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Dedicated to Dr. Robert Mackenzie on the occasion of his 75th birthday

EGA – A FINGERPRINT CHARACTERIZATION OF MINERALS AND ROCKS

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Abstract

Detailed studies of the gas release profiles of minerals and rocks reveal differences in the degassing rates and degassing temperatures and also in the compositions of the fluids evolved from the samples.

The use of special equipment for the determination of gas release profiles demonstrated that these profiles are characterized either by a continuous change in the partial pressure or by a spiky degassing process. It is shown that the gas release profiles are governed by the physico-chemical conditions influencing the formation of and alterations in the solid sample. Determination of the gas release profiles is therefore an effective tool for the identification and characterization of minerals and rocks.

Keywords: EGA, minerals, rocks

Introduction

The characterization of geological materials has played an important role in the development of thermal analysis. As pointed out by Mackenzie [1], conversely, thermal analysis has contributed significantly to developments in the earth sciences. Nevertheless, the place of thermoanalytical techniques in the geosciences at the present time is disappointing.

Whereas the DTA card index, for example, is frequently used in pharmaceutic and organic research and industrial applications, the SCIFAX DTA Data Index edited by Mackenzie and the Atlas of Thermoanalytical Curves edited by Liptay [2] are rarely employed in the majority of geoscience laboratories. The reasons for this situation differ, but in general results from the complex information provided by most thermoanalytical methods. This leads to a strong dependence of the experimental results on the equipment used. Only by a rigorous standardization of the experimental processes can a significant contribution to the study of geological materials be achieved [3]. The present paper shows that a combination of integral and selective thermal methods such as thermogravimetric analysis (TG) and mass-spectrometric evolved gas analysis (MS-EGA) can result in implications concerning the

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origins of minerals and rocks. The aim of the study is to present gas release profiles for crystalline and glassy rocks, while special consideration is devoted to the release of H_2O, CO_2, hydrocarbons and sulfur species, which are difficult to correlate with a distinct mineral structure.

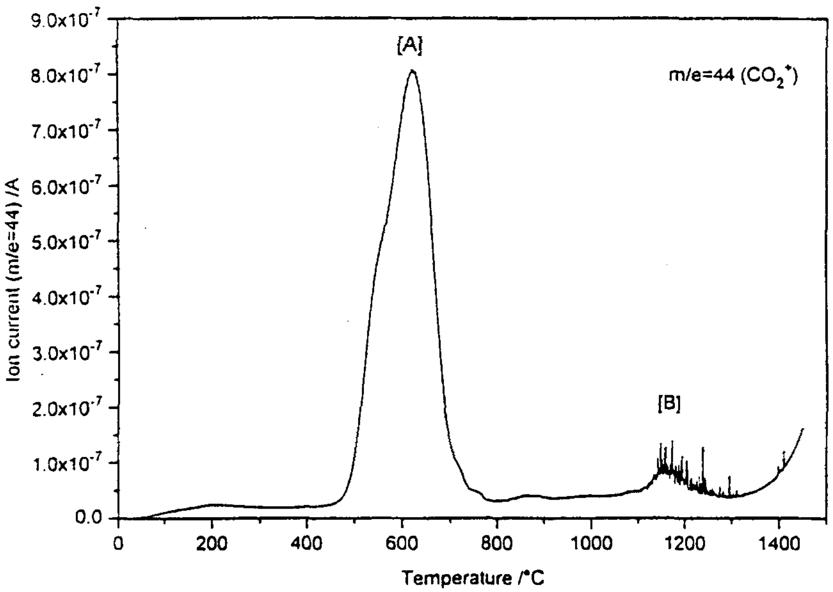

Fig. 1 Gas release profiles (m/e=44, CO_2^+) for a cutting from the 8850 m level of the continental deep drilling (KTB)

The degassing curves of crystalline and vitreous rocks point to two characteristic processes:

– a continuously changing degassing rate, which is characteristic, for instance, of the decompositions of hydrates, hydroxides and carbonates (Fig. 1 [A]), and

– an abrupt change in partial pressure due to the bursting of bubbles formed in a melt (Fig. 1 [B]).

