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A new purge and trap headspace technique to analyze low volatile compounds from fluid inclusions of rocks and minerals

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ABSTRACT

A new method for the analysis of trace gases from fluid inclusions of minerals has been developed. The purge and trap GC–MS system is based on the system described by Nolting et al. (1988) and was optimized for the analyses of halogenated volatile organic compounds (VOCs) having boiling points as low as −128 °C (carbon tetrafluoride). The sample preconcentration cold trap consists of a U-shaped glass lined steel tube (GLT™), that is immersed into a small liquid nitrogen Dewar vessel for cooling. A rapid desorption step heats up the preconcentration tube in <30 s from −196 °C to 200 °C. The process is carried out by using a pressurized air stream to dissipate the liquid nitrogen followed by resistive heating of the trap. The design of the cold trap and the direct transfer of desorbed analytes onto the GC column via a deactivated capillary column retention gap made sample refocusing within the GC oven unnecessary. Furthermore, a special air-tight grinding device was developed in which samples ranging from soft halite (hardness 2, Mohs scale) to hard quartz (hardness 7) are effectively ground to average diameters of 1000 nm or below, thereby releasing gases from fluid inclusions of minerals. The gases are then purged from the grinding chamber with a He carrier gas flow. The detection and quantitative determination of gases, such as SF_6 and CF_4 released from fluorites and CH_3Cl from halite samples is demonstrated.

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1. Introduction

Volatile organic compounds (VOCs) released from fluid inclusions (FIs) of rocks and minerals, especially the halogenated volatiles (VOXs), are of pivotal importance for stratospheric and tropospheric chemistry. Currently there are discrepancies in the fundamental understanding of the sources and sinks for these compounds in the atmosphere. Here, we describe briefly the fundamental objectives of FI research, which provides a historical context in addition to the environmental focus of our application. It also compares previous methods in the area of FI and environmental research regarding the detection of VOXs.

Fluid inclusions can be gaseous, liquid or solid and are present in practically all terrestrial minerals. They are formed either during crystal growth or later on in the minerals' life along the annealing cracks in the presence of fluid phases (Samson et al., 2003). The FIs are only infrequently larger than 1 mm, in most samples their size ranges from 1 to 100 μm. The very small size fraction of FIs usually outnumbers all inclusions larger than 10 μm at least by a factor of 10 (Roedder, 1984). Current FI research spans a wide array of topics: phase relations and thermodynamic properties include the study of complex brines. Laser Raman techniques are increasingly employed in the investigation of mixed water/gas systems and with special emphasis on the analysis of single inclusions. Also, FIs provide evidence about the character of early geological processes, are used in the study of modern (sub)-volcanic processes and supply information on ore formation. Frezzotti and van den Kerkhof (2007) summarized that about 20% of published work on inclusions dealt with the use of melt inclusions to study the highly complex relationship between magma and fluids during crystallization. Bulk analysis of volatiles in FI, are predominantly concerned with the detection of O_2, CO_2, SO_2, N_2, H_2, H_2S, HCl, HF, He, Ar, CH_4 and heavier hydrocarbons, which can be found in the literature as summarized by Salvi and Williams-Jones (2003). Typical contents of these compounds are reported to be in the ppb to ppm mass range, i.e. ng to μg per gram of mineral.

Mass spectrometric (MS) methods were mainly applied in noble gas analysis and detection of sulfur bearing compounds whereas gas

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chromatography (GC) was particularly used for the separation of hydrocarbons, as well as H_2 and N_2 (Salvi and Williams-Jones, 2003). Plessen and Lüders (2012) and Lüders et al. (2012) report the measurement of gas isotopic compositions of fluid inclusion gases (N_2, CH_4, CO_2) from 0.2 to 1 g of sample chips crushed with an on-line piston crusher followed by GC, an elemental analyzer and continuous-flow isotope ratio MS. The most recent developments are in the application of laser ablation GC–MS, focusing on higher molecular weight hydrocarbons from single blue or yellow fluorescing FIs, and co-occurring molecular composition in order to gain insights on thermal maturity, paleo-oil charges and oil migration (Greenwood et al., 1998; Volk et al., 2010; Zhang et al., 2012). Zhang et al. (2012) summarized the GC–MS based procedures in this sector as follows: (1) offline mechanical crushing of (sedimentary) material in organic solvent to release hydrocarbons into solution and subsequent injection; (2) use of purpose-designed injectors that crush samples online via thermal decrepitation; and (3) laser opening of selected inclusions with on- and offline GC–MS analysis.

Online crushing stages are employed before MS detection for the analysis of noble gases or stable isotope ratios. Principally, they consist of stainless steel cylinders with grains or cut cuboids of rock that are manually pounded several hundred times by a moveable piston (or ball) via a handheld magnet. For example, applications in the study of FIs from speleothems have been used to reconstruct paleoclimate (Dennis et al., 2001; Kluge et al., 2008) or in cosmochemistry (Scarsi, 2000). Less frequently, an alternative method is reported in which the sample is squeezed using a vice to release contained gases while in a copper tube under vacuum (Harmon et al., 1979; Scheidegger et al., 2006). Isidorov et al. (1993) detected chlorine and sulfur containing compounds from halite and sylvinite mining emissions which they also partly measured after dissolution of the salt crystals by GC–MS headspace analysis. Most recently, Svensen et al. (2009) reported the extraction of $CHCl_3$, $CHBr_3$ and 1-chloro- and 1-bromobutanes from halites using GC–MS and a heating procedure at 225 °C as well as a crushing procedure, but little details were reported on the latter one.

