (5–1000 °C/h). Cooling rates higher than 100 °C/h produce $K_d^{\text{Eu}/\text{Eu}^*}$ on the order of the observed >45 kyr Cpx value. The difference between starting T (1250 and 1265 °C) and crystallization T (1100 and 1125 °C) in both studies is similar (140 and 150 °C) and they were both run at 1 atm conditions. The main difference between the Mollo *et al.* (2013) and Lofgren *et al.* (2006) experiments is the $f\text{O}_2$, so that at more reducing conditions a larger amount of Eu is in 2+ valence state, and thus larger Eu-anomalies can be produced in Cpx. Moreover, Lofgren *et al.* (2006) also investigated larger cooling rates, and thus the effect is more extreme.

The ratio of $K_d^{\text{Eu}/\text{Eu}^*}$ between the different sectors of the Cpx crystals in Lofgren *et al.* (2006) is about one when Cpx crystallized in equilibrium conditions, but the ratio increases with increasing cooling rate. To test the effect of growth rates on REE Kds it is useful to look at the slope of K_d^{REE} ($K_d^{\text{La}}/K_d^{\text{Lu}}$). This is about 0.25–0.29 in equilibrium crystallization conditions in the non-sector zoned (i.e. Mollo *et al.*, 2013) and in both sectors of the sector zoned Cpx in both sectors (i.e. Lofgren *et al.*, 2006), and close to the model of Wood & Blundy (2002), which gives similar $K_d^{\text{La}}/K_d^{\text{Lu}} = 0.23$ (at 1265 °C and 1 atm). Thus, it seems that equilibrium crystallization gives similar REE patterns under similar equilibrium conditions. The $K_d^{\text{La}}/K_d^{\text{Lu}}$, however, decreases with increasing cooling rate (e.g. Lofgren *et al.*, 2006; Mollo *et al.*, 2013) due to kinetics of rapid crystal growth. The same decrease is observed in the sector-zoned >45 kyr Cpx in the $K_d^{\text{La}}/K_d^{\text{Lu}}$ between the low-REE sector (S1) and the high-REE sector (S2) ($K_d_{\text{S1}}^{\text{La}/\text{Lu}}/K_d_{\text{S2}}^{\text{La}/\text{Lu}}$). Assuming the different K_d of the sectors is the result of growth kinetics and not that of an inhomogeneous melt around the crystal (e.g. Adam & Green, 1994; Lofgren *et al.*, 2006;

Hammer, 2008 and references therein), the ratio of La/Lu between sectors 1 and 2 ($X_{S1}^{La/Lu}/X_{S2}^{La/Lu}$) equals to that of the Kd between the sectors ($Kd_{S1}^{La/Lu}/Kd_{S2}^{La/Lu}$). This ratio is therefore characteristic of the cooling rate. In the >45 kyr sector-zoned Cpx crystal we find that $Kd_{S1}^{La/Lu}/Kd_{S2}^{La/Lu}$ increases from 0.84-1.05 from core to rim, suggesting a decrease in cooling rate and probably reaching equilibrium. Eu-anomaly values also follow a trend, but one where Eu/Eu* increases with increasing cooling rates (Fig. 7). This means that faster grown crystals will generate more negative Eu-anomalies. When compared to the natural Cpx crystal we see that the Eu/Eu* decreases towards the rims, and thus implies a decreasing cooling rate in accord with the La/Lu ratios between sectors. Crystal chemistry and f_{O_2} causing negative Eu-anomaly in Cpx rather than plagioclase crystallization was also proposed by Shearer & Papike (1989) in lunar basalts (IW buffer).

Fig. 7. (a) La/Lu, and (b) Eu/Eu* between the sectors (S1 and S2) of sector zoned clinopyroxenes plotted against cooling rate from the experiments of Lofgren *et al.* (2006) (solid grey symbols) and clinopyroxene from this study (open symbols). Gede clinopyroxene cooling rates are inferred from the experimental ones, and show a decrease from core to rim implying that finally crystallization (and the magmatic system) reached equilibrium.

As a summary, from this section it is apparent that only plagioclase crystallization cannot reproduce the observed moderate Eu-anomalies in the mafic Cpx. A reduced f_{O_2} close to the QFM buffer can partly explain the Eu-anomaly by affecting the Eu Kd in

clinopyroxene. However, we have also found evidence for fast growth in sector zoned

Cpx and this will affect the REE and tend to produce a more negative Eu-anomaly. We, thus, conclude that Eu-anomaly in mafic Cpx do not necessarily reflect the effect of plagioclase crystallization. Mafic Cpx rims of younger (4 kyr and 1.2 kyr) units have similar geochemical characteristics to the >45 kyr crystals, and thus are probably the result of a combination of the same parameters.

7.2. Eu-anomalies in evolved clinopyroxene and silicic liquids

The moderately negative Eu-anomalies in the mafic >45 kyr Cpx is the result of the combination of relatively high growth rates (likely upon rapid decompression), relatively reduced condition ($< \text{QFM}$), and perhaps also some plagioclase crystallization. For the REE patterns in evolved Cpx cores in Holocene units the kinetic factors and oxygen fugacity likely played a lesser role, since sector zoning is not common and $f\text{O}_2$ was 0.5-1 log unit above NNO (see Table 10 in chapter 1). Moreover, there is plenty of textural and geochemical evidence for plagioclase growth before and during Cpx crystallization. Here we assess the evolution of Eu/Eu* in the evolved rhyodacitic liquid and the evolved Cpx and sodic Plag in equilibrium with it. Plagioclase co-crystallization with Cpx is recorded in the decreasing Sr and increasing Eu-anomaly shown by the Cpx compositions (Fig. 5.b), but below we perform some models to better quantify the processes.

We have shown a possible differentiation path from the >45 kyr high-aluminium basaltic andesite (HABA) to the rhyodacite whole rock (Table 12 in chapter 1). It involves 60 wt% plagioclase and 5.5 wt% olivine with low water contents (≤ 3 wt%) and at low pressure (≤ 100 MPa). We have also demonstrated that the evolved cores from the 4 kyr and 1.2 kyr reversely zoned Cpx are in equilibrium with the rhyodacite whole rock composition (Fig. 23 in chapter 1). The appearance of pyroxenes in the rhyodacitic liquid is likely due to low temperatures and changing chemistry as the system evolves. The calcic plagioclase plus olivine assemblage for this amphibole-free differentiation (>45 kyr

Stage 2) turns into a sodic plagioclase plus two-pyroxenes mineral assemblage mostly as the residual liquid becomes more evolved. This change in the mineral assemblage happens late, probably after the liquid reaches phosphorus and apatite saturation at about $\text{SiO}_2 = 67 \text{ wt\%}$ (at about 910°C) since the most evolved pyroxene cores ($\text{Mg\#} < 67$) have plenty of apatite inclusions. Thus, plagioclase crystallization occurred before and during the appearance of evolved pyroxenes, and therefore a significant negative Eu-anomaly can be produced. We tested this hypothesis by modeling the Eu/Eu^* evolution of the liquid and the minerals in a similar manner we have shown it in the case of the $>45 \text{ kyr}$ Cpx. According to the mineral assemblage of the HABA (G130) sample, it experienced mixing with the rhyodacitic evolved melt, and thus, its composition is likely to be already a mixture (see chapter 1). We therefore choose to use the REE concentrations obtained from the $>45 \text{ kyr}$ Stage 1 modeling (chapter 1).

Fig. 8. Modeled REE and Sr abundances in plagioclase, clinopyroxene, and the residual liquid at different percentage of plagioclase crystallization in Stage 2 differentiation. Note that at 40 wt% of plagioclase and subsequent clinopyroxene and apatite crystallization reproduce the REE abundances in both minerals and approximates them in the residual liquid are similar to the natural values, except for Sr, which is lower than the natural ranges. In cases where plagioclase crystallizes it precedes clinopyroxene. For details see main text.

We used the Bindeman *et al.* (1998) to calculate Kd^{REE} in the plagioclase, except for Eu, which we calculated using the measured plagioclase compositions ($Eu/Eu^* = 7-12$ in the 4 kyr and the 1.2 kyr low-An plagioclase) and the rhyodacite bulk-rock (Table 3). Although these latter Kd^{Eu} are about an order of magnitude larger than other REE, they are in agreement with published values from dacite-rhyolite systems (e.g. Bacon & Druitt, 1988). Thus, we calculated a minimum and maximum Kd^{Eu} ($Kd1$ & $Kd2$). Using these Kds we first crystallized 40% and 60% plagioclase and 6.5 wt% Cpx (Fig. 8.a&b; Table 3). The calculated Eu concentrations (1.13-1.36) in plagioclase, independently of the amount of crystallization, are in agreement with the natural low-An plagioclase range (i.e. 0.77-1.27 ppm) using both $Kd 1$ and $Kd 2$ (Table 3). Calculated LREE (i.e. La and Ce) abundances are somewhat lower than the observed range, whereas the MREE and HREE fit in the observed range (Fig. 8, Table 3). The mismatch shows that either the calculated Kd is not entirely appropriate, or the starting liquid REE pattern is slightly different. The calculated Sr concentrations in both Plag and residual liquid (compared to the rhyodacite) are underestimated. This might be because our calculations are made for a large amount of evolution and crystallization, but we only use a single temperature and anorthite content. Moreover, we also model all plagioclase being crystallized first, while crystallizing small amounts of Cpx (and olivine) would probably raise Sr in the residual liquid from which sodic Plag could form with the observed Sr concentration.

The Eu-anomaly in the residual liquid ($Eu/Eu^* = 0.29 - 0.63$) is much lower than the measured value of the rhyodacite whole rock (0.71), with Eu concentrations being rather high (Fig. 5, Table 3). MREE (e.g. Sm and Gd) are also higher than those in the rhyodacite whole rock. These subtle differences may be due to the crystallization of accessory minerals (e.g. apatite) since even a small amount ($\ll 1\text{wt}\%$) can significantly modify the REE pattern in the liquid. The presence and formation of apatite is well constrained (Chapter 1), we will discuss its role in the following paragraphs.

Table 3. *Eu/Eu* calculation in >45kyr Stage2 plagioclase and clinopyroxene*

element	La	Ce	Sm	Eu	Gd ^s	Eu/Eu*	Lu	Sr
<i>CI chondrite</i>								
<i>C₀</i>	10.04	22.07	0.153	0.058	0.2055	0.98	0.33	373
Plag (An60)	2.5-6.85	4.31-8.59	0.31-0.95	0.77-1.27	0.23-0.83	7.0-12.0	0.036	484-623
Cpx	2.76-4.29	13.36-20.45	7.82-11.77	1.46-1.75	9.71-14.15	0.377-0.509	0.8-1.2	16-19
<i>C_d (PATA-7)</i>	22.9	44.6	4.1	0.9	3.6	0.716	0.3	224.7
apparent Kd Plag	0.09-0.30	0.097-0.192	0.076-0.231	0.85-1.41	0.064-0.231		0.07-0.09	2.15-2.77
apparent Kd Cpx	0.12-0.187	0.30-0.46	1.91-2.87	1.62-1.94	2.70-3.93		2.6-4.0	0.07-0.08
Kd Plag	0.147	0.098	0.095	0.912	0.071	11.083	0.053	2.695
Kd 1 Cpx	0.137	0.234	0.895	1.037	1.155	1.020	1.026	
Kd 2 Cpx	0.259	0.466	2.014	2.362	2.652	1.022	2.274	
Kd apatite	5.4	16.6	62.8	30.4	56.3	0.511	16.0	
F = 40% plag								
in Plag (ppm)	2.28	3.41	0.55	1.13	0.43	7.091	8.502	422.9
<i>in liquid (ppm)</i>	15.53	35.00	5.79	1.24	6.11	0.640	0.496	156.92
in Cpx 1 (ppm)	2.25	8.62	5.22	1.29	6.98	0.652	0.505	0.548
in Cpx 2 (ppm)	4.23	16.90	10.90	2.68	14.50	0.653	0.506	1.117
<i>in liquid 1 (ppm)</i>	16.45	36.85	5.84	1.24	6.04	0.639	0.496	0.53
<i>in liquid 2 (ppm)</i>	16.32	36.28	5.41	1.14	5.47	0.639	0.495	0.49
<i>liq after apatite</i>	15.19	32.36	3.97	0.98	4.14	0.739	0.573	0.20
F = 60% plag								
in Plag (ppm)	3.22	4.92	0.80	1.18	0.63	5.068	0.147	212.696
<i>in liquid (ppm)</i>	21.94	50.46	8.36	1.29	8.90	0.457	0.290	78.92
in Cpx 1 (ppm)	3.19	12.43	7.54	1.33	10.17	0.466	0.295	0.80
in Cpx 2 (ppm)	5.97	24.37	15.73	2.78	21.13	0.466	0.295	1.64
<i>in liquid 1 (ppm)</i>	23.25	53.13	8.42	1.29	8.81	0.457	0.289	0.78
<i>in liquid 2 (ppm)</i>	23.06	52.30	7.81	1.18	7.97	0.456	0.289	0.72
<i>liquid after apatite</i>	20.99	43.14	4.20	0.88	4.57	0.612	0.387	0.29

Cpx Kd¹ & ² is after Wood & Blundy (1997, 2002) at 0.1 GPa, anhydrous, at 910 and 810 °C, respectively; C₀ is the parent, C_d is the daughter magma
apparent Kd = C_{mineral}/C_d
^s Gd for Plag is from Rollinson (1993)

REE partition coefficients for Cpx are calculated after Wood & Blundy (1997, 2002). The set of K_d is calculated at 910 °C and yields K_d s lower than apparent ones (those calculated by the ratio of measured Cpx and rhyodacite bulk-rock; Table 3). If we decrease the temperature by 100 °C, the calculated K_d s are similar to the apparent ones (Table 3). It might also be that the effect of the liquid composition being much higher in SiO₂ is not well captured by the Wood & Blundy (1997, 2002) models. Clinopyroxene that crystallized from the residual liquid after 40 % plagioclase crystallization using K_d has REE concentrations within the observed natural ranges. However, if crystallization increases to 60% the REE abundances are much higher than observed, and the calculated Eu concentrations as well (Fig. 8. c&d; Table 3). Therefore, K_d^{Eu} in Cpx should be lower than predicted so that it promotes a negative Eu-anomaly (e.g. Sun *et al.*, 1974) and would give lower Eu concentrations in Cpx. Huang *et al.* (2006) have experimentally shown that Cpx crystallizing from a dacitic melt with no Eu-anomaly also develops negative Eu-anomaly due to oxygen fugacity. Thus, the lower K_d^{Eu} (compared to neighboring REE) in Cpx from silicic systems reported in the literature is not only the ‘inherited’ liquid signature. Therefore, we could lower the K_d^{Eu} in Cpx to find the exact K_d^{Eu} value to fit our natural data, but it would be only a few per cent lower than the calculated one from Wood & Blundy (1997, 2002).