The continuous change in the gas release is strongly influenced by alterations in the processes and environmental factors.

Instrumentation

Degassing experiments on geological specimens were carried out by using a thermobalance combined with a quadrupole mass spectrometer. Fluid species could be determined in high-vacuum degassing experiments, with a controlled heating rate from room temperature up to 1600°C. The escaping gases were analysed in a multiple ion detection (MID) mode and correlated with the total pressure change in the sample chamber during the heating process. Different commercial systems were modified as described in detail elsewhere [4, 5].

In contrast with the majority of MS-EGA systems, the degassing of the sample occurs under extreme non-equilibrium conditions (no Knudsen conditions). This allows detection of the primary fluid species escaping from the sample without any mutual interaction of fluid volatiles derived from the sample and gases from the reaction chamber. For a comparison of the results, careful standardization of the analytical conditions is necessary [6]. The standard deviation due to the experimental procedure was determined to be less than 5%. It is obvious that data obtained under high vacuum and with relatively small sample masses cannot be compared directly with results obtained with conventional equipment.

Table 1 Depth and composition of the cutting samples from KTB [7]

Depth	Rock
3002 m	garnet-sillimanite, biotite gneiss
5012 m	(garnet) amphibolite
6600 m	amphibolite-dominated alternation of amphibolite, biotite-gneiss, hornblende-biotite gneiss
8850 m	gneiss-dominated alteration of garnet-sillimanite-biotite gneiss, biotite-hornblende gneiss, amphibolite

The experimental conditions are summarized as follows: sample mass 10–100 mg, ground to 0.63–0.40 mm, Al_2O_3 crucible, preheated to incandescence in a gas flame, vacuum $<10^{-3}$ Pa, heating rate 10 K min^{-1}.

The specimens analyzed were selected from different levels in the continental deep drilling project (Kontinentale Tiefbohrung, KTB) in Germany (Oberpfalz, Bavaria). The washed, sieved and dried cutting samples from the hole were tested by EGA (Table 1). Further materials investigated were crystalline rocks from West-Eifel, Germany (juvenile lapilli from phreatomagmatic tephra of the Ulmener Maar and a fragment of a comagmatic bomb from the lapilli-tuff of the Hinkelsmaar, Mosenburg, volcanic system), and vitreous pyroclastite from Komorni Hurka (Kammerbühl) near Cheb (Eger), The Czech Republic.

Crystalline phases were identified by X-ray diffractometry. Biotite from the granite pluton at Henneberg in Thuringia was used as a reference material.

Results

Degassing experiments on specimens from different levels in the continental deep drilling (KTB) showed that the gas release results on rocks were comparable for H_2O, but slightly different for carbon and sulfur species.

H_2O release was characterized by three main maxima. Maximum temperatures are listed in Table 2. The curves for H_2O release were similar to those for the de-

Table 2 H_2O, CO_2 and SO_2 release of amphibolites and gneiss from the KTB, Windischeschenbach, Bavaria, Germany

Depth	H_2O-release (decomposition)	CO_2-release	SO_2-release
3002 m	310–610°C	1010–1400°C single bubbles	no bubbling
			1250–1330°C decomposition
(Fig. 2a)	610–777°C	1150–1400°C bubbling	
	777–1000°C		
5012 m	435–625°C	1110–1270°C single bubbles	1045–1295°C single bubbles
	625–815°C	1160–1190°C bubbling	1140–1215°C bubbling
	815–1100°C		
6600 m	430–640°C	1010–1310°C single bubbles	1050–1340°C single bubbles
	640–800°C	1140–1260°C bubbling	1140–1250°C bubbling
	800–1100°C		
8850 m	421–631°C	500–700°C decomposition	1070–1300°C single bubbles
	631–790°C	1110–1310°C single bubbles	1120–1220°C bubbling
	790–1041°C		

hydration of clay minerals and silicates containing OH groups, such as micas and amphiboles, respectively (Fig. 2a and b).

The release of CO_2 demonstrated two degassing processes, the decomposition of carbonates and the formation of CO_2 bubbles in a melt (>1100°C) (Fig. 1). SO_2 release occurred in the temperature range from 1100 up to 1300°C through the bursting of bubbles (Fig. 3).

