

# High-temperature experiments on silicate melt inclusions in olivine at 1 atm: inference on temperatures of homogenization and H<sub>2</sub>O concentrations

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## Abstract

A series of heating stage experiments, at ambient atmosphere and high temperature, were conducted in order to detail the change in the homogenization temperature and the behavior of H<sub>2</sub>O of melt inclusions in olivine phenocrysts (Fo<sub>82–89</sub>). The samples were collected at different volcanic sites (Piton de la Fournaise [PdF], Réunion Island; Stromboli, Aeolian Islands; FAMOUS zone) expected to have a range of magmatic water contents. The melt inclusions vary in composition from basaltic to shoshonitic, with H<sub>2</sub>O content from 0.14 to 2.9 wt.%. Temperatures of homogenization ( $T_h$ ) of melt inclusions systematically increase with time during heating experiments, regardless of their major element composition and their H<sub>2</sub>O. It is proposed that  $T_h$  changes with time in response to the deformation of the host crystal and change in the volume of the cavity. The FTIR spectra successively acquired on the same inclusion repeatedly heated at constant temperature clearly demonstrated that the relative absorbance ( $Abs_n/Abs_0$ ) measured at 3535 cm<sup>-1</sup> corresponding to hydroxyl group and molecular H<sub>2</sub>O decreases with time. The H<sub>2</sub>O-rich melt inclusions may have lost from 20% to 80% H<sub>2</sub>O after the first homogenization and almost total dehydration of melt inclusions may occur within few hours or less, at 1 atm. Water loss driven out of olivine-hosted melt inclusions possibly exists to some extent in natural large dunitic bodies or in mantle xenoliths. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Silicate melt inclusions; Olivine; Homogenization

## 1. Introduction

Melt inclusions in olivine offer the opportunity to assess temperatures of entrapment, major and trace element compositions, and pre-eruptive volatile abundance of magmas from mantle depths to the surface.

Over the last 10 years, the interest for basaltic melt inclusions in primitive olivine crystals [ $Mg/(Mg + Fe) > 0.80$ ] has been growing, particularly to estimate the volatile content of magmas in hot-spot (Anderson, 1974; Sobolev and Nikogosian, 1994; Wallace, 1998; Bureau et al., 1998a,b; Sobolev et al., 2000), and subduction-related volcanoes (Sobolev et al., 1993; Sobolev and Danyushevsky, 1994; Sobolev and Chaussidon, 1996; Kamenetsky et al., 1997; Roggensack et al., 1997; Sisson and Bronto, 1998; Métrich et al., 2001) among others. However, precipitation of the

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host olivine on the inclusion walls is commonly described in naturally quenched glassy basaltic inclusions, and the extent of olivine growth may approach 10–12% (Anderson, 1974; Sisson and Layne, 1993; Sobolev et al., 1993). Depending on the cooling rate, MgO and H<sub>2</sub>O-rich basaltic melt inclusions may partially crystallize to an extent that necessitates heating stage experiments prior to any analytical investigation. High-temperature treatment of melt inclusions, either to estimate the temperature of entrapment or to get homogenized inclusions, may cause irreversible chemical or textural changes, possibly water loss, and over-estimation of homogenization temperature (Sobolev et al., 1983; Kamenetsky et al., 1997; Bureau et al., 1998a,b; Gioncada et al., 1998), particularly for water-rich melt compared to the dry systems (Sobolev et al., 1993).

In the present work, different heating stage experiments were conducted and systematic infrared spectra were acquired before and after heating treatments at 1 atm on glassy basaltic inclusions hosted in olivine grains, in order to determine whether the temperature of homogenization ( $T_h$ ) is a function of the initial water concentrations dissolved in the trapped melt, and whether it is related to the water loss during 1 atm heating-stage experiments. The starting inclusions were carefully selected to be preserved as glass and representative of low pressure basaltic melts with variable concentrations in H<sub>2</sub>O. The possible implications for natural systems are evaluated.

## 2. Sample description

The olivine grains used in this study were collected from the lapilli levels at Piton de la Fournaise (PdF) volcano in Réunion Island (P. Vincenzo pyroclastic cone, sample PF92-17), at Stromboli in the Aeolian island arc (lower deposits of Vancori sequence, sample Str94-5), and from submarine basalts from the FAMOUS zone on East Atlantic Ridge (sample ARP10.03). The starting inclusions were selected to have basaltic compositions, with variable H<sub>2</sub>O concentrations from one sample set to the other. All of them have been preserved as glass inclusions because of rapid natural cooling rate.

The PdF olivines (Fo<sub>83–84</sub>) display one or several inclusions, whose largest dimension is between 80

and 100  $\mu\text{m}$ , rarely 150  $\mu\text{m}$ . They contain only glass, or glass associated with mechanically trapped spinel (Fig. 1A,B). The largest inclusions have a bubble, with a ratio between the volume of the bubble and that of the whole cavity ( $V_b/V_{\text{incl}}$ ) close or less than  $1 \times 10^{-2}$ . In Stromboli olivines (Fo<sub>83–84</sub>), the inclusions commonly form clusters and their size vary between 100 and 120  $\mu\text{m}$  (Fig. 1C,D). A bubble is always present with a  $V_b/V_{\text{incl}}$  ratio  $\geq 1 \times 10^{-2}$ . In FAMOUS olivines (Fo<sub>90</sub>), the inclusions are 80  $\mu\text{m}$  in size, isolated, with no bubble in most of them (Fig. 1E,F). When the bubble exists, the  $V_b/V_{\text{incl}}$  ratio is  $1 \times 10^{-3}$ .

The  $V_b/V_{\text{incl}}$  ratio is constant within a group of inclusions suggesting that the bubble nucleation occurs during cooling, whereas heterogeneous trapping should have resulted in variable proportions between the gas bubble and the silicate melt (Clocchiatti, 1975; Roedder, 1984; Anderson et al., 1989).

