

CYCL'HAL 2023

Friday 20th October

Third Scientific Workshop on Halogens

from mantle processes to emissions
and their impact on the atmosphere



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Campus Pierre et Marie Curie
4, Place Jussieu, 75005 Paris
Conference room : 46-56, 2d floor

Video-conference

Zoom N° : 943 1217 7370

Psswd : D7MSsT



CYCL'HAL

October 20th, 2023

Campus Pierre et Marie Curie – Sorbonne Université

Salle de conférence Tower 46, corridor 46-56, 2nd floor

Zoom N° : 943 1217 7370 ; Password : D7MSsT

Invited speakers

Claudia D'Oriano (INGV-Pisa)

Anne-Sophie Bouvier (Lausanne)

Kirstin Krüger (Oslo University)

Stam Flemetakis (Muenster University)

Martyn Chipperfield (Leeds university)

9h – Welcome coffee

9h30 Introduction

- 9h35 :** **Stam Flemetakis** (Muenster University): “The solidus of peridotites in the presence of F and other volatiles - Do we need more complex experiments?”
- 10h00 :** **Mara Miranda** (University of Geneva) “Development of new methods to track magma degassing and fluid fluxing in complex magmatic systems: The study of heavy halogens”
- 10h15 :** **Tobias Grützner** (Frankfurt, Germany) “Heavy halogen impact on Raman water bands at high pressure”
- 10h30 :** **Sami Soudani** (University of Nantes) “The effect of iodine on the local environment of network forming elements in aluminoborosilicate glasses : an NMR study”

10h45 coffee break

- 11h15 :** **Elliott Carter** (Trinity College Dublin) “Multi-stage carbonation of mantle peridotites in the Oman Ophiolite: tracing fluids using halogens and trace elements” *-remote-*
- 11h30 :** **Claudia D'Oriano** (INGV-Pisa) “High-resolution compositional mapping reveals degassing dynamics during major explosions at Stromboli”
- 11h55 :** **Yann Morizet** (University of Nantes) “Iodine dissolution mechanisms in high-pressure aluminoborosilicate glasses and its relationship to oxygen speciation”
- 12h10 :** **Anne-Sophie Bouvier** (Lausanne) “Chlorine isotope behavior in subduction zone settings: insights from olivine- hosted melt inclusions and bulk rocks”

12h35 : General discussion + poster time

13h : Lunch time

- 14h30 :** **Slimane Bekki** (LATMOS) “Halogen and atmosphere”
- 14h45 :** **Kirstin Krüger** (Oslo University): “Initial meteorological conditions and eruption source parameters control on volcanic forcing”
- 15h10 :** **Martyn Chipperfield** (Leeds university) “Impact of halogens on ozone in the lower stratosphere”
- 15h35 :** **Marion Louvel** (ISTO) “Br degassing mechanism investigated by X-ray absorption spectroscopy”
- 15h50 :** **Bastian Joachim** (Innsbrück) “Bromine partitioning between olivine, orthopyroxene and melt at MORB and OIB source conditions”
- 16h05 :** **Sarah Figowy (Oslo)** *-remote-* “Crystal chemistry and partitioning of halogens in hydrous silicates”
- 16h20 :** **Daniele Pinti** (Géotop, Montréal) *-remote-* “Elemental and isotopic systematics of chlorine and other elements (b, li) in geothermal fluids of Mexico”

16h35 : final discussion

The solidus of peridotites in the presence of F and other volatiles –
Do we need more complex experiments?

Abstract

References

Development of new methods to track magma degassing and fluid fluxing in complex magmatic systems: The study of heavy halogens

Mara Miranda¹, Alexandra Tsay¹, Michael Schirra¹ and Zoltan Zajacz¹

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Magma degassing and fluid fluxing within trans-crustal magma reservoirs play an important role in the transport of volatile elements and ore metals. Tracking the migration of magmatic fluids within such systems is challenging, yet essential for the understanding of magmatic-hydrothermal ore genesis and volcanic degassing.

