ELSEVIER

Thermochimica Acta 354 (2000) 165–172

thermochimica
acta

www.elsevier.com/locate/tca

The detection of an inorganic hydrocarbon formation in silicate melts by means of a direct-coupled-evolved-gas-analysis-system (DEGAS)

K. Heide*, K. Gerth, E. Hartmann

Institut für Geowissenschaften Friedrich-Schiller-Universität, Jena, Germany

Received 7 June 1999; received in revised form 2 August 1999; accepted 16 August 1999

Abstract

In an attempt to determine the volatile components in various industrial, laboratory and natural glasses, the gas release from the silicate melts in high vacuum — high temperature extraction experiments were analyzed by simultaneous TG and mass spectrometry. In the temperature range from 800 to 1200°C molecular fragments with m/z=13, 15, 27, 28, 29, were detected, which are possible fragments of hydrocarbon molecules.

Similar behaviour could be demonstrated by analysis of glass samples synthesized in the laboratory. The formation of hydrocarbons during the heating process was successfully controlled by the carbon concentrations in the batches, through appropriate additions of carbon bearing reagents — graphite, Al- and Ca-carbides, di- and polysaccharides, or Na-acetate.

Based on the degassing profiles (DP) it is possible to deduce a mechanism for the formation of hydrocarbons, e.g. of methane in systems containing graphite or carbides and hydroxideions:

$$C + 4(OH)^- \Rightarrow CH_4 + 2O^{2-} + O_2$$

The oxygen formed during this process is dissolved in the melt and escaped again in the form of oxygen bubbles with a further temperature increase.

With the DP of laboratory prepared melts, it was possible to give an interpretation of the observed degassing maxima of m/z 13, 15, 27, 28, 29, on the one hand, by the formation of molecular fragments of CH_4 and C_2H_6 and, on the other hand, by the carbon isotopic relations, e.g. m/z 13=$^{12}CH^+$ or $^{13}C^+$; m/z 28=$^{12}C_2H_4{}^+$ or $^{12}C^{13}CH_3{}^+$.

Keywords: Evolved-gas-analysis; Silica melts; Hydrocarbon formation; Mass spectrometry

1. Introduction

The detection of volatile species of mass number m/z=15 during degassing experiments of different industrial glasses indicates the formation of hydrocarbons, obviously derived from C- and H_2O-relicts in the melt, as was shown by Hartmann et al. [1].

The inorganic formation of methane can be induced by the action of water on Al_4C_3

$$Al_4C_3 + 6H_2O \Rightarrow 2Al_2O_3 + 3CH_4 \qquad (1)$$

or by reaction between acetates and NaOH

$$CH_3COONa + NaOH \Rightarrow Na_2CO_3 + CH_4 \qquad (2)$$

---

* Corresponding author. Fax: +49-3641-948602.
E-mail address: ckh@rz.uni-jena.de (K. Heide)

PII: S0040-6031(00)00418-4

Table 1
Starting materials and carbon components for preparation of different glasses

	Chemical composition of the starting materials	Purity	Produced by
Oxide components			
Na_2O	Na_2CO_3	p.a.	Merck AG
	Na_2CO_3	supra pure	Merck AG
	Na_2CO_3	p.a.	Laborchemie Apolda
CaO	$CaCO_3$	'reinst f.opt.Zwecke'	Leuchtstoffwerk Bad Liebenstein
	$Ca(NO)_2$	p.a.	Own preparation
SiO_2	SiO_2	'reinst f. opt. Zwecke'	IGW Jena
	SiO_2	'optipur'	Merck, Darmstadt
Carbon components			
Graphite	C	'reinst'	Laborchemie Apolda
	Al_4C_3	'reinst'	Riedel de Haen AG Hannover
Disaccharide	$C_{12}H_{22}O_{11}$	p.a.	Merck AG Darmstadt
Polysaccharide	$(C_6H_{10}O_5)_n$	p.a.	Merck AG Darmstadt
Sodium-acetate	CH_3COONa	p.a.	Merck AG Darmstadt
Calcium-carbide	CaC_2	'reinst'	Laborchemie Apolda