The post-trapping crystallization of olivine on the walls of the cavities is quite limited and does not exceed 4 wt.%, assuming olivine–liquid equilibrium (Table 1), in agreement with the well-preserved morphology of the cavities. For these calculations, the  $K_D$  [(Fe/Mg) olivine/(Fe/Mg) melt] values were in the range 0.30–0.29, according to previous works on these samples (Métrich and Clocchiatti, 1996; Bureau et al., 1998a,b).

The concentrations of H<sub>2</sub>O determined by systematic FTIR measurements vary from 0.14 wt.% in the basaltic inclusions from FAMOUS to 2.9 wt.% in the shoshonitic inclusions from Stromboli (Table 1). The basaltic inclusions in PdF olivines contain 0.74 wt.% H<sub>2</sub>O (Bureau et al., 1998b). Besides their total H<sub>2</sub>O concentrations, their OH/H<sub>2</sub>O<sub>mol</sub> ratios are also distinct. Water is mainly dissolved as OH<sup>−</sup> in the FAMOUS and PdF inclusions, whereas the shoshonitic inclusions from Stromboli contain both OH<sup>−</sup> and molecular H<sub>2</sub>O in agreement with rather high total H<sub>2</sub>O content.

## 3. Experimental procedure

### 3.1. Heating stage and FTIR apparatus

The heating stage used for high-temperature experiments consists of a small size platinum heater

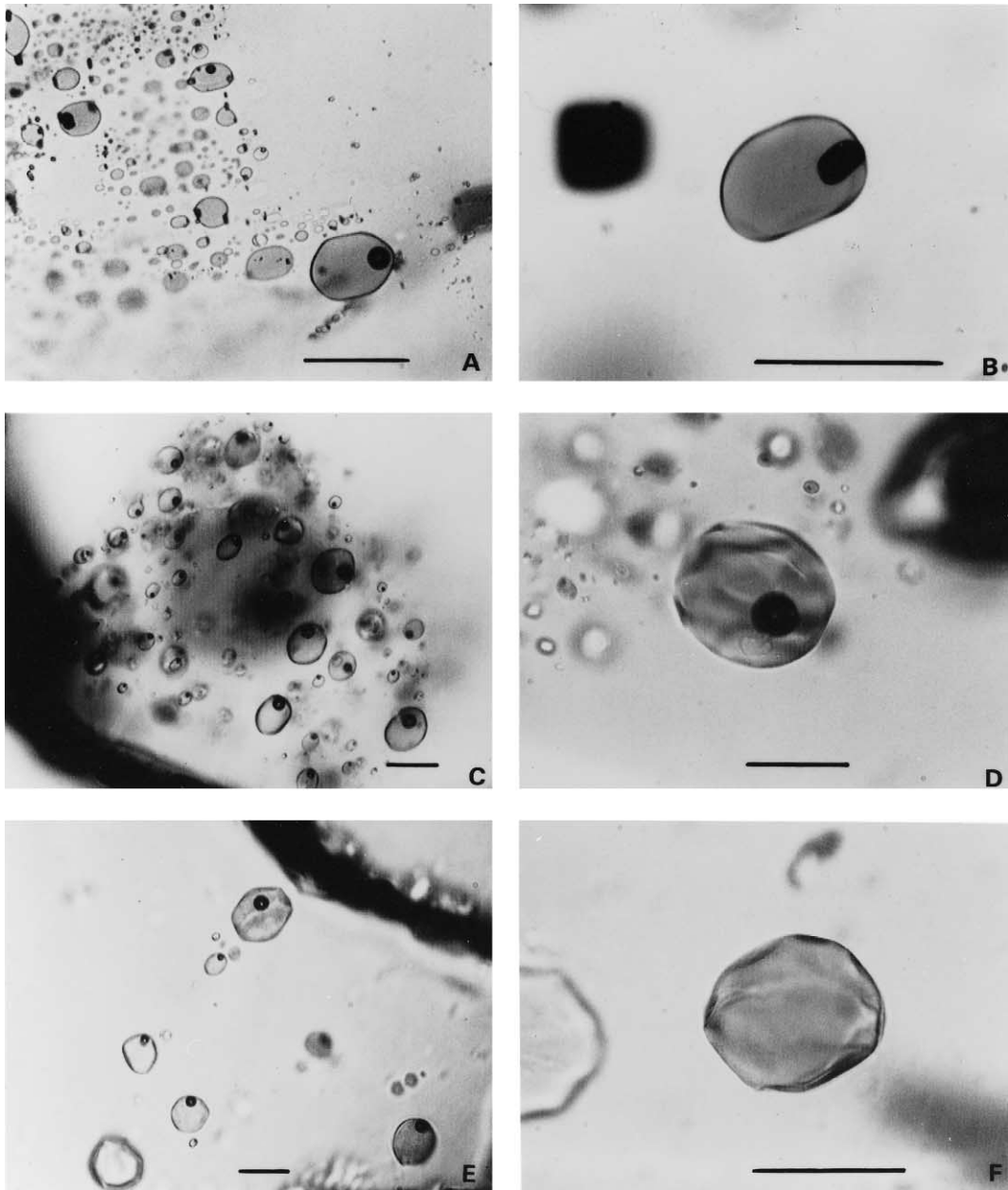


Fig. 1. Transmitted-light photomicrographs of inclusions in olivines. Piton de la Fournaise (PdF) samples: most of the inclusions contain glass associated with one or two bubbles (A) and/or a mechanically trapped spinel (B); Stromboli samples: the inclusions consist of glass and a bubble (C, D); FAMOUS samples: inclusions with glass+one bubble (E) or only glass (F). The scale is 100  $\mu\text{m}$ .

