Basylevska, M., & Bogillo, V. (2021). The impact of volcanic emission
of halogenated compounds on the Southern Hemisphere
and Antarctic environment.
*Ukrainian Antarctic Journal*, 2, 12—34.
https://doi.org/10.33275/1727-7485.2.2021.675

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# The impact of volcanic emission of halogenated compounds on the Southern Hemisphere and Antarctic environment

**Abstract.** The study aims to estimate and compare the global emission for 20 halocarbons from volcanic and hydrothermal sources into the Earth's atmosphere. It follows from the results that the contribution of volcanic emission for these species in the depletion of stratospheric ozone in the catalytic halogen cycles does not exceed 0.1%. Still, they significantly impair the level of tropospheric ozone near the volcanoes. The scheme of gas-phase free radical chain halogenation of the hydrocarbons is proposed and confirmed by thermodynamic and kinetic calculations. This explains the experimental ratios between concentrations of $CH_3I : CH_3Br : CH_3Cl$ and $CCl_4 : CHCl_3 : CH_2Cl_2 : CH_3Cl$ in the volcanic gases. The possible volcanic emission of halocarbons from Erebus and explosive eruptions in the Southern Hemisphere during the Holocene do not have a notable impact on their content in the Antarctic ice. However, volcanic emission of hydrogen halides (HX, X = Cl, Br or I) from powerful eruptions in the Southern Hemisphere during Holocene could deplete the stratospheric ozone substantially, causing a drastic impact of the harmful UV-B radiation on the biota of continents and ocean. We calculated the injected Equivalent Effective Stratospheric Chlorine values and estimated the column ozone percentage change, $\Delta\%O_3$, for 20 known volcano eruptions in the tropical belt and Southern latitudes. The estimates lead to more than 50% depletion of stratospheric ozone after past powerful volcanic eruptions. The range is estimated for possible ozone depletion after the eruption of Deception Island's volcano occurred near 4000 BP (from 44 to 56%), which is comparable with those from Krakatoa, Samalas, and Tambora eruptions. A similar analysis was carried out for 192 yrs series of Mt Takahe (West Antarctica) halogen-rich volcanic eruptions at 17,7 kyr, showing extensive stratospheric ozone depletion over Antarctica. Crude estimations of stratospheric ozone depletion ($\Delta\%O_3$) after Ferrar Large Igneous Province eruptions (183 Ma) in Antarctica were performed, considering the whole LIP volume of basaltic lavas, and they range from 49 to 83%. Given the very low emission rate of HCl due to non-eruptive degassing of the Mt. Erebus volcano, the volcanic emission of Erebus could not be a fundamental reason for modern springtime ozone hole formation over Antarctica.

**Keywords:** halocarbons, hydrogen halides, free-radical chain reactions, stratospheric ozone depletion, volcanic emission

## 1 Introduction

Volcanoes release many gases, heavy metals, and sulfate aerosols into the atmosphere due to rare explosive eruptions and prolonged non-eruptive degassing. Volcanic emission plays a vital role in the exchange of many trace components between land and atmosphere and in the biogeochemical cycles of essential elements. In recent years, the influence of large volcanic eruptions on the Earth's climate and the stratospheric ozone layer depletion and destruction of tropospheric (surface) ozone has been studied in detail.

The volcanoes are significant sources of sulfur, nitrogen, halogen, and carbon compounds in the atmosphere (Halmer et al., 2002). Volcanic hydrated sulfate aerosols in the stratosphere ($H_2SO_4 \times nH_2O$) act as active sites for heterogeneous atmospheric reactions in which passive halogen compounds (HCl, HBr, HI, HOCl, HOBr, HOI, $ClONO_2$, $BrONO_2$, $IONO_2$) are converted into active particles (Cl, Br, I, ClO, BrO, IO), which then efficiently react with ozone ($O_3$). These heterogeneous reactions lead to the depletion of the ozone layer in the stratosphere over the Antarctic and the Arctic in the spring. Although volcanoes can be a significant source of passive chlorine compounds in the stratosphere, HCl, due to its high solubility in water, is effectively washed out in a volcanic column and deposited on the Earth's surface. However, it was shown (Textor et al., 2003) that, at a low water content, relatively dry aggregates of particles form in this column and, despite trapping by ice particles, over 25% HCl and 80% sulfur-containing gases reach the stratosphere.

The studies of the atmospheric chemistry and climate impacts of volcanic emissions have mostly focused on $SO_2$ and its oxidation to sulfate particles in both the stratosphere and troposphere. Volcanic sulfates also catalyse gas-aerosol reactions leading to depletion of stratospheric ozone (Berthet et al., 2017; Ivy et al., 2017). However, the volcanic release contains volcanic halogens such as HBr and HCl (Aiuppa et al., 2009). Volcanic halogens can occasionally be injected into the stratosphere as evidenced by observations of HCl, OClO, BrO, and IO by satellite (Rose et al., 2006; Carn et al., 2016; Schönhardt et al., 2017). Volcanic halogens that reach high altitudes may cause reductions in stratospheric ozone levels. This has been observed (Rose et al., 2006) and simulated by numerical models (Millard et al., 2006; Lurton et al., 2018). The discovery of BrO in a volcanic plume in the troposphere (Bobrowski et al., 2003) showed that volcanic HBr emissions could transform into reactive bromine over very short time scales. Volcanic BrO has subsequently been observed in many tropospheric volcano plumes globally (Boichu et al., 2011). Volcanic OClO has also been reported in some tropospheric plumes (Bobrowski et al., 2007; General et al., 2015).

The ozone destruction potential of stratospheric iodine is significantly higher than that of the other halogens. Bromine is about 60 times more effective in destroying ozone than chlorine and, for iodine, the factor is about 150 to 300. As a result, reactive iodine may impact stratospheric ozone chemistry even at sub-pptv levels. Recently, Koenig et al. (2020) provided quantitative evidence that total inorganic iodine may exist in the stratosphere at mixing ratios of 0.8 pptv and that reactions of iodine may account for as much as a third of halogen-induced chemical ozone loss in the lower stratosphere. Large column amounts of IO have been observed in satellite measurements following the major eruption of the Kasatochi volcano, Alaska, in 2008 (Schönhardt et al., 2017). Following the eruption, strongly elevated levels of IO whole columns of more than $4 \times 10^{13}$ molecules $cm^{-2}$ for several days. The column amounts of IO are approximately one order of magnitude lower than BrO. The model developed in Karagodin-Doyennel et al. (2021) suggests the strongest influence of iodine in the lower stratosphere with an ozone loss of up to 30 ppbv at low latitudes and up to 100 ppbv at high latitudes. Globally averaged, the model suggests iodine-induced chemistry to result in an ozone column reduction of 3—4%, peaking at high latitudes.

The discovery of mutated palynomorphs in end-Permian rocks (~252 Ma) led to the hypothesis that the eruption of the Siberian Traps through older organic-rich sediments synthesized and released massive quantities of halocarbons (HC), which caused widespread $O_3$ depletion and allowed increased terrestrial incidence of harmful ultraviolet-B radiation (UV-B). A 2-D model was used in (Beerling et al., 2007) to evaluate this possibility quantitatively. According to the simulations, $CH_3Cl$ released from the heating of coals alone caused minor $O_3$ depletion (5—20%). The explosion of the Siberian Traps, combined with the direct release of HCl, depleted the model $O_3$ layer in the high northern latitudes by 33—55%, given a main eruptive phase of 200 kyrs. The $O_3$ depletion was most extensive when HCl release was combined with $CH_3Cl$ release formed from organic matter in Siberian rocks, and it led to column $O_3$ depletion of 70—85% and 55—80% in the high northern and southern latitudes, respectively, given eruption durations of 100—200 kyrs. Calculated year-round increases in total near-surface biologically effective (BE) UV-B radiation following these reductions in $O_3$ layer range from 30—60 (kJ $m^{-2}$ $d^{-1}$) BE up to 50—100 (kJ $m^{-2}$ $d^{-1}$) BE.

By combining petrologic constraints on eruption volatile yields with a global atmospheric chemistry-transport model, it was shown that the Bronze-Age 'Minoan' eruption of Santorini Volcano released far more halogens than sulfur and that, even if only 2% of these halogens reached the stratosphere, it would have resulted in strong global ozone depletion (Cadoux et al., 2015). The erupted magma volume was assumed to be 39 $km^3$ (i.e., a mass of $9 \times 10^{13}$ kg). In a scenario with melt degassing only, the Minoan eruption would have released 0.34 Tg of S, 50.6 Tg of Cl, 23 Tg of F, 0.1 Tg of Br, and 0.002 Tg of I (Cadoux et al., 2015).

Petrological analysis of the 1257 Mt. Samalas eruption suggests as much as 227 Tg of HCl and 1.3 Tg of HBr could have been emitted into the atmosphere alongside 158 Tg of $SO_2$ (Vidal et al., 2016; Wade et al., 2020). Despite efficient scavenging, direct stratospheric injection of volcanic halogens predicted by theory and sophisticated plume models suggest that between 10% and 20% of the HCl could reach the stratosphere. Klobas et al. (2017) simulated hypothetical Mt. Pinatubo-sized eruptions with stratospheric injection HCl : $SO_2$ mixing ratio of ~0.14 and reported global ozone depletion lasting ~2—3 years with a peak of 20%. Ming et al. (2020) simulated explosive tropical eruptions. They found that a volcanic halogen emission of 0.02 Tg (HCl : $SO_2$ = 0.04) into a preindustrial background state had little impact on column ozone, but 2 Tg (HCl : $SO_2$ = 0.4) showed significant and prolonged ozone depletion above both poles. Brenna et al. (2019) simulated an average eruption of a Central American Volcanic Arc volcano with a 10% halogen injection efficiency (2.5 Tg Cl, 9.5 Gg Br). They found ozone depletion of up to 20% globally for ten years, with ozone hole conditions over the tropics and Antarctica. Consequently, UV radiation increases of >80% were simulated for two years.

The super eruption of Los Chocoyos (14.6 N, 91.2 W) in Guatemala 84 kyrs was one of the largest volcanic events of the past 100 000 years. Recent petrologic data show that the eruption released vast amounts of S (523 Tg), Cl (1200 Tg), and Br (2 Tg). Simulations of the impacts of the S, Cl, and Br-rich eruption on the preindustrial Earth system were performed in Brenna et al. (2020). They show that elevated sulfate burden and aerosol optical depth (AOD) persists for five years, while the volcanic halogens stay elevated for nearly 15 years. The eruption leads to a collapse of the ozone layer, with global column ozone values dropping to 50 DU (80% decrease) and leading to a 550% increase in surface UV over the first five years, with potential impacts on the biosphere. The surface climate is impacted globally due to peak AOD of > 6, which leads to a maximum surface cooling of > 6 K, precipitation and terrestrial net primary production decrease of > 25 %, and sea ice area increases of 40% in the first three years. Recovery to pre-eruption ozone levels and climate takes 15 and 30 years, respectively.