For the analysis of VOXs, most expertise has been accumulated in atmospheric research. Advanced GC–MS systems with multiple traps and columns have been developed (Sive et al., 2005; Miller et al., 2008; Bahlmann et al., 2011). Crucial development was the employment of effective sample preconcentration traps. The low boiling point analytes of interest from air samples of up to several liters have to be enriched in order to detect their trace level amounts mostly in the ppt-range (mole fractions).

Little is known on the geogenic origin of CF_4 and SF_6. The largest scientific community that has recognized and measured their natural occurrence is environmental physicists, who used CF_4 and SF_6 as age tracers in groundwater. Assumption of the underlying method was that both compounds are of purely anthropogenic origin and have gradually increased and partitioned into younger groundwater since their industrial production in the 1950s. However, natural disturbances have been noted and reported, first by Busenberg and Plummer (2000). Literature on the topic is still scarce but the occurrence of SF_6 from basaltic aquifers (Koh et al., 2007), from granitic alluvium of the Mojave Desert (Deeds et al., 2008) and sedimentary aquifers of the North China Plain (von Rohden et al., 2010) have been reported, putting restrictions on the groundwater dating if SF_6 is taken as a tracer. Deeds et al. (2008) also mentioned CF_4 as of terrigenic origin and stated that fluxes of CF_4 and SF_6 when extrapolated from their measurements to a global scale could be consistent with the fluxes required to sustain the preindustrial atmospheric abundances of CF_4 and SF_6.

Busenberg and Plummer (2010) presented results on a new groundwater dating method using the environmental tracers SF_5CF_3, $CClF_3$ (CFC-13), SF_6, and CCl_2F_2 (CFC-12). However, Harnisch et al. (2000) reported values of up to 1200 pg g^{-1} CCl_2F_2 released from fluid inclusions in fluorites and Jordan et al. (2000) reported detection of this compound from volcanic gas samples. An extensive screening of geologic materials has simply not taken place yet, so maybe even these newly developed methods encounter limitations in some natural environments where there is a terrigenic source of these compounds.

The studies of Harnisch and Eisenhauer (1998) and Harnisch et al. (2000) are ground-breaking in VOX analysis from FIs of rocks and minerals. Harnisch and Eisenhauer (1998) demonstrated that CF_4 and SF_6 are commonly present in natural fluorites and granites, and the publication by Harnisch et al. (2000) provided a detailed description of their grinding procedure. They were using a grinding device emulating a "peppermill"-design in which samples were ground from 5 mm down to around 100 μm diameter and released gases were transported directly onto the preconcentration sample loop by using a vacuum. After desorption, analytes were separated using a packed column and detected by MS. By using this technique they were able to detect CF_4, CF_2Cl_2, $CFCl_3$ and SF_6 from a number of natural samples and additionally CF_3Cl, CHF_3 and NF_3 from one fluorite sample. Levels of CF_4 were determined to be up to 5600 pg g^{-1} and those of SF_6 reached 340 pg g^{-1}. On the one hand, their measurements, although in good agreement with old results from Kranz (1966), have apparently not been replicated by other groups or expanded to a larger set of samples. On the other hand, their papers are cited quite frequently, whenever authors acknowledge a natural origin in discussions on the atmospheric concentration of the corresponding compounds (e.g. Muhle et al., 2010).

In order to contribute to a larger scientific basis for natural background estimates of VOXs, the major goal of this work was to develop a simple, inexpensive and robust method to detect VOX and organosulfur compounds from FIs. Objectives were to develop a grinding device that crushes mineral samples to a specific final grain size, to install a cooling trap that is capable of concentrating released gases with particularly low boiling points (as low as −128 °C) prior to measurement and to assure high analytical performance of the GC–MS system by protecting it from mineral particles.

In this paper, we first describe an alternative purge-and-trap GC–MS method to analyze the chemical composition of VOXs from FIs using an adapted dynamic headspace approach that accommodates all types of minerals and rocks across the entire Mohs scale of hardness while maintaining high sensitivity.

2. Experimental section

2.1. Grinding device

In order to analyze the volatile organohalogen and organosulfur compounds of FI using GC–MS the first step was to develop a grinding device that was able to crush and release the target gases from the rocks and minerals. Our approach was to create a purgeable grinding container mimicking a dynamic headspace vial, and at the same time, incorporate already existing infrastructure of our laboratory. The resulting grinding device consisted of a 80 mL tempered steel grinding bowl (Fritsch, Idar-Oberstein, Germany) equipped with a lid and a Viton seal ring. The lid was chosen in stainless steel and we constructed two brass orifices on top, which could be sealed by conventional crimp caps (diameter 8.4 mm) with Sil/PTFE septa (thickness 1.5 mm).

After inserting the sample and five tempered steel grinding balls (diameter 15 mm) to the bottom bowl the crimp cap sealed lid was pressed via a clamping plate onto the bowl. The Viton seal allowed for an air-tight closure. The whole fixture with grinding vessel and sample then fits into a regular planetary mill (Fritsch, Pulverisette 5).

In order to effectively grind samples, materials needed an initial particle size below 3 mm (preferentially between 2 and 3 mm), otherwise larger particles were not sufficiently ground to appropriate sizes.

