

Diffusive emission of halocarbons from volcanic flanks and craters

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Current global atmospheric budgets of ozone-depleting substances (ODS) are not balanced by known anthropogenic and natural sources (Butler, 2000). Volcanic emissions have been suggested as a source of stratospheric chlorine (Stolarski and Cicerone, 1974), but it was limited to episodic explosive HCl and HF emissions that wash out by dissolution and vapour condensation on ash before they can reach the stratosphere. Quiescent fumarolic degassing of less soluble halocarbons was suggested as a quasi-continuous source (e.g., Wahrenberger et al., 1996), but quantification was limited by inadequate sampling and analytical protocols, leading to air contamination (Jordan et al., 2000). We have developed new sampling and analytical techniques in order to reliably measure the concentration of halocarbon compounds in volcanic gases (Schwandner et al., 2002). The question arises to what extent diffusive emissions contribute to the volcanic source strength of organic trace gases.

We have sampled soil gas emissions of organic compounds and determined CO₂-fluxes along a profile spanning from the vegetated base of the active La Fossa cone (Vulcano Island, Italy) over the unvegetated crater rim and -base into fumarolic areas. The results show that a) emissions of CFC-11 (CCl₃F) correlate well with soil CO₂-flux ($R^2=0.91 \pm 0.02$), and b) diffusive emissions contribute significantly to the volcanic halocarbon source strength. Other ODS significantly above air, field and system blanks include CH₃Br, CH₃Cl, CH₃I, C₂H₅Br, and chlorinated benzenes. Abundances range from upper pptv to ppmv (e.g. CFC-11: max. 1200 pptv diffusive, 3700 pptv fumarolic/dry gas, dry air: 268 pptv).

References

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Dating of hydrothermal alteration by the ⁴⁰Ar/³⁹Ar step heating method using plagioclase-sericite intergrowth

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K-Ar dating of younger hydrothermal alteration products is often difficult because the minerals are closely intergrown. A quantitative separation is mostly impossible because of the extremely small grain sizes of at least one of the components. In the case of two components pairs of differently enriched separates yield total argon data which can be evaluated for the ages of the mixing end members (Lippolt and Kirsch 1994), provided that the minerals have different K contents. In case that the argon kinetics of the two minerals during in-vacuo step degassing differ significantly, argon and thus the age information of the two components may be separated by applying ⁴⁰Ar/³⁹Ar step heating on a single separate, combined with microprobe chemical analysis (Lippolt and Kirsch 1994, Villa et al. 1997). Analytical problems may turn up if nucleogenically redistributions of activated argon isotopes occur and methodical when more than two components are present.

This single-sample ⁴⁰Ar/³⁹Ar step heating approach was used with sericitized plagioclases from two regions: the Frankenstein gabbro in the NW-Odenwald (Germany) and the Bande-Médiane andesite in the Vosges (France). Separates of sericitized plagioclase were analysed for their chemical composition and neutron-irradiated aliquots for the argon isotope concentrations. The determination of end-member ages was performed by extrapolations in three-isotope correlations diagrams and by numerical calculations.

Based on several independent measurements the intrusion age of the Frankenstein gabbro (c. 360 Ma) was confirmed and two sericitization (alteration) ages of the plagioclases were determined, of which the younger one coincides with the time frame of late Jurassic given by Lippolt and Kirsch (1994). The older age is approximately equal to the intrusion age.

The andesite results are more complex, indicating the existence of more than two components. Indications of excess-argon in the plagioclase prevented the determination of the plagioclase age. However, several sericitisation phases were determined, of which the oldest happened more than 330 Ma ago and the youngest c. 140 Ma ago, nearly simultaneously with the Frankenstein alteration.

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