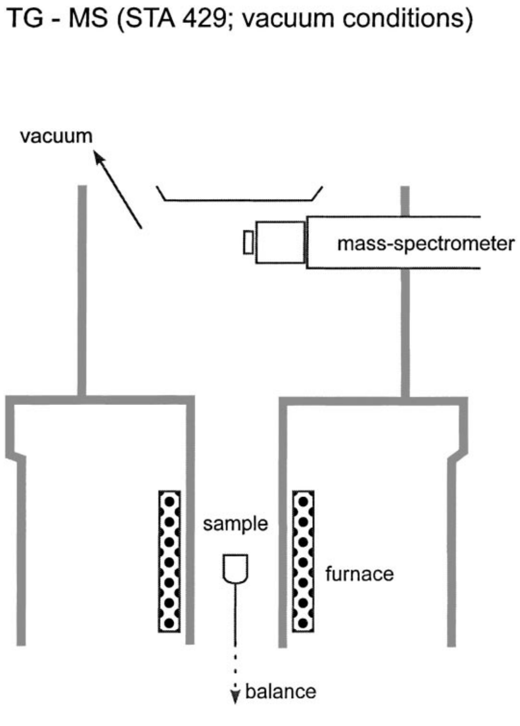


Fig. 1. Schematic of the main components of the DEGAS-devices. To minimize the loss of information by condensation in the system, the distance between the sample holder and the MS-gas detection was about 20 cm.

Furthermore, formation of methane can result from a two-step process between carbon and water

$$C + H_2O \Leftrightarrow CO + H_2 \qquad (3)$$
$$C + 2H_2 \Leftrightarrow CH_4$$

Higher C–H species, e.g. ethyne (acetylene), result from the reaction, e.g. between Ca-carbide and water

$$CaC_2 + 2HOH \Leftrightarrow Ca(OH)_2 + C_2H_2 \qquad (4)$$

In the following investigations it was tested whether the addition, e.g. of Al_4C_3, results in the formation of methane during the heating process in the temperature range above 800°C, and whether the carbon and water

Table 2

m/z	Isotopes
2	H_2
12	$^{12}C^+$
13	$^{12}CH^+$, $^{13}C^+$
14	$^{12}CH_2{}^+$, $^{13}CH^+$, N^+
15	$^{12}CH_3{}^+$, $^{13}CH_2{}^+$, NH^+
16	$^{12}CH_4{}^+$, $^{13}CH_3{}^+$, $NH_2{}^+$, $^{16}O^+$
18	H_2O^+, $NH_4{}^+$
27	$^{12}C_2H_3{}^+$, $^{13}C_2H_2{}^+$
28	$^{12}C_2H_4{}^+$, $^{13}C_2H_2{}^+$, $^{12}C^{16}O^+$, $^{12}C^{13}CH_3{}^+$, N_2
29	$^{12}C_2H_5{}^+$, $^{13}C_2H_3{}^+$, $^{12}C^{13}CH_4{}^+$, $^{13}C^{16}O^+$

concentration in an industrial silicate melt and in natural glasses is sufficient to form such C–H volatiles.

2. Experiments

Sample preparation for the degassing experiments, a soda-lime-silica glass with a standard composition: $Na_2O=16.0$ wt.%, $CaO=10.0$ wt.%, $SiO_2=74.0$ wt.% was prepared. The batches were prepared from pure and supra pure raw materials and melted in air in an alumina crucible at 1480°C, for 1 h in a special electric furnace.

The various carbon bearing components (Table 1) were added in concentrations between 1 and 5 wt.% to discrete 100 g batches of this glass.

One of these batches was kept without any additions and used as ‘reference glass’ in the further investigations.