Corresponding to the hardness of the minerals under investigation the grinding times were adjusted accordingly. Initially, tests were performed with quartz (Mohs hardness 7) and fluorite (hardness 4) samples for which grinding times, grinding intensities in revolutions per minute (rpm), amount of sample and amount of grinding balls were varied. The particle sizes of subsequently obtained fine powders

were analyzed from suspensions of 50 mg sample in 100 mL^{-1} deionized water using a ZetaPals (Brookhaven Instruments, Holtsville, NY) in multiple angle particle sizing mode. For the particle size determination, commercial quartz gravel (Quarzkies Natur, MK-Handel, Düren, Germany) of grain size 2 to 3.15 mm and of a fluorite of same grain size from the mine Marienschacht nearby Wölsendorf, Bavaria, Germany, were used. The particle size distribution was determined in the range from 0.5 to 5000 nm. From the data of triplicate measurements mean values were calculated and standard deviations were found to be < 15%. For easily soluble salt minerals, such as halite, this particle size determination was not carried out. Halite showed a ductile behavior upon intensive grinding with "smearing out" along the rim of the grinding bowls and clogging of the orifices. Therefore, we based the selection of grinding conditions on observations made during the grinding procedure.

After setting the basic grinding conditions, temperature evolution during grinding operation was determined for quartz and fluorite. After different grinding times, the lid was taken off quickly and temperatures were determined instantaneously by an infrared thermometer (Voltcraft, IR 1200-50). Additionally, temperatures on the outer surface of the grinding vessel were recorded. Temperatures were recorded in triplicate from each 10 g of a commercially available Dead Sea salt (August Töpfer & Co. KG, Hamburg, Germany) was utilized.

2.2. Analytical system

The MAGNUM™ GC–MS system (Finnigan MAT, San Jose, CA) consists of three main components: the gas chromatograph (GC, Varian Model 3400), the ion-trap mass spectrometer (MS, Finnigan MAT, ITS40) and the data processing system and software (Saturn 5.4, Saturn 2000). Additionally, we employed a custom built temperature control unit (Newig GmbH, Ronnenberg, Germany) that was originally developed by Nolting et al. (1988) and also described more recently by Siekmann (2008) as well as the self-constructed inlet system comprising the sample preconcentration tube that bridged the GC injection port. All gas carrying components of the setup consisted of 1/8-inch stainless steel tubing and 2 mm outer diameter Swagelok® compression fittings. Fig. 1 provides a schematic of the analytical system.

2.2.1. Purge and trap unit

The regulation of the ultra high purity He carrier gas flow affects the measurement reproducibility. Helium flow is controlled by two 3-way solenoid valves (valves 1 and 2), two 2-way solenoid valves (valves 3 and 4) and one manual 2-way needle valve. Solenoid valves were obtained from Kuhnke AG, Malente, Germany (Micro-Solenoid Valves type 65). The first four valves are controlled by the external event relays of the GC computer. Under standby as well as desorption conditions, equivalent to a non-purge sequence, valves 1 and 2 are directly connected to each other and valve 3 is closed as represented by the solid lines in Fig. 1. This means that the sample loop, i.e. the grinding vessel and connecting lines, are not purged by He, but instead the cooling trap made of glass lined tubing (GLT™) and GC columns are constantly flushed with He at a rate of 2.0 mL min^{-1}.

Analysis of a ground sample is started by piercing two stainless steel needles as inlet and outlet through the septa of the crimp caps on the grinding vessel. We used 16 gauge, point style hubless needles of custom length (10 cm; Hamilton Bonaduz AG, Bonaduz, Switzerland). To avoid rupture and leakage at the thin Sil/PTFE septa employed, it is advisable to pre-pierce them with a thin needle before punching through with the 16 gauge needle. The cooling trap consists of a 215 mm long piece of GLT™ (SGE Analytical Science, Melbourne, Australia), which is bent in the middle to form a U-shaped section of the tube. This U-shaped part of the tube is installed above a Dewar vessel (80 mL, KGW Isotherm, Karlsruhe, Germany), and is submerged in liquid nitrogen during sample preconcentration. Liquid nitrogen was added manually before each measurement. A thermocouple connected to a temperature controller was attached to the submergible part of the GLT™ using PTFE-tape. The temperature control device monitors the temperature of the trap. During the sample preconcentration step valves 1 and 2 switch so that the He purges the grinding vessel (dotted lines, Fig. 1). At the same time, valve 3 is opened to permit a high purge
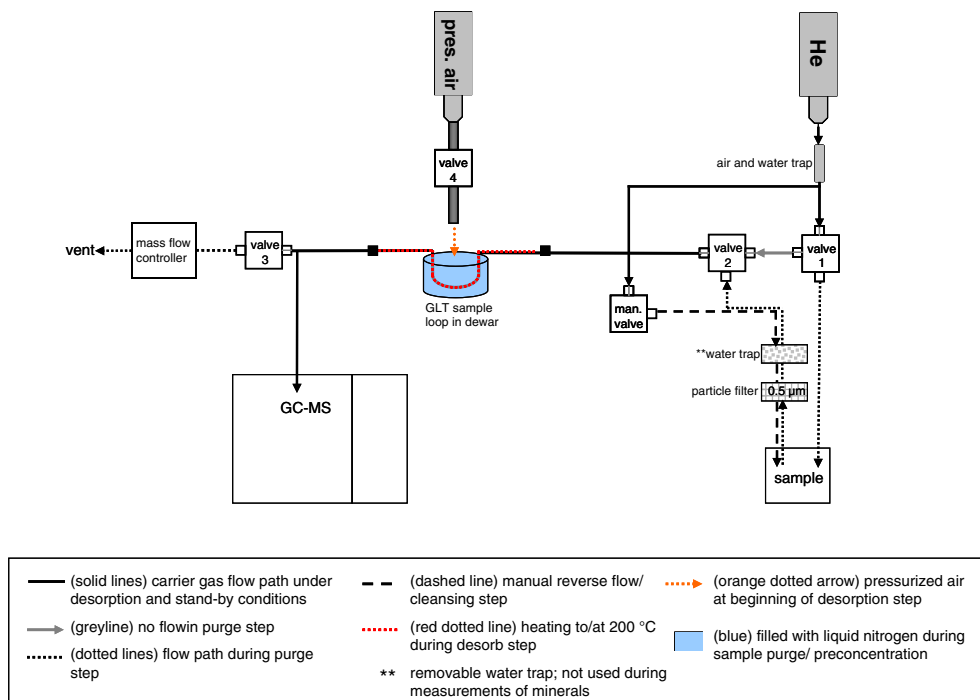

