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Igneous Rock Associations 22. Experimental Petrology
Methods, Examples, and Applications

Cliff S.J. Shaw

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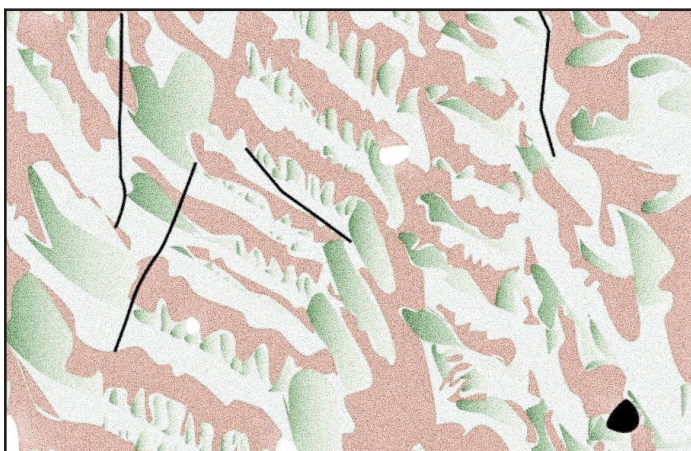
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Shaw, C. S. (2018). Igneous Rock Associations 22. Experimental Petrology:
Methods, Examples, and Applications. *Geoscience Canada*, *45*(2), 67–84.

SERIES

Igneous Rock Associations 22. Experimental Petrology: Methods, Examples, and Applications

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SUMMARY

Experiments are an important source of basic information in petrology, from thermodynamic data used to develop predictive models to physical property data used to understand magma ascent and eruption. Since we all use experimental data in our work as geoscientists, it is important that we have a basic understanding of the methods used to prepare and perform experiments on rocks and minerals and their synthetic analogues. In this review I examine how the observational science of geology changed in the late 1800's with the development of the interdisciplinary science of physical chemistry. The second part of the paper discusses what factors need to be considered in designing an experimental study; it focuses particularly on the problems of reaching equilibrium on the short timescales available in the laboratory. In the final section, I give four examples of geological problems that have been solved using experimental methods and make some suggestions about the directions that future experimental campaigns might take.

RÉSUMÉ

L'expérimentation est une source importante d'information de base en pétrologie, qu'il s'agisse de données thermodynamiques pour développer des modèles prédictifs, ou des propriétés physiques utilisés pour comprendre la montée et l'éruption d'un magma. Puisque nous utilisons tous des données expérimentales dans notre travail de géoscientifique, il est important que nous ayons une compréhension minimale des méthodes utilisées pour préparer et réaliser des expériences sur les roches, les minéraux et leurs analogues de synthèse. Dans la présente étude, je me suis penché sur les changements survenus en science d'observation qu'est la géologie, à la fin des années 1800, avec le développement de la science interdisciplinaire de la chimie physique. La deuxième partie de l'article traite des facteurs à prendre en compte dans la conception d'une étude expérimentale; elle porte en particulier sur les problèmes d'atteinte d'un équilibre sur les temps courts du laboratoire. Dans la dernière section, je donne quatre exemples de problèmes géologiques qui ont été résolus à l'aide de méthodes expérimentales, et je fais des suggestions sur des orientations qui pourraient être adoptées lors de campagnes expérimentales à venir.

Traduit par le Traducteur

INTRODUCTION

"The test of all knowledge is experiment. Experiment is the sole judge of scientific "truth". But what is the source of knowledge? Where do the laws that are to be tested come from? Experiment, itself, helps to produce these laws in the sense that it gives us hints" (Feynman et al. 1963). Strong words indeed from one of the great theoreticians of science. In the Earth sciences, we experiment when we subject a geological material to a simulation of the conditions in or on the Earth. But what purpose do experiments serve? After all, they cannot simulate the passage of geological time, emplacement of a large magma body or even an entire lava flow.

Medawar (1968) described two types of experiment that are relevant to Earth scientists:
Baconian experiments, which he describes as contrived experiences designed to determine what will happen if we do x to y, and *Critical experiments*, designed to test a hypothesis.

In petrology, our experiments are often of the first type and most are done to increase the stockpile of knowledge, without which we would be hard-pressed to interpret our field data. Such experiments often provide the building blocks for models that allow us to calculate the pressure, the temperature, or some other property of real rocks. For example, the ther-

modynamic data derived from experiments has been of critical importance to the development of internally consistent thermodynamic models such as the widely used MELTS models first developed by Ghiorso and Sack (1995). In a similar vein, experiments to measure magma properties, such as viscosity, have provided us with a robust model that can be used to calculate the viscosity of natural melts (Giordano et al. 2008) to aid in modelling and understanding of volcanic processes. Critical experiments are also a major part of experimental petrology. Classic examples are the experimental studies done in the late 1960's and throughout the 1970's to test Ringwood's (1966) hypothesis that basaltic magma is generated by melting of peridotitic mantle.

Experimentation on rocks has a long history. Sir James Hall, sometimes referred to as the Father of Experimental Petrology, was melting rocks in gun barrels in the early 1800's (Hall 1805). However, the utility and power of experimental petrology has not always been fully appreciated. In 1861, Darwin commented "*About thirty years ago there was much talk that geologists ought only to observe…*" (in a letter to H. Fawcett, 18 September 1861; Burkhardt and Secord 1985). It took another 60 years for experimental studies to be widely accepted. F.D. Adams noted in his Presidential Address to the Geological Society of America that "*Observation is the great basis and foundation stone of the science of geology; but as a companion and helper on this delightful, but sometimes toilsome, path – and more especially in the later years – observation has had the support of experiments, which while of distinctly subordinate and collateral value as compared with observation, has nevertheless rendered many important services in the development of geological knowledge*" (Adams 1918).

EXPERIMENTAL PETROLOGY AS AN OFFSHOOT OF PHYSICAL CHEMISTRY

In the late 1800's physical chemistry became one of the first interdisciplinary fields in science. Between 1875 and 1878, J.W. Gibbs published his papers on equilibria in heterogeneous systems including a derivation of the phase rule (Gibbs 1874–1878). Ostwald, Van't Hoff and Arrhenius developed critical concepts in physical chemistry that are still applied in Earth sciences today. The idea that the phase rule could be used to predict the behaviour of chemical systems undergoing melting or crystallization was developed by Roozeboom (1901) who established the phase relations of a large number of systems both theoretical and based on metallurgical experiments (Eugster 1971; Cahn 2000). The stage was set for the application of thermodynamics to geological systems.

Harker (1909) recognized that "*recent developments of physical chemistry indicate at least the general lines upon which a more systematic treatment may be attempted*" and "*we may hope that the petrologist will soon be provided with data enabling him to introduce into the discussion of rock genesis the quantitative element, which hitherto has been almost wholly lacking*". At that time, there was very little information available on the melting and freezing points of igneous rocks, let alone information on the nature of solid solutions and phase relations of minerals. At best, there were experiments on metallurgical slags (Vogt 1903) and Roozeboom's (1901) theoretical work on solid solutions. An understanding of the

melting and crystallization temperatures and the nature of solid solution in minerals would only come after the studies of Day et al. (1905) and Bowen (1913).

Before there could be any systematic study of the temperature dependence of phase relations in geological systems the problem of temperature measurement had to be solved. Early attempts at measuring high temperatures relied on the Wedgewood pyrometer, which related temperature to the change in shape of clay cylinders in pottery kilns (see Young 1998, p. 17), but these were not very precise. The discovery of the Seebeck effect led to the development of thermocouples, in particular, the platinum–rhodium thermocouple (Le Châtelier 1886) but the lack of a reliable calibration hampered further development. The systematic work of Day and Allen (1904) and Day and Sosman (1911, 1912) to calibrate platinum–rhodium thermocouples against nitrogen gas thermometers allowed precise temperature measurement to 1755°C. This, and the early phase equilibria experiments of Shepherd et al. (1909) in the CaO–MgO–Al$_2$O$_3$–SiO$_2$ system, prepared the way for subsequent systematic studies, mostly led by Bowen (see Young 1998 for a detailed account).

Up to the 1960's, most of the work on analogue and natural melts relevant to basaltic systems focused on phase relations during crystallization at atmospheric pressure. This culminated in the development of the basalt tetrahedron and recognition of the thermal divide that separates the alkaline basalt series from the tholeiitic series (Yoder and Tilley 1962). This is not to say that research at high pressure had not been considered. Bridgman had been experimenting with a variety of apparatus, though his work was at relatively low temperature and focused mainly on the behaviour of simple compounds (Bridgman 1914, 1915, 1916, 1918). Goranson (1931, 1932) examined the high-pressure phase equilibria of granitic compositions and Hall and others developed apparatus capable of creating high pressure and temperature simultaneously in their pursuit of synthetic diamonds (Hall 1954, 1957, 1958, 1959, 1964; Hall et al. 1958; Hall and Kistler 1958), but it was not until the development of the piston-cylinder press (Boyd and England 1960) that high pressure and high temperature studies of geological systems became feasible. This new apparatus resulted in hundreds of studies in synthetic and natural systems.

In experiments on simple synthetic systems, such as those by Bowen and Andersen (1914) the phases were easily identified with the polarizing microscope or with x-ray diffraction techniques. In more complex natural systems, the small size of the experimental charges meant that the wet chemical techniques that were applied to real rocks were not feasible for routine chemical analysis of mineral phases in experimental materials. However, at about the same time that the piston-cylinder press became generally available, experimental petrologists were given a new tool – the electron microprobe. The ability to analyze samples at the micron scale for a wide range of elements drove experimentalists to work in natural systems using real rocks (Green 1976).

By 1974, the phase relations of peridotite were well enough defined to warrant inclusion in a classic petrology text (Carmichael et al. 1974). Igneous petrology was now a multi-

disciplinary field that combined field geology, geophysics, geochemistry and experimental studies. In particular, the results of mantle melting experiments have provided a firm basis for interpreting subtle variations in basalt composition and mineralogy (Basaltic Volcanism Study Project 1981). Most studies of igneous rocks now incorporated knowledge from experiments in the interpretation of field-based petrologic and geochemical data.

As more experimental data entered the literature, the descriptions of the methods used by the experimentalists became increasingly technical and jargon-filled and, thus, difficult for the uninitiated to follow. Edgar (1973) and Holloway and Wood (1988) provided essential guides to the techniques and equipment used in experimental petrology. Since then there have been numerous specialized volumes that outline the state of the art in experimental petrology, e.g. Luth (1993).

