Experimental and petrological studies of melt inclusions in phenocrysts from mantle-derived magmas: an overview of techniques, advantages and complications

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Abstract

Melt inclusions in phenocrysts are a potentially powerful tool in petrological research that can provide the only direct information available on the physical parameters (P, T and melt composition) of crystallisation at various stages in the evolution of magmatic systems. However, melt inclusions also differ in principle from other parts of the magmatic system in that their composition, after trapping, may be controlled by the composition of the host phenocryst and therefore the direct application of our understanding of macro-scale magmatic processes to the interpretation of melt inclusion data can lead to erroneous conclusions. Our results indicate that the compositions of melt inclusions in early formed phenocrysts (olivine, pyroxene, plagioclase and spinel), often of most interest in petrological studies, can be affected by processes such as volatile dissociation, oxidation and/or partial re-equilibration with their host, both during natural cooling and homogenisation experiments. In particular, melt inclusions in all minerals are prone to hydrogen diffusion into or out of the inclusions after trapping and prior to eruption, and during homogenisation experiments. If not taken into account, this can significantly affect the crystallisation temperatures derived from the homogenisation experiments. Melt inclusions in high-magnesian olivine phenocrysts commonly have lower Fe contents compared to the initially trapped composition due to re-equilibration with the host at lower temperatures. This often leads to the appearance of sulphide globules and in some cases high-magnesian clinopyroxene daughter crystals, and may cause an increase in the oxidation state of the inclusions. Homogenised melt inclusions in plagioclase phenocrysts in MORB usually have lower Ti and Fe, and higher Si contents compared to the melt composition at the moment of trapping. However, homogenisation experiments can provide reliable estimates of trapping temperature and the MgO, Al_2O_3, CaO, Na_2O, and K_2O contents of the host magma at the moment of trapping. Some of these processes can be identified by observing the behaviour of melt inclusions during homogenisation experiments using low-inertia visually controlled heating stages, and their effects can be minimised by using appropriate experimental conditions as determined by kinetic experiments, ideally completed for each phenocryst type in every sample. We also discuss general aspects of melt inclusion studies aimed at recovering H_2O content of primary mantle-derived magmas and demonstrate that, in cases of low-pressure crystallisation, it is important to identify the

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first liquidus (most magnesian) olivine that crystallised from these magmas. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The existence of melt inclusions, small portions of melt trapped by growing crystals during magma evolution prior to and during eruptions, has been recognised for many years (Anderson, 1974; Clocchiatti, 1975; Sobolev and Kostyuk, 1975; Sobolev, 1983; Roedder, 1984 and references therein). As summarised by Roedder (1979), melt inclusion studies can provide valuable information on crystallisation temperatures, the sequence of phase changes in the host magma during cooling, constraints on cooling rates, the composition and volatile content of the host magma and liquid line of descent.

However, the importance of melt inclusions for petrological and geochemical studies of magma genesis has only been fully realised in the past two decades following the development of microbeam analytical techniques. A large number of recent studies have described the compositions of melt inclusions in various phenocrysts from different magma types (e.g., Sobolev and Shimizu, 1993; Nielsen et al., 1995; Gurenko et al., 1996; Sobolev and Chaussidon, 1996; Sobolev, 1996; Kamenetsky et al., 1997; Metrich et al., 1999; Sobolev et al., 2000; and references therein). However, since the pioneering works summarised by Roedder (1984), the methodological aspects of melt inclusion research have received considerably less attention (see Sobolev, 1983; Sobolev et al., 1983, 1990; Qin et al., 1992; Tait, 1992; Sobolev and Danyushevsky, 1994; Lu et al., 1995; Nakamura and Shimakita, 1998; Danyushevsky et al., 2000a; Gaetani and Watson, 2000).

In this contribution, we discuss the techniques used in experimental studies of melt inclusions and some processes that may affect the compositions of melt inclusions after trapping. We do not attempt to cover all problems associated with melt inclusion studies. Correspondence of the trapped composition to the host magma, coexistence of compositionally contrasting melt inclusions in a single grain and origin of 'exotic' melt inclusions are outside the scope of this paper (see Lu et al., 1995; Sobolev et al., 1990; Sobolev, 1996, 2001).

2. Experimental studies of melt inclusions

The purpose of experimental studies of melt inclusions is to reheat the inclusions to the temperature at which they were trapped, thus reversing the phase changes that occurred during natural cooling, i.e., crystallisation and formation of the shrinkage/fluid bubble, and then quench the restored trapped composition for further analysis. A detailed description of the theory of the homogenisation of melt inclusions is given in Roedder (1979, 1984 and references therein). The following discussion assumes that the composition of the host phenocryst does not change after the inclusion is trapped, and that the melt was fluid-saturated at the moment of trapping.

Important differences may exist between the physical conditions of the phenocryst, and any melt inclusions it hosts, during crystallisation and experimental reheating. For example, the pressure on the phenocryst during 1 atm experiments is always different (lower) than during natural cooling. The pressure inside melt inclusions at high temperatures will tend to increase toward the pressure at the time of trapping. If the phenocryst is capable of containing the high pressure, a pressure gradient (which is absent at the moment of trapping) will result. If the phenocryst cannot preserve the pressure inside the melt inclusions during an experiment, the pressure inside inclusions will be lower than the pressure of trapping (see Tait, 1992 for further discussion). In both cases, differences between experimental and natural conditions will result.

Another important difference between experimental and natural conditions is that during homogenisation experiments the phenocryst may control the composition of melt inclusions due to its dominant size (i.e., when chemical equilibrium is established during an experiment, the composition of a melt inclusion is a function of the physical conditions of

the experiment and the phenocryst composition), whereas during crystallisation in macro systems, the melt composition controls the composition of crystallising phases (i.e., the composition of a phenocryst is a function of the physical conditions and melt composition). As the physical parameters of homogenisation experiment may differ from the trapping conditions (see above), it is undesirable to equilibrate a melt inclusion with its host, as this may result in a change in the inclusion's composition.

An ideal homogenisation experiment is shown on Fig. 1. A typical melt inclusion at room temperature comprises a rim of the host mineral, a shrinkage/fluid bubble, and the recrystallised residual melt (Roedder, 1979; Fig. 1a). The host mineral always crystallises as an overgrowth on the walls of the melt inclusion because the pre-existing phase boundary (inclusion wall) has a low nucleation energy (e.g., Roedder, 1979). As the rim of the host mineral is usually optically indistinguishable from the host phenocryst, the observed size of the inclusion is smaller that its real size. The phase composition of a melt inclusion will depend on the temperature gap between trapping and eruption and the efficiency of quenching during eruption (Roedder, 1979).

With increasing temperature, during a homogenisation experiment, crystalline phases inside the inclusion melt and the bubble decreases in size (Fig. 1b). At a certain point, all microlites inside the inclusion will melt but the bubble is still present and there is some overgrowth remaining on the host phenocryst (Fig. 1c). Eventually, all crystalline phases inside the inclusion will have melted and the bubble disappears (Fig. 1d). At this moment, the experiment should be quenched.

From this simple analysis, it is clear that the kinetics of melting during a homogenisation experiment are important. If the temperature is increased too rapidly (i.e., the rate of heating is faster than the rate of melting within the inclusion), then the melting process will lag behind, and at any given moment, the conditions inside the inclusion will correspond to a lower temperature than the experimental temperature. Thus, rapid heating results in overheating (i.e., homogenisation is observed at a higher temperature than it occurs; note, however, that if the experiment is quenched immediately after homogenisation, the composition of an overheated inclusion should correspond
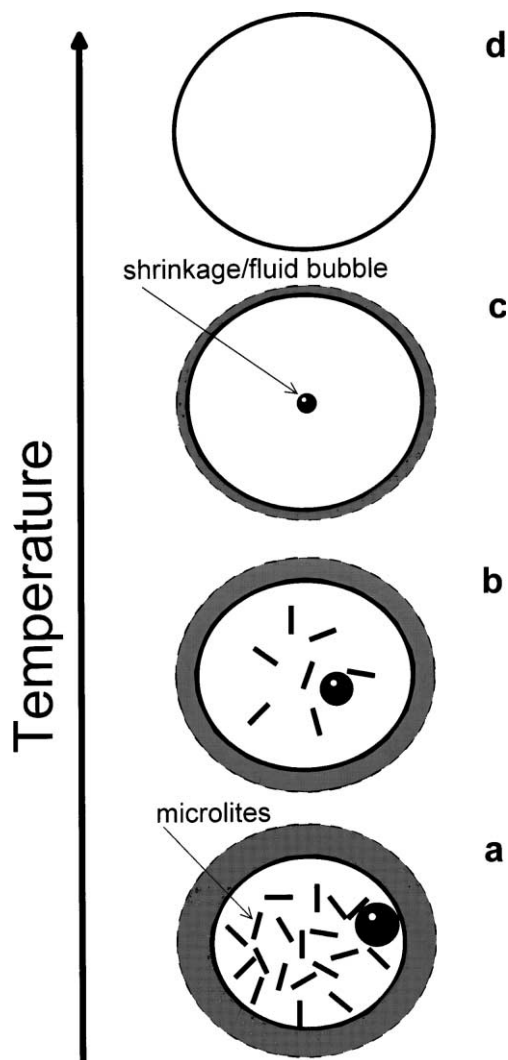

Fig. 1. Illustration showing an ideal melt inclusion homogenisation experiment. The solid bold line represents the visible boundary of the melt inclusion. Dashed bold line shows the actual size of the melt inclusion. Shaded grey area on the walls of the inclusion represent the host mineral that crystallised from the inclusion volume after trapping forming an overgrowth on the walls of the inclusion. See text for discussion.

to the trapped composition). Slow heating, on the other hand, will lead to re-equilibration (i.e., equilibration at conditions different to those at the moment of trapping) of a melt inclusion with its host.

