AN EXPERIMENTAL STUDY OF SULPHUR ISOTOPE FRACTIONATION DURING MAGMATIC DEGASSING

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ABSTRACT

The sulphur isotopic evolution of basaltic melts degassed under disequilibrium conditions was investigated experimentally at temperatures of 1225 °C and oxygen fugacities between 0.5 and 1.9 log₁₀ units above that defined by the Ni-NiO buffer. Melts were equilibrated at a pressure of 550 MPa in a piston-cylinder apparatus and degassed at ~490 to 0 MPa. Water concentrations in the experimental glasses varied from 1.5-10 wt %. Extents of degassing were quantified by comparing sulphur concentrations in the experimentally degassed (DG) glasses to those in isobarically quenched (IQ) glasses, and ranged from 0 to \sim 40%. Degassed glasses were systematically more enriched in ³⁴S than IQ glasses, and the degree of enrichment correlated positively with the extent of degassing. Predicted fractionation factors between the gas and the melt $({}^{34}\alpha_{g-m})$ for open-system degassing under conditions of local gas-melt equilibrium ranged from 0.9986 to 0.9996. Our empirical fractionation factor was found to be 0.9987, which lies near the low end of the predicted range, suggesting that another process is contributing to S isotope fractionation. Modelling results indicate that a possible explanation for this behaviour is the diffusion of S during bubble growth; however consideration of the mechanistic details of bubble growth show that more sophisticated models than those employed in this study are needed to fully quantify this effect.

RÉSUMÉ

Une investigation de l'evolution isotopique du soufre dans les liquides basaltiques a été effectuée à une temperature de 1225 °C et à une fugacité d'oxygène entre 0.5 et 1.9 unités log₁₀ au-dessus du tampon Ni-NiO. Les matières fondues ont été équilibrées à une pression de 550 MPa dans un appareil pistoncylindre et dégazées de ~490 à 0 MPa. Les concentrations de l'eau dans des verres expérimentaux ont varié entre 1.5 et 10 % (en masse). Le taux de dégazage (variable de 0 à ~40 %) a été quantifié en comparant les concentrations de soufre dans les verres dégazés experimentalement (DG) à celles de verres trempés de façon isobarique (IQ). Les verres DG étaient systématiquement plus enrichis en ³⁴S que les verres IQ, et cet enrichissement montrait une corrélation positive avec le degré de dégazage observé. Les facteurs de fractionation théoriques entre la phase gazeuse et la phase fondue ($^{34}\alpha_{g-m}$) pour dégazage d'un système ouvert sous conditions d'équilibre localisé (phase gazeuse-phase fondue) ont varié entre 0.9986 to 0.9996. Notre facteur de fractionation empirique était de 0.9987, vers le bas de la gamme prédite, ce qui suggère qu'un processus additionel contribue à la fractionation isotopique de soufre. Nos résultats de modélisation suggèrent la diffusion du soufre pendant la croissance de bulles de gaz comme possible explication; néanmoins, la prise en compte des détails mécanistiques de la croissance des bulles montre que des modèles plus complexes que ceux utilisés ici sont nécessaires pour une quantification complète de cet effet.

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1.0 Introduction

In the first section of this chapter we discuss several reasons why the study of sulphur in volcanic systems is important. In the second section we discuss S isotope systematics in natural igneous systems and the usefulness of S isotope data for understanding the processes that form volcanic rocks. The final section discusses the goals of this study and presents a brief overview of the research.

1.1 Motivation

Humans have coexisted with volcanoes for thousands of years. The land surrounding volcanoes is often very fertile due to the high amounts of volcanic ash, and provides great opportunities for farming and agriculture (Stevens, 1964). Volcanic ore deposits provide abundant economic opportunities (Naldrett, 1989). Volcano tourism is a source of income to countries rich with volcanic activity (Aylward *et al.* 1996). On the other hand, volcanic eruptions pose threats to the lives and livelihoods of those living in proximity. An estimated 500 million people worldwide are at risk from volcanic hazards (Tilling and Lipman, 1993). Despite the growing body of knowledge of volcanic systems, we are still far from having a complete understanding of volcanism.

Magmatic volatiles are an integral component of all volcanic systems. Many studies have been undertaken to asses the volatile abundances in magmas, their degassing paths, and the magmatic volatile budgets of active volcanoes (Metrich and Wallace, 2008). Understanding the degassing of volatiles in a particular volcano is critical to the determination and mitigation of the risks posed by that volcano because the degassing of the volatiles within a volcanic system determines in part the eruptive style of a volcano: whether the volcanic eruption is explosive, effusive, or somewhere in between (Sparks *et al.* 2004). In particular it is important to distinguish the irreversible loss of gas from the magmatic system degassing, where gas lost from the magma is not removed from the magmatic system. Closed-system degassing paths are characteristic of explosive eruptions, whereas open-system degassing paths characterize effusive eruptions (Adams *et*

al. 2006). Prior to an explosive eruption, the high rate of ascent of the gas and melt causes a thermodynamic and chemical disequilibrium if the volatiles cannot exsolve at the same rate as the magma ascends (Mangan and Sisson, 2000). This could happen in a closed system, where the volatiles remain in contact with the melt. In an open system, once the volatiles leave the melt they do not remain in equilibrium with the melt, and the volatiles and melt may become decoupled and the gas is able to flow out the conduit, leading to a more effusive eruption (Melnik and Sparks, 2002).

Studying the gasses emitted by volcanoes before, during, and after eruptions and during times of quiescent degassing has improved our ability to predict volcanic eruptions. For example, data obtained from real-time monitoring of volcanic gas at Mount Etna found that there is a spike in the CO₂/SO₂ ratio prior to an eruption: this may indicate that the magma chamber is filling up with CO₂-rich magmas that soon erupt (Aiuppa *et al.* 2007). The sampling of volcanic gas at vents and remote sensing of volcanic plumes are useful tools in eruption forecasting, but the correct interpretation of field data requires modelling of volatile degassing from magmas.

Water and carbon dioxide are the most abundant volatiles in magmatic systems (Symonds *et al.* 1994). Although sulphur is the third most abundant volatile, it plays an important role in many igneous processes (Symonds *et al.* 1994). The typical concentrations of volatile species in volcanic gasses (including convergent-plate, divergent-plate, and hot-spot volcanoes) are H₂O (35-90 mol%), CO_2 (5-50 mol%) and SO_2 (2-20 mol%) (Schmincke, 2004).

The "excess S" problem demonstrates the complexity of the degassing behaviour of volcanic systems. The excess S problem comes from observations that the amount of S gas measured during volcanic eruptions is often an order of magnitude or greater than the amount of S expected to result from the degassing of melt (Wallace, 2001). There are several theories that may partially explain this phenomenon. One such theory is mixing of basaltic and dacitic magmas, in which a reduced magma mixes with an oxidized magma (Kress, 1997). This proposed mixing would lower the oxidation state of the magma to a point of minimal S

solubility. This has the effect of exsolving most of the S from the dacitic and basaltic liquids, and also reduces the stability of any anhydrite crystals possibly present in the oxidized liquid, thus driving S out of the major non-volatile sulphur-bearing phases (Kress, 1997). Another theory is that there exists a separate C-O-H-S vapour phase at the top of the magma chamber that is not reflected in the volatile contents obtained from melt inclusions (Wallace and Gerlach, 1994).

On average, volcanoes emit ~13 Mt of SO₂ per year (Symonds *et al.* 1994). Most of the SO₂ (~9 Mt) is emitted by passive degassing (Symonds *et al.* 1994). Sulphur dioxide injected into the stratosphere during large volcanic eruptions converts to sulphuric acid aerosols that block solar radiation and contribute to ozone destruction (Pollack *et al.* 1976). This can be especially problematic during eruptions which release large amounts of SO₂, such as the eruption of Mount Pinatubo in 1991. An estimated 17 Mt of SO₂, the largest measured stratospheric cloud of SO₂, were erupted, and had a significant impact on climate and the ozone layer (Bluth *et al.* 1992). Another well-known example of volcanoes and climate change comes with the 1883 eruption of Krakatau, to which a drop in mean annual northern hemisphere temperature of 0.3-0.4°C has been attributed (LaMarshe and Hirschboeck, 1984).

As alluded to above, sulphur isotopes in volcanic rocks have the potential to allow us insight into the formation of those rocks. The usefulness of the interpretations of volcanic processes in terms of S isotope systematics depends in part on our depth of knowledge of S isotope fractionation during these processes. In a typical study of volcanic degassing, field data (volcanic rocks) are collected and S is extracted and analyzed (e.g., Marini *et al.* 1998). Using a degassing model that incorporates the S isotopic composition and the amount of S remaining in the melt after degassing, researchers may make inferences on the style and extent of degassing that has occurred. In this study we experimentally constrain the style and extent of degassing, and measure the resulting S isotopic composition of the melt, thus quantifying the process of magmatic degassing.

The following section discusses examples of how this idea has been applied to natural volcanic systems.

1.2 Sulphur isotope fractionation in natural volcanic systems

The materials used to study S isotopic fractionation in volcanic systems are extrusive volcanic rocks such as lavas and pumices. The composition of the rocks studied depends on the location of interest. Sakai et al. (1982) concluded in their study of submarine and subaerial Kilauea basalts that the degassing of SO₂ is a very important process governing S chemistry and isotopic ratios of these rocks. Equilibrium isotopic fractionation theory holds that, in general, basaltic magmas will become isotopically heavier during degassing (de Hoog et al. 2001). Low measured sulphur contents in many volcanic rocks points to extensive degassing of sulphur (Marini et al. 1998, de Hoog et al. 2001). By measuring the isotopic values of sulphur extracted from these rocks and fitting these data to models for fractionation under conditions of local gas-melt equilibrium, researchers can infer the general characteristics of the degassing process. Examples of this technique include Torssander (1989), Marini et al. 1998, Mandeville et al. 1998, de Hoog et al. 2001, and Luhr and Logan (2002). The list of examples cited is not a complete list of studies of this nature, but rather a selection of literature relevant to this work.

Marini *et al.* (1998) studied the S-isotopic signatures of phonolitic rocks from Vesuvius, Italy. They determined the pre-eruptive temperatures (T) of the lavas to be 1100 to 1200 °C. They used δ^{34} S and degassing models to constrain the oxygen fugacities of the samples to be 0.85 to 1.20 log units above the nicklenickle oxide buffer (Δ NNO = 0.85-1.20) The S-isotope signatures of the lavas ranged from -0.8 - +6.4 ‰ V-CDT (Vienna-Canyon Diablo Troilite). Most samples followed the trend of increasing δ^{34} S and decreasing S concentration in the rock caused by inferred increased degassing. They found that a model of open-system degassing under conditions of local gas-melt equilibrium provided the best fit to their data. Their data and interpretations are plotted together in Figure 1.1. Marini *et al.* (1998) also concluded that because the key parameter

controlling the ${}^{34}S/{}^{32}S$ ratio is the average magma oxidation state, the S concentrations and $\delta^{34}S$ values could be used to estimate average redox conditions.

de Hoog *et al.* (2001) studied basaltic lavas from Indonesian arc volcanoes that are strongly degassed (estimated >90% S loss during degassing) and are enriched in δ^{34} S relative to basalts from non-subduction related settings. The range in δ^{34} S was +2.0 - +7.8 ‰ V-CDT. At their determined P,T, *f*O₂ conditions, the model of isotopic fractionation during open-system degassing under conditions of local gas-melt equilibrium was not able to explain their measured data. Instead, the higher values of δ^{34} S were inferred to be imparted by slab enrichment.

Luhr and Logan (2002) used measurements of S isotopes from anhydrite crystals in trachyandesite pumices from El Chichón, Mexico to evaluate various mixing scenarios. The δ^{34} S values in the different anhydrite crystals ranged from 2.5 – 10.9 ‰ (CDT), and were homogeneous to within 1 σ within a given crystal. It was concluded using open-system degassing models that progressive degassing alone could not account for such high δ^{34} S values, because at the degree of degassing needed to produce such fractionations there wouldn't be enough S left to precipitate the anhydrite crystals.

Mandeville *et al.* (1998) studied rhyodacitic and dacitic rocks from the 1883 eruption of Krakatau. They measured whole-rock δ^{34} S values of +2.6 - +4.0 ‰ (V-CDT) and tephra δ^{34} S values of +6.3 - +16.4 ‰. Using the model of equilibrium isotopic fractionation they concluded that the high δ^{34} S values could be explained by open-system or multi-stage degassing at low pressures, along with other factors such as the pre-eruptive temperature and the efficient partitioning of S into the water-dominated vapour phase.

In most of the cited studies, isotopic fractionation during open-system degassing under local gas-melt equilibrium does not adequately explain the results. Exception are Marini *et al.* (1998) and Mandeville *et al.* (1998) who conclude that a model of open-system degassing can explain their data. Inspection of Figure 4 in Mandville *et al.* (1998) results in the observation that

many of their data points lie above fractionation curves predicted by open-system degassing, potentially indicating that the model is not completely adequate. This serves to highlight the need for controlled experimental investigations of the degassing process, which would enable us to better interpret the S isotopes measured in natural volcanic rocks.

1.3 Purpose of this study

Magma chambers are inaccessible to direct observation but the processes that occur in magmatic systems, such as degassing and diffusion, are often isotopically sensitive (e.g., Marini *et al.* 1998; Richter *et al.* 2006). Accordingly, the S isotopic consequences of these phenomena may be used to indirectly constrain processes occurring in magmatic systems. In order to achieve this goal, however, laboratory studies of must be performed to investigate the efficacy of sulphur isotopic fractionation during magmatic degassing.

It is well known that S plays a major role in many magmatic processes, yet a full picture of sulphur behaviour prior to, and during, eruptions remains unknown. Many studies rely on local gas-melt equilibrium isotopic fractionation, such as Rayleigh fractionation in the interpretation of their results (e.g. Marini *et al.* 1998, Mandeville *et al.* 1998, Torssander 1989, de Hoog *et al.* 2001, and Luhr and Logan, 2002). This study is designed to test whether local gas-melt equilibrium fractionation holds in a laboratory setting.

To study the effects of degassing on sulphur isotope fractionation, a series of degassing experiments were performed on basaltic melt. Degassing was induced by reducing the pressure on a hydrous melt such that it became saturated with an aqueous phase that exsolved and extracted sulphur from the melt. The degassing occurred at disequilibrium conditions at various pressures. Disequilibrium degassing is a stochastic process and occurs when the gas and melt are not allowed sufficient time to equilibrate. The longer it takes for the sample to be degassed, the closer the sample gets to equilibrium, but this did not happen in our study because the timescales of degassing (minutes) are much less than that required for the system to achieve equilibrium, which requires hours

(Liu *et al.* 2007). The melt was quenched to a glass by quickly dropping the temperature after degassing. The range in degassing was designed to correspond to a range in sulphur isotopic composition of the melt, as Rayleigh fractionation predicts that larger amounts of degassing cause larger sulphur isotopic fractionation (Marini *et al.* 1998). The glasses produced from these experiments were analysed for S concentration and δ^{34} S values. The resulting data were compared with widely used models of volcanic degassing, and provide laboratory quantification of S isotope fractionation during magmatic degassing.

Magmatic processes drive volcanic eruptions, thus this research will be a valuable tool in hazard management through isotopic characterisation of S degassing. We believe that studying the fractionation of sulphur during degassing can improve our knowledge of magmatic systems by helping to interpret field data and better understand past eruptions. To date, very little has been done to experimentally constrain S isotopic fractionation factors during disequilibrium magmatic degassing. This research will help to evaluate the interpretation of S isotopic data from volcanic rocks.



Figure 1.1: Sulphur isotope measurements from lava and pumice vs fraction of S remaining in the melt after degassing. Lavas and pumices from Somma-Vesuvius, Italy are plotted as filled circles and rectangles, respectively. Redrawn from Figure 2A in Marini *et al.* (1998).

2.0 Theory

2.1 Factors that control isotopic fractionation during degassing

The magnitude of an equilibrium isotopic shift during degassing of a silicate melt is primarily controlled the fractionation factor, ${}^{34}\alpha_{g-m}$, between the gas and the melt, by the degree of degassing (F = [S]_{melt after degassing}/[S]_{melt before degassing}), and by the mode of degassing. The fractionation factor is controlled by the temperature of the system and S speciation, which is a function of the oxidation state of the magma as well as the water fugacity (Marini *et al.* 1998).

As originally recognized by Sakai *et al.* (1982), speciation of S within coexisting gas and melt phases is a critical control on the magnitude of ${}^{34}\alpha_{g-m}$ under conditions of local gas-melt equilibrium. A particularly lucid presentation of the technique for calculating ${}^{34}\alpha_{g-m}$ can be found in Marini *et al.* (1998), and the discussion here relies heavily on this paper. The functional relationship between the fractionation factors that govern isotopic partitioning among individual species in the gas and melt and the overall fractionation factor ${}^{34}\alpha_{g-m}$ is:

$$1000 \ln \alpha_{g-m} = Ygs1000 \ln \alpha_{SO_2-H_2S} + Yis1000 \ln \alpha_{S^{2^-}-SO_4^{2^-}} + 1000 \ln \alpha_{H_2S-S^{2^-}}$$
(1)

The quantities " Y_{is} " and " Y_{gs} " represent S speciation in the melt (S²⁻, SO₄²⁻) and in the gas (H₂S, SO₂), respectively. The fractionation factors between S species ($\alpha_{SO2-H2S}$, $\alpha_{S2--SO42-}$, $\alpha_{H2S-S2-}$) are temperature dependent (Taylor, 1986). Conventional statistical mechanics predicts that there should not be a pressure effect under these conditions.

Temperature dependencies of fractionation factors between various species have been compiled by Taylor (1986) and are listed below (as they appear in Marini *et al.* 1998):

 $1000 \ln \alpha_{SO_2 - H_2S} = -0.42 (10^3 / T)^3 + 4.367 (10^3 / T)^2 - 0.105 (10^3 / T) - 0.41$ (2)

$$1000 \ln \alpha_{S^{2^{-}} - SO^{2^{-}}} = -7.4 (10^{3} / T)^{2} + 0.19$$
(3)

$$1000 \ln \alpha_{H_2 S - S^{2-}} = 1.1 (10^3 / T)^2 - 0.19$$
⁽⁴⁾

Equation (2) has been calibrated over a temperature range of 400-1300 °C, whereas equations (3) and (4) may be used for temperatures between 600-1000 °C (Taylor, 1986). Marini *et al.* (1998) have used equations (3) and (4) up to 1200 °C, and we have used them up to 1225 °C. Experimental data to extend the temperature ranges of these fractionation factors is lacking in literature, thus we have no choice but to extrapolate these equations beyond their calibrated range of accuracy.

The SO_4^{2-} (S⁶⁺) fraction of total ionic S in the melt, (Y_{is}) is defined as:

$$Yis = \frac{X_{SO_4^{2^-}}}{X_{SO_4^{2^-}} + X_{S^{2^-}}} .$$
⁽⁵⁾

This value is related to the oxidation state of the magma and can be calculated from the oxygen fugacity following Wallace and Carmichael (1992):

$$Yis = 10^{0.48* \Delta NNO - 0.70}$$
(6)

where Δ NNO is calculated from the oxygen fugacity (fO_2) following Huebner and Sato (1970):

$$\Delta NNO = \log fO_2 - 9.38 + 24930/T.$$
⁽⁷⁾

We did not find that this method of calculation provided a good fit with our data (discussed below). Instead, we use equation (4) from Jugo *et al.* (2005) to calculate Y_{is} at a given Δ NNO as follows:

$$\log\left(\frac{X_{s^{6+}}}{X_{s^{2-}}}\right) = 1.02\Delta NNO - \frac{18.60}{T} - 0.45$$
(8)

The ratio $[X(S^{6+})/X(S^{2-})]$ can be converted to equation (5) as follows:

$$Yis = \frac{X_{SO_4^{2^-}}}{X_{SO_4^{2^-}} + X_{S^{2^-}}} = \frac{1}{\frac{1}{[X(S^{6^+})/X(S^{2^-})]} + 1}$$
(9)

 Y_{gs} represents the SO₂ fraction in total gaseous S and is defined as:

$$Ygs = \frac{X_{SO_2}}{X_{SO_2} + X_{H_2S}}.$$
 (10)

This value depends on the ratio of the mole fraction of SO_2 to the mole fraction of H_2S in the gas which can be calculated from the following equation (Marini *et al.* 1998):

$$\log \frac{X_{SO_2}}{X_{H_2S}} = \frac{27377}{T} - 3.986 - \log(fH_2O) + 1.5\log(fO_2)$$
(11)

Equation (7) can be used to calculate fO_2 at a given Δ NNO, while the equilibrium fH_2O in the degassing experiments can be calculated using Volatilecalc (Newman and Lowenstern, 2002).