(2.5 mm in diameter), purged with purified He as described by Sobolev et al. (1980). Using He as carrier gas, whose thermal conductivity ( $k=3.63$

$\text{mW cm}^{-1} \text{K}^{-1}$ ) is relatively high, at 1000 °K and  $P=1$  bar, compared to that of Ar ( $k=0.434 \text{ mW cm}^{-1} \text{K}^{-1}$ ), significantly improves the cooling rate

Table 1  
Representative compositions of the olivines and their melt inclusions

Sample	Stromboli		PdF <sup>a</sup>		FAMOUS	
	Str94-5		PF92-17		ARP10.03	
SiO <sub>2</sub> <sup>b</sup>	47.63	0.55	48.21	0.58	50.00	0.32
TiO <sub>2</sub>	0.97	0.04	2.65	0.08	15.79	0.02
Al <sub>2</sub> O <sub>3</sub>	17.33	0.25	14.31	0.28	0.46	0.11
FeO	8.34	0.24	10.73	0.61	7.55	0.09
MnO	0.16	0.03	0.17	0.02	0.16	0.05
MgO	5.79	0.18	6.76	0.17	9.47	0.05
CaO	10.83	0.29	10.88	0.19	13.63	0.12
Na <sub>2</sub> O	2.42	0.06	2.85	0.14	1.48	0.07
K <sub>2</sub> O	1.66	0.08	0.75	0.06	0.03	0.02
P <sub>2</sub> O <sub>5</sub>	0.40	0.07	0.28	0.03	nd	
Total	95.53		97.59		98.66	
H <sub>2</sub> O	2.9 <sup>c</sup>	0.6	0.74 <sup>d</sup>	0.07	0.14 <sup>e</sup>	0.03
N <sup>c</sup>	40		13		5	
<i>Host olivine</i>						
SiO <sub>2</sub>	39.79		39.65		40.85	
FeO	15.89		15.86		9.68	
MnO	0.29		0.29		0.20	
MgO	44.11		43.82		49.16	
Mg <sup>#f</sup>	0.83		0.83		0.90	
X <sub>Fo</sub> <sup>g</sup>	–		0.04		0.025	

<sup>a</sup> PdF: Piton de la Fournaise.

<sup>b</sup> Electron microprobe analyses (Cameca SX50, Camparis, Univ. Paris 6), 15 kV, 10 nA, 10 μm as beam diameter.

<sup>c</sup> The H<sub>2</sub>O concentrations in the starting material were measured by FTIR against H<sub>2</sub>O-rich glass fragments, similar in compositions measured at 3.05 and 3.6 wt.% H<sub>2</sub>O by Karl Ficher Tritation (data from B. Scaillet, Orléans).

<sup>d</sup> From Bureau et al. (1998b).

<sup>e</sup> Number of analyses.

<sup>f</sup> [Mg/(Mg + Fe)] olivine.

<sup>g</sup> Fraction of olivine that crystallized after entrapment, calculated on the basis of  $K_D$  value (see text).

(500 °C/s; Sobolev et al., 1980). Temperatures were measured with a Pt–Pt<sub>90</sub>Rh<sub>10</sub> thermocouple, and calibrated against the melting points of Ag (961.8 °C) and Au (1063.8 °C). The error on measurements is about 15 °C. The oxygen fugacity was monitored in the outgoing gas flux, with a Zirconia probe, calibrated with an Ar + 1% H<sub>2</sub> gas and calculated to be close to 10<sup>-10</sup> and 10<sup>-9</sup> atm at 1200 °C.

The FTIR measurements were performed using a Nicolet Magna-IR 550 spectrometer equipped with a Global source, an MCT/A detector cooled with liquid N<sub>2</sub>, a XT-KBr beam splitter, and coupled with a Spectra-Tech microscope (Pierre Süe laboratory-Saclay).

### 3.2. Heating stage experiments

Different heating stage experiments were done in order to determine the temperature of disappearance of the last daughter crystal ( $T_m$ ) as defined by Roedder (1984), and the homogenization temperature ( $T_h$ ) of inclusions in different crystals (PdF, Stromboli, FAMOUS). In the studied samples, the daughter crystals have nucleated and grown during the experiments; they do not exist prior to the heating treatment. A specific attention has been paid on the variation of the  $T_h$  with duration of experiment by repeated cycles of heating (52 °C min<sup>-1</sup>) in order to get homogenization with bubble disappearance and cooling (30 °C min<sup>-1</sup>) down to the temperature of bubble nucleation.

Two types of heating experiments were conducted and FTIR measurements were acquired in order to assess the H<sub>2</sub>O loss after heating treatment.

#### 3.2.1. Type I experiments

They consisted of cycles on the same inclusion. Every cycle included successively (1) in situ IR measurement through olivine + inclusion, (2) sample heating at constant temperature, (3) quench, and this cycle was repeated 8 to 12 times until the inclusion was partially crystallized. The cumulative time for the whole experiment on one inclusion was about 8 h. For each experimental cycle, the same grain was heated at 1130 °C (Stromboli) and 1190 °C (PdF), with a 52 °C min<sup>-1</sup> heating rate and cooled from experimental to room temperature in a few seconds. The experiment temperatures were chosen to be close to the temperature of melting of the last daughter crystals ( $T_m$ ) previously measured for every composition. For these experiments, each olivine grain was prepared as a section, polished on each of the six faces, in order to get a 3D image of the inclusion and its exact position ( $x$ ,  $y$ ,  $z$ ). The inclusion was kept completely enclosed within the crystal as illustrated in Fig. 2. The thickness between the inclusion walls and the polished surface of the host olivine was always  $\geq 100$  μm, so as to preclude decrepitation during heating. Great attention has been paid to get reproducible in situ FTIR measurements before and after each experimental cycle. The IR beam is masked to be smaller than the inclusion to avoid any contribution of the bubble. The successive FTIR measurements were made, ex-