Fig. 1. Schematic of the analytical system. The sample is attached by piercing through the sealing septa and the sample is purged by the He carrier gas flow. Grinding of mineral samples is realized offline in a conventional planetary mill. The sample trap temperature is controlled via a thermocouple by the temperature control device. The thermocouple is attached at the deepest point of the U-shaped sample loop, but this is omitted in the scheme for simplicity. The resistance heating is attached to the GLT™ sample loop via copper clamps symbolized by the black squares and also regulated by the temperature control device.

flow controlled by the flow controller (GFC17, Analyt-MTC), additionally to the existing flow through the GC column. Volatile compounds from the grinding vessel are purged for 6 min with a He flow at 10 mL min^{-1}, as regulated by the flow controller and enriched on the pre-cooled trap (-196 °C). An important aspect of this step in the process is the intercalated particle filter (Swagelok® Series F, mesh size 0.5 μm) that prevents fine mineral dust particles from entering the delicate GC–MS system. The sintered filter element should be exchanged every 20 to 30 measurements. Optionally, the scheme shows a (magnesium perchlorate) water trap. This has to be installed when measuring with a standard headspace technique (water vapor phase) or other sample requiring a moisture control system and is added here to demonstrate the versatility of the experimental setup. After sample preconcentration is finished valve 4 is opened for 10 s and allows pressurized air to dissipate the liquid nitrogen from the Dewar vessel. A resistance heating that is controlled by the temperature control device is directly attached onto the GLT™ with two copper clamps, symbolized by the small black boxes in Fig. 1. After liquid nitrogen is blown off, heating from -196 °C up to 200 °C is accomplished within 30 s and this temperature is held for 2 min. The optimum heating rate is regulated by the temperature control device, permitting on the one hand a fast desorption of the volatile compounds, but preventing the thermal decomposition of the trapped compounds. During the desorption sequence, valves 1, 2 and 3 switch back into the stand-by conditions as described above. While the measurement is running, the sampling line with the filter element was cleaned by opening the manual valve to allow He backflush.

2.2.2. GC–MS

After desorption the sample is transferred by the carrier gas flow through a 15 cm long retention gap (0.53 mm diameter fused silica capillary column, deactivated) perpendicular to the GLT™ directly onto the GC columns. A graphite ferrule is used for the connection between retention gap and GLT™, whereas a retention gap and two capillary columns were installed in series using quartz Press-Fit®-connectors (Mega s.n.c, Legnano, Italy). The first capillary column employed is a DB-624, ID 0.53 mm, df 3 μm, 30 m. The second capillary column is a BP-5, ID 0.32 mm, df 1 μm, 60 m. Due to the choice and length of chromatographic columns in combination with the cold trap design, no further sample refocusing on the column or GC oven cooling was needed to achieve good retention of very low boiling point compounds such as CF$_4$ or SF$_6$.

The GC oven was programmed at 35 °C for 22 min, 35 °C to 150 °C at 5.5 °C/min, 150 °C are held 5 min, 150 °C to 210 °C at 30 °C/min, hold 10 min (Fig. 2). The MS detector was operated at 170 °C with electron ionization of 70 kV. Signals were acquired between 11 and 50 min in scan mode for masses from 49 to 132 m/z at a scan rate of 0.17 s. Signal response and chromatographic performance of a reference gas mix (Crystal Mixture, Air Liquide) was controlled daily and electron multiplier voltage adjusted if necessary.

In order to achieve best analyte recoveries, the purge flow speed and time were varied and the measurement conditions were set for both, the grinding vessel and a 20 mL empty standard headspace vial.

Isobutene, 1,3-butadiene, *cis*-2-butene and *trans*-2-butene were contained in a mixed calibration standard (15 ppm in N$_2$, Crystal Mixture, Air Liquide). For optimization of purge flow and time 2.8 ng CF$_4$ (99.9%, Sigma-Aldrich) and 0.7 ng of Crystal components were employed.

Calibration was performed subsequently according to optimum conditions using pure gas standards. The following chemicals were used: chloromethane (99.5%, Sigma-Aldrich), sulfur hexafluoride (5.0, Linde AG), carbon tetrafluoride (99.9%, Sigma-Aldrich). Pure gases were diluted via injection into Erlenmeyer flasks, on top of which a thread for closure with screw caps and Sil/PTFE septum was mounted. Calibrations were performed at 25 °C.

The solvent EPA 624 calibration mix 1 (Sigma-Aldrich) was used to determine retention times while the water trap was installed. Before samples were measured, mineral material was washed 3 times with bidistilled water or ethanol (p.a., Sigma Aldrich) and then evacuated at pressures below 10^{-4} mbar for at least 24 h in order to remove contaminants adsorbed to the mineral surfaces.

2.3. Measurement of samples

A 10 g mineral sample was measured in the closed grinding device before and after grinding. Samples were ground corresponding to their specific grinding conditions, e.g. 15 min at 400 rpm, 10 min at 400 or 5 min at 200 rpm for quartz, fluorite or halite, respectively. Sample results presented later on originate from a purple-green banded hydrothermal fluorite from the mine Marienschacht, Wölsendorf, Germany, and a halite from a recent salt crust of the salt pan Lake Kasin, South Russia.