An aerosol-chemistry-climate model was confronted in Staunton-Sykes et al. (2021) with four stratospheric volcanic eruption emission scenarios (56 Tg $SO_2 \pm$ 15 Tg HCl & 0.086 Tg HBr and 10 Tg $SO_2 \pm$ 1.5 Tg HCl & 0.0086 Tg HBr) to understand how co-emitted halogens may alter the life cycle of volcanic sulfur, stratospheric chemistry and the resulting effective radiative forcing (ERF). The eruption sizes simulated in this work are hypothetical Volcanic Explosivity Index (VEI) 7 (e.g., 1257 Mt. Samalas) and VEI 6 (e.g., 1991 Mt. Pinatubo) eruptions. It was shown that co-emission of volcanic halogens and sulfur into the stratosphere increases the ERF by 24—30 % compared to sulfur-only emission. Co-emission of volcanic halogens results in significant stratospheric ozone, methane, and water vapor reductions, and thus in substantial increases in peak global-mean ERF (>100%), predominantly due to ozone loss. The dramatic global-mean ozone depletion simulated in both co-emission simulations (22%, 57%) would result in very high levels of UV exposure on the Earth's surface, with important implications for the biosphere.

The most important source of active halogen atoms in the modern stratosphere is the photolysis of HCs of anthropogenic and natural origin, in particular, Freon 11 ($CFCl_3$) and 12 ($CF_2Cl_2$), $CH_3Cl$, $CH_2Cl_2$, $CHCl_3$, $CCl_4$, $CH_3CCl_3$, $CH_3Br$, $CH_2Br_2$, and $CHBr_3$. If for $CH_3Cl$, $CHCl_3$, $CH_3Br$, $CH_2Br_2$, and $CHBr_3$ their natural sources (oceanic biota, coastal salt marshes, terrestrial plants, wood-rotting fungi, soils, biomass burning, photochemical production in near-surface snow) are established, then the remaining compounds are believed to be mainly of anthropogenic origin. This conclusion was confirmed by analyzing these compounds in firn air and ice samples from the Antarctic and the Arctic (Butler et al., 1999; Bogillo et al., 2003).

However, the results of the analysis of fumarole, solfataric, and diffusion gases, performed in 1971–2005 for volcanoes of Santiago (Guatemala) (Stoiber et al., 1971), Kilauea and Mauna Loa (Hawaii, USA) (Rasmussen et al., 1980), St. Helens (USA) (Rasmussen et al., 1982), Mendeleev, Golovnina, Tyatya (Kunashir Isl.), Curly (Iturup Isl.) (Russia) (Isidorov et al., 1990), Volcano Isl. (Italy) (Wahrenberger, 1997), Kuju and Satsuma Iwojima (Japan), Etna and Vulcano Isl. (Italy) (Jordan et al., 2000), Volcano Isl. (Italy) (Schwandner et al., 2004), Momotombo (Nicaragua) (Frische et al., 2006) indicate the existence of many HCs in the volcanic gases, including Freon 11 and 12, in high concentrations with an enrichment ratio (the ratio of the compound in the volcanic gas to its concentration in the background air) reaching $1.5 \times 10^5$ (Rasmussen et al., 1980; Rasmussen et al., 1982; Isidorov et al., 1990; Wahrenberger, 1997; Jordan et al., 2000; Schwandner et al., 2004; Frische et al., 2006). Thus, volcanoes can be significant natural sources of these compounds, and it is necessary to assess the contribution of the volcanoes to the global HCs inventory.

In the present study, the estimates of emissions of the HCs from volcanic and hydrothermal sources were performed, and the mechanisms of the HCs formation in the volcanic column were considered. Estimates were also made of the possible effect of volcanic emissions of HCs from Mt Erebus (East Antarctica) and explosive eruptions in the Southern Hemisphere during the Holocene on their airborne firn and ice core content in the Antarctic. Also, possible stratospheric ozone depletion caused by the hydrogen halides released after powerful volcanic eruptions in the Southern Hemisphere and Antarctica was estimated.

## 2 Results and discussion

### 2.1 Ranges of volcanic and geothermal emissions of halogenated hydrocarbons

The ranges of volcanic emission of 20 HCs were calculated using the volcanic emission of $SO_2$ (7.5—19 Tg yr$^{-1}$), its volume concentration in volcanic gas (1—25%) (Halmer et al., 2002), and the average and maximum volumetric mixing ratios of the HCs in volcanic gases (Rasmussen et al., 1980; 1982; Isidorov et al., 1990; Wahrenberger, 1997; Jordan et al., 2000; Schwandner et al., 2004; Frische et al., 2006). These data are presented in Table 1. It also shows the global emissions of the HCs (GE) and their ozone-depleting potential in the stratosphere (ODP), assuming ODP = = 1 for $CFCl_3$.

One can recognize from Table 1 that the volcanic emission of HCs makes an extremely insignificant contribution to their global atmospheric emission. The maximum contribution of volcanic emission can be for $CH_3CClF_2$ (0.8%), $CF_2Cl_2$ (0.3%), $CFCl_3$ (0.25%), $CCl_4$ (0.2%) and $CH_2Br_2$ (0.1%). This contribution ranges from 0.0001% to 0.03% for the other compounds. Since the contribution of the HCs to the depletion of stratospheric ozone is different, we estimated the possible maximum total volcanic emission of all compounds from Table 1, taking into account their ODP value. This emission in the equivalent of the ODP of freon 11 is 0.00116 Tg yr$^{-1}$. In comparison, the global emission of these HCs from all sources in the equivalent of the ODP of freon 11 is 1.029 Tg yr$^{-1}$, i.e., the contribution of volcanic emission of HCs to the depletion of stratospheric ozone in catalytic halogen cycles does not exceed 0.1%.

Another geological source of HCs is the emission from hydrothermal sources in seismically and volcanically active regions. Based on the concentrations of the compounds in spontaneous gases given in (Isidorov et al., 1997), the global annual flux of methane from these sources (2.5—6.3 Tg yr$^{-1}$) (Etiope, 2004), its volume concentration in spontaneous gases (up to 15%) (Isidorov et al., 1997), we estimated the emission ranges of HCs from these sources (in tons yr$^{-1}$): 3.5—480 ($CHCl_3$), 0.1—4.2 ($CCl_4$), 0.2—3.0 ($ClHC = = CCl_2$), 0.2—0.5 ($CCl_2 = CCl_2$), 0.1—66 ($CF_2Cl_2$) and 0.05—0.9 ($CFCl_3$). Comparing these ranges with those from Table 1 shows that hydrothermal sources are also insignificant natural sources of HCs in the atmosphere.

Despite the insignificant contribution of the HCs volcanic emission to the stratospheric ozone depletion, the photochemical reactions of the compounds and their hydrolysis with the formation of active species such as Cl, Br, I, ClO, BrO, and IO can deplete the tropospheric ozone in the vicinity of volcanoes. So, in Lee et al. (2005), the rate of ozone depletion in the area of the Sakurajima volcano crater (Japan) is 31 ppbv $h^{-1}$, caused by high concentrations of ClO (1 ppbv) and BrO (20 pptv) in the volcanic column.

## 2.2 The genesis of volcanogenic halocarbons

The high concentrations of HCs in volcanic gases (Rasmussen et al., 1980; Rasmussen et al., 1982; Isidorov et al., 1990; Wahrenberger, 1997; Jordan et al., 2000; Schwandner et al., 2004; Frische et al., 2006) indicate the abiotic origin of these compounds. The main natural source of the HCs is the halogenation of organic substances by biota of land and oceans, catalyzed by various enzymes. So far, only two abiotic sources of HCs have been identified. The first of them relates to the alkylation of halogen ions in soils and bottom sediments during the oxidation of the organic matter by $Fe^{3+}$ ions (Keppler et al., 2000), while the second involves the haloform reaction of HOBr and HOI with organic matter in the quasi-liquid layer of snow cover on the sea ice surface (Carpenter et al., 2005).

The formation of organic compounds, including HCs, under magmatic conditions, contradicts the

**Table 1.** Ozone Depleting Potential (ODP) of halocarbons (HC), their global emission from all sources (GE), and their volcanic emission (VE)

| HC | ODP | GE, Tg $yr^{-1}$ | VE, tons $yr^{-1}$ | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | 4 | 5 | 6* | 7 |
| $CH_3Cl$ | 0.02 | 3.7 | 4.7–299 | 192 | – | – | 2.8–180 | 78 | 5.6 |
| $CH_2Cl_2$ | <0.001 | 0.6 | – | – | 177 | 327 | 0.02–1.2 | 21 | 0.027 |
| $CHCl_3$ | 0.008 | 0.6 | – | – | 147 | 0.6 | 0.3 –20 | 95 | 0.02 |
| $CCl_4$ | 1.2 | 0.02 | | – | 7.4 | 17 | 0.7–42 | 3.4 | 0.003 |
| $C_2H_5Cl$ | – | – | – | – | – | – | – | – | 0.3 |
| $CHCl = CCl_2$ | <0.001 | 0.6 | – | – | – | – | 8.6 | – | – |
| $CCl_2 = CCl_2$ | 0.006 | 0.5 | – | – | – | – | 7.4 | – | – |
| $CH \equiv CCl$ | – | – | – | – | – | – | 1.4–88 | – | – |
| $C_6H_5Cl$ | – | – | – | – | – | – | 1.6–100 | 13 | – |
| п-$C_6H_4Cl_2$ | – | – | – | – | – | – | – | 7.3 | – |
| $CH_2 = CHCl$ | – | – | – | – | – | 18.6 | 0.44–28 | – | 0.007 |
| $CH_3CClF_2$ | 0.065 | 0.05 | – | – | – | 390 | – | – | – |
| $CF_2Cl_2$ | 0.9 | 0.19 | – | – | 75 | 0.1 | 2.1 | – | – |
| $CFCl_3$ | 1.0 | 0.13 | – | – | 327 | 306 | 4.0 | 8.6 | – |
| $CH_3Br$ | 0.57 | 0.2 | – | 615 | – | – | 12.1 | 1.0 | 0.72 |
| $CH_2Br_2$ | – | 0.04 | – | – | – | – | 0.7–46 | – | – |
| $CHBr_3$ | – | 0.2 | – | – | – | – | 0.3 | – | – |
| $C_2H_5Br$ | – | – | – | – | – | – | – | – | 0.055 |
| $CH_3I$ | – | 2.1 | – | 460 | – | – | 0.6–38 | 1.3 | 1.7 |
| $C_2H_5I$ | – | – | – | – | – | – | – | – | 0.13 |

1 — (Rasmussen et al., 1980); 2 — (Rasmussen et al., 1982); 3 — (Isidorov et al., 1990); 4 — (Wahrenberger, 1997); 5 — (Jordan et al., 2000); 6 — (Schwandner et al., 2004); 7 — (Frische et al., 2006).

* Data from (Schwandner et al., 2004) based on average $CO_2$ volcanic emission (78 Tg $yr^{-1}$); Tg = $10^{12}$ g.

thermodynamic equilibrium calculations (Wahrenberger, 1997). The difference between the concentration of HCs detected in volcanic gases and their fugacity, calculated under the assumption of thermodynamic equilibrium is 5 ÷ 25 orders of magnitude. Therefore, in Rasmussen et al. (1980), high concentrations of $CH_3Cl$ found in volcanic gas during the Kilauea eruption were explained by its formation during the biomass burning on the volcano slopes.