Experimental studies of melt inclusions will produce reliable results when no mass transfer has occurred through the inclusion–host interface. In such

cases, using an appropriate heating rate that precludes re-equilibration with the host during the experiment, the composition of an inclusion at the moment of homogenisation (Fig. 1d) corresponds to the trapped composition. However, if some mass transfer has occurred (i.e., re-equilibration of the inclusion with its host after trapping, but before natural quenching), then the composition of the homogenised melt inclusion will differ from the trapped composition and will not be in equilibrium with the host. If the compositions of the host mineral and the homogenised melt inclusion are known, such disequilibrium can be deduced using mineral–melt equilibrium models (e.g., Ariskin et al., 1993). Currently, these models are most reliable for major elements, but our understanding of trace element partitioning as a function of pressure, temperature and other physical parameters is constantly improving (e.g., Blundy et al., 1996; Libourel, 1999; Sugawara, 2000).

The foregoing discussion highlights the danger of re-equilibrating a melt inclusion with its host during an experiment. When re-equilibration occurs, the composition of the melt inclusion is forced into equilibrium with the host at the experimental conditions, depriving us of any means to reveal changes in the inclusion composition after trapping and before natural quenching. It is important to note that re-equilibration with the host during an experiment will not necessarily return the composition of the melt inclusion to its initially trapped composition, as the physical parameters of an experiment may differ from the trapping conditions, as discussed above. We are not suggesting that re-equilibration equally affects all elements in an inclusion or that every experiment results in noticeable re-equilibration of inclusions with their host. For example, elements that are incompatible with the host are prone to re-equilibration significantly less than compatible elements, and their concentrations are unlikely to suffer any changes during reheating experiments. We would like to emphasise the main underlined principle of experimental studies: melt inclusions should be kept at high temperatures for a minimum possible time during an experiment.

The appropriate heating rate for homogenisation experiments can be established from kinetic experiments (e.g., Sobolev and Kostyuk, 1975; Sobolev et al., 1988; Sobolev and Danyushevsky, 1994). Kinetic experiments involve the continuous reheating a melt inclusion at different rates and then observing the homogenisation temperature obtained at each rate. Fig. 2a shows an example of kinetic experiments for plagioclase phenocrysts from MORB. The melt inclusion is first heated at the highest rate (50 °C/min). After homogenisation, the inclusion is cooled and recrystallised and then homogenised again at a slower
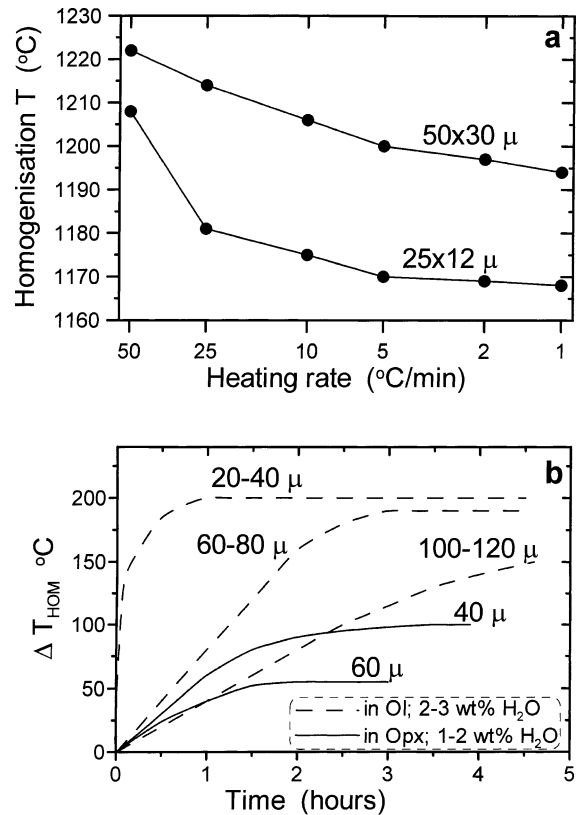

Fig. 2. (a) Kinetic experiments using a plagioclase phenocryst from MORB (ODP Hole 504B). Homogenisation temperatures were recorded for two inclusions of different size as indicated on the figure. The larger inclusion requires significantly slower heating rates than have been used in the experiment since all inclusions in one grain are expected to be trapped at a similar temperature. Heating rates are effective from temperatures 50 to 70 °C lower than the true homogenisation temperature. (b) Kinetic experiments using melt inclusions of different sizes in olivine and orthopyroxene phenocrysts from Tongan boninites (Sobolev and Danyushevsky, 1994). Experiments indicate an increase of the homogenisation temperature caused by dissociation of H_2O within inclusions when they are kept at high temperatures (> 1150 °C). Note there is a smaller effect from H_2O dissociation in larger inclusions. See text for discussion.

Table 1
Approximate heating rates for melt inclusions from several magma types

Phenocryst	Inclusion size (μm)	Magma type	Homogenisation temperature (°C)	Heating rate (°C/min)	Comments
Olivine	~ 30	"anhydrous" tholeiitic	1190–1250	1–2	heating rate is effective from temperatures ~ 50 to 70 °C below expected homogenisation temperature[a]
Plagioclase	~ 30	"anhydrous" tholeiitic	1190–1250	2	heating rate is effective from temperatures ~ 50 to 70 °C below expected homogenisation temperature[a]
Clinopyroxene	~ 30	"anhydrous" tholeiitic	1190–1250	0.5–1	heating rate is effective from temperatures ~ 50 to 70 °C below expected homogenisation temperature[a]
Olivine	100–150	tholeiitic, boninitic, 1.5–3 wt.% H_2O	1250–1350	100–200	heating rate is effective above 1060–1100 °C[b]
Orthopyroxene, clinopyroxene	50–80	tholeiitic, boninitic, 1.5–3 wt.% H_2O	1150–1250	50–100	heating rate is effective above 1060–1100 °C[b]
Plagioclase	50–80	tholeiitic, boninitic, 1.5–3 wt.% H_2O	1050–1100	100	heating rate is effective above 950 °C[c]

[a] Sobolev et al., 1988.
[b] Sobolev and Danyushevsky, 1994.
[c] Danyushevsky et al., 1997.

rate. This process is repeated until the homogenisation temperature becomes asymptotic, and the rate at which this happens is deemed the appropriate heating rate (between 2 and 5 °C/min for the smaller inclusion on Fig. 2a). Heating inclusions at a slower rate will not result in a lower homogenisation temperature, but will lead to re-equilibration of the inclusions with their host (as discussed above). The optimal heating rate is strongly dependent on the size of inclusions (Fig. 2a). Ideally, kinetic experiments should be conducted for every phenocryst type (i.e., olivine, plagioclase, etc.) in every sample studied.

Table 1 presents experimentally determined heating rates for "anhydrous" tholeiitic melt inclusions, ~ 30 μm in diameter, with homogenisation temperatures in the range 1190–1250 °C. These rates are effective from ~ 50 to 70 °C lower than the expected homogenisation temperature. Thus, the melt inclusions are kept at temperatures close to homogenisation for durations of ~ 30 min to 1 h. Melt inclusions in clinopyroxene require the slowest heating rate (longest time at high temperature), whereas inclusions in plagioclase generally allow the fastest heating rate. The heating rate at lower temperatures (< 1150 °C) does not influence the homogenisation temperature.

Although kinetic experiments provide important information on optimal heating rates, the rate of melting of individual melt inclusions can vary and some inclusions may be overheated even when the heating rate was constrained by kinetic experiments. Overheated melt inclusions can be identified by comparing the homogenisation temperatures of inclusions in phenocrysts of a similar composition (Fig. 3). A
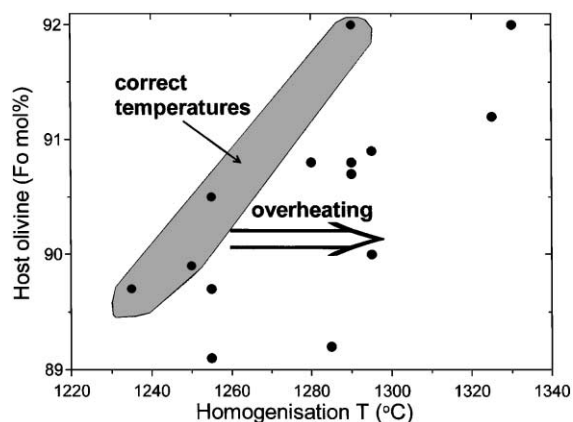

Fig. 3. Homogenisation temperatures of melt inclusions in olivine phenocrysts from Tongan boninites. The range of homogenisation temperatures at a given host composition is caused by overheating. See Sobolev and Danyushevsky (1994) for a detailed description of experimental procedures. See text for discussion.

necessary requirement for such a comparison is that inclusions have similar compositions, i.e., they represent a single liquid line of descent.