The release of hydrocarbon species (*m/e* 15) was noteworthy (Fig. 4). The differences between the various localities were significant. As shown in Fig. 5, the degassing of hydrocarbons is only remotely correlated with the dehydration process.

In a second series, vitreous and cryptocrystalline rocks from different geological localities were investigated in order to demonstrate the liberation of H_2O, CO_2 and SO_2. Figures 6 and 7 depict the gas release profiles for CO_2 and SO_2 from volcanic rocks from West-Eifel (Germany), while Fig. 8 relates to a rock from a Bohemian area (The Czech Republic). The specimen from the Hinkelsmaar was embedded in lapilli-tuffs of more or less magmatic origin, whereas the material from the Ulmener Maar represents pyroclastic rocks of strong phreatomagmatic origin. The pyroclastics from the Komorni Hurka (Kammerbühl) near Cheb (Eger) are a vitreous basaltic slag. As shown in Figs 6, 7 and 8 and Table 3, there were no significant differences in the temperature of beginning of gas release, but differences were observed in the quantities of gas released from the volcanic rocks from the different localities.

Whereas the formation of CO_2 bubbles from the melt was similar for the rocks from the different locations, differences in high-temperature dehydration were observed between the phreatomagmatic material and the magmatic specimens.

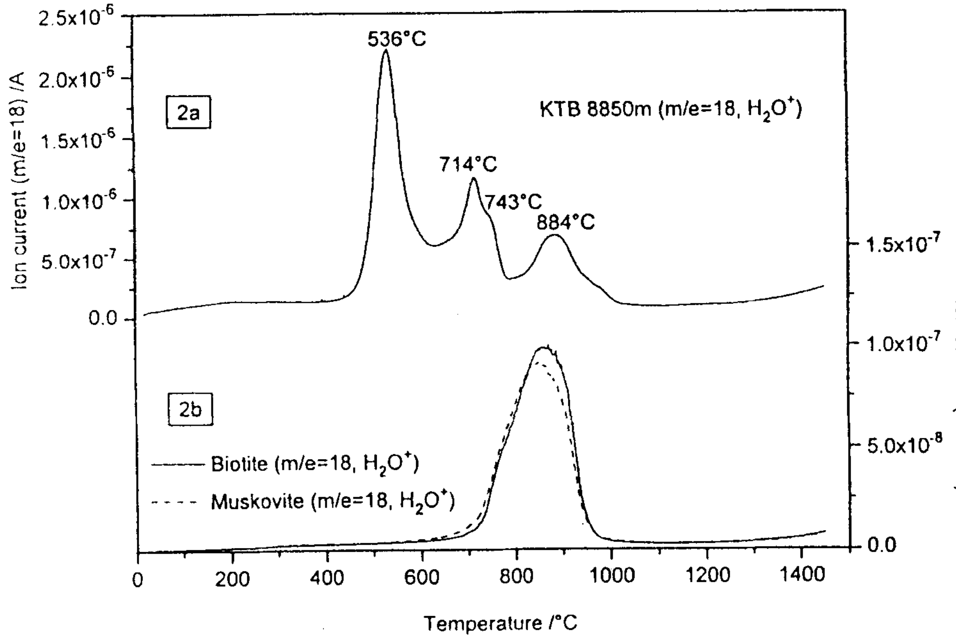

Fig. 2 H_2O release from KTB cuttings from the 8850 m level (a)
H_2O release profiles of micas from a granite (Henneberg, Thüringen) (b)

