

## Natural fluorinated organics in fluorite and rocks

Jochen Harnisch<sup>1,2</sup>, Matthias Frische<sup>1,3,4</sup>, Reinhard Borchers<sup>1</sup>,  
Anton Eisenhauer<sup>3,4</sup> and Armin Jordan<sup>1,5</sup>

**Abstract.** Results of measurements of fluorinated compounds in gasses extracted from igneous and metamorphic rocks are reported. A new extraction method analogous to a pepper mill for geological samples is described. It permits extraction at low temperatures and ensures a rapid transfer of extracted gases from active surfaces to cryogenic pre-concentration loop. Values for CF<sub>4</sub>, CF<sub>3</sub>Cl, CF<sub>2</sub>Cl<sub>2</sub>, CFC<sub>13</sub>, CHF<sub>3</sub>, SF<sub>6</sub> and NF<sub>3</sub> in fluorites, granites, basalts and other igneous and metamorphic rocks are reported. It is proposed that trifluoroacetic acid (TFA) that was recently discovered in various environmental archives could also origin from similar geogenic sources.

### Introduction

For decades synthetic fluorinated organics have been widely used as refrigerants, blowing agents in foam production, propellants for aerosol applications, solvents, surfactants pesticides and anaesthetics. The annual production and release of many of these compounds is well established [McCulloch and Midgley, 1999] while their natural occurrence has remained a matter of scientific debate.

After Lovelock [1971] established the extraordinary environmental stability of chlorofluorocarbons (CFC) through his pioneering atmospheric measurements the effect of their atmospheric accumulation has been thoroughly assessed. A milestone on this road has been the work by Rowland and Molina [1975] who predicted significant losses of stratospheric ozone as a consequence of a continuing release of CFCs. In combination with the discovery of the Antarctic ozone hole these research efforts led to the phase-out scheme of the production and use of CFCs under the Montreal Protocol starting in the late 1980's. The potential contribution of fluorocarbons to the anthropogenic warming of the global climate was first addressed by Wang *et al.* [1980]. Subsequently emissions of hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulfurhexafluoride have been included into the Kyoto-Protocol in 1997. The issue of a potential phytotoxic effect of an accumulation of trifluoroacetic acid (TFA) – a degradation product of atmospheric HFCs – in freshwaters has also been a matter of scientific discussion during recent years [Tromp *et al.*, 1995].

Only a limited number of naturally occurring organofluorine compounds has been detected in the biosphere, all of which contain only one fluorine atom. The best known example is

monofluoroacetate (MFA) that is produced by several plant species [Key *et al.*, 1997] as part of their defense strategy against grazing animals. In addition ω-fluorooleic acid and ω-fluoropalmitic acid have been isolated from the African plant *Dichapetalum toxicarium*. Two species of fungi are also known to produce the fluorine containing compounds nucleocidin and 4-fluorothreonine.

Kranz [1966] presented the first scientific evidence for the natural occurrence of abiotic organic fluorocarbons. His mass-spectrometric identification method however was not unambiguous and his results not widely received. Stoiber *et al.* [1971] detected several organofluorine compounds in gases collected from dilute volcanic fumaroles gases on Santiaguito volcano in Guatemala. Subsequently Rasmussen *et al.* [1979] rejected a volcanic formation of CF<sub>4</sub>, CF<sub>2</sub>Cl<sub>2</sub> and CFC<sub>13</sub> in fumarolic gases at Mauna Loa, Hawaii. This was later corroborated by the modeling results of Symonds *et al.* [1988] who excluded a gas phase formation of CFCs, CF<sub>4</sub> or SF<sub>6</sub> in a volcanic gas phase. However, Isidorov *et al.* [1993 a and b] reported the occurrence of highly elevated concentrations of different chloromethanes and trichlorofluoromethane (CFC-11) in gases extracted from halite (NaCl) and sylvite (KCl) samples, air from salt mines and dilute volcanic fumaroles at various sites in Russia. Again, these results were not accepted widely [Gaffney, 1995; Gribble, 1995; Isidorov, 1995]. Harnisch and Eisenhauer [1998] demonstrated that CF<sub>4</sub> and SF<sub>6</sub> are commonly present in natural fluorite and granite samples. Jordan *et al.* [2000] report the occurrence of a large number of chlorinated, brominated and iodated compounds in fumarolic and magmatic gases collected on Mt. Etna and Vulcano in Italy and Satsuma Iwojima and Kuju in Japan. Interestingly, they detected no significant enrichment above atmospheric background values of fluoroorganics. Recent measurements in environmental archives suggest that tetrafluoromethane (CF<sub>4</sub>) [Harnisch *et al.*, 1996a] and trifluoroacetic acid (CF<sub>3</sub>COOH) [Scott *et al.*, 1999] accumulated naturally in air and marine and fresh waters up to concentrations which are comparable to anthropogenic pollution levels.