DESIGNING A GOOD EXPERIMENT

Fortunately, it is not necessary to understand all of the technical details of an experimental study in order to make use of the results. Nevertheless, a basic understanding of experimental design is required for petrologists to understand the limitations of the results. In this review, I concentrate on the experimental design considerations and the issues that have to be faced in interpreting the results, with only a brief review of the equipment. The interested reader can find detailed descriptions of the construction and operation of various types of apparatus in Edgar (1973), Holloway and Wood (1988) and Luth (1993). I focus on experiments applicable to mafic igneous systems. This is not to say that experiments have not been done on intermediate and felsic igneous rocks or on metamorphic rocks, it simply reflects my personal interests and experience.

Experiments are both time consuming and expensive, so it is essential to ensure that they are well designed so as to minimize uncertainties in pressure and temperature and unnecessary complexity in the composition of the materials being studied. Modern experimental studies are typically designed to test a hypothesis or to define the rate of a geological process. Regardless of the aim, there are nine major issues that need to be considered before beginning an experimental campaign.

The Experimental Charge

Experiments are designed to reproduce conditions within the Earth at the laboratory scale. We can generate the physical conditions of pressure, temperature, etc. relatively easily, but it is of course not practical to perform our experiments over geological timescales. This means that the material (i.e. the charge) in our experiment should be reactive enough to reach chemical equilibrium in a reasonable time frame, ideally hours to days. One way to obtain such a reactive material is to ensure that the charge is very finely powdered before loading into the experiment. Figure 1a shows an example from Fyfe (1960). In this system there are two complex silicate phases $A.H_2O$ and B whose stability curves are shown. The ideal starting material for experiments to examine the stability of these phases will have a higher free energy than either of the phases, i.e. it will be less stable at the pressure and temperature conditions of
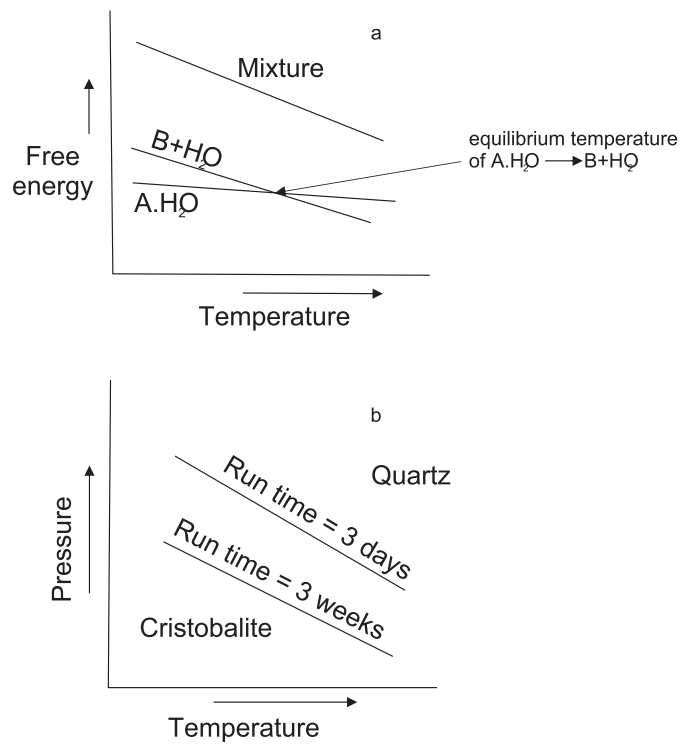

Figure 1. a) Ideal temperature – free energy relationship for a reactive starting mixture that will be used to examine the position of the equilibrium temperature of $A.H_2O \rightarrow B + H_2O$. The reaction curves intersect at the equilibrium temperature of $A.H_2O \rightarrow B + H_2O$. (Redrawn from Fyfe 1960). b) Results of cristobalite synthesis experiments as a function of run duration. Top boundary curve shows the quartz–cristobalite reaction curve for experiments run for three days. Bottom curve shows the quartz–cristobalite reaction curve for experiments run for three weeks. Without a method to test for equilibrium it is impossible to tell which curve is correct. It is possible that experiments run for months might give a different reaction curve. (Redrawn from Fyfe 1960)

the experiment. Importantly, however, the phase that forms first depends not on the equilibrium temperature, but rather on the interplay between nucleation and grain growth.

Our experiments aim to help us understand igneous rocks, but using a natural sample may not be the best option. In some cases, it is necessary to simplify the composition of the system, perhaps by leaving out trace elements, water, or another component to make the results of the experiment easier to interpret. If we choose not to use a natural sample as our starting material, then we need to prepare a synthetic composition. There are a number of options for a synthetic starting material (Edgar 1973):

1. Co-precipitated gels
2. Oxide mixtures
3. Pure minerals mixed in the desired amounts
4. A synthesized glass

Which one do we use? Fyfe (1960) reviewed this issue as it pertains to subsolidus reactions, in particular showing that experiments with highly reactive, amorphous gels can produce metastable assemblages that can persist for many months in an experiment. Figure 1b shows Fyfe's example of the shift in the position of the quartz–cristobalite phase boundary depending

on the duration of the experiments. Which, if either, of these phase boundaries is closest to the real one? If one's goal is to determine the equilibrium phase relations, then clearly avoiding such metastability is crucial and a method of assessing the approach to equilibrium is essential. Of the choices above, most experiments in igneous systems have chosen glass or a partially to completely crystallized glass prepared from oxide/hydroxide/carbonate mixtures. For example, Bowen and Anderson (1914) did their experiments in the $MgO–SiO_2$ system on glasses prepared from quartz and decarbonated $MgCO_3$. Their procedure was as follows:

1. Prepare mixtures of the desired composition by weighing the oxides/carbonates, grind in an agate mortar to mix, and fuse to produce a melt, holding at temperature for one hour before rapid cooling to produce a glass.
2. Crush the resulting glass and repeat the fusion.
3. Analyze the glass to ensure that it has the desired composition.
4. Hold the glass at a temperature below the melting temperature to crystallize. For silica-poor compositions, crystallization takes a few minutes, but for silica-rich compositions, which can remain free of crystals at temperatures significantly below their liquidus, crystallization can take several days.
5. Grind the crystallized material to a fine powder and store in a desiccator.

This procedure is by far the most common method used to prepare materials for experiments. Even, so there can be problems in using the crystallized material. If it is ground too finely, the powdered crystals may have very large surface energies which can lead to metastability and thus to disequilibrium.

If a volatile, such as water or CO_2 is required as part of the sample charge, the experiment must be done in a sealed capsule at greater than atmospheric pressure. Water can be added in liquid form before sealing the sample capsule (see below), but if CO_2 is required it is usually added as a solid that will decompose at the experiment conditions to give the required amount of volatile.

The Containment Problem

The sample must be contained in something and this container must: 1) be stable at the conditions of the experiment, and 2) not react with any of the materials being used – the furnace walls or elements, the thermocouple, or the material under investigation. The most common sample container is a platinum crucible or capsule but a variety of other materials, such as graphite, gold, silver, and molybdenum can be used. Platinum has a high melting temperature (1768°C), it is stable in both oxidizing and reducing conditions and it is unreactive to silicate melts, except those containing iron (Merrill and Wyllie 1973). In experiments that produce melt, iron in the melt will alloy with a Pt sample container so that over time the composition of the melt will change. This is a significant problem in older studies and a variety of methods have been developed to overcome it including pre-saturating the capsules with iron, using silver–palladium (AgPd), gold, graphite, or molybdenum
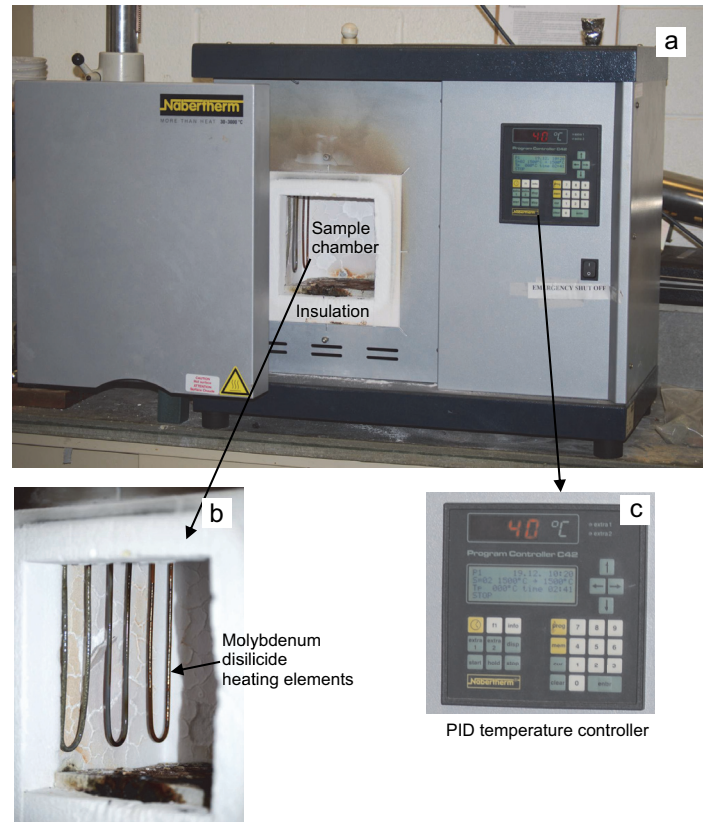
Figure 2. The Nabertherm 1650°C muffle furnace in the experimental petrology laboratory at University of New Brunswick. The sample chamber (a) has a working volume of around 3000 cm³. It is heated with U-shaped $MoSi_2$ elements (b) and the heating rate, heating duration and final temperature are controlled by the built in digital controller (c).

containers, or replacing iron in the starting material with cobalt which does not alloy with platinum.

If the sample contains volatiles, the encapsulating material must be able to be tightly sealed prior to the experiment and remain sealed during the experiment. Volatile-bearing experiments are typically done in welded platinum, AgPd, or gold capsules, depending on the temperature of the experiment.