An example of the readjustments of the melt inclusion–host phenocryst pair to experimental conditions is shown on Fig. 4. When melt inclusions in plagioclase from MORB are kept at temperatures close to their trapping temperatures (between stages b and c, Fig. 1) longer than it is necessary, olivine microlites inside inclusions may recrystallise to form a single crystal. Once such a crystal is formed, it would not melt at temperatures at least 20 °C higher than the true homogenisation temperature, and in some cases, the shrinkage/fluid bubble disappeared before the olivine crystal melted. Our preferred explanation is that this results from a decrease of pressure inside such inclusions due to the inability of the host crystal to contain the pressure gradient during experiments, as

discussed above. Since MORB melts are olivine + plagioclase cotectic (e.g., Grove et al., 1992), the olivine microlites inside inclusions should melt simultaneously with complete melting of the plagioclase rim on the walls and homogenisation of the inclusion, as is often observed in experiments (McNeill, 1997). If the effect of pressure on the olivine liquidus temperature is slightly less than it is on the plagioclase liquidus temperature, than the decrease of pressure inside an inclusion during an experiment will enhance olivine stability and produce the observed effect.

The preceding discussion highlights the importance of visual control during homogenisation experiments, which is possible when using a microscope-mounted heating stage (see Sobolev et al., 1980 for a description of a low-thermal inertia heating stage). However, when experiments are conducted in a 1 atm vertical furnace without visual control, it is impossible
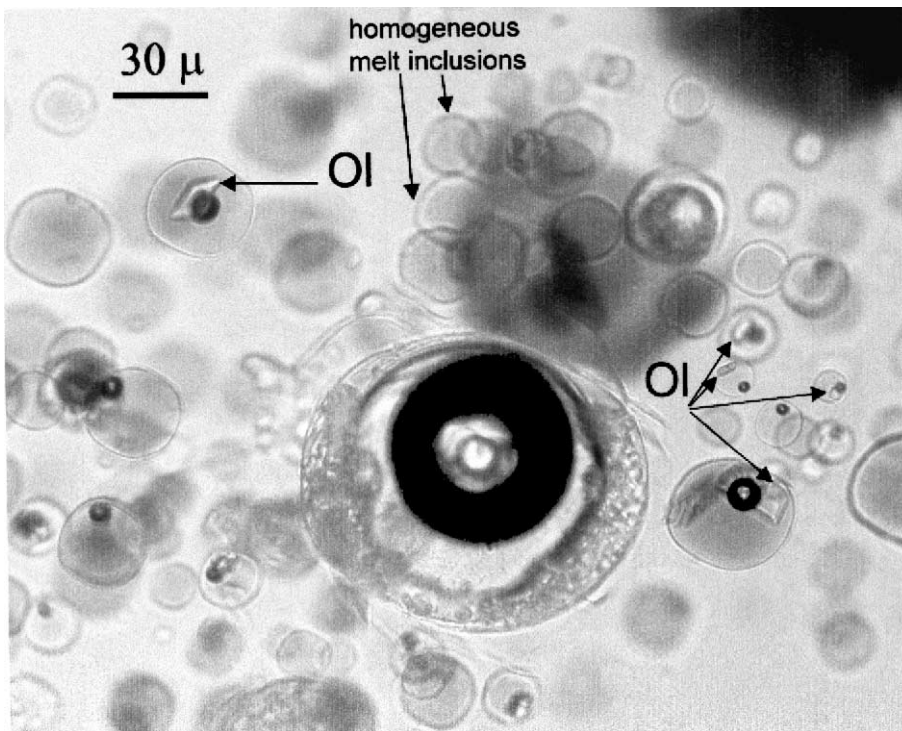

Fig. 4. Melt inclusions in plagioclase phenocryst P118 from MORB sample D9-1 (Gorda ridge) quenched from 1200 °C. Since most inclusions have homogenised at this temperature, it is considered the true trapping temperature of these inclusions. Several of the inclusions contain a large olivine crystal that would not melt at the inferred trapping temperature. These olivine crystals formed during the experiment as a result of recrystallisation of small olivine microlites initially present in all inclusions. The large air bubble in the centre formed in place of a melt inclusion that leaked during the experiment. See text for discussion.

to observe phase transformations within inclusions or to determine the appropriate duration/heating rate for the experiments.

If phase transformations cannot be observed, the presence of large olivine crystals inside some melt inclusions, as discussed above (this issue is taken as an example), may be interpreted as an indication that the inclusions were trapped at a higher temperature. Indeed, such olivine crystals have been observed in a number of studies of melt inclusions in MORB plagioclase which have used 1 atm vertical furnaces (e.g., Johnson et al., 1995) and have resulted in an overestimation of trapping temperatures (a detailed discussion of this issue is presented in McNeill, 1997).

A further consequence of the lack of visual control is that trapping temperatures cannot be obtained independently but must instead be inferred from the chemical and/or phase compositions of the melt inclusion after an experiment. In other words, the melt inclusions are forced into reacting with their host phenocryst which leads, as discussed above, to irreversible changes in inclusion composition and the loss of information about possible re-equilibration during natural cooling.

In contrast, homogenisation experiments performed under visual control will yield an independent estimate of the trapping temperature. Models of mineral–melt equilibrium can then be used to assess whether the composition of the homogenised melt inclusion is in equilibrium with its host at the conditions of the experiment. If they are in equilibrium, then the temperature of homogenisation is the true crystallisation temperature of the phenocryst as re-equilibration was prevented during the experiment.

Potentially, the trapped melt composition and trapping temperature may also be reconstructed from the composition of the residual melt (i.e., glass) inside inclusions using numerical modelling (e.g. Sobolev and Shimizu, 1993; Danyushevsky et al., 2000a; Gaetani and Watson, 2000). However, today this approach is accurate for olivine-hosted melt inclusions only, and the results are strongly dependent on the extent of mass exchange between the melt inclusion and its host and/or outside magma after trapping, and require knowledge of the oxidation state and volatile contents of the melt.

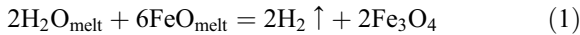# 3. Estimation of parental magma H_2O contents using melt inclusions

Melt inclusions in phenocrysts from mantlederived magmas have been recognised as a useful tool for studies of volatile contents of primary melts (e.g., Roedder, 1979; Metrich and Clocchiatti, 1989; Sobolev and Danyushevsky, 1994; Sobolev and Chaussidon, 1996; Sisson and Layne, 1993; Sisson and Bronto, 1998; Hauri, 2002). Isolated by the host at relatively high pressure, melt inclusions may preserve original, or less degassed, volatile contents when compared to the erupted magmas (e.g., Sobolev and Chaussidon, 1996; Sobolev, 1996). When efficient quenching during eruption converts the residual melt inside inclusions into glass with no shrinkage/fluid bubble, volatile contents can be measured without experimental reheating. If a shrinkage bubble is present in a glassy inclusion, an estimation of the volatile content is also possible, but the amount of volatiles in the bubble should be measured or calculated and added to the total volatile content (e.g. Sobolev et al., 1990; Anderson and Brown, 1993). However, efficient quenching is usually limited to samples from sea floor eruptions of relatively H_2O-poor magmas, and in general, experimental homogenisation of melt inclusions is required to recover trapped volatile contents.

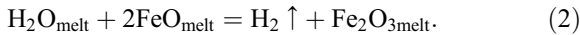## 3.1. H_2O loss during experimental reheating of melt inclusions

During reheating experiments, H_2O can be lost from melt inclusions by dissociation and hydrogen diffusion through the host crystal (Roedder, 1979; Sobolev et al., 1983; Sobolev and Danyushevsky, 1994). Diffusion occurs because experiments are performed in an inert atmosphere (to prevent oxidation at high temperatures) at a low hydrogen fugacity (to prevent reaction with the platinum heater). The relatively high pressures inside melt inclusions at high temperature (see above) results in a higher hydrogen fugacity within inclusions than in the inert atmosphere around the crystal even when the inclusions have low H_2O contents.

Sobolev et al. (1983) showed that during experiments with H_2O-bearing melt inclusions, a continuous increase in homogenisation temperature occurs when

an inclusion is kept at high temperatures (>1100 °C). This process is often accompanied by precipitation of magnetite inside an inclusion as described by the reaction:

$$2H_2O_{melt} + 6FeO_{melt} = 2H_2 \uparrow + 2Fe_3O_4 \qquad (1)$$

or at temperatures higher than magnetite stability,

$$H_2O_{melt} + 2FeO_{melt} = H_2 \uparrow + Fe_2O_{3melt}. \qquad (2)$$

These reactions are limited by the ability of the melt to oxidise, and as the main component of natural melts that can be oxidised is Fe^{2+}, the maximum amount of H_2O that may dissociate can be calculated:

$$H_2O(wt.\%) = 0.125 * C_{(FeO)}, \qquad (3)$$

where $C_{(FeO)} = $ wt.% FeO in the melt. For basaltic melts, the maximum amount of "lost" H_2O is therefore < 1 wt.%.

