Crystallization and Oxidation of Kilauea Basalt Glass: Processes during Reheating Experiments

DOROTHEE J. M. BURKHARD†*

SCIENTIFIC CENTRE FOR MATERIALS RESEARCH AND INSTITUTE FOR MINERALOGY, UNIVERSITY OF MARBURG, D-35032 MARBURG, GERMANY

RECEIVED OCTOBER 4, 1999; REVISED TYPESCRIPT ACCEPTED JUNE 16, 2000

INTRODUCTION
Numerous studies have been performed in the past on processes related to the thermal evolution of magmas (cooling path and degree of undercooling) and to the energetics of the exothermic process of crystallization. The cooling history could be related to crystallization on the basis of detailed investigations of textures and microtextures of volcanic materials for both terrestrial and lunar basalts (e.g. Dowty et al., 1974; Lofgren et al., 1974; Kirkpatrick, 1981; Lofgren, 1983), supported by experimental research (Walker et al., 1978; Cashman & Marsh, 1988) and by theoretical modelling (e.g. Lasaga, 1981; Brandeis & Jaupart, 1987; Marsh, 1988; Toramaru, 1991). The energetics that characterizes thermal evolution has been accessed in calorimetric studies, among which differential scanning calorimetry (DSC) has been used to quantify the latent heat during crystallization and melting of minerals and rocks (e.g. Lange & Navrotsky, 1992; Lange et al., 1994). Tholeiitic basalts from Hawaii are ideal for studies relating cooling history and crystallization (e.g. Anderson & Wright, 1972), and specifically the Hawaiian lava lakes provided a natural laboratory par excellence (Moore & Evan, 1967; Wright & Okamura, 1977). Drill cores and downhole temperature measurements at the Makaopuhi and Alae lava lakes challenged studies on nucleation and growth rate of

KEY WORDS: microcrystallization; oxidation process; kinetics; basalt glass; Kilauea

Crystallization and oxidation are usually considered as a consequence of cooling and emplacement of a magma, whereas little is known about crystallization upon reheating. However, the common eruption of basalt on the Earth and other rocky planetary bodies results in reheating at the interface. To explore the range of possible processes of crystallization and oxidation, reheating experiments were carried out on basalt glass from Kilauea in air and in argon atmosphere. In air, interface-controlled crystallization starts with the formation of pyroxene dendrites and Fe–Ti oxides at their apices below 840°C. Above 920°C, crystallization of the bulk glass occurs and includes in addition growth of plagioclase. In argon, the growth of only pyroxene is observed between 850 and 936°C. Crystallization is interface controlled below 890°C, and occurs within the bulk above 890°C. On the basis of T-dependent studies of the formation of Fe³⁺ (detected by Mössbauer spectroscopy), AG of oxidation is estimated to −165 and −67 kJ/mol (± 7 kJ/mol) for glass chunks and powder, respectively. The activation energy is 100 kJ/mol for glass chunks, and 32 and 20 kJ/mol for powders, below and above the glass transition temperature, respectively. However, oxidation does not involve an exchange with the environmental atmosphere, as shown by the constant δ¹⁸O (4·6–5·8 ± 0·2‰) for any reheating below the liquidus. Significant cation diffusion of mainly Ca⁺⁺ to the sample–air interface forming time (rather than anion diffusion of O²⁻ into the sample), may account for the charge balance and explain at least the high rate of surface oxidation. Although the extent of diffusion processes to the sample’s interior cannot be observed (but is at least 80 µm) because of overlapping effects by crystallization, an increase in cationic mobility, dependent on the oxygen gradient between sample and environmental atmosphere, might be the reason for an increasing degree of crystallization observed.

*Telephone: +49-6421-282-7026. Fax: +49-6421-282-8919. e-mail: burkhard@mailer.uni-marburg.de © Oxford University Press 2001
pyroxene and plagioclase (e.g. Kirkpatrick, 1976, 1977), and the application of crystal size distribution analyses opened a new dimension for a quantitative understanding of crystallization in relation to magmatic processes (Cashman & Marsh, 1988; Maaløe et al., 1989; Mangan, 1990; Cashman et al., 1999). At the most recent pahoehoe flows produced at Kilauea East rift, Pu‘u O‘o, direct temperature measurements on cooling provided insight into thermal evolution in relation to atmospheric convection, occurring on surfaces, and the consequences for crystallization (Keszthelyi, 1995; Keszthelyi & Denlinger, 1996). A detailed petrological characterization of these lavas has been given by Garcia et al. (1996, and references therein).

An important parameter related to the thermal evolution of magmas is derived from redox equilibria [e.g. Reviews in Mineralogy, edited by Rumble (1976) and Lindsay (1991)]. Redox equilibria of melts and magmas were studied, for example, by Johnston (1964), Fudali (1965), Goldman & Gupta (1983), Kilinc et al. (1983), Mysen et al. (1985), Schreiber (1986), Paul (1990), Kress & Carmichael (1991) and Wilke et al. (2001). However, the relation between temperature path and oxygen fugacity during cooling has a long history of debate. The question of concern is whether the system is open or closed to oxygen and how this may affect redox conditions and the stability of minerals [see, for example, summary by Snyder et al. (1993)]. Recent conclusive experiments illustrated that titanomagnetite precipitates before ilmenite above FMQ (fayalite–quartz–magnetite) buffer conditions, and the order is reversed below FMQ conditions (Snyder et al., 1993; Toplis & Carroll, 1995). Compared with an open system, more ilmenite than magnetite precipitates in a closed system and Fe–Ti oxides are stabilized at higher temperatures in a closed system (Toplis & Carroll, 1996; Partzsch & Lattard, 1999). However, the process of oxidation in terms of kinetics is largely unknown. In principle, it involves a coupled reaction of oxygen acceptance and an electron loss. Kinetics of oxygen diffusion has been considered to be rate limiting (e.g. Schreiber, 1986). Diffusion experiments are either oxygen tracer diffusion experiments, looking at oxygen self-diffusion (e.g. Canil & Muehlenbachs, 1990), or chemical diffusion experiments, applying a chemical gradient between sample and environment (e.g. Dunn, 1983; Wendlandt, 1991). Most of these studies are restricted to melts above the liquidus, and only few data are available on glasses (e.g. Muehlenbachs & Schaeffer, 1977; Cooper et al., 1996). In line with the suggestions by Dunn (1982) that oxygen diffusion mechanisms resemble those of cation diffusion, Cooper et al. (e.g. 1996) recently suggested that oxidation mechanisms in glass are dominated by diffusion of cation rather than oxygen species. As to the electron loss during oxidation (Fe$^{3+} \rightarrow$Fe$^{2+}$), determinations are in most cases of a qualitative nature and correlations with oxygen diffusivity are assumed.

Although crystallization and oxidation during cooling have attracted much attention, little is known about possible reactions during reheating. Reheating of lava should occur on a regular basis during eruption of flows, whenever lava, cooled or partially cooled, is covered by a subsequent flow. Such reheating is particularly efficient between pahoehoe flows. The importance of pahoehoe as a primary emplacement mode has recently been recognized by Hon et al. (1994) and Self et al. (1996). Reheating may induce a post-eruptive alteration including crystallization and oxidation, as shown by preliminary experiments (Burkhard, 1997, 1999). Although a conclusive answer to this question has to come from investigations across interfaces of flows (and this is subject of forthcoming studies) such investigations will benefit from experimental work that evaluates qualitatively and quantitatively the kind of processes and reactions to be expected. The basic questions that arise are: What are the temperatures of crystallization and oxidation and what is the role of environmental atmosphere? An evaluation of these questions involves a number of aspects of which the present paper provides an outline, presenting phenomena of crystallization as a function of temperature and environmental atmosphere while concentrating on the process of oxidation. The studies consider basalt glass from Kilauea, Hawai‘i, obtained from hammer-dipping and subsequent quenching. Glass characterizes the chilled margin of lava flows at the contact to air, but most important, it is of advantage for the intended studies to consider non-crystalline material, i.e. glass without any preceding crystallization history. To obtain information about crystallization temperatures, and particularly the minimum temperature required for crystallization, glass samples are investigated by DSC, in air and in argon atmosphere. Results serve as a basis for static heating experiments of glass chunks (in air and argon), which are subsequently investigated with the optical microscope, with back-scattered electrons (BSE) and with the electron microprobe (EMP). To tackle the question of oxidation, glass chunks are heated at various temperatures and periods of time, and are subsequently investigated with Mössbauer spectroscopy. A treatment of glass powder allows one to evaluate by comparison the effect of surface oxidation. As redox reactions involve an electron exchange and a concomitant exchange of oxygen, the oxygen isotope composition was determined for some samples.