Apatite co-crystallization increases the Eu/Eu* in the liquid (e.g. Deering & Bachmann, 2010) due to its high aptitude for negative Eu-anomaly (e.g. Fujimaki, 1986; Rollison, 1993), thus, it could counterbalance the effect of plagioclase crystallization on Eu-anomaly in the liquid. Crystallizing 0.5-1 wt% of apatite would increase the Eu-anomaly of the liquid significantly, as well as decrease Sm and Gd concentrations closer to the observed ones in the rhyodacite whole rock (Table 3).

We, thus, conclude that the Stage 2 fractionation trend starts with probably highly calcic Plag formation, which becomes more sodic, and Cpx (and Opx) follows with

deeply negative Eu-anomalies. Due to the low anorthite in plagioclase and the low crystallizing temperature, it effectively depletes the Eu from the melt compared to the other REE. Clinopyroxene precipitates from this residual melt with significant negative Eu-anomalies and may partially ‘inherit’ it, or make it even more negative if the Eu partition coefficient promotes it. Apatite crystallization balances back the very negative Eu-anomaly in the melt caused by plagioclase crystallization (e.g. Deering & Bachmann, 2010).

9. CONCLUSIONS AND IMPLICATIONS

We have shown that negative Eu-anomalies in the >45 kyr mafic, sector zoned clinopyroxenes is not necessarily the result of extensive plagioclase crystallization –in contrast to the traditional interpretation–, but rather a combination of a relatively low fO_2 (around QFM) of the magmas and fast crystal growth. It is likely that the >45 kyr Cpx started to grow in a deep water-rich magma reservoir and thus plagioclase was absent, and likely continued during transport and storage at shallower depth at which point plagioclase joined the crystallizing assemblage. We also suggest that REE characteristics (e.g. La/Lu) of the >45 kyr sector-zoned phenocryst and especially its Eu-anomaly, are indicative of fast growth and of progressively decreasing crystal growth rates towards the rims. This might reflect the movement of the magma from a deep to a shallow reservoir and thus decreasing degrees of disequilibrium after the transport. On the other hand, at the shallow level, the dry crystallization of sodic plagioclase incorporates Europium to such an extent that it causes remarkable depletion in the residual liquid. Crystallizing evolved clinopyroxenes from such a liquid shows strongly negative Eu-anomaly. However, for such evolved compositions, apatite crystallization may also start to play a major role and obscure the effect of plagioclase crystallization.

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CHAPTER

3

THE EFFECTS OF 3D DIFFUSION ON RETRIEVED TIME SCALES FROM FE-MG ZONING IN ORTHOPYROXNE AND APPLICATION TO MAFIC-SILICIC MAGMA MIXING AT GEDE VOLCANO, WEST-JAVA, INDONESIA

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ABSTRACT

The determination of time scales of magmatic processes from modeling the chemical zoning patterns is increasingly being used by volcano petrologists and geochemists. Most determinations are done using one-dimensional traverses across a crystal. However, crystals are three-dimensional objects, and diffusion and re-equilibration occurs in multiple dimensions. Given that we can mainly study the crystals in two-dimensional petrographic thin sections, the determined time scales could be in significant error if multiple dimensional effects are not identified or minimized. Here we show the results of a numerical study of the effects of diffusion of Fe-Mg in orthopyroxene in three-dimensions and evaluate what are the best suited two-dimensional sections, and one-dimensional traverses that can lead to the most accurate calculated time-scales. We apply the findings to orthopyroxene crystals from Gede volcano that reflect magma mixing and mafic recharge in a silicic reservoir. We found that when choosing the most appropriate crystals the time scales from different eruptions are very similar, and indicate that the times since the last magmatic intrusion and eruption are less than one month. Such time should be informative for taking actions to mitigate volcano hazards at Gede during possible forthcoming unrest and eruptions.

1. INTRODUCTION

Diffusion in different geological materials has long been the interest of scientists (e.g. Bowen, 1921; Li & Gregory, 1974; Sutton, 1932). Petrologists and volcanologists have

been using diffusion to understand and explain processes such as crystal growth (e.g. Hammer, 2008; Lasaga, 1982) or dynamic magma mixing (e.g. Fourcade & Allegre, 1981; Morgavi *et al.* 2013). In the last decade, modeling chemical diffusion in minerals has helped to understand the timing and duration of certain magmatic process recorded in the volcanic crystal cargo (e.g. Costa *et al.*, 2003, 2008, and 2010). 1D diffusion models are commonly used among volcanologists dealing with active and actively monitored volcanoes to gain an improved understanding, and this recently became a very practical and modern tool in interpreting monitoring signals, which is essential for forecasting volcanic behavior (e.g. Kahl *et al.*, 2011; Kligour *et al.*, 2014; Martí *et al.*, 2013; Oeser *et al.*, 2015; Saunders *et al.*, 2012).

Modeling diffusion to retrieve the duration of magma mixing (e.g. Costa *et al.*, 2013), magma residence time (e.g. Allan *et al.*, 2013, Fabbro, 2014), and the timing of other magmatic processes is now routinely done. This is partially due to a better understanding of the variables (e.g. composition (X), temperature (T), pressure (P), and redox state (fO_2) of the magma) governing the diffusion in solid crystalline materials (e.g. Crank, 1975), and also the many new experiments aimed to establish diffusion coefficients (D) of many elements (e.g. Mg, Fe, Mg-Fe, Cr, Ni, REE, etc.) in many minerals (e.g. olivine, pyroxenes, garnet, plagioclase, magnetite; e.g. Zhang, 2010; and references therein).

It is also well known that elements diffuse at differing paces parallel to different crystallographic axes in most minerals, i.e. diffusion is anisotropic (e.g. Fe-Mg in olivine; Chakraborty, 2010). Several studies have shown that even though compositional traverses are taken along the same crystallographic orientation from crystals presumed from the same population, the estimated time-scales show a rather large scatter (e.g. Fabbro, 2014; Kahl, *et al.*, 2011; Saunders *et al.*, 2012). This opens the question of whether the scatter is a real feature of the magmatic process or some sort of artifact. Yet, the traditional

approach of diffusion modeling is using unidimensional data (e.g. Allan *et al.*, 2013; Druitt *et al.*, 2012) and, apart from some preliminary studies on the effect of crystal shape on diffusion (e.g. Ganguly & Tirone, 1999; Watson *et al.*, 2010), no comprehensive study has been investigating the effect of three-dimensional (3D) geometries. Costa *et al.* (2010) showed that 2D zoning patterns modeled in different orientations yield different results. Most recently, Shea *et al.* (in press) conducted simulations on olivine with various shapes (from sphere to polyhedral) demonstrating that crystal shape (3D) affects the diffusion pattern, and that 1D modeling cannot always retrieve the correct times. Thus, part of the scatter in time scales determinations from 1D diffusion modeling may be artifacts resulting from the simplification of the real situation of diffusion in 3D.

In this chapter we focus on differences in between 1D and 2D models and how successfully they return the 3D diffusional pattern in orthopyroxene revealed by numerical modeling. We present the first simulation results conducted on the typical orthopyroxene polyhedral shape (i.e. Deer *et al.*, 1992) in order to compare simulated 3D diffusion patterns under both isotropic (i.e. Ganguly & Tazzoli, 1994) and anisotropic conditions (i.e. Schwandt *et al.*, 1998) to natural observations. We reveal the importance of crystal zoning and shape, the location of 1D traverses and 2D planes, and the advantages and disadvantages of 1D and 2D model applications. At the end we model some natural orthopyroxene crystals from Gede volcano that have recorded the mixing between mafic and silicic magmas (Chapter 1).

2. COMMONLY USED TERMS AND DEFINITIONS

Some of the expressions used in this contribution may be synonyms, or have meanings different from everyday use. To avoid confusion, below we list and define the often-used terms, some of which are also illustrated in Figure 1 and 2.

Fig. 1. Cartoon illustrating the main components of our models. (a) schematic view of orthopyroxene used in simulations and its 2D projections in different orientations; (b) cartoon of the four compositional settings used in simulations; (c) schematic 1D traverse and its components (plateau, profile, boundary position) changing with time. C and x are concentration and distance, where the subscript refer to the moment in time, i.e. 0 = initial conditions. For instance, at $t=1$, the initial C profile is a step function (darkest blue line), its maximum and position is indicated by the red arrows. At $t=1$, the maximum C equals to the initial one ($C_0 = C_1$), but the inferred ('apparent') boundary position (x_1) (judged from the profile – grey line) is significantly different from the initial one. At $t=2$, both the inferred ('apparent') boundary position (x_2) and the inferred ('apparent') maximum concentration (C_2) is different from the initial ones.

3D (three-dimensional) or 'real' data: data obtained by 3D diffusion simulation of orthopyroxene crystals.

3D or 'real' time (t_{3D}): the duration of the above-mentioned diffusion simulation.

1D (one -dimensional) model/estimate: data from 1D diffusion modeling.

2D (two-dimensional) model/estimate: data from 2D diffusion modeling.

Traverse (tr.): array of points in 1D (independently of concentration); 1D section.

Plane (section): a 2D array of concentrations (independently of their absolute value).

Plateau: a flat 1D array of **constant** concentrations (independently of their absolute value); part of a traverse.

Profile: that part of a traverse or plane where the concentration is **not constant** (i.e. the part of the crystal that is affected by diffusion).

'Initial' (concentration or boundary location): relates to the 3D crystal **before** diffusion and is used for 1D and 2D models as starting model input.

'Apparent' (concentration or boundary location): observed/evaluated in the 3D crystal **after** diffusion (of a given duration) and used for 1D and 2D models as starting model input; corresponds to measured/observed values in natural crystals (after diffusion).

Time-scale: the estimated duration of 3D diffusion by 1D/2D models.

Mismatch (ΔC): the difference between the '*real*' concentration dataset and the estimated 1D/2D concentration dataset calculated at every corresponding data point ($\Delta C = C_{3D} - C_{1D/2D}$).

3. METHODS

In this paragraph we describe all models (1D, 2D, and 3D) built and used in orthopyroxene diffusion simulations, including variables such as the crystal shape and size, zoning patterns, diffusing elements and diffusion coefficients, and numerical methods.

3.1. Model variables

3.1.1. Crystal shape and aspect ratio

Shea *et al.* (in press) has shown that the crystal shape of olivine has a great influence on the details of the equilibration of the chemical zoning and can cause significant differences when comparing natural data to 1D and 2D diffusion modeling and estimated

time-scales. Orthopyroxene habit depends on the environment and conditions it formed from (e.g. Durant & Fowler, 2002, Grégoire *et al.*, 2001). Deer *et al.* (1992) identifies three different polymorphic types of orthopyroxene with the most common shape of well developed crystal faces being {100}, {010}, {101}, and {210}, and with an approximate unit cell ratio of 1:1.7:3.5 (a-axis : b-axis : c-axis) commonly occurring in magmatic environments. Two out of these three polymorphs show orthorhombic symmetry (protoenstatite and orthoenstatite) and one is monoclinic (clinoenstatite). Protoenstatite is unknown in nature and clinoenstatite occurs below the temperature range of typical volcanic systems (700-1200 °C). Orthoenstatite is stable below about 1300 °C both in magmatic and metamorphic environment, therefore we adopt the crystallographic and morphological parameters of the orthoenstatite by Deer *et al.* (1992).

