

Dedicated to Prof. Dr. H. J. Seifert on the occasion of his 60th birthday

THE DEGASSING BEHAVIOUR OF NATURAL GLASSES AND IMPLICATIONS FOR THEIR ORIGIN

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Degassing experiments showed that a remarkable difference exists between glasses from a range of geological environments. The released gases were thermally analysed by a simultaneous thermogravimetric, mass spectrometric (partial pressure), and total pressure measurements of evolved gases by heating from room temperature to 1450°C. Detailed degassing studies on natural glasses from various terrestrial environments show that the degassing behaviour of glasses differs strongly, also in respect of the manmade glasses. The gas release profiles of natural glasses can be divided into three groups: 1) volcanic glasses, 2) impact glasses and 3) silica glasses and tectites.

The degassing behaviour of manmade glasses is determined by the melting technique, the raw materials, and the fining agents. Gas release curves are suitable tools for the identification of vitreous samples of unknown origin but it is impossible to gain data of physico-chemical conditions of the glass formation process or for the polymerization state of the melt.

Detailed studies of gas release profiles of volcanic glasses from various geological environments show significant differences between lava types [1-3]. These differences are attributed to the different physical properties of the glass samples (such as viscosity, diffusion rate and solubility of gases) which are determined directly both by the bulk chemistry and the genesis. An attempt was made to find a correlation between the temperatures at which the different gases are released (gas release temperature profiles) and the melting structure (degree of polymerization) [2].

Numerous investigations of manmade glasses show that both the analytical techniques and the physico-chemical conditions of glass formation strongly influence the gas release profiles [4, 5]. In the following investigations experiments were carried out in order to get more detailed informa-

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tion about the process of bubble formation. A consequent standardization of measurements allows to compare quantitatively the results of degassing experiments.

Recently O'Keefe [6] published a review describing half a dozen different natural glasses which he classified according to the mechanism by which they were formed. This is a suitable starting point to show how it is possible to deduce from glass release profiles the formation history of vitreous bodies.

In terms of petrography, natural glass formation processes can be classified into three different groups:

1.) glass formation in connection with magmatic activities (volcanism):

In this case, vitreous bodies are quenched parts of magmatic melt and represent a frozen state of the bulk composition, not only of the major elements but in part also to the volatiles (obsidians, slags, [7]). In the case of foamed slags as well as in the case of the 'snowflakes' in obsidian a partial or total degassing of the melt occurs before the glass transformation. As microphotographs show in differential phase contrast, the homogeneity of the vitreous fraction is high, also in the surroundings of the crystals [8].

Glass inclusion in minerals are discussed as remains of the original melt composition too [9].

2.) glass formation by metamorphism (pyrometamorphism, shock metamorphism).

Here the composition of the glasses represents the composition of the whole rock or part of the rock (e.g. frictionites, fulgurites [10] or impact glasses, tectites) or of a single mineral (e.g. the feldspars composition in the maskelynite glass [11]).

3.) glass formation by solidification of silica-gels like hyalite. The composition is mainly silica and water [12].

In the present paper gas release profiles are presented for different natural glasses. The possibility of interpretation of these profiles on the basis of glassmaking experience is discussed.

Experimental

Degassing experiments were carried out using a TA1 Thermoanalyzer (Mettler, Switzerland) combined with a quadrupol mass spectrometer (QMG 101 Balzers Liechtenstein). The system was described in detail elsewhere [1]. In this way it was possible to determine simultaneously the change in total pressure within the vessel, the partial pressure of selected volatiles

by single ion detection, and the mass loss of a sample as a function of the temperature.

Table 1 Chemical composition of specimens for evolved gas analysis

Sample Nr.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O
1	72.26	15.83	0.04	0.57	0.02	0.22	4.14	3.66
2	76.68	12.84	1.18		0.22	1.26	3.11	3.34
3	76.37	12.99	1.47		0.33	1.65	3.27	2.86
4	76.08	12.76	1.45		0.32	1.53	3.25	2.81
5	75.93	12.59	0.92		0.65	0.34	3.50	4.32
6	72.11	13.16	1.82		0.05	0.69	4.11	5.05
7	73.63	13.15	1.82				4.00	5.07
8	74.30	13.26	1.85				4.06	5.14
9	36.6	8.0	6.2	5.6	18.2	15.1	2.8	1.4
10	72.01	15.55	5.50		1.11	0.55	1.10	2.83
11	74.28	10.16	5.60		2.93	2.36	0.97	2.00
12	78.30	10.18	3.75		1.43	1.21	0.92	2.41
13	97.58	1.54	0.11	0.23	tr	0.38	0.34	
14	65.77	15.56	4.76		2.74	3.98	2.60	3.36