We find three mineral phases upon reheating in air: (1) pyroxene and (2) Fe–Ti oxides starting around 850°C, and (3) plagioclase above 920°C. In argon, only pyroxene crystallization is observed up to 936°C. Treatment in air leads to oxidation, which is detected as an electron loss by Mössbauer spectroscopy (Fe$^{3+} \rightarrow$Fe$^{2+}$); however,
oxidation does not involve atmospheric oxygen. In surface regions, to at least 80 μm depth, an extensive diffusion of specifically Ca$^{2+}$ is recorded that depends on the oxygen gradient between sample and environmental atmosphere.

**EXPERIMENTAL**

**Sampling and sample description**

The Pu‘u O‘o–Kupaianaha eruption on Kilauea’s east has been erupting tholeiitic basalt lava since January 1983. In 1996, the lava was erupted from Pu‘u O‘o and transported about 10.5 km in tubes to La‘iapuki, the ocean entry. A few hundred metres inland, samples were taken by hammer-dipping and subsequent quenching in air or water on 12 April 1996. Additional samples erupted during the following months of 1996 were kindly provided by Carl Thornber from the US Geological Survey’s Hawaii Volcano Observatory. All samples contain olivine phenocrysts, and the larger ones may be recognized with the naked eye. Under the optical microscope, the basalt glass consists of >95% glass, light yellow in colour, with olivine phenocrysts, augite, plagioclase laths and occasionally Cr-spinel. The spinel is usually associated with olivine. According to independently determined, wet chemical analyses, kindly provided by G. C. Ulmer and G. Jarsowitch, this glass contains <1 wt % Fe$_2$O$_3$.

**Dynamic (high-temperature DSC) and static heating experiments**

For dynamic heating experiments, larger olivine phenocrysts were removed from the glass before it was carefully ground under acetone. Powder (40–50 mg) with a grain size larger than 300 μm was pressed into Pt pans and investigated by high-temperature DSC with a Sciko instrument between 400 and 1300°C against an empty Pt crucible of the same weight as reference. The grain size may be critical because it affects the surface to bulk ratio and hence the dominant contribution of the one or the other. A grain size of 300 μm was reported as the critical value in the Li$_2$O–SiO$_2$ system above which one observes the bulk effect (Ray & Day, 1990). The heating rate was 20°/min or 10°/min. The sample chamber was flushed with air or with 99.999% pure argon. Experiments included two heating cycles to 1300°C; during the first cycle the powder was heated, and in the second cycle the same sample, now as solid glass in the Pt crucible, was reheated. Although melting was relatively short and the amount of Fe in the sample large, one has to expect a loss of Fe to the Pt crucible during melting, which may affect the second cycle but not the thermal events below melting of the first cycle. DSC experiments provided minimum temperature ranges for crystallization, subsequently applied in static heating experiments. Glass chunks of the April 1996 sample, about 0·8 cm × 0·5 cm × 0·5 cm in size, were heated in Pt–5%Au crucibles at various temperatures between 775 and 1200°C (± 3°C), usually for 24 h. To consider the surface effects of oxidation, glass was powdered to a size of <80 μm and heat-treated between 430 and 800°C for different lengths of time. Heating experiments are summarized in Table 2. For comparison, five reheating experiments in argon atmosphere were carried out between 835 and 935°C (± 5°C), in a 99.995% pure argon flow.

**Chemical characterization of experimental products**

Investigations with the electron microprobe utilized an SX 80 Cameca, applying an accelerating voltage of 15 keV. The beam current was 18 nA and defocused to 20 μm for glass and focused to ~1 μm for distinct phases. Standards used include albite, periclase, corundum and orthoclase for Na, Mg, Al and K, respectively. Wolastonite was used for Ca and Si, and MnFeO$_3$, Cr$_2$O$_3$ and haematite for Mn, Ti and Fe, respectively; the error is estimated to ~1% relative to SiO$_2$. In addition to EMP analyses, samples were usually also studied with an attached BSE system. Images of elemental distribution of Mg, Ca, Fe, Al and Na were obtained with an SX100 Cameca applying a scanning stage, and conditions of 15 keV and 40 nA. A size of 256 × 256 pixels or 256 × 192 pixels were chosen, and, depending on the required resolution, the time involved was 20–200 ms/pixel.

The chemical composition of minerals in the basalt glasses shows olivine of Fo$_{81}$ and plagioclase between An$_{68.5}$ and An$_{69.5}$. Two different pyroxenes may be distinguished, px1 and px2; px1 is the common type, a few millimetres in size and relatively rich in CaO and MgO (17 and 20 wt %), typical for augite; px2 is very rare, even smaller in size, and contains less than half the amount of Mg compared with px1, but ~10 wt % AlO$_3$ and more FeO. XRF analyses of the bulk and EMP results for the glass are identical within systematic error and suggest therefore that the crystalline fraction has a negligible effect on the bulk composition (Table 1). Table 1 also gives average analyses of the crystalline phases.

Several heat-treated samples were investigated with $^{57}$Fe Mossbauer spectroscopy, using 14·4 keV from a $^{57}$Co source embedded in Rh. The voltage was triangular, and transmitted γ-rays were collected with a conventional spectrometer and a multi-channel analyser with 1024 channels. All spectra were first collected on a large velocity scale. If no magnetic interactions was identified,
Table 1: XRF analyses of the bulk and electron microprobe analyses (EMP analyses of the glass and mineral phases (<5% in tholeiitic basalt glass, Kilauea)

<table>
<thead>
<tr>
<th>EMP analyses, Kilauea basalt glass, 1996</th>
<th>EMP analyses of minerals in Kilauea basalt glass, 12 April 1996</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location:</td>
<td>px1</td>
</tr>
<tr>
<td></td>
<td>12 Apr 96</td>
</tr>
<tr>
<td>SiO₂</td>
<td>51.49</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.77</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>13.33</td>
</tr>
<tr>
<td>FeO</td>
<td>11.56</td>
</tr>
<tr>
<td>MnO</td>
<td>0.21</td>
</tr>
<tr>
<td>MgO</td>
<td>6.30</td>
</tr>
<tr>
<td>CaO</td>
<td>11.40</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.05</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.32</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.41</td>
</tr>
</tbody>
</table>

XRF analyses, bulk rock

| SiO₂ | 50.82 | 50.69 | 50.77 | 50.74 | 50.94 | 50.97 |
| TiO₂ | 2.45  | 2.4   | 2.43  | 2.4   | 2.41  | 2.46  |
| FeO  | 11.32 | 11.51 | 11.42 | 11.43 | 11.3  | 11.1  |
| MnO  | 0.18  | 0.17  | 0.17  | 0.17  | 0.17  | 0.18  |
| MgO  | 8.61  | 8.52  | 8.07  | 8.38  | 7.99  | 7.87  |
| CaO  | 10.68 | 10.91 | 11.01 | 10.86 | 11.00 | 10.97 |
| Na₂O | 2.08  | 2.02  | 2.24  | 2.18  | 2.19  | 2.15  |
| K₂O  | 0.41  | 0.41  | 0.42  | 0.42  | 0.42  | 0.42  |
| P₂O₅ | 0.21  | 0.24  | 0.23  | 0.25  | —     | —     |
| NBO/T| 0.858 | 0.829 | 0.831 | 0.840 | 0.818 | 0.818 |

Based on 24 oxygens

a smaller velocity scale was chosen to improve resolution. Spectra were fitted with one to three doublets of Lorentzian shape. For five samples Jochen Hoefs from the University of Göttingen kindly provided δ¹⁸O analyses and four samples were checked by Harald Behrens from the University of Hannover with IR spectroscopy.