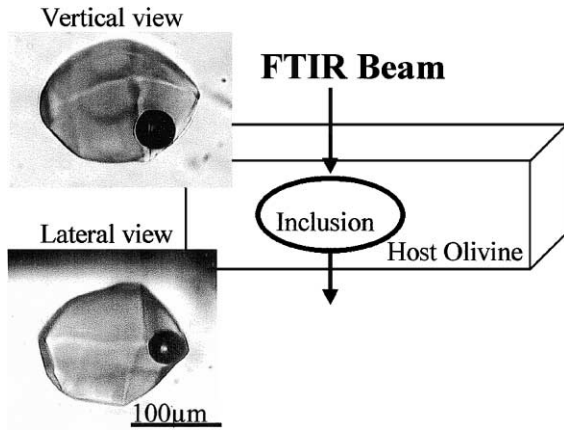


Fig. 2. Schematic experimental device. The FTIR spectra were systematically acquired through olivine+inclusion, after each heating experiment (see text). The thickness of the olivine grain is between 300 and 400  $\mu\text{m}$ , depending on the size of the inclusion.

actly in the same conditions (position, focus, spot size) and the absorbance ( $\text{Abs}_{1,2,\dots}$ ) centered at  $3535\text{ cm}^{-1}$  assigned to the fundamental OH-stretching vibration (Inhinger et al., 1994, for review) was normalized to the initial absorbance ( $\text{Abs}_0$ ) obtained on the sample prior to any heating treatment. Further discussion is based on variation of the relative absorbance ( $\text{Abs}_n/\text{Abs}_0$ ) over the whole experiment. The peak heights at  $3535\text{ cm}^{-1}$  were measured graphically relative to a linear baseline drawn between 3800 and  $2500\text{ cm}^{-1}$ . The absorption peaks at 5200 and  $4500\text{ cm}^{-1}$ , resulting from the combination of stretching+bending modes of molecular water and combination vibration of bound hydroxyl groups (Inhinger et al., 1994, for review), are not high enough to get reliable measurements over the whole duration of the experiments, even for the water-rich samples.

### 3.2.2. Type II experiments

Some experiments were performed, especially on the  $\text{H}_2\text{O}$ -rich melt, in order to measure the  $\text{H}_2\text{O}$  concentration in the inclusion after one or several successive homogenization(s). In this case, the olivine and its inclusion were heated with heating rate  $52\text{ }^\circ\text{C min}^{-1}$  up to about  $900\text{ }^\circ\text{C}$  and  $14\text{ }^\circ\text{C min}^{-1}$  until homogenization was obtained. After quenching, they were double-face polished and the FTIR spectra were obtained on inclusion exposed at the surface. The total  $\text{H}_2\text{O}$  concentrations were calculated on the basis of

the asymmetric band at  $3535\text{ cm}^{-1}$ , and according to Beer–Lambert’s law:  $C=100AM/[\epsilon\rho e]$ , where  $A$  is the absorbance,  $M$  is the molar mass ( $\text{g}\cdot\text{mol}^{-1}$ ),  $\epsilon$  is the molar absorptivity ( $\text{l}\cdot\text{mol}^{-1}\text{ cm}^{-1}$ ),  $\rho$  is the glass density ( $\text{g}\cdot\text{cm}^{-3}$ ), and  $e$  is the thickness (cm). The sample thickness was measured with an error of  $\pm 2\text{--}3\text{ }\mu\text{m}$  using a Mitutoyo digital comparator. The density and the molar absorptivity values are from Bureau et al. (1998b) except for the  $\text{H}_2\text{O}$ -rich shoshonitic inclusions, in which an average value  $2.69 \pm 0.02\text{ g cm}^{-3}$  was determined on a series of  $\text{H}_2\text{O}$ -rich basaltic glasses fragments by the Archimedes method using distilled water, and the molar absorptivity coefficient estimated to be  $65.7\text{ mol}^{-1}\text{ cm}^{-1}$  for the broad band at  $\epsilon^{3535}$  (Métrich, unpublished data).

## 4. Results

### 4.1. Temperature of melting ( $T_m$ ) and temperature of homogenization ( $T_h$ )

The temperatures ( $T_m$ ) are reported in Table 2, when the melting of the last crystals was clearly observed during the experiment. They are  $1187\text{ }^\circ\text{C}$

Table 2  
Temperatures of the first homogenization ( $T_{ho}$ ) and melting of daughter crystals ( $T_m$ )

Sample	PdF	Stromboli	FAMOUS
$T_{ho}$ ( $^\circ\text{C}$ ) <sup>a</sup>	1199 [9]	1210 [65]	1270 [90]
	1208 [18]	1220 [75]	1275 [95]
	1225 [35]	1230 [85]	1292 [112]
	1240 [50]	1234 [89]	1308 [128]
	1255 [65]	1304 [159]	1323 [143]
	1270 [80]	1314 [169]	1326 [146]
	1270 [80]	1320 [175]	
		1323 [178]	
		1345 [200]	
Mean <sup>b</sup>	1238 (SD=29)	1278 (SD=53)	1300 (SD=24)
$T_m$ ( $^\circ\text{C}$ ) <sup>c</sup>	$1150 \pm 15$ ( $N=3$ )	$1055 \pm 15$ ( $N=5$ )	$1187 \pm 10$ ( $N=5$ )
$T_{calc}$ ( $^\circ\text{C}$ ) <sup>d</sup>	1190	1145	1180

$N$  is the number of measurements.

<sup>a</sup> Temperature of the first homogenization with  $[\Delta T$  ( $^\circ\text{C}$ )] =  $[T_{ho} - T_{calc}]$ .

<sup>b</sup> Mean value and standard deviation (SD).

<sup>c</sup> Temperature of melting of the daughter crystals.

<sup>d</sup> Temperature calculated with MELTS (Ghiorsso and Sack, 1995).

for FAMOUS, 1150 °C for PdF, and 1055 °C for Stromboli inclusions, with a relative error of  $\pm 15$  °C.