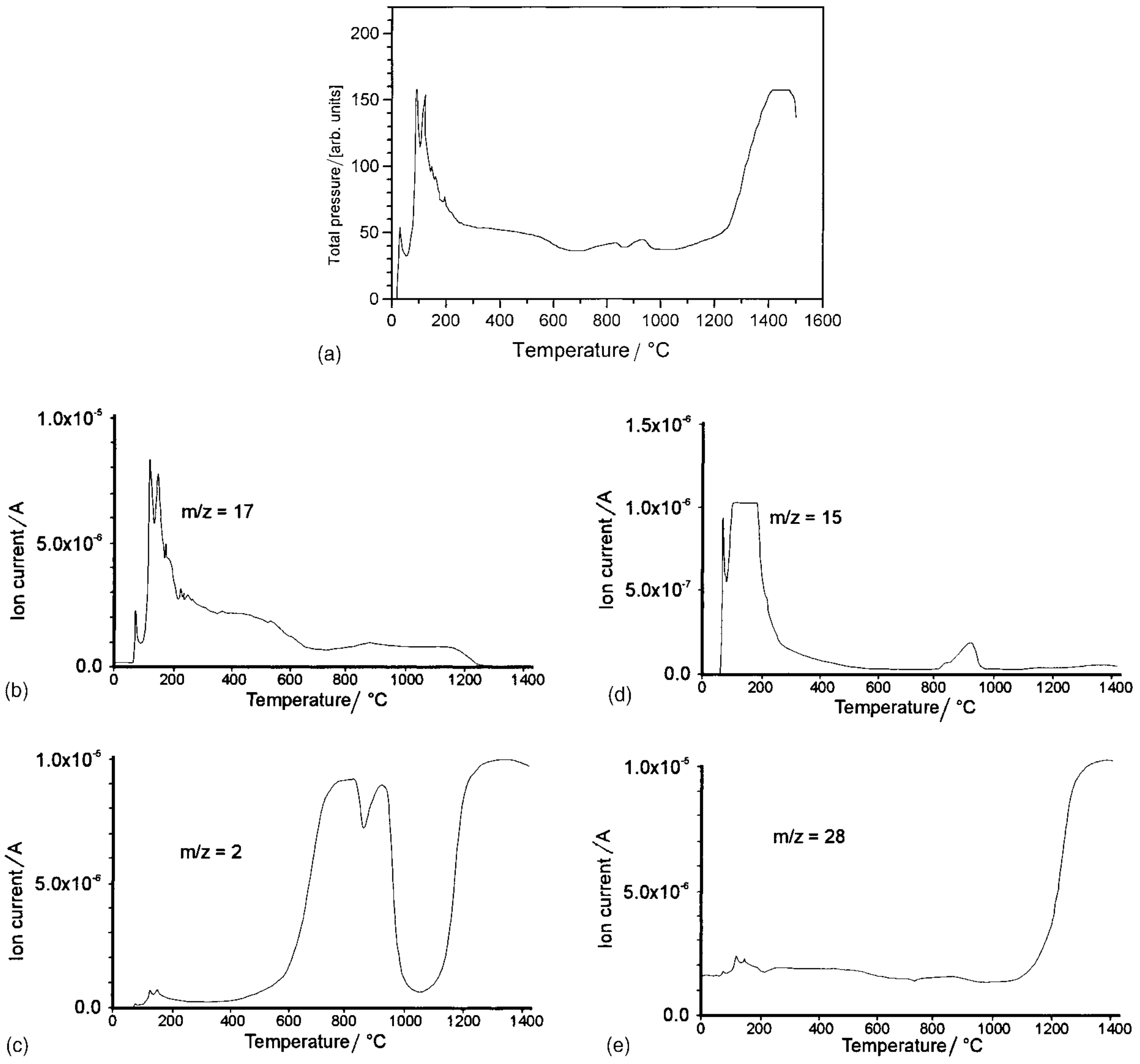


Fig. 2. Degassing profile (DP) of Al_4C_3 (a) total pressure run (b) gas release of water ($m/z=17$) (c) hydrogen ($m/z=2$) (d) hydro carbons ($m/z=15$) and (e) carbon monoxide ($m/z=28$).

The final melting of the samples was carried out in a vertical electric furnace flushed either with air or with gas mixtures with controlled H_2/CO_2 ratios or with pure Ar.