It is generally believed that hydrocarbons are not formed at great depths in the Earth's mantle. As the compounds are not thermally stable, they should quickly decompose at temperatures of hot lava (1000–1300 °C). Indeed, our kinetic calculations indicate a very short atmospheric lifetime of the hydrocarbons ($CH_4$: 159 ÷ 0.14 s, $C_2H_6$: $0.02 \div 3.1 \times 10^{-5}$ s, n-$C_3H_8$: $2.1 \times 10^{-4} \div 4.3 \times 10^{-7}$ s) and HCs ($CHCl_3$: $3.1 \times 10^{-4} \div 8.9 \times 10^{-6}$ s, $C_2H_5Cl$: $7.1 \times 10^{-5} \div 8.0 \times 10^{-7}$ s, $CH_3Br$: $0.01 \div 7.0 \times 10^{-5}$ s, $CH_3I$: $5.0 \times 10^{-5} \div 8.5 \times 10^{-7}$ s) in the temperature range. In addition, at such high temperatures, water decomposes to form highly reactive H· and ·OH. The ·OH radical easily oxidizes hydrocarbons up to $CO_2$. As our calculations show, the atmospheric lifetime of $CH_4$, $C_2H_6$, and n-$C_3H_8$ in the reaction with ·OH radical (mixing ratio of 10 ppmv) are 5, 0.9, and 0.6 s, respectively, at 1000 °C.

The primary organic precursor in the formation of the HCs can be methane, produced by the interaction of subvolcanic fluids with organic matter of sedimentary rocks or formed in the hydrothermal system by the catalytic Sabatier reaction: $CO_2 + 4H_2 = CH_4 + 2H_2O$.

With decreasing temperature and under high pressure in the hydrothermal system, the equilibrium of this reaction shifts to the right. In contrast, as the magma temperature rises, it shifts to the left. The latter explains the fact that only a small amount of methane is in equilibrium at magma temperature. The fact that the source of methane is sedimentary rocks is confirmed by the high negative values of $\delta^{13}C$ (−25 ‰) ÷ (−40 ‰) obtained for volcanogenic methane in (Symonds et al., 2003), exceeding the (−15 ‰) ÷ (−20 ‰) range characteristic of the carbon of mantle origin.

The main sources of halogens in volcanic gases are hydrogen halides HX (X = F, Cl, Br, and I). When fluid is released from rising magma, chlorine, bromine, and iodine are largely redistributed between the fluid and magma. The reason for this redistribution is an increase in the ionic radius upon transition from $F^-$ to $I^-$, which prevents the penetration of the ions into most minerals. The relative halogen content in high-temperature magmatic fluids is a function of their concentration in the molten magma and the fluid/melt partition coefficient. The partition coefficients for the albite melt are 8.1, 17.5, and 104 for Cl, Br, and I, respectively (Bureau et al., 2000). This indicates that Cl, Br, and I entering the magmatic system should emit into the atmosphere during magma degassing at shallow depths. Strong enrichment of the halides in the fluid phase promotes the formation of hydrogen halides at the shallow depths.

In Frische et al. (2006), the following mechanism was proposed for the formation of HCs from $CH_4$ and $C_2H_6$, which are formed upon decomposition of organic matter at shallow depths in volcanic and hydrothermal systems. In the reaction cycles, the hydrocarbons can react with the Cl·, Br· and I· species generated upon degassing of magma at shallow depths (Lee et al., 2005):

$$X\cdot + CH_4 \rightarrow CH_3\cdot + HX \ (X = Cl,\ Br,\ I)$$
$$CH_3\cdot + \cdot X \rightarrow CH_3X$$
$$X\cdot + C_2H_6 \rightarrow C_2H_5\cdot + HX$$
$$C_2H_5\cdot + \cdot X \rightarrow C_2H_5X$$
$$CH_3X + \cdot X \rightarrow CH_2X\cdot + HX$$
$$CH_2X\cdot + \cdot X \rightarrow CH_2X_2$$
$$CH_2X_2 + \cdot X \rightarrow CHX_2\cdot + HX$$
$$CHX_2\cdot + \cdot X \rightarrow CHX_3$$
$$CHX_3 + \cdot X \rightarrow CX_3\cdot + HX$$
$$CX_3\cdot + \cdot X \rightarrow CX_4$$

It should be noted that the recombination reactions ($CH_3\cdot$ + ·X, etc.), proposed in Frische et al. (2006) as the main routes for the HCs formation, in the theory of free radical-chain reactions are a rather exotic cross-recombination of two different free radicals, leading to chain termination. The reactions are possible only under strong concentration and kinetic restrictions, and they cannot be the main routes for the HCs formation.

Obviously, any proposed reaction scheme should explain the distribution of the products of methane and ethane halogenation (Schwandner et al., 2004; Frische et al., 2006). Thus, the molar ratios of $CH_3I$ : $CH_3Br$ : $CH_3Cl$ are 1 : 0.6:59 in fumarolic and 1 : 2 : 37 in diffusion gases (Schwandner et al., 2004), 1 : 1.3 : 5 and 1 : 0.7 : 13 in gases from fumaroles F2 and F3 (Frische et al., 2006). The molar ratios of $CH_3CH_2I$ : $CH_3CH_2Br$ : $CH_3CH_2Cl$ in fumarolic gases from F2 and F3 are 1.0 : 1.1 : 7.6 and 1 : 0.7 : 9 (Frische et al., 2006). The molar ratios $CCl_4$ : $CHCl_3$ : $CH_2Cl_2$ : $CH_3Cl$ in the gases are 1 : 27 : 4 : 43, 1 : 29 : 8 : 2, 1 : 1.2 : 2.8 : 194, 1 : 44 : 49 : $2.0 \times 10^4$. As the ratio between the halogens concentrations in Etna's volcanic

**Table 2.** Enthalpies ($\Delta H^0_{298\ K}$, kJ mole$^{-1}$) and rate coefficients of gas-phase reactions ($k_2$, cm$^3$ molecule$^{-1}$ s$^{-1}$) at 300 °C

| No. | Reaction | X = Cl | | X = Br | | X = I | |
|---|---|---|---|---|---|---|---|
| | | $\Delta H^0$ | $k_2$ | $\Delta H^0$ | $k_2$ | $\Delta H^0$ | $k_2$ |
| r1 | $HX + OH \rightarrow X + H_2O$ | –67.4 | $1.3 \cdot 10^{-12}$ | –136.8 | $4.0 \cdot 10^{-12}$ | –200.8 | $3.2 \cdot 10^{-11}$ |
| r2 | $HX + O_2 \rightarrow X + HO_2$ | 234.1 | — | 95.8 | — | 100.8 | $<1.0 \cdot 10^{-11}$ |
| r3 | $X + O_2 \rightarrow XO + O$ (I) | 229.5 | $9.8 \cdot 10^{-10}$ | 262.8 | — | 287.4 | — |
| | $+ M \rightarrow M + XO_2$ (II)$^{(b)}$ | –23.8 | $1.0 \cdot 10^{-33}$ | –4.0 | | –10.3 | — |
| r4 | $X + O_3 \rightarrow XO + O_2$ | –163 | $2.0 \cdot 10^{-11}$ | –128.4 | $4.0 \cdot 10^{-12}$ | –85.4 | $5.0 \cdot 10^{-12}$ |
| r5 | $XO + HO_2 \rightarrow HOX + O_2$ | –213.8 | $4.0 \cdot 10^{-12}$ | –225.1 | $1.7 \cdot 10^{-11}$ | –271.1 | $4.4 \cdot 10^{-11}$ |
| r6 | $X + HO_2 \rightarrow HX + O_2$ | –234.3 | $2.4 \cdot 10^{-11}$ | –164.9 | $5.3 \cdot 10^{-12}$ | –153.6 | — |
| r7 | $HOX + HX \rightarrow X_2 + H_2O$ | –57.7 | — | –97.1 | — | –117.2 | — |
| r8 | $X_2 \rightarrow 2X$ $^{(a)}$ | 242.7 | $2.0 \cdot 10^{-9}$ | 190.0 | $5.4 \cdot 10^{-4}$ | 148.5 | 10.1 |
| r9 | $CH_4 + X \rightarrow CH_3 + HX$ | 3.3 | $1.5 \cdot 10^{-12}$ | 72.8 | $9.1 \cdot 10^{-18}$ | 136.8 | $7.7 \cdot 10^{-23}$ |
| r10 | $CH_3 + X_2 \rightarrow CH_3X + X$ | –100.8 | $1.8 \cdot 10^{-12}$ | –101.7 | $6.2 \cdot 10^{-12}$ | –85.4 | $4.4 \cdot 10^{-12}$ |
| r11 | $CH_3 + X \rightarrow CH_3X$ (298 K) | –343.5 | $2.6 \cdot 10^{-10}$ | –291.6 | $1.2 \cdot 10^{-10}$ | –234.3 | $1.0 \cdot 10^{-11}$ |
| r12 | $CH_3 + HX \rightarrow CH_4 + X$ (I) | –3.3 | — | –72.8 | $2.0 \cdot 10^{-12}$ | –136.8 | $5.0 \cdot 10^{-12}$ |
| | $\rightarrow CH_3X + H$ (II) | 81.6 | $6.3 \cdot 10^{-16}$ | 1.7 | — | 63.2 | — |
| r13 | $CH_3X + OH \rightarrow CH_2X + H_2O$ | –73.6 | $2.7 \cdot 10^{-13}$ | –80.3 | $2.4 \cdot 10^{-13}$ | –64.9 | $4.3 \cdot 10^{-13}$ |
| r14 | $CH_3Cl + X \rightarrow CH_2Cl + HX$ | –5.9 | $3.2 \cdot 10^{-12}$ | 132.2 | $2.5 \cdot 10^{-16}$ | 127.2 | — |
| r15 | $CH_2X + HX \rightarrow CH_3X + X$ (I) | 6.3 | $1.0 \cdot 10^{-14}$ | –125.5 | $4.4 \cdot 10^{-13}$ | –136.0 | — |
| | $\rightarrow CH_2X_2 + H$ (II) | 93.7 | | 14.2 | — | 79.1 | — |
| r16 | $CH_2X + O_2 \rightarrow CH_2O + XO$ | –135.6 | $1.8 \cdot 10^{-12}$ | –153.6 | $4.9 \cdot 10^{-12}$ | –200.8 | $5.1 \cdot 10^{-13}$ |
| r17 | $2CH_2X \rightarrow CH_3X + HX$ | –421.3 | $>1 \cdot 10^{-10}$ | –327.6 | — | –419.9 | — |
| r18 | $CH_3X + Cl \rightarrow CH_3Cl + X$ | 0 | — | –58.3 | $2.0 \cdot 10^{-15}$ | –114.9 | $5.1 \cdot 10^{-11}$ |
| r19 | $CH_3X \rightarrow CH_3 + X^{(a)}$ | 343.5 | — | 291.6 | $5.4 \cdot 10^{-13}$ | 234.3 | $6.4 \cdot 10^{-8}$ |
| r20 | $2X + M \rightarrow M + X_2^{(b)(c)}$ | –242.7 | $1.5 \cdot 10^{-32}$ | –190.0 | $2.3 \cdot 10^{-32}$ | –148.5 | $1.2 \cdot 10^{-31}$ |
| r21 | $CH_3 + CH_2X \rightarrow C_2H_5X$ | –375.3 | $8.3 \cdot 10^{-11}$ | –369.4 | — | –380.7 | $5.2 \cdot 10^{-11}$ |
| r22 | $X + C_2H_6 \rightarrow C_2H_5 + HX$ | –21.3 | $6.3 \cdot 10^{-11}$ | 47.7 | $3.2 \cdot 10^{-15}$ | 112.1 | $2.0 \cdot 10^{-20}$ |
| r23 | $C_2H_5 + X_2 \rightarrow C_2H_5X + X$ | –98.3 | — | –92.9 | — | –74.1 | — |
| r24 | $CH_3C(O)CH_3 + HOX \rightarrow$ $\rightarrow CH_3COOH + CH_3X$ | –220.2 | — | –195.4 | — | –238.7 | — |

(a) Rate coefficient of first-order reaction, $k_1$ has dimensionality s$^{-1}$.