Generating High Temperatures

In the early days of experimental petrology, samples were heated in platinum-wound furnaces powered by storage batteries and controlled by large street-car-type banks of resistor coils (Yoder 1998). A wide variety of furnace designs have been developed since (e.g. Strong et al. 1942; Edgar 1973) and today, there are many commercial suppliers of furnaces that will easily reach temperatures in excess of 1600°C (Fig. 2, e.g. www.nabertherm.com/produkte/labor/laboratory_english.pdf). These furnaces come in a variety of shapes and sizes from the typical muffle furnace used for preparing large quantities of glass to tube furnaces in which samples can be heated under high vacuum or in a variety of gas mixtures (Fig. 3, see below). The heating elements are typically molybdenum disilicide ($MoSi_2$) or less commonly silicon carbide. $MoSi_2$ elements are extremely stable up to 1800°C with long service lifetimes in a variety of furnace atmospheres.
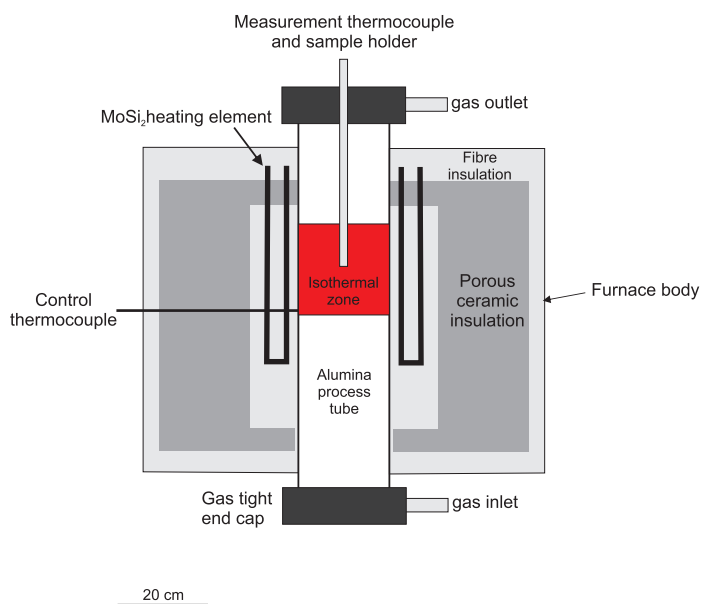
Figure 3. Schematic diagram of a one atmosphere tube furnace. The furnace is heated with MoSi₂ elements and temperature is controlled with a thermocouple attached to the outside of the process tube. The process tube is made of gas tight Al₂O₃ and is sealed at both ends. Ports in the seals allow mixtures of gases to be pumped into the tube to control oxygen fugacity. The upper cap also has ports for a measurement thermometer and a sample holder. The isothermal zone of the furnace is approximately 20 cm long.

Measuring and Controlling Temperature

The most common temperature measurement instrument is the thermocouple. When two metals of different composition are joined at one end, any temperature difference between the joined and free ends of the wire will generate a small, but measurable electromotive force (*emf*) that is proportional to temperature. The choice of thermocouple depends on the temperature range of interest. In experimental petrology, type s and r platinum–rhodium thermocouples are the most common, but other types such as chrome–alumel and tungsten–rhenium are used as well. In most studies, the quoted precision on temperature is usually $\pm$ 5°C for experiments at 1 atmosphere and $\pm$ 10°C for high pressure experiments. The larger range for the high-pressure experiments is because usually no correction is made for the effect of pressure on the *emf* of the thermocouple.

Oxygen Fugacity Control and Measurement

The availability of oxygen to the sample during an experiment controls the ratio of ferrous (Fe^{2+}) to ferric (Fe^{3+}) iron and other multivalence elements through redox reactions such as:

$$2Fe^{2+}O + 0.5\ O_2 = Fe^{3+}_2O_3$$
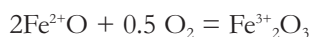
The equilibrium oxygen fugacity (fO_2) of a reaction varies with temperature and there are numerous reference reactions that define a range of fO_2 values that are petrologically useful. In practice, we use these reactions (often referred to as buffers; Eugster 1957) to communicate information about the redox state of a rock or experiment. The relationship between fO_2 and temperature of two commonly used buffer reactions:
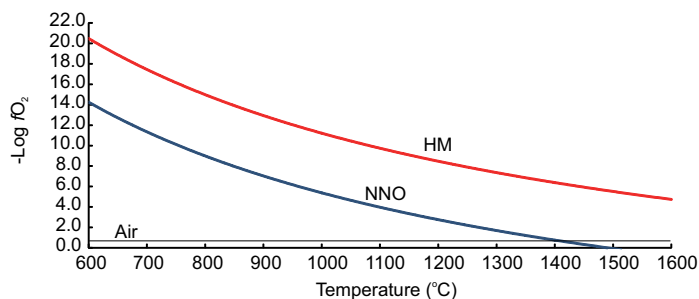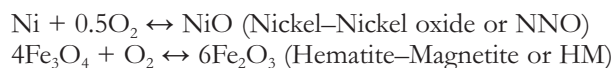

Figure 4. Temperature vs –Log fO_2 plot showing the position of the relatively reducing Nickel–Nickel oxide (NNO) and oxidizing Hematite–Magnetite (HM) buffer curves. The oxygen fugacity of air is shown for reference.

$$Ni + 0.5O_2 \leftrightarrow NiO\ (\text{Nickel–Nickel oxide or NNO})$$
$$4Fe_3O_4 + O_2 \leftrightarrow 6Fe_2O_3\ (\text{Hematite–Magnetite or HM})$$

is shown in Figure 4.

In one atmosphere experiments, fO_2 is controlled by redox reactions in gases, e.g. carbon monoxide and carbon dioxide:

$$CO + 0.5O_2 \leftrightarrow CO_2$$

To fix fO_2 the partial pressure of the two gases is varied as shown below:

$$fO_2 = (PCO_2/(PCO*k))^2$$

where P is the partial pressure of the gas phase and k is the equilibrium constant (Darken and Gurry 1945, 1946). The equilibrium constant can be determined from thermodynamic tables (kinetics.nist.gov/janaf/) and we use the partial pressure of the gases, rather than fugacity, since they can be considered to be ideal at the high temperature of most experiments.

Solid buffers are commonly used in high pressure experiments where the use of gas mixtures is impractical. In this case, the encapsulated experiment charge is placed into a larger capsule that contains the buffer assemblage. Holloway and Wood (1988) note that when solid buffers are used, it is actually water that controls the oxygen fugacity:

$$e.g.\ \ Ni + H_2O \leftrightarrow NiO + H_2$$
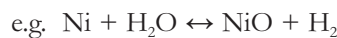
For the solid buffer method to work, the sample capsule must be platinum or silver–palladium as they are permeable to hydrogen. Hydrogen formed in the buffer reaction can diffuse through the capsule walls to control fO_2 in the experiment. However, this means that the solid buffer method cannot be applied to anhydrous experiments. In such experiments, oxygen fugacity can be controlled by using a graphite capsule sealed inside a platinum capsule. In this approach, oxidation of the graphite produces carbon monoxide and the equilibrium between the two defines fO_2 (Médard et al. 2008).

Generation of Pressure

Pressure can be applied to an experimental charge by a gas, liquid or deformable solid. Internally heated gas pressure vessels are used in some laboratories, e.g. Spickenbom et al. (2010);
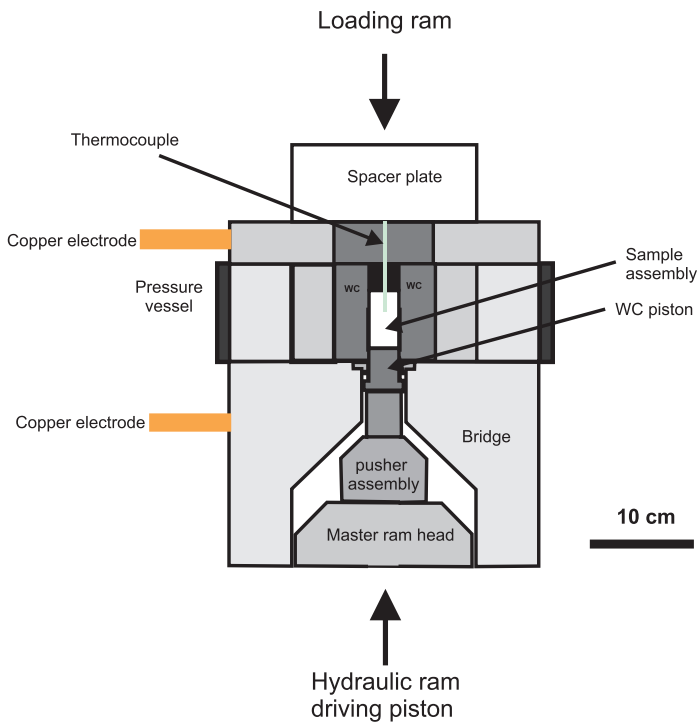
Figure 5. Components of the piston cylinder press showing the pressure vessel its supporting bridge which contains the mechanism for pushing the piston into the vessel. The pressure vessel is covered by a thermocouple plate topped with a spacer plate. This assembly is placed in a large press frame that holds two hydraulic rams. The upper ram compresses the entire assembly to add strength. The lower ram pushes the piston into the pressure vessel.

however, they are expensive, and require extensive shielding as failure of the pressure containment system will lead to a large explosion – the vessels are commonly referred to as 'bombs' for good reason! Pressure generation by a liquid, usually water, is limited to about 10 kilobars (Tuttle 1949; Wyllie and Tuttle 1960; Walter et al. 1962). At this pressure, the maximum temperature is limited to around 600°C by the hot rupture strength of the pressure vessel which means that hydrothermal pressure vessels are not particularly useful for studies of mafic igneous rocks.

The work horse of the experimental petrologist interested in mantle melting processes is the solid-media piston-cylinder apparatus (Fig. 5). This was designed by Boyd and England (1960) based on earlier designs by Coes (1955) and Hall (1958). The piston-cylinder can generate pressures from 0.5 to 6 GPa, though the most common range is 0.5 to 3 GPa. Samples are heated in a graphite resistance furnace that is contained within the solid pressure medium. Compared to one atmosphere experiments, the sample size is quite small, with a maximum capsule size of ~1 cm long and ~5 mm in diameter (Fig. 6). In early designs, the samples had to be much smaller because the graphite furnaces produced large thermal gradients. New furnace designs have decreased the gradient to around 10°C over the length of a 1 cm capsule (Schilling and Wunder 2004).