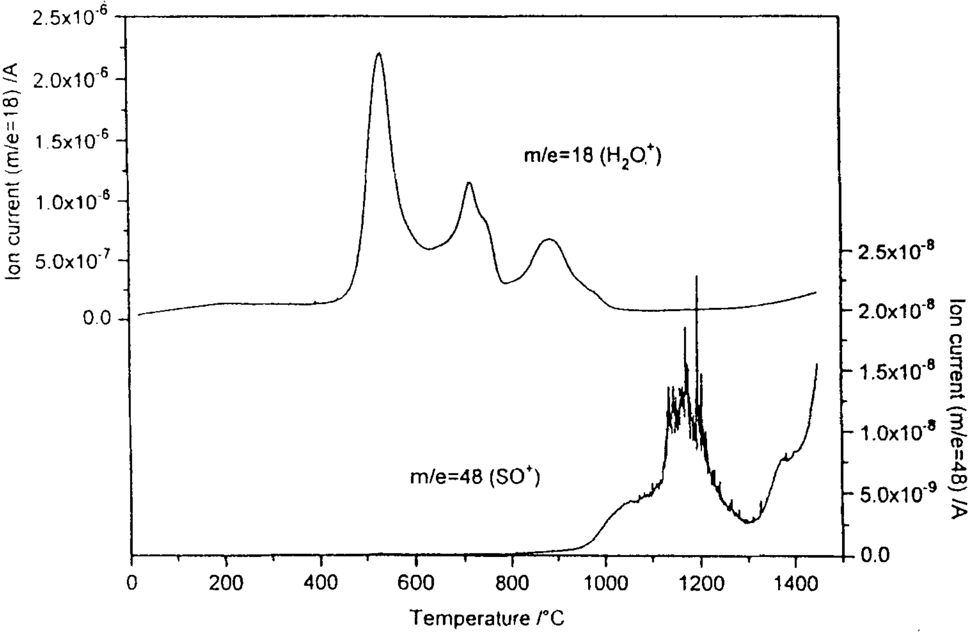

Fig. 3 Gas release profiles for H_2O and SO_2 from a cutting from the 8850 m level of the KTB

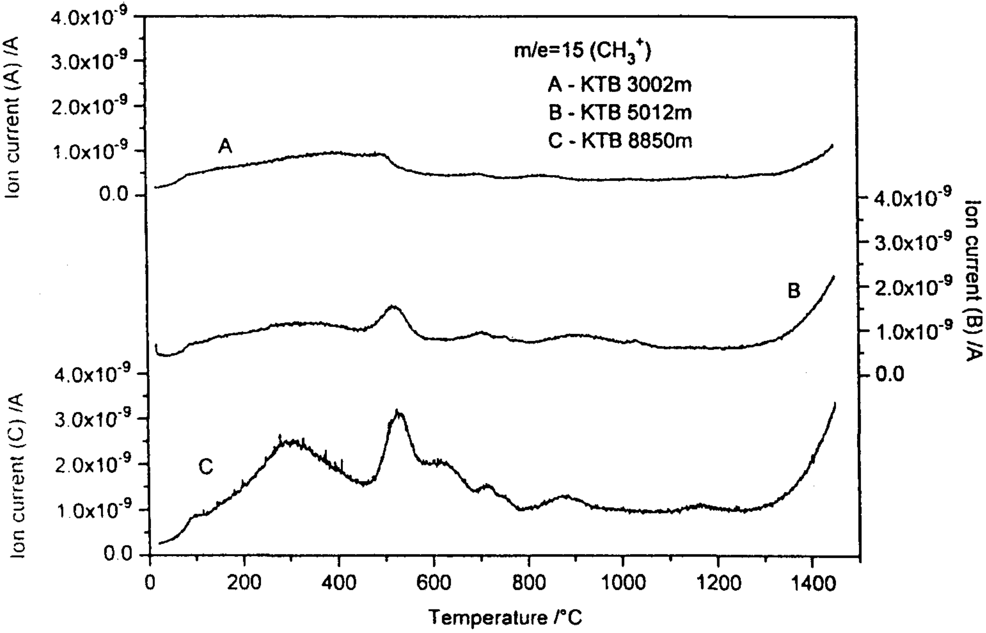

Fig. 4 Hydrocarbon evolution during the heating process of cuttings from the 3002 m, 5012 m and 8850 m levels of the KTB