Equilibrium isotopic fractionation between a melt and coexisting gas phases at varying temperatures and oxidation states and at an fH_2O of 300 MPa have been calculated following the above procedure and the results are plotted in Figure 2.1. To obtain Figure 2.1, we first calculate Y_{is} and Y_{gs} at the desired T, Δ NNO, and fH_2O . We can then use equations (2, 3, and 4) and equation (1) to calculate a value for $1000ln^{34}\alpha_{g-m}$ for our specified conditions.

Figure 2.1 demonstrates the strong control that temperature has on fractionation factors. From this figure we see that as the temperature increases, less isotopic fractionation is expected. To calculate this figure, Y_{is} and Y_{gs} are calculated as above. The range of Δ NNO represented in Figure 2.1 is representative of what is observed in natural volcanic environments (Carmichael, 1991, Wallace and Carmichael, 1992). The calculated equilibrium S-isotope fractionation factor is plotted against Δ NNO. It is clear from this figure that in very reduced igneous environments such as mid-ocean ridges (Wallace and Carmichael,1994) we do not expect large fractionation factors, but in oxidized igneous environments such as island and continental arcs (Haggerty, 1976) sulphur isotopic fractionation can be significant. An important feature to note is that at the high temperature of our experiments (1225 °C), and at an average oxidation state of ~ 0.9 log units above the NNO buffer, that the calculated equilibrium fractionation is quite small, and we would expect δ^{34} S values for a co-existing gas and melt that differ by only about ~ - 0.7‰.

The change in isotopic composition of the melt during degassing as conditions change from reduced to oxidized is presented in Figure 2.2. This calculation was performed at 1225 °C over a range of water fugacities to test the effect of fH_2O on S isotope fractionation. Within the experimental conditions of this study, the effect of fH_2O on ${}^{34}\alpha_{g-m}$ is insignificant (highlighted in the figure); Figure 2.2 illustrates, however, that the depth of degassing can influence the magnitude of ${}^{34}\alpha_{g-m}$, especially at reduced conditions.

In a closed system the exsolved vapour remains in contact with the melt during degassing. In an open system, infinitesimal amounts of exsolved vapour are immediately removed from contact with the melt. The isotopic shifts in the melt caused by equilibrium open- and closed- system degassing can be approximated using equations (12) and (13), respectively (Marini *et al.* 1998):

$$\delta^{34}S_f = \delta^{34}S_i + 1000(F^{\alpha - 1} - 1)$$
(12)

$$\delta^{34}S_f = \delta^{34}S_i + (F - 1)1000\ln\alpha$$
(13)

Where the subscripts "f" and "i" stand for the "final" and the "initial" melt, and F is the fraction of sulphur remaining in the melt. In our study we normalize all $\delta^{34}S_f$ values to the $\delta^{34}S_i$ of the melt, so while equations (12) and (13) are approximate because they are cast in terms of δ values, the differences between their predictions and those of more exact forms is non-existent (Gat *et al.* 2000). Plotting each of these equations at identical F and ${}^{34}\alpha_{g-m}$ on the same figure (Figure 2.3) it can be seen that all other factors being equal, isotopic fractionation

in an open system will be greater than in a closed system. This is true in general, but especially true for smaller values of F (greater degrees in degassing).



Figure 2.1: Effect of temperature on ${}^{34}\alpha_{g-m}$ at $fH_2O = 300$ MPa. As the temperature increases less fractionation occurs. In general, at more reduced conditions, fractionation will be less than at more oxidized conditions.



Figure 2.2: Effect of varying fH_2O on ${}^{34}\alpha_{g-m}$ at T = 1225 °C. Maximum and minimum fH_2O plotted are slightly wider than the range encountered in our experiments. The widest shaded area represents the Δ NNO range of our experiments to one standard deviation on the population (Δ NNO 0.5 to 1.3). The darker grey shaded area represents the Δ NNO range covered by the 99% error on the weighted mean (Δ NNO 0.7 to 1.1), and the dark grey line represents the weighted mean of our calculated oxygen fugacity: Δ NNO = 0.9. Changing fH_2O within the range encountered in our experiments does not affect the isotope fractionation to a significant degree.



Figure 2.3: Open (dashed line) versus closed (solid line) system degassing. The fractionation factor is equal to 0.9993 in both cases. Open-system degassing is capable of producing larger fractionation among the S isotopes than closed-system degassing. The $\delta^{34}S_{melt}$ values are referenced to the initial composition of the melt.

3.0 Methodology

3.1 Decompression Experiments

The initial material (basalt glass powder) for all decompression experiments was composed of a mixture of basalt glass and gypsum. The glass was synthesized by melting basalt from Mount Etna, Italy (erupted during 122 BC) in a 1 atm furnace for 1 hour. The glass was quenched, powdered ($< 10 \,\mu m$) and mixed with enough reagent grade gypsum (CaSO₂·2H₂O) to give the final mixture approximately 0.2 wt % S. The mixture was ground under ethyl alcohol in an agate mortar and pestle for 30 minutes. The resulting mixture was stored in an oven at 110 °C. Platinum capsules (0.3 cm diameter) were loaded with approximately .005 ml de-ionized water and approximately 0.045 g basalt glass gypsum powder and welded closed without volatile loss. Water contents before the experiments ranged from 1.5 to 10.5 wt %. Experiments were performed in a piston-cylinder apparatus. Loaded capsules were placed into crushable-aluminapyrex NaCl assemblies (Baker, 2004), and any free space was filled with finely powdered ($< 10 \,\mu$ m) pyrophyllite. Temperatures were measured with W26%Re and W5%Re thermocouples. The temperature in the piston cylinder was automatically controlled to within 2 °C.

Twenty-three samples were synthesized by submitting aliquots of basalt glass powder at 550 MPa and 1225 °C for two hours. The uncertainty in the temperature readings is ± 10 °C (Hudon *et al.* 1994), and the pressure is calibrated to within ± 25 MPa (Baker, 2004). After this step some samples were isothermally decompressed to final P between ~ 490 and ~0 MPa and quenched. Decompression rates were approximately 740 kPa s⁻¹. Other samples were isobarically quenched at ~550 MPa. Quench rates at the termination of the experiment were approximately 2000 °C/min. Oxygen fugacities of the experiments (discussed below) measured relative to the Ni-NiO buffer (Huebner and Sato, 1970) range from 0.5 to 1.9 Δ NNO. This variation is most likely imparted by the experimental conditions and not experimental error, as the general trend in our data shows that samples which are more degassed have lower

oxidation states than less degassed samples. A complete list of experimental conditions used during this study can be found in Appendix 1. Material from the isobaric experiments was used for two purposes: (1) it provided an estimate of the initial S content and S isotopic composition prior to degassing and; (2) it provided the starting material for three 1-atmosphere in-situ degassing experiments. For the 1 atm experiments, aliquots of the isobarically quenched glasses were placed in a boron nitride capsule, which was placed in an alumina furnace wrapped with Kanthal wire attached to an AC power supply. The furnace and wire were insulated by a block of alumina ceramic. Temperature inside the furnace was measured by a type S thermocouple. The uncertainty of these measurements is less than 15 °C. Samples were heated above 1100 °C and held for 30 -60 s. The power supply was then switched off and the samples cooled to 600 °C within 120 s. Because the 1-atm degassing experiments were an attempt to produce large amounts of degassing, they are discussed along with the piston cylinder experiments. Sample numbers DG31, DG32, and DG33 all represent degassing in the 1-atm furnace.

3.2 Quantitative Analytical Procedures

3.2.1 Electron microprobe

Following the degassing experiments, quantitative analyses were obtained by wavelength-dispersive spectrometry using a JXA JEOL-8900L electron microprobe in the Department of Earth and Planetary Sciences, McGill University. Glass analyses were performed with an accelerating voltage of 15 kV, a beam current of 10 nA, and a beam size of 5µm. For major elements a counting time of 20 s on the peak was used. For S analysis, a Johanssen crystal and an Hspecrometer were used with a counting time of 240 s, achieving a detection limit of approximately 80-90 ppm. Both pyrite and pyrrhotite were used as the standards for S analysis at different times. In all cases, BMAK (a basalt glass) was the standard for Na, Al, Fe, Si Mg, Ca, Ti; a rhyolite glass was the standard for K; spessartine was the standard for Mn, and apatite was the standard for P. All raw data were reduced with a ZAF correction routine. To ensure the accuracy of the measurements of our unknowns, a secondary standard (basaltic glass VG-2) was analyzed. Our measured S concentration in VG-2 was 1440 ± 46 ppm. This agrees with previous measurements on VG-2: 1420 ± 20 ppm (Wallace and Carmichael, 1992), 1416 ± 36 ppm (de Hoog *et al.* 2001), 1414 ± 30 ppm (Liu *et al.* 2007), therefore the measurements of the electron microprobe do not introduce any bias into our analysis. For each sample, approximately 10-15 spot measurements were made in order to quantify the homogeneity of each glass. Running duplicate analyses of some samples provided an empirical estimate of the analytical reproducibility. In select samples, S contents were measured along transects between neighbouring bubbles. A 5 µm step size was used along the transects.

The amount of S in each sample was used to calculate a quantitative degree of degassing (F). The F-value represents the fraction of sulphur remaining after degassing and is calculated as follows:

$$F = \frac{S_{ppm} (\text{degassed sample})}{\text{average } S_{ppm} (\text{isobaric quench experiments})}$$
(14)

The relative error on F was calculated as follows:

$$\frac{Error(F)}{F} = \sqrt{\left(\frac{\sigma \ avg \ S_{ppm} \ (isobaric \ quench)}{S_{ppm} \ (isobaric \ quench)}\right)^2 + \left(\frac{\sigma \ S_{ppm} \ (degassed)}{S_{ppm} \ (isobaric \ quench)}\right)^2}$$
(15)

where σ represents one standard deviation. Estimates of water content of synthesized glasses were obtained using the "difference from 100" technique (Devine *et al.* 1995) with electron microprobe data and are accurate to better than 1 wt%. To determine the F values for each sample, points both near and far from vesicles were analyzed to get the mean F value for each experiment. The above procedure uses the S concentration in the bulk glass to estimate F values and does give individual attention to the variability associated with S depletion at bubble rims (where present). The variability in the mean S concentration for each experiment is consistent with the microprobe variability. It is noted here that as a result, F values reported in this thesis are maximums.

3.2.2 Determination of the experimental oxidation state

Variations in the wavelength of sulphur SK α X-ray radiation [λ (SK α)] are directly related to changes in the oxidation state of sulphur dissolved in silicate glasses (Carroll and Rutherford, 1988) and can be used to not only investigate sulfur speciation, but also to determine the oxygen fugacity of the experiments. In order to calculate the oxidation state of the silicate glasses we assumed that (a) all of the S in the glass occurs as S²⁻ and S⁶⁺, and (b) that $\Delta\lambda(SK\alpha)$ increases linearly with $S^{6+/}S_{tot}$. These assumptions have been successfully employed in previous studies (Carroll and Rutherford; 1988 Wallace and Carmichael, 1994; Baker and Rutherford, 1996; Jugo et al. 2005). Measurements of the peak position of the sulphur K α radiation, λ (SK α) in the synthesized glasses were made using a PETH crystal on 1 spectrometer. Measurements of DG30 were made on 2 spectrometers using both PETH and PETJ crystals, and the calculated oxygen fugacity for this sample represents an averaging of the two datasets. Approximately 10 measurements were made on each sample analysed. Operating conditions were an accelerating voltage of 15 kV, a beam current of 10 nA, beam diameters from 1 to 10 µm, and counting times from 3 to 9 minutes. Beam diameters varied according to how clean the glass was. A crystal-free glass or a glass with very few crystals allowed us to use a larger beam diameter than glasses that contained closer-spaced crystals. Measurements were made over a 2-day period. On the first day a counting time of 3 minutes of used, and this was increased to 9 minutes on the second day to get a more accurate count. Reference samples containing S of a known valence state were sphalerite (ZnS) for S^{2-} and barite (BaSO₄) for S^{6+} . References and samples were counted for 3 minutes before and after measuring $\lambda(SK\alpha)$ for each unknown. For each sample, $\lambda(SK\alpha)$ was determined by fitting

background-subtracted wavelength scan data with a Gaussian function to estimate the SK α peak centre. Average values for wavelength shifts relative to ZnS [$\Delta\lambda$ (SK α)] are listed in Table 4.1. The total SK α wavelength shift between sulphide and sulphate for barite (λ SK α _{barite}- λ SK α _{sphalerite}) is consistent with previous determinations (Wallace and Carmichael, 1994).

Following Carroll and Rutherford (1988) and taking $\Delta\lambda(SK\alpha)$ for barite to represent 100% sulphur as sulphate, we use the relationship:

% sulphate in total sulphur =
$$\frac{\Delta\lambda(SK\alpha)_{unknown}}{\Delta\lambda(SK\alpha)_{barite}} x 100$$
 (16)

to calculate % sulphate in the total sulphur for each spot measurement on a sample. This is equivalent to S^{6+}/S_{tot} if we omit the multiplication by 100 in equation (16). An average value was taken to obtain our value for S^{6+}/S_{tot} , which is equivalent to Y_{is} . S^{6+}/S_{tot} is used to calculate the ratio of $X_{SO_4^{2-}}/X_{S^{2-}}$ in the following way:

$$\frac{1}{\frac{1}{S^{6^+}/S_{tot}} - 1} = \frac{X_{SO_4^{2^-}}}{X_{S_{2^-}}}$$
(17)

The oxygen fugacity of the experiments relative to the nickel-nickel oxide buffer, Δ NNO, was calculated using the following equation from Jugo *et al.* (2005):

$$\log\left[\frac{X_{SO_4^{2-}}}{X_{S^{2-}}}\right] = 1.02\Delta NNO - \frac{18.6}{T} - 0.45$$
(18)

where T is the temperature in K. Equation (18) is calculated using equation (7), the NNO buffer expression of Huebner and Sato (1970). Huebner and Sato (1970) include a correction term for the pressure effects in their equation, however for our experimental conditions the change in Δ NNO it produces (± 0.1) is less than uncertainly of these measurements.

Our determination of Δ NNO using this method was found to be consistent with Figure 2 of Wallace and Carmichael (1994). To estimate the uncertainty associated with the calculation of Δ NNO we used the following equation derived from standard propagation of error techniques:

$$\sigma_{\Delta NNO}^{2} = \left(\frac{1}{1.02}\right)^{2} \left[\sigma_{M}^{2} \left(\frac{M}{\left(1-M\right)^{2}} + \frac{1}{\left(1-M\right)}\right)^{2} \left(\frac{1}{\ln 10} \times \frac{1}{\frac{M}{1-M}}\right)^{2}\right]$$
(19)

where M equals the measured value of S^{6+}/S_{tot} .

3.3 Qualitative Analytical Procedures

3.3.1 Backscatter electron Images

Backscatter electron images were obtained for each of the experimental run products. The run products ranged from almost crystal- and/or bubble-free, to bubble-rich and/ or containing crystals. Examples of backscatter electron images of the glasses may be found in Chapter 3. The crystals observed in the glass are thought to be quench crystals due to their skeletal morphology and common presence in experiments (O'Hara and Humphries, 1977). The crystals are composed of Fe-Ti oxides, which are commonly found in experiments with basaltic melts. Additional backscatter electron images of experimental glasses are found in Appendix 3 and 4.

3.3.2 Bubble size distributions and porosity

The two-dimensional porosity was measured using the program ImageJ (Abramoff *et al.* 2004). Using this software, a black and white backscattered electron image is uploaded, and the brightness, contrast and threshold are manually adjusted until the bubbles are highlighted separately from the background. Outliers were manually removed by selecting the desired threshold and size. Outliers were selected by comparing the threshold image to the original backscattered electron image, and include objects such as scour pits or pieces of dust that were darker in colour than the glass and were mistaken for bubbles. The dark area on the screen (the bubbles) was calculated as a percentage of the total area of the image, which is the porosity of the sample. To obtain an estimate of the uncertainty of this process, repeat analyses were performed on most samples, yielding an average reproducibility for porosity determinations of about ± 2.5 %.

Bubble size distributions also were obtained using ImageJ. During this procedure the scale (pixels/ μ m) was set from the original SEM image, and a histogram was produced from the black and white threshold images, excluding those on the edges. No correction was made to convert the two-dimensional measurements to three-dimensional measurements. As a result, true bubble sizes, and therefore porosity, may be larger than measured from the two-dimensional images (Morton, 1830).

3.4 Isotope analysis

3.4.1 Sulphur extraction

Sulphur was extracted from the glasses for isotopic analysis following a modified version of the procedure described in Hong et al. (2000). A schematic of the sulphur extraction line used is presented in Figure 3.1. Kiba reducing reagent (Kiba, 1955) was prepared by boiling 500 g of phosphoric acid (H_3PO_4) with 40 g of sodium chloride (NaCl) and 40 g stannous tin dihydride (SnCl₂·2H₂O) at 300 °C in a 500 ml fused quartz flask. Boiling was conducted under a stream of N₂ gas and continued until ~100 ml of condensed vapours were collected in an ice-water trap. Due to the corrosive nature of the Kiba reagent it was stored in the same vessel in which it was prepared, requiring that it be prepared in small batches. Sulphur extracted from samples using one Kiba batch produced anomalously high δ^{34} S (V-CDT) values and resulted in the loss of these data, which have not been included in this text. The failure of this Kiba batch can most likely be attributed to incomplete dissolution of the reagents during its preparation. This theory is supported by several lines of evidence suggesting that this batch was different from the others: (a) the reaction time to collect 100 ml of condensed vapours in the bad batch was significantly less than for the good batches, (b) the presence of a significant amount of white powder (both the NaCl and the SnCl₂·2H₂O were white) at the bottom of the reaction vessel, and (c) the overall consistency of the bad batch was less viscous than the good batches. To extract the sulphur from the experimental glasses, glass samples were ground under ethanol in an agate mortar and pestle and dried. This yielded a range in

sample mass from approximately 0.015 to 0.056 g. The sample was placed in a 200 ml fused quartz flask containing ~15 ml Kiba reagent. This mixture was heated to 280 °C for 40 to 60 minutes, with a constant stream of nitrogen flowing through the system. A one-step capture of the evolved sulphur was employed. Liberated H₂S passed through an ice-water trap to condense any acidic vapours, and subsequently carried through a trap filled with 0.1 M silver nitrate (AgNO₃) and converted to silver sulphide (Ag₂S). The precipitated Ag₂S was washed twice in milli-Q water, once in a 1.0 M ammonium hydroxide solution, and twice more in milli-Q water. Yield tests conducted prior to the experiments consistently showed 92% +/- 3% recovery with this procedure. We assume that this level of recovery was maintained throughout the experiments reported here.