Though the above reports remain contradictory, sufficient evidence has accumulated to challenge conventional wisdom according to which polyfluorinated organic compounds are exclusively man-made. This study continues the work initiated by Harnisch and Eisenhauer [1998]. An improved extraction technique is applied on a wider set of geologic samples to narrow the large uncertainties existing regarding the occurrence of fluorinated gases in fluid inclusions of minerals and rocks.

### Methods

Gases were extracted by grinding samples from roughly 5 mm diameter down to 100 μm diameter. This was accomplished by means of a grinding device similar to a pepper mill made out of steel (Figure 1). The mill was generally operated at room temperature. Seals were made from pure graphite. Driven by an electric motor set to 25 rotations per minute it permits to grind roughly 30 grams of a sample in less than one minute. The whole

<sup>1</sup> Max-Planck-Institut für Aeronomie (MPAE), Katlenburg-Lindau, Germany

<sup>2</sup> Now at: ECOFYS energy & environment, Cologne, Germany

<sup>3</sup> Geochemisches Institut, Universität Göttingen, Göttingen, Germany

<sup>4</sup> Now at: GEOMAR, Forschungszentrum für Marine Geowissenschaften, Kiel, Germany

<sup>5</sup> Now at: Max-Planck-Institut für Biogeochemie, Jena, Germany

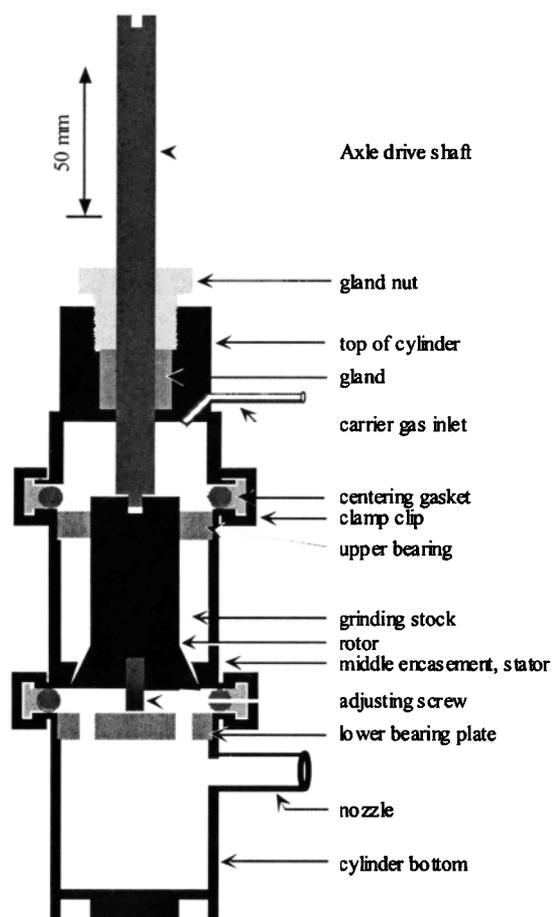


Figure 1. Schematic overview of the grinding device.