Systematic measurements of the temperatures of the first homogenization ( $T_{h0}$ ) were carried out on 22 inclusions, each of them hosted in different crystals. They indicate temperatures from 1199 to 1270 °C and from 1270 to 1326 °C for PdF and FAMOUS inclusions, respectively (Table 2). There is no clear relationship between the occurrence of a bubble and  $T_h$  either in FAMOUS or PdF samples. One may note that the inclusions from FAMOUS do not contain a

bubble, or when the bubble exists, it appeared during the cooling and is of very small size (Fig. 1E,F). For example, the  $T_h$  was measured to be 1240 and 1270 °C for PdF inclusions containing a bubble and a bubble associated with a mechanically trapped spinel, respectively. Similar values (1255–1270 °C) were obtained for monophase inclusion containing only glass without a bubble. In the case of Stromboli, every inclusion displays a bubble, and homogenization is achieved at temperature higher than 1200 °C and up to 1345 °C (Table 2).

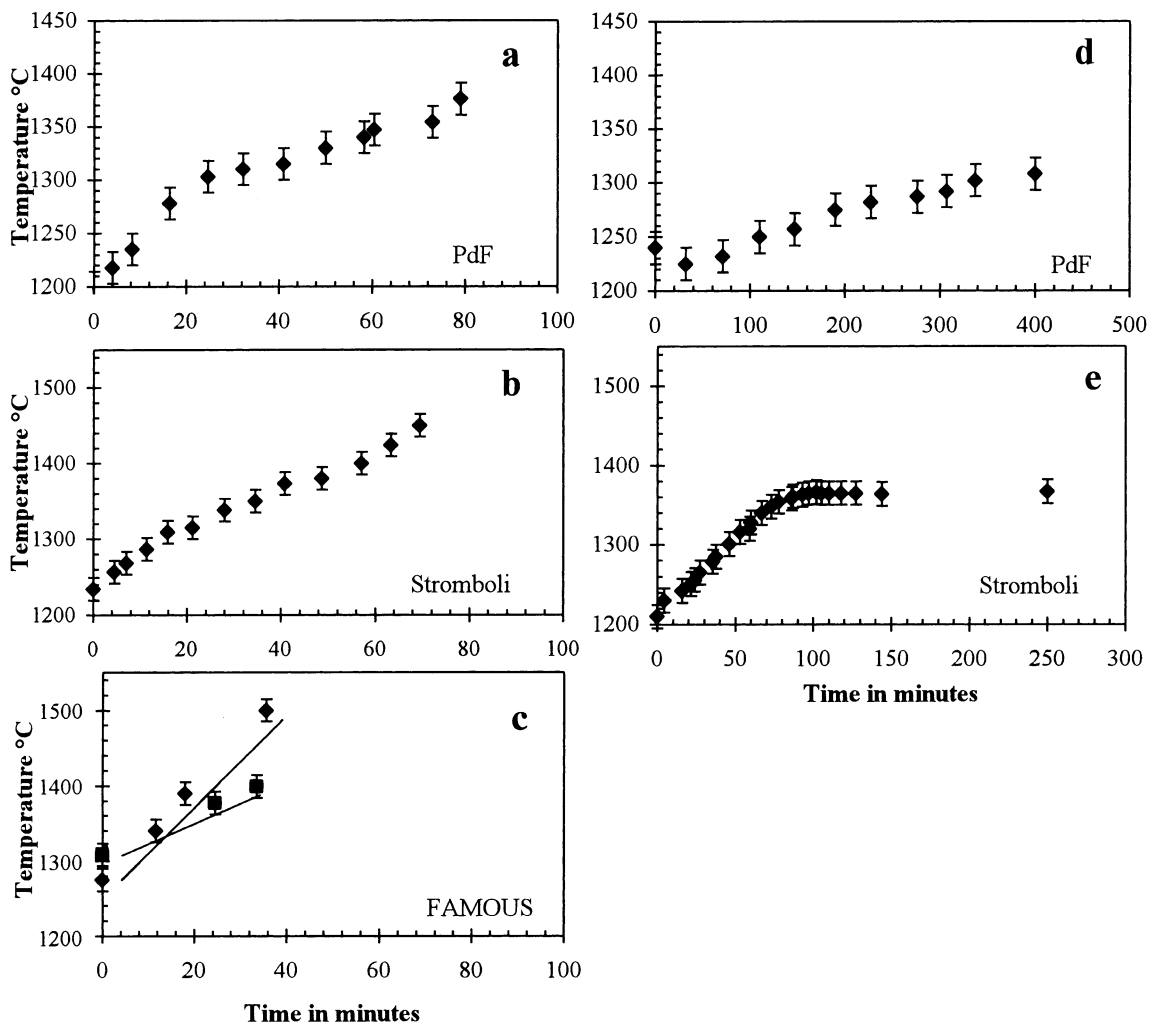


Fig. 3. Variation of the temperature of homogenization ( $T_h$ ), measured by optical thermometry, as a function of time. Each curve represents the variation of  $T_h$  determined for the same inclusion by repeated cycles of heating until the homogenization is reached and cooling down to temperature of bubble nucleation (see text). Samples are from (a, d) Piton de la Fournaise (PdF); (b, e) Stromboli; (c) FAMOUS.

Repeated heating experiments on the same inclusions demonstrate a sharp increase in the temperature of homogenization ( $T_h$ ) with time, regardless of the composition of the trapped melt and of its host. These results are valid for every studied sample from PdF (Fig. 3a), Stromboli (Fig. 3b), and FAMOUS (Fig. 3c), although  $T_h$  may vary from one inclusion to another one.  $T_h$  is still increasing after long time experiments (500–300 min) and it may reach a plateau (Fig. 3d,e).