3.4.2 Mass Spectrometry

Sulphur isotope analyses were performed at the University of Toronto Geobiology Stable Isotope facility. Abundances of ³⁴S and ³²S in each Ag₂S sample were determined by Elemental Analysis Continuous Flow Isotope Ratio Mass Spectrometry (EA-CF-IRMS) with a Thermo Scientific MAT 253, equipped with a Conflo-III device and a Eurovector Elemental Analyzer. Between 101 and 501 µg of Ag₂S were analysed from each sample. Scale compression and sample size effects monitored through a series of analyses on Ag₂S standard powders. Analyses were calibrated to the V-CDT scale according to IAEA-S-1 ($\delta^{34}S_{V-CDT} =$ -0.3‰), IAEA-S-2 ($\delta^{34}S_{V-CDT} = 22.67\%$), and IAEA-S-1 ($\delta^{34}S_{V-CDT} = -32.55\%$) standards (Ding *et al.* 2001). The internal precision of $\delta^{34}S$ measurements by continuous flow introduction of SO₂ into the Thermo Scientific MAT 253 is 0.1‰ (1 σ). Repeat unknown analyses (n = 11) of the IAEA-S-1 standard material returned an average $\delta^{34}S$ value (V-CDT) of -0.29‰ with 1 σ uncertainty of 0.2‰.

3.4.3 External Reproducibility

A natural Mid-Ocean Ridge Basaltic glass from the Juan de Fuca ridge (P1326-2, Stix *et al.* 1995) was used to quantify the external reproducibility of the extraction and isotope analysis procedure. This sample was chosen because it contained a similar amount of S as our samples (approximately 1600 ppm). Splits of P1326-2 were measured out to span the range of total S extracted from our experimental glasses in order to test the effects of sample size on measured δ^{34} S. Using the above extraction procedures, sulphur from the sample was converted to Ag₂S, and analyzed for its S isotope composition. The three samples of P1326-2 yielded a mean isotopic composition of 1.73 ±0.65‰ (V-CDT) [P1326-2-KGST11 = 2.36‰; P1326-2-KGST12 = 1.79‰; P1326-2-KGST13 = 1.05‰]. Taking into account the standard deviation, the S isotopic composition of P1326-2 is within the range of values previously measured for MORB glasses, which demonstrates that our analytical procedure does not appear to introduce any measurement biases. Accordingly, we take the standard deviation of these measurements (0.65 ‰) as our best estimate of the external reproducibility of the total analytical procedure.



Figure 3.1: Laboratory set up of sulphur extraction.

All tubes are ¼" o.d. Teflon[®]. Thermometer (A). Aluminum block (B). 250 ml fused silica flask (C). Teflon-coated magnetic stir bar (D). Magnetic hot plate with ceramic top (E). Silicon stopper (F). Teflon connectors (G). Heating coil (H). Borosilicate vessel used for acid trap (I). Styrofoam container (J). Cold water filled with ice (K). Borosilicate test tube S-trap (L).

4.0 Results

4.1 Electron Microprobe

4.1.1 Sulphur contents of synthesized glasses

Sulphur concentrations were measured for 8 isobarically quenched (IQ), and 18 degassed (DG) experiments. Results are presented in Table 4.1 along with the microprobe analyses explained in this section. All microprobe data is available in Appendix 2.

Samples DG1 through to DG16 were prepared with a different batch of starting material (powdered basalt glass + gypsum) than samples DG19 through to DG33. The addition of slightly more gypsum to the second batch of starting material explains the overall lower sulphur content of the first 11 samples. Sulphur concentrations of the 2 IQ samples from batch 1 are 1598 ±119 ppm and 1719 ± 115 ppm. Unless otherwise stated, all uncertainties reported are 1σ . Applying a reduced χ^2 test (Mahon, 1996) we find that these values are consistent within a single uncertainty-weighted mean value. The average S concentration of IQ samples from batch 1 is 1658 ± 86 ppm (un-weighted mean). Sulphur concentrations of IQ samples in batch 2 range from 1993 ± 85 ppm (IQ19) to 2165 ± 262 ppm (IQ 27), and were found to be consistent within a single uncertainty-weighted mean value as above. We conclude that the S distribution in our IQ samples is homogeneous at the levels of uncertainty in our measurements. The un-weighted mean S concentration of IQ samples from batch 2 is 2031 ± 91 ppm.

In general, the DG experiments have lower sulphur concentrations than the IQ experiments. Sulphur concentrations of DG experiments from batch 1 range from 1336 to 1718 ppm. Batch 2 yielded DG S concentrations between 739 and 2044 ppm. In DG4 and DG22, S concentrations are 1718 ± 111 and 2044 ± 97 ppm, respectively. Although these concentrations are equal to or higher than the average S concentration of the IQ glass from their batch, their S concentrations fall within one standard deviation of the average S concentrations of the associated IQ glass.

The fraction of sulphur remaining in the melt after degassing (F) and associated error were calculated according to section 2.2.1. and results are listed in Table 4.1. Calculated values for F ranged from 0.36 to 1.07. A histogram showing the frequency of F values is presented in Figure 4.1. Our experiments were designed under the assumption that higher values of ΔP should produce lower values of F (less S remaining in the melt, therefore more degassed). Results demonstrate that this assumption may not be valid (Fig. 4.2). For values of ΔP less than about 400 MPa the trend is straightforward. At values of ΔP of approximately 400 MPa or greater, there is more variability in the F values than would be expected. Some variability is expected due to the disequilibrium nature of the degassing. This is expected to depend on the timescales of degassing. All experiments were degassed over time intervals within 10 minutes of an average (mean degassing time based on 2 measurements is approximately 8.5 minutes), but more accurate data for the range of degassing rates does not exist.

4.1.2 Oxidation state of synthesized glasses

Microprobe analyses of SK α for selected samples are listed in Table 4.1. Calculated values of S⁶⁺/S_{tot} for the synthesized glasses range from 0.50 – 0.97, with a mean of 0.78 (± 0.14). Sulphur in these samples is present, therefore, dominantly as S⁶⁺. Applying a reduced Chi-squared test (Mahon, 1996) to our calculated Δ NNO, we find that they are consistent within a single uncertainty-weighted mean value of Δ NNO = 0.9. The 99% error on the weighted mean value is 0.2, and 1 standard deviation on the population is 0.40.

The variability in the fO_2 measurements, is most likely a function of the counting statistics of the electron microprobe measurements I think that your fO_2 variations are a function of counting statistics. Degassing or H loss during experiments could potentially cause fO_2 to change, but we have evidence that suggests that this is not the case. In the case of degassing, we might expect to see a trend of fO_2 vs. F, and this trend is very weak. In the case of H loss, an experiment of longer duration would correlate positively with fO_2 because it would be losing more H. All of our experiments were equilibrated for the same
amount of time and degassed within a few minutes of one another, and we do not observe such a trend. Additionally, one might expect to see a slightly higher fO_2 in the 1 atm experiments, but again, this was not observed. With this reasoning, we consider the variability in the fO_2 measurements, although seemingly quite high, as consistent within a single weighted mean value. The effects of the fO_2 variation on our model is discussed in section 5.1.

4.1.3 Porosity and bubble size distribution

The results of calculations performed with ImageJ are presented in Table 4.2. Only those samples that contained bubbles and had a good polish were analyzed. A more complete record of bubble size distributions can be found in Appendix 3. For illustration purposes, Figure 3.3 shows 4 backscattered electron images representative of the range in degassing of the samples. Porosity in the experiments varied from 5-55 area %. Minimum bubble diameters ranged from approximately 1 to 33 μ m, with the majority (75%) being 4 μ m or less. The maximum bubble diameter ranged from approximately 9 μ m to570 μ m. Figure 4.4 shows the relationship between average bubble diameter and the degree of degassing. There is a broad trend that higher degrees of degassing correlate to larger average bubble diameter. There are several samples (DG16, DG24a, DG 33) that span wide F values yet maintain small (< 10 μ m) diameters. This variation is expected due to the disequilibrium nature of the degassing experiments.

Histograms of bubble size distribution can be found in Appendix 4. Counts for the histograms range from 6 (bubbles) to 121, while the majority of the analyses counted approximately 50 bubbles. Many of the samples are unimodal with the peak occurring at the minimum bubble diameter and tapering towards the larger diameters. This suggests a power-law distribution, indicative of disequilibrium conditions (Bai *et al.* 2008). A few samples (DG4, DG6, DG26) are more evenly distributed and show signs of multimodality, with peaks occurring in the mid-range of bubble diameter as well.

4.1.4 Transects in S content

Bubble to bubble transects of S do not show any consistent trends, either among samples or within a given sample. Some traverses (DG21, DG25, DG26) demonstrate depletion haloes around the bubbles (see Appendix 3), whereas others do not. If the profiles in S content record the influence of a diffusional boundary layer around the bubbles without depletion haloes, this boundary layer must be thinner than the step size of the transects (5 μ m).

4.2 S Isotopic compositions of synthesized glasses

The measured isotopic composition of 5 IQ and 7 DG samples are listed in Table 4.3A and 4.3B, respectively. Isotopic compositions were normalized relative to the average isotopic composition of the IQ glasses according to the procedure outlined below. The IQ glasses were consistent with a single mean δ^{34} S (V-CDT) value of -0.40 ± 0.34 ‰ (Table 4.3). Standard delta notation for each sample can be expressed using equations (20) and (21):

$$\delta^{34} S_i = \left(\frac{{}^{34} R_i - {}^{34} R_{VCDT}}{{}^{34} R_{VCDT}}\right) \times 1000$$
(20)

$$\delta^{34} S_{IQ} = \left(\frac{{}^{34} R_{IQ} - {}^{34} R_{VCDT}}{{}^{34} R_{VCDT}}\right) \times 1000$$
(21)

Where $R = {}^{34}S/{}^{32}S$, *i* refers to the degassed sample, and IQ refers to the isobarically quenched sample. Rearranging (20) and (21) we obtain:

$$\frac{{}^{34}R_i}{{}^{34}R_{VCDT}} = \frac{\delta_i^{34}S}{1000} + 1$$
(20')

$$\frac{{}^{34}R_{IQ}}{{}^{34}R_{VCDT}} = \frac{\delta_{IQ}^{34}S}{1000} + 1$$
(21')

A delta notation for a DG sample relative to an IQ sample can be expressed as:

$$\delta_{i/IQ}^{34} S = \left(\frac{{}^{34}R_i - {}^{34}R_{IQ}}{{}^{34}R_{IQ}}\right) \times 1000$$
(22)

Equation (22) may be rearranged to obtain equation (22').

$$\left(\frac{{}^{34}R_i}{{}^{34}R_{IQ}} - 1\right) \times 1000 = \delta_{i/IQ}^{34}S$$
(22')

By dividing (20') by (21') we obtain ${}^{34}R_i/{}^{34}R_{IQ}$ which is used in (22') to calculate final values of $\delta^{34}S$ (IQ).

The DG glasses exhibited δ^{34} S (IQ) values that ranged from -0.27 to 1.10 ‰. When plotted against calculated degree of degassing the δ^{34} S (IQ) values of the DG samples show a positive correlation. In terms of the degree of degassing, low F values indicate a higher degree of degassing resulting in a negative correlation with F (Figure 4.5). Our observation that more degassing leads to greater fractionation is what would be expected from simple models of isotopic fractionation during degassing under local gas-melt equilibrium (Marini *et al.* 1998).

				F	Wt % H ₂ 0	Wt% H ₂ 0			<i>C</i> .				ΔΝΝΟ
	S	S		(relative	(after	(before	$\Delta\lambda(SK\alpha)$	<i>(</i>)	S ⁶⁺ /S _{tot}		2		(relative
Sample	(ppm)	(lo)	F	error)	experiment)	experiment)	$(A \times 10^3)$	S^{6+}/S_{tot}	(lo)	S^{6+}	S^{2-}	ΔNNO	error)
Batch 1	_												
IQ2	1719	115	1.04	0.09	6.2	4.9	0.0024	0.80	0.08	1375	344	1.0	0.23
DG4	1718	111	1.04	0.09	3.2	3.6	N.D.*	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
DG6	1697	138	1.02	0.10	5.5	4.8	0.0029	0.97	0.09	1641	57	1.9	1.24
IQ1	1598	119	0.96	0.09	5.1	4.4	0.0027	0.90	0.09	1438	160	1.4	0.41
DG11	1568	90	0.95	0.07	8.3	7.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
DG5	1540	109	0.93	0.08	6.9	6.1	0.0021	0.72	0.08	1104	436	0.8	0.17
DG15	1508	125	0.91	0.09	2.5	10.6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
DG8	1468	362	0.88	0.22	5.4	11.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
DG3	1444	168	0.87	0.11	3.0	4.6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
DG12	1409	81	0.85	0.07	8.7	9.9	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
DG16	1336	124	0.81	0.09	5.4	10.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Batch 2	_												
IQ27	2165	262	1.07	0.14	10.5	11.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
DG22	2044	97	1.01	0.07	7.5	10.4	0.0023	0.14	1567	477	0.96	1.0	0.33
IQ20	2040	69	1.00	0.06	9.7	11.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
IQ19	1993	85	0.98	0.06	9.8	13.2	0.0019	0.60	0.10	1193	800	0.6	0.18
IQ28	1967	85	0.97	0.06	8.2	10.7	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
IQ29	1960	80	0.97	0.06	9.4	9.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
IQ30	1944	56	0.96	0.05	9.1	9.5	0.0022	0.71	0.07	1385	559	0.8	0.14
DG31	1926	77	0.95	0.06	2.1	9.7	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
DG25	1843	267	0.91	0.14	4.8	11.1	0.0029	0.91	0.07	1677	166	1.4	0.37
DG21	1740	60	0.86	0.05	5.7	9.5	0.0026	0.82	0.08	1421	320	1.1	0.22

TABLE 4.1. ELECTRON MICROPROBE RESULTS

				F	Wt % H ₂ 0	Wt% H ₂ 0							ΔNNO
	S	S		(relative	(after	(before	Δλ(SKα)		S^{6+}/S_{tot}				(relative
Sample	(ppm)	(lo)	F	error)	experiment)	experiment)	$(\dot{A} \times 10^3)$	S ⁶⁺ /S _{tot}	(1 o)	S^{6+}	S^{2-}	ΔNNO	error)
DG26	1313	218	0.65	0.11	4.2	11.8	0.0027	0.90	0.14	1182	131	1.4	0.66
DG24b	1132	101	0.56	0.06	5.0		N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
DG33	1135	597	0.56	0.29	3.2	9.1	0.0015	0.50	0.22	771	771	0.5	0.38
DG32	965	329	0.48	0.16	1.5	8.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
DG24a	739	153	0.36	0.08	5.1	11.9	0.0022	0.73	0.22	542	197	0.9	0.49
N.D. = not determined													

The uncertainty-weighted mean of the Δ NNO values presented in this table is 0.9, calculated using a reduced χ^2 procedure (Mahon, 1996).



Figure 4.1: Histogram showing the frequency of calculated experimental F values of DG samples. The majority of experiments were less than 20% degassed.



Figure 4.2: Fraction of S in the melt after degassing (F) vs drop in pressure (ΔP). This graph demonstrates that larger drops in pressure did not necessarily correspond with greater degrees of degassing. The variability in this relationshipt might be expected because of the stochasitc nature of the disequilibrium degassing experimetns.



Figure 4.3: Representative backscattered electron images of experimental run products.

A = IQ2 (F = 1.04), B = DG22 (F = 1.01), C = DG26 (F = 0.65), D = DG33 (F = 0.56). Additional information on experimental conditions can be found in Table 4.1 and Appendix 1. Scale bars are found at the bottom of each panel. Panel A has a scale bar of 10 μ m, panels B, C, and D have 100 μ m. Bright spots in panels A, B, and D are crystals of Fe-Ti-Mg oxides (EMP analysis on the electron microprobe). Small holes adjacent to the crystals in panel A and B are thought to be scour pits caused by polishing rather than bubbles. Bubble size ranges from ~5 μ m to greater than 100 μ m.



Figure 4.4: Mean bubble diameter (μ m) vs fraction of S remaining in the melt after degassing (F). Bubble diameter shows a general increase in size at larger amounts of degassing. There are some bubbles which remain small (less than 10 μ m diameter) over a wide range of degassing. This variability is expected under our conditons of disequilibrium degassing.

	Bubble	Bubble	Minimum		Average
	area 1 st	area 2 nd	bubble	Maximum	bubble
	count	count	radius	bubble	radius
Sample	(%)	(%)	(µm)	radius	(µm)
Batch1					
DG4	47	44	2	14	9
DG6	8	6	3	9	6
DG15	20	23	3	14	8
Batch2					
DG31	69	N.D*	33	571	53
DG32	48	N.D	3	212	44
DG33	66	N.D	1	127	30
DG21	40	39			
DG22	19	22	8	34	19
DG24a	17	18	2	9	5
DG24b	45	45	3	17	9
DG25	43	49	4	161	27
DG26	53	55	5	53	80

TABLE 4.2. RESULTS OF IMAGEJ ANALYSIS

*N.D. = not determined

Sample	δ ³⁴ S(V-CDT)							
	(-)							
IQ 2	-0.09							
IQ 19	0.06							
IQ 20	-0.85							
IQ 27	-0.56							
IQ 29	-0.59							
The IQ samp	les are							
consistent wit	thin a single							
mean (δ ³⁴ S(V-CDT) = -0.40).								
The 95% confidence interval								
is -1.21 to 0.40								

TABLE 4.3A. ISOTOPIC ANALYSIS OF IQ SAMPLES

 TABLE 4.3B. ISOTOPIC ANALYSIS OF DG SAMPLES

Sample	F	δ ³⁴ S(V-CDT)	δ ³⁴ S(IQ)
DG 6	1.02 ± 0.01	-0.36	0.04
DG 22	1.01 ± 0.07	-0.67	-0.27
DG 25	0.91 ± 0.14	-0.43	-0.03
DG 26	0.65 ± 0.11	0.33	0.74
DG 32	0.48 ± 0.16	0.70	1.10
DG 16	0.81 ± 0.09	0.06	0.46
DG 33	0.56 ± 0.29	0.45	0.85



Figure 4.5: Isotopic composition of experimental DG glasses versus F. The degree of enrichment correlates negatively with F and therefore positively with the extent of degassing, which is expected for fractionation of S isotopes by open-system degassing under conditions of local gas-melt equilibrium at our experimental conditions.

5.0 Discussion

5.1 Degassing Model

In order to better interpret our experimental results, a model of isotopic fractionation during the degassing processes is needed for comparison. The model initially employed considers isotopic fractionation under conditions of local gas-melt equilibrium, and is comparable to those used in studies of natural volcanic systems (Torrsander, 1989; Marini *et al.* 1998; Mandeville *et al.* 1998). The P, T, and Δ NNO conditions used in our experiments define our system, which will be modelled as an open system, even though all high pressure degassing experiments were performed in sealed capsules. We may consider our system as open because the time scale of degassing (seconds) is much less than that of the equilibration (hours); thus re-equilibration of the gas and melt is not expected to occur (Shinohara, 2009).

Hypothesizing that Rayleigh distillation is occurring, we may insert our predicted fractionation factor calculated from equations (1, 2, 3, 4, 7, 8, 10, 11) into equation (12) to predict the isotopic shift during degassing. The model was calculated using a Δ NNO of 0.9 (the average oxygen fugacity determined for our experiments), *f*H₂O of 3000 bars (representative of the mid-range of our experimental degassing pressures), and the experimental temperature of 1225 °C. The uncertainties in the temperature and oxygen fugacity are \pm 10 °C and \pm 0.22, respectively. The effects of varying the temperature, oxygen fugacity, and *f*H₂O within their uncertainties on the calculated fractionation factor are discussed in more detail in section 2.3. Our experimental results are plotted in Figure 5.5 along with the isotopic fractionation model discussed in Section 5.1. These conditions yield a predicted ³⁴ α_{g-m} value of 0.9993. This calculation was repeated for varying *f*H₂O to account for varying experimental pressures. To estimate our uncertainties in the modelled value of ³⁴ α_{g-m} we calculate the minimum and maximum ³⁴ α_{g-m} values that are possible within our experimental uncertainties.

The minimum ${}^{34}\alpha_{g-m}$ was calculated at a temperature of 1200 °C, a Δ NNO 1.1 and fH₂O of 7126 bars and is equal to 0.9986. The maximum ${}^{34}\alpha_{g-m}$ was calculated at 1250 °C, a Δ NNO of 0.7, and fH₂O of 1140 bars and is equal to 0.9996.