Our model crystal has a volume of $103 \times 173 \times 355$ voxels (along x , y , z coordinates, corresponding to the a , b , and c crystallographic axes, respectively) with the aspect ratio described above, and with an orthorhombic symmetry where crystallographic axes meet at an acute angle ($\alpha=\beta=\gamma=90^\circ$) (Fig.1.a). In our model crystals, each voxel is assigned to 2-by-2-by-2 μm cube, thus it has a volume of $206 \times 346 \times 710 \mu\text{m}^3$.

3.1.2. Investigated zoning patterns

We investigated four different chemical zoning configurations. Two different reverse and normal zoning patterns both with and without overgrowth rims: (1) zoning pattern A is reverse zoning without overgrown rim, (2) pattern B is reverse zoning with overgrown rim, (3) pattern C is normal zoning without overgrown rim, (4) and pattern D is normal zoning with overgrown rim (Fig.1.b). The different initial enstatite concentrations (Mg-rich orthopyroxene end-member, $\text{En} = \text{Mg}/(\text{Mg}+\text{Fe})$ in mols) for core–melt (or overgrowth rim) relations were 0.75 and 0.60 in normal zoning patterns, and the other way around for reverse zoning patterns. In both zoning patterns, open boundary

conditions apply at all boundaries, i.e. element exchange by diffusion is not limited (Costa *et al.*, 2008). However, there is a fixed concentration at the boundary between crystal rim surrounding melt, which equals to the concentration in the melt, whereas for crystal core and rim boundary there is no such a restriction. Moreover, the melt is treated as an infinite reservoir of constant Fe-Mg, its concentration never changes, independently of actual En values, which is intended to simulate a natural system where significant amount of recharge magma remobilizes existing (cumulate) crystals. We chose the contrasting En values of 0.6 and 0.75 to make sure that there is a chemical gradient that is high enough to see changes after relatively short diffusion times, but that the time to reach the point where initial concentration vanishes from the entire crystal is not too long.

3.1.3. Investigated orientation of traverses and planes

We compared 1D and 2D diffusion models to 'real' 3D data along two main types of sections (Fig.1.a&c): (1) sections parallel to the crystallographic axes (i.e. *a*, *b*, and *c*, parallel to *x*, *y*, and *z* respectively) and running through the crystal center (along-axis and on-center sections); (2) sections parallel to the crystallographic axes but not slicing through the center (along-axis and off-center sections). There are only 3 principal orientations of the 1st configuration, but endless of the 2nd. We sampled the along-axis off-center sections every 6 μm (every third grid step) parallel to the axis in question and perpendicular to the other two axes.

3.1.4. Nature of diffusion and diffusion coefficients

Diffusion coefficients (*D*) in orthopyroxene for Fe-Mg (Ganguly & Tazzoli, 1994), for Mg^{2+} (Schwandt *et al.*, 1998) and several trace elements (Cr, La, Nd, Eu, Gd, and Yb Cherniak & Liang, 2007; Ganguly *et al.*, 2007; Sano *et al.*, 2013) have been experimentally determined. Their dependence on composition (*C*) and other factors (*T*, *P*,

and f_{O_2}) has also been extensively studied. However, diffusion anisotropy (variation of D along different crystallographic axes) in orthopyroxene is poorly understood. Ganguly & Tazzoli (1994) proposed isotropic D for Mg-Fe along the b -, and c -axes, and lower D (anisotropic) for the a -axis, whereas Schwandt *et al.* (1998) proposed unambiguously anisotropic D , where D_c being the highest and $D_c > D_b > D_a$. Experimentally established diffusivities for trace elements also show an anisotropic behavior where D_c is the highest (e.g. Ganguly *et al.*, 2007; Sano *et al.*, 2013). Thus, we investigate both isotropic and anisotropic D , where D is calculated following Ganguly & Tazzoli (1994) and modified by Allan *et al.* (2013):

$$D^{Fe/Mg} = \left(-5.44 + (1 - X_{En}) - \frac{12530}{T} \right) \times \left(\frac{f_{O_2}(NNO,T)}{f_{O_2}(IW,T)} \right)^{\frac{1}{6}} \quad (1)$$

where $D^{Fe/Mg}$ is the concentration dependent isotropic diffusion coefficient (m^2s^{-1}), f_{O_2} is the oxygen fugacity (Pa), NNO stands for nickel-nickel-oxide buffer, IW stands for iron-wüstite buffer, X_{En} is the molar enstatite fraction (En), and T is temperature (K). Anisotropic D has been speculated based on natural observations (e.g. Tomiya & Takahashi, 2005) and observed in D^{Cr} by Ganguly *et al.* (2007), and that is $D_a^{ani} = \frac{D^{Fe/Mg}}{3.5}$; $D_b^{ani} = \frac{D^{Fe/Mg}}{1.7}$; and $D_c^{ani} = D^{Fe/Mg}$ (*ani* is for anisotropy, $D^{Fe/Mg}$ is as described above). For all models, we used $T = 1000$ °C and $f_{O_2} =$ NNO buffer, as is representative of a magmatic environment where orthopyroxene is common.

3.2. Numerical methods and diffusion equation

For the diffusion simulation experiments we used the same finite-difference method and theoretical considerations on diffusion as Shea *et al.* (in press; and references therein). We give only a brief summary here:

Diffusion equation (in 3 spatial dimensions) takes the form, in regard to Fick's 2nd law (Crank, 1975):

$$\frac{\partial C^i}{\partial t} = \frac{\partial}{\partial x} \left(D_a^i \frac{\partial C^i}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_b^i \frac{\partial C^i}{\partial y} \right) + \frac{\partial}{\partial z} \left(D_c^i \frac{\partial C^i}{\partial z} \right) \quad (2)$$

where C^i is the concentration of element i , and D_a , D_b , and D_c are the diffusion coefficients along a , b , and c axes (axes are parallel to a spatial direction). The second derivative of the above equation (Eq. 2), using central approximation, in respect to the x coordinate writes as (after Ismail-Zadeh & Tackley, 2010):

$$\left. \frac{\partial^2 C}{\partial x^2} \right|_{x,y,z} = \frac{C_{x+1,y,z} - 2C_{x,y,z} + C_{x-1,y,z}}{\Delta x^2} \quad (3)$$

where Δx is the spatial step (here it is 2 μm); C is the concentration; and x , y , and z are the numerical matrix coordinates. From Eq. (3), incorporating the time derivative and the concentration dependence of the diffusion coefficient, we end up with the following numerical formulation in 1D along the x -direction (e.g. Costa *et al.*, 2008):

$$C_x^{t+1} = C_{x+1}^t + \Delta t \left(\frac{D_{x+1}^t - D_i^t}{\Delta x} \right) \left(\frac{C_{x+1}^t - C_i^t}{\Delta x} \right) + D_x^t \Delta t \left(\frac{C_{x+1}^t - C_x^t + C_{x-1}^t}{\Delta x^2} \right) \quad (4)$$

where C is the concentration; D is the diffusion coefficient; Δt is the timestep; Δx is the spatial step; superscript t denotes the time step; and subscript x is for the matrix coordinate. For 2D and 3D, the expression on the right side of the equation, without the first term in the addition ((C_{i+1}^t)), needs to be added once or twice, with respect to the y and z directions, respectively.

3.3. Simulation protocol and preparation of the 1D & 2D models

In this paragraph we detail our approach for the simulation protocol, which is similar to that in Shea *et al.* (in press), with some modifications in the comparison of the 1D (and 2D) model results to the 3D 'real' data.

3.3.1. Protocol for obtaining 3D ('real') and 1D & 2D models

Figure 2 schematically illustrates the simulation protocol. We started each simulation with different zoning patterns (A to D) by diffusing the given 3D crystal for 14600 days (i.e. 40 years) with daily time-steps ($\Delta t = 1$ day) employing the above-described conditions (section 3.1). Time-steps were chosen to fulfill the stability criterion (e.g. Press *et al.*, 2007; Costa *et al.*, 2008) for the numerical method described above. As the matrix containing the crystal is 64,481,201 voxels (approx. 1.7 MB in MATLAB® matrix file format), we did not save and store the data for every time-step (i.e. every day), but only every 200th, which somewhat limits the data continuity, but still gives enough details. We used the multicore computing facility at the Earth Observatory of Singapore to conduct the 3D and the 2D simulations. As parallelization of the Laplace part of the concentration dependent diffusion equation in MATLAB® is not fully possible, we used only one core (CPU) with 128 GB RAM. A full (i.e. 40 years) simulation of the 3D crystal with the parameters above took over 3 weeks time and resulted in a dataset of approximately 9 GB in size.

The obtained 3D results are used as our ground-truth data. After obtaining the 3D concentration matrix, we sliced both the initial (pre-diffusional) and simulated (post-diffusional) crystal matrix in desired orientations in 1D (traverse) and 2D (plane). Subsequently, we set up the starting conditions for the 1D (and 2D) model based on the 1D (and 2D) slice obtained from the 3D simulation. Next, we ran the diffusion model in 1D (and 2D) with the starting model inputs inferred from the 1D (and 2D) data obtained from the simulated 3D crystal. Finally, we compared the results of the 3D simulation and the 1D (and 2D) model in the same orientation (Fig. 2).

Fig. 2. Flow chart of comparison protocol of different diffusion modeling approaches. Step 1) Building the 3D crystal, filling it with compositional data, and diffuse it in 3D for t time – acquire simulated natural data. 2) Selecting a 1D traverse (or 2D plane) from both the initial (prior to diffusion) and diffused crystal, and apply 1D (or 2D) diffusion on the initial section for t time, as well. Step 3) Compare the simulated natural data to the that obtained by 1D (or 2D) diffusion modeling on the initial (prior to diffusion) traverse (or section) through calculating mismatch in between each corresponding data point (in 1D or 2D). Note that 1D and 2D profiles are not usually identical even if taken from the same location (see text).

3.3.2. 1D and 2D model settings

To make our simulation realistic and applicable to natural systems, we investigate the effect of 1D and 2D starting conditions (C and *apparent location* of the core-rim boundary) in this paragraph.

Initial concentrations (C). It is a difficult parameter to constrain in natural samples because of the unknown amount of diffusion that might have occurred. It is, therefore, common to use the measured maximum and minimum concentrations for modeling (e.g. Allan *et al.*, 2013; Costa & Chakraborty, 2004; Costa *et al.*, 2008; Druitt *et al.*, 2012; Kahl *et al.*, 2011; Morgan *et al.*, 2006; Tomiya & Takahashi, 2005). Insights into the ‘initial’ concentrations of a crystal affected by diffusion might be calculated by using concentrations of a slow diffusing element (e.g. Ca, Al, or REE) with known partition coefficients. As the effects of using apparent values in diffusion modeling are a priori unknown, we consider two setups for the 1D and 2D model inputs: (1) the ‘initial’ concentration directly from the 3D crystal before diffusion, and (2) the ‘apparent’ concentration as it can be inferred from the 1D traverse (2D plane) taken from the post-diffusional 3D crystal (Fig.1.d). This latter one corresponds to the measured concentrations in many studies of natural samples. This distinction is necessary to account for cases where diffusion has reached the crystal center (see later).

Starting boundary conditions & positions. It is important to have an a priori knowledge of boundary conditions or at least fairly good constraints on them (e.g. Costa *et al.*, 2008). A closed boundary condition refers to a situation where exchange of matter is not possible even if there is chemical gradient present. This mostly manifests in very slow diffusion rates or insufficient partitioning of the given element in one of the phases in question (e.g. Al in olivine, or La in orthopyroxene). In open boundary condition, there is diffusive communication in between the participating parties and it is much more common in magmatic systems (Costa *et al.*, 2008), and this is mostly the case for Fe/Mg diffusion in orthopyroxene. However, the boundary location – position of the boundary in space – is very influential in certain cases. These cases involve the traverses (and planes) that run into junctions of crystal faces, places where diffusion fronts merge (the angle is less than 180°) and diffusion intensifies. In orthopyroxene, such a typical orientation is a traverse

parallel to the *c*-axis that runs parallel to the *ac*-plane slicing through the crystal center (Fig.1.a). Any such traverse runs into the prism of {101} and $\{\bar{1}01\}$ faces (Fig.1.a) would imply ‘*apparent*’ boundary locations that are different from the ‘*initial*’ ones due to an effect of 3D diffusion. Thus, the results of modeling critically depend on the boundary location in the 1D (and 2D) models. We investigated two scenarios: (1) ‘*initial*’ location and (2) ‘*apparent*’ location (Fig.1.d). This is a significant issue in natural samples, since a slowly diffusing element (e.g. Al or Ca) may indicate the position of the initial boundary location (‘*initial*’ position), whereas the fast diffusing Fe/Mg indicates it to be somewhere else (‘*apparent*’ position), i.e. as it can be inferred from the Fe/Mg concentrational profile (e.g. Allan *et al.*, 2013).