3. Results and discussion

3.1. Grinding procedure

Compared to previous crushing stages in FI analysis, our grinding is used in offline MS detection because of the need for chromatography
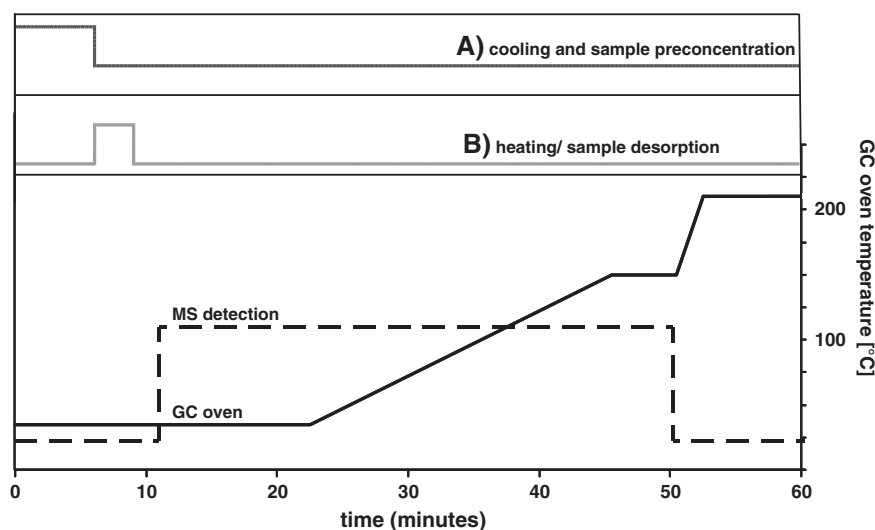

Fig. 2. GC oven program and MS detection. (A) indicates the duration of the sample pre-concentration and (B) the desorption step.

and detection of trace amounts of volatiles. Hence, bulk released VOC composition is determined rather than the release of individual fluid inclusions. Crushing yielded mean average diameters of 1000 and 740 nm for quartz and fluorite, respectively. Response of particle size to selected grinding treatments is depicted in Fig. 3. Quartz showed no further decrease of particle sizes after 15 min grinding time at 400 rpm, which was then chosen as the standard grinding condition for quartz and similar materials, such as granites. Fluorite summation curves of particle distribution clustered for the 10, 15 and 20 min of grinding time at 400 rpm. Longer grinding times did not yield smaller particles, which is typically observed (Jefferson et al., 1997; Kano et al., 2000) with final grain sizes apparently depending on the choice of grinding method and the properties of ground material (Kumar et al., 2006). Therefore, 400 rpm and 10 min were chosen as the standard grinding condition for fluorite and minerals of similar hardness, such as calcite or dolomite. Our grinding device avoids the tedious manual work done in the use of a crushing stage and ball. Also the cleaning of the grinding vessel is relatively easy as compared to the "peppermill"-design (Harnisch et al., 2000). At the same time the whole analytical setup only needed minor adjustments in order to accomplish the detection of volatiles from FIs and can be easily adjusted for a variety of other applications.

The observation of temperature development within the grinding device during grinding was crucial in order to evaluate the potential risk of de-novo volatile compound formation. As seen in Fig. 4, the interior temperature of the grinding chamber with sample and balls did not exceed $\Delta T = 10$ K for the quartz. However, an apparent plateau appeared to be reached. This can be explained by the high heat conductance of the tempered steel of 47 W m^{-1} K^{-1} (at 20 °C). After 15 min the maximum temperature difference on the outside of the vessel amounted to Δ 5 K. This means that heat had been transported away from the grinding vessel's interior, heating up the whole steel container. For the halite sample, the obtained curve in Fig. 5 shows a similar behavior, but temperatures on the outside of the vessel essentially remained constant, likely because of the higher deformation and plastic behavior of the salt. Energy input during grinding was lower as halite was only ground at 200 rpm (quartz at 400 rpm). After 5 min of grinding the temperature increase was less than half for the halites as compared to the quartz. When calculating the energies released during impacts and
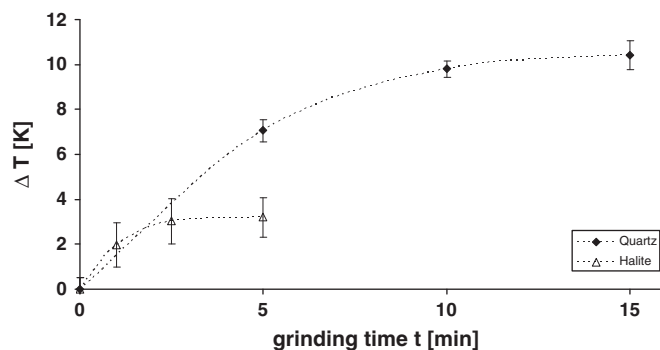

Fig. 4. Temperature development inside the grinding vessel after different grinding times for quartz and halite.

friction of balls with sample and walls, time of heat conductance was considered to yield a linear energy development over time. The energies were calculated approximately based on the equation,

$$Q = m \cdot cp \cdot \Delta T \qquad (1)$$

with Q being the heat energy (kJ/J), m the total mass of ground material, grinding balls and factored in the heated material of the grinding vessel, cp the respective specific heat capacities (kJ kg^{-1} K^{-1}) and ΔT the temperature difference (K). The calculated thermal energies released during grinding were 7.62 ± 0.47 kJ for quartz after 15 min and 0.87 ± 0.24 kJ for halite after 5 min. A larger error for the calculations for the halite crystal is probably due to its ductile behavior with energies being partly converted into deformation. Bond energies are for example 347 kJ mol^{-1} for C–C, 414 kJ mol^{-1} for C–H and 485 kJ mol^{-1} for C–F bonds (Mortimer and Müller, 2007). Although the values for the released energies can only be understood as approximations, they demonstrate that the energies developed within the grinding vessel are insufficient to break and form new covalent bonds. The grinding process should therefore not contribute to additional amounts of volatile compounds measured, thus we assume that the compounds measured after grinding are released directly from the fluid inclusions of the materials.