When the host mineral contains Fe^{2+}, it may potentially diffuse to the oxidised inclusion causing further dissociation of H_2O in excess of the amount predicted from Eq. (3). At temperatures higher than magnetite stability, this will result in an artificially high total Fe content of the inclusion (Sobolev, unpublished data). In some cases, hydrogen diffusion can cause oxidation not only of the melt inclusion but also of the host phenocryst (Roedder, 1979). These cases of extreme oxidation are readily detectable when inclusions are examined under the microscope and can be easily avoided.

The dissociation of H_2O in a melt inclusion increases the experimental homogenisation temperature in two different ways (Sobolev and Danyushevsky, 1994). First, the volume of melt is reduced due to loss of a component with large molar volume, thus decreasing pressure inside the melt inclusion, and second, the increase in the melting temperature of crystalline phases inside the melt inclusion. As discussed by Sobolev and Danyushevsky (1994), the effect of the reduction in melt volume is significant at low pressures (<2 kbar) and at high temperatures (>1100 °C) and can lead to a dramatic increase in homogenisation temperature. For small inclusions (~20 μm) the homogenisation temperature may increase by 150 °C during the first few minutes of an experiment (Fig. 3b). At higher pressures, this effect decreases, due to the volume reduction of H_2O in melt, and the second factor dominates. This latter factor is pressure-independent but is a function of the composition of the host mineral and the total amount of H_2O in the melt inclusion. If all the Fe in an olivine-hosted inclusion is oxidised (i.e., ~1 wt.% H_2O dissociates, Eq. (3)), and the initial H_2O content of the inclusion was 1 or 3 wt.%, then the effect will be to increase the homogenisation temperature by ~75 or ~15 °C, respectively (Falloon and Danyushevsky, 2000). The effect on plagioclase is expected to be significantly larger (Danyushevsky, in press).

As homogenisation temperature is highly sensitive to dissociation of H_2O, determining crystallisation temperatures from homogenisation experiments on H_2O-bearing melts is relatively difficult. However, several experimental studies (e.g., Sobolev et al., 1990; Sobolev and Danyushevsky, 1994) have shown that the use of heating rates, established from kinetic experiments, and optimal inclusion sizes, as discussed below, makes it possible to establish the temperature of crystallisation and the trapped melt composition with an accuracy close to that obtained for "dry" melts.

For each sample, the effect of H_2O dissociation on the homogenisation temperature can be estimated using kinetic experiments (Fig. 3b). An inclusion is heated rapidly (e.g., 100 °C/min) from 1100 °C until homogenisation is achieved. The temperature is then decreased to 1150–1200 °C and held for 15–30 min. The temperature is then decreased to 1100 °C and heating is repeated at the initial rate until homogenisation occurs. These steps are repeated until the homogenisation temperature becomes asymptotic (Fig. 3b). The effect of H_2O dissociation is clearly less for larger inclusions, and in general, inclusions as large as possible should be used for homogenisation experiments with H_2O-bearing magmas. As the lower viscosity of H_2O-bearing melts results in significantly faster kinetics of melting (Sobolev and Danyushevsky, 1994), the effect of H_2O dissociation on homogenisation temperature completely overrides the effect of melting rates inside the inclusions. A summary of appropriate experimentally determined heating rates for H_2O-bearing magmas is presented in Table 1. In general, melt inclusions from H_2O-bearing magmas should be kept at high temperatures for very short times (in order of minutes).

3.2. Changes of initial H_2O contents of melt inclusions after trapping and prior to natural quenching

Diffusion of hydrogen can affect H_2O contents of melt inclusions not only during experimental reheating but also in nature, both before and during eruption, a result of the differing hydrogen fugacity inside inclusions and in the surrounding magma.

As decreasing temperature causes crystallisation of melt inclusions, it also results in decreasing pressure inside the inclusions, because the liquidus minerals of basaltic melts (olivine, pyroxene and plagioclase) are denser than the melt (Niu and Batiza, 1991; Lange and Carmichael, 1987). Cooling in a magma chamber after trapping may thus result in a lower hydrogen fugacity inside inclusions and diffusion of hydrogen into the inclusions from the host magma, thus increasing the H_2O content of melt inclusions following the reverse of reaction (2). This reaction is limited by the ability of the melt to be reduced, and as Fe^{3+} is the main component of natural melts that can be reduced, the maximum amount of H_2O that may be formed is:

$$\Delta H_2O(wt.\%) = 0.113 * Fe_2O_3. \qquad (4)$$

As the Fe_2O_3 contents of natural magmas rarely exceed 1 wt.%, the amount of 'gained' H_2O is petrologically negligible.

Alternatively, if a magma rises without substantial cooling after an inclusion was trapped, then the pressure inside the inclusion will remain close to the pressure of trapping (as no significant crystallisation will occur). However, as the pressure on the host magma decreases, there will be a higher hydrogen activity within inclusions than in the host magma, a situation similar to that which occurs during homogenisation experiments (see above). In this case, hydrogen may diffuse out of the melt inclusions causing H_2O dissociation following reactions (1) or (2). A clear indication of this process is the appearance of magnetite 'dust' in some naturally quenched inclusions (Verbeeten, 1996). When magnetite 'dust' is not observed in inclusions, the loss of H_2O can be assumed to be negligible as magnetite stability is very sensitive to melt Fe_2O_3 content (Ariskin and Barmina, 1999), and the appearance of the magnetite 'dust' has been observed in homogenisation experiments with

virtually anhydrous ($H_2O \sim 0.1$ wt.%) reduced (fO_2 < quartz–fayalite–magnetite buffer) melt inclusions in MORB phenocrysts (Sobolev et al., 1988).

Under certain circumstances, e.g., when melt inclusions in olivine have undergone significant Fe loss resulting from prolonged cooling (as discussed by Danyushevsky et al., 2000a), magnetite "dust" may be prevented from forming due to low melt Fe contents, even when a significant amount of H_2O has been dissociated. In such a case, it may therefore not be obvious that H_2O has been lost. However, the D/H values of melt inclusions are a potential indicator of hydrogen diffusion, as hydrogen diffuses faster than deuterium, and therefore higher D/H values may indicate H_2O loss (Hauri, 2002). In general, two characteristics of inclusions that have undergone extensive Fe loss make it unlikely that significant H_2O will also have been lost. First, the low Fe contents (in some cases as low as 3 wt.%; Danyushevsky et al., 2000a) will reduce the oxidation potential of the inclusion; and second, prolonged cooling will lead to extensive crystallisation of the inclusion, reducing the pressure inside the inclusion and making H_2O gain more likely (as discussed above) than H_2O loss.

Qin et al. (1992) demonstrated that on geological time scales, H_2O can be lost from inclusions by diffusion of molecular H_2O through the host crystal. Diffusion can happen when the phenocryst which trapped the inclusion at high pressures is retained in a low-pressure magma chamber as the host magma degasses. This process is difficult to detect as it does not result in oxidation and the formation of magnetite in melt inclusions. However, Qin et al. (1992) also demonstrated that the diffusion of H_2O is significantly slower than the diffusion of major elements in the host phenocryst. Therefore, any significant loss of H_2O must be preceded by the re-equilibration of the host phenocryst with the more evolved, degassed magma. However, re-equilibration of phenocrysts is usually not observed in primitive mantle-derived magmas, as numerous studies have reported original primitive phenocryst compositions (e.g., Eggins, 1993, their Table 10; Sobolev, 1996; Sobolev and Chaussidon, 1996). Molecular H_2O diffusion is more likely to occur in melt inclusions of more evolved andesite–dacite–rhyolite melts where the long residence time of phenocrysts in magma chambers is well-documented (e.g., Christensen and DePaolo, 1993).

It is therefore unlikely that any petrologically significant amount of H_2O will have been lost or gained by melt inclusions, after trapping and prior to natural quenching, if magnetite 'dust' is not present in the naturally quenched inclusion. The general representativeness of the H_2O contents of melt inclusions that were homogenised using optimal experimental conditions can be demonstrated by their correlation with other petrological parameters (e.g., Danyushevsky et al., 1995, 1997; Sobolev and Chaussidon, 1996). However, some of the processes described above can lead to geochemically significant changes in the H_2O content of melt inclusions, i.e., the H_2O/(incompatible element) values of melt inclusions can be significantly different from those of the trapped liquid. For example, discrepancies between the H_2O/K_2O values of melt inclusions and pillow-rim glasses in depleted MORB from the Mid-Atlantic Ridge have been reported by Sobolev (1996) and Kamenetsky et al. (1998).