Sample 1 Macusani glass [13] (F=1.30%, H₂O=0.46%, CO₂=0.09%, Li₂O=0.74%, B₂O₃=0.62%, P₂O₅=0.53%, TiO₂=0.04%); 2 Obsidian Milos (SN3) [14]; 3 Obsidian Milos (D12) [14]; 4 Obsidian Milos (D13) [14]; 5 Obsidian Antiparos (D5) [14]; 6 Obsidian Lipari (R35) [15]; 7 Obsidian Lipari (R26) [15]; 8 Obsidian Lipari (R34) [15]; 9 Kammerbühl, Melilith-Nephelinitbasalt [19] TiO₂=2.5%; 10 Zhamanshinit (Si-reich) [17]; 11 Irghisit ('sauer') [17]; 12 Muong Nong [16]; 13 Lybisches Wüstenglas [16]; 14 Suevit, Ottingen, Nördlinger Ries [18]

In Table 1 the chemical compositions (in weight percent) of the glasses studied are presented. More detailed description of the samples including geological aspects and formation, is given in Ref. [13–19].

The degassing behaviour of the samples (the temperature of bubble formation, the bubble number, and the bubble size) is affected by the sample preparation, the starting pressure, and the crucible material.

In the present study the experimental conditions were as follows:

- sample size: 30–120 mg, single broken piece, without any handling,
- crucible: Al₂O₃, pretreated to incandescence in a gas flame,
- vacuum: <10⁻³ Pa, left overnight at room temperature,
- heating rate: 10 (up to the main gas release) and 2 deg/min (range of the main gas release for samples with high gas content),

– MS analysis: single ion mode (m/e 17, 32, 44, 28, 14, 12 for H₂O, O₂, CO₂, CO/N₂).

The gas release profiles of glasses are characterized by the number of spikes and the volume of the released gas which was evolved by bursting of bubbles (the intensity of spikes). Each spike represents the bursting of a bubble from the melt. A calibration of the intensities of the spikes by injection of known volumes of gas into the sample chamber allows a semiquantitative estimation to be made of the volume of gas evolved (critical value = 1 nl) [5].

Results and discussion

The gas release from glasses can occur in two different processes, in that involving degassing with a continuous change in the partial pressure, and that with spiky gas release pattern (Figs 1a and 1b). The continuous gas release can be explained by the diffusion of the volatile species from the surface of the sample and the degassing spikes by the burst of the bubbles.

As it is demonstrated in Figs 2–5 the gas release profiles differ for glasses of different genesis both in the temperature and in the range of bubble forming. On the basis of analysis of more than 50 specimens a classification of a glass specimen is possible by means the gas release in the 1000–1250° range.

Manmade glasses show a separation in the gas release temperature for volatiles resulting from the raw materials (as lime), and gas inclusions (as air) and from chemical reactions of the fining agents (Fig. 1) [4, 5].

The relation between the temperature of bubble formation and the bulk chemistry or the viscosity is complicated, as was discussed by Hampton and Bailey [2]. It means that the gas release is not determined only by the degree of the formal polymerization state of the melt structure calculated from the bulk composition (Table 2), but also by extrinsic factors of the glass formation such as the cooling rate and p – T –conditions during cooling.

The interpretation of the gas release curves should depend on the changes in the composition of specimen, especially on the change of water concentration during heating. In this case the viscosity is changed not only by the heating but also by the loss of volatiles. Calculation of the viscosity plots, p.e. by means of Shaw's empirical method [20], is irrelevant in respect to the interpretation of gas release profiles.

The temperature of the 'main gas release' is strongly affected by the analytical conditions. Further characteristic data in the gas release of vol-

canic glasses are the temperatures of "explosion". But this effect is observed only with volcanic glasses.

As it was demonstrated for basaltic glass and crystalline basalt from Eger (Kammerbühl) the influence of phenocrysts in glass on the gas release profiles is not significant in contrast to observations by Götze [3] for a felsic glass from Jerevan and by Hampton [2] for mafic glass. The gas release in the basalt glass from Kammerbühl (Figs 6 and 7) is not correlated with the exothermic crystallization effect in the DTA curve.