#### 4.2. Evidence for $H_2O$ loss after heating stage experiments

##### 4.2.1. Type I experiments

Repeated heating cycles on one inclusion result in progressive lowering of the relative absorbance ( $Abs_n/Abs_0$ ) with time (Fig. 4). Although, FTIR spectra were carefully acquired at the same place for each successive measurement, some error on the determination of the relative absorbance cannot be ruled out because of the irregular shape of the inclusion. However, we may conclude that the relative absorbance significantly decreases with time that occurs either at 1190 °C in inclusion containing 0.7 wt.% total  $H_2O$  or at 1130 °C in inclusion with 2.9 wt.% total  $H_2O$  (Fig. 4). Almost total dehydration occurs regardless of either the total water concentrations or the relative proportions of  $OH^-$  and molecular  $H_2O$  prior to heating experiments. The size of these nuclei precludes any determination of their composition, but they are suspected to represent the paragenesis of the evolved,  $H_2O$ -poor compositions from either PdF and Stromboli magmas, which is mainly composed of clinopyroxene, plagioclase ( $\pm$  titanomagnetite) in association with olivine.

##### 4.2.2. Type II experiments

The few FTIR measurements made after the first homogenization ( $T_{h0}$ ) of  $H_2O$ -rich shoshonitic melts indicate that the total  $H_2O$  concentration decreases from 2.3 to 1.5 wt.% when  $T_{h0}$  are 1230 and 1304 °C, respectively. After three successive homogenizations obtained on the same inclusion at 1345, 1393 and 1405 °C, the remaining  $H_2O$  concentration dissolved in glass is 0.56 wt.%. These concentrations are significantly lower than the initial content, prior to any

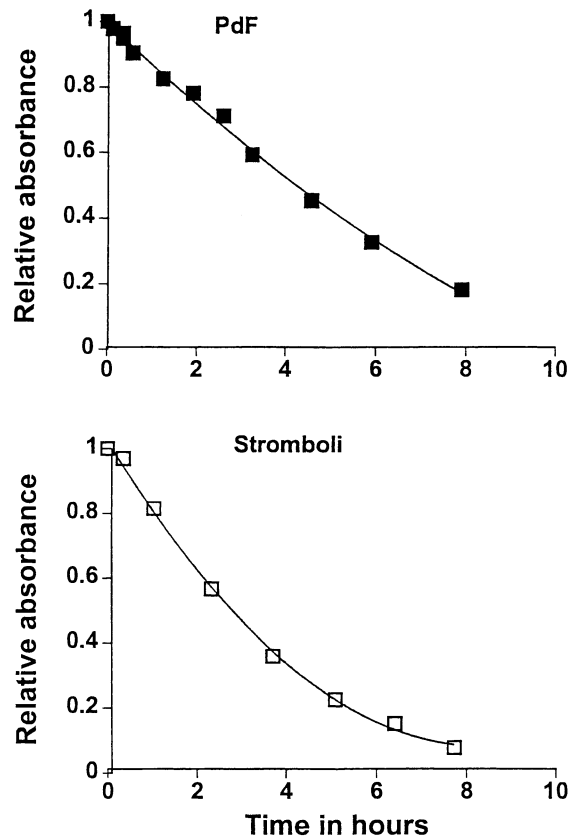


Fig. 4. Plots showing the decrease of the relative absorbance ( $Abs_n/Abs_0$ ) with time in inclusions from Piton de la Fournaise (PdF) and Stromboli volcanoes. The FTIR spectra are acquired through olivine + inclusion (see text).

heating treatment, expected to be  $2.9 \pm 0.6$  wt.% total  $H_2O$ .

The presence of either hydroxyl group or molecular  $H_2O$  in the host olivine itself has never been detected after heating experiments by FTIR. If these species exist, their concentrations are below the detection limits.

## 5. Discussion

### 5.1. Systematic over-estimation of the temperature of homogenization in olivine at 1 atm

Olivine is the liquidus phase with spinel in the PdF basaltic magmas, between 1180 and 1270 °C, from 1

atm to 600 MPa (Fisk et al., 1988). The olivine (Fo<sub>83–84</sub>)–liquid equilibrium is calculated to be 1190 °C (Albarède et al., 1997; Bureau et al., 1998a). On the basis of MELTS calculations (Ghiorso and Sack, 1995), it is expected to be nearly 1190 °C for PdF, 1180 °C for FAMOUS Fo<sub>90</sub> and 1145 °C for Stromboli Fo<sub>83</sub>, with  $f_{O_2}$  buffered close to FMQ or Ni–NiO (Table 2). In addition, the liquidus temperature of a hawaiite-like magma containing 2.9 wt.% H<sub>2</sub>O would be closely 1150 °C according to experimental results (Métrich and Rutherford, 1998).

The difference between the calculated and experimental values is highly variable, from one crystal to another one, between up to 146 °C in FAMOUS and 200 °C in Stromboli inclusions (Table 2). It becomes larger with duration of experiment and, therefore, as  $T_h$  is getting higher (Table 2). The range of  $T_h$  from 1210 to 1345 °C is strongly over-estimated and cannot be considered as the temperature of the trapping event. Similarly, 1270 °C is the highest temperature of dry liquidus experimentally obtained for the PdF basaltic magmas (Fisk et al., 1988), whereas  $T_h$  are measured between 1199 and 1270 °C for basaltic inclusion containing 0.7 wt.%. Similar results were recently reported for PdF samples (Bureau et al., 1998a).

The present experiments bring new evidence of systematic over-estimation of  $T_h$  by more than 140–200 °C after 80-min heating cycles regardless of the total H<sub>2</sub>O concentrations of the inclusions (Fig. 3);  $T_h$  also varying from one inclusion to another one in the same sample. Increasing  $T_h$  during long time experiments with a possible effect of H<sub>2</sub>O has been invoked by Sobolev et al. (1983), who obtained no difference between  $T_h$  and temperatures calculated on the basis of the olivine–melt equilibrium for H<sub>2</sub>O-poor MORB-type melt, but a systematic shift up to 100 °C for H<sub>2</sub>O-rich basaltic inclusions. Although the largest discrepancy corresponds to H<sub>2</sub>O-rich composition in our experiments, there is no systematic relationship between the H<sub>2</sub>O concentrations and  $T_h$  for inclusions whose sizes do not significantly differ. The steady state conditions are not obtained; in most of the cases, there is no plateau (Fig. 3).