The evolved gas analyses (EGA) were carried out using a special device of high-temperature mass-spectrometry. A schematic diagram of the equipment used is shown in Fig. 1. The system has been described in detail by Heide [2] and Stelzner et al. [3]. The degassing process occurs under highly non-equilibrium conditions. Reverse reactions between the volatiles and the melt thus cannot occur. The samples are heated under a vacuum of 10^{-4} to 10^{-3} Pa at 10 K min^{-1} up to 1500°C. Hence secondary interactions between the evolved gases were minimized and determination of the primary volatile species is possible.

A special problem results from the contamination of furnace and the gas analysis system by the oil from the vacuum devices. To reduce the content of hydrocarbons in the background, turbomolecular pumps are used.

Analyses of the volatiles were carried out using a quadrupole mass spectrometer (QMG 420 C; Balzers) operated in rapid scan mode, or in multiple ion detection mode, during the entire heating period.

The measurements yield ion currents at distinct mass numbers (*m*/*z* 1–100), which are proportional to the partial pressure of the various volatiles escaping from the melt during the heat treatment. Fragmentation of molecules occurs during the ionization in the ion source of the mass spectrometer. Isotopic abundances and background contributions were taken into consideration for the interpretation of the gas release curves (Table 2).

To test the system, background measurements were carried out before and after a cycle in a 'placebo' experiment, i.e. degassing profiles of the equipment without a sample. All results are discussed on the basis of such runs.

3. Results

The thermal behaviour of the pure carbon-additives was tested in separate experiments, as shown, e.g. for Al_4C_3, in Fig. 2. The total pressure change in three temperature ranges

1. 20–250°C with two maxima between 100 and 200°C;
2. 700–1000°C with two maxima at 800 and 950°C;
3. Above 1250°C with a maximum at 1450°C.

The interpretation of these EGA-curves is given from the partial pressure registration. As shown in Fig. 2a and b, the maxima result for the first range for an ion with $m/z=17$, indicative of the escape of water, together with hydrocarbons ($m/z=15$). The second range is determined by release of $m/z=2$, that is hydrogen release, and the two maxima are a result of the superposition of hydrogen release and CH_4 ($m/z=15$, CH_3^+) at ca. 900°C. In the third range, hydrogen ($m/z=2$) and carbon monoxide ($m/z=28$) escaped from the sample.

The gas release curves of the glass specimen ('reference glass') made from the pure raw materials are quite similar to the degassing profiles of industrial

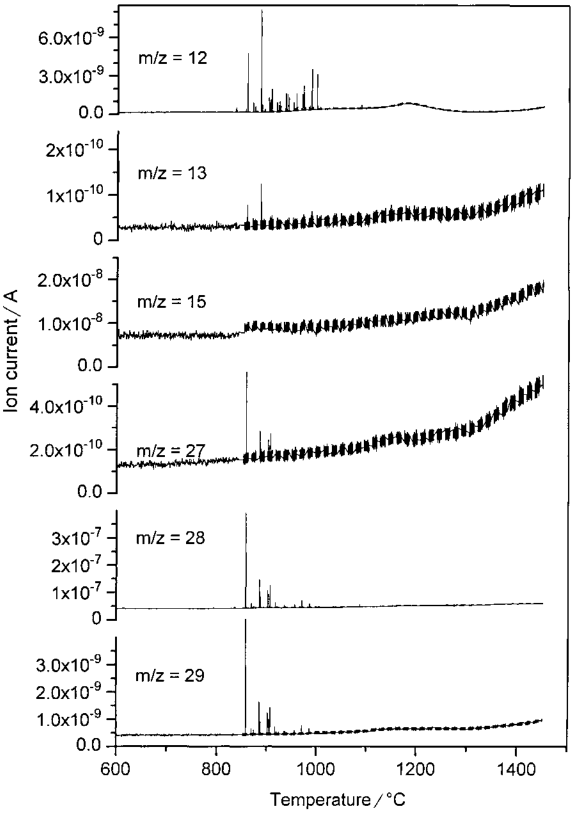


Fig. 3. DP of the soda-lime-silica (NCS) reference glass, molten from pure raw materials.