**RESULTS**

Dynamic heating, differential scanning calorimetry

High-temperature DSC patterns of Kilauea basalt glasses are dependent on whether experiments are undertaken in air or in argon atmosphere. Six observations are made (see Figs 1 and 2):

1. Air and argon experiments show an endotherm dip at the glass transition temperature \( T_g \), around 640°C, exotherm events of crystallization at \( T_c \), and endotherm dips at \( T_m \) (melting event). Melting in air occurs in one event, and in argon in two events.

2. Crystallization occurs in air in two events, and in argon in one single event, approximately at an intermediate temperature between the two peak temperatures of the air run.

3. In runs at 10 K/min, \( T_c \) and \( T_g \) are shifted to lower temperatures by about 7°C and 23°C, respectively, compared with runs at 20 K/min.

4. In second runs (molten–in glass), \( T_c \) is shifted to lower temperatures compared with the first run if the first run was in air, and \( T_c \) is shifted to higher temperatures if the first run was in argon (\( T_c \) shifts are of the order of 60–70°C).
### Table 2: Experimental conditions for isothermal reheating, chunk and powder; Fe³⁺/Fe²⁺ from Mössbauer spectroscopy (only for glassy material)

<table>
<thead>
<tr>
<th>Chunk</th>
<th>Powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C, ± 3°C)</td>
<td>Time (h)</td>
</tr>
<tr>
<td>T16</td>
<td>700</td>
</tr>
<tr>
<td>T13/1</td>
<td>775</td>
</tr>
<tr>
<td>T13/2</td>
<td>775</td>
</tr>
<tr>
<td>T13/4</td>
<td>775</td>
</tr>
<tr>
<td>T13/3</td>
<td>775</td>
</tr>
<tr>
<td>T13/5</td>
<td>775</td>
</tr>
<tr>
<td>T8</td>
<td>850</td>
</tr>
<tr>
<td>T15/1</td>
<td>850</td>
</tr>
<tr>
<td>T15/2</td>
<td>850</td>
</tr>
<tr>
<td>T4</td>
<td>900</td>
</tr>
<tr>
<td>T14/1</td>
<td>900</td>
</tr>
<tr>
<td>T14/2</td>
<td>900</td>
</tr>
<tr>
<td>T3</td>
<td>913</td>
</tr>
<tr>
<td>T7</td>
<td>919</td>
</tr>
<tr>
<td>T9</td>
<td>924</td>
</tr>
<tr>
<td>T1</td>
<td>935</td>
</tr>
<tr>
<td>T5</td>
<td>936</td>
</tr>
<tr>
<td>T2</td>
<td>950</td>
</tr>
<tr>
<td>T10</td>
<td>970</td>
</tr>
<tr>
<td>T12</td>
<td>1013</td>
</tr>
<tr>
<td>T1</td>
<td>1033</td>
</tr>
<tr>
<td>T6</td>
<td>1090</td>
</tr>
<tr>
<td>Ar 1</td>
<td>835°C, in argon</td>
</tr>
</tbody>
</table>

*No Fe²⁺ apparent, estimated as 4%.

(5) For the various samples, T_g and T_m are rather constant, around 640°C and 1150°C, respectively; some more significant variations are found for the crystallization temperature T_c (Fig. 2).

(6) The degree of crystallization, reflected in the intensity of the T_c peaks, is higher for the first run, if both runs were in argon, and higher for the second run, if the first run was in air and the second in argon (Fig. 1).

All these observations reflect the kinetic dependence of the occurring events. For example, a temperature shift of T_g and T_c, as a result of heating rate, mentioned in (3) is well known from the literature (e.g. Moynihan, 1995). The shift of T_c in the second run, point (4), is likely to be related to the stability of iron-bearing phases, as the shift depends on environmental atmosphere. Variations noted under (5) should reflect different amounts and/or ratios of phenocrysts present, or different thermal histories, as samples were collected at various distances from the vent. These effects have been discussed, for example, by Kirkpatrick (1981) or Mishima et al. (1996). The most important observation for the present study is made in point (2). Peak temperatures of crystallization around 850°C and 924°C for the run in air, and at ~890°C for the run in argon were the basis for the static heat treatment. Run products of DSC experiments were too difficult to recover and analyses therefore considered products of static heat-treatment experiments.

**Products of static heat treatment**

Chemical and textural features as a result of a static heat treatment in air (Table 2) are illustrated in Figs 3–5. Although the minimum temperatures for crystallization derived from DSC experiments should be around 650°C, investigations of chunks included also one treatment at 775°C (T13). Here, worm-like features were produced at the surface of the chunk and in its interior. Between
Elemental distribution images show a major enrichment in Ca, and suggest a minor enrichment in Mg and Fe at the surface (outermost 1–2 μm). Na cannot be detected at the surface, but Na increases sharply at ~10 μm towards the interior. Line profiles (Fig. 3) also show the major increase in Ca, and minor decreases in Al towards the sample–air interface, whereas changes in Mg and Fe are not apparent. After a treatment at higher temperatures (Fig. 5, T8, 850°C and T7, 919°C) dendritic features are visible. These dendrites are enriched in Mg and Ca and may have Fe-enriched apices (because heavy elements back-scatter electrons better than light elements; i.e. Fe enrichment is white in these BSE images). Fe enrichments may in places also occur at inherited crystals or vesicles. These worm-like features, or dendrites at higher temperatures, seen in BSE imaging, outline spherulites, as may be recognized when comparing BSE images with optical microscopy (Fig. 5, T7, 919°C). Line profiles do not change significantly compared with those of samples heated to 775°C. However, these elemental distribution patterns are less refined with temperature, disappearing above 900°C (Fig. 3), as a result of an increasing degree of crystallization. The two Al peaks in Fig. 1. Dynamic (high-temperature differential scanning calorimetry) experiments on Kilauea glass, prepared as powder with a grain size of ~300 μm. Two runs are shown whereby the second run was carried out on the glass that formed in the Pt crucible during cooling of the melt of the first run. The first run (heavy line) was either in air (upper graph) or in argon (lower graph); the second run was in argon in both cases.

the surface and the interior is a texturally relatively homogeneous zone of glass ~5–7 μm wide (Fig. 4).

Fig. 1. Dynamic (high-temperature differential scanning calorimetry) experiments on Kilauea glass, prepared as powder with a grain size of ~300 μm. Two runs are shown whereby the second run was carried out on the glass that formed in the Pt crucible during cooling of the melt of the first run. The first run (heavy line) was either in air (upper graph) or in argon (lower graph); the second run was in argon in both cases.

Fig. 2. Comparison of the glass transition temperature \( T_g \) (diamonds), the crystallization temperature \( T_c \) (triangles), and the melting temperature \( T_m \) (circles) for a series of basalt glass samples collected during a time period of half a year in 1996. Temperatures given are average values of the first run (filled symbols). For comparison, values of the second run are shown with open symbols. Variations occur mainly for \( T_c \).