(b) Rate coefficient of third-order reaction, $k_3$ has dimensionality cm$^6$ molecule$^{-2}$ s$^{-1}$.

(c) The log $A$ estimated from the relationship: $\log A = 16.3 - 0.012 \cdot E_{A}$, where $A$ is the pre-exponential factor. M = $Cl_2$, $Br_2$, and $I_2$, respectively.

gases is I : Br : Cl = 1 : 60 : 6.0 × $10^4$ (Aiuppa et al., 2005), the iodine concentrations in volcanic gases (Schwandner et al., 2004; Frische et al., 2006) are abnormally high.

To verify the scheme in Frische et al. (2006), we calculated the enthalpies of possible reactions of the halogen compounds in the volcanic column using the standard enthalpies of atoms, free radicals, and molecules formation (Luo, 2007) as well as their rate coefficients at 300 °C using the activation parameters from Atkinson et al. (2006; 2007; 2008). The results are given in Table 2.

As follows from Table 2, the most efficient way of the X· (X = Cl, Br, I) formation in the volcanic column is the exothermic reaction (r1) of hydrogen halides (HX) with the ·OH radical. From the thermodynamic calculations (Gerlach, 2004; Martin et al., 2006), it follows that ·OH equilibrium concentration can reach 2 ppmv in magmatic gas and 100 ppmv in a mixture of magmatic gas with 15% air at 1200 °C. A less efficient source of X atoms is the endothermic decomposition of $X_2$ (r8). The $Cl_2$, $Br_2$, and $I_2$ equilibrium concentrations in a mixture of magmatic gas with 10% air at 1000 °C are 0.4 ppmv, 2.5 ppbv, and 0.1 pptv, while the Cl, Br, and I atomic concentrations formed from them are 6.3 ppmv, 4.3 ppmv, and 0.2 ppmv. In the free radical chain halogenation of hydrocarbons, reactions r1 and r8 are chain initiations. Reactions r1, r4–r8 determine the catalytic cycle of ozone depletion in the volcanic column, and all of them, except r8, are characterized by high exothermicity and large rate coefficients.

The main chain growth reactions in Table 2 are r9, r10, and the reverse of r9, reaction r12.I. From thermodynamic calculations and kinetic data, it follows that reaction r9 in the case of methane iodination has a high potential barrier and proceeds at a slow rate. Thus, the scheme proposed in (Frische et al., 2006) does not agree with these data and the low ratios of $CH_3I : CH_3Br : CH_3Cl$ and $C_2H_5I : C_2H_5Br : C_2H_5Cl$. However, the reaction of $CH_3$· with $I_2$ proceeds even more easily than with $Cl_2$. Therefore, $I_2$ (and probably, $Br_2$) in the volcanic column will act as a sink for the $CH_3$· radicals and reduce the chain length of methane chlorination. In addition, the sources of halogen atoms are most likely to be thermal dissociation of hydrogen halides, their oxidation by oxygen, and reactions with ·OH radical.

Given this scheme, we can write the expression for the ratio of free radicals in the stationary state of the chain reactions:

$$\theta = (CH_3/X)_{stat} = k_9\,[CH_4] \,/\, (k_{12}\,[HX] + k_{10}\,[X_2]). \quad (1)$$

When substituting in Eq. 1 the concentrations of $X_2$ and HX from Martin et al. (2006) (the ratio of atmospheric and magmatic fluids is equal of 0.1; $T$ = 1000 °C), as well as the rate coefficients from Table 2, we obtain the ratio of θ for chlorination, bromination, and iodination as 1 : 0.0024 : 0.00013. The low relative concentrations of methyl radicals in methane bromination and iodination are primarily associated with much lower $k_9$ than the chlorination $k_9$. However, compounds of chlorine, bromine, and iodine are present simultaneously in the volcanic column. Therefore, the θ for the bromination and iodination in the volcanic column will depend only on the products of $k_{10}$ × $[X_2]$ and the products of $k_9$ × $[CH_4]$, $k_{12}$ × [HCl] for chlorination. Indeed, substitution into Eq.1 of the $k_9$ × $[CH_4]$ and $k_{12}$ × [HCl] for the chlorination and $k_{10}$ × $[X_2]$ for the corresponding halogenation leads to almost the same θ (1.875 for X = Cl, Br and I; $[CH_4]_0$ = 2.5 × $10^{17}$ molecules $cm^{-3}$). Simultaneously with an increase in θ (rise of $CH_3$· concentration compared with X·), the activation energy of the halogenation decreases, and the reaction rate rises.

If the main reaction of chain termination is the quadratic recombination of X· atoms, then the chain length ($F$) of the methane halogenation is equal to the ratio of the concentration of the $CH_3X$ formed to the number of radicals formed:

$$F = k_9\,[CH_4] \,/\, (2[M](k_8\,k_{20}\,[X_2])^{1/2}). \quad (2)$$

When substituting in the Eq. 2 the concentrations of $X_2$ from Martin et al. (2006) and the rate coefficients from Table 2, with $[CH_4]$ / [M] = 10, we obtain the chain length $F$ = 433 (X = Cl), $F$ = 5 × $10^{-5}$ (X = Br) and $F$ = 21 × $10^{-10}$ (X = I). Obviously, the bromination and iodination of methane under such a mechanism is impossible. If we assume the simultaneous existence in the volcanic column of chlorine, bromine, and iodine compounds and the predominant formation of methyl radical in the reaction of a chlorine atom with methane, then the calculation leads to the same value of $F = 433$ for X = Cl, Br and I. Therefore, bromine chemistry operates in synergy with iodine and chlorine chemistry to increase the halogenation rate.

The most effective chain termination reaction may be the reaction of methyl radicals with oxygen: $CH_3\cdot + O_2 + M \rightarrow CH_3O_2\cdot + M$ ($k_{25}$) with rate coefficients $k_0$ (300 °C) = $6.5 \times 10^{-32}$ cm$^6$ molecules$^{-2}$ s$^{-1}$ at low pressures and $k_\infty$ (300 °C) = $6.0 \times 10^{-13}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ at high pressures. Then, the ratio of the concentrations of the methyl halides is equal to the ratio of the reaction rates of r10 chain growth

$$[CH_3Cl] : [CH_3Br] : [CH_3I] = k_{10}\,[CH_3]\,[Cl_2] : k_{10}\,[CH_3]\,[Br_2] : k_{10}\,[CH_3]\,[I_2], \tag{3}$$

$$[CH_3] = \frac{\acute{\omega}_i}{k_{10}\,[Br_2] + k_{10}\,[I_2] + k_{25}\,[O_2]\,[M]}. \tag{4}$$

Here $\acute{\omega}_i$ is the chain initiation rate (for example, the sum of reactions r1 and r8). The ratio between the halogen concentrations in volcanic gases is I : Br : Cl = 1 : 60 : $6.0 \times 10^4$ (Aiuppa et al., 2005). Taking into account the rate coefficients $k_{10}$, the ratio of $[CH_3I] : [CH_3Br] : [CH_3Cl]$ is 1.0 : 84 : $2.5 \times 10^4$. The ratio far exceeds those in the fumarolic gases (Schwandner et al., 2004; Frische et al., 2006). One possible explanation for the low $[CH_3I] : [CH_3Br] : [CH_3Cl]$ ratio (Schwandner et al., 2004; Frische et al., 2006) could be an effective reaction for termination of the methane chlorination chains in the reaction of r11 for Br and I atoms. The source of a high atoms concentration can be reactions r1 and r8, which are more favorable in the case of I and Br than for Cl atoms. Calculating the relative concentration of halogen atoms formed under equilibrium by reaction r8 at $T = 300$ °C leads to the ratio Cl : Br : I as 1 : 168 : 13720.

The various ratios of polychloromethanes, $CCl_4 : CHCl_3 : CH_2Cl_2 : CH_3Cl$ in gases of different volcanoes obtained in Frische et al. (2006), Jordan et al. (2000), Schwandner et al. (2004) can be explained as follows. Suppose that the initiation of chains of the methane chlorination occurs in reactions r1 and r8 at a rate of $\acute{\omega}_i$, and chain termination occurs mainly in reactions r3.II and r20 at a rate of $\acute{\omega}_t$. The rate coefficients of the chlorine atom reactions with $CH_4$, $CH_3Cl$, $CH_2Cl_2$, and $CHCl_3$ to form methyl and corresponding polychloromethyl radicals are within narrow limits $k_9 = (1.3 \div 3.5) \times 10^{-2}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, (Atkinson et al., 2007; 2008) and in a first approximation, they can be considered the same. Then the methane sequential chlorination scheme is reduced to a simple sequence of first-order reactions with the same pseudo-constant $k' = k_9 \times \acute{\omega}_i / \acute{\omega}_t$, and the system of coupled linear differential equations for this kinetic scheme has a simple analytical solution:

$$\frac{C_{t(i)}}{C_{1(0)}} = \frac{(k' \times t)^{i-1}}{(i-1)!} \exp(-k' \times t), \tag{5}$$

where $t$ is the reaction time, $i = 1$ – $CH_4$, 2 – $CH_3Cl$, 3 – $CH_2Cl_2$, 4 – $CHCl_3$, 5 – $CCl_4$, $C_{t(i)}$ is the current concentration of methane or the corresponding polychloromethane, and $C_{1(0)}$ is the initial concentration of methane at $t = 0$.

Figure 1 shows the calculated dependencies of the relative concentration of methane and polychloromethanes during the radical chain chlorination of methane on the product $k' \times t$. The same parameter could be calculated using Eq.5 based on the experimental ratios $CCl_4 : CHCl_3$, $CCl_4 : CH_2Cl_2$, and $CCl_4 : CH_3Cl$ in the volcanic gases (Jordan et al., 2000; Schwandner et al., 2004; Frische et al., 2006). Figure 1 shows lines parallel to the $C_{t(i)} / C_{1(0)}$ axis with coordinates corresponding to the calculated average $k' \times t$ products following data from Jordan et al. (2000), Schwandner et al. (2004), Frische et al. (2006). They lie in a fairly narrow range from 0.2 to 3.3. The minimum of the $k' \times t$ products corresponds to high relative concentrations of $CH_3Cl$ in the volcanic gas, while the maximum values of the parameter are characteristic of high relative concentrations of $CCl_4$ and $CHCl_3$. Obviously, the $k' \times t$ product depends on temperature, total pressure, composition, partial pressure of the reactants, and the volcanic column depth.

Although the considered scheme is too simplified and does not take into account many other cross-reactions of polychloromethyl radicals with polychloromethanes or with HCl, HBr, and HI, it can satisfactorily explain the various concentration ratios of polychloromethanes, halomethanes, and haloethanes in volcanic gases (Jordan et al., 2000; Schwandner et al., 2004; Frische et al., 2006).