To test the validity of our claim that the measured fO_2 from the experiments could be expressed in our model as $\Delta NNO = 0.9$, we calculated ${}^{34}\alpha_{g.m}$ m for each experiment where both fO_2 and isotope data were available. These ${}^{34}\alpha_{g.m}$ m were determined at T = 1225 °C, $fH_2O = 3000$ bar, and fO_2 according to the dataset. The highest and lowest ${}^{34}\alpha_{g.m}$ calculated were 1.0003 (DG33) and 0.9967 (DG6). These ${}^{34}\alpha_{g.m}$ correspond to the highest and lowest fO_2 measurements ($\Delta NNO = 1.9$, $\Delta NNO = 0.5$). The shaded region in figure 5.1 represents this range in ${}^{34}\alpha_{g.m}$. If the variability of the fO_2 measurements was real, then we would expect that each experiment would lie on the curve predicted by its corresponding fO_2 . Given our range in fO_2 , the data points should be scattered around the plot. What we find, however, is that the data points lie along one curve, suggesting that a single fO_2 is governing the fractionation over all experiments. Therefore, it is likely that the range in fO_2 that we estimate represents true uncertainty in the fO_2 determinations rather than actual variability in the fO_2 of the different experiments.

5.2 Interpretation of results

We used an alternative formulation of equation 12 to estimate an empirical fractionation factor that is consistent with the experimental data.

$$\ln\left(\frac{\delta^{34}S_{final} - \delta^{34}S_{initial}}{1000} + 1\right) = (\alpha - 1)\ln F$$
(23)

We transformed measured $\delta^{34}S(IQ)$ and F values as shown in equation 23, and made a linear best-fit to the transformed quantities. The slope of the best-fit line ($^{34}\alpha_{g-m}$ -1) yielded an empirical of 0.9987. Thus, our empirical value falls just within the calculated ranges of experimental uncertainty.

Taking into consideration measurement uncertainties, Figure 5.1 illustrates that the experimental results are consistent with the prediction of an isotopic fractionation model for open-system degassing under conditions of local gas-melt equilibrium. Discrepancies between the measurements and the model are almost uniformly one-sided, however. In order to explore the reasons for this feature, we vary the main parameters that control the model: T, Δ NNO, and F. In particular, we would like to see what changes are necessary for the model predictions to match the experimental results.

We know that a lower temperature will result in more fractionation (discussed above). By lowering our temperature to 1100 °C the measurements and the prediction coincide (Figure 5.2). However, we have good control of our experimental temperatures (± 10 °C) and a temperature change of 125 °C falls too far out of our uncertainty to be a realistic option. An interesting and potentially meaningful point to re-state is that in our model we applied equations 3 and 4 beyond the range for which experimental data exists. Thus, the extrapolation of the fractionation equations to temperatures beyond their calibration may be partially responsible for the differences between the predicted and measured S isotopic compositions of the degassed glasses.

Increasing the oxidation state in our model has the potential to increase the magnitude of fractionation. Raising the average oxidation state of our model to Δ NNO + 1.3 (Figure 5.3) would allow most of the experimental data to coincide with the theoretical line. It is important to note that the range in oxidation state of our experiments falls within a range where a small change in oxidation state leads to a large change in fractionation. However, our average oxidation state is Δ NNO = 0.9, even with the uncertainty of 0.22 we do not approach Δ NNO = 1.3.

A bias in our estimates for F values could also cause the model predictions to match our experimental results. We remember from our discussion that lower values of F (greater degrees of degassing) will result in a larger fractionation. Figure 5.1 shows that a constant shift in F would not produce the desired results. In order for the experimental data to coincide with the theoretical degassing trend, the changes in F must be proportional to the original values of F, that is, for small degrees of degassing the shift would be small, and for large degrees of degassing the shift would need to be larger (around 30%). Due to the relationship between F and S (ppm), larger degrees of degassing are an indication that less S was measured in the DG samples. There is the potential that smaller concentrations of S in the glass are more difficult to measure than larger concentrations. This might suggest that the error associated with smaller values of F is greater. An inspection of our calculated uncertainties in F reveals that this is not the case. Additionally, our measured S concentrations were well above the detection limits on the electron microprobe. Both of these observations indicate that the F value estimates are not biased.

5.3 Other processes affecting S isotope fractionation

The experimentally measured fractionation path is steeper than the path calculated for open system isotopic fractionation (Figure 5.1), suggesting that other processes are fractionating the S isotopes in our experiments by a small amount. The formation of a bubble may be subdivided into two stages: nucleation and growth. Bubble nucleation in these experiments begins when the pressure of the system is decreased, as a response to superstauration of the melt (Gardner et al. 1999). This is facilitated if there are heterogeneities present in the melt, such as microlites of Fe-Ti oxides (Hurwitz and Navon, 1994). Mass balance arguments demonstrate that if isotopic fractionation occurs during bubble nucleation, it is unlikely that it will be significant. Assuming a bubble can be represented by a sphere, the volume of the bubble is $4/3\pi r^3$. Typical bubble nuclei have diameters that are less than 1 µm (Mangan and Sisson, 2000). When the bubble nucleates, it will have very little H₂O in it, and since H₂O is much more abundant in typical melts than S, the bubble will also contain very little S. As the bubble grows in diameter, material will be added to it on the order of the radius cubed. Thus, any S isotope fractionation that occurred during nucleation will quickly be overpowered and erased by the relatively large influx of new material from the melt

Eliminating fractionation during bubble nucleation, it is most likely that fractionation occurs during bubble growth. Continued bubble growth can occur in 2 ways: diffusional growth and decompressional growth (Sparks, 1978).

Diffusion-controlled growth of a bubble is controlled mainly by the composition, concentration, and solubility of dissolved volatiles, as well as the degree of supersaturation of the volatiles in the melt (Sparks. 1978). Bubble growth by decompression occurs as a response to a decrease in hydrostatic pressure of the magma (Sparks, 1978). As magma moves towards the surface, pressure decreases. The growth rate of the bubble is controlled by the ascent velocity of the magma, as well as the rate at which overlying pressure (such as tephra) is removed from the system. Bubble size itself is also a limiting factor (Sparks, 1978). It is thought that bubbles stop growing when bubble: liquid ratios reach proportions of 3:1 to 5:1 (Sparks, 1978). In these conditions, the viscosity of the melt has increased such that the bubbles can no longer expand, and transport of material along very thin paths between neighbouring bubbles becomes too difficult (Sparks, 1978). The bubble growth in our experiments is thought to be dominated by decompression expansion growth of gases within the bubbles, as the duration of the pressure drops was most likely to short to allow for significant diffusive growth to occur.

5.4 Diffusion

The diffusion coefficient, D (in m^2s^{-1}), for sulphur in a hydrous (3.5 wt% H₂O) basalt has been experimentally determined by Freda *et al.* (2005) to fit the equation:

$$D = 5.91 \times 10^{-7} \exp\left(\frac{-130.8 \pm 82.6}{RT}\right)$$
(24)

where R is the gas constant, the activation energy is in kJmol⁻¹ and T is the temperature in Kelvin. Using equation (24) and a temperature of 1225 °C, we can calculate $D = 1.93 \times 10^{-11} \text{ m}^2 \text{s}^{-1}$. Following the lead of Watson (1994), who reported a linear dependence for S diffusion on water concentration in andesitic melts, Freda *et al.* (2005) found that at 1300 °C, D increases at a rate of 0.6 x 10⁻¹¹

 m^2s^{-1} for every wt % H₂O added. Our basalt glasses have an average H₂O content of 9.0 ± 2.7 wt % before the experiments, thus we would expect that diffusion coefficients from our experiments would be 5.5 x 10⁻¹¹ m²s⁻¹. Using this estimated diffusion coefficient and the approximate decompression timescales of our experiments (8.5 minutes), we calculate a diffusive lenghscale of approximately 167 µm. This lengthscale is too small to apply to the whole capsule, but is larger than any measured distance between bubbles, implying that the S is able to travel between bubbles within the timescales of our experiments.

To conceptualize the mechanics of S diffusion within our melts we use the model of Alletti et al. (2007), who present a model of diffusion based on their experimental work on diffusion of halogens within basaltic melts combined with existing experimental knowledge of diffusion of other volatiles within melts in order to investigate the role of diffusion during magmatic degassing. The result of their work was an illustrative model of the behaviour of F, Cl, Br and S during rapid growth of water bubbles in basaltic melts at 1250 °C where bubbles were assumed to be one dimensional and maintain a constant growth rate, and that the water concentration in the bubble remained constant and dominated the composition. While we will not apply the mathematics of this model to our study, we draw general parallels between our experiments and this model: Both instances investigate basaltic melts at similar temperatures (within 25 °C), and both parties are interested in the behaviour of S. The main conclusions of Alletti et al. (2007) relevant to our study are: melts closer to the growing bubble are depleted in S compared to melts at greater distances due to sulphur's relatively high partition coefficient and slow diffusion coefficient (Alletti et al. 2007). These properties of S suggest that during rapid bubble growth diffusive fractionation will occur.

Supported by the findings of the Alletti *et al.* 2007 model, namely, that during rapid bubble growth diffusive isotopic fractionation (that is, fractionation between ionic species owing to differences in diffusion coefficients) is expected to occur at growth rates as low as 10^{-10} ms⁻¹ (growth rates estimated from our experimental data are on the order of 10^{-7} ms⁻¹), we have reason to believe that

our bubbles have not grown in equilibrium with the melt and as a result S is likely to undergo diffusive fractionation during bubble growth. In addition, a few of our measured S profiles in the melt show depletions near the bubble-melt interface (discussed in Section 4.1.4). The isotopic consequences of fractionation during diffusion are discussed in the following section.

5.5 Sulphur isotope fractionation during diffusion

It is well documented that mass-dependent kinetic fractionation can occur during chemical diffusion (Richter *et al.* 2006). We may employ simple physical properties of particles to explain mass-dependent fractionations. The kinetic energy of a free particle must equal its thermal energy (Young *et al.* 2002)

$$\frac{1}{2}mv^2 = \frac{3}{2}kT$$
(25)

where m is the mass of the particle, v is the velocity, k is Boltzmann's constant and T is the temperature. If T is constant in a system, the velocity of a particle will depend only on its mass. A particle with larger mass will have a smaller velocity than a particle with a smaller mass. Considering a system composed of a dilute gas containing ³²S and ³⁴S, the slightly heavier ³⁴S will move slowly relative to ³²S. Although the situation is more complex in condensed systems, such as silicate melts, this same general principle of the energy equivalence applies to sulphur isotopes during diffusion. Therefore the diffusion of ³⁴S is expected to be slower than that of ³²S.

In order to constrain S isotopic fractionation occurring during the diffusion of S through the melt to the bubble-melt interface, it will be useful to have a simple model, at least to predict the direction and order-of-magnitude of the expected fractionation. The assumptions of this model should fit the results and experimental conditions of this study. Necessary assumptions include that we observe homogeneous S distribution within the melt prior to bubble growth, that the modelled diffusional isotopic fractionation is greater than that under conditions of local gas-melt equilibrium alone. As the variability of S concentration in our transects is, in general, no larger than that of the spot measurements of S concentration in our glasses, we believe that the S distribution at the initiation of bubble growth in our experiments is homogeneous. Although we are not aware of the existence of a model, nor have we attempted to create a model during this work, parallels may be drawn between our experimental degassing and the simplified model Richter *et al.* (2006) used to illustrate the possible effects of diffusion on isotopic fractionation. This model was chosen because of its simplicity and the ability to make first-order estimates of kinetic fractionation during diffusion of S during bubble growth. Figure 5.4 shows conceptually how our experiments may be thought of in terms of this model.

Despite the fact that the conditions of the Richter et al. (2006) model are quite different from ours, their model provides a phenomenological description of S isotopic fractionation during diffusion. In their model, Richter et al. (2006) track an ionic species (i) (in water) travelling from a smaller container, V_1 , to a larger container, V_2 through a tube (Figure 5.4). The tube length is adjusted to control the speed of diffusion, as the rate depends on the cross-sectional area (A) and the length (L) of the tube. In this model at time = 0, *i* is located completely within V_1 and V_2 is $\gg V_1$. At time progresses, *i* moves from V_1 to V_2 through the tube. The fundamental assumptions of the Richter *et al.* (2006) model are that (1)diffusion between the two reservoirs is rate-limiting and (2) the concentration of iin reservoir 2 is much less than the concentration of *i* in reservoir 1. The mathematics behind the model can be found in Richter et al. (2006). We conceptualize the Richter et al. (2006) model as governing transport between a melt reservoir and a bubble reservoir. For this study, the tube of Richter et al. (2006) represents an effective average diffusion path. Though the conditions of our experiments are not completely similar to those of Richter et al. (2006), the match is sufficiently close to give a general sense of the isotopic consequences of diffusion in our experiments. Accordingly the change in isotopic compositions of the melt over time may be expressed as:

$$\ln\left(\frac{\delta^{34}S_{final} - \delta^{34}S_{initial}}{1000} + 1\right) = \left(\frac{D_1}{D_2} - 1\right) \ln F$$
(26)

Equation (26) is another form of the Rayleigh distillation (open-system degassing) equation described in Chapter 4, where in this specific case, ${}^{34}\alpha_{g-m}$ =

 D_1/D_2 . The empirical ${}^{34}\alpha_{g-m}$ of 0.9983, therefore, constrains the ratio of the diffusivities of the isotopomers.

In the simplified case of Richter et al. (2006), $D_1/D_2 = \alpha$. The ratio of diffusion coefficients of 2 chemically or isotopically distinct species can be expressed as:

$$\frac{D_1}{D_2} = \left(\frac{m_2}{m_1}\right)^{\beta} \tag{27}$$

where m_1 and m_2 are the masses of the two species and β is an experimentally determined parameter. In an ideal gas with elastic collisions, β is equal to 0.5 (Graham's Law, Graham, 1850). In a solution, the collisions are not elastic and therefore β will be less than 0.5 (Graham, 1850). Currently we are not aware of published values of β for sulphur, but experimentally determined β values for several other elements do exist. Results of diffusion experiments performed in molten oxides, rhyolite melts, and basalt melts suggest that in general as atomic number increases, the magnitude of β decreases (Richter *et al.* 1999, Richter *et al.* 2003, Richter *et al.* 2009). Richter *et al.* (2008) determined that β for Mg was 0.05±0.01, and Richter *et al.* (1999, 2003) determined that β for Ca was 0.06 ± 0.02. Since the atomic number of S lies between that of Mg and Ca, we assume that the value of β for S will fall between 0.05 and 0.06.

The choice of D_1 and D_2 in equation (27) will affect the magnitude of the isotopic fractionation. Sulphur within the melt is present as either S²⁻ or S⁶⁺ (Wallace and Carmichael 1994, Wilke *et al.* 2008). There is evidence to support that if S⁴⁺ exists in a glass, it is an analytical artefact caused by the irradiation of the sample with an x-ray beam (Wilke *et al.* 2008). A large number of studies conclude that in a wide range of melt compositions, oxygen fugacities, temperatures and pressures it is S²⁻ that dominates S diffusion (Baker and Rutherford, 1996, Watson *et al.* 1993, Watson, 1994). Even in melts where S⁶⁺ is the dominant S species, it is believed that S²⁻ is the species that diffuses (Baker and Rutherford, 1996).

We would like to compare our experimental results to the fractionation predicted by Richter *et al.* 2006. We may estimate an $\alpha_{diffusion}$ using equation (27). According to the discussion above where sulphur ions are widely thought to be the diffusing species, we use National Institute of Standards and Technology values for the molecular weights of ³²S and ³⁴S (31.97207069 and 33.96786683, respectively) and $\beta = 0.055$ to calculate $\alpha_{diffusion}$ to be approximately equal to 0.9967. We recognize that the choice of β affects the overall fractionation. If we set $\beta = 0.05$ we obtain an $\alpha_{diffusion}$ of 0.9970. A β of 0.06 yields an $\alpha_{diffusion}$ of 0.9964. For F values above 0.6, the effect of these $\alpha_{diffusion}$ values on fractionation is less than 0.2 ‰. The effects become more pronounced at lower F values, however the majority of our samples are less than 40 % degassed.

The estimated ${}^{34}\alpha_{g-m}$ value of 0.9967 represents the fractionation we would see if diffusion were the only factor affecting S isotope fractionation for the model investigated. It is lower than all the ${}^{34}\alpha_{g-m}$ values discussed in Chapter 5, which indicates that diffusion is more effective at fractionating isotopes than open-system equilibrium degassing alone. In Figure 5.5, fractionation factors for open-system equilibrium degassing alone and diffusion alone are plotted against our empirical fractionation factor. Our empirical fractionation lies between the fractionation produced by these two end-member processes, which is indicative that the kinetic fractionation of S isotopes by chemical diffusion of S occurs during our degassing experiments. However, in order to be able to make better inferences about isotopic fractionation during diffusion, more realistic and detailed models of bubble growth and diffusion are needed.

To evaluate our experimental results in terms of kinetic isotope fractionation during diffusion, we again turn to equation (27), this time solving for β under our experimental conditions. As before, we assume that ionic S is the diffusing species, giving us m³²S/m³⁴S = 0.9412. We set $\alpha_{diffusion} = \alpha_{empirical}$ and obtain $\beta = 0.028$. Comparing this value to the previously determined values for β collected in Figure 8 of Richter *et al.* (2009), we find that our estimate of β falls within the range of what would be expected from kinetic isotope fractionation

during diffusing. This demonstrates that our experimental results are consistent within a wide range of experimentally determined β , and also within the current theories on diffusing species within a melt.

5.6 Implications

In Chapter 1 we pointed out that in many studies of S isotopes in natural volcanic systems the data could not be explained by open- or closed-system degassing of S under conditions of local gas-melt equilibrium alone. This was also found to be true for our experiments, as the degassing model employed did not provide an adequate explanation of our data.

Marini et al. (1998) concluded that their data was consistent with opensystem degassing. We found over the course of this study that their methods of estimating predicted fractionation may not be applicable to all systems. Whereas the data sets of both studies (the current work and Marini et al. 1998) consist of S concentrations, and δ^{34} S values, *Marini et al.* (1998) did not independently constrain their oxygen fugacity. We had the benefit of additional information about our oxygen fugacities in the form of SK α measurements of our glasses. We found that our calculated oxygen fugacities and our measured values of S^{6+}/S_{tot} were not in agreement with equation (6), the same equation Marini et al. (1998) used in calculating the predicted isotopic fractionation at a given degree of degassing. In addition, our experiments show that even using our updated S^{6+}/S_{tot} relationship for calculating oxygen fugacity, it is not possible to accurately estimate Δ NNO from measured δ^{34} S and F relationships. Given their data limitations, Marini et al. (1998) made the best possible interpretation of their data, however in light of this thesis it is shown that their model needs to be refined. The conclusion of Marini *et al.* (1998) that S concentration and δ^{34} S values could be used to estimate average redox conditions may be an oversimplification of the processes governing S speciation in natural silicate melts, and we have shown that it is not applicable to this study.