Results of investigations in argon atmosphere after treatment at 835°C (45-5 h), 880°C (41 h), 913°C (39.6 h) and at 936°C (43 h) are illustrated in Figs 6 and 7. The choice of temperatures was derived from the DSC pattern (Fig. 1). At 835°C the formation of worm-like
no evidence is seen for the formation of Fe-oxides or plagioclase. Elemental profiles from the surface to the interior show a minor decrease in Ca and a small increase in Mg towards the surface (Fig. 6). A sharp increase in Na, as observed in air experiments, may be recognized best after the heat treatment at 835°C, but it gradually disappears towards higher temperatures.

Mineral phases produced in air

Pyroxene. Heat treatment has two effects on pyroxene: (1) the average chemistry of inherited pyroxene adjusts to heating temperatures with a decrease in Mg and Ca and increase in Al and Fe (e.g. sample 940); (2) new pyroxene grows, initiated by Mg and Ca phase separation and formation of dendrites. In BSE images, the pyroxene usually has a darker (Fe-poor) core, gradually changing to a lighter, Fe-richer margin. This zonation is the reverse of that commonly observed in pyroxene from basalt lava (e.g. Clague et al., 1995). Measurements taken in the centre of pyroxene show a change of chemistry with temperature of heat treatment (Table 3, Fig. 8a; Ti changes minimally and is therefore ignored in the figure). Pyroxene compositions expressed in components according to the projection by Lindsley (1983) are plotted in a quadrilateral in Fig. 8b. The compositions of the inherited pyroxene plot in the augite field; this suggests a precipitation temperature between 1100 and 1200°C, which is in agreement with temperatures obtained by the Gibbs free energy minimization program MELTS (Ghiorso & Sack, 1995). The melting temperature of 1170°C obtained here is consistent with the melting temperature derived by high-T DSC (see Fig. 1), as well as by the Mg-glass thermometer (Helz & Thornber, 1987). Pyroxenes that grew at temperatures below 850°C scatter between the augite, pigeonite and ortho-pyroxene region. There are several reasons for this scatter, all of which are probably related to a limited resolution by EMP analysis; the main reason is that the pyroxene minerals have a size of a few microns only and one measures mixed values of margin and centre. In addition, the scatter in composition may be due to an intergrowth of two pyroxenes. Px2 is rare and probably has not changed composition with temperatures of treatment. Estimating the ionic abundance from Fig. 8a, taking into account charge balance as well as general structural constraints, the temperature-dependent chemical variation may be described with the substitution reaction:

\[ \text{Fe}^{3+}\text{M}_{1} + \text{Fe}^{2+}\text{M}_{2} + \text{Al}^{3+}\text{IV}_{\text{M}_{1}} \leftrightarrow \frac{1}{2} \text{Si}^{4+}\text{IV}_{\text{M}_{1}} + \text{Mg}^{2+}\text{M}_{1} + \text{Ca}^{2+}\text{M}_{2}. \]

This reaction has an equilibrium slightly at the right side at temperatures around 1100°C, and at the left side at lower temperatures.

Fe–Ti oxides. Fe enrichment at the apices of pyroxene dendrites shows that Fe-oxide phases start to grow already below 850°C. Occasionally, a separation of Fe-rich oxides
Elemental distribution and BSE images of glasses treated in air at 775°C for 163 h. The BSE image shows a phase separation and the start of crystallization of dendrites at the grain boundary and in the interior (the grain to the right is an olivine). Corresponding textures are observed for Mg and Ca distribution images, but for Fe and Al, an outline of these textures becomes weak. This initial state of microcrystallization may be assigned to pyroxene formation. Na is low in pyroxene and reheating has developed a ‘Na-front’ at ~10–15 μm from the grain boundary (see also Fig. 3). The light grain border in the Ca distribution image should be noted. This marks a Ca enrichment at the sample–air interface (see also Fig. 3).

is seen along cracks in inherited olivine, without measurable effect on the olivine composition. Fe-oxides become observable with BSE in the 1 μm range around 924°C or 950°C, but are large enough for analysis without a dominant matrix effect only after a treatment at 1013°C.

After the heat treatment at 1090°C, four oxide phases are observed (Fig. 9). However, their small size precludes their identification under the optical microscope. The chemical composition and crystal habit in BSE images are the only tools available. Although only poor and qualitative probe analyses may be obtained, it is apparent that the main difference in composition is the FeO, MgO and TiO₂ content. TiO₂ around 40 wt % is likely to refer to ilmenite, and phases with MgO content around 12–13 wt % should be geikielite. Oxides with FeO(tot) of 70–80 wt % classify as haematite, and with TiO₂ of <20 wt % and ~65 wt % FeO should be ulvöspinel. All analyses have a total of several percent below 100%, indicating that at least some of the FeO in FeO(tot) is Fe₂O₃ (Table 3). Non-stoichiometric defect structures and intergrowth on a scale that cannot be resolved with back-scattered electrons should be expected. No sulphides could be detected, neither in the original samples nor in the heat-treated aliquots.

Plagioclase. Two different types of growth are observed. BSE images and elemental distribution pictures showing Al, Ca and Na suggest that a new phase grows on inherited plagioclase below 900°C, although with a composition that differs from that of the inherited plagioclase. Above ~925°C, plagioclase grows as needles within the glass, that is, without apparent relations to pre-existing interfaces. Above 935°C these phases are large enough to be analysed and show an anorthite content that is less than that of the inherited plagioclase. At temperatures of treatment as high as 1033°C the anorthite content increases again with rising temperature, to values that are comparable with those of the original plagioclase phenocrysts (see Fig. 10 and Table 3). The anorthite content of plagioclase, reflecting the temperature of formation, was used as geothermometer (Marsh et al., 1990). The plagioclase composition of the inherited phases around An₆₉ suggests a temperature of formation around 1180°C; the anorthite content of the new-grown phases around An₁₃ would suggest a formation temperature that is ~100°C higher than that applied in the experiments.

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**Fig. 4.** Elemental distribution and BSE images of glasses treated in air at 775°C for 163 h. The BSE image shows a phase separation and the start of crystallization of dendrites at the grain boundary and in the interior (the grain to the right is an olivine). Corresponding textures are observed for Mg and Ca distribution images, but for Fe and Al, an outline of these textures becomes weak. This initial state of microcrystallization may be assigned to pyroxene formation. Na is low in pyroxene and reheating has developed a ‘Na-front’ at ~10–15 μm from the grain boundary (see also Fig. 3). The light grain border in the Ca distribution image should be noted. This marks a Ca enrichment at the sample–air interface (see also Fig. 3).
Fig. 5. BSE images of samples after reheating in air (usually for 24 h). At 850°C: start of formation of dendrites (pyroxene), which surround more homogeneous areas (glass). The crystal in the centre is an olivine phenocryst. At 919°C: enhanced formation of dendrites with Fe enrichment at their apices (white spots), which have grown to grains of pyroxene (light grey) with Fe–(Ti) oxides (white) during reheating at 950°C. Areas that correspond to homogeneous glass in the previous images show a phase separation, and hence the crystallization of the bulk at 919°C, with a spherulitic growth of silicates and Fe–oxides at the apices (950°C). Black areas refer to plagioclase or residual glass, which are not resolved in grey levels. At 970–1090°C: with rising $T$ of treatment the crystal size increases (note the larger inherited plagioclase, which served as a nucleation centre for plagioclase growth at 1013°C; this may be observed also at much lower temperatures). At 1040 and 1090°C, a basalt texture of pyroxene (light grey), Fe–Ti oxides (white) and plagioclase (dark grey) is found. (Black areas are holes.)
Spectra of samples heat-treated above 950°C are complex, reflecting a variety of local environments for iron in Fe-oxides and pyroxene. Quantitative investigations of spectra are therefore restricted to samples treated no higher than 900°C. Spectra from samples heat-treated in argon atmosphere show some minor effect of oxidation probably below 10% Fe$^{3+}$ (835°C, 45.5 h, Fig. 11d) that increases with temperature of treatment. Reheating at temperatures above 890°C produces a magnetic splitting related to the increasing formation of pyroxene. Whereas the fit model, i.e. number of doublets and their assignment, is a matter of discussion, the determined ferric–ferrous ratio is largely independent of the model used (e.g. Helgason et al., 1992; Dunlap, 1997; Burkhard, 2000; Wilke et al., 2001). The error of redox estimates is of the order of 3–4%, derived from the fit residuals. Results are given in Table 2.