Table 2 also shows the calculated enthalpies of haloform reactions for the HCs formation (r24). Although these reactions usually proceed in the liquid phase in an alkaline medium (Carpenter et al., 2005), the calculation shows that is very energetically favorable in the gas phase and may be an alternative to the proposed free radical-chain scheme. The heterogeneous catalytic formation of the HCs in a volcanic column during the interaction of hydrocarbons with hydrogen halides, mentioned in Isidorov et al. (1990), Jordan et al. (2000), cannot be ruled out as well. The catalysts for this process can be aluminosilicates, metal oxides, and transition metal halides in the volcanic rocks.

In (Isidorov et al., 1990; Jordan et al., 2000), the main pathway for the formation of Freon 11 is the heterogeneous catalytic reaction of $CCl_4$ with HF. As follows from the concentrations of HCs in the volcanic gases (Isidorov et al., 1990; Wahrenberger, 1997; Jordan et al., 2000; Schwandner et al., 2004; Frische et al., 2006), $CCl_4$ concentrations are much lower than other polychloromethanes. Therefore, the following reaction in a heterogeneous system can be a more suitable way of $CCl_4$ and freons 11 and 12 formation: $4CH_4 + 16Cl_2 + 4HF \rightarrow 2CFCl_3 + CF_2Cl_2 + CCl_4 + 20HCl$.

## 2.3 The impact of HCs volcanic emission on their airborne firn and ice core content in Antarctica

The stratovolcano Mt. Erebus (77°33′ S, 167°10′ E, 3794 m above sea level) is the most southern active volcano globally and is currently the most active volcano in Antarctica. It became a passively degassing volcano after 1841, and even much earlier (Kyle et al., 1982). Continuous passive emission of gases, liquid, and solid aerosols from Mt. Erebus considerably influence the content of different metals and inorganic ions in the Antarctic snow and ice samples (Zreda-Gostynska et al., 1997). Here we examine possible effects of volcanic emission of the HCs, in particular, freon-11, on its content in the air from Antarctic firn and ice cores. The average $SO_2$ emission from Mt. Erebus equals 25.9±7.3 Gg $yr^{-1}$ (Zreda-Gostynska et al., 1997). Because global volcanic emission of the $SO_2$ ranges from 14 to 19 Tg $yr^{-1}$, then the contribution of Mt. Erebus to global $SO_2$ emission is negligible (0.16 %). The highest possible freon-11 emission from Mt. Erebus does not exceed 0.5 t $yr^{-1}$. Emissions of $CH_3Cl$, $CH_2Cl_2$, and $CH_3I$ are close to the estimation.

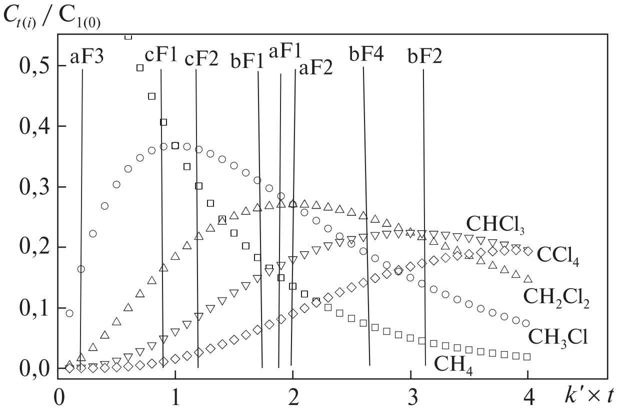

**Figure 1.** Dependence of relative concentration of methane and polychloromethanes during the radical chain chlorination of methane on the product $k' \times t$ (Eq. 5). The coordinates of lines parallel to the $C_i / C_{10}$ on the $Y$-axis correspond to the calculated $k' \times t$ products on $X$-axis in accordance with analytical data for the fumaroles (F) from a: (Frische et al., 2006); b: (Jordan et al., 2000); and c: (Schwandner et al., 2004)

To calculate the budget of trace gases over Antarctica, we employ a simple block model in which the Antarctic atmosphere is defined as a rectangular block with a square base with area $A = 14 \times 10^6$ km$^2$ (~3700 km × 3700 km) and height $h = 5$ km (Zreda-Gostynska et al., 1997). The current global emission of freon-11 is 0.13 Tg $yr^{-1}$. Its average concentration in the Antarctic atmosphere is 0.29 ppbv or 1.66 μg $m^{-3}$. The contribution ($Q$) of the freon to the atmosphere over Antarctica can be estimated as

$$Q = C_A v_w A_c, \quad (6)$$

where $C_A$ is the gas concentration in the air, $v_w$ is the average wind speed (5 m $s^{-1}$), $A_c$ is the vertical area of the Antarctic atmosphere (3700 km × 5 km).

The estimation shows that up to 4.8 Tg yr$^{-1}$ of freon-11 can be "pumped" through the Antarctic atmosphere. Thus, the contribution of possible emission of freon-11 from Mt. Erebus is 7 orders of magnitude lower than its global contribution to the Antarctic atmosphere, and it cannot significantly affect its concentrations in air of firn and ice cores. The results of glaciochemical studies (Butler et al., 1999; Bogillo et al., 2003) confirm this conclusion.

As the volcanic emission of $SO_2$ accounts for up to 14% of its total emission from anthropogenic and natural sources, the molar ratio of the test gas to $SO_2$ ($SO_2 + SO_4^{2-}$) in volcanic gas and the global volcanic emission of $SO_2$ (average, 14.6 Tg yr$^{-1}$ (Aiuppa et al., 2005)) are commonly used to estimate the global volcanic emission of a test gas. This approach was applied both here and in Rasmussen et al. (1980; 1982), Isidorov et al. (1990), Wahrenberger (1997), Jordan et al. (2000), Frische et al. (2006) to estimate the global volcanic emission of HCs. These estimates show that the volcanic emission of HCs is negligible compared to their emission from known natural and anthropogenic sources.

However, during the powerful explosive volcanic eruptions, the emission of the compounds, especially directly into the stratosphere, should increase significantly. The consequence of such eruptions is the deposition of $nssSO_4^{2-}$ (ions of non-sea salts) and volcanic tephra on the snowpack surface of Antarctica and Greenland and the further formation of acidic layers in the ice with a high content of tephra, $nssSO_4^{2-}$ ions, and elevated electrical conductivity. Thus, to understand the scale of HCs emission from past volcanic eruptions in the Southern Hemisphere, it is necessary to consider the data on the content of $nssSO_4^{2-}$ ions in the snowpack and ice cores in Antarctica ice and to estimate the $nssSO_4^{2-}$ fluxes.

Measurement of sulfate ions along the profile of a 200-meter ice core (Pole of Relative Inaccessibility, Plateau Remote, 84° S, 43° E, 3330 m above sea level) revealed the signals of 54 eruptions of explosive volcanoes that occurred in the Southern Hemisphere over the past 4100 years until 1986 (Cole-Dai et al., 2000). For 14 of them, the calculated sulfate deposition fluxes on the Antarctic snow surface ($F_S$, in kg km$^{-2}$) turned out to be comparable, or higher than for Tambora volcano eruption, Indonesia in 1815 (volcanic explosivity index, VEI) 7 ($F_S$ = 22.4 kg km$^{-2}$). Such eruptions include Kuwae volcano (Hawaiian Isls) in 1454 ($F_S$ = 133.4 kg km$^{-2}$), an unknown volcano in 1277 ($F_S$ = 55.4 kg km$^{-2}$), of El Chichon volcano, Mexico in 1259 ($F_S$ = 46.3 kg km$^{-2}$), unknown volcanoes in 1234 ($F_S$ = 31.2 kg km$^{-2}$) and 742 ($F_S$ = 45.0 kg km$^{-2}$), as well as Taupo volcano, New Zealand in 186 ($F_S$ = 69.4 kg km$^{-2}$).

In Castellano et al. (2005), the $F_S$ value for the Tambora volcano eruption is 39.3 kg km$^{-2}$, and for Kuwae it is 31.7 kg km$^{-2}$ (the ice core EDC96 at Dome C, 75°06′ S, 123°24′ E, 3233 m above sea level). Higher $F_S$ values are characterized by eruptions in 1255–1259, possibly of El Chichon volcano, Mexico ($F_S$ = = 60.4 kg km$^{-2}$) and unknown volcanoes in 4523 and 5538 B.C.E. ($F_S$ = 61.5 and 52.5 kg km$^{-2}$, respectively).

In Kurbatov et al. (2006), a chronology of powerful volcanic eruptions and the magnitude of the fluxes formed (the SDMA ice core from the Siple Dome, 81°39.53′ S, 148°48.72′ W, 621 m above sea level) is different from that considered in Cole-Dai et al. (2000), Castellano et al. (2005). So, traces of the Tambora volcano eruption were not observed in this core, but the range of $F_S$ = 18–21 kg km$^{-2}$ was estimated for the Kuwae volcano eruption. However, the sulfate layers for numerous volcanic eruptions in the Antarctic volcanic belt, the South Shetland and South Sandwich Islands were found in the core, such as of Bristol volcano in 1936 ($F_S$ = 5 kg km$^{-2}$), Deception volcano in 1871 ($F_S$ = 8–11 kg km$^{-2}$), Buckle volcano in 1839 ($F_S$ = 9–10 kg km$^{-2}$) and in 1809 ($F_S$ = 19–26 kg km$^{-2}$). The maximum sulfate deposition fluxes were noted for the eruption of Mt. Melbourne volcano in 1262 ($F_S$ = 32–39 kg km$^{-2}$).

Tephra fingerprinting identified sources of tephra particles contributed by previously unknown Holocene eruptions of Mt. Melbourne, the Pleiades, Balenny Isl., Mt. Berlin, Mt. Melbourne, and Mt. Takahe volcanic centers (Antarctica). From the 35 volcanic events detected in the SDMA ice core in the time interval 0–2000 B.C.E., only four events contained tephra particles, and these were found in 1334, 1783, 1805, and 1815 B.C.E. One tephra layer is geochemically close to the volcanic rocks of the Takahe volcano. Ten volcanic signals, including a single tephra horizon geochemically similar to the tephra layer collected near Mt. Berlin, were found in the interval 2001—4000 B.C.E. Two visible tephra layers (6217 and 6231 B.C.E.) correlate with episodes of known volcanic activity of Mt. Takahe. The 756 B.C.E. tephra layer is chemically similar to tephra derived from Mt. Berlin. The tephra layer from 9346 B.C.E. is similar to the tephra composition at 7756 B.C.E., also derived from Mt. Berlin.

Obviously, powerful volcanic eruptions at low latitudes and much less powerful local eruptions of the volcanoes in Antarctica or the Sub-Antarctic islands can lead to similar fluxes of $F_S$. Therefore, in Kurbatov et al. (2006), in addition to the nss-$SO_4^{2-}$ ions concentration in SDMA ice core, geochemical analysis of volcanic tephra in the core and a comparison of its elemental and mineralogical composition with possible volcanic sources in Antarctica were also used to identify volcanic sources in South and Central America, New Zealand and Oceania.