3.3.3. Comparison of 1D & 2D model results with 3D (‘*real*’) data

An important decision to make with our simulation experiment is how to compare the 3D data with the 1D (and 2D) models and their evaluation. Shea *et al.* (in press) compared ‘*real*’ time to *best-fit* time (t_{1D}^*) of 1D models. It means that the 1D model runs as long as it reaches a concentration profile that is statistically the closest to the corresponding one taken from the crystal after simulated 3D diffusion. The two times (t_{3D} and t_{1D}^*) are then compared and interpreted. This is potentially problematic in some cases of our approach where we use ‘*initial*’ position and/or ‘*initial*’ concentration inputs for the 1D (and 2D) model (Fig.1.c). In order to avoid situations where objective judgment cannot be assured we chose to compare concentration profiles instead of times (duration of diffusion). To this end, we designed the simulations accordingly: each 1D (and 2D) model was run for the same time as the 3D simulation (t_{3D}) to be compared to, and concentrations of each corresponding points in both traverses (and planes) [3D ‘*real*’ and 1D (and 2D)] were compared via the root-mean square deviation (RMSD) method (e.g. Girona & Costa, 2013; Shea *et al.*, in press). RMSD calculates as follows:

$$RMSD_{1D} = \sqrt{\frac{\sum_M (C_{3D}^i - C_{1D}^i)^2}{M}} \quad (5)$$

$$RMSD_{2D} = \sqrt{\frac{\sum_M \sum_N (C_{3D}^{i,j} - C_{2D}^{i,j})^2}{M \cdot N}} \quad (6)$$

for 1D traverses [Eq. (5)] and 2D planes [Eq. (6)]; where M and N are the number of total cells in the x and y direction respectively, i and j are the spatial coordinates of the traverse or plane, C_{3D} is the ‘real’ concentration obtained from the 3D simulation, and C_{1D} or C_{2D} is the concentration estimated by the 1D or 2D model. This statistical method smoothens the deviations within the dataset. It means, for example, that if there are only few data points with striking differences in C , the RMSD can be low; and if all corresponding data points (1D – 3D) deviate a little from each other, the RMSD is low, as well. Because of the nature of the RMSD formulation, it always yields a positive natural number (or zero), therefore it reflects only the fact of deviation (if any) and does not supply information on whether it is positive or negative (i.e. over- or underestimation of the 3D concentration). However, visual inspection of the two concentration profiles [3D and 1D (or 2D)] allows deciding if the 1D (or 2D) model over- or underestimates the ‘real’ data. As all comparison in the experiments are for the same duration, an underestimation of C_{3D} by the 1D (or 2D) model means the time (t_{1D} or t_{2D}) required for reaching C_{3D} would be larger than the ‘real’ time (t_{1D} or $t_{2D} > t_{3D}$), and the opposite is true for an overestimation of C_{3D} .

Given the nature of the RMSD method, comparison between ‘real’ and estimated datasets requires additional evaluation. Therefore, RMSD is rather used to track the trajectory of deviation from ‘real’ values than to evaluate the ‘goodness’ of an estimate. We also evaluate the absolute maximum difference in C between a given 1D or 2D dataset and the corresponding 3D data (ΔC_{max}). When in any estimated (1D or 2D) dataset

of C , at least one data point exceeds the arbitrary chosen threshold of C , the estimation is rejected (i.e. considered as an inadequate estimate) (Fig. 3; Appendix 1).

Fig. 3. Illustration of assessing the goodness of a diffusion model estimate. Top panel shows the modeled traverses within the 3D crystal (on left hand side), RMSD of the estimates (in the middle), and legend (on the right). Three different traverse locations (A, B, and C) are highlighted, and along them the corresponding concentration distributions (bottom panel) with $t_{3D} = 200$ days (on the left) and $t_{3D} = 14000$ days (on the right) using anisotropic D . 'Real' (grey line) and 1D modeled (dark blue dotted line) concentration profiles, as well as mismatches (red line) are shown for each traverse location (e.g. A, B, and C) at both selected t_{3D} . On the mismatch plot tolerance interval for acceptable estimates is indicated (dashed black line). Acceptable estimates are marked with green ticks, whereas unacceptable (reject) estimates are with a red cross.

4. RESULTS AND INTERPRETATIONS

Below we describe the results of the simulation according to section orientation (starting with along-axis models) and subdivided by modeled dimension (1D and 2D). Note that any exact values (i.e. t_{3D} , RMSD, ΔC) given here are valid only for the models with the above-described parameters (i.e. most importantly T , C , aspect ratio and size of the crystal; c.f. Shea *et al.*, in press). The description below is based on a detailed investigation of crystals with patterns A and B; patterns C and D were not explored in as much detail as the effect of the zoning pattern in such a case is negligible (Shea *et al.*, in press). As we noted above the exact values of D^{Fe-Mg} in orthopyroxene are still debated, thus we carried out simulations with both isotropic and anisotropic D , when every other condition (T , C , f_{O_2} , and shape and size of the crystal) is identical. This allows us later to compare the model concentration profiles results to those observed in natural samples. We shall note here that differences between ‘*real*’ and modeled concentrational profiles are of variable importance in time-scale estimates, however uncertainties arising from T , and –less importantly– from f_{O_2} estimates can always lead to erroneous time-scale calculations when modeling natural crystals.

4.1. 1D along-axes and on-center traverses

These are along the central symmetry axes of the crystal, in other words, the three main crystallographic axes: a , b and c (Fig. 4, crystal cartoons). Independently of whether D is anisotropic or isotropic or the zoning pattern, 1D models along the b -axis show the best results and the smallest overall RMSD values ($< 2 \times 10^{-4}$) when ‘*apparent*’ initial C is used, (Fig. 4). Also, the 1D model parallel to the a -axis retrieves almost a perfect match (RMSD $< 10^{-5}$) if isotropic D is used. However, 1D models parallel to the c -axis perform badly even for the shortest duration ($t_{3D} = 200$ days) (Fig. 4). We come back to this point and discuss it in more detail in the next section. Although on-center 1D models

along the *a*- and *b*-axis yield concentration profiles different from the corresponding 3D simulation, and the differences become larger as the diffusion duration (t_{3D}) increases, these 1D models give acceptable estimates of the 'real' concentration distributions for almost the entire timespan investigated here.

The RMSD values of the individual models increase over time in any considered direction (Fig. 4). The most important observation is that there is a time (t_x) when any model for a given orientation (i.e. parallel to *a*-, or *b*-, or *c*-axis) has a significantly increased RMSD (Fig. 4). This corresponds to the time when the concentration plateau is lost, i.e. the diffusion reaches the crystal core along the axis in question (i.e. Fig. 1.c). The time (duration) it requires is proportional to the length of the axis, thus along the *a*-axis it occurs somewhat sooner than along the *b*-axis, in the case of isotropic *D*. This however, occurs much earlier than the time after which no acceptable estimates can be retrieved (i.e. at least two points of mismatch exceed the tolerable limit). This time is $t_{3D} > 12000$ days, for traverses along the *a*-axis and *b*-axis. However, for the *c*-axis the result is more complex. The *c*-axis is the longest, and thus it is expected to give good estimates (i.e. $\text{RMSD} \approx 0$) for the longest durations of diffusion (t_{3D}) relative to the other axes, but the 1D model along the *c*-axis performs the worst. This is because of the effect of merging diffusion fronts, an extreme 3D effect (c.f. Shea *et al*, in press). As the traverse parallel to the *c*-axis runs into the prism formed by $\{101\}$ & $\{\bar{1}01\}$ and $\{10\bar{1}\}$ & $\{\bar{1}0\bar{1}\}$ faces where interacting diffusion fronts meet, it experiences additional diffusion coming from two directions (i.e. the two prism faces). In 1D models this effect is absent, because diffusion operates only along the traverse. Therefore, if the 1D model is allowed to diffuse for the same time as the 3D, the two traverses (the one of 1D model and traverse taken from 3D data) are quite different in *C* between corresponding points and in the shapes of the profiles. We will address this matter in detail below.

Fig. 4. Plot of t_{3D} versus RMSD in various settings of parameters along the principal axes retrieved from 1D models. (a) simple reverse zoning (pattern A) (b) reverse zoning with overgrowth rim (pattern B). Crystallographic orientation is coded with colors. Y-axis of each plot corresponds to maximum observed RMSD at any t_{3D} . Symbols are same as in Fig. 3

As we mentioned above, 1D models employing ‘*apparent*’ initial C yield appropriate estimates even after the center is affected by diffusion, whereas models using ‘*initial*’ input C give increasing RMSD with time (Fig. 4). This is not a finding that we were anticipating. The reason for this is that diffusion in 1D models is allowed to modify C (‘remove’ material) with respect to one dimension only, therefore C towards the middle of the traverse can be modified from its ends only. This also results in the loss of the plateau. Whereas in 3D it is possible to modify C from the other two dimensions along the entire traverse at the same time, so that the plateau is maintained and C is effectively modified along the entire traverse. As a result, if the ‘*apparent*’ initial C is used, diffusion in the 1D model needs to recover only the profile shape, whereas the real ‘*initial*’ C ought to keep up with maintaining C of the plateau (see details in section 5.1.2.). Although

diffusion reaches the core from more than one direction, the additional effect is not significant enough for the 1D model to become unacceptable, although it definitely performs worse (c.f. *a*-axis and *b*-axis at a given t_{3D} ; Fig.4).

Our results agree with the findings of Shea *et al.* (in press) and show that crystal shape and aspect ratios have a major effect on modeling diffusion time-scales in 1D. Consequently, the 1D diffusion models estimate the ‘*real*’ diffusion duration correctly, as long as the compositions along the given 3D traverse are not affected by diffusion from other direction(s) significantly. When using 1D models on traverses through the crystal center and parallel to any of the crystallographic axes, ‘*apparent*’ conditions should be used for initial settings. Unfortunately, being sure whether the section slices through the center of the crystal is almost impossible when studying natural crystals in a 2D petrographic thin section.

4.2. 1D along-axes and off-center traverses

The possibility of working on traverses in this category are numerous, therefore, we need to organize them in order to show the systematics of 1D model estimates. The most explicit way is when traverses parallel to one selected axis are sampled from the crystal core to the edge within the plane defined by two axes (Fig. 5). For example, traverses parallel to the *a*-axis can be sampled starting with the one running through the center up till the crystal edge on the principal *ac*-plane, or on the principal *ab*-plane (Fig. 5). This exercise then can be repeated at one (or some or all) t_{3D} , so systematics of the 1D model estimates can also be examined with increasing diffusion duration (t_{3D}). Results shown here are from crystal with pattern A (reverse zoning, no overgrowth rim) with ‘*apparent*’ concentrations and both isotropic and anisotropic D , at $t_{3D} = 200$ and $t_{3D} = 14000$ days. At $t_{3D} = 200$, traverses from various distances relative to the center returns acceptable

estimates, but no traverse gives back an acceptable estimate of concentration distribution at $t_{3D} = 14000$, not even the center cuts (c.f. Fig. 5).

Fig. 5. RMSD plotted against location of traverse (distance from crystal center) for simple reverse zoning settings (pattern A) yielded by 1D models using ‘apparent’ C . Grey dashed line (or band) denote jointing faces. Symbols are same as in Fig. 3. Maximum of diagram y-axes reflects the maximum of RMSD, which is associated with a t_{3D} different from minimum and maximum t_{3D} .

Figure 5 shows the result of a sampling exercise of along-axis and off-center traverses. It is apparent that RMSD values change depending on the traverse’s orientation, i.e. parallel to which crystallographic axis and within which plane the traverse is taken.

Traverses taken parallel to the *a*-axis, on the *ac*-plane show good results ($\text{RMSD} \ll 10^{-4}$) up to $\sim 240 \mu\text{m}$ from crystal center ($< 70\%$ of *c*-axis half length), just before the corner where faces meet (dashed grey line, Fig. 5.a, right panel). Just after this point RMSD values abruptly increase and peak at $\sim 250 \mu\text{m}$ from the center then drop and increase again in various patterns depending on the duration of diffusion (t_{3D}) (Fig.5.a). Similar patterns of RMSD are shown for traverses parallel to the *a*-axis sampled on the *ab*-plane, with the exception of the peak RMSD position ($\sim 110 \mu\text{m}$ from center, 63.5% of *b*-axis half length). These patterns of traverses parallel to the *a*-axis show a systematic change with time (t_{3D}) independently of sampling orientation (on *ab*- or *ac*-planes). The position (in center-rim relation) where RMSD values start to steeply deviate from an acceptable value is shifted towards the crystal center, as well as there is an overall increase in RMSD with time (Fig. 5.a).

RMSD values associated with traverses parallel to the *b*-axis exhibit very similar patterns, albeit with lower overall RMSD values (Fig.5.b). Traverses sampled on the *ab*-plane show a generally higher scatter of RMSD values, and a much shorter range around center (max. $>60 \mu\text{m}$, about 60% of the *a*-axis half length; at $t_{3D} = 200$ days) with ΔC_{max} within an acceptable range (Fig. 5.b, left panel). However, traverses on *bc*-plane provide a much wider range (up to about $330 \mu\text{m}$ from center, $< 90\%$ of the *c*-axis half length; at $t_{3D} = 200$ days) where 1D model of traverses yield appropriate estimates (Fig. 5.b, right panel). As diffusion duration (t_{3D}) progresses RMSD values increase and the range of suitable traverses for 1D modeling shrinks on the *ab*-plane, whereas it extends to the entire length of the *bc*-plane at $t_{3D} = 14000$ days (Fig. 5.b). On the *ab*-plane 1D models return estimates within error in the vicinity of the crystal center and toward the edges, with a widening range of unacceptable 1D estimates around the joint of the corresponding crystal faces (Fig. 5.b, left panel). That is about $30\text{--}50 \mu\text{m}$ (about $30\text{--}50\%$) along the *a*-axis, with isotropic and anisotropic *D*, respectively. A more important observation,

however, is that for $t_{3D} = 14000$ days, all traverses parallel to the b -axis on the bc -plane give estimates within acceptable error (Fig. 5.b). In general, 1D models of traverses parallel to the b -axis yield closest estimations of C_{3D} (and therefore t_{3D}) with RMSD being $\sim 2 \times 10^{-4}$ and ΔC_{max} of 1.4×10^{-3} even at $t_{3D} = 14000$ days (about 38 years).