The piston-cylinder works by pressing a piston into a cylinder that contains a solid pressure medium, a heater and the sample (Fig. 6). The force applied by a large hydraulic ram, usually with a capacity of between 50 and 200 tonnes, is mul-
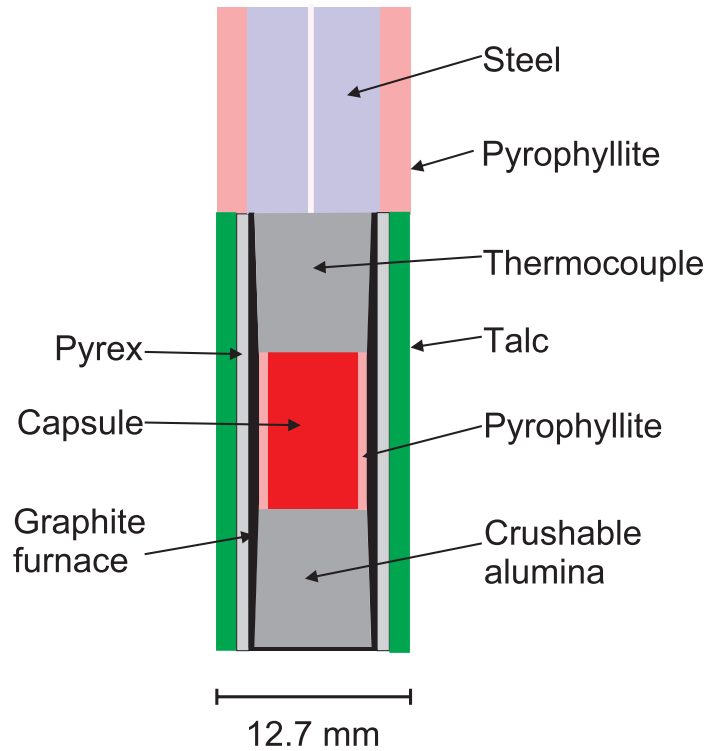

Figure 6. Schematic sketch of the solid pressure medium used in the piston cylinder press. The cell parts are produced in-house and a new cell is required for each experiment.

tiplied by the ratio of the ram area ($A1$) to the piston area ($A2$) as shown in Figure 7. Since the ram area is much larger than that of the piston, which has a diameter of either 0.5 or 0.75 inches, there is a significant multiplication factor for pressure (P):

> Force = Pressure * Area
> $P1*A1=P2*A2$
> $P2=P1*(A1/A2)$

For example, at a pressure of 1000 pounds per square inch (69 bars), a hydraulic cylinder with a radius of 1.75 inches pushes a piston with a radius of 0.25 inches, the pressure multiplication factor is 49, so that the pressure applied to the sample in contact with the piston is 3381 bars or 0.338 GPa.

Calibrating Pressure

Pressure generated by gas or water is hydrostatic and the pressure on the sample is simply the measured pressure within the pressure containment vessel. In a solid media apparatus like the piston-cylinder, the relative simplicity and greater safety come at a cost as the pressure experienced by the sample may be higher or lower than the nominal pressure depending on how the experiment is performed and the pressure medium used. Most of the deviation from the nominal pressure is due to the shear strength of the pressure medium which is usually made from either talc which has a significantly more shear strength than the alternative – NaCl. The deviation from nominal pressure, commonly referred to as being due to 'friction'
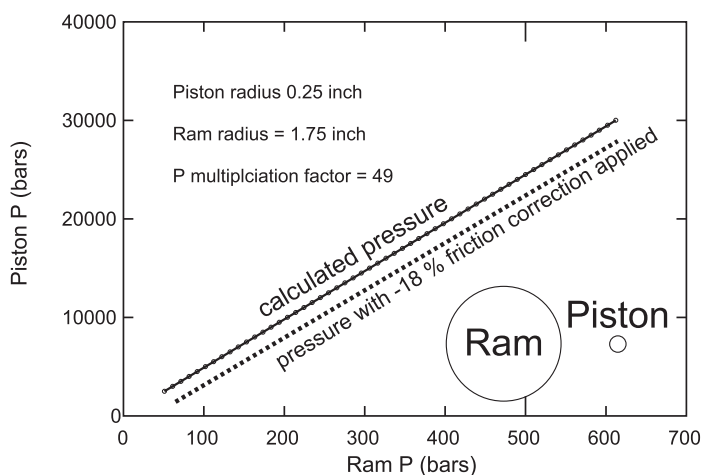
Figure 7. A plot of ram pressure vs piston pressure for the 150 tonne piston cylinder press at the University of New Brunswick. The piston radius is 0.25 inches and the ram radius is 1.75 inches, giving a pressure multiplication factor of 49. The solid line shows the calculated pressure based on the load applied by the hydraulic ram. The dashed line shows the corrected pressure after calibration using the melting point of diopside.

Figure 8. The *P–T* relations in the albite–water system (data from (Bohlen et al. 1982). The albite melting curve is shown by the dashed line. Reversal experiments were carried out to check for equilibrium at 1 and 1.5 GPa. Reversal experiments were first heated to the temperature above the melting curve and held there for ~7 hours after which they were cooled by 10°C. These reversals showed that the experiments at 670°C and 1 GPa and 635°C and 1.5 GPa had reached equilibrium. Note that at 0.5 GPa the position of the melting curve is not well defined and there appears to be one experiment at 735°C in which melt-free albite persists metastably.

(see Johannes et al. 1971 for details), requires that the piston-cylinder be calibrated against a *P–T* curve for a reaction that has been determined by some other means, either from thermodynamic data or from experiments in a gas pressure vessel.

Inside the talc or salt cell is a Pyrex glass liner that prevents reaction between the graphite furnace and pressure medium. The sample capsule is placed inside an alumina, pyrophyllite, or quartz glass sleeve to electrically insulate it from the furnace (Fig. 6). The entire pressure assembly is placed in a high-strength tungsten carbide (WC) cylinder that is surrounded by press-fit steel rings which apply a radial force that counteracts the extensional forces that occur during pressurization.

Time: Equilibrium vs Kinetics

One atmosphere experiments can be run indefinitely if there is a stable power source. High pressure experiments can also be for stable days or even weeks at temperatures below 1500 as long as there is a stable power supply and the thermocouple does not suffer contamination. Above 1500°C high pressure experiments are somewhat less stable but experiments may still have durations of 10's of hours with careful preparation.

In experimental studies of phase equilibria, it is essential that we know that the experimental charge reached thermodynamic equilibrium. But how do we prove that equilibrium has been attained, and what is the minimum time that is needed to attain equilibrium? One way to try to attain equilibrium quickly is to have a very finely ground starting material, so that the distance that elements have to diffuse to attain equilibrium is small. However, as noted earlier, there can be issues with metastability if the powders are too fine. Another way is to do two experiments, using the same material and conditions but at widely different durations. If the two experiments, one run for 1 hour and another for 100 hours, have the same homogeneous phases and phase compositions, then equilibrium is suggested. However, this approach does not prove that phases are in equilibrium. Fyfe (1960) noted that in experiments prepared
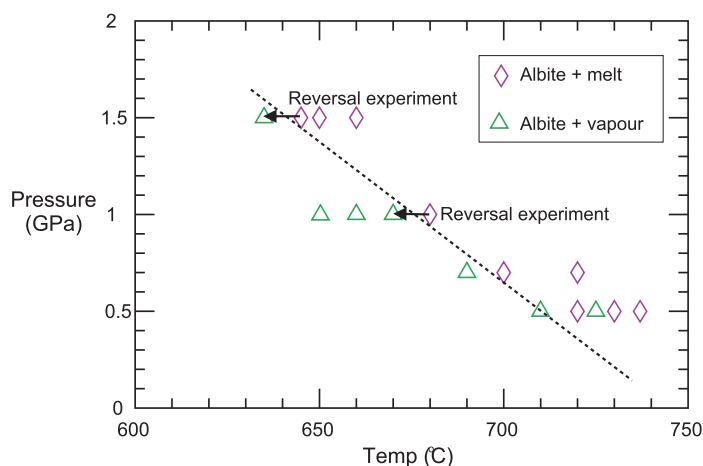
from gels, cristobalite can exist metastably in the quartz stability field for months!

The only way to properly assess equilibrium is to perform reversal experiments. In their simplest form, these involve taking the composition of interest toward the boundary curve from two different directions. For example, in their experiments to determine the melting point of albite at 1 and 1.5 GPa in a H_2O fluid, Bohlen et al. (1982) did a series of experiments as shown in Figure 8. From these they estimated that the melting point of albite lies between 670 and 680°C at 1 GPa and between 635 and 645°C at 1.5 GPa. However, in both cases, the melting point is not well defined. The duration of the low temperature experiments might have been too short for melt to be generated. In other words, albite + vapour could have existed metastably. To determine if the melting temperature actually lies in the suggested range, Bohlen et al. (1982) did two additional experiments. They knew that at 1 and 1.5 GPa they had albite plus melt at 680 and 645°C respectively, so they started their experiment by heating their sample to the temperature at which melt was present and running it for the same time as in the first experiment after which they decreased the temperature by 10°C. If they were correct about the position of the melting curve, the decrease in temperature should have caused crystallization giving only albite + vapour. In both experiments, there was no melt present in the reversed experiment confirming the location of the melting curve.

In more complex systems, where there is one or more solid solution, reversal experiments require a more complex methodology. This is well illustrated by the work of Klemme and O'Neill (2000). In their experiments, rather than having a single starting material composition and changing pressure or temperature to change the direction of the approach to an equilibrium curve, they used two slightly different compositions. In detail, their approach to determining the position of

the garnet to spinel transition in peridotite involved having two starting materials with slightly different compositions of clino- and orthopyroxene. They showed that equilibrium was attained when the composition of the two pyroxenes in the two different starting materials was the same after the experiment.

Maintaining Equilibrium During Cooling

Most reactions in geological materials are slow, so that the rate of cooling will not significantly affect their composition. There is a major exception to this; quench crystallization of silicate melt. This is a particular problem for mafic and ultramafic melts; in particular those that have even relatively low volatile contents. If cooling is not fast enough, these melts can show significant amounts of crystallization (Fig. 9). These crystals were not present at the experiment conditions, and their presence changes the composition of the equilibrium liquid.

In experiments at one atmosphere, very rapid cooling can be achieved by dropping the sample into a container of coolant – water is the most common, though mercury baths and even liquid nitrogen have been used (Edgar 1973; Xu and Zhang 2002), this rapid cooling quenches the high temperature assemblage and transforms any melt present to a glass. For most compositions, this is an effective technique. However, even with cooling rates of a few hundreds of degrees per second, crystallization during quenching of the experiment can still be a problem. In their quest to produce a glass of peridotite composition, Dingwell et al. (2004) used a very rapid quenching technique, the splat quencher, in which the sample is dropped from the furnace and 'splatted' between two cold copper discs. This increases the surface area of the sample and so increases cooling rate.