mill was repeatedly evacuated and flushed with blank tested synthetic air prior to the start of the grinding process. During grinding a continuous gas flow through the mill transferred the released gases to a concentration loop filled with Spherosil<sup>®</sup> XOB adsorbent cooled to liquid nitrogen temperature. The carrier gas which was not trapped in the loop was removed by a vacuum pump. After the end of the grinding process the trapped gases were de-sorbed by rapidly heating the loop to 95°C. By switching a multi-port valve, the carrier gas flow then transported the pre-concentrated de-sorbed gases into a gas chromatograph-quadrupole mass spectrometer system [see Harnisch *et al.*, 1996b]. Detection was carried out in single ion detection mode on respective characteristic masses, e.g. 69amu for  $\text{CF}_3^+$ , 127amu for  $\text{SF}_5^+$ , 52 amu for  $\text{NF}_2^+$ , 85amu for  $\text{CClF}_2^+$  or 101amu for  $\text{CCl}_2\text{F}^+$ . To identify substances gas chromatographic retention times were used as inferred from analyses of mixtures of pure compounds in blank tested air. The identity of compounds was also confirmed by operating the mass spectrometer in scan mode (33-250amu) on high concentration samples, e.g. WF (see below). The calibration of the system was carried out by several injections of a working standard gas mixture per day. The working standard had been calibrated against calibration gases prepared in a three step static dilution technique. Detection limits for  $\text{CF}_4$ ,  $\text{CF}_3\text{Cl}$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCl}_3$ ,  $\text{CHF}_3$ ,  $\text{SF}_6$  and  $\text{NF}_3$  were mass contents of 0.2, 0.3, 0.5, 0.3, 0.5, 0.1, 0.2 ppt, respectively taking into account residual air contamination in samples pores as inferred from  $^{126}\text{Xe}$  and  $^{128}\text{Xe}$ . The precision of individual measurements generally was  $\pm 10\%$ . Please refer to Harnisch *et al.* [1996b] and Harnisch and Eisenhauer [1998] for further analytical details.

## Results

In this study it is reported that  $\text{CF}_4$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCl}_3$  and  $\text{SF}_6$  can be extracted from a number of natural geologic samples (Table 1).  $\text{CF}_3\text{Cl}$ ,  $\text{CHF}_3$  and  $\text{NF}_3$  were detectable exclusively in a purple variety of fluorite (WF) with mass contents of 0.8, 3.7 and 60 ppb, respectively.

Fluorites are found to be rich in  $\text{CF}_4$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCl}_3$  and  $\text{SF}_6$ , while in granites  $\text{CF}_4$  is the only compound detectable in all samples. Interestingly,  $\text{CF}_4$  and  $\text{SF}_6$  remain undetectable in volcanites while some samples exhibit traces of CFCs.

The results for  $\text{CF}_4$  and  $\text{SF}_6$  derived in this study agree quite well with the ranges of mass contents reported by Harnisch and Eisenhauer [1998] for granites ( $\text{CF}_4$  2-55ppt /  $\text{SF}_6$  0-2ppt) and fluorites ( $\text{CF}_4$  0-5600ppt /  $\text{SF}_6$  0-340ppt).

## Discussion

As already discussed by Harnisch and Eisenhauer [1998] there are several factors that influence the content of fluorinated compounds in a geological sample. Among them are the rates of formation and destruction within the sample and the magnitude of fluxes across the sample boundaries.

Due to its extreme electronegativity the activation of fluorine from the ionic state is energetically disfavoured under most common conditions on Earth. Model calculations [Symonds *et al.*, 1988] suggest that the fluorinated compounds considered in this paper cannot be formed in a gas-phase equilibrium under plausible volcanic gas-phase equilibrium conditions.