3.3. General aspects of melt inclusion studies aimed at recovering H_2O content of primary mantle-derived magmas

Consider a melt formed in the mantle under H_2O-undersaturated conditions (Fig. 5, point 1). The slowest possible thermodynamic ascent rate for this melt that will not cause compositional changes is defined by the pressure dependence of the olivine liquidus (~ 5 °C/kbar, Ford et al., 1983; path 1–2, Fig. 5). If the rate of ascent is thermodynamically slower (i.e., it cools faster than 5 °C/kbar), the melt will start to crystallise. Point 2 (Fig. 5) indicates the minimum depth that this melt can reach without changing its composition, as at this pressure, the melt will be H_2O-saturated and any further ascent will cause degassing and crystallisation. However, the actual ascent rates of mantle-derived magmas are believed to be ~ 3 °C/kbar (Nisbet, 1982) corresponding to the adiabat of a high Mg liquid (path 1–3, Fig. 5), and point 3 represents the minimum depth that such a melt can reach without degassing. The grey envelope 1–2–3 (Fig. 5) thus represents the P–T range where a melt can exist without any changes in its initial composition. Note that at any temperature above line 1–2 on Fig. 5, the melt is overheated, i.e., its temperature is higher than its liquidus temperature for a given pressure, and
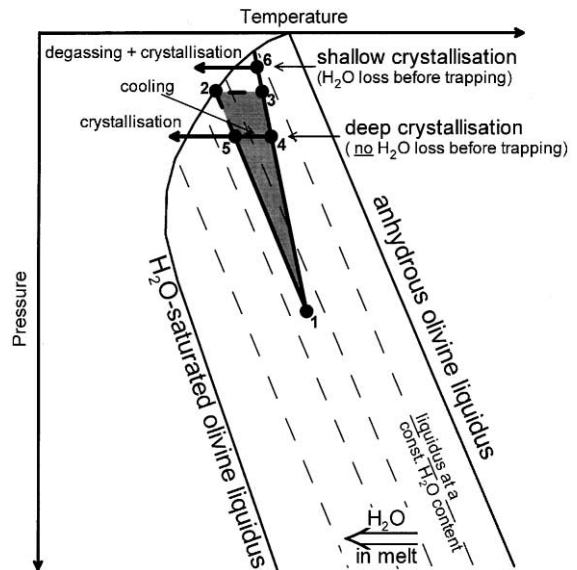

Fig. 5. Diagram illustrating the two end-member cases of crystallisation of a melt formed in the mantle under H_2O-undersaturated conditions. The effect of H_2O on olivine liquidus is from Falloon and Danyushevsky (2000) and references therein. 1 Represents the point of melt generation in the mantle; path 1–2— melt ascent along olivine liquidus (~ 5 °C/kbar); path 1–6— melt ascent along an adiabat (~ 3 °C/kbar); grey envelope 1–2–3— the P–T range where the melt can exist without changing its initial composition including its H_2O content; level 2–3— the minimum depth which the melt can reach without degassing; path 4–5—a case of deep crystallisation that proceeds initially without degassing at a depth where the melt is undersaturated in H_2O; path 6— a case of shallow crystallisation that commences after initial degassing. See text for discussion.

cooling at a constant pressure will not cause immediate crystallisation.

Two end-member cases of crystallisation of a mantle-derived melt are shown on Fig. 5. Deep crystallisation (point 4, Fig. 5) refer to crystallisation at pressures higher than the saturation pressure for the initial melt H_2O content (point 2, Fig. 5), whereas shallow crystallisation occurs at pressures less than the saturation pressure for the initial H_2O content (point 6, Fig. 5).

In the case of deep crystallisation, when melt ascent is interrupted (point 4, Fig. 5), cooling occurs at a constant pressure and crystallisation will begin when the melt reaches its liquidus (point 5, Fig. 5). As crystallisation proceeds under H_2O-undersaturated conditions, no H_2O loss will occur along path 4–5

(Fig. 5) and a melt inclusion trapped by the first most magnesian olivine phenocryst that crystallises will preserve the H_2O content of the primary melt (point 1, Fig. 5). If the first liquidus olivine did not trap any melt inclusions, or was not recovered in the studied samples, the H_2O content of the primary melt can be confidently estimated from melt inclusions in near liquidus olivine phenocrysts (formed at temperatures below point 5 along path 4–5, Fig. 5). This is because the rate of olivine crystallisation for high Mg melts is ~ 1% per 8 °C temperature drop (Ford et al., 1983), and thus changes in melt H_2O content caused by olivine-only crystallisation over ~ 40 °C (~ 5%) are within analytical uncertainties.

In the second case, i.e., shallow crystallisation at pressures less than the saturation pressure at the initial H_2O content (point 6, Fig. 5), adiabatic ascent over 10 kbar (for example) results in overheating of the melt by ~ 20 °C (see above). If such a melt becomes H_2O saturated, degassing will not cause immediate crystallisation and some H_2O may be lost before crystallisation begins. Due to the non-linear effect of H_2O on olivine liquidus temperature (Falloon and Danyushevsky, 2000), the amount of lost H_2O will depend on the initial H_2O content of the melt. For example, if the initial H_2O content was 1 wt.%, then 20 °C overheating will result in 0.6 wt.% H_2O loss prior to crystallisation. However, if the initial melt H_2O content was 4 wt.%, the same overheating will result in 1.6 wt.% H_2O loss (see Falloon and Danyushevsky, 2000). As low-pressure crystallisation is often accompanied by degassing (i.e., degassing does not stop when crystallisation begins; e.g., Danyushevsky et al., 1995), it is vitally important to identify the most magnesian olivine that crystallised from the melt and to analyse the H_2O contents of its melt inclusions. In contrast to the case of deep crystallisation, a failure to identify the composition of the first liquidus olivine can lead to a substantial underestimation of the initial melt H_2O content. If the H_2O content at the onset of crystallisation is known, a correction for degassing before crystallisation began can be estimated from (1) the major element composition of the primary melt, to determine the pressure of melting (Falloon and Danyushevsky, 2000), and (2) an assumed ascent rate of the melt from the depth of melting to the depth of crystallisation, to estimate overheating.

The pressure of crystallisation can be estimated if both the H_2O and CO_2 contents of the melt are known (Dixon et al., 1995). For a fluid-saturated melt, increasing CO_2 content, at a given H_2O content, corresponds to increasing pressure. Alternatively, crystallisation pressure can be estimated from the composition and/or density of primary fluid inclusions in phenocrysts (e.g., Roedder, 1984). In general, a high proportion of H_2O in the fluid indicates low-pressure crystallisation, whereas a high proportion of CO_2 indicates high-pressure crystallisation (see Dixon et al., 1995 for the effect of CO_2 on H_2O solubility).

4. Effect of Fe loss by melt inclusions in olivine phenocrysts on sulphur solubility and oxidation state

As discussed above, the re-equilibration of melt inclusions with their host during natural cooling results in changes in inclusion compositions. An example of such re-equilibration is the Fe loss suffered by some melt inclusions in olivine (e.g., Sobolev, 1983; Sobolev and Danyushevsky, 1994), described in detail by Danyushevsky et al. (2000a). In brief, most melt inclusions in magnesian olivine phenocrysts (generally $> Fo_{85}$) from subduction-related and within-plate lavas have a significantly lower FeO content and a higher
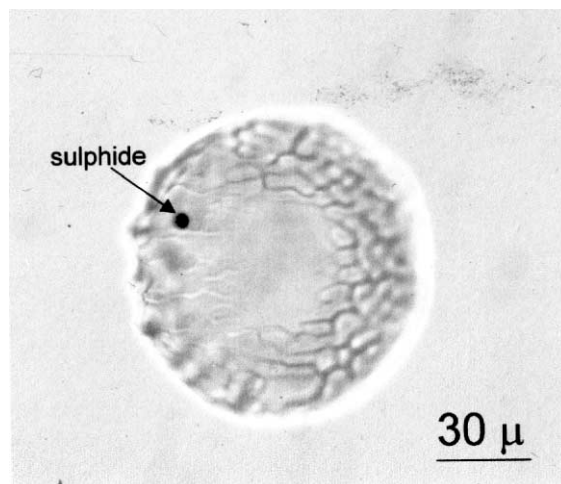

Fig. 6. Sulphide globule in a homogenised melt inclusion in an olivine phenocryst from MORB (southern Mid-Atlantic Ridge, Kamenetsky, unpublished).

MgO content than the originally trapped melt. Low FeO contents are less common in MORB and back-arc basin basalts.

Many homogenised melt inclusions in OIB and MORB olivine phenocrysts, which have experienced Fe loss, contain small sulphide globules (Fig. 6), the size of which is proportional to the size of the melt inclusions in a given sample (Gurenko et al., 1987; Metrich et al., 1999). In some cases, such globules are observed in naturally quenched melt inclusions (Sobolev, unpublished data). Despite clear indications that the sulphide is a daughter phase (e.g., proportionality of size), the globules will not melt even after homogenisation of an inclusion (i.e., melting of microlites and dissolution of the gas/shrinkage bubble).

The sulphide globules are a consequence of Fe loss, rather than indicating sulphide saturation of the trapped melt, or changes in the fO_2 or H_2O content after trapping (Gurenko et al., 1987; Metrich et al., 1999). As sulphur solubility is strongly dependent on the Fe content of a melt (Wallace and Carmichael, 1992); decreasing the Fe content of a melt inclusion may lead to sulphur saturation and exsolution of the sulphide globule. This also results in artificially low melt sulphur contents within such inclusions.