The interpretation of measured values of δ^{34} S in volcanic rocks in terms of the process of only open-system isotopic fractionation alone may lead to over-

estimates of the degree of degassing. For example, if you calculated fractionation under conditions similar to those in our experiments and you had a sample with δ^{34} S = 1 ‰, you would estimate that the sample was approximately 60 % degassed, whereas these experiments would tell you that the sample was only about 43 % degassed, an over-estimation of about 17%. To see an example of how this overestimate may come about, we look at the work of de Hoog et al. (2001). In their study, they estimate that their samples are about 90% degassed based on independent estimates of initial S concentration (primitive melt inclusions) and measured S concentrations in the samples. However, using a model of open-system degassing under conditions of local gas-melt equilibrium, they find that even degassing of up to 99% under their T, fH_2O and ΔNNO conditions do not explain their measured δ^{34} S values. This demonstrates that it would not be possible to interpret their results in terms of degassing alone, as reproducing the observed δ^{34} S shift in the samples would require that over 100% of the S had degassed. Fractionation factors calculated using the conditions of de Hoog et al. (2001) (T = 1100 °C, fH_2O from 100 to 1000 bars, and ΔNNO from 0.5 to -1.0) range from 1.0002 to 1.0011 and can only explain their measured δ^{34} S values if a relatively high initial δ^{34} S value is assumed (5-7 ‰; de Hoog *et al.* 2001). The broad trend in their data is similar to our study, however, and suggests another process may be fractionating S isotopes. de Hoog et al. (2001) hypothesize that slab enrichment is contributing to high initial δ^{34} S values. Given the results of our study, it is possible that kinetic S isotope diffusion during degassing may have also contributed to these trends, especially since de Hoog et al. (2001) observe the presence of common vapour bubbles in melt inclusions in most basalt samples, pointing to an exsolved vapour phase. When interpreting S isotope data from ancient eruptions, an overestimation of the degree of degassing could greatly alter the results of a study. As discussed in the introduction, the difference between open and closed-system degassing leads to differences in eruptive style. If an eruption was thought to have been more degassed than it was, the eruption may be recorded as being less explosive than it was in reality. Incorrect interpretations of the explosivity of a particular volcano could have a

direct impact on hazard mitigation efforts for that volcanic system. When studying the effects of volcanic eruptions on climate change an overestimation of the degree of degassing would result in the conclusion that an eruption released more SO_2 than it did in reality. Consequently, this may result in attributing more climatic effects to an eruption than may be warranted.



Figure 5.1: Predicted S isotope fractionation under open-system degassing where the gas and melt are in local equilibrium (${}^{34}\alpha_{g-m} = 0.9993$) compared with experimental results. The solid line represents our empirical ${}^{34}\alpha_{g-m}$. It falls within the maximum and minimum ${}^{34}\alpha_{g-m}$ predicted based on experimental uncertainty, but is well above the average fractionation predicted for our conditions. Error bars for F are discussed in the text. Error bars in δ^{34} S-IQ are the uncertainties based upon repeat analysis of an external standard (P1326-2). The shaded grey region represents the range of fractionation expected as a result of the apparent fO_2 variability. The fact that the data points can be described by a single curve implies that all the experiments were run under a single fO_2 value, and that the observed variability is representative of the variability in the fO_2 determinations.



Figure 5.2: The effect of changing the temperature in our open-system degassing model to 1100° C. This expected fractionation provides a better fit for our data but is out of range for what we would expect given the small uncertainty (± 25 °C) on our T measurements.



Figure 5.3: The effect of changing the oxidation state in our model of S isotope fractionation under conditions of local gas-melt equilibrium from $\Delta NNO = 0.9$ to $\Delta NNO = 1.3$. This provides a better fit to our data. One standard deviation on the population gives a range of $\Delta NNO = 0.5$ to 1.3.



Figure 5.4: The diffusion straw model (after Richter *et al.* 2006). In this model, a substance is diffusing from a smaller container (V_1) in which the substance is distributed homogeneously, to a much larger area (V_2) through a tube of length L and cross-sectional area A. The distribution of the substance in V_2 is assumed to be homogeneous.



Figure 5.5. Open-system degassing of S under conditions of local gas melt equilibrium is represented by the dotted line (${}^{34}\alpha_{g-m}$ = 0.9993). The solid black line represents end-member diffusion of S²⁻ (with β = 0.055) which gives = ${}^{34}\alpha_{g-m}$ = 0.9967. Our empirical fractionation factor (${}^{34}\alpha_{g-m}$ = 0.9987) is represented by the wide dashed line. The fact that our observed fractionation lies between the other two end-member scenarios is a good indication that both processes play a role in the observed isotopic signature in degassed rocks.

6.0 Conclusion

A series of sulphur isotopic compositions from basaltic melts degassed under disequilibrium conditions were reported over ranges in degassing from ~490 to 0 MPa, and an oxygen fugacity range of NNO+0.5 to NNO+1.9, and a temperature of 1225 °C. Water concentrations in the experimental glasses varied from 1.5-10 wt %. Extents of degassing measured by comparing degassed to isobarically quenched samples ranged from 0 to ~40%.

The degree of degassing was found to correlate positively with δ^{34} S values. Degassed glasses were systematically more enriched in ³⁴S than isobarically quenched glasses. The empirical fractionation factor (³⁴ α_{g-m}) was found to be 0.9987, which is lower than the ³⁴ α_{g-m} predicted for our general (T=1225 °C, fO_2 = NNO+0.9, and fH_2O = 3000) experimental conditions of 0.9993. Because our $\alpha_{empirical}$ falls within the maximum and minimum ³⁴ α_{g-m} expected for our experimental uncertainties (0.9996 and 0.9986, respectively), we conclude that our results are consistent with the theory of fractionation during degassing under local gas-melt equilibrium. However, the data points lie consistently above predicted fractionation lines, suggesting that a model of open-system degassing under conditions of local gas-melt equilibrium does not provide a complete explanation of the observed trends.

It was demonstrated in this thesis that the process of kinetic S isotope fractionation is a very likely candidate for having additional control on S isotopic fractionation during degassing. This is suggested by the fact that our observed fractionation lies between the fractionation predicted under open-system degassing of a system in local gas-melt equilibrium and the fractionation expected under kinetic S isotope diffusion during degassing. Further evidence for this idea is provided by the β value (a controlling parameter in kinetic isotope fractionation) calculated from our experimental data that is consistent with the findings of other researchers. We recognize that more realistic models of bubble growth and S diffusion are needed to provide a better idea of the contribution of S diffusion to the observed isotopic fractionation.

While our results agree within error of a model of open-system degassing under conditions of local gas-melt equilibrium, they also would lead us to caution against interpreting S isotope data from natural systems in terms of equilibrium isotopic fractionation alone, as it may lead to over-estimates of the degree of degassing. At the minimum, ranges in fractionation resulting from analytical and experimental uncertainties should be considered due to their effect on the overall trends of the data.

This study provides a good base for the laboratory investigation of sulphur isotope fractionation during magmatic degassing. To get the best use out of the results presented here, more work must be done to further our findings. The following paragraphs present suggestions as to how similar studies in the future might be expanded and improved.

The study should be repeated to test if the results are consistently reproducible. We have postulated in this thesis that many of the variations in degassing we observe are due to the stochastic nature of the disequilibrium degassing process, meaning that exact replications of data points would not be possible. However, repeating the experiment would give us a better idea of the results and consequences of this study.

The relationship between F and average bubble size is not well defined in this thesis. Future experiments could attempt to control the bubble nucleation process. This might be achieved by adding a uniformly-sized insoluble powder (such as platinum) to the starting material. To better understand bubble nucleation and growth rates, future studies should focus on defining the solubility curve of the diffusing species under experimental conditions.

It would be useful to have data on S isotopic fractionation during magmatic degassing in other melt compositions, such as andesite or rhyolite. The resulting fractionation in the more viscous nature of these melts might be able to tell us more about the mechanics of S diffusion to a bubble within a melt during degassing.

In the range of Δ NNO of our experiments, a small change in oxygen fugacity corresponded to a larger shift in isotopic composition. To reduce the error window in a future study we would suggest running buffered experiments so that ne oxygen fugacity was controlled. It would also be interesting to see if the results are consistent under more oxidizing or reducing conditions.

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Sample	S (ppm)	1σ	F	1σ	H ₂ O content before experiment (wt%)	H ₂ O content of glass (wt%)	Tempe rature (°C)	P initial (Mpa)	P Final (Mpa)	ΔP (Mpa)	Quench rate (°C/min)	Approximate decompression Rate (MPa/s)	<i>f</i> H₂O (bar)
Batch 1													
IQ1	1598	119	0.96	0.09	4.4	5.1	1225	554	554	0	2000		7126
IQ2	1719	115	1.04	0.09	4.9	6.2	1225	554	554	0	2000		7126
DG3	1444	168	0.87	0.11	4.6	3.0	1225	554	178	376	2000		1810
DG4	1718	111	1.04	0.09	3.6	3.2	1225	554	178	376	2000		1810
DG5	1540	109	0.93	0.08	6.1	6.9	1225	554	194	360	2000		1984
DG6	1697	138	1.02	0.10	4.8	5.5	1225	554	194	360	2000		1984
DG8	1468	362	0.88	0.22	11.3	5.4	1225	554	490	64	2000		5989
DG11	1568	90	0.95	0.07	7.1	8.3	1225	554	322	232	2000		3504
DG12	1409	81	0.85	0.07	9.9	8.7	1225	554	322	232	2000		3504
DG15	1508	125	0.91	0.09	10.6	2.5	1225	554	290	264	2000		3099
DG15	1336	124	0.81	0.09	10.3	5.4	1225	554	290	264	2000		3099
Batch 2													
DG31	1926	77	0.95	0.06	9.7	2.1	1190	554	0	554	349		
DG32	965	329	0.48	0.16	8.2	1.5	1117	554	0	554	263		
DG33	1135	597	0.56	0.29	9.1	3.2	1200	554	0	554	222		
IQ19	1993	85	0.98	0.06	13.2	9.8	1225	554	554	0	2000		7126
IQ20	2040	69	1.00	0.06	11.2	9.7	1225	554	554	0	2000		7126
DG21	1740	60	0.86	0.05	9.5	5.7	1225	554	114	440	2000	0.72	1141
DG22	2044	97	1.01	0.07	10.4	7.5	1225	554	114	440	2000	0.72	1141
DG24a	739	153	0.36	0.08	11.9	5.1	1225	554	146	408	2000		1471

APPENDIX 1: FULL EXPERIMENTAL CONDITIONS

AFFENDI		INVEL	,										
Sample	S (ppm)	1σ	F	1σ	H ₂ O content before experiment (wt%)	H₂O content of glass (wt%)	Tempe rature (°C)	P initial (Mpa)	P Final (Mpa)	ΔP (Mpa)	Quench rate (°C/min)	Approximate decompression Rate (MPa/s)	<i>f</i> H₂O (bar)
DG24b	1132	101	0.56	0.06	14.4	5.0	1225	554	146	408	2000		1471
DG25	1843	267	0.91	0.14	11.1	4.8	1225	554	146	408	2000	0.74	1471
DG26	1313	218	0.65	0.11	11.8	4.2	1225	554	146	408	2000	0.74	1471
IQ27	2165	262	1.07	0.14	11.5	10.5	1225	554	554	0	2000		7126
IQ28	1967	85	0.97	0.06	10.7	8.2	1225	554	554	0	2000		7126
IQ29	1960	80	0.97	0.06	9.3	9.4	1225	554	554	0	2000		7126
IQ30	1944	56	0.96	0.05	9.5	9.1	1225	554	554	0	2000		7126

APPENDIX 1 CONTINUED

APPENDIX 2. MICROPROBE DATA

Excluded based on low total (*)

Excluded based on high total (**)

Excluded based on $AI_2O_3(\$)$

Excluded based on SiO₂ (\$\$)

Comment	Na ₂ O Al ₂ O	FeO	K ₂ O	SO ₃	S(ppm)	SiO ₂	MgO	MnO	CaO	P_2O_5	TiO ₂	Total
Sdegas1_c1_s1	4.287 18.49	7.411	1.726	0.409	1638.08	48.86	3.108	0.097	8.728	0.674	1.313	95.1
Sdegas1_c1_s2	4.425 18.55	57.248	1.787	0.438	1754.23	49.08	3.071	0.157	8.691	0.734	1.459	95.64
Sdegas1_c1_s3	4.323 18.38	8 7.126	1.683	0.366	1465.87	48.87	3.007	0.094	8.659	0.751	1.319	94.58
Sdegas1_c1_s4	4.282 18.51	7.425	1.7	0.414	1658.11	48.77	3.065	0.174	8.615	0.724	1.448	95.13
Sdegas1_c1_s5	4.433 18.4	7.165	1.763	0.391	1565.99	48.89	3.072	0.16	8.618	0.759	1.416	95.06
Sdegas1_c1_s6 (\$)	4.382 18.13	8 7.389	1.678	0.398	1594.03	49.09	3.025	0.197	8.687	0.708	1.28	94.96
Sdegas1_c2_s1	4.249 18.47	7.6	1.925	0.369	1477.88	49.2	3.204	0.153	8.027	0.668	1.442	95.31
Sdegas1_c2_s2	4.275 18.42	2 7.09	1.775	0.378	1513.93	49.58	3.018	0.194	8.295	0.638	1.398	95.06
Sdegas1_c2_s3	4.19 18.46	6.886	1.807	0.372	1489.9	49.52	2.94	0.203	8.347	0.675	1.415	94.81
Sdegas1_c2_s4	4.314 18.46	6.787	1.798	0.403	1614.05	49.45	2.993	0.12	8.227	0.714	1.297	94.57
Sdegas1_c2_s5	4.154 18.36	57.106	1.841	0.462	1850.35	49.1	3.008	0.093	8.31	0.724	1.433	94.59
Sdegas1_c2_s6 (\$)	4.143 18.13	3 7.406	1.72	0.559	2238.85	48.6	3.092	0.174	8.49	0.728	1.4	94.43
Sdegas1_c2_s7 (\$)	4.272 17.96	67.261	1.682	0.518	2074.64	48.6	3.073	0.1	8.684	0.716	1.389	94.25
Sdegas1_c3_s1	4.109 18.35	57.096	1.65	0.421	1686.15	49.12	2.932	0.197	8.482	0.633	1.327	94.32
Sdegas1_c3_s2 (\$)	4.226 18.2	2 7.075	1.671	0.356	1425.81	49.28	3.084	0.144	8.274	0.73	1.406	94.45

Sdegas1_c3_s3 (\$)	4.152	18.29	6.944	1.644	0.367	1469.87	49.2	3.009	0.14	8.364	0.715	1.417	94.24
Sdegas1_c3_s4	4.183	18.48	6.98	1.725	0.397	1590.02	49.11	2.942	0.1	8.331	0.705	1.461	94.42
Sdegas1_c3_s5 (\$)	4.267	18.13	7.059	1.7	0.381	1525.94	49.27	2.968	0.1	8.495	0.701	1.364	94.44
Sdegas1_c3_s6	4.146	18.39	7.104	1.661	0.366	1465.87	49.17	3.057	0.147	8.474	0.681	1.369	94.57
Sdegas1_c3_s7 (\$)	4.009	18.09	7.163	1.642	0.36	1441.83	48.97	2.848	0.144	8.552	0.702	1.37	93.86
Average	4.253	18.35	7.166	1.733	0.409	1597.73	49.09	3.035	0.144	8.463	0.7041	1.387	94.73
Standard deviation	0.096	0.163	0.209	0.074	0.054	119.209	0.278	0.068	0.039	0.195	0.0346	0.056	0.395
Sdegas2_c1_s2 (\$\$)	4.174	18.22	6.634	1.314	0.441	1766.25	48.28	2.754	0.191	9.077	0.683	1.355	93.13
Sdegas2_c1_s3	4.313	18.15	6.817	1.574	0.441	1766.25	48.79	3.039	0.171	8.809	0.694	1.438	94.23
Sdegas2_c1_s4	4.384	18.11	6.747	1.543	0.393	1574	48.63	2.888	0.13	8.714	0.741	1.426	93.7
Sdegas2_c1_s5	4.381	18.24	6.54	1.545	0.459	1838.34	48.95	2.6	0.144	8.999	0.72	1.379	93.95
Sdegas2_c1_s6	4.376	18.11	6.824	1.261	0.453	1814.31	48.47	2.659	0.147	9.046	0.717	1.345	93.4
Sdegas2_c1_s7	4.481	18.26	7.135	1.471	0.422	1690.15	48.73	2.91	0.127	8.94	0.67	1.379	94.52
Sdegas2_c2_s1 (\$)	4.453	17.94	6.692	1.454	0.402	1610.05	48.63	3.052	0.151	8.848	0.727	1.325	93.68
Sdegas2_c2_s2 (\$\$)	4.315	18.21	6.212	1.397	0.374	1497.91	49.29	2.341	0.244	9.164	0.729	1.3	93.57
Sdegas2_c2_s3	4.317	18.13	6.668	1.379	0.389	1557.98	48.45	2.717	0.137	8.968	0.67	1.383	93.21
Sdegas2_c2_s4	4.363	18.12	6.639	1.334	0.448	1794.28	48.81	2.423	0.141	9.503	0.673	1.326	93.78
Sdegas2_c2_s5 (\$\$)	4.224	18.05	6.848	1.261	0.391	1565.99	48.3	2.619	0.201	9.436	0.679	1.402	93.42
Sdegas2_c2_s6 (\$)	4.325	17.84	7.288	1.502	0.383	1533.95	48.31	2.817	0.11	9.045	0.641	1.38	93.65
Average	4.342	18.11	6.754	1.42	0.416	1719.33	48.64	2.735	0.158	9.046	0.6953	1.37	93.69
Standard deviation	0.086	0.123	0.274	0.111	0.031	114.752	0.3	0.222	0.038	0.234	0.0308	0.041	0.404

Comment	Na ₂ O	Al ₂ O ₃	FeO	K ₂ O	\mathbf{SO}_3	S(ppm)	SiO ₂	MgO	MnO	CaO	P_2O_5	TiO ₂	Total
Sdegas3_c1_s1	4.629	18.52	8.081	1.815	0.382	1529.95	48.84	3.176	0.153	8.825	0.667	1.452	96.54
Sdegas3_c1_s2	4.725	18.57	7.73	1.828	0.339	1357.73	48.87	3.321	0.157	8.802	0.652	1.365	96.36
Sdegas3_c1_s3	4.694	18.74	7.814	1.754	0.3	1201.53	49.37	3.234	0.19	8.672	0.715	1.288	96.77
Sdegas3_c1_s4 (*)	4.48	18.5	7.685	1.766	0.367	1469.87	48.98	3.227	0.15	8.905	0.687	1.35	96.09
Sdegas3_c1_s5	4.516	18.75	8.181	1.816	0.403	1614.05	49.38	3.307	0.124	8.813	0.689	1.415	97.4
Sdegas3_c2_s1 (*)	4.676	18.4	7.432	1.828	0.433	1734.21	49.08	3.193	0.22	8.687	0.709	1.461	96.12
Sdegas3_c2_s2 (*)	4.762	18.3	7.615	1.831	0.405	1622.06	48.81	3.108	0.173	8.73	0.712	1.353	95.8
Sdegas3_c2_s3 (*)	4.62	18.55	7.463	1.92	0.371	1485.89	49.4	3.118	0.11	8.602	0.707	1.312	96.17
Sdegas3_c2_s4	4.653	18.62	7.902	1.896	0.372	1489.9	49.43	3.269	0.17	8.741	0.773	1.398	97.23
Sdegas3_c2_s5 (\$)	4.442	19.02	7.445	1.986	0.266	1065.36	48.87	2.966	0.2	8.544	0.757	1.506	95.99
Sdegas3_c2_s6	4.59	18.65	7.894	1.863	0.297	1189.51	49.08	3.268	0.097	8.68	0.662	1.283	96.37
Sdegas3_c2_s7	4.556	18.57	7.473	1.888	0.367	1469.87	49.39	3.237	0.07	8.785	0.686	1.371	96.39
Sdegas3_c2_s8 (*)	4.572	18.6	7.839	1.767	0.388	1553.98	48.7	3.2	0.13	8.814	0.693	1.381	96.09
Sdegas3_c3_s1	4.5	18.61	7.7	1.822	0.28	1121.43	49.29	3.25	0.19	8.615	0.741	1.294	96.29
Sdegas3_c3_s2	4.558	18.79	7.817	1.81	0.325	1301.66	49.38	3.234	0.147	8.648	0.67	1.443	96.82
Sdegas3_c3_s3 (*)	4.58	18.63	7.379	1.82	0.245	981.249	49.2	3.234	0.114	8.658	0.708	1.447	96.02
Sdegas3_c3_s4	4.659	18.62	7.559	1.827	0.359	1437.83	49.55	3.189	0.16	8.786	0.71	1.425	96.84
Sdegas3_c3_s5	4.783	18.79	7.29	1.857	0.334	1337.7	49.48	3.322	0.187	8.659	0.752	1.478	96.93
Sdegas3_c3_s6	4.673	18.77	7.586	1.871	0.439	1758.24	49.29	3.294	0.167	8.685	0.728	1.397	96.9
Sdegas3_c3_s7	4.581	18.63	7.536	1.877	0.375	1501.91	49.49	3.36	0.187	8.718	0.655	1.313	96.72
Sdegas3_c3_s8	4.711	18.66	7.533	1.865	0.393	1574	49.26	3.247	0.211	8.759	0.651	1.362	96.65