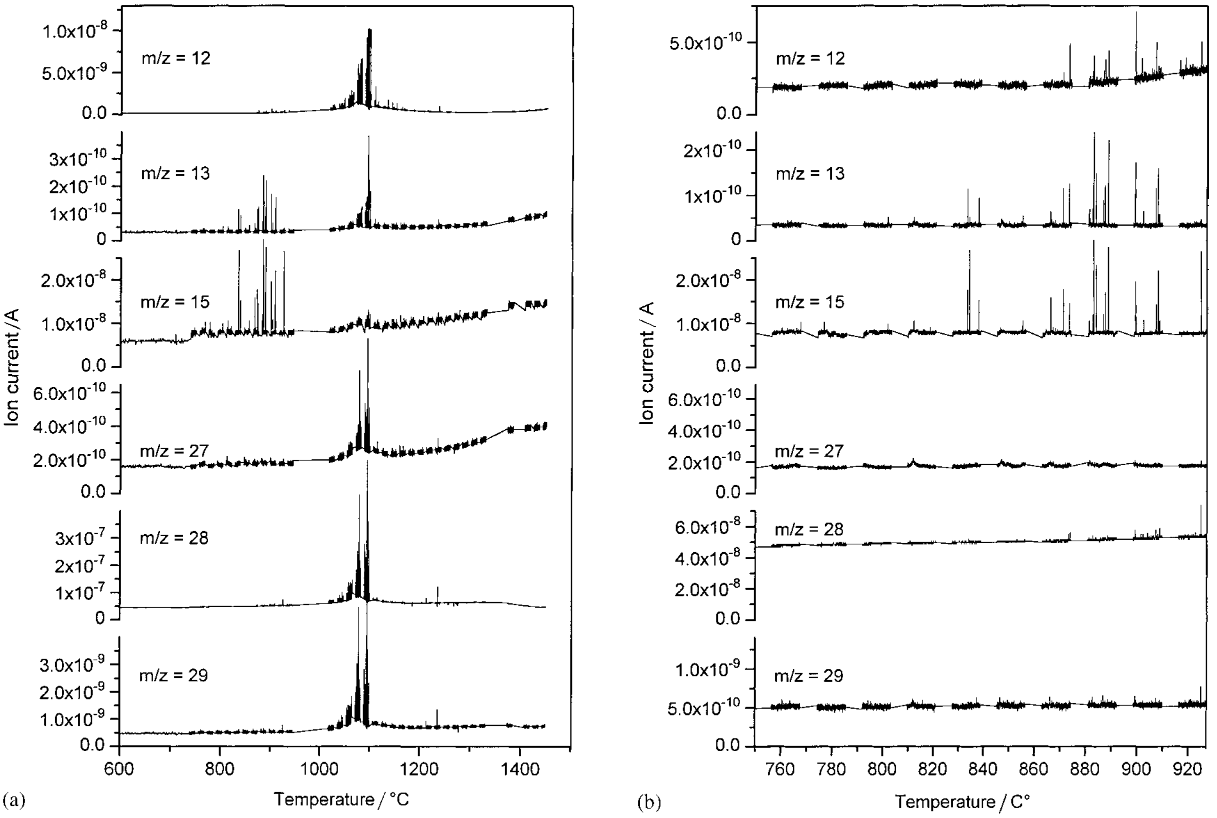


Fig. 4. DP of NCS glass with addition of 1 wt.% Al_4C_3 in the glass batch (a) DP between 600 and 1400°C, obviously the formation of methane occurs between 830 and 920°C and the formation of C_2H_n between 1010 and 1100°C (b) DP detail between 750 and 920°C, where it is shown that the formation of CH_4 does not depend on the formation of CO (*m*/*z* 12 in correlation to *m*/*z* 28).

soda-lime-silica (NCS)-glasses. That means that the bubbling occurs in two temperature ranges (Fig. 3). Between 810 and 1000°C CO_2-release occurs, but above 1100°C pure oxygen bubbles escape. This phenomenon is due to the carbonates in the raw material and the to refining additives. It has previously been explained by Stelzner et al. [3].

Addition of 1 wt.% of Al_4C_3 to the glass batch changed the degassing behaviour drastically. Bubbling of hydrogen and C–H species (m/z=12, 13, 15, 27, 28, 29) occurs between 750 and 930°C (Fig. 4).