The results from the c -axis traverses are fundamentally different (Fig.5.c). Traverses sampled on the ac -plane exhibit constant RMSD ($< 2 \times 10^{-4}$) and ΔC_{max} with the exception of an about 10 μm wide area at the crystal edge at $t_{3D} = 200$ days with anisotropic D (Fig. 5.c, left panel). RMSD pattern on the bc -plane is similar and values are somewhat higher ($\sim 4 \times 10^{-4}$); there is no acceptable traverse in this setup, independently of D (Fig.5.c). As diffusion duration (t_{3D}) increases, the constant values of RMSD also increases, and gradually more traverses sampled on bc -plane deviate from those showing a constant value. RMSD patterns of these traverses resemble the shape of a logarithmic function (mirrored to y -coordinate-axis). With increasing t_{3D} , RMSD of traverses sampled on the ac -plane towards the edge of the crystal increase, however this upturn corresponds to an overestimation of the 'real' time (see section 3.3.3.). There is, however, a segment on the ac -plane (between 30 and 70 μm from the crystal center) where both D gives acceptable estimates at $t_{3D} = 14000$ days.

These results also demonstrate the interesting feature of merging diffusion fronts (e.g. Shea *et al.*, in press), and its variable effects through time. At $t_{3D} = 200$ days, the peaks of RMSDs (from the center towards the rim) correspond perfectly to the position where crystal faces meet (indicated by the grey line on Fig. 5). As the diffusion duration increases these peaks also become more significant, and the distance grows between the position of the last perfect matching traverse (RMSD ≈ 0 , from the center) and the peak position. This is the result of the increasing effect of interacting diffusion fronts. However, after a significant amount of time the diffusion modifies the *initial* C to an

extent that the strong effect of ‘additional’ diffusion is less important when 1D models are performed using ‘apparent’ C .

Fig. 6. Plot of t_{3D} versus RMSD in various settings of parameters along the principal planes retrieved from 2D models. Symbols and settings are same as in Fig. 3.

4.3. 2D on-center planes

2D planes sliced along the core of the crystal are the three center of symmetry planes: ab -, bc -, and ac -planes (Fig. 6). The 2D diffusion modeling exercises yielded results very similar to those of the 1D models. The results from the ab -plane somewhat resemble those of the a -axis, the bc -plane is akin to the c -axis, and the ac -plane is vaguely follows the pattern drawn by the b -axis. However RMSD values of 2D are at least an order of magnitude lower than corresponding 1D estimates. This, however, does not mean they would yield better estimates than 1D models; it is simply due to the nature of the RMSD method (see Appendix).

Not surprisingly, the *bc-plane* yields the largest mismatch of concentration, independently of D , starting C , or zoning pattern (Fig.6). This is because the section is affected by additional diffusion from the prism of $\{101\}$ and $\{\bar{1}01\}$, but this effect cannot be incorporated into the 2D model (cf. 1D *c-axis*). On the other hand, diffusion along the *b-axis* is taken into account, thus the overall RMSD is half an order of magnitude lower than for the 1D model along the *c-axis*. Yet the maximum difference (at any given position) between the ‘*real*’ and the estimated (2D model) C is always higher than the acceptable error (Fig. 6).

Although the *ac-plane* also contains the *c-axis* and therefore the model estimates of such a section might be expected to perform badly, the involvement of the *a-axis* compensates and takes the additional diffusion effect at the prisms into account (Fig. 1.a). In other words, the effect of 3D merging diffusion fronts is accounted for in these 2D models. Consequently, the *ac-plane* yields fairly good estimates almost until 12000 days in the chemically homogenous crystal (pattern A) and the reverse zoned crystal (pattern B) (Fig. 6). In contrast to the 1D models, the 2D models generally perform better if the ‘*initial*’ C is used (Fig. 6). 2D models along the *ac-plane* yield acceptable estimates throughout the entire investigated timespan (14600 days) in both crystal pattern A and pattern B independently of what D is used (Fig. 6).

The results of 2D models on the *ab-plane* are similar to those of the *ac-plane* under the same conditions (i.e. zoning pattern or starting C) (Fig. 6). In general, if the ‘*apparent*’ C is used, the *ab-plane* gives slightly worse estimates than the *ac-section*, independently of the anisotropic effect of D . In contrast, if the ‘*initial*’ C is used, models along the *ab-plane* yield the best estimates independently of zoning pattern, diffusion anisotropy, or duration (t_{3D}) with ΔC_{max} less than 10^{-8} , four orders of magnitude lower than the acceptable error (Fig. 6).

It is important to note that – if the ‘initial’ C is used – the *ac-plane* model starts to deviate from the acceptable error when diffusion along the non-modeled *b-axis* reaches the crystal center and thus affects the modeled section itself. Also, models along *ab-planes* give inaccurate estimates when diffusion along *c-axis* reaches the modeled *ab-plane*. The *ac-plane* models fail earlier than the *ab-plane* ones, because the *b-axis* is shorter than the *c-axis*.

4.4. 2D off-center planes

2D models along the *bc-plane* produce the most incorrect estimates close to the crystal center as well as close to the crystal edge (Fig. 7.c). RMSD values also peak at 70 μm from the crystal center where the $\{010\}$ and $\{210\}$ faces meet and diffusion fronts merge. At 200 days, the RMSD values are among the lowest, but the absolute mismatches (AC_{max}) are not in the acceptable error, irrespectively of which C (‘apparent’ or ‘initial’) and D (isotropic or anisotropy diffusion coefficients) are used (Fig. 7.c right panel). RMSD values increase exponentially with time towards the crystal edge (Fig. 7.c). When the ‘apparent’ C is used, the lowest RMSD are found closest to the core with increasing time (Fig. 7.c left panel). In the case of an ‘apparent’ C , models using anisotropic D yield estimates with overall lower RMSD, and between about 35 and 45 μm from the crystal center, the estimates are acceptable at $t_{3D} = 14000$.

Models along the *ac-sections* yield adequate estimates up to about 90 and about 100 μm from the crystal center in the case of ‘apparent’ and ‘initial’ C , respectively, at $t_{3D} = 200$ days independently of the choice of D (Fig. 7.b). These models also show that at about 110 μm from the center the RMSD values have a local maximum. This is the position of intersecting faces of $\{210\}$ and $\{100\}$ and merging diffusion fronts along the *b-axis* (Fig. 7.b), which effect is not accounted for in the *ac-section*. Results from both the anisotropic and the isotropic D models are similar at any given time independently of the

choice of starting C . There is, however, a striking contrast between the goodness of estimates using the 'apparent' or the 'initial' starting C . 2D models along *ac*-sections with 'apparent' C yield estimates of progressively increasing RMSD values with time, whereas models employing 'initial' C return satisfactory estimates with acceptable mismatch (ΔC) even at $t_{3D} = 14000$ days (Fig. 7.b). We shall note, however, that these satisfactory results are limited to a narrow spatial range around the crystal center of about $< 90 \mu\text{m}$ ($< 50\%$ of the *b*-axis half length) if D is isotropic and about $25 \mu\text{m}$ ($< 15\%$ of *b*-axis half length) if D is anisotropic.

Models on the *ab*-planes show very similar patterns to those of *ac*-planes (Fig.7). Generally, results from *ab*-sections yield lower RMSD values at larger distance from the crystal center than *ac*-sections at any given time. For instance, at $t_{3D} = 14600$ days and for models using 'initial' C and isotropic D , the *ab*-plane model give estimates with acceptable maximum mismatch until about $180 \mu\text{m}$ (more than half of the core-rim distance along *c*-axis), whereas *ac*-sections cannot reproduce the concentration distribution within acceptable error (cf. Fig. 7.a&b right panels). It is because the third crystallographic axis (*c*-axis for *ab*-sections) is much longer than the third axis (*b*-axis) for *ac*-planes, therefore diffusion along the third axis takes more time to reach the crystal center and affect the diffusion pattern in the *ab*-planes. This changes if D is anisotropic, and thus the range of acceptable estimate localizes to the immediate vicinity of the center (Fig. 7.a&b). If 'initial' C are used in *ab*-section models, then estimates are satisfactory to about $150 \mu\text{m}$ (about 45%) and $195 \mu\text{m}$ (about 60%) from the crystal center using anisotropic and isotropic D , respectively, at $t_{3D} = 14000$ days (Fig. 7.a). 2D models of *ab*-sections yield the best estimates between the crystal center and the junction of the $\{101\}$ and $\{100\}$ faces, and the worst from the prismatic ($\{101\}$ and $\{\bar{1}01\}$) area (Fig.7.a). It is due to the influence of merging diffusion fronts that act at the prism and cause additional diffusion from the *c*-axis.

The simulation results unambiguously show that along-axis 1D models, independently of zoning pattern or anisotropy of D , generally give better results if ‘apparent’ C is employed, whereas along-axis 2D models yield overall better estimates if ‘initial’ C is used as model starting input. Also, most models – 1D or 2D – show worst misfit if the c -axis involved, except for models of ac -section under certain conditions.

Figure 7. RMSD plotted against location of traverse (distance from crystal center) for simple reverse zoning settings (pattern A) by 2D models using ‘apparent’ C . Symbols are same as in Fig. 3. Maximum of diagram y-axes reflects the maximum of RMSD, which is associated with a t_{3D} different from minimum and maximum t_{3D} .

5. DISCUSSION

A very important effect of the interacting diffusion fronts in 3D is that it becomes more complex with time and more complicated with complex crystal shape. Thus, the longer the diffusion duration and the smaller and more complex the crystal is, the less chance one stands to conduct successful diffusion modeling and calculate reliable time-scales. Here we discuss the most important issues that need to take into account when one models the diffusion to obtain time-scales of inferred magmatic processes.

5.1. 1D or 2D model, what is more applicable in different cases?

5.1.1. The role of the position of initially abrupt concentration change – ‘apparent’ or ‘initial’?

We have shown above that in certain cases (e.g. 1D models involving the *c*-axis), the boundary (between zones of different composition) appears to shift from its initial position as diffusion duration (i.e. t_{3D}) increases significantly. This is potentially problematic, because to obtain proper time-scale estimates the essential parameter of initial location of the boundary has to be correct (e.g. Costa *et al.*, 2008, Saunders *et al.*, 2014). Otherwise erroneous time-scale estimates will be acquired.

Figure 8 shows the 1D estimated concentration traverses on the principal *c*-axis done by various initial conditions compared to the ‘real’ traverse taken from the 3D simulation done on the pattern A (initially chemically homogenous) crystal for $t_{3D} = 1000$ days with isotropic *D*. The largest misfit between ‘real’ data and estimated 1D concentration traverse is seen if the ‘initial’ boundary position is used and $t_{1D} = t_{3D}$. Consequently, if t_{3D} is not known (as in a natural crystal), probably one would keep diffusing the crystal to reach a better fit between the 1D estimated profile and the ‘real’ one. It can be seen that the ‘initial’ boundary position (dotted black line) does not coincide with an apparent

boundary position (dashed black line) inferred from the 'real' traverse (grey) (Fig. 8.b top panel). As in this simulation the initial crystal is chemically homogenous and diffusion is isotropic, the sole factor that can be accounted for the apparent shift in boundary position is the effect of the merging diffusion fronts at the prisms (i.e. $\{101\}$ & $\{\bar{1}01\}$ and $\{10\bar{1}\}$ & $\{\bar{1}0\bar{1}\}$).

Fig. 8. Schematic illustration of traverses and mismatches obtained by different boundary conditions applied. (a) the ac -plane shows the different penetration depth (x) due solely to additional diffusion; (b) 1D model conducted with 'initial' boundary position for $t = t_{3D}$; (c) 1D model conducted with 'initial' boundary position for $t = t_{ID*}$; (d) 1D model conducted with 'apparent' boundary position for $t = t_{3D}$. Grey traverse is simulated natural data, yellow traverse is 1D model data, and red traverse is mismatch (3D-1D). Grey bands in the traverse show melt surrounding the crystal. Thick dashed lines show the position of 'apparent' boundary. Note the similar shape of 1D model and mismatch in (c) and (d) as well as the difference in absolute ΔC . Note the massive difference between time obtained by models (c) and (d). t_{ID*} stands for best fit.

Allowing the above 1D model (using the ‘*initial*’ boundary position when other conditions are the same) to keep on diffusing, the best-fit concentration distribution estimate is obtained, i.e. the lowest overall mismatches, when $t_{1D}^* = 2943$ days, where * refers to the best-fit time (Fig. 8.c). Although the inflection points of the modeled profiles approximately fall onto the apparent boundary positions of the ‘*real*’ profiles, the absolute maximum error ($\Delta C > 0.015$) is more than twice as much as the acceptable threshold (0.0075). Therefore, this estimate should probably be rejected because of the too large associated mismatches ($\Delta C > 2\%$) (Fig. 8.c, bottom panel). The differences between the modeled traverse and the ‘*real*’ one become more obvious with increasing time.