We compared the petrological estimates of total $SO_2$ emission during powerful eruptions ($F_V$) of the Pinatubo volcano (1991, 17 Tg), Agung volcano (1963, 9 Tg), Krakatoa volcano (1883, 32 Tg), Tambora volcano (1815, 130 Tg) and Kuwae volcano (1454, 500 Tg) from Graf et al. (1997) with fluxes of sulfate deposition on the snowpack of Antarctica after these eruptions, $F_S$ (Cole-Dai et al., 2000; Castellano et al., 2005; Kurbatov et al., 2006). We found a satisfactory relationship between the $F_S$ values from Cole-Dai et al. (2000) and the $F_V$: $F_V = 7.7 + 3.7 \times F_S$; $N = 4$, $R = 0.993$. With the data from Castellano et al. (2005) and especially from Kurbatov et al. (2006), the $F_V$ values are weakly correlated (the correlation coefficients, $R$ are 0.642; $N = 5$ and 0.464; $N = 3$, respectively). Using the relationship between $F_V$ and $F_S$ as well as $F_S$ fluxes from Cole-Dai et al. (2000), we estimated the $SO_2$ emission from the most powerful volcanic eruptions over the past 4100 years. The estimates range from 91 Tg (Tambora) to 501 Tg (Kuwae).

From the data in Castellano et al. (2005), Kurbatov et al. (2006), it follows that the signals from powerful explosive volcanic eruptions in the ice cores of West and East Antarctica exceed two-fold the signal from the Kuwae volcano eruption. However, this is most likely due to the proximity of these volcanoes to Antarctica compared to Kuwae, Vanuatu. The value of 1000 Tg $SO_2$ can be chosen as an upper limit of the gas emission from powerful eruptions throughout the Holocene. If we assume that such an amount of $SO_2$ was formed during the year of the eruption, then a comparison with the average value of global volcanic emission (14.6 Tg year$^{-1}$) implies that the level of $SO_2$ emission at the most powerful eruption in the Holocene may exceed the average annual level of volcanic emission over 70 times. The highest value of volcanic emission known is $SO_2$ emission during the eruption of Toba volcano (Sumatra Isl.) 75000 years ago — from 70 Tg to 6000 Tg, which corresponds to a maximum 410-fold excess of the average annual volcanic emission. Thus, from the data above, it follows that the maximum possible contribution of volcanic emission in the past could reach up to 40% of the level of current anthropogenic emission and up to 6% of it over the past 12000 years.

However, it should be noted that the lifetime of the HCs in the atmosphere varies from 0.006 ($CH_3I$) to 0.7 ($CH_3Br$), 1.3 ($CH_3Cl$), 50 ($CCl_3F$), and up to 100 yrs ($CCl_2F_2$). Therefore, the most significant change in the atmospheric HCs content during the pre-industrial and industrial periods was contributed by volcanic eruptions over the past 250 years, such as the Pinatubo (1991), Agung (1963), Krakatoa (1883), and Tambora volcanoes (1815). A comparison of the estimates of $SO_2$ emissions from these volcanoes with the emission of HCs from natural and industrial sources shows that the contribution of these volcanogenic HCs could not exceed 1% of their budget from total sources.

## 2.4 The impact of the hydrogen halides' volcanic emission on the stratospheric ozone depletion over the Southern Hemisphere and Antarctica

Explosive volcanic eruptions inject large amounts of sulfur and other aerosols, often including halogens, into the stratosphere, frequently leading to stratospheric ozone depletion even for small eruptions and an increase in UV radiation at Earth's surface. The release of gases ($CO_2$, $SO_2$, HF, HCl, HBr, HI, $H_2O$, etc.) accompanying such great eruptions must have tremendous consequences for the composition of the ocean and atmosphere, with dramatic impact on climate and environment.

Detailed estimates of magmatic degassing were used in Black et al. (2014) to complete the first 3-D global climate modeling of atmospheric chemistry during the eruption of a Large Igneous Province (LIP). The results show that both strongly acidic rain and global ozone collapse are possible transient consequences of volcanism. The thermal metamorphism could result in peak annualized production (over $10^2$ yrs) of 0.87–1.65 Tg $CH_3Cl$ (Aarnes et al., 2011). Methyl chloride fluxes in this range produce steady-state ozone depletion of 60% –70% globally.

Apart from the organic HCs, discussed above, the main inorganic halogen-containing volcanic gases are the hydrogen halides HX (X = Cl, Br and I), which in gas-phase reactions r1 (Table 2, $HX + OH \rightarrow X + H_2O$) release halogen atoms and subsequently deplete the stratospheric ozone (reactions r2). However, significant ozone losses that occur over the Arctic and Antarctic regions result directly from heterogeneous reactions involving inorganic halogens on the surface of cold sulfate-water aerosols (Chartrand et al., 1999):

$$XONO_2 + HX \rightarrow X_2 + HONO_2 \text{ (X = Cl, Br and I)}$$
$$XONO_2 + H_2O \rightarrow HOX + HONO_2$$
$$HOX + HX \rightarrow X_2 + H_2O.$$

These reactions primarily transform inorganic chlorine (principally HCl and $ClONO_2$, which constitute ~97% of available inorganic chlorine) into the rapidly photolyzed intermediates $Cl_2$ and HOCl, followed by reaction of the product Cl atoms with ozone to form the primary catalytically active chlorine oxide radical ClO. Similar heterogeneous reactions are known also for Br- and I-consisting compounds (Chartrand et al., 1999; Gutmann et al., 2018; Gerlach, 2004; Aiuppa et al., 2005; Bureau et al., 2000; Lee et al., 2005).

Antarctica is one of the least volcanically active regions in the world, with the highest number of volcanoes listed as uncertainly active and many others hidden beneath the ice sheet. Antarctica has undergone several phases of volcanism throughout its long history. As a consequence, volcanism was important for the formation of both West and East Antarctica. It was a driver of several global continental and oceanic biotic extinctions during the past 300 Ma and potentially driven Antarctica climatically, both into and out of glacials (Smellie et al., 2021 and references therein).

The Proterozoic and Paleozoic records of Antarctica's volcanism are comparatively poorly known. Gondwana break-up volcanism (at c. 190 Ma) is represented in Antarctica by two major volcanic provinces: a mafic LIP that crops out throughout the Transantarctic Mountains and in Dronning Maud Land, with correlatives in South Africa, Tasmania, Australia, and New Zealand, and the other consisting of a series of felsic flareups that affected the entire Antarctic Peninsula and extended into southern South America (Chon Aike province). The mafic volcanism in Antarctica is known as the Ferrar Supergroup, but representatives in Dronning Maud Land show greater affinities to mafic lavas and sills in the Karoo of South Africa. The mafic LIP had a total volume of more than $0.5 \times 10^6$ km$^3$, but it was emplaced in a very short time (~100 kyrs). By contrast, the felsic Chon Aike province has erupted in three major pulses, individually c. 6–10 Ma in duration, between 189 and 153 Ma.

Over a period in the Cretaceous, Antarctica's magmatism shifted from arc-related to rift-related during the latest stage of Gondwana break-up (c. 90–83 Ma). The presence of relict heat (Mt. Berlin, Mt. Melbourne, and Mt. Rittmann) and abundant englacial and marine tephras sourced in Mt. Takahe, Mt. Berlin, Mt. Waesche, Mt. Rittmann, and the Pleiades indicate that many others were active in recent geological time (<10 kyrs). Subduction is active today only at the northern tip of the Antarctic Peninsula. From c. 12 Ma, an extensive back-arc mafic alkaline volcanic field developed in the James Ross Island region. It is dominated by a very large shield volcano of Mt. Haddington. Several small monogenetic alkaline volcanic fields were constructed from c. 7.5 Ma, mainly along the flanks of the Antarctic Peninsula.

The ice-sheet bed-elevation data were used in (De Vries et al., 2018) to locate individual conical edifices protruding upwards into the ice across West Antarctica. It was proposed that these edifices represent subglacial volcanoes. Of the 138 volcanoes, 91 had not been identified before, and they are especially concentrated and orientated along the >3000 km central axis of the West Antarctic Rift System. The identified cones range in height between 100 and 3850 m, with an average relief of 621 m, including 29 structures >1 km tall, mainly in Marie Byrd Land and the central rift zone. The basal diameter of the cones ranges between 4.5 and 58.5 km, with an average diameter of 21.3 km. Conversely, high regional heat fluxes, geomagnetic anomalies, and evidence of recent subglacial volcanism suggest that the rift is currently active. The largely uneroded nature of the cones indicates that many may be of Pleistocene age or younger.

LIP eruptions are implicated in environmental and climatic changes, including global warming, ozone layer depletion, acid rains, oceanic anoxia and/or increased oceanic fertilization, calcification crises, mass extinction, and potentially the release of gas hydrates. Every 1 $km^3$ of basaltic magma emplaced during a subaerial LIP eruption releases ~3.5–6.5 Tg $SO_2$ and estimates for entire LIPs yield $3.5–68 \times 10^6$ Tg $SO_2$ (Mather, 2015).

The volume of the combined Karoo-Ferrar province ($\sim 2.5 \times 10^6$ $km^3$) makes it one of the largest continental flood basalt events in the world (Storey et al., 2013). The timing of this event correlates with a moderate mass extinction (Toarcian-Aalenian), affecting primarily marine invertebrates. Mercury (Hg) was emitted to the atmosphere as a trace constituent of volcanic gas and distributed globally before being deposited in sediments. Percival et al., 2015, explore the use of Hg in sediments as a possible direct link between the Karoo-Ferrar LIP and the coeval Toarcian Oceanic Anoxic Events (T-OAE). It was suggested that extrusive igneous activity caused increased Hg flux to the Early Toarcian sedimentary realm, supporting the Hg potential as a proxy for ancient volcanism. The interpretation is consistent with a relationship between LIP formation and a perturbed carbon cycle during the Pliensbachian-Toarcian transition and T-OAE. The recording of these two distinct Hg excursions may also indicate that the Karoo-Ferrar LIP released volatiles in temporally distinct episodes due either to multiple phases of magmatic emplacement or sporadic release of thermogenic gaseous products from the intrusion of igneous material into volatile-rich lithologies.

Combined analysis of available geochronologic, paleomagnetic, and geochemical data from the entire Karoo-Ferrar LIP allows an improved reconstruction of its eruptive history (Moulin et al., 2017). This emplacement chronology is in good agreement with the discontinuous rhythm of environmental and biotic perturbations during the late Pliensbachian-Toarcian interval. Pulsed emissions of volcanic gases could have been the main trigger of the multiple phases of extinction. The ensemble of available data is consistent with a scenario in which the two main phases of extinction at the Pliensbachian-Toarcian boundary and Tenuicostatum/Falciferum zone boundary corresponded to the largest pulse (Phase 2, 183 Ma) of volcanism, and possibly lasted a short time, on the order of 100 kyrs or less.

A relationship between the column ozone percentage change against the injected Equivalent Effective Stratospheric Chlorine (EESC) (EESC = [Cl] + 60 [Br] + 300[I]) from Staunton-Sykes et al. (2021) and a number of previous studies (Brenna et al., 2019; 2020) is available:

$$\Delta\%O_3 = -16{,}3\ln(\mathrm{EESC}) - 5{,}3, \qquad (7)$$

where $\Delta\%O_3$ is the column ozone percentage change and EESC is the Equivalent Effective Stratospheric Chlorine (in Tg).