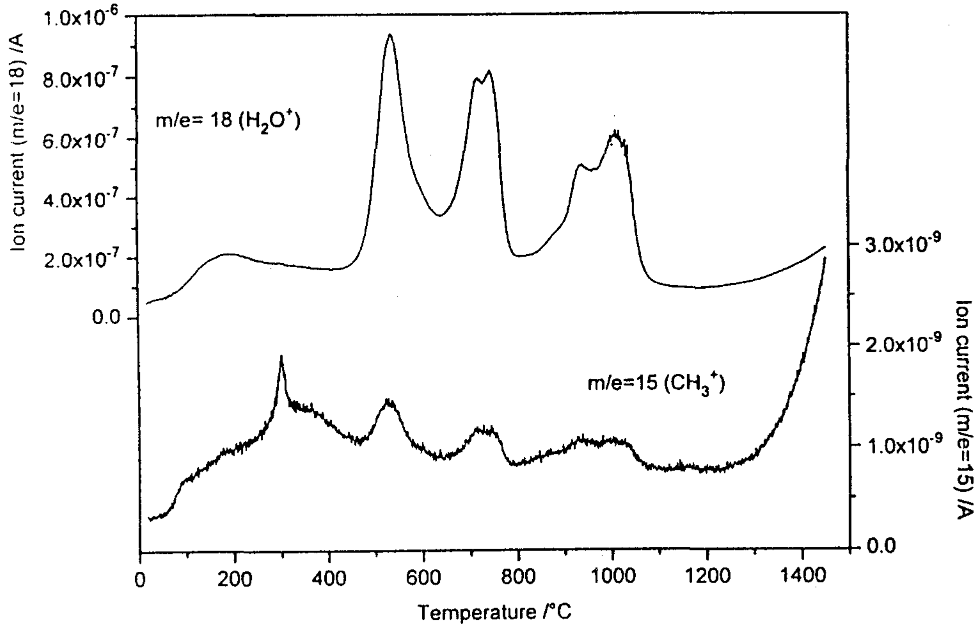

Fig. 5 Hydrocarbon and H_2O evolution during the heating process of a cutting from the 6600 m level of the KTB

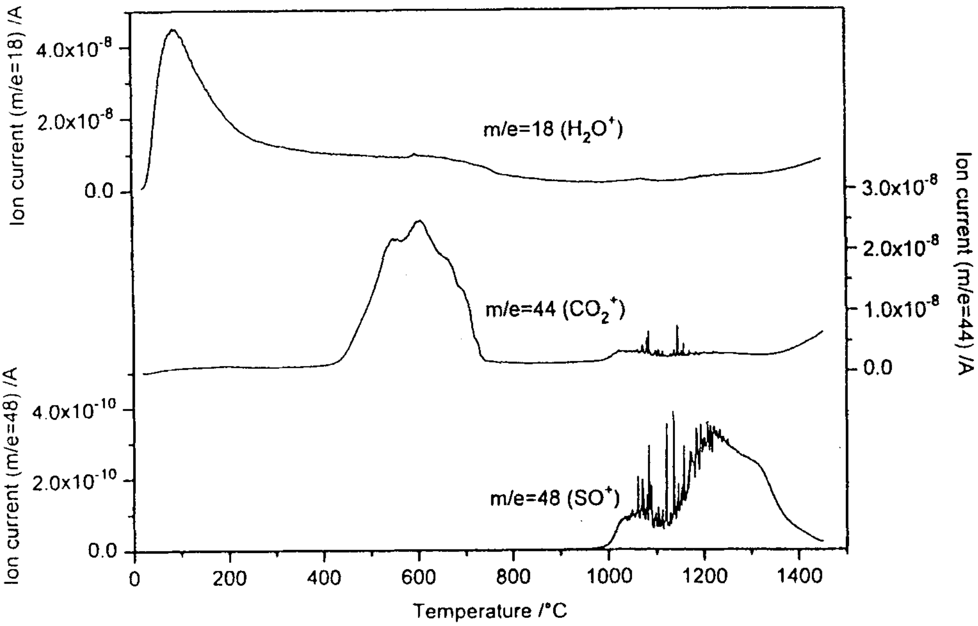

Fig. 6 H_2O and CO_2 release from a phreatomagmatic pyroclastite (Ulmener Maar, West-Eifel, Germany)