Moreover, as an olivine is unlikely to buffer the oxidation state of any melt inclusion it hosts (as indicated by commonly observed H_2O loss from inclusions, see above), Fe loss will lead to a higher oxidation state (i.e., higher Fe^{3+}/Fe^{2+} values) for
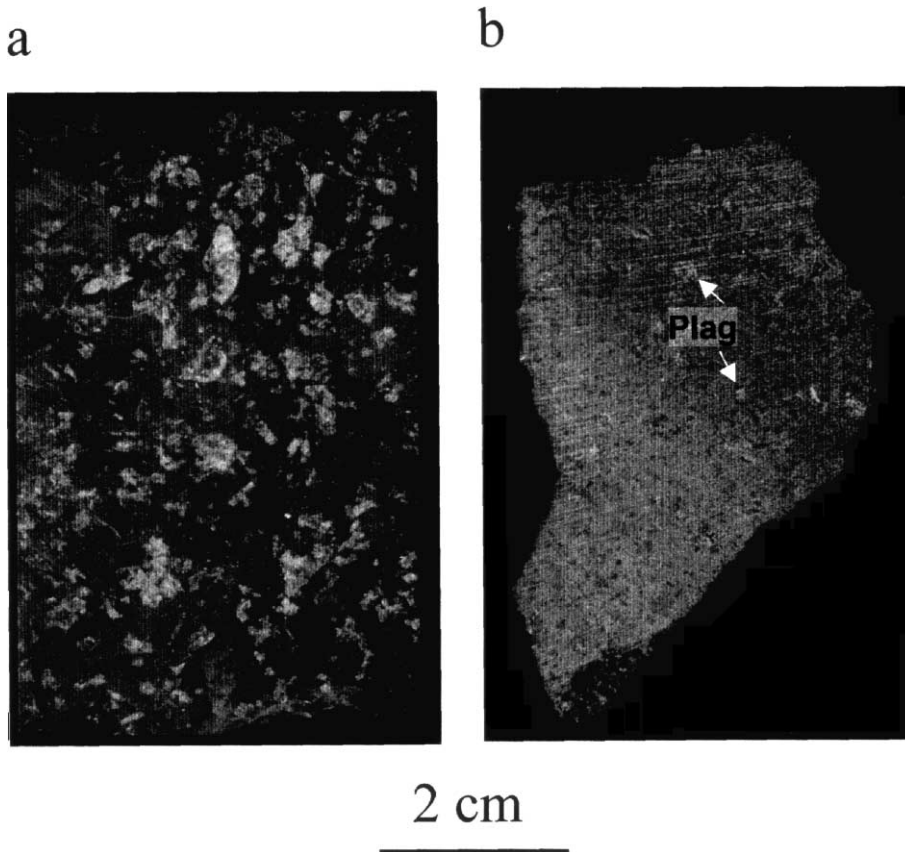

Fig. 7. (a) A typical example of a plagioclase-phyric MORB (sample MW8801-D5-2, Australia–Antarctic Discordance, Southern Ocean). Note obvious accumulation of plagioclase, i.e. the composition of this sample does not represent the melt composition being enriched in plagioclase components. (b) Sample 5-2-5 from ODP Hole 896A. Note a small size of plagioclase phenocrysts and the lack of any significant plagioclase accumulation. See text for discussion.

the melt inclusions. This will in turn affect the oxidation state of sulphur in inclusions, and therefore, the S^{2-}/S^{6+} values of melt inclusions in olivine, for which the extent of Fe loss has not been constrained (e.g., Metrich and Clocchiatti, 1996; Gurenko and Schmincke, 2000), should be treated with care.

Another consequence of Fe loss is reported by Sobolev (1983). Since Fe/Mg values of the affected inclusions are significantly lower, this increases stability of Fe−Mg daughter phases inside inclusions. Clinopyroxene in melt inclusions in olivine from Siberian meimechites melts at 100 °C higher temperatures than is observed in the macro-system. Thus, melting temperatures of clinopyroxene inside inclusions affected by Fe loss cannot be used as an indicator of the cotectic relationships in the macro system.

5. Some examples of poorly understood reequilibration processes or trapping of non-representative compositions

A number of studies of plagioclase phenocrysts from MORB have described melt inclusion compositions that are more primitive (i.e., more MgO-rich) than pillow-rim glasses from the studied area (Sobolev et al., 1988; Sinton et al., 1993; Nielsen et al., 1995; Sours-Page et al., 1999). These studies report a number of features (e.g., a range of TiO_2 contents at a given MgO content) that are not seen in more evolved pillow-rim glasses. It is possible to reconcile these observations by invoking intensive mixing of a variety of primitive magmas prior to the eruption that transported the plagioclase phenocrysts to the surface
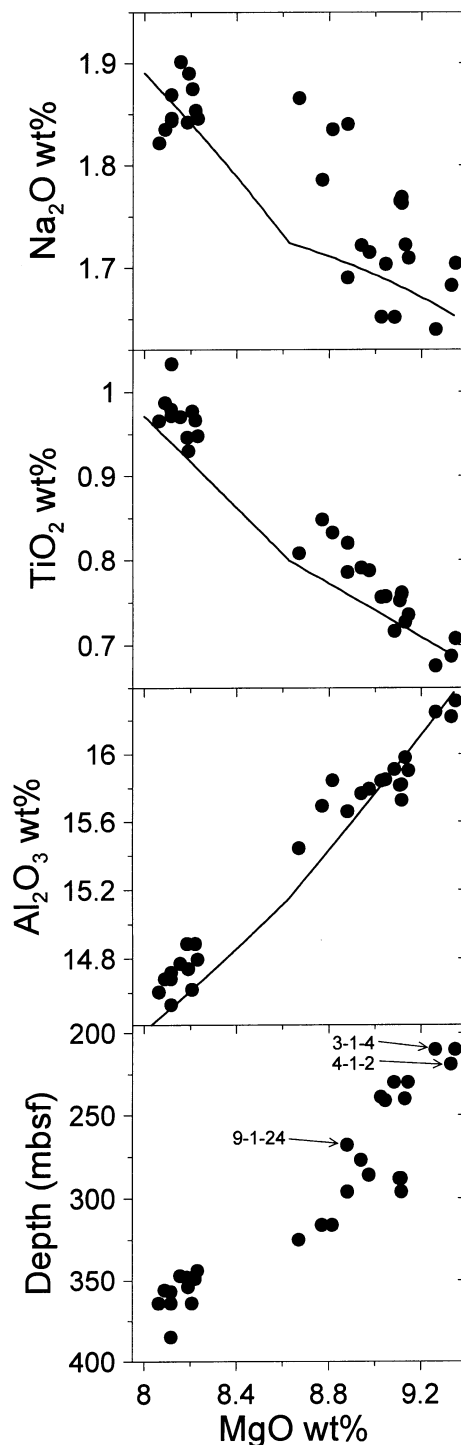

Fig. 8. Compositions of pillow-rim glasses from ODP Hole 896A (McNeill and Danyushevsky, 1996). Glasses from samples used in the melt inclusion study are identified on the lower plot. Solid lines show a fractionation trend calculated from the average most primitive glass composition. Calculations were carried out using the model of Danyushevsky (in press) assuming crystallisation pressure of 0.05 GPa, melt Fe^{2+}/Fe^{3+} value of 11, and the olivine + plagioclase cotectic nature of the starting composition. At these conditions, clinopyroxene appears on the liquidus at ∼ 8.6 wt.% MgO as can be seen by the inflection on the trend. The figure demonstrates that glass compositions from this Hole closely follow an olivine + plagioclase ± clinopyroxene fractionation trend. See text for discussion.

and produced the more evolved pillow-rim glasses. However, it is important to consider if the studied melt inclusion compositions are representative of the melt composition at the time of trapping. We can address this problem by studying melt inclusions with compositions within the range covered by pillow-rim glasses (McNeill and Danyushevsky, 1996). In a suitable suite of samples, the compositions of pillow-rim glasses must form a well-defined liquid line of descent (to enable comparison with melt inclusion compositions), and the samples must not have undergone extensive plagioclase accumulation. The latter is important as, if accumulation had occurred (Fig. 7a), it can be argued that phenocrysts present in the rock crystallised from a different melt than that represented by the pillow-rim glasses and thus the compositions of melt inclusions will not match the compositions of the glasses.

The criteria outlined above are satisfied by MORB samples from ODP Hole 896A (McNeill and Danyushevsky, 1996). Samples from this hole underwent no plagioclase accumulation (Fig. 7b) and it cannot be argued that phenocrysts found in these rocks crystallised from a different melt. The compositions of glasses recovered from 200 to 400 mbsf follow a fractionation trend formed by low-pressure cotectic crystallisation of olivine and plagioclase with clinopyroxene joining the liquidus at $\sim$ 8.5 wt.% MgO (Fig. 8).