We aim to develop new geochemical tools to track magma degassing and fluid fluxing over a broad melt composition range. We hypothesize that halogen ratios may be useful for this purpose because previous studies have found that the fluid/melt partition coefficients ($D^{f/m}$) of halogens significantly increase with increasing halogenide ion radius (Bureau et al., 2000; Bureau and Métrich, 2003; Cadoux et al., 2018). However, the data available on Br and I partitioning is limited; therefore, we are experimentally studying the $D^{f/m}$ of halogens as a function of melt composition, pressure, and fluid salinity.

The experiments presented here were conducted at $T=785^{\circ}\text{C}$ and $P=200$ to 500 MPa. We used synthetic peralkaline, metaluminous, and peraluminous haplogranitic starting glasses and starting fluids with 7 different salinities. The experiments were performed in rapid-quench externally heated René 41 and Molybdenum-Hafnium Carbide (MHC) pressure vessel apparatuses, as well as an end-loaded piston cylinder apparatus with a 19.05 mm diameter assembly.

Halogen concentrations in the run product glasses were determined by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) at the University of Geneva and Secondary Ion Mass Spectrometry (SIMS) at the SwissSIMS facility in Lausanne. The concentration of halogens in the equilibrium fluids was then estimated by mass balance calculation using the method by Zajacz et al., 2012 which allowed us to determine the $D^{f/m}$ for Cl, Br and I as a function of fluid salinity, confining pressure, and melt composition. On average, for the metaluminous composition, the $D^{f/m}$ of Br and I are 2 and 5 times higher than that of Cl, respectively. Moreover, the $D^{f/m}$ of all three studied halogens increases by a factor of 3 to 5 with fluid salinity increasing from 0.5 to 32 molal, with $\text{Cl} > \text{Br} > \text{I}$. Moreover, the effect of pressure on the $D^{f/m}$ of halogens depends on the salinity of the fluid phase. With increasing pressure at low-fluid salinities, all three halogens partition stronger towards the fluid phase but the opposite trend was observed at high-fluid salinities. This difference can be rationalized by taking the much lower compressibility of high-salinity fluids into account. Overall, our results up to date indicate that I/Cl and Br/Cl ratios in the silicate melt will decrease during progressive magma degassing. The I/Cl ratio is more sensitive and thus more applicable during the early stages of magma degassing. Br/Cl is well-suited to address crystallization-driven degassing in more crystalline/felsic systems. The I/Cl ratios may serve as a sensitive indicator of fluid fluxing.

Bureau, H., Métrich, N., 2003. An experimental study of bromine behaviour in water-saturated silicic melts. *Geochimica et Cosmochimica Acta* 67, 1689–1697. [https://doi.org/10.1016/S0016-7037\(02\)01339-X](https://doi.org/10.1016/S0016-7037(02)01339-X)

Bureau, H., Keppler, H., Métrich, N., 2000. Volcanic degassing of bromine and iodine- experimental fluid melt partitioning data and applications to stratospheric chemistry.pdf. *Earth and Planetary Science Letters* 183, 51–60.

Cadoux, A., Iacono-Marziano, G., Scaillet, B., Aiuppa, A., Mather, T.A., Pyle, D.M., Deloule, E., Gennaro, E., Paonita, A., 2018. The role of melt composition on aqueous fluid vs. silicate melt partitioning of bromine in magmas. *Earth and Planetary Science Letters* 498, 450–463. <https://doi.org/10.1016/j.epsl.2018.06.038>

Zajacz, Z., Candela, P.A., Piccoli, P.M., Sanchez-Valle, C., 2012. The partitioning of sulfur and chlorine between andesite melts and magmatic volatiles and the exchange coefficients of major cations. *Geochimica et Cosmochimica Acta* 89, 81–101. <https://doi.org/10.1016/j.gca.2012.04.039>