3.2. Chromatographic optimization

Results from the optimized measurement conditions are shown in Fig. 5. First, the purge flow rate as regulated by the flow controller downstream of valve 3 (Fig. 1) was varied for both the grinding vessel (a) as well as a regular empty 20 mL headspace vial (c) and purge flow as mL min^{-1} is plotted on the x-axis. The purge time was held constant at 6 min. The bars of the diagram in Fig. 5 show the response of each compound that was added in equal amounts each time. After 6 min with a purge flow of 10 mL min^{-1} CF_4 was recovered with highest intensities from the grinding vessel even though under these conditions the volume of the grinding vessel was not purged completely. Apparently, even at trapping temperatures of −196 °C the adsorption of low boiling compounds is not absolute but can be optimized by adjustment of the purge flow. Recoveries for butenes were generally higher from the 20 mL headspace vial than from the grinding vessel. This may be caused by the different purge volumes and geometries of the purged containers and by the different boiling points of the calibrated substances.

As we were striving to optimize the system for the lower boiling compounds and butenes did not show significant increase with higher purge rates, the purge rate was set at 10 mL min^{-1}. When varying the purge times it was remarkable that with 4 min signals for all five compounds were too low to be detected. After 6 min highest values were observed for CF_4, but recoveries for butenes between 6 and 10 min remained nearly constant from the grinding vessel (b). When looking at the headspace vial (d), clearly best results were achieved for the
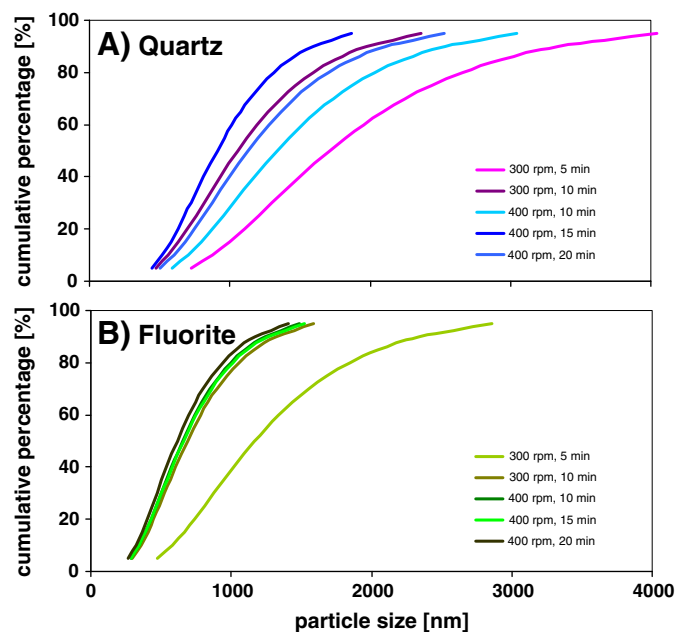