In real geologic environments, however, generally many chemically differentiated conditions exist close to each other in mineral assemblies. In most cases apart from high temperature magmatic gases one would expect a significant impact on gas compositions from surface and non-equilibrium effects and from a chemical differentiation on the mineral grain level. Figure 2 shows a grain of accessory fluorite in the granite matrix of sample CG2. A variety of loci for distinctly different reactions exists even within and around this one grain.

Thus several processes can be envisioned that could yield the compounds found in fluorites and rocks. A) Gas phase formation

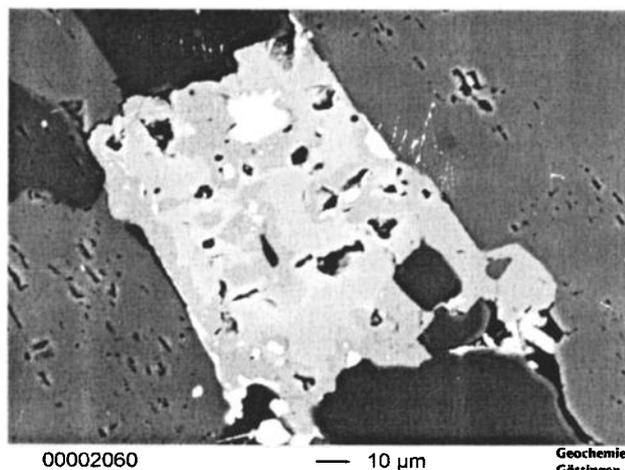


Figure 2. Accessory fluorites in Granite - fluorite (light grey) with fluid inclusions embedded in feldspar and quartz (dark grey and black) in granite sample CG2 from Battersen (Canada) identified by means of an electron microprobe in 30-35  $\mu\text{m}$  thin film.

Table 1. Mass-content of fluorinated gases in fluorite and rocks [ppt].

Sample type and location	sample	CF <sub>4</sub>	CF <sub>2</sub> Cl <sub>2</sub>	CFCl <sub>3</sub>	SF <sub>6</sub>
<b>Fluorites</b>					
Fluorite, Lavrio, Greece	GF1	120	110	46	42
Fluorite, Kazakstan	KF1	230	34	13	12
Fluorite, Kazakstan	KF2	480	24	11	13
Fluorite, Kazakstan	KF3	23	820	120	n.d.
Fluorite, Wölsendorf, Germany	WF	61,000	1,200	460	30,000
<b>Plutonites</b>					
Granite, Guenotte, Canada	CG-1	130	n.d.	n.d.	n.d.
Granite, Battersen, Canada	CG-2	265	n.d.	0.5	45
Granite, Brocken, Germany	BG-1-D	16	0.9	2.6	0.8
Granite, Jotunheimen, Norway	NNG	5.1	3.9	1.7	n.d.
Granite, Eknö, Sweden	SG-1	42	1.3	2.2	2.0
Granite, Eknö, Sweden	SG-2	12	1.8	1.8	0.6
Granodiorite, Khao Chmao N.P, Thailand	TG	29	n.d.	0.5	n.d.
Granite, Barre, USA	UG-1	1.9	n.d.	n.d.	n.d.
Granite, Minot, USA	UG-2	1.8	n.d.	0.4	n.d.
Granite, Rockport, USA	UG-3	39	1.1	0.7	0.7
Quartzmonzonite, Jotunheimen, Norway	NHQM	2.1	2.0	0.4	n.d.
Syenite, Skane, Sweden	SS	n.d.	n.d.	0.7	n.d.
<b>Volcanites</b>					
Andesite, Tungnafellsjökull, Iceland	IbAf	n.d.	n.d.	n.d.	n.d.
Andesite, Bakening, Kamtchatka	KaA	n.d.	n.d.	n.d.	n.d.
Basalt, Tungnafellsjökull, Iceland	IBd	n.d.	0.9	1.7	n.d.
Basalt, Tungnafellsjökull, Iceland	IBf	n.d.	n.d.	n.d.	n.d.
Basalt, Tungnafellsjökull, Iceland	IBp	n.d.	n.d.	0.6	n.d.
Basalt, Hoher Hagen, Germany	HHB	n.d.	n.d.	2.2	n.d.
Basalt, Bakening, Kamtchatka	KaB-1	n.d.	n.d.	n.d.	n.d.
Dacite, Tungnafellsjökull, Iceland	IDd	n.d.	1.2	1.4	n.d.
Dacite, Andes, Chile	AD	n.d.	1.0	1.1	n.d.
Mg-Andesite, Shivelnch, Kamtchatka	KaMgA	n.d.	n.d.	n.d.	n.d.
Rhyolite, Tungnafellsjökull, Iceland	IRp	n.d.	-	0.9	n.d.
Rhyolite, Andes, Chile	AR	n.d.	n.d.	n.d.	n.d.
Rhyolite, Bakening, Kamtchatka	KaR	n.d.	n.d.	n.d.	n.d.
<b>Metamorphic Rocks</b>					
Gneiss, Gamsberg, Namibia	NG-4	6.3	1.6	0.5	0.7
Meta-Rhyolite, Gamsberg, Namibia	NG-1	n.d.	1.8	4.0	n.d.
Meta-Rhyolite, Gamsberg, Namibia	NG-2	n.d.	0.9	0.8	n.d.