Oxygen isotope composition, δ$^{18}$O, and IR spectroscopy
The original glass of the hammer-dipped sample from 12 April 1996 has a δ$^{18}$O value of 4.76 (± 0.2‰) relative to SMOW, i.e. standard mean ocean water, where δ$^{18}$O (‰) = [(18O/16O_sample)/(18O/16O_SMOW)] - 1] × 10³. A Kilauea basalt from a 1974 eruption, analysed for comparison, has a value of 5.35 (± 0.2‰). These data are typical for Kilauea basalt lava, for which literature values are given between 4.6 and 5.8‰ (e.g. Kyser et al. (1982); more recent investigations of O-isotope compositions from Kilauea are those by Harmon & Hoefs (1995) and Garcia et al. (1998)). After heat treatment of chunks in air at temperatures between 850 and 1090°C for ~70 h, O-isotope compositions scatter within the range of 4.6–5.8 (± 0.2‰). Only after melting in air at 1250°C does δ$^{18}$O increase significantly to 10–79‰ (see Fig. 12). This means that an exchange with air of an O-isotope composition of 23.5‰ (e.g. Hoefs, 1997, and references therein) occurred only after melting. If the scatter of δ$^{18}$O observed for the sample of 12 April 1996 after heating is not related to this heat treatment, the scatter does occur in fact in the very same sample and illustrates local inhomogeneity of the lava. The data are in agreement with inhomogeneities in O-isotope compositions of basalt from various geotectonic settings (Harmon & Hoefs, 1995) that correlate with other geochemical characteristics (e.g. Eiler et al., 1998), and were assigned by those workers to a heterogeneous mantle (e.g. Harmon & Hoefs, 1995; Eiler et al., 1998).

Of the four samples investigated with IR spectroscopy, only the original, untreated glass was sufficiently transparent. For this glass, a water content of 688 ppm was determined. Heat treatment resulted in heterogeneous transparency and finally its loss, as a result of crystallization. Quantitative analyses of these samples were therefore not possible. However, qualitatively, the loss of water was noticed already after a treatment at 850°C.
BURKHARD REHEATING EXPERIMENTS ON KILAUEA BASALT GLASS

DISCUSSION

Results of the investigation of heat-treated basalt glass reveal that the alteration involves three interrelated phenomena: (1) crystallization, (2) oxidation and (3) diffusion. All of these depend on temperature, time and environmental atmosphere. Here, we will mention some general aspects and focus on the kinetics of oxidation processes. A more quantitative treatment of crystallization and its kinetics is the subject of a forthcoming paper and will be based on the application of crystal size distribution theory.

Crystallization

Relation between static heat treatment and dynamic (DSC) experiments

Interpretation and assignment of exothermic events observed for the DSC pattern around 850° and 920°C in air and 890°C in argon benefits from a correlation with static heating experiments. During static heat treatment in air pyroxene and Fe-Ti oxides occur above 850°C. This suggests that the low-T exothermic peak of the DSC pattern (Fig. 1) is related to the crystallization of these minerals. Textures, however, show that the crystallization at these temperatures is confined to certain areas situated among glassy and comparatively homogeneous parts (Fig. 5). The arrangement of these crystallized parts suggests a relation to interfaces such as, for example, microcracks. After a heat treatment above 910°C, the bulk is crystallized, showing plagioclase and an enhanced occurrence of pyroxene and Fe-oxides. Hence, crystallization is interface-independent above ~910°C, suggesting that this event relates to the 920°C peak in the DSC pattern (Fig. 1). The onset of crystallization, as derived from the onset of the exotherm DSC peak, should occur at least as low as 800°C (Fig. 1). Figure 4, with images of single heat treatment at 775°C, shows already at this temperature first indications of phase separation in the glass as a precursor for crystallization.

Fig. 7. BSE pictures of samples after reheating in argon. An interface-controlled growth of pyroxene occurs up to 880°C with textures comparable with those observed after reheating in air (see Figs 4 and 5, reheating at 775°C and 850°C). At higher temperatures a fine texture within formerly homogeneous areas of glass indicates crystallization within the bulk. No Fe-oxides but Fe enrichments (light spots) are identified at these temperatures.
Table 3: Averaged electron microprobe analyses of pyroxene, Fe-oxides and plagioclase, grown in reheated glass

<table>
<thead>
<tr>
<th>T8</th>
<th>T9</th>
<th>T2</th>
<th>T2</th>
<th>T10</th>
<th>T11</th>
<th>T6</th>
</tr>
</thead>
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<tr>
<td>SiO2</td>
<td>52.75</td>
<td>47.99</td>
<td>47.01</td>
<td>47.81</td>
<td>46.71</td>
<td>47.02</td>
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<tr>
<td>TiO2</td>
<td>0.92</td>
<td>5.28</td>
<td>3.31</td>
<td>3.48</td>
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<td>2.96</td>
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<tr>
<td>Al2O3</td>
<td>2.66</td>
<td>6.05</td>
<td>9.75</td>
<td>7.83</td>
<td>7.41</td>
<td>6.58</td>
</tr>
<tr>
<td>FeO</td>
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<td>19.26</td>
<td>15.73</td>
<td>14.20</td>
<td>17.23</td>
<td>14.38</td>
</tr>
<tr>
<td>MnO</td>
<td>0.23</td>
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<td>0.25</td>
<td>0.29</td>
<td>0.31</td>
<td>0.30</td>
</tr>
<tr>
<td>MgO</td>
<td>17.78</td>
<td>9.44</td>
<td>8.89</td>
<td>10.83</td>
<td>11.53</td>
<td>13.19</td>
</tr>
<tr>
<td>CaO</td>
<td>18.07</td>
<td>10.57</td>
<td>12.70</td>
<td>15.18</td>
<td>13.22</td>
<td>15.47</td>
</tr>
<tr>
<td>Cr2O3</td>
<td>0.70</td>
<td>0.04</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Na2O</td>
<td>0.22</td>
<td>0.84</td>
<td>0.77</td>
<td>0.57</td>
<td>0.52</td>
<td>0.23</td>
</tr>
<tr>
<td>K2O</td>
<td>0.00</td>
<td>0.62</td>
<td>0.22</td>
<td>0.29</td>
<td>0.15</td>
<td>0.03</td>
</tr>
<tr>
<td>Sum</td>
<td>101.23</td>
<td>100.20</td>
<td>98.82</td>
<td>100.46</td>
<td>100.94</td>
<td>100.16</td>
</tr>
</tbody>
</table>

