



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



Ines Mulder^{a,*}, Stefan G. Huber^b, Torsten Krause^a, Cornelius Zetzsch^c, Karsten Kotte^a, Stefan Dultz^d, Heinz F. Schöler^a

^a Institute of Earth Sciences, University of Heidelberg, Im Neuenheimer Feld 234-236, 69120 Heidelberg, Germany

^b Robert Bosch GmbH, (CR/ARA1), P.O. Box 10 60 50, 70049 Stuttgart, Germany

^c Bayreuth Center of Ecology and Environmental Research, Atmospheric Chemistry Research Laboratory, University of Bayreuth, Dr. Hans-Frisch-Str. 1-3, 95440 Bayreuth, Germany

^d Institute of Soil Science, Leibniz University Hannover, Herrenhäuser Str. 2, 30419 Hannover, Germany

ARTICLE INFO

Article history:

Received 30 May 2013

Received in revised form 5 September 2013

Accepted 6 September 2013

Available online 17 September 2013

Editor: David R. Hilton

Keywords:

Dynamic headspace purge and trap technique

Mineral grinding

Fluid inclusions

Carbon tetrafluoride

Sulfur hexafluoride

Methyl chloride

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 SF₆ and CF₄ released from fluorites and CH₃Cl from halite samples is demonstrated.

© 2013 The Authors. Published by Elsevier B.V. Open access under [CC BY license](#).

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 outnumbered 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 O₂, CO₂, SO₂, N₂, H₂, H₂S, HCl, HF, He, Ar, CH₄ 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

* Corresponding author at: Institute of Earth Sciences, University of Heidelberg, Im Neuenheimer Feld 234-236, 69120 Heidelberg, Germany. Tel.: +49 6221 546005; fax: +49 6221 545228.

E-mail address: ines.mulder@geow.uni-heidelberg.de (I. Mulder).

chromatography (GC) was particularly used for the separation of hydrocarbons, as well as H₂ and N₂ (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 (N₂, CH₄, CO₂) 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 sylvinitic 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 CHCl₃, CHBr₃ 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 CF₄ and SF₆. The largest scientific community that has recognized and measured their natural occurrence is environmental physicists, who used CF₄ and SF₆ 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 SF₆ 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 SF₆ is taken as a tracer. Deeds et al. (2008) also mentioned CF₄ as of terrigenous origin and stated that fluxes of CF₄ and SF₆ when extrapolated from their measurements to a global scale could be consistent with the fluxes required to sustain the preindustrial atmospheric abundances of CF₄ and SF₆.

Busenberg and Plummer (2010) presented results on a new groundwater dating method using the environmental tracers SF₅CF₃, CClF₃ (CFC-13), SF₆, and CCl₂F₂ (CFC-12). However, Harnisch et al. (2000) reported values of up to 1200 pg g⁻¹ CCl₂F₂ 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 terrigenous 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 CF₄ and SF₆ 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 CF₄, CF₂Cl₂, CFCI₃ and SF₆ from a number of natural samples and additionally CF₃Cl, CHF₃ and NF₃ from one fluorite sample. Levels of CF₄ were determined to be up to 5600 pg g⁻¹ and those of SF₆ 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

Download English Version:

<https://daneshyari.com/en/article/6436819>

Download Persian Version:

<https://daneshyari.com/article/6436819>

[Daneshyari.com](https://daneshyari.com)