under extreme conditions, including elevated pressures and temperatures in combination with high local concentrations of hydrogen fluoride (HF) and low concentrations of water. B) Catalytic surface reactions under similar but less extreme conditions as postulated for pure gas phase reactions. C) Gas phase or heterogenous fluorination of halogenated precursors. D) Radiochemical production of molecular or atomic fluorine which would randomly fluorinate surrounding matter. E) Solid state generation of F<sub>0</sub>/F<sub>2</sub><sup>-</sup> defects [Kiss and Staebler, 1965] and their subsequent migration to the boundaries of fluid inclusions.

It cannot be excluded that two or more of the above fluorination reactions take place simultaneously or subsequently in (accessory) fluorites. Our results unfortunately do not provide strong constraints on the chemical pathways leading to a natural formation of polyfluorinated organics. However, the existence of CFCs in fluorites and the dominance of carbon-fluorine compounds relative to SF<sub>6</sub> or NF<sub>3</sub> in all of our samples suggests that stable (non-hydrolyzable) intermediates may greatly increase the chances for the formation of poly-fluorinated compounds in geologic matrices.

Quantitatively our results for granites confirm the earlier estimates by Harnisch and Eisenhauer [1998] that concluded that

common release mechanisms from granites would yield annual fluxes of CF<sub>4</sub> into the atmosphere of the order of 10<sup>5</sup>-10<sup>6</sup> grams yr<sup>-1</sup>. Assuming a natural atmospheric lifetime of CF<sub>4</sub> of roughly 200,000 years or more [Ravishankara *et al.*, 1993] this flux would sustain the observed natural atmospheric background concentration of CF<sub>4</sub> [Harnisch *et al.*, 1996a] which corresponds to 6×10<sup>11</sup> grams.

Levels of CF<sub>3</sub>COOH - trifluoroacetic acid (TFA) - recently detected in the environment (Frank *et al.* [1996]; Wujcik *et al.* [1999]) exceed the concentrations expected based on known anthropogenic sources [Jordan and Frank, 1999]. Measurements of von Sydow [1998] and Scott *et al.* [1999] in (aged) ocean waters indicate that TFA may exhibit a natural oceanic background concentration of roughly 100 ng per litre.

We here propose the hypothesis that accessory fluorite in granites is a source of natural TFA analogous to natural CF<sub>4</sub>. There are no degradation mechanisms of TFA known in the hydrosphere [AFEAS, 1994] so this concentration level is likely to have accumulated on a geologic timescale

Terrigenous dust could be a significant contributor to TFA in present day precipitation and unfiltered air. Measurements of TFA in fluorite and a range of metamorphic and igneous rocks

including granites are needed to decide whether a geogenic source could have built up detected TFA background concentrations.