Based on 24 oxygens

| Si | 7.659 | 7.315 | 7.171 | 7.174 | 7.051 | 7.103 | 7.186 | 7.541 |
| Ti | 0.101 | 0.606 | 0.380 | 0.392 | 0.440 | 0.337 | 0.314 | 0.149 |
| Al | 0.455 | 1.086 | 1.753 | 1.385 | 1.314 | 1.172 | 1.045 | 0.603 |
| Fe | 0.980 | 2.455 | 2.006 | 1.782 | 2.179 | 1.816 | 1.384 | 0.927 |
| Mn | 0.028 | 0.041 | 0.032 | 0.036 | 0.040 | 0.038 | 0.034 | 0.030 |
| Mg | 3.848 | 2.144 | 2.021 | 2.421 | 2.988 | 2.969 | 3.431 | 3.679 |
| Ca | 2.811 | 1.727 | 2.076 | 2.441 | 2.141 | 2.504 | 2.512 | 3.040 |
| Cr | 0.080 | 0.004 | — | — | — | 0.014 | — | — |
| Na | 0.061 | 0.190 | 0.227 | 0.165 | 0.152 | 0.066 | 0.102 | 0.079 |
| K | 0.000 | 0.120 | 0.042 | 0.055 | 0.029 | 0.006 | 0.003 | 0.002 |
| Al(IV) | 0.341 | 0.685 | 0.829 | 0.826 | 0.949 | 0.897 | 0.814 | 0.459 |
| Al(VI) | 0.114 | 0.402 | 0.924 | 0.559 | 0.368 | 0.274 | 0.231 | 0.144 |
| M1, M2 | 8.004 | 7.689 | 7.708 | 7.851 | 7.946 | 8.011 | 8.023 | 8.049 |
| Cat.* | 18.577 | 19.793 | 20.746 | 14.529 |

*Cations in the oxides; a contribution of pyroxene is subtracted, based on the average pyroxene analyses at this T.
Tetr., tetrahedral position.
Fig. 8. Changes in pyroxene chemistry as a result of reheating: (a) variation in Si, Fe, Al, Mg and Ca in atom percent, as a function of reheating temperatures; (b) pyroxene compositions of inherited pyroxene in the original glass and after reheating were calculated according to Lindsey (1983) and plotted in the quahilateral. For comparison, theoretical compositions (dashes) during cooling to solid conditions were calculated with the program MELTS (Ghiorso & Sack, 1995).

As a result of increasing crystallization, the residual glass changes its composition. It shows increases in SiO₂, Al₂O₃ and K₂O, and decreases in FeO, MgO, CaO and TiO₂ between 850°C and 924°C. The relative amount of residual glass and crystallizing phases may, in principle, be estimated from variation diagrams. However, the quality of such estimates naturally depends on the quality of probe analyses, which is here limited by the size of the crystals (micron range for all phases). The application of variation diagrams to a sample treated around 1033°C, which had produced the best mineral analyses, provides roughly 12% residual glass, ~46–47% pyroxene, 40–43% plagioclase and 9–13% Fe(Ti). This result supports expectations and observations that the residual glass is highly disseminated in the sample and therefore difficult to identify by BSE.

After the static heat treatment in argon, only pyroxene is identified between about 830 and 935°C, suggesting that the DSC peak at 890°C is related to this crystallization. Textures illustrate that crystallization in the bulk occurs only above 890°C whereas, at lower temperatures, crystallization is confined to certain part of the glass (Fig. 7). These textures are comparable with those in air experiments below 900°C and are interpreted to also be the result of interface-controlled crystallization. The contrast to air experiments is apparent: pyroxene is stabilized at temperatures ~40° higher. At temperatures of ~936°C, growth of Fe-oxides cannot yet be observed.
Fig. 11. Mössbauer spectra: (a) of the original glass, showing the absorption peak of Fe$^{2+}$; (b) of a glass chunk, reheated at 700°C for 140 h (notice the shoulder at about 1 mm/s related to Fe$^{3+}$); (c) of a chunk reheated above 940°C for 24 h; this spectrum is shown in a larger velocity range to illustrate the magnetic interaction. This interaction is in agreement with the observed growth of pyroxene and Fe-oxides. (d) Spectrum of a sample reheated in argon flow, at 835°C for 45.5 h.

The observations of heating experiments are largely in agreement with results from cooling experiments. At redox conditions above the FMQ buffer, cooling experiments illustrate a first occurrence of magnetite instead of ilmenite (Snyder et al., 1993; Toplis & Carroll, 1995). The first appearance of Fe–Ti oxides at the pyroxene apices and a rare occurrence of ilmenite, which could be found in some places after the 1090°C treatment in air, is in agreement with the experimental set-up in an oxidizing atmosphere and results from cooling experiments. These experiments showed the dominance of magnetite as indicative of cooling open to oxygen (Toplis & Carroll, 1996). A shift of the stability of oxides to higher temperatures was suggested for cooling in an oxygen closed system (Toplis & Carroll, 1996; Partzsch & Lattard, 1999). This agrees with the observation that Fe–Ti oxides did not grow after a treatment in argon at 936°C.

Pyroxene compositions increase in Ca and Mg and decrease in Fe and Al with rising temperature of treatment (Fig. 8a). In cooling experiments of basalt at temperatures between 1166 and 1050°C, one observes a decrease in Ca in clinopyroxene towards a minimum (Toplis & Carroll, 1995) in agreement with observations from tholeiitic rocks [see references given by Toplis & Carroll].

They are therefore stabilized at temperatures >80°C above those required under atmospheric conditions. This is what one would expect, because oxidizing conditions stabilize Fe in oxides, as is known from buffer reactions (e.g. introduction by Frost, 1991).
(1995). The CaO(cpx) minimum occurring at the maximum of FeO*(cpx) was assigned to saturation of the magma in FeO* as a result of a saturation in magnetite. An analogy of cooling and heating processes would suggest that the Fe–Ti oxides growth occurs above 925°C. Here, however, we observe Fe–Ti oxides already at temperatures of at least 850°C. We therefore feel that the observed CaO and MgO* minima in pyroxene are unlikely to be related to magnetite saturation. One could imagine that the minima are related to redox conditions (see below).

Despite minor deviations, there is a general agreement between heating and cooling experiments. However, heating experiments consider the low-temperature stability of phases and one finds therefore different temperatures for their first appearance. The possible growth of Fe–Ti oxides as a result of reheating should be considered when interpreting natural remanent magnetism (NRM).

Process of oxidation
Electron charge transfer, $Fe^{2+} \rightarrow Fe^{3+}$

Oxidation is a kinetic process and depends on time, temperature, and on the surface area such that the $Fe^{3+}/Fe^{2+}$ ratio increases with surface area, with temperature and with time. The oxidation process in a melt may be described as

$\left(Fe^{2+}\right)_{melt} + \left(\frac{1}{2}O_2\right)_{gas} \rightarrow (Fe^{3+})_{melt} + \left(\frac{1}{2}O^{2-}\right)_{melt}$

The equilibrium constant for this equation is

$$K = \frac{a_{Fe^{3+}} \cdot (a_{O^{2-}})^{1/2}}{a_{Fe^{2+}} \cdot (a_{O_2})^{1/2}}$$

with

$$K = e^{-\Delta G/RT}$$

where $R$ is the universal gas constant, $T$, the temperature in Kelvin and $a_i$ is the activity of component $i$. Re-arranging these terms, one obtains

$$\log \left(\frac{a_{O^{2-}}}{a_{O_2}}\right) = -\frac{\Delta G^o}{2 \cdot 303RT} + \frac{1}{4} \log f_{O_2} - \frac{1}{2} \log a_{Fe^{2+}}$$