Comment	Na₂O	Al ₂ O ₃	FeO	K ₂ O	SO₃	S(ppm)	SiO ₂	MgO	MnO	CaO	P_2O_5	TiO ₂	Total
Line 1	4.647	19.05	7.525	1.844	0.354	1417.8	49.67	3.275	0.204	8.853	0.764	1.344	97.53
Sdegas3_c3_traverse1													
Line 2	4.39	19.13	7.345	1.851	0.38	1521.94	49.47	3.344	0.167	8.739	0.711	1.427	96.95
Sdegas3_c3_traverse1													
Line 3	4.496	18.97	7.302	1.902	0.34	1361.73	49.47	3.302	0.167	8.945	0.763	1.43	97.09
Sdegas3_c3_traverse1													
Line 4	4.532	19.01	7.373	1.916	0.363	1453.85	49.53	3.27	0.194	8.924	0.708	1.441	97.26
Sdegas3_c3_traverse1													
Line 5	4.53	18.93	7.849	1.865	0.388	1553.98	49.34	3.332	0.194	8.895	0.706	1.284	97.31
Sdegas3_c3_traverse1													
Line 6	4.487	18.96	7.552	1.857	0.385	1541.96	49.71	3.214	0.124	8.887	0.76	1.442	97.39
Sdegas3_c3_traverse1	4 500	40.00	7 005	4 000	0.070	4547.00	40.05	0.005	0.007	0.054	0 700	4 400	00.00
	4.569	18.69	7.685	1.893	0.379	1517.93	49.25	3.285	0.097	8.854	0.723	1.436	96.86
	4 500	10.00	7 404	1 000	0.076	1505 00	40.00	2 202	0 1 1 7	0.044	0 70	4 445	07 40
	4.522	18.98	1.424	1.883	0.376	1505.92	49.38	3.303	0.117	8.941	0.78	1.415	97.12
Line 9	4 252	18 89	7 762	1 922	0.379	1517 93	49 35	3 341	0 144	87	0 7 1 9	1 29	96 75
Sdegas3 c3 traverse1	4.202	10.00	1.102	1.022	0.070	1017.00	40.00	0.041	0.144	0.7	0.7 10	1.20	00.70
Line 10	4 497	18 87	7 7 18	1 831	0 404	1618.06	49 45	3 308	0 177	8 947	0 675	1 378	97 26
Sdegas3 c3 traverse1		10.01			0.101	1010.00	10.10	0.000	0	0.0 11	0.010	1.01.0	01.20
Line 11	4.49	18.86	7.301	1.904	0.366	1465.87	49.47	3.232	0.171	8.7	0.772	1.385	96.65
Sdegas3 c3 traverse1	-						-		-	-	-		
Line 12	4.584	19	7.447	1.849	0.322	1289.64	49.91	3.171	0.157	8.836	0.723	1.352	97.34
Sdegas3_c3_traverse1													
Line 13	4.358	18.59	7.459	1.962	0.297	1189.51	49.69	3.271	0.177	8.78	0.758	1.357	96.7
Sdegas3_c3_traverse1													
Line 14	4.347	19.26	7.387	1.947	0.297	1189.51	50.37	3.185	0.218	8.391	0.705	1.334	97.44
Sdegas3_c3_traverse1													
Line 15	4.526	19.13	7.52	1.869	0.255	1021.3	50.13	3.187	0.154	8.709	0.787	1.419	97.69
Sdegas3_c3_traverse1													
Line 16	4.48	19.07	7.5	1.912	0.371	1485.89	49.56	3.297	0.184	8.724	0.766	1.355	97.22
Sdegas3_c3_traverse1													

Comment	Na₂O	AI_2O_3	FeO	K ₂ O	\mathbf{SO}_3	S(ppm)	SiO ₂	MgO	MnO	CaO	P_2O_5	TiO ₂	Total
Line 17	4.449	18.96	7.475	1.857	0.387	1549.97	49.35	3.24	0.124	8.802	0.707	1.384	96.73
Sdegas3_c3_traverse1													
Line 18	4.393	19.1	7.858	1.867	0.449	1798.29	49.21	3.393	0.12	8.944	0.705	1.293	97.33
Sdegas3_c3_traverse1													
Line 19	4.512	18.9	7.719	1.836	0.325	1301.66	49.11	3.296	0.141	8.859	0.71	1.4	96.81
Sdegas3_c3_traverse1													
Line 20	4.544	18.77	7.872	1.88	0.405	1622.06	49.52	3.308	0.141	8.702	0.745	1.393	97.28
Sdegas3_c3_traverse1													
Line 21	4.551	18.94	7.676	1.855	0.392	1570	49.32	3.311	0.197	8.823	0.688	1.35	97.1
Sdegas3_c3_traverse1													
Line 22	4.285	18.94	7.465	1.911	0.345	1381.76	49.77	3.227	0.154	8.659	0.729	1.506	96.99
Sdegas3_c3_traverse1													
Line 23	4.546	18.93	7.538	1.839	0.32	1281.63	49.83	3.183	0.147	8.518	0.696	1.341	96.89
Sdegas3_c3_traverse1													
Line 24	4.539	19.14	7.678	1.775	0.35	1401.78	49.79	3.248	0.184	8.653	0.681	1.359	97.4
Sdegas3_c3_traverse1													
Line 25	4.352	18.95	7.628	1.81	0.344	1377.75	49.44	3.233	0.104	8.863	0.764	1.453	96.94
Sdegas3_c3_traverse1									o . = .				
Line 26	4.28	18.72	7.446	1.909	0.382	1529.95	49.24	3.311	0.151	8.897	0.712	1.445	96.49
Sdegas3_c3_traverse1				=									
Line 27	4.491	19.13	7.591	1.925	0.316	1265.61	49.19	3.311	0.194	9.032	0.764	1.405	97.35
Sdegas3_c3_traverse1	4 405	40.00	7 507	4 050	0.00	4004.00	40	0.070	0.40	0.040	0 000	4 0 4 0	00.4
	4.405	18.68	1.567	1.859	0.33	1321.68	49	3.279	0.13	8.813	0.696	1.346	96.1
Sdegas3_c3_traverse1 (*)	4 205	10.00	7 746	1 770	0 240	1000 77	40.00	2 204	0 4 2	0 0 0 0	0 750	1 200	07
Lille 29 Sdogoo2 o2 troveroo1	4.395	10.90	1.110	1.779	0.340	1393.77	49.32	3.204	0.13	0.932	0.755	1.300	97
	4 2 2 0	10 77	7 0 1 0	1 0 2 7	0.215	1061 61	10.25	2 201	0 174	0 002	0 670	1 1 70	07 10
Second and traversed	4.329	10.77	1.012	1.037	0.315	1201.01	49.35	3.301	0.174	0.995	0.070	1.470	97.12
	4 507	10 06	7 774	1 006	0.26	1111 02	10 11	2.26	0 1 2 7	0 006	0 766	1 260	07.24
Education School and S	4.507	10.00	1.114	1.090	0.50	1441.03	49.44	3.20	0.127	0.000	0.700	1.300	97.24
Line 32	1 511	18.83	7 36	1 865	0 35/	1/17 Q	10 13	3 202	0 18/	8 7 2 7	0 72	1 368	96 64
Sdegae3 c3 traverso1	4.514	10.05	1.50	1.000	0.004	0.11+1	79.40	5.232	0.104	0.121	0.72	1.500	30.04
Suegass_cs_liaveise i													

Comment	Na₂O	AI_2O_3	FeO	K₂O	SO₃	S(ppm)	SiO ₂	MgO	MnO	CaO	P_2O_5	TiO₂	Total
Line 33 Sdegas3_c3_traverse1	4.293	18.66	7.669	1.892	0.383	1533.95	49.19	3.335	0.163	8.735	0.745	1.374	96.43
Line 34	4.35	18.74	7.889	1.843	0.426	1706.17	49.33	3.278	0.154	8.978	0.751	1.409	97.14
Sdegas3_c3_traverse1 Line 35	4.405	18.75	7.755	1.901	0.453	1814.31	48.7	3.289	0.194	8.951	0.701	1.38	96.48
Line 36	4.089	18.91	7.816	1.857	0.359	1437.83	49.33	3.388	0.197	8.86	0.75	1.422	96.98
Sdegas3_c3_traverse1 Line 37	3.89	19.2	7.297	1.86	0.395	1582.01	49.23	3.33	0.137	9.007	0.748	1.514	96.6
Sdegas3_c3_traverse1 Average						1444.16							
Standard deviation						168.372							
Sdegas4_c1_s1 (*)	4.373	17.98	7.846	1.727	0.467	1870.38	49.39	3.084	0.124	8.208	0.685	1.387	95.27
Sdegas4_c1_s2	4.496	18.36	7.217	1.73	0.432	1730.2	50.03	3.125	0.134	8.54	0.71	1.319	96.09
Sdegas4_c1_s3	4.451	18.92	7.421	1.824	0.38	1521.94	50.17	3.223	0.14	8.583	0.723	1.297	97.13
Sdegas4_c1_s4	4.394	19.04	7.328	1.759	0.422	1690.15	50.07	3.192	0.157	8.711	0.726	1.489	97.29
Sdegas4_c1_s5 (*)	4.374	16.07	7.1	1.642	0.386	1545.97	47.08	2.617	0.17	7.896	0.637	1.266	89.23
Sdegas4_c2_s1 (*)	4.082	18.76	7.537	1.758	0.462	1850.35	48.74	3.183	0.154	8.584	0.802	1.353	95.42
Sdegas4_c2_s2 (*)	4.109	17.75	7.426	1.798	0.394	1578.01	47.71	2.885	0.157	8.386	0.737	1.424	92.78
Sdegas4_c2_s3	4.401	18.99	7.243	1.79	0.433	1734.21	50.54	3.077	0.184	8.431	0.761	1.46	97.31
Sdegas4_c2_s4	4.292	19.1	7.281	1.824	0.464	1858.36	49.8	3.121	0.094	8.591	0.693	1.49	96.75
Sdegas4_c2_s5	4.335	18.7	7.354	1.788	0.442	1770.25	50.07	3.232	0.063	8.375	0.729	1.38	96.47
Sdegas4_c2_s6 (*)	3.705	14.38	6.967	1.594	0.47	1882.4	43.51	2.283	0.134	7.93	0.703	1.466	83.14

Average

1717.52

Comment	Na ₂ O Al ₂ O ₃ FeO	K ₂ O SO ₃	S(ppm)	SiO ₂	MgO	MnO	CaO	P_2O_5	TiO ₂	Total
Standard deviation			111.408							
Sdegas5b_c1_s1	4.124 17.96 6.176	1.338 0.399	1598.03	48.54	2.934	0.097	8.549	0.658	1.388	92.16
Sdegas5b_c1_s2	4.131 17.77 6.354	1.213 0.402	1610.05	48.71	2.898	0.124	8.692	0.703	1.403	92.4
Sdegas5b_c1_s3	4.207 18.11 6.124	1.152 0.386	1545.97	48.96	2.9	0.127	8.702	0.726	1.327	92.72
Sdegas5b_c2_s1	4.117 18.01 6.651	1.614 0.375	1501.91	48.92	2.948	0.177	8.257	0.685	1.357	93.11
Sdegas5b_c2_s2	4.139 17.99 6.324	1.554 0.422	1690.15	48.8	3.053	0.127	8.425	0.684	1.389	92.9
Sdegas5b_c2_s3	4.152 18.07 6.266	1.641 0.366	1465.87	49.27	2.935	0.201	8.233	0.735	1.311	93.17
Sdegas5b_c2_s4	4.106 18.17 6.065	1.754 0.38	1521.94	49.51	2.861	0.127	8.208	0.75	1.393	93.33
Sdegas5b_c2_s5	4.191 18.32 6.04	1.62 0.382	1529.95	49.72	2.981	0.107	8.296	0.663	1.318	93.63
Sdegas5b_c2_s6	3.998 18.32 6.064	1.743 0.336	1345.71	49.96	2.855	0.084	8.125	0.796	1.467	93.75
Sdegas5b_c2_s7	4.192 18.33 5.983	1.609 0.391	1565.99	49.39	2.888	0.107	8.084	0.602	1.494	93.07
Sdegas5b_c2_s8	4.134 18.07 5.764	1.587 0.403	1614.05	49.49	2.98	0.154	8.284	0.746	1.323	92.93
Sdegas5b_c2_s9	4.147 18.39 5.99	1.74 0.336	1345.71	49.83	2.975	0.131	7.983	0.756	1.368	93.64
Sdegas5b_c2_s10	4.234 18.16 5.963	1.761 0.422	1690.15	49.59	2.992	0.117	8.178	0.744	1.33	93.49
Average			1540.42							
Standard deviation			108.945							
Sdegas6_c1_s1	4.581 18.33 6.672	1.841 0.413	1654.1	49.48	3.148	0.11	8.484	0.681	1.326	95.07
Sdegas6_c1_s2	4.519 18.48 6.724	1.859 0.413	1654.1	49.05	3.181	0.127	8.594	0.714	1.4	95.06
Sdegas6_c1_s3	4.407 18.13 6.791	1.832 0.457	1830.33	49	3.149	0.127	8.56	0.743	1.382	94.57

Sdegas6_c1_s4 4.604 17.9 6.724 1.884 0.36 1441.83 48.86 3.21 0.14 8.572 0.627 1.362 94.24

Commont	Na.O ALO	E ₀ O	K.O S	0. S/n	nm) SiO	MaO I	MnO	C20	P.O.	TiO.	Total
			N ₂ O 3	503 S(b	piii) 5i0 ₂	wigo i		CaO	F 205		TOLAT
Sdegas6_c1_s5	4.376 18.28	6.614	1.848 (0.47 18	82.4 48.92	3.084 0).124	8.436	0.663	1.424	94.24
Sdegas6_c1_s6	4.652 18.15	6.846	1.897 0	0.38 152	1.94 48.91	3.131 0).134	8.508	0.759	1.258	94.62
Sdegas6_c1_s7	4.616 18.1	6.52	1.791 0.4	431 17	26.2 48.8	3.068 0).147	8.683	0.717	1.39	94.25
Sdegas6_c1_s8	4.421 18.07	6.734	1.799 0.4	424 169	8.16 49.08	3.2 0).127	8.436	0.653	1.337	94.28
Sdegas6_c2_s1	4.613 18.31	6.814	1.727 0.	374 149	7.91 48.71	3.308 0).274	8.5	0.643	1.313	94.59
Sdegas6_c2_s2	4.47 18.35	6.962	1.769 0.	444 177	8.26 48.61	3.179 0).164	8.7	0.71	1.417	94.78
Sdegas6_c2_s3	4.587 18.07	7.015	1.783 0	0.45 180	2.29 48.61	3.182 0).157	8.621	0.674	1.346	94.49
Sdegas6_c2_s4 (*)	4.565 17.83	6.739	1.765 0.	479 191	8.44 48.29	3.089	0.15	8.532	0.688	1.311	93.44
Sdegas6_c2_s5	4.437 18.26	7.106	1.78 0	0.44 176	2.24 48.52	3.128 0).124	8.514	0.657	1.367	94.32
Sdegas6_c2_s6 (*)	4.441 18.07	6.641	1.749 0.	421 168	6.15 48.48	3.117 0	0.077	8.369	0.741	1.308	93.41
Sdegas6_c2_s7	4.555 18.35	6.841	1.852 0.	417 167	0.13 48.48	3.165	0.14	8.373	0.703	1.345	94.22
Sdegas6_c2_s8	4.571 18.22	6.635	1.8 0	0.43 172	2.19 48.46	3.116 0).174	8.505	0.714	1.374	94.01
Sdegas6_c2_s9	4.505 18.49	6.735	1.838 0.	453 181	4.31 48.84	3.131 0).187	8.364	0.72	1.411	94.68
Average				169	7.09						
Standard deviation				138	.448						
Sdegas8_c1_s1	4.416 18.49	6.481	1.86 0.4	432 17	30.2 49.83	3.219 0).191	8.513	0.713	1.287	95.43
Sdegas8_c1_s2	4.441 18.21	6.577	1.866 0.	433 173	4.21 49.03	3.177 0).144	8.254	0.704	1.305	94.14

Sdegas8_c1_s3 Sdegas8_c1_s4

s8_c1_s4 4.446 18.25 6.449 1.843 0.449 1798.29 49.32 3.129 0.1 8.542 0.698 1.414 94.63

4.525 18.2 6.533 1.922 0.427 1710.18 49.04 3.109 0.17 8.34 0.716 1.332 94.32

Comment	Na ₂ O Al ₂ O	, FeO	K ₂ O	\mathbf{SO}_3	S(ppm)	SiO ₂	MgO	MnO	CaO	P_2O_5	TiO ₂	Total
Sdegas8_c1_s5	4.429 18.22	6.615	1.831	0.381	1525.94	49.5	3.196	0.06	8.43	0.763	1.364	94.79
Sdegas8_c2_s1	4.381 18.12	6.386	1.874	0.269	1077.37	49.7	3.173	0.117	8.26	0.733	1.294	94.31
Sdegas8_c2_s2	4.545 18.53	6.643	1.808	0.374	1497.91	49.57	3.289	0.201	8.468	0.706	1.411	95.54
Sdegas8_c2_s4	4.448 18.46	6.771	1.896	0.368	1473.88	49.01	3.156	0.157	8.359	0.709	1.392	94.73
Sdegas8_c2_s5	4.442 18.25	6.571	1.83	0.405	1622.06	48.92	3.223	0.131	8.482	0.678	1.366	94.3
Sdegas8_c2_s6	4.521 18.62	6.042	1.885	0.193	772.984	49.68	3.189	0.151	8.474	0.796	1.321	94.87
Sdegas8_c2_s7	4.496 18.54	6.012	1.84	0.195	780.994	49.29	3.089	0.141	8.484	0.764	1.296	94.15
Sdegas8_c2_s8	4.336 18.6	6.195	1.83	0.217	869.106	49.61	2.983	0.104	8.54	0.711	1.393	94.53
Sdegas8_c2_s9	4.493 18.55	6.588	1.84	0.353	1413.8	49.23	3.236	0.134	8.442	0.731	1.389	94.99
Sdegas8_c2_s10	4.457 18.61	6.509	1.884	0.328	1313.67	49.61	3.136	0.194	8.525	0.699	1.349	95.31
Sdegas8_c3_s1	4.08 18.23	7.011	1.689	0.459	1838.34	49.18	3.146	0.087	8.161	0.709	1.304	94.06
Sdegas8_c3_s2	4.121 18.4	6.446	1.824	0.446	1786.27	49.21	3.018	0.131	7.955	0.758	1.339	93.64
Sdegas8_c3_s3	4.152 18.38	6.815	1.767	0.41	1642.09	49.13	3.046	0.147	8.152	0.724	1.368	94.09
Sdegas8_c3_s4 (\$)	4.043 17.9	6.969	1.735	0.429	1718.19	49.06	3.098	0.117	8.18	0.717	1.375	93.62
Sdegas8_c3_s5 (*)	3.787 18.15	6.76	1.714	0.431	1726.2	49	2.976	0.164	8.206	0.723	1.367	93.28
Sdegas8_c3_s6 (\$\$)	3.919 18.31	7.098	1.666	0.457	1830.33	48.11	3.133	0.234	8.29	0.72	1.321	93.25
Sdegas8_c3_s7	4.102 18.36	7.095	1.77	0.457	1830.33	49.06	3.092	0.147	8.214	0.718	1.434	94.45
Average					1467.65							
Standard deviation					362.058							