## Conclusions

Our findings demonstrate that CFCs and perfluorinated compounds like  $CF_4$ ,  $SF_6$  and  $NF_3$  occur naturally in fluorites and igneous and metamorphic rocks. The natural geological reservoirs of these compounds are estimated to be of similar order of magnitude to the atmospheric reservoirs of their anthropogenic counterparts. Release rates from the crust, however, seem to be many orders of magnitude lower than comparable emission rates from anthropogenic sources. It appears thus quite certain that during the history of Earth natural CFCs and perfluoro-compounds never had any significant effect on the levels of stratospheric ozone or climatic conditions.

For the evaluation of hydrological or oceanographic tracer data using e.g. CFCs or  $SF_6$  it needs to be taken into account that at low concentrations, tracer signals could either be the result of an advection of recent waters or due to natural sources. Measurements of e.g.  $SF_6$  in ground waters could support the prospective search for commercial fluorite deposits.

The measurement of TFA contents in a similar set of geologic samples as analysed for this study would help to decide whether a natural geogenic source is responsible for the observed accumulation of TFA in aged ocean waters.

## Acknowledgements

The authors acknowledge the support by the many individuals who provided geological samples that were used in this study. Many thanks to K. Simon from the Institut für Geochemie in Göttingen for providing the grinding mills which were modified for the applications of this study. This study summarises the results of the master thesis of M. Frische. It was made possible through financial support by the Max-Planck-Society (Munich) and the Institut für Geochemie (Göttingen).