Fig. 3. Particle size distributions obtained at grinding conditions using each 5 grinding balls and 10 g of sample. A) cumulative percentage curves for quartz and B) for fluorite at different grinding conditions. The legend indicates quartz (Q) and fluorite (F), grinding intensities in rpm (300 or 400) and grinding times (min).
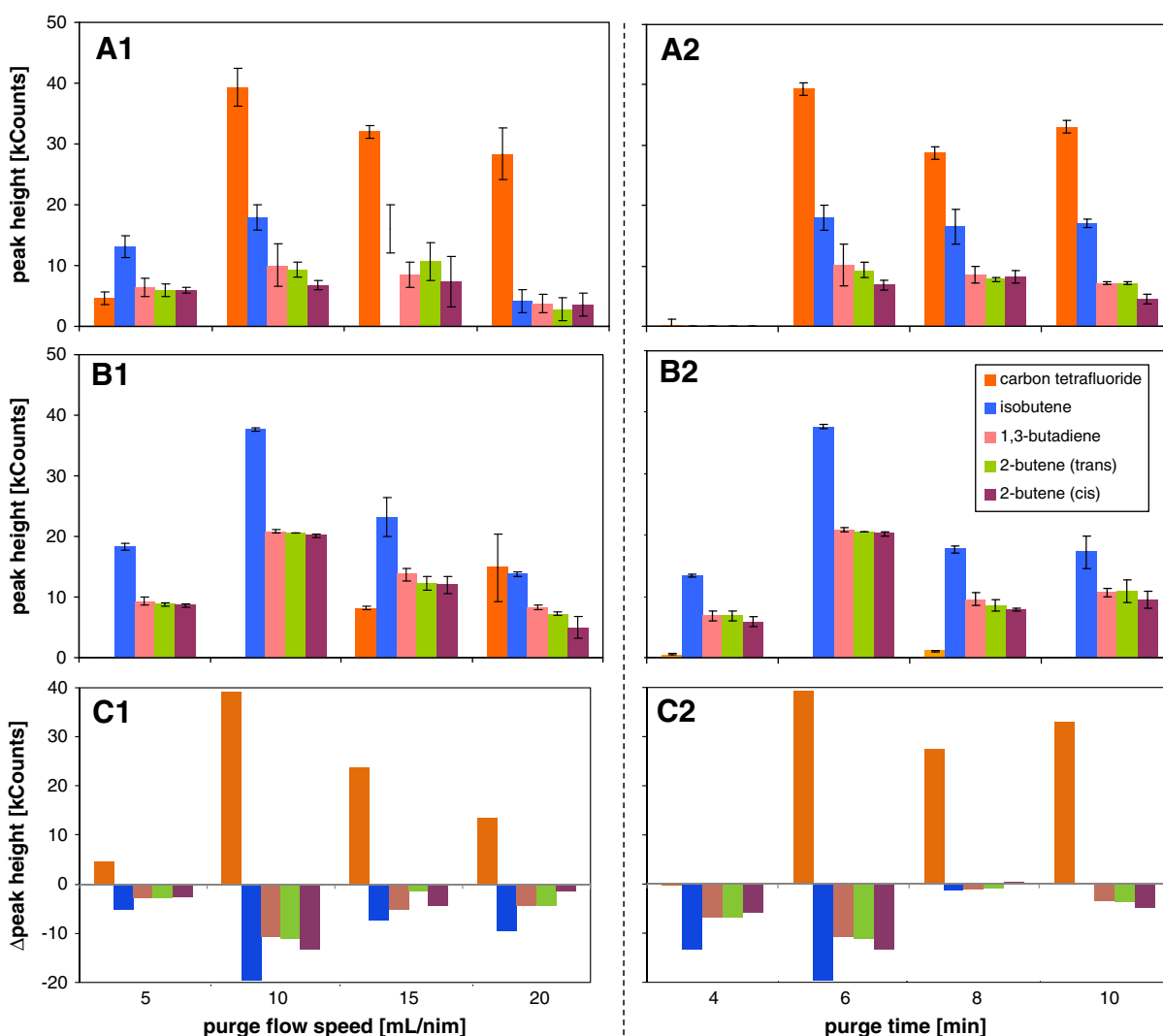
Fig. 5. Chromatographic recoveries of 5 standards at different purge flow speeds and purge times. Results from grinding vessel are on top (A1 and A2) and from headspace vial in the middle (B1 and B2). Plots C1 and C2 show the difference between grinding vessel and purge time (A minus B). Purge flow speed was varied with a constant purge time set at 6 min (left). Subsequently, the purge flow speed was held constant at 10 mL min^{-1} and purge times varied (right).

butenes after 6 min whereas CF$_4$ was not recovered at all, except for near detection limit amounts after 4 and 8 min. In general, purge time did not have such a distinct effect as purge speeds. However, best results were achieved after 6 min already. Hereupon, sample measurements were performed with 6 min purge time and 10 mL min^{-1} carrier gas flow. Detection limits with these conditions for the observed compounds are below 0.5 ng. The system installed at the University of Bayreuth employing a similar sample preconcentration applied to aerosol smog chamber experiments reached detection limits of 70 ppt for n-butanes and other higher molecular weight hydrocarbons (Siekmann, 2008).

The two capillary columns combined with the specificity of the MS detection sufficiently resolved most compounds of interest. Prior to this work, only CF$_4$ and SF$_6$ were quantified in our set of fluorite and granite samples. Table 1 lists the analytes that have been detected from standard and sample measurements with the current system.

The use of the Viton (fluoropolymer) seal ring between grinding bowl and crimp cap lid was not found to additionally augment our samples with CHF$_3$ as was reported previously in the literature (Miller et al., 2008). Also grinding and analysis of FIs did not necessarily need to be performed under inert gas conditions as the concentrations of compounds released from mineral material by far exceed atmospheric

concentrations. The 60 mL aliquot enriched from the grinding vial during the purge-and-trap sequence did not suffice for the detection of atmospheric volatile compounds as observed in blank measurements.

Two examples of the chromatograms after mineral grinding are shown in Fig. 6. The Wölsendorf-fluorite showed peaks for CF$_4$ and SF$_6$ corresponding to 26.3 and 3.4 ng/g, respectively. This shows the effectiveness of the system to trap these low boiling point compounds. Our values lie below those reported for comparable fluorite samples by Harnisch and Eisenhauer (1998) and Harnisch et al. (2000). This can be attributed to large natural variation and the inhomogeneity of the natural samples and is also reflected in the reported values that differ by a factor of 100. The larger abundance of CF$_4$ to SF$_6$ was confirmed from our analyses. Interestingly, chloromethane was released from both, the fluorite and the halite sample, at similar concentrations of around 6 ng g^{-1}. While Isidorov et al. (1993) and Svensen et al. (2009) also reported the measurement of chloromethane after dissolution or heating of halite samples, this is the first time that the release of chloromethane after grinding can be reported. Its observation from fluorite is novel but in both cases its occurrence is conceivable as chlorine as chloride in brines and methane in gases of fluid inclusions are commonly observed. Recent data from different quartz samples (not shown here) also showed that bromomethane can be released from FIs.

Table 1
Selected analytes detectable with the purge and trap system from calibration standards, their boiling points and target qualifier ion masses. Release of carbon tetrafluoride, sulfur hexafluoride, methyl chloride and methyl bromide from FIs can be accounted for thus far.