Crude estimations of $\Delta\%O_3$ value changes after Ferrar LIP eruptions can be performed following Eq. 7, taking into consideration the whole Ferrar LIP volume of basaltic lavas in Antarctica ($0.5 \times 10^6$ $km^3$; Smellie et al., 2021), time of the largest pulse of volcanism (~100 kyrs; Moulin et al., 2017), the release of the $SO_2$ during a subaerial LIP eruption (~3.5 – 6.5 Tg $km^{-3}$; Mather, 2015), mean Cl/S ratio for HCl emission from the Erebus volcano (0.7; Zreda-Gostynska et al., 1997), mean Br/S and I/S ratios in volcanic gases (0.05 and 0.00002, respectively; Gutmann et al., 2018), percent for release of HCl and other hydrogen halides to the stratosphere (25%; Textor et al.,

2003) and 10 yrs mean each eruption duration: the $\Delta\%O_3$ changes range from −49 to −83%. Ozone depletion on this scale (quadratic dependence of UV-B % on the $\Delta\%O_3$; Madronich et al., 1998) would dramatically increase the flux of harmful UV-B radiation to the surface, which could cause DNA damage of animals and plants in ancient Antarctica (part of the Gondwana).

The estimations under the above assumptions and petrological estimates of the $SO_2$ volcanic emission from Graf et al. (1997) lead to the $\Delta\%O_3$ changes as −7% (Agung), −28% (Krakatoa), −51% (Tambora), −73% (Kuwae) and over −100% (Toba). The high limit for the use of Eq. 7 is EESC = 640 Tg when $\Delta\%O_3$ >100%, and the lower limit is 1.38 Tg (taking into consideration the constant term in the Eq. 7 (−5.3)) when $\Delta\%O_3 = 0$. Of course, there are limitations to the empirical relationship.

Assuming the same conditions, mean volcanic flux from Tambora eruption (28.1 Tg S; Toohey & Sigl, 2017), by using the ratio of $SO_4^{2-}$ deposition fluxes in Antarctic ice cores between a volcano and Tambora, we can estimate the $\Delta\%O_3$ changes after volcanic eruptions in the tropical belt and Southern Hemisphere, using the glaciochemical data from Ren et al. (2010), Plummer et al. (2012), Sigl et al. (2013; 2015), Osipov et al. (2014). Results of the estimates are presented in Table 3.

As it is shown, the estimates lead to more than 50% depletion of stratospheric ozone after powerful volcanic eruptions with high VEI values (Huaynapu-

**Table 3.** Changes in stratospheric ozone content after volcanic eruptions

| Eruption | Region | Year | VEI | $\Delta\%O_3$ after volcanic eruptions | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | a | b | c | d | e | f |
| Agung | Indonesia | 1963 | | | −15 | −16 | | −14 | −35 |
| Tarawera | New Zealand | 1887 | | | | | | −10 | |
| Krakatoa | Indonesia | 1884 | 6 | | −9 | −5 | | −23 | −34 |
| Cosiguina | Nicaragua | 1835 | 5 | | −14 | −14 | | −12 | |
| Galunggung | Indonesia | 1823 | | | | | | −6 | |
| Tambora | Indonesia | 1815 | 7 | −43 | | | | | |
| Gamkonora | Indonesia | 1674 | 5 | | −9 | | | −20 | |
| Long Island | New Guinea | 1660 | | | | | | | −19 |
| Parker Peak | Philippines | 1642 | 5 | −35 | −11 | | −24 | −27 | −35 |
| Huaynaputina | Peru | 1600 | 6 | −36 | −21 | | −28 | | −47 |
| Ruiz | Columbia | 1597 | | | | | | −24 | |
| Ruiz | Columbia | 1586 | 4 | | −26 | | | −24 | |
| Kuwae | Vanuatu | 1458 | 6 | | −45 | −37 | | −53 | −60 |
| El Chichon | Mexico | 1345 | | | | | −28 | | |
| Quilotoa | Ecuador | 1286 | | | | | −30 | | |
| Samalas | Indonesia | 1257 | 7 | −55 | | −57 | −25 | | −55 |
| Pago | New Britain | 682 | | | | | −40 | | |
| Rabaul | New Britain | 574 | | | | | −38 | | |
| Ilopango | El Salvador | 540 | | | | | −38 | | |
| Taupo | New Zealand | 232 | 6 | | −12 | −56 | | | |

a: based on the volcanic emission in Tg S from (Toohey & Sigl, 2017); b: (Sigl et al., 2013); c: (Ren et al., 2010); d: (Sigl et al., 2015); e: (Plummer et al., 2012); f: (Osipov et al., 2014): based on the $SO_4^{2-}$ deposition fluxes (kg km$^{-2}$) in West and East Antarctica.

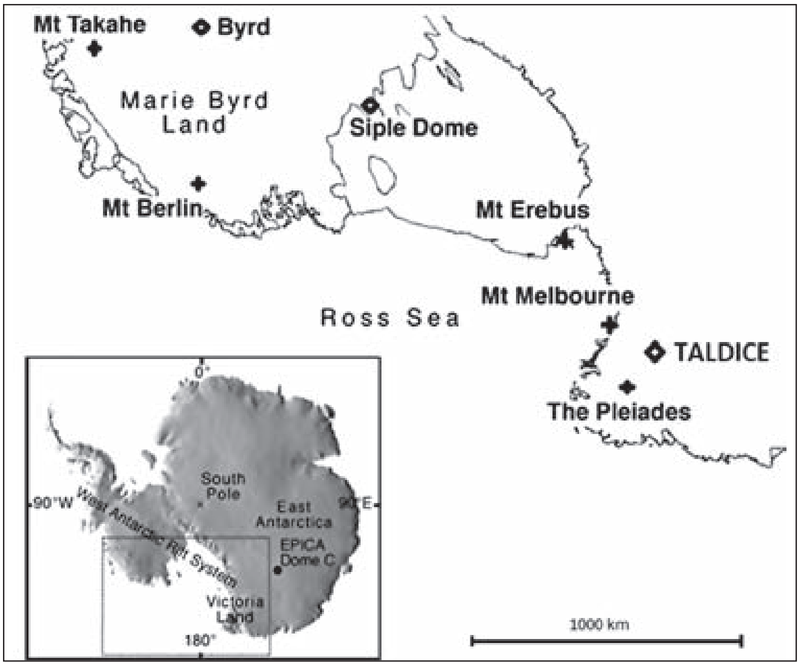

**Figure 2.** Map of Antarctica with the location of the ice cores (rhombs) and main Quaternary volcanoes (crosses) in Victoria Land (Mt. Erebus, Mt. Melbourne, and the Pleiades) and in Marie Byrd Land, West Antarctica (Mt. Takahe and Mt. Berlin). The figure is modified after (Narcisi et al., 2010)

tina, Kuwae, Samalas, and Toba). The chosen Cl/S ratio in the estimates is responsible for low $\Delta\%O_3$ values. For example, the use of 0.06 for $HCl/SO_2$ mass ratio from Mather (2015) leads to lower $\Delta\%O_3$ values: −3% (Tambora), −7% (Huaynaputina), –16% (Taupo), and −17% (Kuwae and Samalas).

Of the dozens of volcanoes located in Antarctica, at least nine (Mt. Berlin, Buckle Isl., Deception Isl., Mt. Erebus, Hudson Mts., Mt. Melbourne, Penguin Isl., Mt. Takahe, and the Pleiades) are known to be active and five of them, all stratovolcanoes, have exhibited frequent volcanic activity in historical times (LeMasurier et al., 1990). Figure 2 shows the main volcanoes and ice cores taken in the region.

Results of the TALDICE ice core (72°49′ S, 159°11′ E, 1620 m depth) study (Narcisi et al., 2010) point to the origin of tephra layers from centers of the Melbourne Volcanic Province (Mt. Melbourne, Mt. Rittmann, and the Pleiades), located 250 km from the coring site. The occurrence of tephra layers suggests that explosive activity was not constant, with a minimum of activity between 20 and 35 kyrs and increased activity back to 65 kyrs. The TALDICE tephra temporal sequence suggests that the Melbourne Volcanic Province was persistently active over the last 70 kyrs.

In Narcisi et al. (2019), fine-grained tephra particles extracted from layers of the AD 1259 major bipolar volcanic signal in four East Antarctic ice cores drilled in different widely-spaced locations on the Antarctic Plateau were analyzed. The extensive database of glass-shard geochemistry combined with grain size analyses consistently indicates that the material was sourced from multiple distinct eruptions. These are the AD 1257 mega-eruption of Samalas volcano in Indonesia, recently proposed to be the single event responsible for the polar signal, as well as a newly-identified Antarctic eruption, which occurred in northern Victoria Land in AD 1259.

The Southern Hemisphere climate conditions persisted until ~17.7 kyrs BP, when nearly synchronous accelerations in deglaciation were recorded in paleoclimate proxies, with many changes ascribed to a sudden poleward shift in the westerlies and subsequent climate impacts. The high-resolution chemical measurements in the West Antarctic Ice Sheet Divide, Byrd, and other ice cores used in McConnell et al. (2017) to document a unique, ~192-yrs series of halogen-rich volcanic eruptions exactly at the start of accelerated deglaciation, with tephra identifying the nearby Mt. Takahe volcano as a source of the eruptions. Estimates of emissions from Mt. Takahe suggest that average and peak chlorine emissions were ~100 Gg $yr^{-1}$ and ~400 Gg $yr^{-1}$, respectively. It was estimated that transport of only 1% of the Mt. Takahe emissions to the high-latitude SH stratosphere would have yielded chlorine concentrations comparable to those responsible for modern chlorofluorocarbon-driven ozone depletion.

Deception Isl. is the largest active volcano in the Antarctic Peninsula region; its basal diameter is 30 km. The caldera collapse of the Deception Volcano was comparable in scale to some of the largest eruptions on Earth. The analysis of nearby lake sediments was done by Antoniades et al. (2018). A singular event was identified for the Deception Isl. caldera collapse that occurred 3980 ± 125 BP. The hitherto undated caldera-forming event ejected a dense-rock equivalent (DRE) of 30–60 $km^3$ of magma, comparable in volume to the catastrophic 1815 Tambora eruption that caused global cooling and resulted in "the year without a summer". During the collapse, rapid volcano-tectonic subsidence along pre-existing faults resulted in a modern 8–10 km-diameter caldera that is of similar dimensions to those of Santorini and Krakatoa volcanoes. Caldera collapses on this scale are often associated with intense seismic swarms, including multiple high-magnitude earthquakes. The volume of magma erupted implies the likelihood of significant, widespread climate impacts. Now firmly established as a Holocene event, the erupted volume and VEI of 6 make the caldera-forming eruption the largest in Antarctica during the Holocene.

Taking the range of ejected magma volume (30–60 $km^3$) for the Deception Isl. caldera collapse (30–60 $km^3$, Antoniades et al., 2018), the erupted magma volume and released Cl, Br, and I amounts (Cadoux et al., 2015), suggesting 25% release of HCl into the stratosphere and by using the Eq.7, we can estimate the range of possible ozone depletion after the eruption (from −44 to −56%). Because Deception caldera possesses similar dimensions to those of Santorini and Krakatoa volcanoes, we can compare the $\Delta\%O_3$ values for those volcanoes (up to −34% for Krakatoa and −57% for Samalas) and Tambora (−43%) with the Deception eruption.