At high pressure, quenching also relies on rapid cooling, although because of the large thermal mass of the apparatus, cooling rates are not as rapid in the piston-cylinder as they are in one atmosphere experiments. This leads to quench crystallization problems, particularly in water and CO_2-bearing basaltic melt and in low percentage partial melts of peridotite. A variety of techniques have been developed to overcome the quench crystallization issues such as melt traps in glassy carbon or diamond or glassy carbon aggregates (Kushiro 1996; Van den Bleeken et al. 2011) or trapping melts as artificial melt inclusions in fractured minerals (Spandler et al. 2007).

USING EXPERIMENTS TO ANSWER PETROLOGICAL QUESTIONS

What Mineral Assemblages and Melt Compositions Form During Melting of the Mantle and Crystallization of Basalt?

To answer this question we need to produce phase diagrams from high pressure and high temperature melting experiments on peridotite and high temperature crystallization experiments on basalt and simple analogue compositions. Although every Earth science student learns to read phase diagrams as part of their undergraduate degree, many do not know how one goes
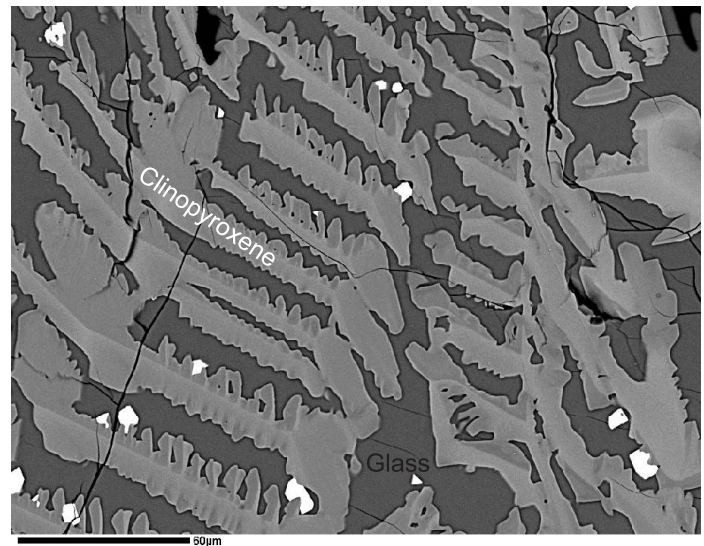

Figure 9. An example of quench crystallization of clinopyroxene in an alkaline basaltic melt. From Mumford (2006).

about 'making' a phase diagram. To illustrate how these diagrams are constructed, we examine two different types of experiment: near solidus melting experiments done at high pressure, and near liquidus crystallization experiments. It is important to realize that just as a geological map is a 2-D representation of the distribution of rocks and the contacts between different lithologies, a phase diagram represents the stability fields of minerals and the 'contacts' are where two or more phases are in equilibrium. As with maps, we never see the entirety of a stability field or a contact and we have to infer their position from a limited number of outcrops (experiments).

Phase equilibrium experiments have been a part of experimental petrology and materials science for more than a century, beginning with studies of metallurgical slags (Vogt 1903) and encompassing the classic studies of Bowen and coworkers (Bowen 1912; Bowen and Andersen 1914; Bowen and Tuttle 1950) to recent studies such as Mitchell and Grove (2016). Thermodynamic modelling software such as FACTSAGE for slag systems (Bale et al. 2002) and MELTS for natural silicate melts (Ghiorso and Sack 1995; Hirschmann et al. 1998; Asimow et al. 2001; Smith and Asimow 2005; Gualda et al. 2012; Gualda and Ghiorso 2014) is the result of almost a century of experiments on a wide variety of materials.

Peridotite Melting Experiments

Experiments just above the solidus of peridotite at high pressure have been essential to our understanding of basalt genesis and the geochemical evolution of the mantle. The study of Jaques and Green (1980) was particularly instructive because it showed how temperature and pressure influence melt composition. For their experiments, Jaques and Green prepared a sintered oxide mixture of pyrolite, the model mantle composition proposed by Ringwood (1966). They modified the pyrolite composition so that it had 40% less olivine than the original. This removal of olivine served two purposes: it made minor

phases easier to detect, and it increased the amount of melt (glass) present in the experiments which decreased the effects of quench crystallization on the melt compositions. A first reaction to this approach might be to wonder how much effect removing the olivine has on the phase equilibria. The answer is almost none because even at the highest temperatures, their experiments were still saturated with olivine. Since the melts were olivine saturated, the removal of the excess olivine made no difference to the results. In fact, they did notice some small effects on the composition of the olivine crystals which were slightly more magnesian than those in equilibrium with the peridotite, but they considered this difference a small cost in order to obtain large pools of glass unaffected by quench crystallization for analysis.

The experiments were done at atmospheric pressure to 1.5 GPa over a temperature range of 1170 to 1550°C in a one-atmosphere furnace and a piston-cylinder press. The high pressure experiments used talc–pyrex cells with the sintered oxide mixtures encapsulated in platinum and temperature was measured with a type-S thermocouple. They calibrated the pressure in their cells against the quartz – coesite and albite = jadeite + quartz transitions and, because of the inherent shear strength of the talc pressure medium, applied a 10% correction to the nominal pressure determined for their piston-cylinder press. Since they were interested in anhydrous melting, they stored their starting materials and pressure cells at 110°C until they were ready to begin the experiment. They did not control the oxygen fugacity of the experiment, but they did note that based on earlier experiments with solid buffers they knew that the fO_2 was below the NNO buffer. The biggest issue that they had to overcome was the alloying of iron with the platinum capsules. They used very short run durations, 20 minutes at 1550°C and 5 hours at 1050°C, and for several P–T conditions they did multiple experiments over a range of durations to examine the effects of progressive iron loss. To test for equilibrium they determined the partition coefficient of Fe and Mg between olivine and orthopyroxene in their experiments and compared it to the accepted value which had been determined in several earlier studies. This is not a particularly robust test of equilibrium and the problems of iron loss meant that it was impossible to do reversal experiments. Although Jaques and Green (1980) considered that their experiments had reached equilibrium, they were unable to prove it conclusively.

Once their experiments were complete, they identified the phases with SEM and determined mineral and melt compositions by electron microprobe analysis. They determined melt compositions in two ways: first by analyzing the pools of glass that were present in the experimental charge, and second by calculating the melt composition by mass balance using the initial pyrolite composition together with the composition and modal abundance of the crystalline phases in the experiment. The calculated melt compositions are more magnesian with higher FeO and lower SiO_2, Al_2O_3 and CaO than the analyzed glass which possibly reflects modification of the glass by quench overgrowths on the surrounding crystals during cooling.

Figure 10 shows the results of their experiments plotted on a P–T phase diagram. Figure 10a shows only the experimental results with no interpretation. Figure 10b shows the interpreted diagram. It shows that once the solidus is crossed that there is a progressive loss of phases with increasing temperature. The first phase to be completely melted is clinopyroxene, which is followed by orthopyroxene. Spinel and olivine are stable at the highest temperatures. Overlain on the interpreted phase relations in Figure 10b are the percentages of melting and curves showing the amount of normative olivine in the melts as well as approximate ranges of pressure and temperature for different magma compositions. Alkaline magmas are produced by the smallest degrees of partial melting, i.e. near the solidus. Increasing pressure increases the amount of normative olivine in the melt causing a transition in melt composition from quartz tholeiite to tholeiitic picrite.

Data on the phase relations of partial melting of anhydrous peridotite have been used to develop models that allow calculation of the volume and composition of magma generated by decompression and extension of oceanic lithosphere (McKenzie and Bickle 1988), as well as to assess the degree of melting of peridotite dredged from mid-ocean ridges (Dick et al. 1984). Most recently, Jaques and Green's (1980) experimental results have been used by Bénard et al. (2017) to develop a petrogenetic model for arc basalts.

Near Liquidus Crystallization Experiments
Systematic study of simple, synthetic systems led Bowen to develop his reaction series and helped pave the way for a deeper understanding of basalt evolution, in particular the role of the thermal divide that separates the alkaline and tholeiitic basalts (Yoder and Tilley 1962). A classic example of such a study of this type is Bowen's (1912) examination of the binary system $Na_2Al_2Si_2O_8$ – $CaAl_2Si_2O_8$ (the nepheline – anorthite system). Bowen applied two techniques in this study: the quench method which is described above and the heating curve method. The heating curve method is really a simplified differential thermal analysis, in which a thermocouple is immersed in the composition of interest. As the temperature is decreased, controlled and measured by a second thermocouple, a difference in temperature between the two thermocouples indicates appearance of a phase, because the latent heat released during crystallization is added to the melt. Bowen used this method to determine the general properties of the system but he had to be careful because Day and Sosman (1911) had shown that some for phases, such as feldspar, cooling rate had a major effect on the temperature at which the phase change occurred because the rate of temperature change affects the rate of crystal nucleation.