The most important finding revealed by our simulations is that if 1D models performed parallel to the *c*-axis using ‘*apparent*’ boundary positions – inferred from the ‘*real*’ data – are used, then satisfactory estimates of *C* can be achieved with minimum errors (Fig. 8.d), and thus, correct time-scales can be calculated. Therefore adequate time-scales can be calculated for the duration of diffusion. This approach even works when absolute *C* at the plateau is lost (i.e. diffusion reached the crystal center from any other direction) as long as a plateau is still present in the *c*-axis traverse (i.e. diffusion reached the crystal center from one direction only). However, the ‘*apparent*’ boundary position is not obvious, because the concentration profile is not symmetric. The appropriate ‘*apparent*’ boundary position results in the lowest and most symmetric mismatch profile (Fig. 8.d bottom panel), thus conducting multiple diffusion models using slightly different positions seems one’s best approach. Consequently, in natural Opx crystals using slowly diffusing elements (e.g. Al or Ca) to determine the position of the boundary for 1D modeling might not be the best approach. The relationship between joint faces with merging diffusion fronts and shifting boundary position is merely a geometric effect, and thus, it should be valid for other minerals or other habits of orthopyroxene.

Crystal with zoning pattern B is somewhat different because diffusion can modify the concentration along the *c*-axis toward the core and toward the edge of the crystal (in contrast to the previous setting where toward the edge the concentration is fixed representing the much faster diffusion in the melt). Therefore, as long as diffusion does not modify the concentration in the entire rim, the boundary position will not shift from the 'initial' position. However, after this point in time the above-described effect occurs as well. How it would modify the shape of the traverse, which already underwent some diffusion by then, is difficult to constrain, but it certainly depends on the quantity of diffusion that affected the profile before, which is proportional to the initial width of the overgrown rim.

Although calculating time-scales from modeled diffusion profiles parallel to the *c*-axis can be challenging due to uncertainties in boundary position, it is also advantageous since diffusion profiles along the *c*-axis are substantially longer than along the *a*- or *b*-axis at any given time (due to what has been explained above). Hence, difficulties and challenges associated with collecting appropriate analytical data in regard to achievable spatial resolution (i.e. Saunders *et al.*, 2014) can be significantly reduced.

In 2D models the choice of boundary position is a complex issue; it does not involve two points only (as in case of a rim-to-rim 1D traverse), but many along the entire section. Along the parallel edge pairs all the boundary positions have to be the same, however selecting positions around the corners is challenging. In sections where the *c*-axis is not involved (*ab*-plane), the known boundary model is preferred, whereas in sections containing the *c*-axis the choice of boundary position is not obvious. Our results show that 2D models from *bc*-sections perform the worst among the possible 2D models when known boundary positions are employed (independently of initial *C* model input). On the other hand, *ac*-planes can be more than satisfactory especially when 'initial' *C* is used (Fig. 6). It is, however, unclear if the *bc*-section models perform better with

apparent boundary input and what the position for the 'apparent' would boundary be along the entire section.

5.1.2. The role of the initial concentration model input – 'apparent' or 'initial'?

We have demonstrated that 1D models give generally better results when 'apparent' concentrations are employed, whereas 2D models yield better overall estimates when 'initial' concentrations are used (Fig. 4-7). It is easy to see that 1D models can return realistic estimates if the diffusion occurs along the modeled direction only, i.e. as long as the modeled dimension is not influenced by diffusion from other directions. However, we found traverses with a concentration plateau, but its absolute value was different from the initial value, an indication that diffusion has reached it from other direction(s), and yet the model yielded adequate estimates. Taking a closer look, it can be seen that as long as there is at least a minimal extent of plateau present in the modeled traverse, 1D models can obtain correct results. However, when the plateau is lost (i.e. diffusion reached the crystal center from the direction in question) 1D models do not yield accurate estimates. We shall note that this is only valid at the immediate time of plateau loss if no error of estimates (see Appendix 1) is applied, i.e. comparison of C_{1D} to C_{3D} in each corresponding point along the traverses is strict. It is because as long as the plateau is present, the diffusion, parallel to the modeled direction, shapes only the profile, the absolute plateau concentration is modified by diffusion from the other direction(s). For instance, diffusion affects the principal *c-axis* only from the direction parallel to it at very short t_{3D} , because diffusion parallel to the other axes cannot influence the principal *c-axis* yet (Fig. 9.a). However, when a plateau loss occurs, the absolute concentration along the traverse is also modified by the diffusion parallel to the traverse. In orthopyroxene, diffusion penetrates the crystal center along the *a-axis* first and effectively alters the concentration of the principal *c-axis* after a given duration (Fig. 9.a). This diffusion

Fig. 9. Comparison of 1D and 2D model estimates and what 3D effects they can account for. Three scenarios considered: (a) at rather short t_{3D} , before diffusion reaches the crystal center from any of the three directions; (b) at an intermediate t_{3D} , after diffusion penetrated through the entire crystal but only along a -axis (the shortest one); and (c) at relatively long t_{3D} , where diffusion reached the center from the two short axes (a - and b -axis), but not from the longest (c -axis). Both 'apparent' (solid line) and 'initial' (dashed line) C model inputs are considered. Note that for the 2D models only the c -axis is plotted instead of the entire ac -section, it is for simplifying reasons and to facilitate direct comparison between the two model results. In (a) both 1D and 2D models give acceptable estimates of concentration distribution along the modeled traverse and plane. In (b) 1D model using 'apparent' C returns good estimate, whereas 2D model does if 'initial' C is used. In (c) 1D model cannot return acceptable estimate, but 2D model is still accurate if 'initial' C model input is used. For details see text.

affecting the principal *c*-axis cannot be taken into account when one conducts a 1D model. However, using ‘*apparent*’ C , the extra flux removed by the *a*-axis is ‘accounted’ for. When diffusion parallel to the *c*-axis reaches the crystal core, the boundaries also appear to shift from their initial positions, and the 1D model cannot realistically reproduce the concentration pattern along the traverse any longer (Fig. 9.a).

If ‘*initial*’ C is used in the 1D model then there is an extra amount of flux to be removed. It is possible only towards the ends of the traverse, which is only possible, however, if 1D diffusion reaches the center of the traverse. This process elongates the profiles and changes the shape of the modeled traverse compared to ‘*real*’ traverse (Fig. 9.b). Thus, if the 1D model is allowed to run for a longer time than t_{3D} , then the profile will flatten and finally reach C_{real} , but its shape will not be similar to that of the ‘*real*’ traverse (Fig. 9.c). This is why 1D models give worse estimates if ‘*initial*’ C is used as a model input. However, there is a special case with the *a*-axis where 1D models yield acceptable estimates after plateau loss, as long as the additional diffusion effect from the merging corners do not influence it (Fig. 3; case A, 14000 days) using ‘*initial*’ C .

The reason why 2D models yield better concentration estimates when ‘*initial*’ C input is used also lies in the interaction of 3D diffusion along the different directions. 2D models account for two out of the three dimensions, therefore they return realistic estimates as long as diffusion along the third (non-modeled) dimension does not play a role in shaping the ‘*real*’ concentration distribution. For instance, 2D models of *ac*-sections yield estimates as reliable as 1D at short durations (Fig. 9). After diffusion has reached the crystal core parallel to the *a*-axis, however, models with ‘*apparent*’ C are not reliable any longer, but using ‘*initial*’ C they can reproduce the actual concentration distribution (Fig. 9.b). After diffusion parallel to the *b*-axis becomes effective in the modeled section, 2D cannot account for the extra diffusion of the third direction and models give poor estimates (fig. 9.b). This happens latest along the on-center *ab*-plane

because of the length of the *c*-axis (even if it experiences additional diffusion). Thus 2D models performed on *ab*-sections are able to yield perfect estimates for the longest time (t_{3D}) when the 'initial' *C* model input is used (Figs. 6&7). When diffusion along the *c*-axis reaches the modeled *ab*-section, t_{3D} is overestimated. The same models perform less well with 'apparent' *C* inputs. Until diffusion first reaches the center of the section along any of the modeled directions, 2D models with 'apparent' *C* input perform excellently (Figs. 6&7). After this, however, they underestimate t_{3D} , because the absolute *C* is also lowered in the crystal center. The overall performance of the 2D models on *bc*-sections is, however, semi-independent on the choice of starting *C*; it is strongly influenced by the position of the *bc*-planes with respect to interacting faces and their effect on boundary position.

2D models, especially the ones parallel to *ab*-sections, perform better when 'initial' *C* input is used. It, however, poses a challenge to decide whether the analyzed *C* is 'apparent' or 'initial' when it comes to natural samples. One's best choice is to perform a 1D model on a traverse that exhibits a plateau using the measured concentrations ('apparent') for model *C* input, then perform a 2D model on the entire section to see if it returns the same inferred time-scale. If it does, diffusion did not alter the measured *C* at the plateau from the third direction yet, and one can be confident about the inferred diffusion duration. However, if the retrieved time-scale is not comparable to the one obtained from the 1D model, then diffusion has reached the crystal center (assuming that the section is from the center of the crystal). This case is tricky, because there appears to be no way to decide if diffusion reached the center from all directions and causes the differing estimates. However, this case also holds a unique opportunity. By conducting a reverse 2D model (i.e. adding mass back to the measured *C*) on the given section for the time-scale calculated from the 1D model (with 'apparent' *C*), one can retrieve the initial (before diffusion) concentration at the plateau in the crystal center, as 2D models on *ab*-

planes gives very good estimates of concentration distribution if 'initial' C used. This means that information of original geochemical characteristics can be estimated even if those are not recorded in the crystal any longer. This information can then be used for other petrological aspects, for instance, to calculate the real concentration of melt in equilibrium with the crystal in question, to refine thermometric calculations, etc.

5.2. Influence of crystal morphology on diffusion

Previous studies (e.g. Ganguly & Tirone, 1999; Watson *et al.*, 2010) have also considered the effect of various crystal morphologies on diffusion and related phenomena (e.g. closing temperature) and found that different shapes (e.g. cylinder, sphere, etc.) yield different results when other parameters are identical. Most recently Shea *et al.* (in press) have performed a series of numerical simulations on polyhedral olivine crystals and have shown that crystal morphology has a significant influence on modifying diffusion gradients through converging diffusion fronts at convex junctions of crystal faces.

Our results of diffusion simulations in orthopyroxene also confirm such an effect and reveal its relationship with respect to progression of diffusion in time. As diffusion progresses in time the additional diffusion also develops in space as well: larger areas around the convex face-joints get involved. As we have shown earlier, 1D models cannot account for its effect, therefore, if the modeled traverse experienced such an impact, likely the calculated time-scales will most not be correct. The lesser the influence of the additional diffusion on a traverse, the smaller the error of an inferred time-scale. Furthermore, 2D models can only keep up with the impact of merging diffusion fronts if 2 crystal faces converge only (e.g. *ab*-sections for merging $\{210\}$ with $\{100\}$ or $\{010\}$; and *ac*-sections for converging $\{101\}$ with $\{100\}$). Hence, the crystal morphology effectively alters the diffusion penetration pattern and creates the impression of the presence of an additional flux.

The same situation happens in an initially zoned crystal (overgrown rim) at the core-rim interface. However, what controls the morphological effect on the diffusion pattern in this case is the shape of the core, not of the entire crystal. As we have shown (e.g. Figs. 6.a&b), a core with the same shape as the crystal itself has the same influence as described above with the exception of the absolute position of joint faces with respect to the crystal. Therefore, for an initially zoned crystal, the morphology of the core and its impact has to be taken into account when modeling diffusion in such a case. Shea *et al.* (in press) showed that 1D (and most probably 2D) diffusion model performed on a spherical crystal will always yield significant overestimations of time-scales (about 30% on average) independently of where the modeled traverse (or section) is taken from (in core-rim relation), orientation, and a priori knowledge of the initial concentration of the core. This setting can potentially lead to incorrect time-scale calculations, therefore when doing diffusion modeling in initially zoned crystals not only the crystal shape has to be considered, but that of the core, as well.

The geometrical effects that we have found for Opx crystals, in particular the effect of merging faces is also relevant for diffusion in other minerals (e.g. Shea *et al.*, in press), even if there is no diffusion anisotropy. Diffusion is isotropic, for example, in garnet, and hence, there is no need of a priori knowledge on crystal orientation as diffusion is not dependent on crystallographic direction (Ganguly, 2002; and references therein). However, Ganguly *et al.* (2000) note that profiles selected for modeling shall be perpendicular to the 3D concentration gradient otherwise ambiguous time-scales may be calculated. Shea *et al.* (in press) and this study demonstrate that crystal morphology substantially influences the diffusional penetration around the convexly converging crystal faces and cause additional diffusion. Furthermore, results of Shea *et al.* (in press) and this study demonstrate that this effect is present in various shapes (e.g. sphere, parallelepiped, different polyhedral habits) and it results mostly in overestimation of

actual diffusion durations estimated by 1D (or 2D) models. Thus, the morphological effect plays an important role in altering diffusional penetration in garnet, as well. The magnitude of differences between estimated and 'real' time, however, depends on the location within the crystal, i.e. where the modeled profile was taken with respect to joint faces and diffusion duration. For instance, diffusion modeled on a 1D profile from a simple sphere-shaped substance almost always yields overestimation of the real time by a minimum of 30% (Shea *et al.*, in press). Therefore, in accord with our findings, it is implied that if diffusion is modeled in rounded (e.g. Ducea *et al.*, 2003) or complexly shaped (e.g. Ganguly, 2000) garnet crystals, it probably yields misleading results. Furthermore, undistorted, naturally occurring garnets mostly manifest in rather spherical habits (e.g. Cherepanova *et al.*, 1992; Jamtveit & Andersen, 1992) and many converging crystal faces, i.e. morphological consideration shall be part of modeling compositional zoning in garnets.