The kinetic effects on  $T_h$  have been documented as a function of the heating rates, inclusion sizes and chemical compositions as summarized in Sobolev and Danyushevsky (1994). However, with appropriate heating rates, the  $T_h$  should reach a plateau as estab-

lished for different compositions of trapped melts and host crystals (Clocchiatti, 1975; Sobolev and Kostyuk, 1975). Increase in the homogenization temperature directly results from the fact that the “shrinkage” bubble is getting bigger along the course of heating experiments. In almost dry system, there is no way to explain such inflation if the whole cavity has kept a constant volume. On the other hand, increasing  $T_h$  is accompanied by morphological modifications of the cavities which are commonly rounded in olivine and progressively have developed faces and a “negative-crystal” shape after long time experiments, which involved dissolution–crystallization mechanisms at the olivine–silicate melt boundary. Note that long time experiments refer to duration a few tenths of minutes (e.g. Fig. 3).

Similarly, an increase of  $T_h$  from a tenth (Gioncada et al., 1998) to 100 °C (Cioni et al., 1995) has been observed after high-temperature experiments on diopside-hosted melt inclusions. Although more systematic studies should be conducted, we suggest that significant increase in  $T_h$  is a main feature of Fe-bearing minerals.

### 5.2. Evidence of H<sub>2</sub>O loss during heating stage experiments

The repeated in situ FTIR measurements of the relative absorbance (Abs.<sub>n</sub>/Abs.<sub>0</sub>) at 3535 cm<sup>-1</sup> on one inclusion together with the very low H<sub>2</sub>O concentration (0.56 wt.%) measured in H<sub>2</sub>O-rich inclusion, after three successive homogenizations, demonstrated that the total H<sub>2</sub>O concentration systematically decreases during heating stage experiments at 1 atm. In addition, one may note that increasing the temperature accelerates the process. This is illustrated by the fact that about 20% to 50% initial H<sub>2</sub>O content in H<sub>2</sub>O-rich inclusion may be lost after the first homogenization occurred at 1230 and 1304 °C, respectively. Water depletion and almost total dehydration of inclusion account for the crystallization after repeated heating experiments (e.g. Stromboli samples). It is in total agreement with the general finding that reducing the H<sub>2</sub>O content strongly increases the liquidus temperature of a basaltic magma (Holloway and Burnham, 1972).

Different mechanisms could be at the origin of this variation. It is well established that the diffusion of



hydrogen as proton in olivine is anisotropic, follows an Arrhenius relationship, and supports the conclusion that “dehydrogenation” of  $\text{CO}_2 + \text{H}_2\text{O}$ -rich fluid inclusions hosted in olivine may occur on time scales

of hours between 800 and 1000 °C and possibly during ascent of mantle xenoliths (Mackwell et al., 1985; Mackwell and Kohlstedt, 1990). Proton diffusion is charge compensated by a possible counter