Heavy halogen impact on Raman water bands at high pressure

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Halogen complexes (e.g., in saline fluids, brines, or molten salts) are major agents for metal transport in ore-forming processes related to hydrothermal systems (Aiuppa et al., 2009). Samples of such fluids can be found entrapped as inclusions in minerals like quartz (Pankrushina et al., 2020) or olivine (Kawamoto et al., 2013) where they are often analyzed with Raman spectroscopy. The impact of dissolved chlorine on the water stretching bands in Raman spectra is studied since about 40 years and is frequently used to determine salinity in fluid inclusions (Georgiev et al., 1984; Mernagh and Wilde, 1989; Pankrushina et al., 2020; Sun et al., 2010). Less is known about the impact of the heavy halogens bromine and iodine, and about the pressure effect on Raman water bands.

We conducted experiments in a hydrothermal diamond anvil cell to study systematically the shift alteration of Raman water bands at different concentration of dissolved chlorine, bromine, and iodine. We conducted these experiments at ambient temperature and varying pressure from 0 to 1.4 GPa.

The strength of the shift change correlates with the ionic size of the halogens: Chlorine shows the smallest shift, iodine the largest shift, and bromine is in between for comparable concentrations. Increasing pressure diminishes the effect of halogen concentration and causes a shift change in opposing direction relative to the change caused by halogen concentration and ionic size.

In consequence, salinity determination in fluid inclusions with Raman spectroscopy can strongly underestimate the salinity in the inclusion, if the pressure effect is not considered.

Aiuppa et al., 2009. *Chem. Geol.*, 263(1-4), 1-18.

Georgiev et al., 1984. *Appl. Spectrosc.* 38(4), 593-595.

Kawamoto et al., 2013. *PNAS*, 110(24), 9663-9668.

Mernagh, and Wilde, 1989. *Geochim. Cosmochim. Acta* 53(4), 765-771.

Pankrushina et al., 2020. In: Votykov et al. (eds.), *Minerals: Structure, Properties, Methods of Investigation*. Springer Proceedings in Earth and Environmental Sciences, 175-183.

Sun, Q., 2009. *Vib. Spectrosc.* 51, 213-217.

The effect of iodine on the local environment of network forming elements
in aluminoborosilicate glasses : an NMR study

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Among radioisotopes produced by nuclear power plants, halogens (¹²⁹I and ³⁶Cl) represent a major trouble as their high volatility makes them impossible to immobilize through classical nuclear waste vitrification. The approach we have recently developed using high-pressure synthesis conditions is able to incorporate large quantities of iodine (I) in aluminoborosilicate glass that could potentially be used as a matrix for ¹²⁹I immobilisation.

The I incorporation in the structure of aluminoborosilicate glasses is strongly dependent on the presence of alkali or alkaline-earth cations needed to charge compensate the iodide (I⁻) and/or iodate (IO⁻) molecular groups. It is currently accepted that the incorporation of volatile species in the glass structure may induce large structural change that, by extent, could influence the physical properties of the glass (i.e. chemical durability). This aspect is of prime importance for nuclear waste that requires a geological disposal for a long period of time. However, the effect induced by I dissolution on the glass structure is actually not apprehended.

We have investigated the change in the glass network structure as a function of I content. We conducted a series of high-pressure experiments (1.0 GPa) on several aluminoborosilicate glasses in the SiO₂-Al₂O₃-B₂O₃-Na₂O system. The starting glass was equilibrated with an iodine fluid phase using either I₂ or I₂O₅ as a starting source. XPS analyses revealed that iodine in the recovered glass (reaching up to 1 mol.%) appears mainly under I⁻ form, co-existing with I⁵⁺ when samples were loaded with I₂O₅.