To avoid this nucleation problem, Bowen used the newly developed quench method to work out the details of the phase diagram. A second reason for using the quench method is that in this method the charges were completely enclosed in platinum which avoided the issue of loss of sodium due to vapourization at the high temperatures of the experiments. For each composition of interest, the samples were held at the
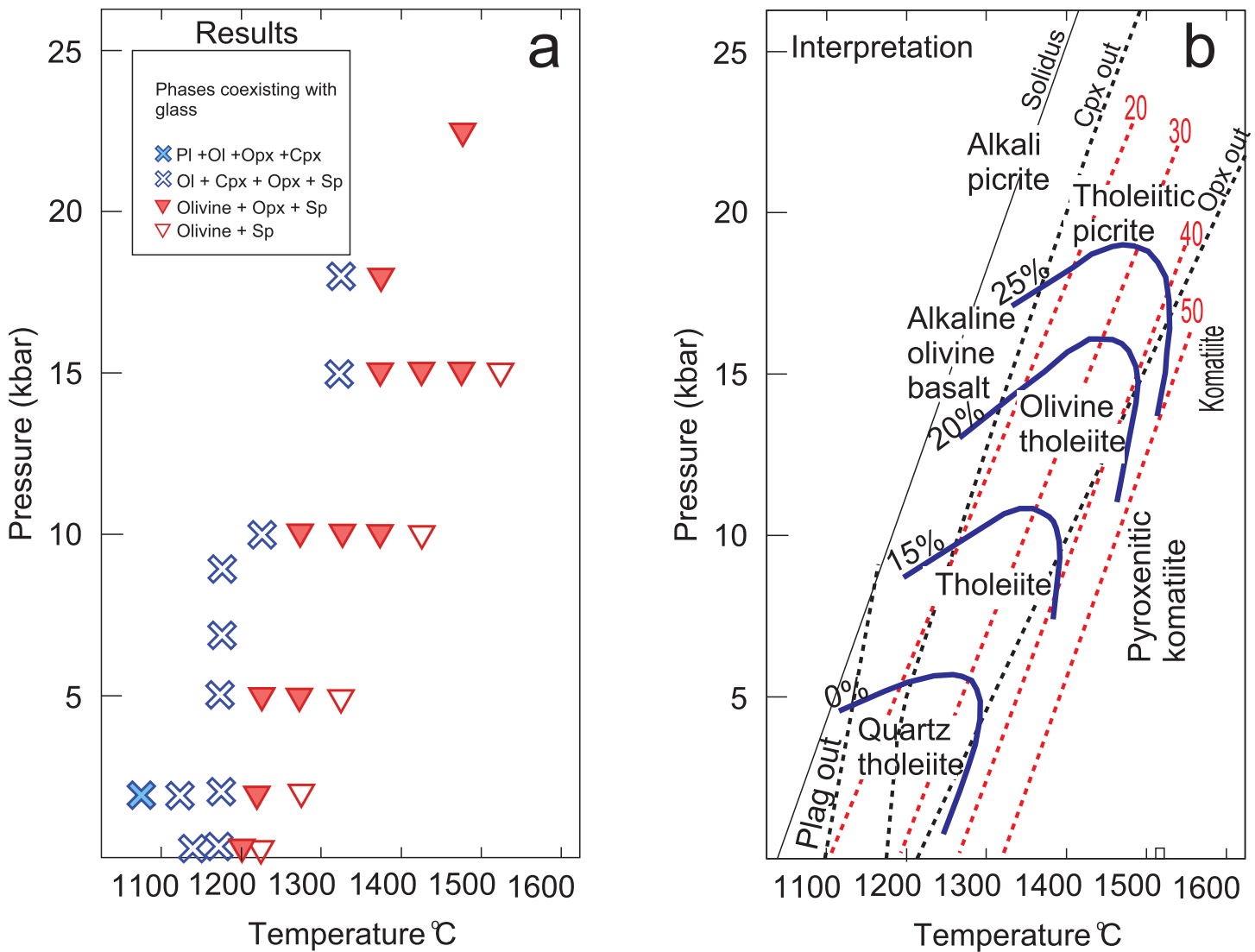
Figure 10. a) The results of phase equilibria experiments on pyrolite (Jaques and Green 1980). b) The interpreted phase diagram showing the solidus and mineral out lines. Dotted line with numbers indicates the percentage of melt present in the experiments. The solid lines with percentages show the amount of normative olivine in the melt. Cpx - clinopyroxene, Pl - plagioclase, Ol - olivine, Opx - orthopyroxene, Sp - spinel.

desired temperature for at least an hour, though some of the experiments had to be held at the run temperature for several days to ensure nucleation and crystallization under equilibrium conditions. Given the technology of the day and the banks of resistors that were used for temperature control, this must have presented significant challenges. At the end of each experiment, the platinum wrapped charges were opened and the contents crushed and examined under the microscope to allow identification of the phases.

Overall Bowen did 'several score' experiments, the results of which are plotted in Figure 11. The top diagram in this figure is the 'raw' phase diagram with only the data and no interpretation. The bottom is the phase diagram we are more used to seeing – a complete map of the phase boundaries with no experimental information given. It is interesting to note that portions of the phase diagram calculated using independently determined thermodynamic data give very close reproductions of the diagram produced by Bowen.

What Are The Transport Times for Mafic Magmas From Source To Eruption?

This is a critical question for volcanologists interested in making eruption predictions at dormant volcanoes. The natural samples that help to answer the question must preserve reactions that have not reached equilibrium because these potentially preserve information on reaction time in the form of compositional zonation or reaction rim growth. As an example of such reactions, Shaw and Klügel (2002) examined peridotite xenoliths that have zoned olivine in contact with basaltic melt. They measured the compositional variation in the olivine crystals with the electron probe (Fig. 12a), but could not determine how long the zoning took to develop without access to experimental data. Zoning can develop during growth or as a mineral re-equilibrates with magma. Shaw and Klügel (2002) showed that olivine was a stable liquidus phase in the lavas they examined. This meant that the olivine in the peridotites, which has a much higher forsterite content than the liquidus olivine,
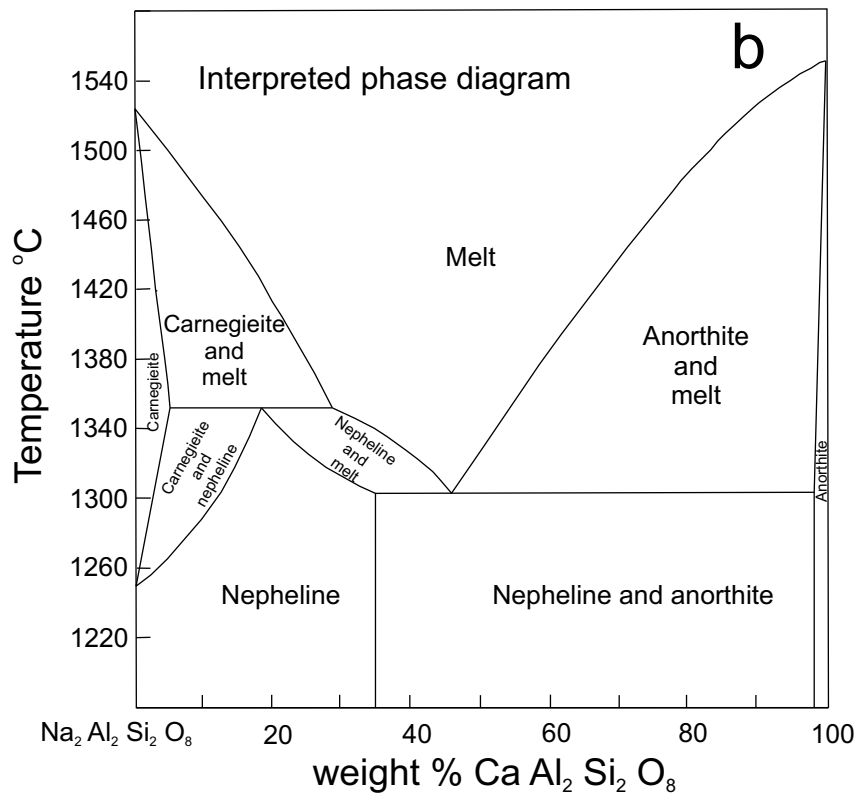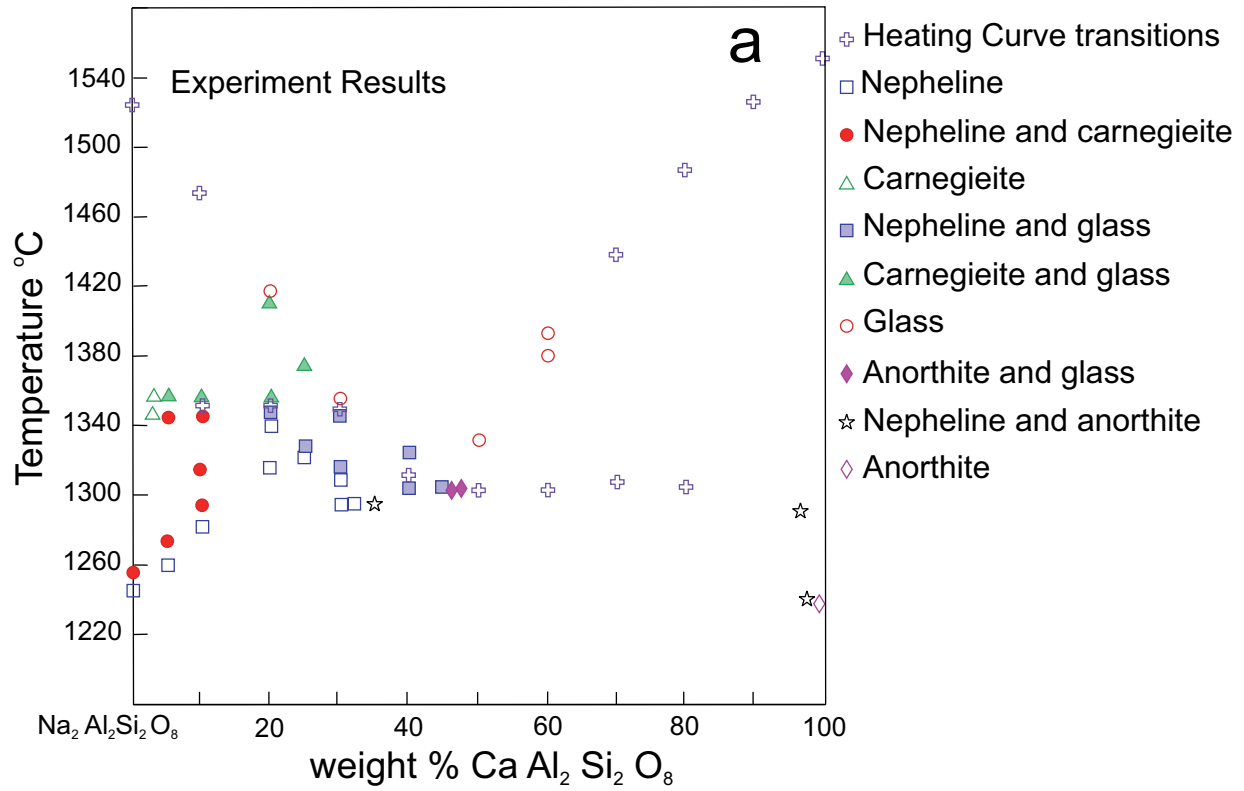
Figure 11. a) The results of Bowen's experiments on the $Na_2Al_2Si_2O_8$–$CaAl_2Si_2O_8$ system showing the position of transitions defined by the heating curve method and the phases present in long duration quench experiments (Bowen 1912). b) The interpreted phase diagram with no experimental results shown. This is typically the way that phase diagrams are presented to students.
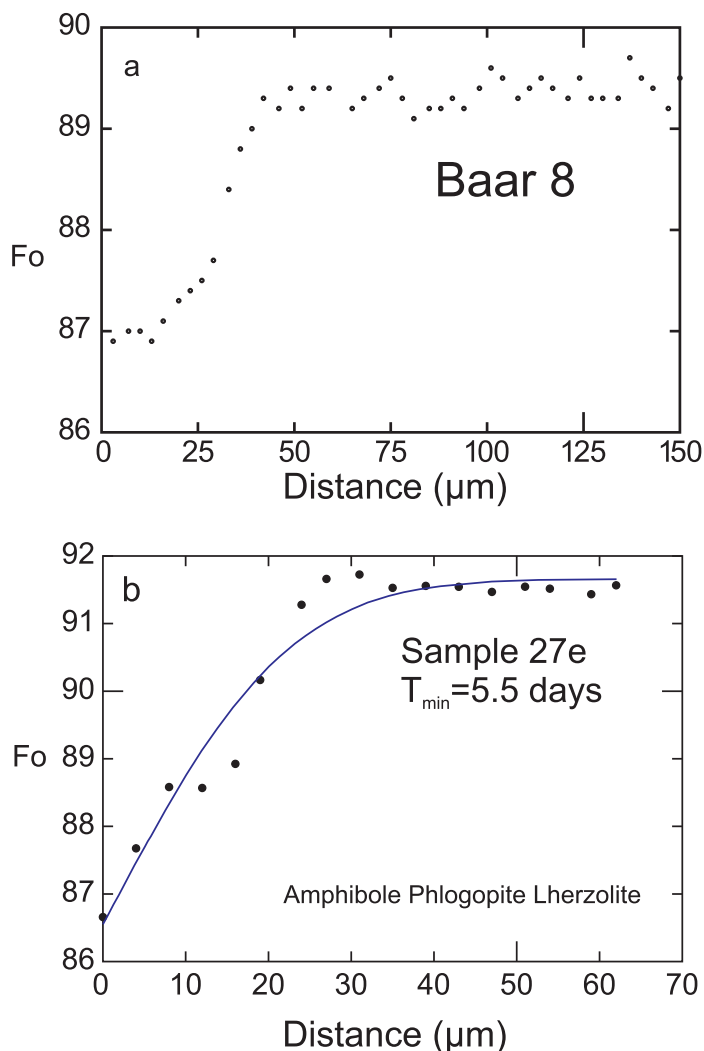
Figure 12. a) A compositional profile in olivine in contact with basaltic melt (Shaw and Klügel 2002). b) A diffusion profile in olivine from the Rockeskyllerkopf volcano in the West Eifel region of Germany (Lebert 2012). The curve shows a binary diffusion model for the profile that was calculated using the experimental data of Chakraborty (1997).