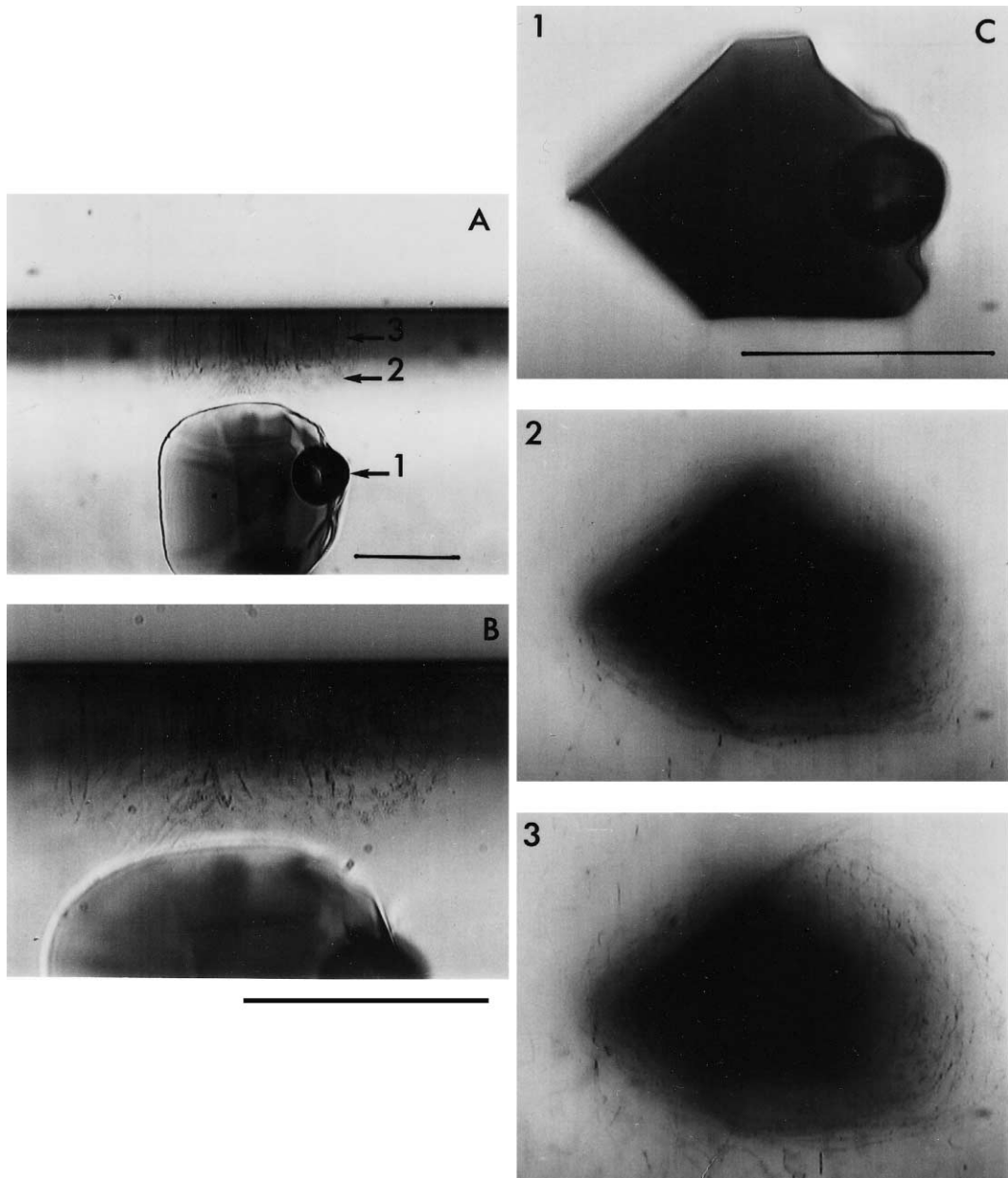


Fig. 5. Dislocations surrounding an H<sub>2</sub>O-bearing silicate melt inclusion revealed because of oxidizing conditions during a high-temperature experiment. (1) Melt inclusion with a shrinkage bubble; (2) host olivine; (3) dislocations towards the surface of the mineral. Scale = 25 μm.

flux of electrons (Mackwell et al., 1985; Kohlstedt and Mackwell, 1998). During heating stage experiments at 1 atm, the  $f_{\text{H}_2}$  and  $f_{\text{H}_2\text{O}}$  is imposed by the furnace atmosphere that may induce hydrogen diffusion gradient between the inclusion and the olivine surface. Water dissociation and hydrogen migration, driven by an  $f_{\text{H}_2}$  gradient, may be efficient in dehydrating the  $\text{H}_2\text{O}$ -rich melt inclusions to some extent. This mechanism has been invoked (Sobolev et al., 1983; Sobolev and Danyushevsky, 1994) following the reaction  $\text{H}_2\text{O} + 2\text{FeO} = \text{H}_2 + \text{Fe}_2\text{O}_3$  (with possible crystallization of Fe-oxides). Based on this reaction, the authors estimated the amount of  $\text{H}_2\text{O}$  that dissociated to be less than 1 wt.% in basaltic melts. However, additional mechanism may be efficient in driving water-derived species off the melt inclusions at high temperature. Water in silicate melt is mainly dissolved as  $\text{OH}^-$  at high temperature (Eckert et al., 1987; Kohn et al., 1989; Pichavant et al., 1992). Preferential diffusion along dislocations or propagation of defect points in the host olivine could be consistent with fast water-derived species (hydroxyl group) loss, regardless of the composition of the silicate melt. Such an assumption seems to be supported by the fact that each crystal has its own behavior, together with the development of dislocations surrounding melt inclusions which may be revealed as exemplified in Fig. 5. The deformation of olivine together with the development and propagation of dislocations are also suitable mechanisms that may explain the volume expansion of the whole cavity during experiment together with variations in  $T_{\text{h}}$ .

### 5.3. Implications for natural volcanic systems

Although the mechanisms may still be under debate, the significant depletion of melt inclusion hosted in olivine phenocrysts with respect to  $\text{H}_2\text{O}$  is clearly demonstrated during heating stage experiments at 1 atm. In nature, re-equilibration prior to the eruption has been invoked to account for possible  $\text{H}_2\text{O}$  content decrease in melt inclusions trapped in natural quartz from Bishop Tuff (Qin et al., 1992). Re-equilibration of  $\text{H}_2\text{O}$  between the inclusions in quartz, olivine and other crystals and a partially degassed magma, which has lost  $\text{H}_2\text{O}$  because of magma accumulation and storage in upper level of a

volcano, should be accompanied by a significant change in the liquidus temperature and crystallization paths of such magmas.

Conversely, it seems realistic to consider that dehydration of inclusion in olivine could occur to some extent. One may note that olivine crystallizes over a wide range of pressure and depth in shield and stratovolcanoes, and the development of large cumulate bodies, percolated by  $\text{CO}_2$ -rich fluids, has been identified at Piton de la Fournaise (Albarède et al., 1997; Bureau et al., 1998b, 1999) and Kilauea (Clague and Denlinger, 1994). These conditions, when crystals are isolated from the magmas from which they are growing, are favorable to partial dehydration of the silicate melts trapped in olivine and possibly clinopyroxene, inducing a variability of the  $\text{H}_2\text{O}$  concentrations. Dehydrogenation mechanism should result in oxidation and thus change in the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio in silicate melt or possibly precipitation of iron oxides. Accordingly, we may expect that the most likely representative  $\text{H}_2\text{O}$  concentrations of magmas are the highest as stipulated by Bureau et al. (1998b). One may also note that processes as leakage and  $\text{H}_2\text{O}$ -loss debated for  $\text{CO}_2$ -rich fluid inclusions in olivines of xenoliths (Pasteris, 1987) together with dehydrogenation and dehydration during decompression and ascent (Mackwell et al., 1985; Mackwell and Kohlstedt, 1990) cannot be ruled out for silicate melt trapped in olivines from mantle xenoliths.

## 6. Conclusions

The present experiments bring new evidence of systematic over-estimation and increasing  $T_{\text{h}}$  of melt inclusions hosted in olivine crystals, during 1 atm heating experiments. The interpretation of the  $T_{\text{h}}$  of melt inclusions hosted in olivine is rather delicate, independently of the  $\text{H}_2\text{O}$  content of the trapped melt. Such a characteristic is valid for olivine, possibly for clinopyroxene and Fe-bearing minerals. We propose that  $T_{\text{h}}$  increase may be mainly related to the deformation of the host mineral itself, in relation with possible propagation of defect points, and a subsequent augmentation of the volume of the cavity.

The experimental dehydration of melt trapped in olivine indicates that water may be lost very rapidly, on time scale of heating experiment, regardless of

their H<sub>2</sub>O initial concentrations. Increasing the temperature hastens the process.

Although these results are obtained at ambient pressure, they may suggest that water-derived species could be driven off silicate melt entrapped in olivine grains from large dunitic bodies and possibly mantle xenoliths.

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