5.3. Isotropic or anisotropic diffusion of Fe-Mg in orthopyroxene? – comparison of natural and simulated data

The results from previous studies do not agree about the nature of diffusion in orthopyroxene (i.e. Ganguly & Tazzoli, 1994; Schwandt *et al.*, 1998). Ganguly & Tazzoli (1994) suggest isotropic D for the c - and b -axis and probably slower D along the a -axis, thus overall an anisotropic behavior. In contrast, Schwandt *et al.* (1998) demonstrated clearly anisotropic D ($D_c > D_b > D_a$). Likewise, anisotropic behavior of D has been shown with respect to several trace elements (e.g. Cr, Nd, Yb) in orthopyroxene (e.g. Cherniak & Liang, 2007; Ganguly *et al.*, 2007; Sano *et al.*, 2011). We have shown that the choice of the diffusion coefficient (i.e. isotropic or anisotropic D) does not influence the general outcome of the compositional distribution pattern with respect to the entire crystal. Simulations performed in either isotropic or anisotropic D show the same correlation with

respect to crystal morphology and goodness of 1D/2D model estimations (Figs. 3-6). The only difference lies in the progress of diffusion along individual crystallographic axis. For isotropic D at any given time (before diffusion reaches the center of crystal) progress of diffusion is identical along the the a - and b -axes, i.e. diffusion penetration distance (x) is equal and profile lengths are identical. However, if D is anisotropic, at any given time (before diffusion penetrates the crystal center) x is shorter along the a -axis than it is along the b -axis. Accordingly, the profile length is also shorter along the a -axis than it is along the b -axis. Diffusion penetration distance (x) or profile length along the c -axis is not definitive in this comparison since it is influenced by other factors, also independently of the choice of D .

Observations on natural, chemically zoned orthopyroxenes revealed that the profile lengths along the different axes (from the same grain in thin section) are not equal and calculated time-scales along those axes may be significantly different (e.g. Allan *et al.*, 2013; Chamberlain *et al.*, 2014; Tomiya & Takahashi, 2005). Tomiya & Takahashi (2005) noted that diffusion along the c -axis is seemingly faster than parallel to the other two axes, and from this observation they concluded that anisotropic behavior of diffusion is the most probable explanation. Allan *et al.* (2013) and Chamberlain *et al.* (2014), however, attribute this to a combination of diffusion and growth. As we show below, the Fe-Mg zoning patterns of Opx from Gede suggest that diffusion of Fe-Mg is significantly anisotropic and supports the Schwandt *et al.* (1998) experimental data.

5.4. Preparation guidelines for diffusion modeling in orthopyroxene

Although there are some ways to correct for sectioning (orientation) effect, it is effective only under certain conditions and cannot be applied generally to all 2D sections. Therefore it seems most useful to try to identify the most reliable crystal sections. Proper

section selection is still a guarantee for correct time-scale estimates, because other factors may introduce uncertainties (e.g. Costa *et al.*, 2008).

- When searching for suitable grains **neglect small, asymmetric crystals**. These sections, by the highest odds, are from the crystal corners, non-parallel to any crystallographic axes.
- Select **intact, euhedral crystals**, the ones that are free from signs of resorption and that show high degree of symmetry. These sections most probably preserve the zoning result of diffusion.
- Avoid euhedral and symmetric sections with obviously asymmetric concentration patterns. These sections may be too close to converging faces.
- **Aim for *ab*-sections and *ac*-sections**. Ignore *bc*-sections because they are the toughest to evaluate for their absolute boundary position within the crystal, and if oblique they were most presumably affected by diffusion along *a*-axis.
- Look for **grains displaying a clearly flat, non-tilted concentration plateau**. Check for high compositional symmetry in the grain. Fe-Mg content of orthopyroxene can be easily assessed by exploiting the relationship between the grey-scale of a BSE image and the Fe-Mg composition (i.e. Allan *et al.*, 2013).
- **Avoid sections of twin or coalescing grains**; conjugated surfaces may result in sector-zoning-like concentration patterns.
- **Assess the orientation** of the selected section by any micro-analytical technique (e.g. electron backscattered diffraction (EBSD) – Costa & Chakraborty, 2004), discard sections with high degree of inclination.
- **Traverses** should be taken **away from crystal corners** in order to avoid the influence of additional diffusion.
- **1D models** should target traverses **parallel to *b*-axis or *c*-axis** (on *ac*-sections) and use '**apparent**' concentration values; collect data of concentration of slowly

diffusing element(s) (i.e. Al, Ca) to evaluate initial boundary positions (i.e. Allan *et al.*, 2013; Saunders *et al.*, 2014).

- **2D models** should aim for *ab*-sections, if possible. Also check for the initial boundary position and zoning in slow diffusing element(s) (i.e. Allan *et al.*, 2013; Saunders *et al.*, 2014). Note that 2D models perform best if '*initial*' *C* is employed.

The guidelines above should lead to better time estimations, but one cannot be sure whether the selected section cuts through the center of the crystal or not. If, however, one has the possibility and laboratory background, one should prepare individually mounted orthopyroxene grains sectioned along *ab*-planes as well as along *ac*-planes in the center of the crystal. These sections certainly hold the highest probability of obtaining correct time-scale estimates. Although sample preparation might be tedious, all sectioning effects can surely be avoided. This approach is especially recommended and advantageous for samples with pumiceous texture.

6. MODELING NATURAL CRYSTALS

In this section we follow the guidelines outlined above and model Fe-Mg diffusion in several reversely zoned orthopyroxene crystals from Gede volcano to estimate time-scales of magma mixing observed in all Holocene deposits (see chapter 1). We are going to (1) select the best crystal candidates and assess the orientation of the selected crystals using EBSD, (2) estimate the initial concentration distribution and the initial boundary conditions and positions, and (3) conduct 1D diffusion modeling.

6.1. Selecting crystals for diffusion modeling and assessing their crystallographic orientations

It has been shown that crystal orientation plays a significant role in obtaining reliable time-scale estimates (e.g. Costa & Chakraborty, 2004; Shea *et al.*, in press). After

filtering out the non-symmetric, broken, and oddly zoned crystals, we assessed the crystal orientations in the 2D petrologic thin-sections using EBSD (Prior *et al.*, 1991). For diffusion modeling we selected only those grains which orientation is ideal. At least one axis of these grains is (almost) parallel to one of the crystallographic axes, and ideally it is either the *c*- or the *a*-axis (Fig. 10). By carefully selecting the to-be-modeled grains, we can minimize the error of estimated time-scales (e.g. Shea *et al.*, in press).

6.2. Estimating the initial Fe-Mg concentration distribution and the boundary conditions in the selected orthopyroxene crystals

Evaluating the initial concentration distribution is more difficult, but the recently gained knowledge of concentration distribution in crystals can be used to make robust estimates. Here we model diffusion in 1D, thus the absolute initial concentration is not of great importance, since 1D models give better estimates when ‘*apparent*’ initial distribution is applied. Further, the selected crystals are quite large ($> 200\ \mu\text{m}$ along the short axis) and concentration profiles are very steep ($< 40\text{--}50\ \mu\text{m}$) suggesting short time-scales of diffusion, thus initial concentration in the crystal center is most likely preserved (Fig. 10). Moreover, plateaus in the concentration traverses (along long and short axes) are present indicating that diffusion did not penetrate through the entire grain. We took the average concentration of the plateau as initial input for the 1D models (Fig. 10). Although the compositional profile of the rim in certain cases shows cyclical repeating changes suggesting multiple magma recharge or dynamic mixing, these events do not effectively affect the diffusion through the core-rim boundary, unless the thickness of the first cycle overgrowth rim is too thin (e.g. Shea *et al.* in press). Thus we take the maximum concentration of the first overgrowth rim as initial input for the 1D models (Fig. 10). We assume that the rim grew very quickly and in equilibrium with the mafic recharge magma, and thus the concentration at the core-rim boundary was initially abrupt

(step function, Fig. 10). By investigating the concentration profile of a slow diffusing element (e.g. Al), the initial boundary positions can be assessed. On the other hand, when modeling diffusion parallel to the *c*-axis, one should take ‘*apparent*’ boundary position as it is inferred from the modeled element’s profile, here Fe-Mg (e.g. section 5.1.1.).

The reversely zoned orthopyroxene crystals indicate mafic magma recharge (see chapter 1). The compositional difference between core and rim is significant, but is negligible at the rim-matrix boundary; therefore a large flux exists at the core-rim boundary, but virtually no flux at the rim-groundmass (matrix) boundary. The relation between the core and the rim indicates open boundary conditions, i.e. diffusion can modify the concentration in both sides to find equilibrium (i.e. Costa *et al.*, 2008). However, assuming the groundmass as an infinite reservoir of constant Fe-Mg concentration (at least compared to the individual crystal in question), if there is exchange of mass through the rim-groundmass boundary, i.e. the equilibrium Fe-Mg value is that of the groundmass (e.g. Costa *et al.*, 2008).

6.3. Modeling Fe-Mg diffusion profiles

As the initial concentration profile is assumed to be a step function change between core and rim, the observed deviation from it is due to diffusion. To model this diffusion and calculate time-scales of it we need to know conditions of *T*, *P*, *f*O₂. We have good constraints on *T* and *f*O₂, but a bit of uncertainty on *P*, however its effect is negligible at subvolcanic pressure (Costa *et al.*, 2008). We used *T* = 1035-1075 °C) and *f*O₂ (> NNO) for modeling, as summarized in Table 1. For detailed description on how these were obtained see Chapter 1.

We have modeled five compositional profiles of four orthopyroxene crystals parallel to the *a*- and *c*-axis (Fig. 10). In two of these crystals we modeled diffusion employing both isotropic and anisotropic diffusion coefficients (e.g. section 5.3.) parallel to the *a*-

axis, and in one crystal we modeled compositional profiles parallel to both the *a*- and *c*-*axis*, and this allows us to show the effects of diffusion anisotropy on calculated time-scales. We have used the concentration dependent diffusion equation shown earlier (Eqn. 4). The results of best fit concentration models are illustrated in Figure 10 and the retrieved time-scales (< 1 month) are summarized in Table 1. The results are self-consistent through the different Holocene units, especially if the error on *T* estimates is considered. The 4 kyr C3O7 orthopyroxene crystal is ideally orientated and thus it is a good target to show the large difference in between time-scales obtained with isotropic and anisotropic *D* parallel to the *a*-*axis*. Time-scales calculated along the *c*-*axis* (25 days) and the *a*-*axis* (6 days) are significantly different when using isotropic *D* (e.g. Ganguly & Tazzuli, 1994) (Table 1). Supposing that the different sectors of the crystal record the same growth history, the retrieved time-scales from them should be identical. It is significant to note that the width (thickness) of the overgrowth rim is proportional to the aspect ratio of the crystal (and the unit cell ratio) indicating anisotropic growth (Fig. 10). Therefore, anisotropy of diffusion is the most likely effect to explain the differences in time-scales. When using anisotropic *D* (section 3.1.4.) the calculated time-scale parallel to the *a*-*axis* (21 days) is, in fact, similar to that parallel to the *c*-*axis* (Table 1), and it explains why the time-scale calculated from the *a*-*axis* traverse seemed much shorter (e.g. Allan *et al.*, 2013). A 10 kyr orthopyroxene crystal (C6O1) yields similarly different calculated time-scales with isotropic and anisotropic *D* (Table 1).

Data in Table 1 show a consistent picture of estimated time-scales, when all crystals and factors are taken into account. Our results show that the investigated crystals record the magmatic interaction that prompted rim growth and started about a month before each eruptions, and thus the trigger mechanism and dynamics must have been very similar in the Holocene eruptive episodes (see chapter 1) However, the magma mixing event could have started earlier and not initially been recorded by the studied crystals.

Fig. 10. Lower hemisphere projection of the orientation of the crystallographic axis (a, b and c), representative photomicrographs of orthopyroxene crystals, and diffusion models of the concentration profiles. Arrows on the photomicrographs show the position and direction of the compositional traverse. (a) Orthopyroxene from the 10 kyr unit. (b & c) Orthopyroxenes from the 4 kyr unit. Note that in (c) two traverses are modeled, for detail see text. (d) Orthopyroxene from the 1.2 kyr unit. Note the very sharp change at composition and the reverse zoning at all crystals. Note also that the rims show slight oscillation in composition in contrast to the cores, which is negligible in modeling. $Mg\# = 100 \cdot Mg / (Mg + Fe^t)$ in mols, Fe^t = total iron as FeO. Calculated time-scales are summarized in Table 1.