with $a_{O^{2-}}$ the activity of oxygen in the glass, which is related to its basicity (e.g. Fraser, 1975). If the activity of ferrous and ferric iron is approximated by their concentration in the glass and the oxidation has reached equilibrium, then the free energy of oxidation ($\Delta G$) may be estimated from the slope of a line in an Arrhenius plot of $\log (Fe^{3+}/Fe^{2+})$ vs $1/T$. The investigation of the time-dependent change of percent $Fe^{3+}$ permits the determination of time required for equilibration. An initial value of $\sim 7% Fe^{3+}$ of total Fe, as derived from wet chemical analyses, was used throughout the calculations. Figure 13 illustrates the oxidation behaviour as a function of time. The powder, here shown for that heated at 600°C, is characterized by a rapid increase and overshooting of the final $Fe^{3+}$ equilibrium, whereas chunks heated at 850 and 900°C approach their equilibrium smoothly. Chunks heated at 775°C and below show a different pattern that suggests a sluggish and heterogeneous equilibration. For powder and chunks heated at 850°C, $\Delta G$ was estimated to $-67 \pm 7$ kJ/mol and $-105 \pm 7$ kJ/mol, respectively (Fig. 14). Comparable estimations are known only from melts. Johnston (1964), investigating the reduction equilibrium of Na$_2$O·2SiO$_2$ melts, with traces of a variety of multivalent elements ($\sim $0.01 wt %) at 1100°C, found in the case of iron about 26 kJ; Mysen et al. (1985) concluded reduction experiments at $\sim 1550°C$ with more iron than Johnston and found for a set of Na silicate melts 9–16 kJ/mol, and for CaO·SiO$_2$–Fe$_2$O$_3$–Al$_2$O$_3$ melts, 16–32 kJ/mol. Schreiber (1986) determined for a multi-component melt with almost 60 wt % SiO$_2$ 188 kJ/mol for 10 wt % Fe and 305 kJ/mol if this melt contains only 1 wt % Fe. These data suggest that $\Delta G$ depends on the amount of iron and that a smaller amount of iron relates to higher $\Delta G$ for oxidation. Further, it appears that $\Delta G$ is larger in systems with a complex chemistry than in simple systems. $\Delta G$ of intervalence charge transfer ($Fe^{2+} \rightarrow Fe^{3+}$) for crystals is of the order of 116–221 kJ/mol (Burns, 1993). This is larger than $\Delta G$ of Fe$^{3+} \rightarrow Fe^{4+}$ in glasses, where bond structures are less defined.

Time-dependent studies allow one to derive the rate constant of oxidation, $k$. If $k$ has been determined at different temperatures, the activation energy $E_a$ for oxidation may be determined from an Arrhenius plot based on

$$ln k = ln A - \frac{E_a}{RT}$$

where $A$ is the pre-exponential factor. We used for $k$ the unit of percent $Fe^{3+}$ formed per second and considered the rapid oxidation within the first 24 h (Fig. 13). For powder, Fig. 15a shows two different lines with different pre-exponential factors and different slopes controlled by the $T$ regime. Below 586°C, $E_a$ and $ln A$ are about 32 kJ/mol and $\sim 3$, whereas above 600°C, $E_a$ and $ln A$ are about 20 kJ/mol and $\sim 4.5$, respectively. Inspection of the DSC pattern in Fig. 1 suggests that the temperature where a change of slope occurs is at the glass transition. Hence, as one might have expected, below $T_c$ a higher $E_a$ is required to obtain oxidation than above $T_c$. For chunk samples, oxidation kinetics is more gradual (Fig. 15b). $E_a$ and $ln A$ are found to be 100 kJ/mol and $+1.2$, respectively. Because of the sluggish kinetics already at
Fig. 13. Increase in Fe$^{3+}$ as a function of time: (a) for glass powder samples treated at 600°C; (b) for chunk samples treated at 900°C, 850°C and at 775°C.

Fig. 14. Arrhenius plot to determine $\Delta G$ of oxidation (induced by reheating) of powdered Kilauea glass.

Fig. 15. Arrhenius plot to determine $E_a$, the activation energy of oxidation, (a) for powder (note that $E_a$ is different above and below $T_g$) and (b) for chunk samples.

degree of polymerization. An increasing amount of network modifier cations increases diffusion of oxygen (e.g. Oshi et al., 1975), but also the kind of modifier cation is important. May et al. (1974) and May & Wollast (1974) observed that in a Na-rich melt oxygen diffusion is 2–3 times faster than in K-rich melts. A tholeiitic magma such as that from Kilauea is comparatively very fluid and one should expect a relatively good mobility of oxygen. However, the process of oxidation appears to be more complicated; for example, redox kinetics was significantly affected by the type of atmosphere applied during redox experiments. Faster redox kinetics was observed when the atmosphere contains hydrogen rather than CO as a reducing agent (Ulmer et al., 1992).

Results from O-isotope compositions show that during heat treatment in the laboratory an exchange with atmospheric oxygen occurred only during melting at ~100°C above $T_g$ over a period of 2 weeks (Fig. 13), data were not obtained from below $T_g$.

Role of oxygen

The observation that O-isotope exchange with air is restricted to high-temperature melting leads to another conclusion. Unless the magma was more reduced before eruption, the basalt lava does not oxidize during eruption.
and transport to the ocean, although exposed to air. Conditions of transport and/or temperatures apparently do not allow the energy barrier for oxidation to be overcome. One reason may be that exposure to air caused the immediate formation of a thin quenched film (microns thick) on the lava surface that prevents acceptance of oxygen. The flowing lava is typically a good fraction of a metre thick, meaning that only ~0.001% of the lava has a chance to oxidize.

Results from O-isotope compositions show that during heat treatment at temperatures at least up to 1090°C no exchange with atmospheric oxygen occurred. On the other hand, results from Mössbauer spectroscopy clearly illustrate that oxidation did take place. The process of oxidation below melting cannot be related to oxygen diffusion. This is also evident from a comparison of activation energies, $E_a$ values for tracer and self diffusion and for chemical diffusion in silicate melts are of the order of 377 and 215 kJ/mol [see discussion by Wendlandt (1991)], which is significantly higher than 100 kJ/mol, the highest value found in the present study for oxidation that is for chunks.

**Mechanisms of oxidation**

The mechanism of oxidation Fe$^{3+} \rightarrow$Fe$^{4+}$ requires in principle a charge balance for the excess electron. Although the occurrence of the classical coupled reaction that includes the acceptance of oxygen is not readily apparent, one could also imagine that cation diffusion, rather than the diffusion of the O$^{2-}$ anion, is involved. Diffusion as a result of heat treatment in air and argon is illustrated in Figs 3 and 6, which need to be compared with Figs 4 and 7. In air, a major enrichment of Ca occurs at the sample–air interface. A similar enrichment at the sample–argon interface is not observed. Pyroxene growing at the surface shows a decrease in Ca towards the interior, and Ca and Mg are about equal in the subsequent texturally homogeneous glass. In argon, Ca increases and Mg decreases in pyroxene that grows at the surface. (We compared here relative positions of the line profiles but units of intensity of the line profile are not calibrated.) In the untreated glass, concentrations of CaO are about twice that of MgO (Table 1, XRF and EMP analyses of glass). If heating in argon has any effect on the Ca and Mg distribution, then it is significantly less than that of heating in air. This suggests that the oxygen gradient between sample (reduced) and environmental atmosphere is a driving force for the observed diffusion. The sensitivity of CaO concentration in pyroxene growing at the surface to the oxygen gradient implies that the temperature-dependent CaO variations in clinopyroxene and the Ca valley of Fig. 8a may also have some relation to redox conditions.