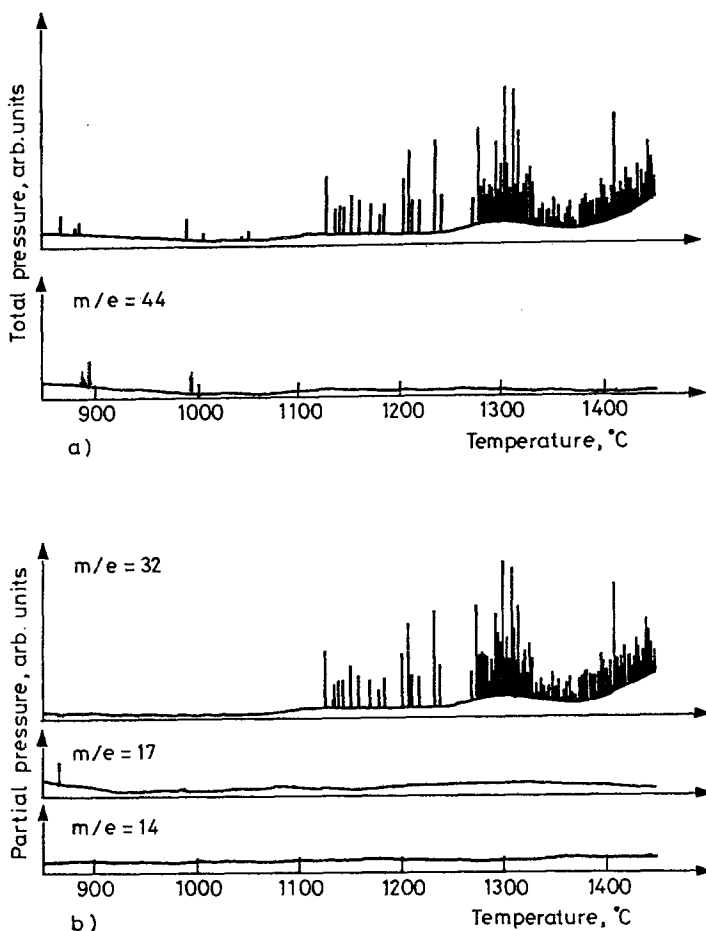


Fig. 1 a) Gas release profile (total pressure and CO₂ [*m/e* 44]) of a soda-lime-silica glass with Sb₂O₃ for fining; b) O₂, [*m/e* 32], H₂O [*m/e* 17] and N₂ release of the same specimen as in Fig. 1a

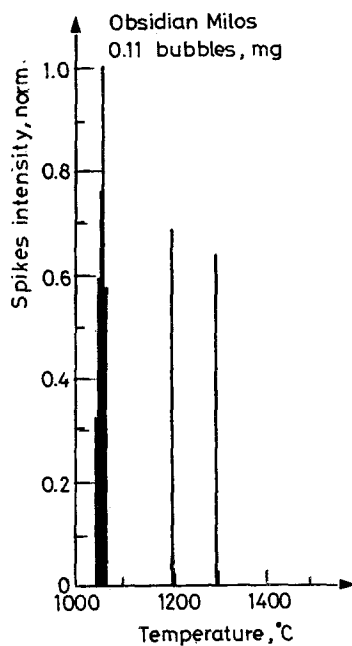


Fig. 2 Bubble release profile for volcanic glass (Obsidian Milos Greece)

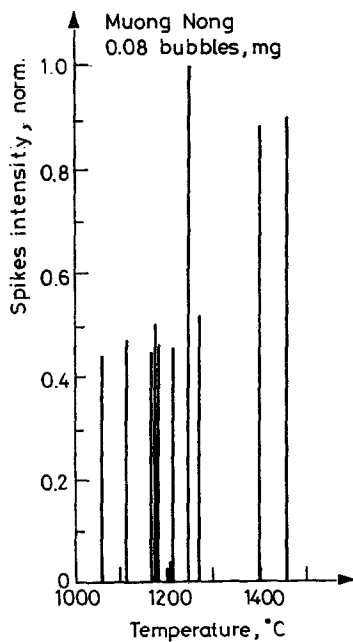


Fig. 3 Bubble release profile for Muong Nong tektite (Thailand)

The gas release from impact glasses such as Suevit from Nördlingen shows a similarity to the degassing behaviour of perlites [21].

A remarkable difference between manmade glasses and obsidians is the explosive water release of obsidians. This 'explosion' temperature cannot be calculated from the viscosity on the basis of the bulk chemistry. Possibly this

Table 2 R₂O : Al₂O₃ relations, water content, and 'explosion' temperature for natural glasses

Sample Nr.	R ₂ O : Al ₂ O ₃	mass loss % up to 1100°C	'explosion' temperature °C
1 (Macusani)	0.66	0.50	833
2 (Milos)	0.67	0.46	1045
5 (Antiparos)	0.83	3.32	—
7 (Lipari)	0.92	0.12	965
10 (Zhamanshinit)	0.69	0.64	1030
12 (Muong Nong)	0.42	0.02	—
14 (Suevit)	0.52	—	1085
9 (Glassy Basalt Eger)	0.76	0.11	1185