## References

- AFEAS; Proceedings of the Workshop on the environmental fate of trifluoroacetic acid, 3-4 March 1994, Miami Beach 1994.
- Frank, H., A. Klein, D. Renschen; Environmental Trifluoroacetate; *Nature*, 382, p. 34, 1996.
- Gaffney, J.S.; Volcanic CFCs; *Environ. Sci. Technol.*, 29, p. 8A, 1995.
- Gribble, G.; Volcanic CFCs - author's response; *Environ. Sci. Technol.*, 29, p. 8A, 1995.
- Harnisch, J., R. Borchers, P. Fabian, H.W. Gäggeler, U. Schotterer, Effect of natural tetrafluoromethane, *Nature*, 384, p. 32, 1996a.
- Harnisch, J., R. Borchers, P. Fabian, M.Maiss; Tropospheric trends for  $CF_4$  and  $C_2F_6$  since 1982 derived from  $SF_6$  dated stratospheric air; *Geophys. Res. Lett.*, 23, pp. 1099-1102, 1996b.
- Harnisch, J. and A. Eisenhauer; Natural  $CF_4$  and  $SF_6$  on Earth, *Geophys. Res. Lett.*, 25, pp. 2401-2404, 1998.
- Isidorov, V.A.; Volcanic CFCs - author's response, *Environ. Sci. Technol.*, 29, p. 8A, 1995.
- Isidorov, V.A., V.G. Povarov., E.B. Prilepsky; Geological sources of volatile organic components in regions of seismic and volcanic activity; *J. Ecol. Chem.*, 1, pp. 19-25, 1993a.
- Isidorov, V.A., E.B. Prilepsky, V.G. Povarov; Photochemically and optically active components of minerals and gas emissions of mining plants; *J. Ecol. Chem.*, 1, pp. 201-207, 1993b.
- Jordan, A. and H. Frank; Trifluoroacetate in the environment. evidence for sources other than HFC/HCFs; *Environ. Sci. Technol.*, 33, pp. 522-527, 1999.
- Jordan, A., J. Harnisch, R. Borchers, H. Shinohara; Volcanogenic Halocarbons; *Environ. Sci. Technol.*, 34(6), pp. 1122-1124, 2000.
- Key, B.D., R.D. Howell, C.S. Criddle; Fluorinated organics in the biosphere; *Env. Sci. Tech.*, 31, pp. 2445-2454, 1997.
- Kiss, Z.J. and D.L. Staebler; Dynamics of oxidation-reduction processes in rare-earth doped  $CaF_2$ ; *Phys. Rev. Lett.*, 14, pp. 691-693, 1965.
- Kranz, R.; Organische Fluorverbindungen in den Gaseinschlüssen der Wölsendorfer Flußspäte; *Naturwissenschaften*, 53, pp. 593-600, 1966.
- Lovelock, J.E.; Atmospheric fluorine compounds as indicators of air movements; *Nature*, 230, p. 379, 1971.
- Midgley P. and A. McCulloch; Production, sales and emissions of halocarbons from industrial sources; in 'Reactive halogens in the atmosphere' edited by P. Fabian and O. Singh, Handbook of Environmental Chemistry, pp. 155-190, Springer-Verlag, Berlin, 1999.
- Rasmussen, R.A., S.A. Penkett, N. Prosser; Measurement of carbon tetrafluoride in the atmosphere; *Nature*, 277, pp. 549-551, 1979.
- Ravishankara, A.R., S. Solomon, A.A. Turnipseed, R.F. Warren; Atmospheric lifetimes of long-lived halogenated species; *Science*, 259, pp. 194-199, 1993.
- Rowland, F.S. and M.J. Molina; Chlorofluoromethanes in the environment; *Rev. Geophys. Space Sci.*, 13, pp. 1-35, 1975.
- Scott, B.F., D.C.G. Muir, C. Spencer, R. MacDonald, A. Witter, A. Flak; Haloacetic acids in the freshwater and marine environment; lecture held at the First International Symposium on Atmospheric Reactive Substances, Bayreuth 14-16 April 1999.
- Stoiber, R.E., D.C. Leggett, T.F. Jenkins, R.P. Murrmann & W.I. Rose; Organic compounds in volcanic gas from Santiaguito volcano, Guatemala, *Geol. Soc. Am. Bull.*, 82, pp. 2299-2302, 1971.
- v. Sydow, L.; PhD thesis, University of Linköping, 1998.
- Symonds, R.B., W.I. Rose, M.H. Reed; Contribution of Cl- and F-bearing gases to the atmosphere by volcanoes; *Nature*, 334, 415-418, 1988.
- Tromp, T.K., M.K.W. Ko, J.M. Rodriguez, N.D. Sze; Potential accumulation of a CFC-replacement degradation product in seasonal wetlands, *Nature*, 376, pp. 327-330, 1995.
- Wang, W.C., J.P. Pinto, Y.L. Yung, Climatic effects due to halogenated compounds in the Earth atmosphere; *J. Atmos. Sci.*, 37, pp. 333-338, 1980.
- Wujcik, C.E., T.M. Cahill, J.N. Seiber; Determination of trifluoroacetic acid in 1996-1997 precipitation and surface waters in California and Nevada; *Environ. Sci. Technol.*, 33, pp. 1747-1751, 1999.

J. Harnisch, ECOFYS energy & environment, Eupener Str. 137, 50933 Cologne, Germany, j.harnisch@ecofys.de  
 R. Borchers, Max-Planck-Institut für Aeronomie, Max-Planck-Str. 2, 37191 Katlenburg-Lindau, Germany, borchers@linmpi.mpg.de  
 M. Frische and A. Eisenhauer, GEOMAR, Forschungszentrum für Marine Geowissenschaften, Wischhofstr. 1-3, 24148 Kiel, Germany, mfrische@geomar.de / aeisenhauer@geomar.de  
 A. Jordan, Max-Planck-Institut für Biogeochemie, Postfach 100164, 07701 Jena, Germany, ajordan@bgc-jena.mpg.de

(Received December 26, 1999; accepted May 4, 2000.)