An enrichment in CaO (and MgO) at the air–sample interface was also observed, by Cooper *et al.* (1996), in a ‘nepheline normative olivine basalt’ by Rutherford backscattering spectroscopy. After equilibration below FMQ buffer conditions, they heated the glass in air at 50–100°C below $T_s$ (655°C). (The fast kinetics at these low temperatures should be due to a lower degree of polymerization of their silicate glasses.) These workers suggested that these diffusion processes of cations are related to oxidation of the glass without the need of O diffusion, with a model that is based on their observation of an ‘Na-front’. We suspect that this ‘Na-front’ is equivalent to the sharp increase in Na that we observe at ~10–15 μm from the air–argon sample interface. A comparison with Figs 4 and 7 reveals that this increase marks the end of pyroxene growth at the transition to the non-crystalline glass. For this reason, this sharp increase in Na disappears at higher temperatures (above 900°C in air, and 880°C in argon) where crystallization included the bulk. A modified model of Cooper *et al.* is suggested in Fig. 16. Ca$^{2+}$ and Mg$^{2+}$, having moved to the surface, react with oxygen from the atmosphere to produce lime and periclase. The diffusion of Ca$^{2+}$ (and Mg$^{2+}$) from the interior is charge balanced by a counter flux of electron holes $h^+$ that oxidizes Fe$^{2+}$ to Fe$^{3+}$. The result of Ca diffusion is well observable in the surface regions; in all profiles that extend to >80 μm to the interior, Ca concentration is less than that of Mg, but in the original glass, Ca is higher than Mg. More to the interior, crystallization hides such possible compositional variations. Cooper *et al.* (1997), who performed heating experiments in argon atmosphere, described a minor increase in Mg at the sample–argon interface. The profiles of Fig. 6 suggest such an increase but this reflects a change in pyroxene composition.

Ca$^{2+}$ apparently has a extraordinary reactivity in the presence of an oxygen gradient, which has been observed previously. For example, Chaskar *et al.* (1993), investigating iron-bearing silicate slags, found a dramatic increase in ferric iron if such slags contained CaO. Fe$^{3+}$ decreased from the air–sample interface to the interior. This stabilization of Fe$^{3+}$ in the presence of Ca had been assigned to the formation of ferric anion complexes [see, e.g. Chaskar *et al.* (1993) and references therein]. During recent studies on iron-bearing silicate melts, an inhomogeneity, possibly occurring in zones sub-parallel to the air–sample interface, was found (Burkhard, 2000). We expect that the extremely negative standard free energy of formation of CaO, as compared with other oxides, is the reason for the observed Ca diffusion to the air–sample interface. The occurrence of free lime and its precipitation during slow cooling during slag preparation is known from metallurgy (e.g. Verein Deutscher Eisenhüttenleute, 1995).

Diffusion processes are apparently triggered by the oxygen gradient between sample and environmental atmosphere and are particularly evident at the surface.
Relaxation does play a role. Specifically, structural relaxation occurs upon heating and may release some of the dissolved OH, forming H₂O and oxygen. Or, if degassing is selective, a preferential escape of hydrogen formed by dissociation of water vapour may occur (Sato, 1978). Relaxation might also activate oxygen that might have been trapped as molecular species. The few percent of oxidation observed after treatment in argon atmosphere might be related to such degassing processes. Mass-spectrometric investigations will clarify this issue and are discussed in a forthcoming paper.

The amount of ferric iron formed (oxidation as charge transfer) is higher for a larger oxygen gradient. The fact that oxidation is particularly effective for high surface area samples suggests that oxidation is most effective in the surface region. These relations suggest that oxidation, and at least surface oxidation of the outer 80 μm, is related to cationic diffusion. In that case, one should expect comparable activation energies for oxidation and Ca²⁺ diffusion. E, for Ca²⁺ diffusion was determined to be 210 kJ/mol (Cooper et al., 1996), which compares well with results from tracer diffusion experiments from similarly polymerized slags below T_g (see references of Cooper et al. [1996]). This value is, however, significantly larger than E, of 32 and 20 kJ/mol for powder below and above T_g, and larger than 100 kJ/mol for chunks. The main reason for this discrepancy might be that the activation energies are derived in different procedures. For example, Ca²⁺ diffusion was not observed in view of the time needed for equilibration, as shown for Fe³⁺ formation in Fig. 13.

Independent of considerations about surface oxidation one should keep in mind that oxidation may be related to the structural relaxation of the glass. The differences in E, below and above T_g demonstrate that structural relaxation does play a role. Specifically, structural relaxation might result in a concomitant exsolution of dissolved water. Water solubility is a function of pressure, temperature and composition (e.g. Silver et al., 1990). For a water content as low as 688 ppm, found for Kilauea glass, all water should be dissolved as OH. The equilibrium constant of the reaction H₂O + ½O₃ = 2OH is strongly T dependent and favours OH at higher temperatures of equilibration (Dingwell & Webb, 1990; Zhang et al., 1991, 1995). Because glass is in disequilibrium by definition with a frozen-in high-T structure, structural relaxation occurs upon heating and may release some of the dissolved OH, forming H₂O and oxygen. Or, if degassing is selective, a preferential escape of hydrogen formed by dissociation of water vapour may occur (Sato, 1978). Relaxation might also activate oxygen that might have been trapped as molecular species. The few percent of oxidation observed after treatment in argon atmosphere might be related to such degassing processes. Mass-spectrometric investigations will clarify this issue and are discussed in a forthcoming paper.

Relation between diffusion and crystallization

As discussed above, the degree of crystallization of pyroxene, Fe–Ti oxides and plagioclase is much higher if heating is carried out in air as opposed to heating in argon (compare Figs 2 and 7). In that discussion, the stability of these phases was related to prevailing redox conditions and compared with cooling experiments. In view of the fact that oxygen does not diffuse into the sample, the relation between redox conditions (e.g. oxygen gradient) and degree of crystallization should be indirect. It is also not obvious how redox conditions should affect crystallization of iron-free phases, such as plagioclase. The apparent effect of the oxygen gradient on crystallization suggests that this gradient and/or related degassing processes induce an enhanced cationic mobility to overcome activation energy for diffusion in relation to nucleation and growth.

CONCLUSIONS

Reheating of Kilauea basalt glass results in crystallization, oxidation and diffusion processes, all of which increase with the oxygen gradient between the sample and the environmental atmosphere. In air, pyroxene and Fe (Ti) oxides grow interface controlled below 900°C and they grow in the bulk together with plagioclase above 920°C. In argon, only pyroxene is observed in an interface-controlled growth below 890°C, and in the bulk at higher temperatures. Kinetic parameters of the oxidation processes could be determined for the electron transfer Fe²⁺→Fe³⁺ but an oxygen exchange with the environmental atmosphere, and hence O diffusion into the sample, occurs only at or above melting temperatures. Cationic diffusion of mainly Ca²⁺ to the sample–air interface appears to be related to high surface oxidation...
rates; an increasing mobility of cations with the oxygen-gradient may also be the reason for an enhanced crystallization in air compared with argon.

ACKNOWLEDGEMENTS
The author thanks Carl Thornber for an exciting field trip on 12 April 1996, which allowed me to collect the samples studied here, and he also kindly made available samples collected within the next 6 months. Horst Pentinghaus at the Research Centre Karlsruhe kindly provided access to the DSC equipment, and Stefan Ebener’s help in carrying out these experiments is acknowledged. Wet chemical analyses by Gene C. Ulmer, from Temple University, Philadelphia, and by Gene Jarrossowish from the Smithsonian Institution, are much appreciated. Thin sections were kindly prepared at the Institute for Mineralogy at the University of Hannover and here, also, microprobe analyses could be carried out with the help of Jürgen Koepke. The author very much appreciates the hospitality of this Institute, help by various people, and, specifically the support by Wilhelm Johannes. Hiltrud Müller-Sigmund at the Mineralogical Institute of the University of Freiburg helped to obtain elemental distribution images. Jochen Hoefs from the University of Göttingen kindly determined the oxygen isotopic compositions of some samples, and Harald Behrens from the University of Hannover investigated the water content with IR spectroscopy. My warm thanks go to both. Gerti Steinbach kindly prepared most of the absorbers for Mossbauer spectroscopy. Continuous interest and discussions with Gene C. Ulmer were very valuable, and his critical reading of a first version improved this manuscript. Encouragement and final reading by Laszlo Keszthelyi from The University of Arizona, Tuscon, and suggestions by an anonymous reviewer are much appreciated. The author acknowledges partial funding by the Deutsche Forschungsgemeinschaft (DFG) in the Heisenberg-Program and an additional grant from Switzerland.

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