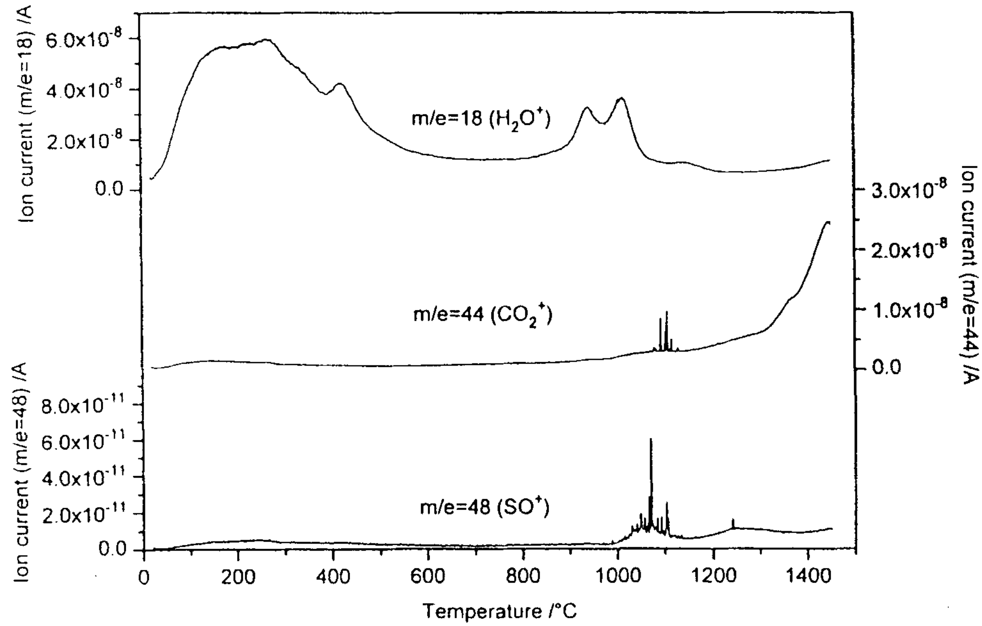

Fig. 7 H_2O, CO_2 and SO_2 release from a lapilli-tuff (Hinkelsmaar, West-Eifel, Germany)

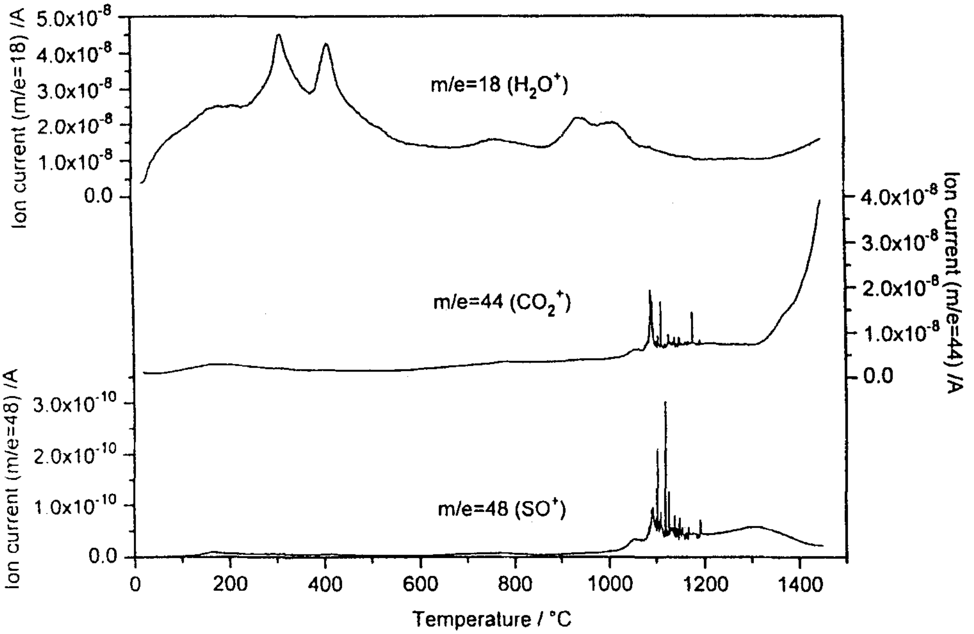

Fig. 8 Gas release profile of H_2O, CO_2 and SO_2 from a vitreous pyroclastite from Komorni Hurka (Kammerbühl) near Cheb (Eger), The Czech Republic

Discussion

The KTB specimen from the 8850 m level has a significant content of carbonates, probably dolomites. The H_2O release curves are characteristic for the decomposition of clays, micas and amphiboles.