The I-bearing glasses were characterized by ¹¹B, ²³Na and ²⁷Al Solid-State NMR. Aluminium in the glass is mainly present as AlO₄ units in agreement with previous works for Na-bearing glasses. Whereas the pressure conditions produce a noticeable effect on the glass structure by increasing the N₄ value (BO₄/[BO₄+BO₃]); the I effect remains weak. In detail, the I incorporation (either I⁻ or IO⁻) does not seem to affect the N₄ value. In contrast, the ²³Na NMR parameters (δ_{iso} and Cq) exhibit a shift towards values indicating a more compensating role for Na⁺ cations. Therefore, Na⁺ acting as network modifiers are scavenged by I species for charge compensation (*figure 1*). It also suggests that the role of Na⁺ cation for charge compensation of AlO₄ and BO₄ unit prevails on its role of network modifiers.

Further additional work is required for investigating the iodine impact on more extended range of glass compositions. Nonetheless, in the present investigated glasses, only little changes are observed on the glass structure upon I dissolution.

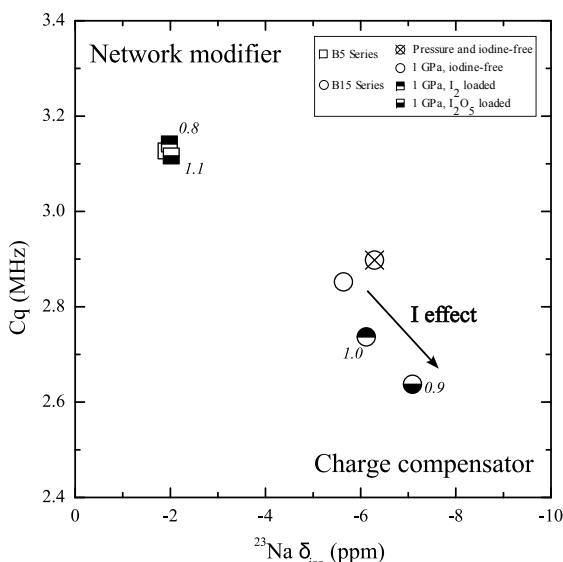


Figure 1: Evolution of the ²³Na parameters as function of iodine source and pressure.

Multi-stage carbonation of mantle peridotites in the Oman Ophiolite: tracing fluids using halogens and trace elements

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Quantifying the carbon budget of subduction zones and the origins of CO₂ in arc magmatism requires an understanding of the lateral trenchward mobility of slab-derived fluids. This can be explored in the Oman Ophiolite where fully-carbonated peridotites overlie the basal thrust fault of the ophiolite and attest to fluxing of the shallow mantle wedge by CO₂-rich fluids.

Listvenites, serpentinites and meta-basalts/-sediments from the carbonated mantle section and the underlying metamorphic sole were sampled by diamond wireline coring during the Oman Drilling Project. Eight four samples were analysed for bulk major, trace and volatile elements. Halogen abundances have been measured in a subset of samples spaced across a carbonation reaction zone by a variety of bulk and *in situ* methods (noble gas method, pyrohydrolysis; electron probe, ion probe).

Rare-earth element patterns vary markedly between different listvenite domains and suggest that, prior to carbonation, the mantle section underwent a phase of high temperature infiltration resulting forming amphibole lherzolites. *In situ* halogen abundances meanwhile indicate two episodes of CO₂-rich metasomatism, the latter being Ca- and F-rich and forming dolomite in discrete horizons. Petrographic observations indicate that dolomite-forming fluids came later, and their chemistry suggests that they derive directly from the underlying metamorphic sole.

In-situ serpentine and bulk listvenite heavy halogen compositions lie along a single tight array, suggesting formation by fluids with a common origin. The serpentine endmember of this array is dissimilar from compositions in the wider literature but can be explained by fractionation of the fluid during carbonation. Modelling this process suggests that the initial carbonating fluid composition was CO₂-rich and Cl-poor suggesting it derived from deep decarbonation reactions in the slab. This implies that much of the CO₂ released from the subducting slab beneath the proto-Oman ophiolite was focussed into the forearc mantle and has important implications for the CO₂ budget of subduction zones through Earth history.