The formation of hydrogen and of the C–H species is the result of different processes, which is supported by the different intensity spikes and release temperatures of the bubbles. Furthermore, the formation of C_2H_n-species near 1100°C is observed (Fig. 4). Through the introduction of C-compounds by disaccharide or by polysaccharide, the formation of C–H species is obviously decreased in favour of the formation of carbon dioxide (Fig. 5).

The addition of Na-acetate does not show a change in the degassing behaviour in relation to the 'reference glass'. In contrast to this, the glasses from batches with an addition of a mixture calcium hydroxide and Na-acetate show a strongly decreased release of carbon dioxide (Fig. 6a,b).

4. Conclusions

The systematic study of the influence of various carbon-bearing compounds in a silicate melt shows that, under high vacuum conditions, C–H species escaped from the melt in the temperature range above 800°C. The formation of higher C–H species is possible, according to the EGA, in the temperature range

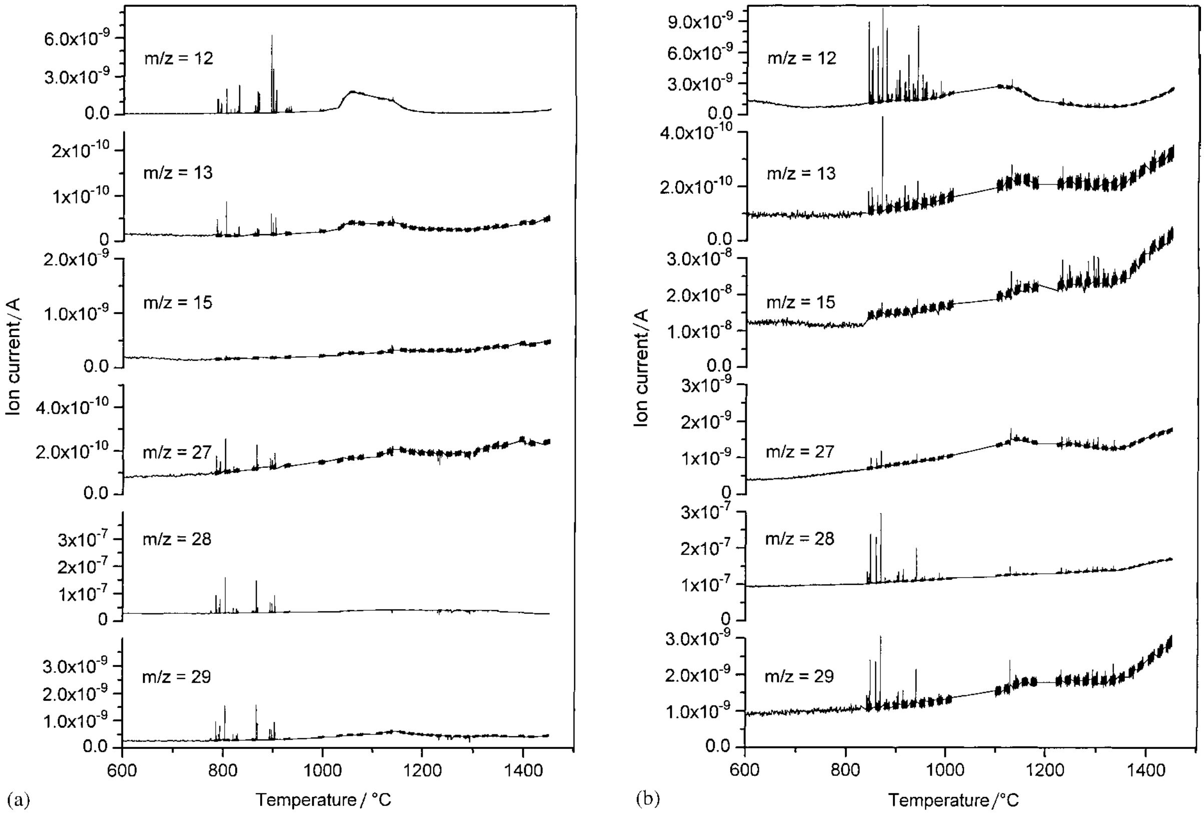


Fig. 5. DP of NCS glass with addition of saccharides in the glass batch (a) DP with addition of 1 wt.% of dissacharide. Only C_2H_n-species are detectable, the spikes *m/z* 12 and *m/z* 13 between 790 and 910°C are explained by the carbon isotopes. (b) DP with addition of 1 wt.% polyssacharide besides the formation of C_2H_n-species in the temperature range between 820 and 920°C, these is also the formation of small quantities of methane above 1200°C.