 Sdegas11_c1_s1 (\$)
 3.661 18.45 6.236
 1.12 0.397 1590.02
 48.2 2.068 0.181 9.891
 0.713
 1.299
 92.21

Comment	Na ₂ O Al ₂ O	₃ FeO	K ₂ O	SO₃	S(ppm)	SiO ₂	MgO	MnO	CaO	P_2O_5	TiO ₂	Total
Sdegas11_c1_s2	3.552 17.9	5 6.838	0.946	0.405	1622.06	48.12	2.39	0.221	9.855	0.687	1.377	92.34
Sdegas11_c1_s3	3.44 17.8	1 6.853	1.652	0.348	1393.77	48.1	2.983	0.141	8.082	0.648	1.223	91.28
Sdegas11_c1_s4	3.615 17.9	3 6.759	1.593	0.375	1501.91	48.49	3.055	0.101	8.141	0.667	1.383	92.11
Sdegas11_c1_s5	3.617 17.9	3 7.007	1.407	0.368	1473.88	48.24	3.003	0.137	8.172	0.746	1.471	92.09
Sdegas11_c1_s6	3.585 17.6	6.7	1.462	0.424	1698.16	48.23	2.94	0.094	8.008	0.734	1.305	91.14
Sdegas11_c1_s7 (*)	1.966 18.0	8 6.91	1.414	0.397	1590.02	48.33	2.813	0.144	8.224	0.722	1.357	90.36
Sdegas11_c1_s8	3.584 17.5	9 7.149	1.51	0.388	1553.98	48	2.909	0.114	8.197	0.708	1.353	91.5
Sdegas11_c1_s9	3.516 17.7	4 6.977	1.437	0.407	1630.07	48.29	2.926	0.097	8.264	0.69	1.363	91.71
Sdegas11_c1_s10	3.605 17.9	2 6.453	1.175	0.398	1594.03	48.14	2.41	0.127	8.727	0.752	1.354	91.06
Sdegas11_c1_s11	3.663 17.8	7 6.517	1.499	0.365	1461.86	48.04	2.981	0.187	8.241	0.744	1.375	91.48
Sdegas11_c1_s12	3.589 17.9	3 6.7	1.529	0.405	1622.06	48.13	2.936	0.124	8.372	0.721	1.454	91.88
Sdegas11_c1_s13	3.712 17.8	7 6.855	1.594	0.383	1533.95	48.29	2.966	0.127	7.966	0.684	1.345	91.8
Sdegas11_c4_s1	3.851 18.	1 5.731	1.148	0.411	1646.09	48.89	2.048	0.137	9.323	0.758	1.377	91.78
Sdegas11_c4_s2	3.637 17.8	5 6.963	1.292	0.414	1658.11	48.21	2.878	0.221	8.697	0.74	1.362	92.27
Average					1568.46							
Standard deviation					90.2486							

Sdegas12_c1_s1	3.49 17.74	16.609 1.683	3 0.362 1449	9.84 47.73 2.8	339 0.157 8.566	0.736	1.318	91.23
Sdegas12_c1_s2	3.392 17.99	9 6.486 1.70 ²	1 0.385 1541	.96 48.1 3.0	075 0.171 8.174	0.696	1.378	91.55
Sdegas12_c1_s3	3.625 18.06	6.586 1.746	6 0.328 1313	8.67 48.08 2.9	997 0.194 8.125	0.71	1.295	91.75
Sdegas12_c1_s4	3.557 17.8	6.28 1.532	2 0.36 1441	.83 47.81 2.9	912 0.144 8.221	0.67	1.422	90.71

Comment	Na ₂ O Al ₂ O ₃ FeC	K ₂ O	\mathbf{SO}_3	S(ppm)	SiO ₂	MgO	MnO	CaO	P_2O_5	TiO ₂	Total
Sdegas12_c1_s5	3.592 18.08 6.70	5 1.457	0.376	1505.92	47.98	2.761	0.181	8.613	0.688	1.377	91.81
Sdegas12_c1_s6	3.644 17.79 6.64	4 1.532	0.366	1465.87	47.69	2.942	0.114	8.435	0.694	1.361	91.21
Sdegas12_c1_s7	3.701 18.07 6.62	2 1.473	0.377	1509.92	48.44	2.835	0.261	8.65	0.678	1.323	
Sdegas12_c1_s8	3.569 17.88 6.76	5 1.558	0.335	1341.71	48.08	3.046	0.214	8.289	0.661	1.47	91.86
Sdegas12_c1_s9	3.618 17.85 6.68	5 1.455	0.352	1409.79	48.02	2.981	0.134	8.133	0.696	1.34	91.26
Sdegas12_c1_s10	3.639 17.85 6.85	5 1.557	0.332	1329.69	48.28	3.076	0.191	8.375	0.687	1.34	92.18
Sdegas12_c2_s1	3.625 17.49 6.57	1 1.482	0.316	1265.61	47.87	3.017	0.12	8.132	0.647	1.318	90.59
Sdegas12_c2_s2	3.613 17.66 6.62	1 1.395	0.346	1385.76	47.56	2.864	0.147	8.54	0.66	1.328	90.73
Sdegas12_c2_s3	3.694 17.33 6.66	3 1.514	0.364	1457.85	47.62	2.998	0.164	8.226	0.671	1.332	90.58
Sdegas12_c2_s4	3.797 17.45 6.59	9 1.406	0.375	1501.91	47.91	2.945	0.114	8.857	0.707	1.301	91.46
Sdegas12_c2_s5	3.677 17.53 6.70	7 1.392	0.335	1341.71	47.91	2.824	0.167	8.488	0.717	1.231	90.98
Sdegas12_c2_s6	3.602 17.41 6.38	5 1.47	0.325	1301.66	47.59	2.899	0.07	8.369	0.695	1.372	90.18
Sdegas12_c2_s7	3.624 17.75 6.30	3 1.41	0.347	1389.77	47.96	2.876	0.147	8.452	0.645	1.395	90.91
Sdegas12_c2_s8	3.607 17.56 6.62	2 1.565	0.35	1401.78	47.95	2.992	0.124	8.469	0.667	1.327	91.23
Average				1408.68							
Standard deviation				81.0715							

Sdegas15_c1_s2	4.849 19.31	5.847 1.8	53 0.348	1393.77	50.92	3.216 0.1	74 8.735	0.712	1.512	97.47
Sdegas15_c1_s3	4.722 18.93	5.571 1.9	26 0.35	1401.78	50.86	3.301 0.1	44 8.771	0.745	1.504	96.82
Sdegas15_c1_s4	4.808 19.18	5.71 1.9	92 0.365	1461.86	51.13	3.291 0.1	31 8.94	0.75	1.555	97.85
Sdegas15_c1_s5	4.753 19.09	5.6 1.9	59 0.361	1445.84	50.81	3.184 0.0	97 8.745	0.668	1.407	96.68

Comment	Na ₂ O	Al ₂ O ₃	FeO	K_2O	SO₃	S(ppm)	SiO ₂	MgO	MnO	CaO	P_2O_5	TiO ₂	Total
Sdegas15_c1_s6	4.68	19.28	5.844	1.893	0.365	1461.86	51.11	3.317	0.204	8.812	0.752	1.467	97.73
Sdegas15_c1_s7	4.65	19.15	5.795	1.856	0.379	1517.93	51.27	3.348	0.121	8.836	0.756	1.403	97.56
Sdegas15_c1_s8	4.692	18.96	5.82	1.904	0.336	1345.71	50.93	3.36	0.15	8.856	0.768	1.407	97.18
Sdegas15_c1_s9	4.699	18.76	6.045	1.889	0.433	1734.21	50.92	3.369	0.167	8.849	0.737	1.406	97.27
Sdegas15_c1_s10	4.832	19.13	5.672	1.873	0.438	1754.23	50.98	3.353	0.214	8.878	0.798	1.436	97.61
Sdegas15_c1_s11	4.732	19.14	5.773	1.89	0.401	1606.04	51.06	3.19	0.15	8.782	0.71	1.357	97.18
Sdegas15_c1_s12	4.807	19.32	5.926	1.92	0.407	1630.07	51.01	3.368	0.141	8.902	0.785	1.45	98.03
Sdegas15_c1_s13	4.666	19.33	6.042	1.906	0.335	1341.71	51.02	3.326	0.147	8.875	0.777	1.472	97.9
Sdegas15_c1_s14	4.672	19.37	5.87	1.866	0.409	1638.08	51.31	3.355	0.117	8.851	0.66	1.398	97.87
Sdegas15_c1_s15	4.718	19.25	5.841	1.972	0.383	1533.95	51.32	3.331	0.127	8.907	0.785	1.456	98.08
Sdegas15_c1_s16	4.802	19.37	5.988	1.858	0.375	1501.91	51.08	3.342	0.201	8.581	0.77	1.427	97.79
Sdegas15_c1_s17	4.668	19.16	5.939	1.909	0.34	1361.73	50.96	3.302	0.144	8.96	0.738	1.376	97.5
Sdegas15_c1_s18	4.791	19.15	5.908	1.919	0.385	1541.96	51.13	3.319	0.161	8.842	0.761	1.335	97.7
Sdegas15_c1_s19	4.741	19.16	5.84	1.835	0.367	1469.87	50.86	3.327	0.171	8.853	0.724	1.342	97.22
Average						1507.92							
Standard deviation						124.732							

Sdegas16_c2_s1	4.578 17.93 7.076	1.544 0.299	1197.52 48.78	3 2.899 0.147 8.772	0.699	1.319	94.04
Sdegas16_c2_s2 (*)	4.212 17.51 7.282	1.374 0.328	1313.67 46.85	5 2.896 0.117 8.792	0.695	1.403	91.46
Sdegas16_c2_s3 (\$)	4.171 20.37 6.637	1.496 0.333	1333.7 46.93	8 2.888 0.131 8.209	0.727	1.225	93.12
Sdegas16_c2_s4	4.465 18.65 7.287	1.62 0.359	1437.83 48.87	3.259 0.144 8.712	0.685	1.361	95.42

2.65
1.24
.83
9.69
99.2
9.19
9.51
6.69
6.76
15
77
04
63
81
.14

Comment	Na₂O	AI_2O_3	FeO	K ₂ O	SO3	S(ppm)	SiO ₂	MgO	MnO	CaO	P_2O_5	TiO ₂	Total
sdegas19_c2_s1	2.65	17.58	6.49	1.11	0.478	1914.44	47.26	1.95	0.165	10.83	0.691	1.36	90.56
sdegas19_c2_s2	2.49	17.62	6.41	1.18	0.467	1870.38	46.39	2.33	0.070	10.55	0.682	1.41	89.60
sdegas19_c2_s3	2.83	17.92	5.56	0.815	0.525	2102.68	48.55	1.33	0.187	11.10	0.788	1.35	90.94
sdegas19_c2_s4	2.59	17.57	6.26	1.11	0.496	1986.53	47.33	2.03	0.085	10.60	0.680	1.33	90.09
sdegas19_c2_s5	2.63	17.43	6.49	1.12	0.505	2022.57	47.03	2.13	0.084	10.43	0.689	1.43	89.97
Average						1993.08							
Standard deviation						85.4555							
sdegas20_c1_s1 (*)	2.69	17.39	6.64	1.26	0.507	2030.58	46.90	2.20	0.137	10.27	0.732	1.25	89.98
sdegas20_c1_s2	2.67	17.67	6.43	1.21	0.506	2026.58	47.48	1.93	0.162	10.14	0.717	1.36	90.26
sdegas20_c1_s3	2.72	17.50	5.72	0.916	0.546	2186.78	47.97	1.51	0.176	10.89	0.697	1.42	90.07
sdegas20_c1_s4	2.45	17.34	6.25	1.08	0.503	2014.56	47.54	1.82	0.102	10.63	0.715	1.34	89.76
sdegas20_c1_s5	2.43	17.68	6.40	1.08	0.498	1994.54	47.39	1.90	0.264	10.85	0.793	1.26	90.56
sdegas20_c1_s6	2.66	17.52	6.30	1.21	0.501	2006.55	47.56	1.91	0.137	10.55	0.722	1.42	90.47
sdegas20_c1_s7	2.65	17.77	6.32	1.15	0.518	2074.64	47.48	1.84	0.200	10.43	0.790	1.46	90.58
sdegas20_c1_s8 (**)	2.91	17.65	5.59	0.827	0.518	2074.64	48.46	1.37	0.169	11.42	0.735	1.39	91.05
sdegas20rep_c2_s5	2.71	17.71	6.90	1.23	0.493	1974.51	47.12	2.62	0.127	9.45	0.696	1.30	90.34
sdegas20rep_c4_s3 (*)	2.97	17.36	6.50	1.31	0.499	1998.54	47.23	2.29	0.207	9.33	0.714	1.40	89.81
Average						2039.74							
Standard deviation						69.2711							

Comment	Na₂O	AI_2O_3	FeO	K ₂ O	SO₃	S(ppm)	SiO ₂	MgO	MnO	CaO	P_2O_5	TiO ₂	Total
sdegas21_c1_s1 (*)	3.29	18.33	3.69	1.24	0.544	2178.77	50.91	1.95	0.138	10.55	0.807	1.50	92.93
sdegas21_c1_s1	3.96	18.29	7.05	1.73	0.378	1513.93	48.84	3.07	0.204	8.72	0.770	1.52	94.53
sdegas21_c1_s2	3.85	18.23	6.69	1.79	0.445	1782.27	48.65	3.14	0.119	8.97	0.681	1.34	93.91
sdegas21_c1_s3	3.87	17.94	7.02	1.79	0.451	1806.3	48.39	2.98	0.147	8.85	0.733	1.52	93.70
sdegas21_c1_s4	3.72	18.01	7.12	1.74	0.411	1646.09	48.55	3.04	0.179	8.77	0.756	1.51	93.80
sdegas21_c1_s5	3.86	18.10	6.81	1.76	0.451	1806.3	49.23	3.15	0.211	8.97	0.740	1.35	94.63
sdegas21_c1_s6	3.93	18.35	7.14	1.77	0.446	1786.27	48.71	3.04	0.126	8.78	0.767	1.36	94.40
sdegas21_c1_s7	3.83	18.45	7.18	1.76	0.431	1726.2	49.57	3.04	0.169	8.49	0.789	1.40	95.10
sdegas21_c2_s1	4.02	18.17	7.06	1.77	0.466	1866.37	48.91	3.24	0.151	8.96	0.772	1.47	95.00
sdegas21_c2_s2	3.85	17.92	6.83	1.83	0.432	1730.2	48.56	3.15	0.211	8.97	0.774	1.49	94.02
sdegas21_c2_s3	4.00	17.91	6.99	1.88	0.434	1738.21	48.68	3.16	0.130	8.79	0.746	1.39	94.10
Average						1740.21							
Standard deviation						60.1657							
sdegas22_c1_s2	3.40	17.74	6.72	1.10	0.504	2018.57	48.07	2.86	0.215	9.87	0.742	1.33	92.56
sdegas22_c1_s3	3.47	17.77	6.70	0.956	0.500	2002.55	48.42	2.31	0.165	10.33	0.724	1.58	92.92
sdegas22_c1_s4	3.53	17.92	7.13	1.09	0.485	1942.47	48.54	2.64	0.190	9.73	0.721	1.39	93.36
sdegas22_c1_s5	3.38	17.50	6.92	1.03	0.473	1894.41	47.99	2.49	0.193	10.14	0.715	1.40	92.22
sdegas22_c1_s6	3.50	18.02	7.00	1.14	0.504	2018.57	48.48	2.62	0.127	9.85	0.721	1.43	93.39
sdegas22_c1_s7	3.36	17.69	6.99	1.20	0.501	2006.55	47.92	2.89	0.175	9.74	0.691	1.37	92.52
sdegas22_c2_s1	3.43	18.19	3.78	1.09	0.554	2218.82	50.34	2.18	0.180	10.24	0.767	1.38	92.12

Comment	Na₂C	Al ₂ O ₃	FeO	K ₂ O	SO3	S(ppm)	SiO ₂	MgO	MnO	CaO	P_2O_5	TiO ₂	Total
sdegas22_c2_s2	3.49	18.32	3.71	1.18	0.536	2146.73	50.19	2.00	0.194	10.32	0.656	1.35	91.93
sdegas22_c2_s3 (\$)	0.19	19.19	3.99	0.533	0.545	2182.78	51.86	2.20	0.159	10.58	0.703	1.45	91.40
sdegas22_c2_s4	3.33	18.17	3.98	1.09	0.522	2090.66	50.11	2.37	0.162	10.45	0.701	1.42	92.31
sdegas22_c2_s5	3.29	18.19	3.82	1.07	0.525	2102.68	50.17	2.32	0.138	10.44	0.714	1.39	92.08
Average						2044.2							
Standard deviation						96.5146							
sdegas24a_c1_s1	4.10	18.28	7.01	1.78	0.193	772.984	49.58	3.22	0.120	8.98	0.757	1.42	95.43
sdegas24a_c1_s2	4.01	18.21	7.20	1.76	0.128	512.652	49.44	3.04	0.123	8.96	0.725	1.39	94.97
sdegas24a_c1_s3	4.12	18.54	7.19	1.84	0.159	636.81	49.39	3.22	0.137	8.99	0.789	1.45	95.81
sdegas24a_c1_s4	4.03	18.34	7.01	1.80	0.180	720.917	49.29	3.09	0.186	9.14	0.790	1.42	95.28
sdegas24a_c1_s5	4.04	17.92	6.47	1.83	0.177	708.902	49.84	3.15	0.077	8.95	0.652	1.41	94.51
sdegas24a_c1_s6	4.03	18.29	6.83	1.75	0.182	728.927	49.45	3.13	0.148	8.91	0.721	1.51	94.95
sdegas24a_c1_s7	4.07	18.24	6.87	1.79	0.251	1005.28	48.88	3.08	0.155	8.95	0.701	1.44	94.41
sdegas24a_c1_s8	3.82	18.17	6.90	1.78	0.244	977.243	48.59	3.18	0.165	9.08	0.813	1.42	94.16
sdegas24arep_c1_s1	4.14	17.76	7.11	1.77	0.180	720.917	49.17	3.20	0.134	9.12	0.701	1.43	94.73
sdegas24arep_c1_s5	3.98	18.33	7.14	1.79	0.151	604.769	49.17	3.13	0.116	9.13	0.682	1.45	95.06
Average						738.94							
Standard deviation						152.816							
sdegas24brep_c1_s1	4.24	18.46	7.01	1.80	0.310	1241.58	49.19	3.22	0.165	9.00	0.780	1.46	95.64