High-resolution compositional mapping reveals degassing dynamics
during major explosions at Stromboli

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Major explosions at Stromboli volcano encompass a wide range of medium to high intensity eruptions. Since the paroxysmal explosions in the summer 2019, these events have occurred with a frequency of about six per year, therefore posing significant hazard on the island, in particular on the upper flanks of the volcano. Nevertheless, their intermediate nature between ordinary and paroxysmal activities make them more elusive to pinpoint in terms of eruptive dynamics and associated precursors.

To better understand the mechanisms that trigger and accompany the evolution of the major explosions at Stromboli, we have linked texture and composition of erupted products to numerical modeling of gas-magma transfer in the upper part of the plumbing system.

High-resolution compositional mappings of residual melts were performed, by means of FEG-EMPA, on Stromboli lapilli and ash emitted during different explosive events, ranging from ordinary activity (11 April and 29 June 2022) to major explosion (13 May 2022) to paroxysms (3 July and 28 August 2019). Areas selected for FEG-EMPA mapping were preventively identified on BSE-SEM images, and in particular we focused our attention on the glasses close to vesicles. Basing on textural evidences, we mapped the zones where a clear compositional contrast was present, highlighted by different gray tones in BSE-SEM images. The occurrence of mingling textures between the two magmas emitted at Stromboli, LP (low-porphyrritic) and HP (high porphyritic) respectively, were present only in the products from paroxysms. The lapilli from the major explosion contains many white filaments, 1-10 microns-thick, close to bubbles, showing irregular and fluidal shapes; ash and lapilli from ordinary activity have a quite homogeneous groundmass glass. Preliminary results suggest complex bubble-melt interaction dynamics during major explosions, evidenced by major elements patterns dictated by well-preserved trails of Cl and K in the elemental maps along the white filaments, that aren't found in products from ordinary and paroxysmal activities. These textures have been interpreted as bubble-driven mingling between LP/evolved LP and HP melts induced by partial gas-melt decoupling. Bubble rise enhances mingling between melts of different composition, and later the resulting filaments are stretched and deformed during fluid motion.

In order to better understand the measured and observational data, we used bubble growth and dynamics models to identify the decoupling time scales and physical parameter (viscosity, volatile contents) ranges leading to the observed distributions characterizing intermediate-intensity eruptions. The diffusion timescale can be estimated as the ratio between the square of the filament thickness (L) and the diffusion coefficient (D). Basing on chlorine signature, and assuming a temperature range: $1200\text{ °C} \leq T \leq 1500\text{ °C}$, a dissolved water content up to 3 wt.%, and a diffusion coefficient of Cl of $10^{-11} \leq D \leq 10^{-10}$ (Alletti et al., 2007), for a filament with $L=10\text{ }\mu\text{m}$, the diffusion timescale is $1\text{ s} \leq \tau \leq 10\text{ s}$. Considering a reasonable bubble ascent rate in the shallow plumbing system of 1-10 m/s, the resulting depth where the filament was formed is $\leq 1\text{ km}$. Thus, the filaments were generated at shallow depth by gas-melt decoupling. This is also consistent with the depletion in Cl (solubility of Cl rapidly decreases at low pressure). Normal activity is characterized by slower timescales; thus these textures are mostly obliterated by diffusion. The fast ascent of LP magma during paroxysms doesn't allow widespread gas-melt decoupling.

The above described textures have been identified also in products of other volcanoes with similar composition, such as in lava fountains from Etna (personal communication) and in the recent Cumbre Vieja 2021 eruption, La Palma (Gonzalez-Garcia et al., 2023). Similarly to what proposed by Gonzalez-Garcia et al., (2023), we conclude that the very short lifetime of these filaments, together with their abundance, suggests a possible trigger mechanism for the major explosions at Stromboli, related to the arrival of many, isolated, small batches of gas-rich magma from depth and degassing at shallow level, inducing a pressurization of the shallow reservoir.