R₂O = Na₂O + K₂O

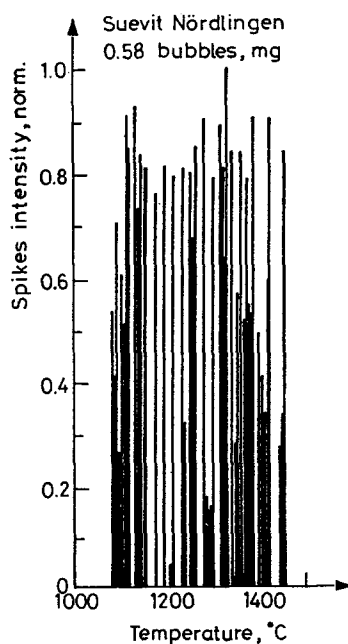


Fig. 4 Bubble release profile for impact glass (Suevit, Ottingen, FRG)

temperature is an indicator for the pressure and temperature conditions in the magma reservoir immediately before the eruption.

Considering the gas release profiles the origin of the 'classic' tektite glasses including that from Muong Nong must be quite different from the formation of impact glasses like Irghizites or Suevites but also from the formation of typical volcanic glasses.

The interpretation of gas release profiles in respect to the glass structure and conditions of formation requires more intensive investigations. But at the present time gas release profiles are useful tools for the characterization of glass specimens of unknown origin.

The gas release profiles of natural glasses can be divided into three groups:

1) volcanic glasses, 2) impact glasses and 3) silica glasses and tectites.

Volcanic glasses are characterized by an 'obsidian' or 'perlite' degassing. In case of obsidians a spontaneous gas emission, mainly of H_2O and CO_2 , in the temperature range of 850 and 1100° is observed.

The main gas release of perlites occurs continuously in the range between 70 and 900° and is accompanied by the evolution of H_2O .

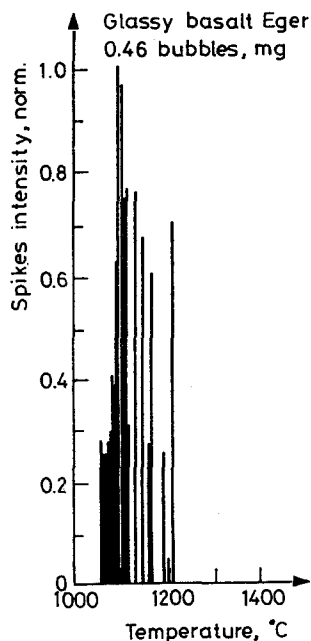


Fig. 5 Bubble release profile for basaltglass (Kammerbühl near Eger, CSFR)

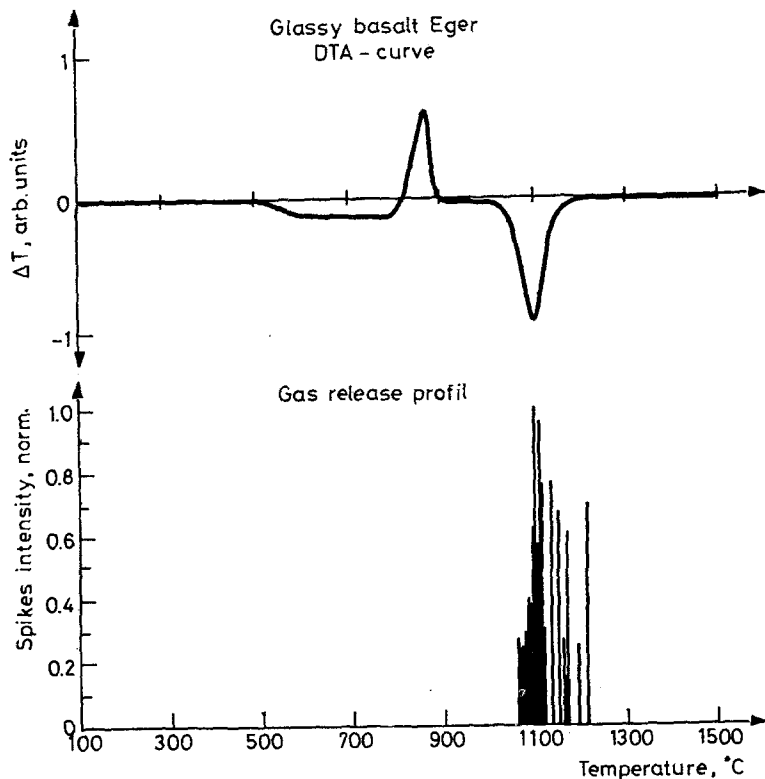


Fig. 6 DTA curve and bubble release profile for basalt (Kammerbühl, CSFR)

Both types of volcanic glasses release bubbles in the range between 1100 and 1600°, whereby mainly water and/or oxygen is evolved.