Comment	Na ₂ O	AI_2O_3	FeO	K ₂ O	SO₃	S(ppm)	SiO ₂	MgO	MnO	CaO	P_2O_5	TiO ₂	Total
sdegas24brep_c1_s2	4.03	18.52	6.74	1.99	0.305	1221.55	49.04	3.16	0.176	8.46	0.695	1.35	94.46
sdegas24brep_c1_s3	3.99	18.27	6.75	1.86	0.235	941.198	49.77	3.13	0.201	8.92	0.772	1.40	95.29
sdegas24brep_c1_s4	4.02	18.13	7.09	1.72	0.273	1093.39	49.52	3.16	0.074	9.06	0.762	1.45	95.26
sdegas24brep_c1_s5	4.18	18.57	6.84	1.73	0.275	1101.4	49.69	3.15	0.137	8.84	0.775	1.41	95.59
sdegas24brep_c1_s6	4.01	18.15	6.09	1.75	0.271	1085.38	50.11	3.14	0.194	8.76	0.694	1.60	94.76
sdegas24brep_c1_s7	4.02	18.32	6.35	1.74	0.307	1229.56	49.58	3.17	0.141	8.89	0.752	1.52	94.77
sdegas24brep_c1_s8	3.98	18.27	6.21	1.77	0.286	1145.46	49.72	3.14	0.095	8.71	0.721	1.41	94.31
Average						1132.44							
Standard deviation						100.521							
sdegas25_c1_s1	4.12	18.22	7.20	1.77	0.437	1750.23	48.78	3.28	0.126	9.17	0.726	1.50	95.32
sdegas25_c1_s2	4.31	18.33	7.83	1.73	0.453	1814.31	49.09	3.30	0.228	9.20	0.723	1.47	96.65
sdegas25_c1_s3	4.07	18.14	7.21	1.66	0.501	2006.55	48.65	3.20	0.183	9.24	0.729	1.42	95.01
sdegas25_c1_s4	4.08	17.75	7.02	1.75	0.486	1946.48	48.66	3.13	0.176	9.09	0.764	1.31	94.21
sdegas25_c1_s5	4.16	18.24	6.80	1.82	0.439	1758.24	49.22	3.14	0.106	9.30	0.709	1.48	95.41
sdegas25_c2_s1	4.14	17.98	6.97	1.74	0.463	1854.36	49.23	3.02	0.179	8.83	0.713	1.34	94.60
sdegas25_c2_s1	4.04	18.15	7.33	1.69	0.503	2014.56	49.09	3.25	0.095	9.38	0.781	1.48	95.81
sdegas25_c2_s2	4.05	18.41	7.33	1.71	0.496	1986.53	48.88	3.15	0.134	9.29	0.733	1.49	95.66
sdegas25_c2_s3	4.01	18.31	6.31	1.79	0.277	1109.41	49.64	3.00	0.165	8.60	0.772	1.38	94.24
sdegas25_c2_s4	4.09	18.27	7.19	1.69	0.488	1954.49	49.05	3.27	0.172	9.06	0.678	1.53	95.48
sdegas25_c2_s5	3.99	18.00	7.06	1.64	0.520	2082.65	48.97	3.25	0.144	9.40	0.733	1.50	95.21

Comment	Na₂O	AI_2O_3	FeO	K ₂ O	SO₃	S(ppm)	SiO ₂	MgO	MnO	CaO	P_2O_5	TiO ₂	Total
Average						1843.44							
Standard deviation						266.879							
sdegas26_c1_s1	5.34	18.50	6.41	1.19	0.344	1377.75	50.53	3.21	0.109	8.12	0.682	1.55	95.99
sdegas26_c2_s1	5.60	18.47	6.70	1.19	0.334	1337.7	50.50	3.10	0.088	8.12	0.674	1.53	96.31
sdegas26_c2_s1	5.59	18.65	6.36	1.19	0.298	1193.52	51.15	3.05	0.130	7.88	0.648	1.48	96.42
sdegas26_c2_s2	5.62	18.67	5.93	1.14	0.275	1101.4	50.42	3.13	0.119	8.33	0.770	1.51	95.92
sdegas26_c3_s1	5.75	18.57	6.42	1.16	0.333	1333.7	50.20	3.14	0.116	8.20	0.720	1.46	96.08
sdegas26_c3_s2	5.76	18.71	6.99	1.05	0.397	1590.02	49.90	3.16	0.119	8.36	0.768	1.60	96.81
sdegas26_c3_s3	5.78	18.50	6.36	1.10	0.390	1561.99	50.02	3.16	0.112	8.26	0.793	1.45	95.92
sdegas26_c3_s4	5.55	18.38	6.65	1.07	0.427	1710.18	49.86	3.24	0.112	8.47	0.754	1.55	96.06
sdegas26_c4_s1	5.72	18.82	5.83	1.23	0.261	1045.33	51.34	2.81	0.067	7.69	0.763	1.47	96.00
sdegas26_c4_s2	5.55	18.94	6.26	1.23	0.308	1233.57	51.22	3.04	0.162	7.92	0.621	1.59	96.83
sdegas26_c4_s3	5.54	18.95	6.14	1.28	0.314	1257.6	51.10	2.85	0.169	7.76	0.754	1.55	96.41
sdegas26_c4_s4	5.54	18.45	6.40	1.19	0.365	1461.86	49.99	3.13	0.060	8.32	0.681	1.50	95.61
sdegas26_c5_s1	4.79	18.35	5.76	1.15	0.219	877.116	49.97	3.05	0.141	8.34	0.797	1.42	93.98
sdegas26_c5_s2	5.00	18.27	6.29	1.14	0.306	1225.56	49.87	3.14	0.063	8.53	0.777	1.45	94.82
sdegas26_c5_s3	5.07	17.91	6.93	1.06	0.378	1513.93	49.12	3.29	0.190	8.67	0.785	1.51	94.91
sdegas26_c5_s4	4.95	18.15	6.42	1.07	0.298	1193.52	49.96	3.28	0.127	8.39	0.780	1.45	94.87
Average						1313.42							
Standard deviation						217.844							

Comment	Na ₂ O	AI_2O_3	FeO	K ₂ O	SO₃	S(ppm)	SiO ₂	MgO	MnO	CaO	P_2O_5	TiO ₂	Total
sdegas27_c1_s1	2.45	17.40	5.90	1.61	0.516	2066.63	47.85	2.90	0.148	8.64	0.673	1.37	89.44
sdegas27_c1_s2	2.46	17.47	5.95	1.56	0.571	2286.91	47.63	2.96	0.169	8.74	0.755	1.43	89.71
sdegas27_c1_s3	2.45	17.35	6.13	1.54	0.559	2238.85	47.31	2.87	0.151	8.75	0.667	1.42	89.19
sdegas27_c1_s4	2.53	17.24	6.04	1.42	0.557	2230.84	47.10	2.89	0.099	8.85	0.655	1.38	88.76
sdegas27_c1_s5	2.47	17.59	6.07	1.54	0.558	2234.84	47.99	3.01	0.169	8.71	0.683	1.42	90.21
sdegas27_c1_s6 (\$)	2.23	22.46	6.69	2.01	0.375	1501.91	42.51	3.57	0.091	6.51	0.685	1.26	88.38
sdegas27_c2_s1	2.59	17.73	5.93	1.38	0.546	2186.78	48.27	2.99	0.236	8.57	0.738	1.43	90.41
sdegas27_c2_s2	2.61	17.31	6.09	1.47	0.477	1910.43	47.23	2.79	0.141	8.60	0.668	1.42	88.82
sdegas27_c2_s3	2.50	17.47	5.84	1.77	0.500	2002.55	47.92	3.02	0.098	8.55	0.733	1.53	89.92
sdegas27_c2_s4	2.34	17.21	5.93	1.75	0.581	2326.96	48.10	2.99	0.095	8.45	0.708	1.31	89.45
Average						2164.98							
Standard deviation						261.819							
sdegas28_c1_s1	3.50	17.93	5.10	1.31	0.494	1978.52	49.21	1.91	0.123	10.22	0.747	1.32	91.87
sdegas28_c1_s2 (*)	3.05	19.94	5.00	1.09	0.496	1986.53	46.66	1.55	0.194	10.03	0.725	1.30	90.04
sdegas28_c1_s3	3.33	17.84	6.02	1.63	0.452	1810.3	49.13	2.82	0.137	9.22	0.696	1.43	92.70
sdegas28_c1_s4	3.39	17.85	5.20	1.02	0.501	2006.55	49.45	1.57	0.152	10.68	0.773	1.45	92.04
sdegas28_c2_s1	3.30	18.08	4.73	1.01	0.496	1986.53	49.94	1.42	0.145	10.54	0.774	1.38	91.81
sdegas28_c2_s2	3.21	17.35	5.01	0.833	0.513	2054.61	48.88	1.37	0.159	11.31	0.847	1.39	90.88
sdegas28_c2_s3	3.11	17.71	5.04	0.743	0.488	1954.49	48.49	1.19	0.173	11.86	0.700	1.38	90.86
sdegas28_c2_s4	3.36	17.46	5.21	0.628	0.534	2138.72	49.01	1.26	0.236	11.95	0.769	1.39	91.80

sdegas28_c2_s5	3.49 17.5	1 5.80	1.25	0.486	1946.48	49.25	1.96	0.183	10.21	0.668	1.40	92.19
sdegas28_c3_s1	3.29 18.8	6 5.50	1.43	0.450	1802.29	49.92	2.60	0.123	9.19	0.657	1.35	93.38
sdegas28_c3_s2	3.18 18.1	8 4.83	1.03	0.478	1914.44	49.19	1.62	0.226	10.63	0.810	1.36	91.54
sdegas28_c3_s3	3.12 18.1	3 4.66	0.831	0.517	2070.63	49.17	1.14	0.152	11.38	0.805	1.30	91.20
sdegas28_c3_s4	3.01 17.7	1 6.33	0.916	0.485	1942.47	48.06	2.40	0.204	9.79	0.706	1.36	90.97
Average					1967.17							
Standard deviation					84.7353							
sdegas29_c1_s1	2.89 17.9	2 4.78	1.03	0.507	2030.58	49.39	1.40	0.127	9.56	0.772	1.31	89.67
sdegas29_c1_s2	3.34 18.3	5 5.40	1.48	0.478	1914.44	48.52	2.43	0.208	8.96	0.626	1.24	91.01
sdegas29_c1_s3	2.70 18.3	7 5.98	1.42	0.483	1934.46	48.51	2.13	0.130	9.19	0.734	1.27	90.92
sdegas29_c1_s4	2.96 18.2	8 4.12	1.19	0.518	2074.64	49.78	1.53	0.109	9.51	0.776	1.24	90.01
sdegas29_c1_s5	2.86 19.1	5.06	1.03	0.479	1918.44	48.74	2.04	0.102	9.43	0.751	1.31	90.91
sdegas29_c1_s6 (\$)	2.68 21.2	1 4.64	1.34	0.457	1830.33	46.81	1.93	0.123	8.57	0.650	1.19	89.59
sdegas29_c1_s7	2.88 17.6	4 6.27	1.15	0.472	1890.41	48.30	1.99	0.187	9.85	0.726	1.52	90.98
Average					1960.49							
Standard deviation					79.6442							
sdegas29rep_c1_s1	2.97 17.9	3 4.61	0.789	0.529	2118.7	49.18	1.10	0.148	11.82	0.834	1.30	91.22
sdegas29rep_c1_s2	3.14 18.1	2 4.84	1.00	0.521	2086.66	49.44	1.47	0.085	10.35	0.730	1.26	90.95
sdegas29rep_c1_s3	3.36 18.5	1 3.53	0.831	0.548	2194.79	50.57	0.894	0.124	10.66	0.782	1.23	91.03
sdegas29rep_c1_s4	3.17 18.1	3 4.31	0.755	0.566	2266.88	50.23	0.932	0.155	11.11	0.815	1.22	91.40

Comment	Na₂O	AI_2O_3	FeO	K ₂ O	SO₃	S(ppm)	SiO ₂	MgO	MnO	CaO	P_2O_5	TiO ₂	Total
sdegas29rep_c1_s5	3.03	18.03	4.29	0.787	0.521	2086.66	49.92	1.08	0.205	11.42	0.768	1.28	91.33
sdegas29rep_c1_s6	2.96	17.76	5.09	0.651	0.501	2006.55	49.00	1.21	0.120	12.06	0.731	1.44	91.52
sdegas29rep_c1_s7	3.17	18.06	4.50	0.757	0.535	2142.73	49.84	1.00	0.244	11.53	0.794	1.31	91.74
sdegas29rep_c1_s8	3.21	18.35	3.51	0.762	0.569	2278.9	50.95	0.634	0.194	11.09	0.860	1.22	91.35
Average						2147.73							
Standard deviation						94.0193							
sdegas30rep_c1_s1	2.91	18.69	4.86	0.726	0.482	1930.46	49.54	1.84	0.088	9.87	0.739	1.28	91.02
sdegas30rep_c1_s2	3.19	18.34	4.57	0.799	0.511	2046.6	49.65	1.05	0.201	10.84	0.771	1.25	91.16
sdegas30rep_c1_s3	2.62	17.66	5.72	1.11	0.479	1918.44	48.85	2.79	0.187	9.42	0.683	1.34	90.86
sdegas30rep_c1_s4	2.58	17.90	5.21	0.830	0.488	1954.49	49.22	2.28	0.190	9.66	0.709	1.33	90.41
sdegas30rep_c1_s5	2.67	17.85	5.60	1.06	0.470	1882.4	48.74	2.67	0.225	9.20	0.777	1.40	90.67
sdegas30rep_c1_s6	2.90	17.91	5.59	0.929	0.482	1930.46	49.01	2.26	0.176	9.75	0.718	1.34	91.07
Average						1943.81							
Standard deviation						55.5925							
1atm20_c1_s1	4.70	19.05	5.13	1.93	0.501	2006.55	51.41	2.94	0.134	9.47	0.783	1.26	97.30
1atm20_c1_s2	4.55	19.85	5.51	1.03	0.437	1750.23	51.48	2.39	0.162	10.64	0.671	1.21	97.93
1atm20_c2_s1	4.68	19.41	5.26	2.00	0.462	1850.35	51.58	3.19	0.123	9.62	0.811	1.28	98.41
1atm20_c2_s2	4.83	19.23	5.75	1.96	0.508	2034.59	51.56	3.30	0.190	9.40	0.753	1.34	98.81
1atm20_c2_s3	4.70	19.00	5.96	1.93	0.495	1982.52	50.73	3.00	0.155	9.73	0.803	1.37	97.87

Comment	Na₂O	AI_2O_3	FeO	K ₂ O	SO₃	S(ppm)	SiO ₂	MgO	MnO	CaO	P_2O_5	TiO ₂	Total
1atm20_c2_s4	4.71	18.89	5.35	1.93	0.475	1902.42	51.23	3.15	0.148	9.60	0.790	1.38	97.65
1atm20_c2_s5	4.78	19.76	5.63	1.92	0.478	1914.44	51.59	3.14	0.148	9.46	0.802	1.31	99.02
1atm20_c2_s6	4.85	19.44	4.84	1.91	0.492	1970.51	52.04	3.09	0.152	9.44	0.780	1.21	98.24
1atm20_c3_s1	4.76	19.31	4.97	1.96	0.478	1914.44	51.94	3.07	0.144	9.17	0.776	1.30	97.87
1atm20_c3_s2	4.69	18.98	5.39	1.96	0.469	1878.39	51.10	2.95	0.123	9.22	0.695	1.31	96.89
1atm20_c3_s3	2.41	19.65	4.93	2.02	0.492	1970.51	52.85	3.08	0.070	9.55	0.708	1.27	97.03
1atm20_c3_s4	4.64	19.07	5.87	1.89	0.484	1938.47	50.75	3.38	0.222	9.27	0.769	1.25	97.59
Average						1926.12							
Standard deviation						77.0482							
1atm28_c1_s1	4.59	18.88	8.91	2.50	0.248	993.264	49.36	3.09	0.197	8.12	0.758	1.54	98.20
1atm28_c1_s2	4.61	19.21	6.20	2.21	0.288	1153.47	51.70	3.08	0.169	9.06	0.735	1.49	98.75
1atm28_c1_s3	4.58	19.44	5.85	2.47	0.184	736.938	52.24	2.62	0.194	8.67	0.706	1.49	98.43
1atm28_c1_s4 (*)	3.68	16.24	4.04	1.75	0.074	296.377	38.46	1.88	0.085	5.56	0.472	0.932	73.17
1atm28_c2_s5	4.62	18.56	7.18	1.95	0.255	1021.3	51.49	3.04	0.127	8.98	0.914	1.73	98.83
1atm28_c2_s1 (\$)	4.82	21.03	5.26	0.885	0.098	392.499	52.24	2.44	0.148	10.66	0.559	1.17	99.31
1atm28_c2_s2	4.56	19.01	6.90	1.79	0.232	929.182	50.82	3.27	0.158	9.28	0.699	1.54	98.25
1atm28_c2_s3 (*)	4.42	18.28	6.09	2.76	0.109	436.555	51.07	3.23	0.113	8.28	0.809	1.47	96.62
1atm28_c2_s4	3.91	17.71	9.71	2.29	0.253	1013.29	48.96	4.06	0.337	8.69	0.846	1.79	98.55
1atm28_c2_s5	4.63	19.62	6.09	1.25	0.227	909.157	52.32	2.47	0.162	9.49	0.956	1.47	98.67
•													

Average

965.228

Comment	Na ₂ O Al ₂ O	₃ FeO	K ₂ O	SO₃	S(ppm)	SiO ₂	MgO	MnO	CaO	P_2O_5	TiO ₂	Total	
Standard deviation	328.62												
1atm30_c1_s1	4.65 19.2	7 8.50	1.82	0.418	1674.13	50.30	3.10	0.221	8.85	0.719	1.70	99.55	
1atm30_c1_s2	4.81 19.2	9 4.80	1.90	0.449	1798.29	51.77	3.04	0.106	9.55	0.784	1.36	97.85	
1atm30_c1_s3	3.29 38.5	5 4.42	1.34	0.366	1465.87	38.69	2.30	0.102	6.83	0.571	0.987	97.45	
1atm30_c1_s4	4.34 19.2	1 6.18	1.74	0.411	1646.09	50.96	3.18	0.169	9.58	0.711	1.31	97.79	
1atm30_c1_s5	4.23 18.43	6.32	1.65	0.111	444.566	49.14	3.22	0.151	9.54	0.779	1.42	94.98	
1atm30_c2_s1	4.44 19.2	6.38	1.79	0.360	1441.83	50.88	3.09	0.162	9.34	0.830	1.30	97.85	
1atm30_c2_s2	4.41 19.14	1 5.21	1.84	0.307	1229.56	51.39	2.89	0.218	9.49	0.807	1.20	96.91	
1atm30_c2_s3	4.92 18.8	7 3.94	2.18	0.021	84.107	51.61	2.68	0.173	7.92	0.756	1.19	94.26	
1atm30_c2_s4 (*)	4.13 17.7	4 6.00	1.64	0.122	488.622	47.65	2.94	0.176	8.65	0.749	1.30	91.10	
1atm30_c2_s5	4.39 18.3	3 6.01	1.86	0.270	1081.38	50.06	2.91	0.155	8.83	0.715	1.42	94.94	
Average					1135.44								
Standard deviation					596.857								

APPENDIX 3: TRANSECTS



DG25 T1. Light grey area around the arrow is the remnants of the original annotation.





DG25 T2













DG26 T1



DG26 T2






DG24b(rep) T1: Direction of the transect was not recorded.



DG31 T1: Direction of the transect was not recorded.



DG22 T1: Direction of the transect was not recorded. Needs black box around it.





APPENDIX 4: BUBBLE SIZE DISTRIBUTIONS



DG4 Chip 1 Backscattered Electron Image

DG4 Chip 1 Threshold Image



DG4 Chip 2 Backscattered Electron Image

DG4 Chip 2 Threshold Image



DG6 Chip 1 Backscattered Electron Image

DG6 Chip 1 Threshold Image



COMP XM8800 15.0KU X1,000 DG6 Chip 2 Backscattered Electron Image

DG6 Chip 2 Threshold Image



COMP XM8800 15.0KU X1,000 DG6 Chip 2 Backscattered Electron Image

DG6 Chip 2 Threshold Image



DG21 Chip 5 Backscattered Electron DG21 Chip 5 Threshold Image



DG22 Chip 1 Backscattered Electron DG22 Chip 1 Image

DG22 Chip 1 Threshold Image



DG22Chip 1-2 Backscattered Electron DG22 Chip 1-2 Threshold Image Image



DG22 Chip 2-1 Backscattered Electron Image

DG22 Chip 2-2 Threshold Image



DG24a Chip 1 Backscattered Electron Image





хмааод 20.0кu ×1.00 DG24a rep Chip 2 Backscattered Electron Image

DG24a rep Chip 2 Threshold Image





DG24brep Chip 2 Backscattered Electron Image

DG24b rep Chip 2 Threshold Image





ХМ8800 20.0KU — 100Рm DG25 Chip 1 Backscattered Electron Image

DG25 rep Chip1 Threshold Image



DG26 Chip 3 Backscattered Electron Image

DG26 Chip3 Threshold Image



DG31 Threshold Image



DG32 Backscattered Electron Image

DG32 Threshold Image



DG33 Backscattered Electron Image

DG33 Threshold Image