Compound name	Boiling point (°C)	Target ions (amu)
Carbon tetrafluoride	−128	69, 50
Sulfur hexafluoride	−64	127
Methyl chloride	−24	49,50,52
Chloroethene	−14	62, 64
Methyl bromide	4	79, 94, 96
Chloroethane	12.3	49, 64, 66
Trichlorofluoromethane	24	66, 101, 103
1,1-Dichlorethene	31.7	61, 96, 98
Methylene chloride	40	49, 84, 86
trans-1,2-dichloroethene	48.7	61, 96, 98
1,1-Dichloroethane	57.4	63, 65
Chloroform	61	83, 85
1,1,1-Trichloroethane	74	61, 97, 99
Carbon tetrachloride	77	117, 119
Benzene	80	77, 78
1,2-Dichloroethane	83.5	62, 64
Trichloroethene	87	95, 130, 132
1,2-Dichloropropane	96	62, 63, 76
Bromdichloromethane	90	83, 85, 129

4. Conclusions

Our GC–MS system together with the newly developed mineral grinding device allows for new compounds of interest in fluid inclusion research and at the same time maintains the high sensitivity of GC–MS measurements. Volatile compounds detected started at the very low boiling point of carbon tetrafluoride up to bromodichloromethane (Table 1), spanning a range of over 200 °C. The cold trap design

constructed of the GLT™ column without further adsorbent material and installed directly before the GC columns made this possible. We report here for the first time the release of CH_3Cl from halites and fluorite following this grinding procedure as compared to previous mineral dissolution or heating experiments.

Mineral grinding as compared to the previous "peppermill"-method by Harnisch et al. (2000) has been improved by a factor of 100, concerning final grain sizes. This also entailed a reduction of sample amount required. Initial measurements of mineral samples with this new system showed that it is able to reproduce SF_6 and CF_4 released from the FI as reported in previous studies by Harnisch and Eisenhauer (1998) and Harnisch et al. (2000).

The adapted dynamic headspace approach accommodates not only all types of minerals and rocks but is still highly versatile. Conventional headspace applications are still feasible by inserting the water trap and since analytes are trapped prior to the GC column, the cold trap could easily be used with different GC configurations or different analytical techniques.

An expanding dataset based upon this method will help to gain new insights into the formation process of VOXs found in FIs and their release to the environment upon weathering.
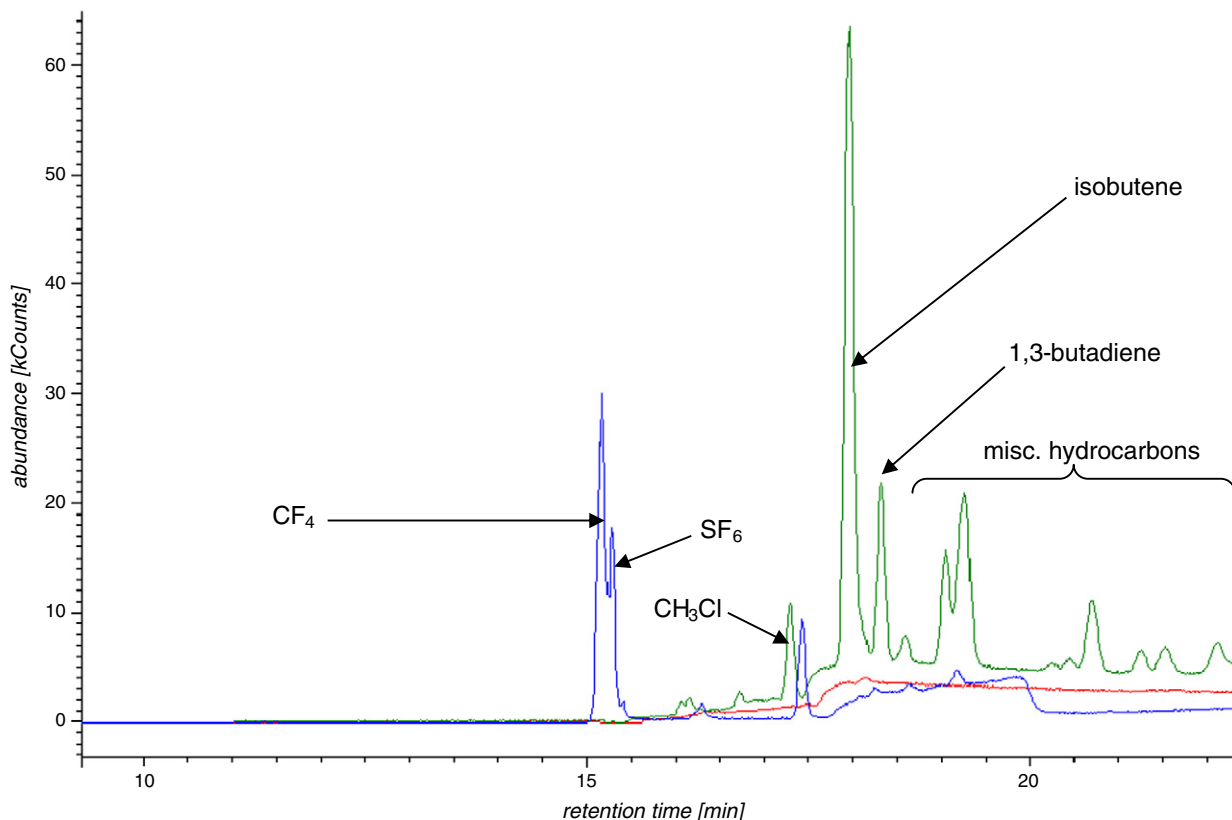
Acknowledgment

Fig. 6. Examples of reconstructed ion chromatograms (RICs) obtained from fluorite (blue) and halite (green) samples after grinding. Blank measurement in red. The samples originate from mine Marienschacht, Wölsendorf, Germany (fluorite), and from a recent salt crust of the salt pan Lake Kasin, South Russia (halite).

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