around 1200°C. A most probable mechanism for the formation in the high temperature melt is the reaction of carbon and water as proposed in the scheme:

$$C + 4(OH)^- \Rightarrow CH_4 + 2O^{2-} + O_2 \qquad (5)$$

As was shown by Hartmann [1], the fragment *m/z*=15 has also been detected in various natural glasses, e.g. tektites (Fig. 7).

These results suggest that, in nature, methane can also be formed by similar inorganic processes in magmatic melts containing carbon and the hydroxyl-group during a subduction process.

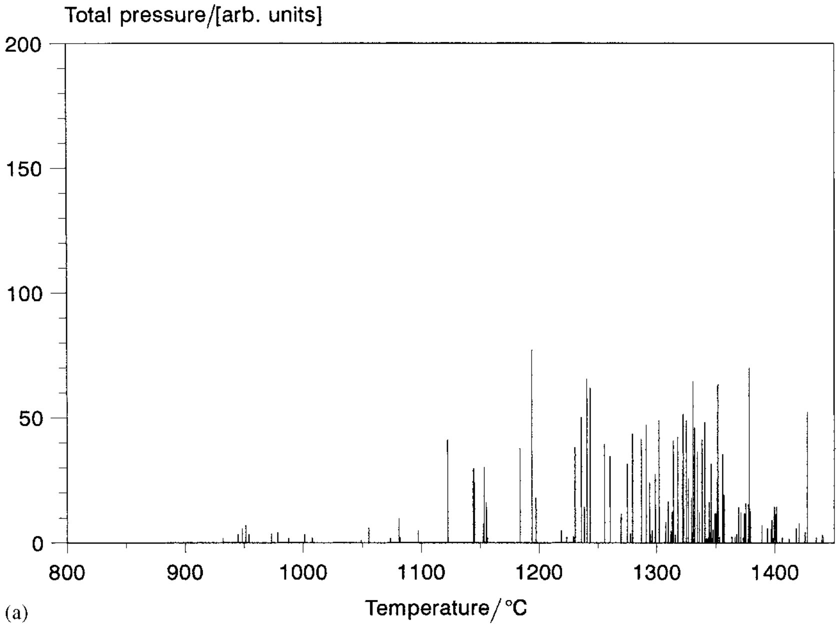
The generation of methane from a silicate melt poses the question of the mechanism for dissolution of methane in silicate melts. Different models have been discussed [4,5]. ‘Oxidized bonds’ of hydrogen or carbon, such as O–H or O–C, are well established in silica melts. At present, no indication of the formation of C–H or metal-H bonds in the relevant silica melts was observed. The formation of Si–C bonds was observed in oxy-carbide glasses. This observation supported the model of methane generation from a network containing Si–C-units:

Mechanism I

$$\{Si{-}C\} + 4[OH]^- + [SiO_2]^0 \Rightarrow 2[SiO_3]^{2-} + CH_4$$
$$\text{(silcon–carbon bond formation)}$$

Mechanism II

A second model for the formation of methane in silica melts is discussed by Taylor and Green [4] on the basis of the generation of methane by a network reduction