A similar estimate for the 192 yrs series of Mt. Takahe halogen-rich volcanic eruptions at 17,7 kyrs BP, with the mean annual volcanic emission of Cl ~100 Gg $yr^{-1}$ (McConnell et al., 2017), yields a 31% stratospheric ozone depletion over Antarctica.

Erebus volcano eruptions are of the Strombolian type, for which the ejecta and gases are known to reach heights of 1–2 km above the volcano summit (3794 m) and, therefore, cannot directly reach the stratosphere (about 9–10 km). However, Erebus volcano gas emissions can ascend to the Antarctic stratosphere via high-latitude cyclones, which are coupled to the stratospheric polar vortex in cold seasons (Zuev et al., 2015). Based on the NCEP/NCAR reanalysis data over the last 35 years and by using the NOAA HYSPLIT trajectory model, it is shown (Zuev et al., 2015) that Erebus volcano gas emissions (including HCl and $SO_2$) can reach the Antarctic stratosphere via high-latitude cyclones with the annual average probability $P_{ann}$ of at least ~0.235 (23.5%). Depending on Erebus activity, this corresponds to an additional 1.0–14.3 kt of annual stratospheric HCl and 1.4–19.7 kt of $SO_2$. Thus, the Erebus volcano is the natural and powerful source of additional stratospheric HCl and $SO_2$, and hence, the cause of the Antarctic ozone depletion, together with industrial halocarbons (Zuev et al., 2015).

It should be noted that such negligibly small annual release of HCl (0.001–0.014 Tg $yr^{-1}$) contradicts the conclusions of (Zuev et al., 2015) that volcanic emission of Erebus is the essential reason for springtime ozone hole formation over Antarctica. In this case, Eq.7 prevents to estimate possible stratospheric ozone percentage change.

The Erebus volcanic activity restarted in 1972. Until the early 1980s, gas emission had gone on at a relatively low rate (e.g., 0.95 kt $yr^{-1}$ $SO_2$ in 1978) (Zuev et al., 2015). However, in 1980 Erebus exhibited anomalously high volcanic activity (69.4 kt $yr^{-1}$ of $SO_2$), and the emission rate reached 83.9 kt $yr^{-1}$ in 1983. The extremely high Erebus activity was synchronous with intense ozone depletion and an increase of the springtime ozone hole area (Zuev et al., 2015). The data lead to the conclusion that the annual average HCl and $SO_2$ emission rates are uniquely associated with the springtime total ozone content. However, it is our opinion that such a conclusion may be erroneous due to the very low emission rate of HCl due to non-eruptive degassing Erebus volcano. In this instance, additional future observation data and computer modelling are required to study the connection between Erebus volcano gases emission rate and springtime ozone hole area as well as the total column ozone amount over Antarctica.

## 3 Conclusion

This study, for the first time, reveals that the volcanic emission of the halocarbons (HCs) makes an extremely insignificant contribution to their global atmospheric emission. The maximum contribution of volcanic emission can be for $CH_3CClF_2$ (0.8%), $CF_2Cl_2$ (0.3%), $CFCl_3$ (0.25%), $CCl_4$ (0.2%) and $CH_2Br_2$ (0.1%). For the remaining 15 HCs examined, this contribution ranges from 0.0001% to 0.03%. The contribution of volcanic emission of HCs to the depletion of stratospheric ozone in catalytic halogen cycles does not exceed 0.1%.

The emission ranges of HCs from hydrothermal sources in seismically and volcanically active regions was also estimated (in tons $yr^{-1}$): 3.5–480 ($CHCl_3$), 0.1–4.2 ($CCl_4$), 0.2–3.0 ($ClHC = CCl_2$), 0.2–0.5 ($CCl_2 = CCl_2$), 0.1–66 ($CF_2Cl_2$) and 0.05–0.9 ($CFCl_3$). Comparing these ranges also shows that they are insignificant natural sources of HCs in the atmosphere.

To verify the scheme of radical-chain gas-phase formation of HCs in a volcanic column (Frische et al., 2006), we calculated the enthalpies of possible reactions and the rate coefficients. It was concluded that the scheme proposed in (Frische et al., 2006) is in contradiction with the data and low ratios $CH_3I$, $CH_3Br$, and $CH_3Cl$ as well as $C_2H_5I$, $C_2H_5Br$, and $C_2H_5Cl$. A synergetic effect acts both the bromine chemistry with iodine and chlorine chemistry to increase the halogenation rates. The methane sequential free-radical chain chlorination explains various ratios of polychloromethanes, $CCl_4$, $CHCl_3$, $CH_2Cl_2$, and $CH_3Cl$ in gases from different volcanoes. The analytical solution for the kinetic equations is proposed, and results are compared with the ratios from different volcanoes.

Continuous passive emission of gases from Mt. Erebus has considerable influence on their content in the Antarctic ice. We examine the possible effects of volcanic emission of the HCs, particularly freon-11, on its content in the air from Antarctic firn and ice cores. The highest possible freon-11 emission from Mt. Erebus does not exceed 0.5 t $yr^{-1}$. The volcano emissions of $CH_3Cl$, $CH_2Cl_2$, and $CH_3I$ are close to the estimate. The estimation shows that up to 4.8 Tg $yr^{-1}$ of freon-11 can be "pumped" through the Antarctic atmosphere. Thus, the contribution of the possible emission of freon-11 from Mt. Erebus is 7 orders of magnitude lower than its global contribution to the Antarctic atmosphere, and it cannot significantly affect its concentrations in the firn and ice cores. To understand the scale of HCs emission from past volcanic eruptions in the Southern Hemisphere, we consider the content of $nssSO_4^{2-}$ ions in the ice cores in Antarctica ice and the $nssSO_4^{2-}$ deposition fluxes. From the data, it follows that the maximum possible contribution of past volcanic emission could reach 40% current anthropogenic emission and up to 6% of it over the past 12000 years. Comparing the estimated $SO_2$ emissions from volcanoes with the HCs from natural and industrial sources shows that the contribution of the volcanogenic HCs could not exceed 1% of their budget from total sources during the past 250 yrs.

Apart from the HCs, the main inorganic halogen-containing volcanic gases are the hydrogen halides HX (X = Cl, Br, and I), which in gas-phase reactions release halogen atoms and subsequently deplete the stratospheric ozone. Large ozone losses that occur over Antarctica result directly from heterogeneous reactions involving halogens from the halides on the surface of cold sulfate-water aerosols. We calculated the injected EESC values by using the Cl/S, Br/S, and I/S ratios, 25% release of HCl to the stratosphere, the S-volcanic flux from Tambora eruption, and petrological estimates of total $SO_2$ volcanic emission as well as the ratio of $nss\text{-}SO_4^{2-}$ deposition fluxes in Antarctic ice cores and Tambora volcano. Using the relationship between EESC and column ozone percentage change, $\Delta\%O_3$, we estimate the last values for 20 known volcanoes in the tropical belt and low latitudes. The estimates lead to more than 50% depletion of stratospheric ozone after the most powerful volcanic eruptions (Huaynaputina, Kuwae, Samalas, and Toba).

Taking the range of ejected magma volume for Deception Island's caldera collapse c. 4000 BP, and amounts of released Cl, Br and I, suggesting 25% release of HCl into the stratosphere, we estimated the range of possible ozone depletion after the eruption, which is comparable with those from Krakatoa, Samalas and Tambora eruptions. A similar estimate for the 192 yrs series of Mt. Takahe halogen-rich volcanic eruptions at 17,7 kyr BP presents extensive stratospheric ozone depletion over Antarctica. Crude estimates of $\Delta\%O_3$ after the Ferrar Large Igneous Province (182 Myrs BP) eruptions in Antarctica, considering the whole LIP volume of basaltic lavas, range from −49 to −83%. The ozone depletion on this scale (quadratic dependence of UV-B % on the $\Delta\%O_3$) would dramatically increase the flux of harmful UV-B radiation to the surface, which could cause damage to animals and plants in the Southern Hemisphere and Antarctica.

Due to very low emission rate of HCl from a unit non-eruptive degassing Erebus volcano, the volcanic emission of Erebus could not be an essential reason for modern springtime ozone hole formation over Antarctica.

*Author contributions*. VB designed research; MB and VB performed research; MB and VB analyzed data; MB and VB wrote paper; and MB and VB reviewed and revised paper.

*Acknowledgments*. The study was supported by the State program in the Department of Antarctic Geology and Geoecology in the Institute of Geological Sciences of National Academy of Sciences of Ukraine "Study of impacts of geological and physicochemical processes on climate change in West Antarctica" (0120U100574).

*Conflict of Interest.* The authors declare that they have no conflict of interest.

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Received: 18 October 2021
Accepted: 5 December 2021

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### Вплив вулканічної емісії галогенопохідних сполук на довкілля Південної півкулі та Антарктики

**Реферат.** Метою дослідження було оцінити та порівняти глобальні викиди 20 галогеновуглеводнів із вулканічних та гідротермальних джерел в атмосферу Землі та їхній вплив на озоновий шар. З'ясовано, що внесок вулканічної емісії цих сполук у руйнування стратосферного озону у каталітичних галогенних циклах не перевищує 0,1%, але вони істотно знижують рівень тропосферного озону поблизу самих вулканів. Запропоновано і підтверджено термодинамічними та кінетичними розрахунками схему газофазного вільно-радикального ланцюгового галогенування вуглеводнів, яка дозволяє пояснити експериментальні співвідношення між концентраціями $CH_3I$ : $CH_3Br$ : $CH_3Cl$ і $CCl_4$ : $CHCl_3$ : $CH_2Cl_2$ : $CH_3Cl$ у вулканічних газах. Можливий вулканічний викид галогеновуглеводнів з Еребуса та вибухові виверження в Південній півкулі протягом голоцену не мали помітного впливу на їх вміст в антарктичному льоді. Однак вулканічний викид галогеноводнів (HX, X = Cl, Br та I) від потужних вивержень тих часів був здатний істотно виснажити стратосферний озон, спричинивши різкий вплив шкідливого випромінювання УФ-Б на біоту материків і океану. Розраховано значення еквівалентного ефективного стратосферного хлору та оцінено відсоткову зміну стратосферного озону ($\Delta\%O_3$) для 20 відомих вивержень вулканів у тропічному поясі та у південних широтах. Здійснені розрахунки демонструють виснаження стратосферного озону більш ніж на 50% після потужних минулих вивержень вулканів. Крім того, діапазон можливого руйнування озонового шару після виверження вулкану острова Десепшен, близько 4000 років тому, (від 44 до 56%) можна порівняти з впливом вулканів Кракатау, Самалас і Тамбора. Оцінка 192-річної серії багатих галогенами вивержень вулкану Такахе (Західна Антарктида) 17,7 тис. років тому свідчить про значне виснаження стратосферного озону над Антарктидою. Окрім зазначеного, враховуючи весь обсяг базальтових лав великої магматичної провінції Феррар, $\Delta\%O_3$ після вивержень в Антарктиді 183 млн. років оцінили від 49% до 83%. Встановлено, що через незначну кількість викидів HCl від нееруптивного дегазуючого вулкана Еребус, такий викид не може бути суттєвою причиною сучасного весняного утворення озонових дір над Антарктидою.

**Ключові слова:** вулканічна емісія, галогеновуглеводні, галогеноводні, радикально-ланцюгові реакції, руйнування стратосферного озону