Table 1. Summary of calculated time-scales (in days) and Fe-Mg modeling conditions

Unit	Crystal	orientation (EBSD)	T (°C)	Δ NNO (log units)	starting D (10^{-18} m ² /s)	t (days)	min. t (max. T)	max. t (min. T)
10ky	C6O1	to a-axis	1075±40		9.90	7	3	13
10ky	C6O1*	to a-axis	1075±40		2.83	22	12	40
4ky	C3O7	to a-axis	1055±20	0.85	10.69	6	3	10
4ky	C3O7*	to a-axis	1055±20	0.85	3.05	21	17	26
4ky	C3O7	to c-axis	1055±20	0.85	10.69	26	20	36
4ky	C3O11	to c-axis	1055±20	0.85	7.86	18	14	26
1.2ky	P5O2	to c-axis	1035±30	0.34	4.89	14	9	24

* denotes anisotropic D (see text for further information)

7. CONCLUSIONS

We have conducted 3D diffusion numerical simulations on orthopyroxene and showed the relationship between crystal shape, initial conditions, and anisotropy of diffusion in 3D and the estimated concentration profiles from 1D and 2D diffusion models. A key finding is that interacting diffusion fronts at joints of crystal faces can significantly modify the diffusion and the concentration pattern. This effect can be accounted for in certain 1D and 2D models, whereas it cannot in others. This effect is universal and not specific only to orthopyroxene, therefore, attention needs to be paid when choosing any crystals and traverse orientations for diffusion modeling. 1D models are most likely to give acceptable estimates if the ‘*apparent*’ *C* is used, whereas 2D models perform better with ‘*initial*’ *C* used. For 1D models the *a*- and *b*-axis, and for 2D models the *ab*- and *ac*-sections should be preferred. These orientations most likely yield appropriate estimates of concentration distribution and thus calculated time-scales.

Applying our results to orthopyroxene crystals from Gede volcano, it indicates that diffusion of Fe-Mg is considerably anisotropic. This reflects why diffusion models parallel to different crystallographic axes give little or excessively different time-scales. Calculated time-scales for Holocene deposits of Gede are about 1 month, indicating that mafic magma recharge and magma mixing occurred just shortly before eruption, and probably – regarding the relatively short time-scales – triggered these eruptions.

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APPENDIX 1

In order to assess the goodness of a concentration estimate along a traverse or a plane, its concentration distribution has to be compared directly to the ‘*real*’ data. Calculating residuals, i.e. subtracting one dataset from the other at each corresponding data point, is a common way (e.g. Shea *et al.*, in press). We chose to subtract the model estimate concentration from the ‘*real*’ data ($\Delta C = C_{3D} - C_{1D/2D}$) (Fig. 3). The residual array (or matrix) is the mismatch. It is easy to see that a perfect model estimate compared to ‘*real*’ data would result an overall zero mismatch ($\Sigma \Delta C = 0$). Most often, however, model estimates are not perfect, therefore, a threshold (a tolerance interval) has to be implemented to distinguish between acceptable and unacceptable estimates. In natural samples most often major elements are analyzed by electron probe micro analyzer (EPMA) for diffusion modeling studies (e.g. Costa *et al.*, 2008). EPMA are associated with a certain uncertainty in respect with accuracy and precision of analyzes, which is commonly >1% relative for major elements. We chose the tolerance interval to be dependent on concentration following the fashion of analytical error, thus it is 1% relative to the ‘*real*’ data, determined at each data point along the traverse (or across the plane) (Fig. 3). An estimated concentration distribution is considered unacceptable and gets rejected if there are at least two (because of symmetry of rim-to-rim traverses) outlier data points (Fig. 3).

Making a verdict based solely on the RMSD value is mostly misleading, because it may not reliably reflect the goodness of an estimate. An acceptable 1D estimate can have higher RMSD value than a rejected 2D estimate. For example, the 1D estimate of pattern A, anisotropic D , ‘*apparent*’ C , and $t_{3D} = 14000$ days (Fig. 4.a, left panel) is a good estimate with a $\Delta C_{max} = 0.0032$ (0.43% relative error) and its RMSD is relatively higher (about 2×10^{-4}). Whereas the 2D model estimate of the same configuration (Fig. 6.a, left panel) is rejected because its $\Delta C_{max} = 0.247$ (about 33% relative error) is way out of

acceptable limit, albeit its RMSD (about 4×10^{-5}) is one order of magnitude lower than that of the 1D estimate. It is because the RMSD calculation averages over the entire dataset, which, in case of the 2D matrix, contains much more data points of $\Delta C \approx 0$, than it does in case of the 1D model. Thus, despite the much higher absolute ΔC values, the 2D model has lower RMSD values. This is why the 2D models, in average, have lower RMSD values than the 1D models, and this is why RMSD by itself is – most of the time – do not support with enough information to decide whether a model estimation is acceptable or not. Although RMSD value is misleading as a standalone parameter in evaluating goodness of an estimate, its change in time (e.g. Fig. 4) or in space (e.g. Fig. 5) gives reliable insights into what tendency operates in respect to concentration estimates. Such as, it is a helpful tool in visualizing the data, because it is a single number and is more suggestive than the absolute ΔC at one data point.

CONCLUSIONS

The volcanological, geochemical and petrological history of Gede volcano before this PhD was only approximately known, despite that it potentially poses a threat to a large population that lives around it. Historical records show that its past activity have caused significant disruption to people's life many times. Thus, improvement of our knowledge on its behavior is necessary in order to interpret ongoing monitoring signals, mitigate the related hazard, and reduce impacts on human life and economics during a future activity. In this spirit, I have performed detailed petrochemical studies based on the deposits collected during field work, and conducted numerical simulations to improve our understanding of diffusion in three dimensions and its effect on commonly used diffusion time-scale modeling.

During detailed fieldwork, samples of pyroclastic flows and debris avalanches from 5 major explosive eruptions (VEI 2 to 4) were collected, four of these eruptions occurred in the Holocene. The collected samples cover a broad range of compositions from basalt to rhyodacite. Several of the Holocene samples show macroscopic mingling and mixing textures. Bulk-rock major and trace element compositions can be explained by a combination of fractional crystallization and magma mixing and mingling. A two-stage differentiation of deep and water-rich basaltic magmas (amphibole-bearing and plagioclase-free; 600 ± 200 MPa, 6 ± 2 wt % H_2O) followed by a drier and shallower differentiation (plagioclase and pyroxene-bearing; < 100 MPa; < 3 wt% H_2O) represents the early (> 45 kyr) magma evolution under Gede. This coupled differentiation leads to high-Si melts (rhyodacitic to rhyolitic) production. In the Holocene, the signature of reservoir processes shifted from the deep reservoir to the shallow and from fractionation to magma mixing. All Holocene magmas have experienced various extents of hybridization and/or mingling between basaltic and rhyodacitic magma types or crystal-

rich cumulates. The hybrid, intermediate magmas may have also undergone plagioclase- and amphibole-bearing fractionation.

I have conducted core to rim electron-probe micro analyses (EPMA) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses (>6000 individual points of EPMA and >450 points of LA-ICP-MS) on the main phenocrysts (amphibole, plagioclase, ortho- and clinopyroxene). This dataset allows unambiguous identification of the processes at play and fingerprint the crystal sources. High concentration of Mg/Fe, Cr, and Ni and low contents of incompatible elements characterize amphiboles from the early units that grew from basaltic liquids. Low Mg/Fe and high incompatible element (e.g. Zr, Rb) cores of ortho- and clinopyroxenes in the older Holocene units are in equilibrium with the rhyodacitic liquid, a much more evolved composition than the bulk-rock they are found in. They probably come from an evolved and shallow crystal-mush. On the other hand, overgrown rims on these pyroxenes are rich in Mg/Fe and compatible elements (e.g. Cr, Ni), and poor in incompatible trace elements (e.g. Zr, Rb), indicating the intrusion of much more primitive melts into the shallow reservoir. Some amphibole cores and intermediate composition pyroxenes record magma hybridization and suggest complete partial mixing between the mafic the silicic magmas. Rims of high Mg/Fe and compatible elements (Cr, Ni) on these hybrid amphiboles also record the mafic magma recharge similarly to the pyroxene rims.

I have shown that rare earth elements (REE) systematics in minerals and residual liquids depend on several factors and not only the crystallizing mineral assemblage. The traditional interpretation of negative Eu-anomaly in clinopyroxene being due to extensive plagioclase crystallization, was shown to not necessarily be the case for the >45 kyr mafic, sector zoned clinopyroxenes. The reason for negative Eu-anomaly is rather a combination of a relatively low fO_2 (about QFM) of the magmas and fast crystal growth. This, however, does not rule out some amount of calcic plagioclase co-crystallization

within the deep source of clinopyroxenes, or rather during transport to the shallow reservoir. I also suggest that REE characteristics (e.g La/Lu) of sector-zoned phenocrysts together with the negative Eu-anomaly are due to fast crystal growth. The gradually increasing La/Lu and decreasing negative Eu-anomaly towards the rims are indicative of decreasing crystal growth rates, and thus the system reaching equilibrium. This can be explained by magma ascending from a deep to a shallow reservoir and thus decreasing degrees of disequilibrium after the transport has been completed.

On the other hand, in the shallow level, dry, and more oxidized differentiation of sodic plagioclase extensively incorporates Europium so that it causes remarkable Eu-depletion in the residual liquid. Crystallization of evolved clinopyroxene from such depleted liquid shows strongly negative Eu-anomaly even in a more oxidized environment. Apatite crystallization in a highly silicic liquid also plays a major role and somewhat obscures the effect of plagioclase crystallization.

I have conducted three-dimensional (3D) numerical simulations on diffusion in orthopyroxene and evaluated the best orientations of two-dimensional (2D) sections, and one-dimensional (1D) traverses than can return the most accurate calculated time-scales. The results show that crystal shape has large influence on chemical zoning patterns created by diffusion, and thus the crystal shape and modeled traverse orientation needs to be taken into account irrespectively of diffusion anisotropy. It can be said that, in general, 1D and 2D models perform better using different initial conditions; therefore one's choice should depend on available information about the crystal.

I have applied the findings to orthopyroxene crystals from Gede volcano that reflect magma mixing and mafic recharge in a silicic reservoir. I found that when choosing the most appropriate crystals the time scales from different eruptions are very similar, and indicate that the time-scales since the last magmatic intrusion and eruption are less than

one month. Such time should be informative for taking actions to mitigate volcano hazards at Gede during possible forthcoming unrest and eruptions.

My work shed new light on the evolution and dynamics of magmatic processes underneath the Gede volcano and their time-scales, and potentially can lead to better hazard mitigation and protecting human life and cultural and economical values around the volcano.

Although my PhD studies have come to an end, my research on volcanic petrology and related topics has hopefully not yet. During my research I addressed many interesting questions, some of these were specific to the Gede volcano, some of them were more general and can be adapted to other volcanic systems or can be of interest not only to hard-core petrologists. I am particularly interested in continuing and extending my research on several topics, two of which I give some perspective below.

I think it is important to better understand the behavior of REE, with particular interest in Eu-anomaly, in pyroxenes, and their relationship to crystal growth rates, disequilibrium crystallization, and sector zoning. I think it should be possible to calibrate a model – based on experimental data – that relates REE systematics and Eu-anomaly in between pyroxene's sectors to growth rates, and maybe to decompression and magma ascent rate. As in-situ determination of REE concentration in minerals is nowadays routinely done (LA-ICP-MS, SIMS), such calibrated model would give a relatively straightforward and universal tool to assess more details on volcanic plumbing systems in general, what is recently more difficult to constrain.

Another important topic that I think is still not well resolved – my personal favorite – is using 3D diffusion models, and results from theoretical works, to be able to fill the gap between the diffusive time-scales (several hundreds or thousand years) and the isotopic time-scales (tens of thousands to millions of years). Using the known relations

between diffusion and 3D crystal shape, and using trace elements to fingerprint parts of a crystal that is not in equilibrium with the major element content link may be made between different zones within a crystal. For instance, is alternating chemical zoning in a single crystal due to a single event or multiple events occurred over a longer time span? Does similar chemical zoning pattern recorded in crystal cargos of different eruptions mean that the same fractionation process is at work over the times or the crystal cargo is 'inherited'? In other words, how can we use diffusion to 'date' different parts of a chemically zoned crystal? In many cases, it can be seen that fast diffusing elements (e.g. Fe/Mg in pyroxenes) show only one event in a zoned crystal, whereas minor (e.g. Al) and trace (e.g. REE) elements show more variations in concentration in core-rim relation. Additionally, these systematic changes in minor and trace elements may coincide with presence of inclusion bands (mineral and/or melt). If changes in major element using the last known – and still recorded – event can be unequivocally associated with minor and trace element abundances, then using the relationship, major element concentrations can be estimated for those inner parts of the crystal where they appear homogenous, but minor and trace elements indicate otherwise, as an example see Chapter 1 Figure 7.e. Reconstructing the 3D shape of a multiple-zoned crystal with the known girth and estimated initial concentration of the chemically different zones, a minimum residence time could be obtained.