Impact glasses show a wide range of degassing by forming mainly water and oxygen bubbles in the range from 1000 and 1450°.

Silica glasses like Lybian Desert glass and tektites exhibit no or very small degassing effects in the temperature range from 1000 up to 1600°.

A marked difference was observed between the gas release curves of manmade glasses and natural glasses. The degassing behaviour in this case is determined by the melting technique, the raw materials, and the fining agents.

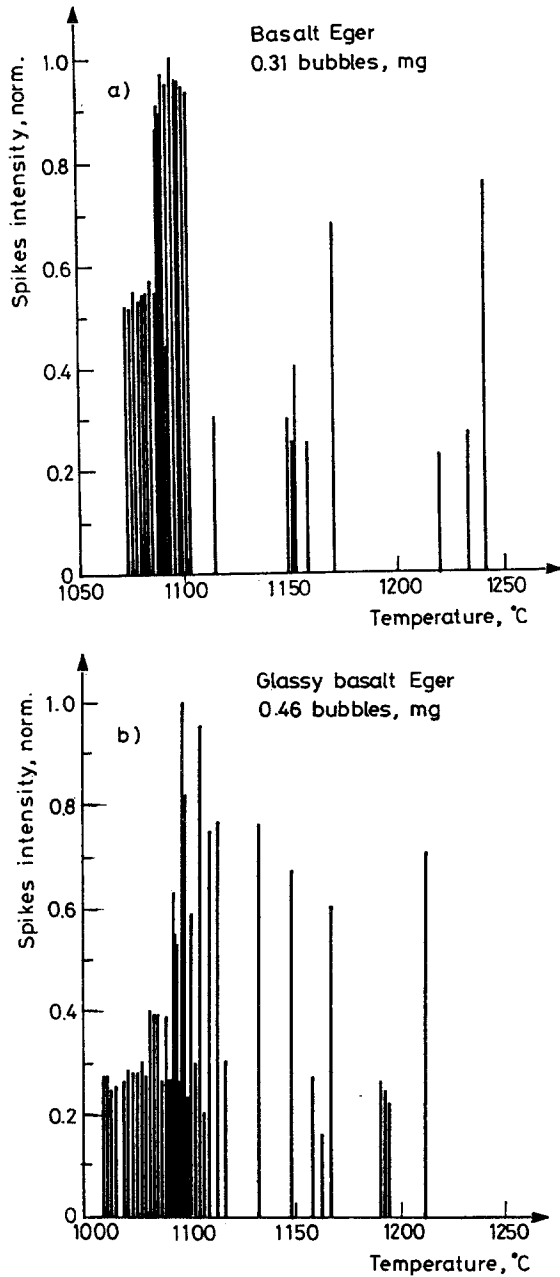


Fig. 7 a) Bubble release profile for basalt of Kammerbühl near Eger, CSFR; b) Bubble release profile for glassy basalt near the location of crystalline basalt of Kammerbühl near Eger, CSFR

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Zusammenfassung — Entgasungsexperimente zeigen, daß zwischen Gläsern von einer Reihe von geologischen Umfeldern bemerkenswerte Unterschiede bestehen. Die beim Erhitzen von Raumtemperatur auf 1450°C freigesetzten Gase wurden thermisch mittels simultanen thermogravimetrischen, massenspektrometrischen (Partialdruck) und Gesamtdruckmessungen analysiert. Ausführliche Entgasungsstudien an natürlichen Gläsern aus verschiedenen Landschaftsgebieten zeigen, daß sich das Entgasungsverhalten der Gläser stark unterscheidet, auch im Vergleich zu künstlich erzeugten Gläsern. Die Gasfreisetzungprofile natürlicher Gläser können in drei Gruppen unterteilt werden: 1.) vulkanische Gläser, 2.) Aufschlaggläser und 3. Silikatgläser und Tektite.

Das Entgasungsverhalten künstlich hergestellter Gläser wird durch die Schmelztechnik, die Rohstoffe und die Läutermittel bestimmt. Entgasungskurven sind ein geeignetes Mittel zur Identifizierung glasähnlicher Proben unbekanntem Ursprunges. Es ist jedoch nicht möglich, Daten über physikalisch-chemische Bedingungen der Glasbildungsprozesse oder über den Polymerisationsgrad der Schmelze zu erhalten.