Homogenisation experiments were carried out with melt inclusions in plagioclase phenocrysts from three samples (Fig. 9) and yielded homogenisation temperatures in the range 1195–1215 °C (see McNeill and Danyushevsky, 1996 and McNeill, 1997 for a detailed description of experimental procedures and results). As the H_2O contents of these glasses are known (McNeill and Danyushevsky, 1996), their crystallisation temperature can be accurately estimated assuming olivine and plagioclase saturation (Danyushevsky, in press). Calculated olivine- and plagioclase–melt equilibrium temperatures, for the most evolved and most

primitive glasses range from 1182 to 1213 °C and from 1179 to 1217 °C, respectively, consistent with the range of experimental homogenisation temperatures.
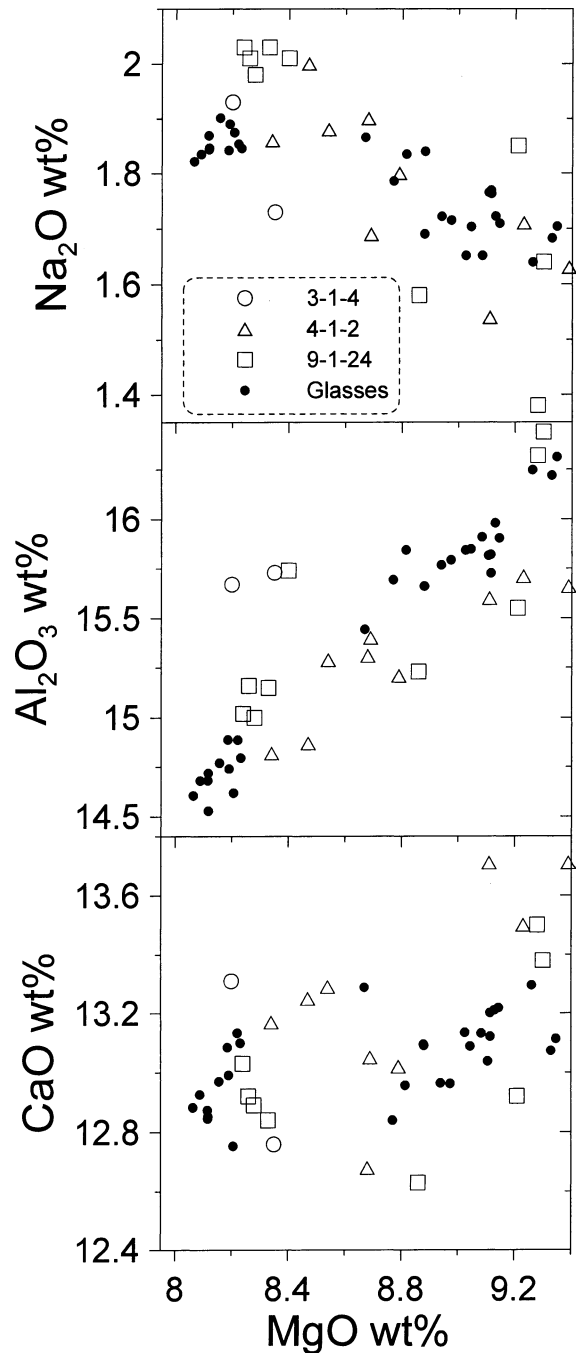

Fig. 9. Comparison of compositions of homogenised melt inclusions in plagioclase phenocrysts with glasses from MORB samples from ODP Hole 896A. Melt inclusions from different samples are shown with different symbols. Glasses from samples used in melt inclusion studies are identified on Fig. 8. Note the good correspondence between compositions of glasses and homogenised melt inclusions for MgO, CaO, Al_2O_3, and Na_2O. See text for discussion.

As can be expected, the MgO contents of the homogenised melt inclusions are similar to those of glasses, as are the CaO, Al_2O_3, and Na_2O contents (Fig. 9). There is also a good correlation between the MgO and Na_2O contents of the melt inclusions and the compositions of their host plagioclase (Fig. 10).

All the foregoing observations indicate that plagioclase phenocrysts crystallised along the liquid line of descent represented by glasses, however, the TiO_2 contents of the homogenised melt inclusions are systematically lower than those along the glass trend, as are their FeO^* contents (Fig. 11). The lower TiO_2 and FeO^* content of the melt inclusions are matched by higher SiO_2 contents (Fig. 11). These compositional variations do not result from processes occurring during the homogenisation experiments, as naturally quenched glassy melt inclusions in plagioclase phenocrysts from these samples also have low TiO_2 contents (McNeill and Danyushevsky, 1996).

Anomalously low TiO_2 and FeO^* contents of melt inclusions in plagioclase phenocrysts are a common feature of MORB. Plagioclase phenocrysts A27-PL8 from sample D9-1 (Gorda Ridge) contains several naturally quenched glassy melt inclusions (Table 2). The phenocryst is not zoned, as can be seen from the low standard deviation of the average host composition for seven melt inclusions (Table 2). The glass compositions have low Al_2O_3 and high MgO contents, a result of plagioclase crystallisation on the walls of the inclusion after trapping. The trapped liquid composition was therefore estimated by modelling the reverse of plagioclase crystallisation on the walls of the inclusions until the composition reached an olivine + plagioclase cotectic (see Danyushevsky et al., 2000a for methods used to calculate the reverse of crystallisation).

Plagioclase phenocryst A27-PL8 also hosts an inclusion of spinel that in turn contains melt inclusions. It is reasonable to assume that plagioclase and spinel crystallised from a single melt and thus melt inclusions in both minerals are expected to have the same composition. The average composition of the melt inclusions in spinel, corrected for Cr interference during microprobe analysis, is shown in the lower part of Table 2. The melt inclusions in plagioclase have substantially lower TiO_2 contents than the inclusions in spinel, and also have lower FeO contents, however, the MgO, Na_2O, CaO and K_2O contents of inclusions
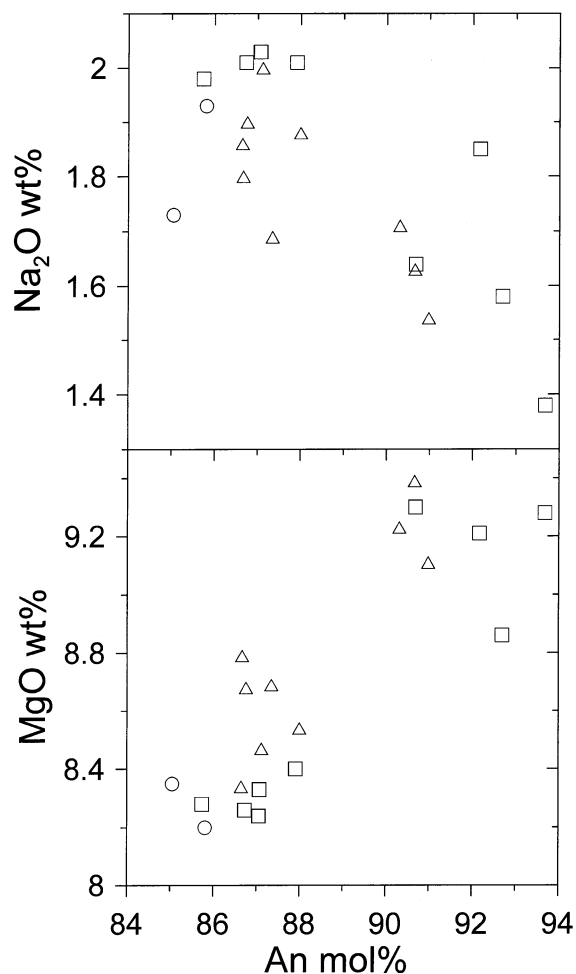

Fig. 10. Correlation between compositions of homogenised melt inclusions and their host plagioclase phenocrysts for samples from ODP Hole 896A. Melt inclusions from different samples are shown with different symbols. Symbols as on Fig. 9. Host plagioclase was analysed at 20–30 μm from the inclusions. See text for discussion.

in both minerals are similar. The lower Al_2O_3 contents in inclusions in spinel most likely indicate re-equilibration of these inclusions with their host.

The pillow-rim glasses from Gorda Ridge samples are significantly more evolved than the compositions of melt inclusions in high-An plagioclase (Nielsen et al., 1995; McNeill, 1997)) and thus a direct comparison with the melt inclusions is not possible. However, if the sample D9-1 pillow-rim glass composition (Table 2) is recalculated along an olivine-plagioclase

cotectic to an MgO content similar to that of melt inclusions, the TiO_2 content of the recalculated glass is similar to that of the melt inclusions in spinel, but is

significantly higher than in the inclusions in plagioclase (see Danyushevsky et al., 2000b for the principles of modelling the reverse of cotectic crystallisation of olivine + plagioclase ± clinopyroxene).

The two examples described above make us confident that low Ti and Fe and high Si contents of homogenised melt inclusions in plagioclase from MORB do not reflect the composition of the host magma and cannot be used to infer petrological processes. We see two possible explanations for these anomalies. Firstly, they may reflect a re-equilibration of the melt inclusions with their hosts during cooling and before eruption (similar to the Fe loss by inclusions in olivine, Danyushevsky et al., 2000a), whereby Fe and Ti diffuse from melt inclusions into the host plagioclase and Si diffuses from the host into the melt inclusions. At the moment, we are unable to provide either a reason or a direct evidence for such re-equilibration. However, an indirect evidence of lower Fe contents, than were trapped, in the homogenised melt inclusions is the common appearance of small sulphide globules, similar to those observed in inclusions in olivine (see Section 4 above). These globules are not observed in naturally quenched glassy melt inclusions and appear during the experiments at high temperatures. As in the case with melt inclusions in olivine, these globules do not disappear when melt inclusions homogenise. The absence of these globules in naturally quenched melt inclusions is explained by high Fe contents in the residual melt inside them, a result of plagioclase crystallisation on the walls of these inclusions. As MORB magmas are saturated in sulphur (Wallace and Carmichael, 1992), only a small decrease in melt Fe content (Fig. 11) is sufficient to form a sulphide globule.