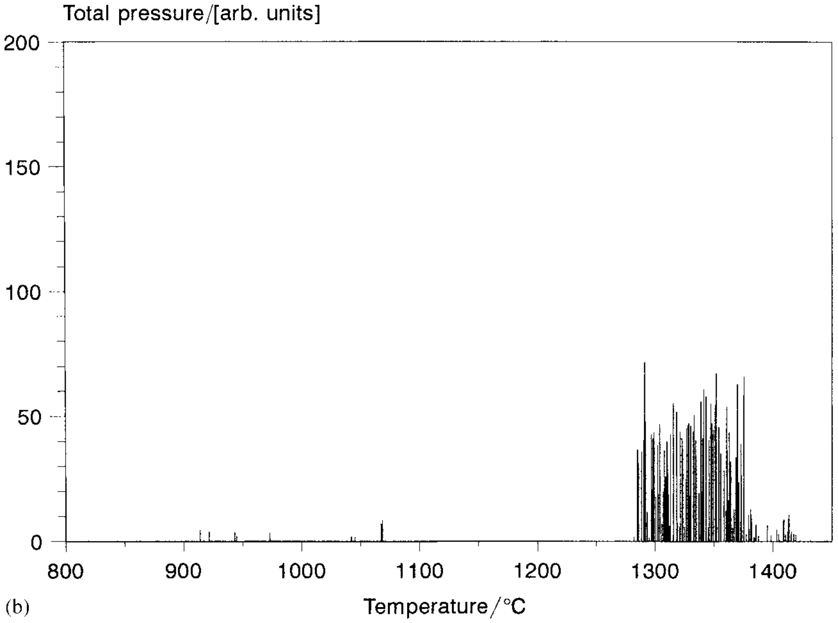


Fig. 6. DP of NCS glass (total pressure) with addition of a mixture of calcium hydroxide and Na-acetate. (a) Total pressure curve of the gas release after substitution of Na and Ca by 1 wt.% of a mixture of Ca-hydroxide and Na-acetate. (b) Total pressure curve of the gas release after substitution of 5 wt.% of Na and Ca.

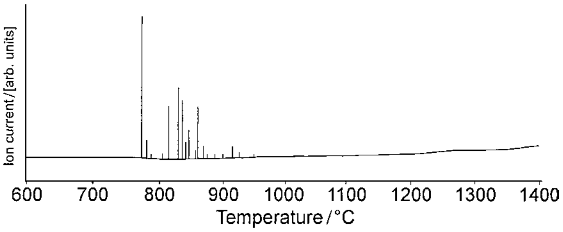


Fig. 7. DP of $m/z=15$ of a natural glass, formed during an impact process on the earth's surface.

$$2\{SiO\} + 4[OH]^{-} + C^{0} \Rightarrow 2[SiO_3]^{2-} + CH_4 \quad \text{(network reduction)}$$

The major difference between the mechanisms is the nature of the reduced bond units. For mechanism (I) we need a reduced carbon component (i.e. Si–C), but mechanism (II) requires the formation of a silicate network with an O:Si ratio <2.

In our experiments it was demonstrated that high-temperature (>800°C) generation of methane occurs in a process of liquid–gas phase separation. For further structural interpretation we need data about the solubility of methane in silica melts.

Both of these processes could be replaced by a more probable reaction in the silica melt

Mechanism III

$$4[Si-OH] + C \Rightarrow 2[Si-O-Si] + CH_4 + O_2 \quad \text{(polymerization by the formation of methane and oxygen)}$$

The generation of hydrogen is not correlated with the formation of methane. It is probably explained by an independent reaction of carbon with water

Mechanism IV

$$C + H_2O \Rightarrow CO + H_2$$

The experiments did show that the high-temperature generation of methane and ethane could be a fundamental process during the formation of silica melts.

Acknowledgements

These investigations were conducted with the kind support of the Deutsche Forschungsgemeinschaft. The authors are also grateful to Prof. E. Woermann for helpful discussions.

References

[1] E. Hartmann, N. Illner, K. Heide, Fundamentals of Glass Sciences and Technology, ESG 1993, pp. 583–586.
[2] K. Heide, Chem. Erde 33 (1974) 195–214.
[3] Th. Stelzner, K. Heide, K. Kothe, Glass Technol. 31 (1990) 236–239.
[4] W.R. Taylor, D.H. Green, in: B.O. Mysen (Ed.), Magmatic Processes: Physicochemical Principles, Spec. Publ. No. 1, The Geochemical Society, pp. 121–138.
[5] E. Woermann, M. Rosenhauer, Fortschr. Min. 63 (1985) 263–349.