had to undergo re-equilibation. The only way for this to occur is via interdiffusion of iron and magnesium between olivine and liquid.

There are two unknowns in even the simplest diffusion equation (see Zhang 2008 for examples), namely, time and the diffusion coefficient (D). If we know the duration of interdiffusion, we can solve for D and vice versa. To determine D, we must perform a diffusion experiment for a known duration and ensure that we quench before equilibrium is attained, in order to preserve the compositional gradients developed during the experiment.

Experiments with crystals or melts can give us the value of D as a function of temperature, oxygen fugacity, pressure, etc. (Zhang and Cherniak 2010). A particularly well designed experimental study of diffusion that is relevant to the example above, is that of Chakraborty (1997) who set out to determine the interdiffusion coefficient of Fe and Mg in olivine. This had been examined by two other groups in the 1970's but there was

significant variability in the determined diffusion coefficients (Buening and Buseck 1973; Misener 1974). Chakraborty's experiments were designed to allow an examination of the diffusion coefficient as a function of crystallographic orientation and temperature. The experimental method is quite simple: place oriented crystals of olivine of different composition in contact and anneal them at the desired temperature and oxygen fugacity, paying close attention to the duration of the experiment. Chakraborty performed 14 experiments that ranged in duration from 2 to 15 days in which he controlled the orientation of the crystals, temperature and oxygen fugacity. Although the experiments themselves are quite simple, the determination of the diffusion coefficients is more complex and beyond the scope of this review. The final result of the experimental study was an equation that allowed calculation of the diffusion coefficient of Fe/Mg in olivine as a function of temperature and orientation. Figure 12b shows an example of a modelled compositional profile in an olivine from a peridotite xenolith from the West Eifel volcanic field (Lebert 2012). A model profile has been fitted to the data using an estimate of the temperature and oxygen fugacity during transport. This shows that the olivine was in contact with its transporting magma for around 5 days. Since the xenoliths were entrained at a depth of around 50 km this gives an average ascent rate for the magma of around 0.5 km/h.

Numerous studies have used Chakraborty's data to model diffusion profile in olivine in order to extract magma–melt contact times and develop models of magma ascent and magma chamber dynamics (Jankovics et al. 2013; Kahl et al. 2015; McGee et al. 2015; Marchev et al. 2017). Clearly, answering these questions in the absence of experimental data would have been impossible.

How Do Melting and Crystallization Influence the Behaviour of Major and Trace Elements?

To answer this question we need to determine whether the element of interest is concentrated in the mineral phase or the melt, i.e. we need to determine its partition coefficient. For some elements we can make a qualitative assessment of this behaviour using simple phase diagrams. For example, from the phase diagram of the Mg_2SiO_4–Fe_2SiO_4 system we can see that olivine crystallizing from any melt that has a composition between the two end members will always be more magnesian than the melt. This behaviour leads to the well-known iron-enrichment trend that is typical of tholeiitic systems.

Olivine/Melt Equilibria

Roeder and Emslie (1970) made a quantitative study of the relative partitioning of iron and magnesium between olivine and melt. Their goal was to use partitioning data to estimate the location of the olivine saturation surface in basaltic melts in temperature–composition space and to use olivine and co-existing glass compositions to estimate magmatic temperatures.

The distribution of Fe and Mg is controlled by the reaction:

$$Mg_{ol} + Fe^{2+}_{liq} \leftrightarrow Mg_{liq} + Fe^{2+}_{ol}$$
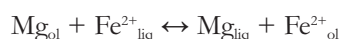
If an equilibrium constant can be defined for this reaction, the composition of olivine can be used to predict the composition of the equilibrium liquid and crystallization temperature. One of the difficulties in dealing with the distribution of major elements between minerals and melts, as opposed to trace elements, is that some assumptions have to be made regarding the ideality of the system under study. In their work, Roeder and Emslie considered the liquid and solid solution to be ideal, in which case the activities of FeO and MgO could be replaced by the mole fraction of components in solid and liquid to calculate the equilibrium constant, i.e.

$$K = X_{ol}^{FeO} / X_{liq}^{FeO} * X_{liq}^{MgO} / X_{ol}^{MgO}$$

They used three different natural basalts from Hawaii that were encapsulated in either platinum, silver–palladium or alumina depending on the temperature and fO_2. Oxygen fugacity was controlled with mixtures of carbon dioxide and hydrogen and calibrated against the Fe–FeO and Ni–NiO reactions. They measured and controlled temperature with a type-S thermocouple and ran their experiments for a minimum of two days. They did not comment on the possibility of iron loss in their runs and the only discussion of the extent of equilibrium is that the minimum of 2 days was " ... *found to be sufficient for equilibrium*" since it confirmed the results of earlier workers. In hindsight it appears that they were correct as the numerous measurements that have followed (e.g. Toplis 2005) have confirmed their results.

They reported on 44 experiments at one atmosphere at 1150–1300°C and controlled fO_2 and used their data (Fig. 13) to define the value of K as 0.30 ± 0.03. The partitioning model was updated to include the effects of pressure, water content and liquid composition by Toplis (2005). Roeder and Emslie's results have been used in more than 1800 published studies. Their partitioning model is commonly used to assess the degree of equilibration of phenocrysts with their host magma or to calculate the degree of fractionation of a magma from the composition of olivine in cumulates. This work was also one of the first to use mineral – melt equilibria as a geothermometer and its influence is shown in the work of Putirka (1997) and Putirka et al. (1996, 2003) who have been developing a wide variety of mineral – melt thermometers using a similar approach.

Trace Element Partitioning

The partitioning behaviour of trace elements is used to model fractionation of magmas (Shaw 1970; Allègre and Minster 1978; Minster and Allègre 1978), or derive magma compositions from mineral chemical data (e.g. Shaw and Eyzaguirre 2000). In the early days of trace-element analyses, most measurements of partition coefficients were made on phenocryst–groundmass pairs in natural volcanic rocks. The authors of these studies recognized that there were potential limitations on their accuracy as the phenocrysts are assumed to be *in situ* and are commonly zoned and therefore may only preserve a local equilibrium with the groundmass. In addition, later studies noted that heterogeneous nucleation and crystallization
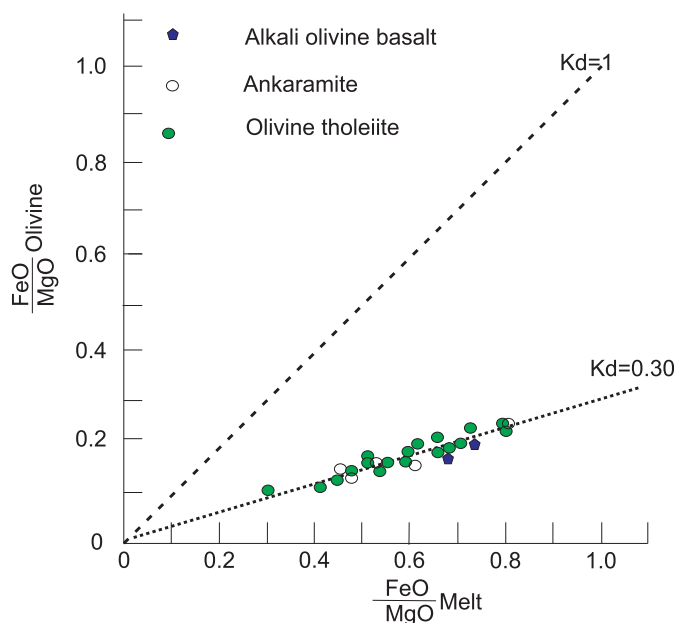

Figure 13. The experimental results of Roeder and Emslie (1970) showing the composition of olivine and coexisting melt for three different basalts over a range of temperatures. The best fit to the data gives the partition coefficient for Fe/Mg between olivine and melt.

during quenching can produce rims on the minerals that are not in equilibrium with the groundmass.