An alternative explanation for the low Ti contents is provided by Michael et al. (2002) who suggested that melt inclusions are trapped by plagioclase in a continuous cycle of growth and dissolution, similar to
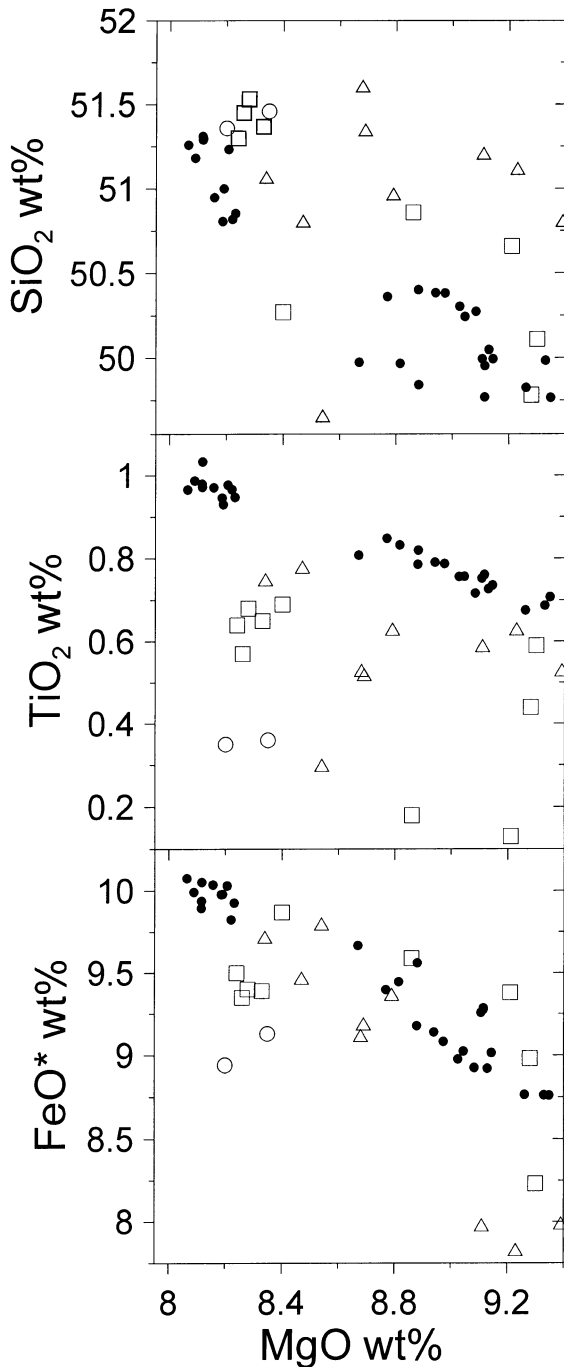

Fig. 11. Comparison of compositions of homogenised melt inclusions in plagioclase phenocrysts with glasses from MORB samples from ODP Hole 896A. Melt inclusions from different samples are shown with different symbols. Symbols as on Fig. 9. Glasses from samples used in melt inclusion studies are identified on Fig. 8. Note large differences between compositions of glasses and homogenised melt inclusions for SiO_2, TiO_2, and FeO^*. See text for discussion.

Table 2

Compositions of melt inclusions in plagioclase phenocrysts A27-PL8 from MORB sample D9-1, Gorda Ridge

	Naturally quenched glassy inclusions in plagioclase		Naturally quenched glassy inclusions in spinel included in plagioclase		Pillow-rim glass of sample D9-1
	Average of 7	S.D.	Average of 2	S.D.	
SiO_2	50.64	0.15	49.44	0.01	50.94
TiO_2	0.33	0.11	0.78	0.05	1.26
Al_2O_3	14.01	0.35	15.93	0.67	15.43
FeO^*	8.42	0.30	8.18	0.55	9.53
MnO	0.16	0.02	0.15	0.03	0.13
MgO	11.96	0.45	9.99	0.43	8.17
CaO	12.67	0.25	12.98	0.69	12.15
Na_2O	1.70	0.08	1.74	0.24	2.31
K_2O	0.03	0.01	0.03	0.01	0.06
Cr_2O_3	0.07	0.03	0.79	0.01	0.03
Host An mol%	92.3	0.42	93.7		
Compositions corrected for fractionation					
SiO_2	49.94	0.20	50.56	0.03	49.18
TiO_2	*0.27*	0.09	*0.79*	0.05	*0.86*
Al_2O_3	17.65	0.44	15.50	0.68	18.15
FeO^*	6.95	0.27	8.02	0.57	7.75
MnO	0.13	0.02	0.15	0.04	0.11
MgO	9.81	0.21	9.81	0.44	9.77
CaO	13.46	0.14	13.28	0.71	12.11
Na_2O	1.70	0.08	1.78	0.24	2.01
K_2O	0.03	0.01	0.03	0.01	0.04
Cr_2O_3	0.06	0.03	0.10	0.00	0.03

the mechanism proposed by Nakamura and Shimakita (1998). In this case, the melt composition surrounding plagioclase after a dissolution phase can be enriched in plagioclase components and depleted in other components, including Ti and Fe. The ability of the melt surrounding a plagioclase phenocryst to recover its original composition will depend on the diffusion coefficients of relevant elements in silicate magmas, and as Ti is expected to diffuse slowly, its concentration in melt inclusions in plagioclase may be low.

In summary, homogenisation experiments with melt inclusions in MORB plagioclase phenocrysts can provide reliable estimates of crystallisation (trapping) temperature and the MgO, Al_2O_3, CaO, Na_2O, and K_2O contents of the host magma at the moment of trapping. However, the concentrations of TiO_2, FeO^*, and SiO_2 in homogenised inclusions do not reflect the composition of the host magma. An important con-

clusion from these results is that Mg# of melt inclusions in MORB plagioclase, widely believed to be unaffected by post-entrapment modification and often used to assess the degree of fractionation of the trapped melts (e.g., Nielsen et al., 1995; Sours-Page et al., 1999), are in fact, not representative of the melt composition at the time of trapping.

A detailed analysis of the processes affecting the compositions of melt inclusions in spinel is beyond the scope of this paper. However, our preliminary results on spinel from MORB, indicate that in general, concentrations of TiO_2, Na_2O, K_2O in homogenised or naturally quenched glassy inclusions reflect the composition of the host magma (McNeill, 1997). At the same time, FeO^*, Al_2O_3, CaO, SiO_2, and MgO contents do not always reflect the composition of the host magma, and the behaviour of these elements varies between samples.

Due to the opaque nature of the host mineral, studies of melt inclusions in spinel are prone to additional complications. During reheating experiments, melting of any accidentally trapped phases can modify the initially trapped melt composition. The compositions of naturally quenched glassy melt inclusions can be affected by crystallisation on the accidentally trapped phases or by crystallisation of daughter phases, both may not be easily identified if they are not present on the opened plane of a sample. Both effects have been identified in melt inclusions in spinel from MORB (McNeill, 1997).

6. Conclusions

Melt inclusions in phenocrysts are potentially a powerful tool in petrological research that can provide the only direct information available on the physical parameters (*P*, *T* and melt composition) of crystallisation at various stages in the evolution of magmatic systems. However, melt inclusions also differ in principle from other parts of the magmatic system in that their composition, after trapping, may be controlled by the composition of the host phenocryst and therefore the direct application of our understanding of macro-scale magmatic processes to the interpretation of melt inclusion data can lead to erroneous conclusions. Our results indicate that the compositions of melt inclusions in early formed phe-

nocrysts (olivine, pyroxene, plagioclase and spinel), often of most interest in petrological studies, can be affected by processes such as volatile dissociation, oxidation and/or partial re-equilibration with their host, both during natural cooling and homogenisation experiments. In particular, melt inclusions in all minerals are prone to hydrogen diffusion into or out of the inclusions after trapping and prior to eruption, and during homogenisation experiments. If not taken into account, this can significantly affect the crystallisation temperatures derived from the homogenisation experiments. Melt inclusions in high-magnesian olivine phenocrysts commonly have lower Fe contents compared to the initially trapped composition. This often leads to the appearance of sulphide globules, and in some cases, high-magnesian clinopyroxene daughter crystals, and may cause an increase in the oxidation state of the inclusions. Homogenised melt inclusions in plagioclase phenocrysts in MORB usually have lower Ti and Fe, and higher Si contents compared to the melt composition at the moment of trapping. However, homogenisation experiments can provide reliable estimates of trapping temperature and the MgO, Al_2O_3, CaO, Na_2O, and K_2O contents of the host magma at the moment of trapping.

Some of these processes can be identified by observing the behaviour of melt inclusions during homogenisation experiments using low-inertia visually controlled heating stages, and their effects can be minimised by using appropriate experimental conditions as determined by kinetic experiments, ideally completed for each phenocryst type in every sample.

The recent literature on melt inclusions is heavily biased toward the interpretation of the melt inclusion compositional data, whereas understanding the process affecting inclusion compositions after trapping receives very little attention. There is a clear need for this situation to change.

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