More significant for the genetic factors are the bubbling processes of the melt. The escaped volatiles are included in the crystalline and glassy matrix of the rocks, and there is no correlation to a distinct mineral. The inter- and intracrystalline solution of the volatiles in the matrix is determined by the *p-T* conditions of solidification. As observed for the different volcanic rocks, the features of CO_2 and SO_2 release can be used as a fingerprint for the identification of rocks from distinct localities and, after the acquisition of more detailed knowledge on the degassing mechanism, for genetic information too.

The gas release curves for the volcanic rocks allow the establishment of a minimum temperature for the formation of a silicate melt from the formation of the first bubbles. These temperatures are given in Table 3.

With the methodology of Mertes and Schmincke [9], the H_2O content in the West-Eifel volcanic rocks was determined to be between 0.2 and 0.5 wt%, while that of CO_2 was generally an order of magnitude lower and quite similar to the SO_2 content. From the EGA, it follows that the release of H_2O and the release of CO_2 and SO_2 are two different processes. The H_2O release is determined by diffusion

Table 3 The temperature of formation of the first bubble in volcanic rocks from different locations

Location	$m/e=44(CO_2^+)$	$m/e=48(SO^+; SO_2$-fragment)
Komorni Hurka (Kammerbühl)	1075°C	1085°C
Hinkelsmaar	1075°C	990°C
Ulmener Maar	1060°C	1010°C

rather than by the formation of bubbles. This indicates a different bonding in the melt. Maares are formed as a highly explosive interactive process between confined ground water and the rising melt. From the gas release profiles, we can conclude that the incorporation of water in the melt structure is insignificant during the interaction of the ground water with the ejected melt. Quite conversely, the phreatomagmatic process obviously occurs by dehydration of the melt.

More systematic investigations are necessary to correlate these results with the conditions of formation of the different rocks.

One of the first results is the determination of the minimum temperature of the volcanic melt before the eruption.

For the lapilli-tuff (Hinkelsmaar) and the pyroclastite (Komorni Hurka), the conditions must be quite similar.

A particularly interesting observation is the mode of release of hydrocarbons from the KTB specimens. The characterization of the starting materials is a task for further studies. The methods of thermal analysis at present provide specific techniques for geoscience, with the special aim of decoding the complex information yielded by the experimental data in respect of the genetic history of the sample.

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References

1 R. C. Mackenzie, Lecture Notes in Earth Sciences Nr. 38 Thermal Analysis in the Geosciences Ed. by W. Smykatz-Kloss and S. St. J. Warne, Springer Verlag, Berlin 1991, p. 2–15.
2 G. Liptay, Atlas of Thermoanalytical Curves, Akadémiai Kiadó, Budapest, Vol. 1–5 1971–1985.
3 W. Smykatz-Kloss, Application and Results in Mineralogy, Minerals and Rocks, Vol. 11, Springer Verlag, Berlin, Heidelberg, New York 1974.
4 K. Heide, Chem. Erde, 33 (1974) 195.
5 Th. Stelzner, K. Heide and K. Kothe, Glass Technology, 32 (1990) 236.
6 R. Franke and K. Heide, Thermochim. Acta, 234 (1994) 263.
7 KTB Report 95–2, Ed. by R. Emmermann, E. Althaus, P. Giese, B. Stöckhert, Schweizerbartsche Verlagsbuchhandlung Stuttgart 1995.
8 M. Földvári, Chemie der Erde, 47 (1987) 19.
9 H. Mertens and H. U. Schmincke, Contrib. Mineral. Petrol., (1985) 330.