There has always been a need for high quality partitioning data for a wide variety of mineral and melt compositions. This need is compounded by the observation from phenocryst–groundmass compositions that partitioning behaviour varies with melt composition. The consequence is the development of a large database of high quality partitioning data from experimental studies (see https://earthref.org/GERM/) that supports trace-element modelling in igneous rocks. However, there are still some significant holes in the database – particularly for unusual compositions such as komatiite, carbonatite and kimberlite. Furthermore, the theoretical understanding of partitioning that has been gained from these studies has led to predictive models of partitioning behaviour (Blundy and Wood 1994; Blundy and Dalton 2000; van Westrenen et al. 2000).

Trace Element Partitioning Experiments

As is the case with the major elements, the charge in trace element partitioning experiments must reach equilibrium. Calculation of the partition coefficient is less complex than for major elements because no assumptions have to be made about the thermodynamic ideality of partitioning. The composition of element i in the mineral is linearly related to the concentration of i in the melt, i.e. the Henry's law region (see Jones 2016 for a detailed treatment).

A widely used study of this type is that by Hart and Dunn (1993) who examined the distribution of 24 trace elements between clinopyroxene and alkali basalt at 1380°C and 3 GPa in an attempt to resolve large discrepancies in measured values for different clinopyroxene–melt pairs in previous studies. Although the study was not able to fully resolve the issues with

the earlier work, it has become an important basis for developing and testing models of partitioning behaviour from the elastic moduli of the minerals of interest (Blundy and Wood 1994). The experiments used a fused chip of a natural basalt placed in a graphite capsule and heated to 1380°C at 3 GPa in a piston-cylinder press. Temperature was monitored by a type R thermocouple and pressure was calibrated against the melting point of NaCl. The experiment charge was not ideal for determination of partitioning behaviour; it comprised two large, zoned clinopyroxene crystals with rims of quench crystals in a matrix of glass, some of which had quench crystallized. The zonation of the clinopyroxene suggests that the charge did not fully equilibrate, though the authors suggest that the zonation represents growth zoning. They used earlier experimental data to argue that the inner zones of the clinopyroxene grains were in equilibrium with the melt and that the outer zones resulted from rapid growth under disequilibrium conditions controlled by the rate of interface attachment. This study shows that even in the controlled world of the experiment, it may not be easy or simple to interpret the results. Interestingly, despite the apparent problems with the experiments, the results of Hart and Dunn (1993) have been confirmed in predictive models of partitioning based on other experimental data (Blundy and Dalton 2000). This latter study is working toward the ultimate goal of a predictive model for partitioning that will account for pressure, temperature, melt composition, oxygen fugacity, volatile content and other intensive variables (Fig. 14). It would appear that the ultimate goal of the experimental petrologist is to put themselves out of work.

What Controls the Eruption Styles of Basaltic vs Andesitic/Dacitic Volcanic Systems?

The differences in the flow characteristics of basaltic vs more silicic magmas are quite obvious, i.e. widespread basaltic flows vs lava domes and spines. Similarly, the effects of temperature on the flow characteristics of basalt can be seen in the transition from pahoehoe to aa flow (Kilburn 1981). The main parameter that controls the flow characteristics of lava is viscosity and since the late 1960's geologists have been interested in finding the relations between magma composition, temperature and viscosity. Shaw (1969) described how the viscosity of a magma can be measured using a concentric cylinder viscometer. This is a common technique that is used to measure the viscosity of oil, paint and other liquids. A spindle is inserted into the liquid whose viscosity is to be determined. The liquid is held in a cylindrical cup and the spindle is rotated at a constant speed and the torque on the spindle is measured. The torque readings and the angular velocity of the spindle can then be used to calculate the viscosity. Viscosity determination at room temperature uses steel spindles and glass cups. Measurements on magma, at temperatures often greater than 1000°C, requires careful choice of materials since they should be strong enough to deal with the applied torque at the temperature of the experiment and should also be unreactive with the liquids to be measured. Temperature control is of particu-
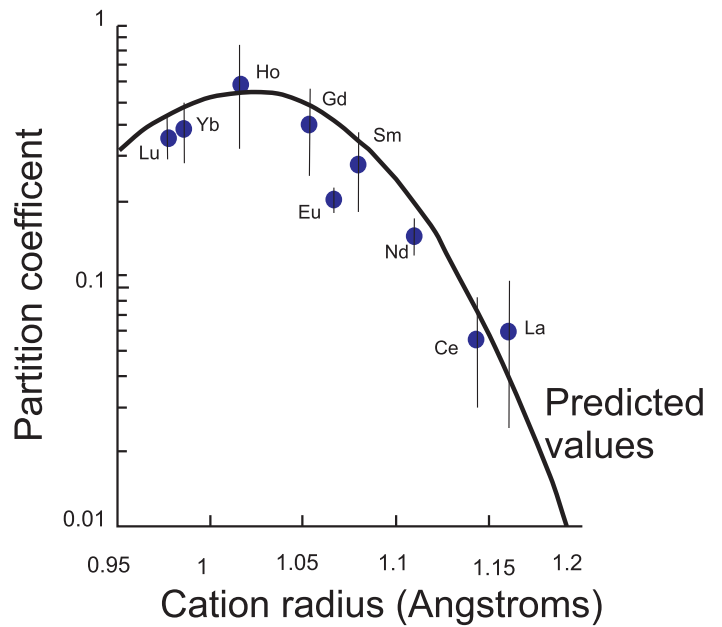

Figure 14. Experimental data of Hart and Dunn (1993) and a model curve calculated using the method of Blundy and Wood (1994). There is close agreement between the measured partitioning values.

lar importance in these measurements, since viscosity varies significantly with temperature.

Shaw's (1969, 1972) systematic experiments on natural compositions using melted samples of erupted materials led to the first empirical model of melt viscosity (Bottinga and Weill 1972). However, it did not take long for geoscientists to apply a Bowenesque approach to the viscosity problem by examining how changes in composition in simple systems affect viscosity (Scarfe and Elderfield 1975; Scarfe 1977a, b; Dingwell et al. 1985; Mysen et al. 1985; Dingwell 1989, 1992; Webb 1991). After several decades of intensive research, we now have models that can be applied to any natural composition at any temperature above the liquidus (Hess et al. 1996; Giordano and Russell 2007; Giordano et al. 2008). Furthermore we have a much deeper understanding of the physics of silicate melts that is helping volcanologists to understand how magma behaves before and during eruption. Figure 15 shows a comparison of measured viscosities in two simple melts and the results of one of the viscosity models. There is extremely good agreement between the two.

Viscosity data are essential in developing models of magma transport and eruption and in the dynamics of lava flows. An excellent example of how viscosity data have been used in interpreting the genesis of real rocks is Holness et al. (2017a) in which they use viscosity data to model the settling and fluid dynamics of cumulate formation in a layered intrusion.

THE FUTURE OF EXPERIMENTAL PETROLOGY

Some aspects of experimental petrology as it relates to the igneous rocks have advanced to the point where we now have robust models that can predict phase equilibria or the physical properties of a magma. In other fields, we are still collecting the basic data that we need to build models, e.g. for partition-
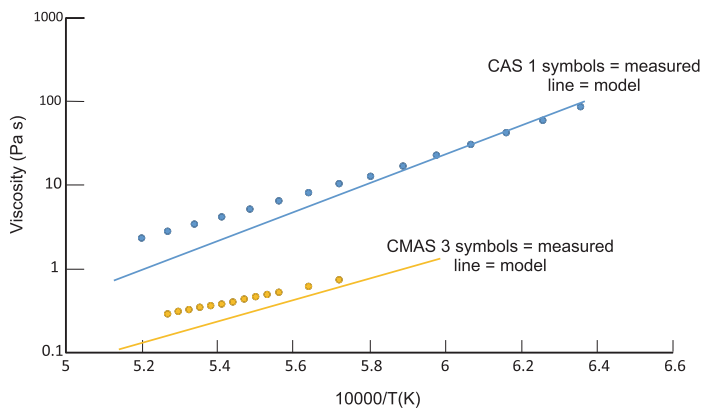
Figure 15. Viscosity measured by rotational viscometry (points) for two synthetic melts in the CaO–Al$_2$O$_3$–SiO$_2$ (CAS) and CaO–MgO–Al$_2$O$_3$–SiO$_2$ (CMAS) systems (Shaw 2006) compared to the viscosity calculated using the model of Giordano and Russell (2007).

ing between minerals and melts as a function of pressure, temperature, melt composition, oxygen fugacity, etc., but we are quite a long way down the road since preliminary models have been proposed.

A major focus of experimentalists should be to help in understanding the origins of microstructure in igneous rocks. Much of what we 'know' about rock microstructure has never been experimentally tested (Vernon 2004). Despite more than 100 years of study, there is still significant debate over the role of crystal accumulation, demonstrated by Bowen and developed into a model to explain layered intrusions (Wager and Brown 1967) vs subsolidus processes in the development of igneous layering even in such classic localities as the Skaergaard intrusion in East Greenland (Holness et al. 2017b). The methods of experimental petrology, in particular experiments in dynamic magmatic systems, will be of critical importance in solving this long standing problem.

There are still phase equilibrium experiments to be done. Though we understand much of the phase relations of the common magmas, the genesis and crystallization behaviour of more exotic compositions such as kimberlites, lamproites and carbonatites requires further study. In addition, the roles of volatiles other than water and carbon dioxide need to be better understood, particularly in alkaline magmas such as those found in the Roman Volcanic Province, which is currently entering a new period of unrest in the Phleagrean fields region (Chiodini et al. 2016). This work will need close coordination between the thermodynamic modelling and experimental petrology communities. The experiments will need to be focused on the areas where critical information is needed to extend the existing models to more exotic composition.

The growing populations around active volcanoes means that we need to have a better understanding of the properties of magma chambers and their contained magma, crystal mushes and the bubble-rich magmas that form as they decompress. As well as continued study of physical properties, experimental petrologists need to scale up experiments so that small scale magmatic systems can be constructed and studied in the laboratory. Some of this work is already in progress, for exam-

ple, Rager et al. (2014) report on experiments that simulate explosive fragmentation of magma during an eruption. However, there is still a need for experimental data on magma behaviour under magma chamber conditions.

Really the future of experimental petrology lies in the hands of petrologists themselves. Imagine a field problem and an experiment can likely be designed to help understand it. All you need to do is contact your nearest experimental petrologist!

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