Iodine dissolution mechanisms in high-pressure aluminoborosilicate glasses
and its relationship to oxygen speciation

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Incorporation of iodine (I) into high-pressure vitrified glasses appears to be a potential solution for the immobilization of ¹²⁹I radioisotopes. Under those conditions, I dissolution is strongly enhanced, however, the impact I dissolution has on the glass structure remains to be determined to assess the matrix durability.

We have studied experimentally the change in I solubility and speciation in a series of sodium aluminoborosilicate glasses (Na₂O ranging from 10 to 40 mol.%) held at 0.25 and 1.0 GPa and 1250°C. As expected, the I solubility increases with pressure conditions, with increasing Na₂O and is positively correlated to the glass optical basicity. The I speciation determined by XPS is changing with the initial loaded source of iodine (either I₂ or I₂O₅) with a predominant iodide form (I⁻) in the glass structure.

The investigation of the oxygen environment in the I-bearing glasses using O 1s XPS revealed that I dissolution induces an apparent oxygen loss within the glass structure. This result is consistent with our current view on I dissolution mechanisms. Furthermore, the subsequent simulations of the O 1s XPS spectra suggest that I dissolution consumes non-bridging oxygen to form bridging oxygen. This change in the oxygen speciation points toward an increase in the glass durability that is an important aspect for nuclear waste immobilization.

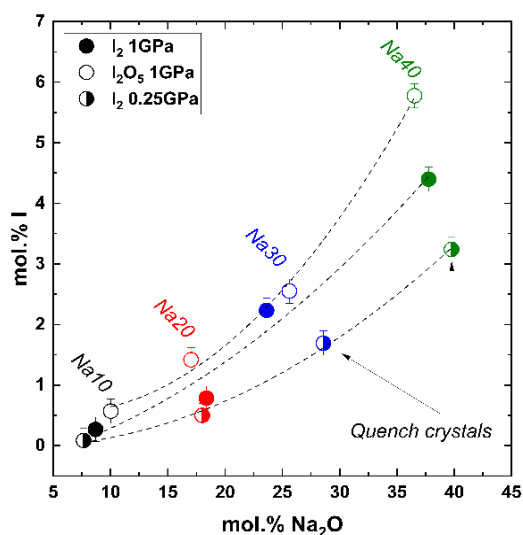


Figure 1: Evolution of the I solubility as a function of the glass Na₂O content expressed in mol.%. There is an increase in the I solubility with 1) increasing Na₂O content, 2) increasing pressure conditions from 0.25 to 1.0 GPa

Chlorine isotope behavior in subduction zone settings: insights from olivine- hosted melt inclusions and bulk rocks

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Chlorine is a highly hydrophile and incompatible element which may provide insights into the transfer of elements from the slab to the surface in subduction zone settings. Bulk rocks data have shown that $\delta^{37}\text{Cl}$ are effective tracers of subducted fluids influence in volcanic rocks, with

$\delta^{37}\text{Cl}$ variation up to 3‰ along an arc (Barnes et al., 2009). Nevertheless, a more profound comprehension is needed to identify the specific contributions from the different slab lithologies. Recent advancements in secondary ion mass spectrometry (SIMS) enable precise determination of $\delta^{37}\text{Cl}$ values at high spatial resolution. In situ measurements of olivine-hosted melt inclusions provide a first order constraint on the $\delta^{37}\text{Cl}$ of primary magmas since these melt droplets are unaffected by near surface processes.

Chlorine isotopes varies by more than 2‰ within a single rock sample. Indeed, combined with either other stable isotopes systems or trace elements within the same melt inclusions, it is possible to trace the signature of the different Cl sources beneath the studied volcanic centers. (Bouvier et al., 2019; Bouvier et al., 2022b). Within an entire arc, the range of $\delta^{37}\text{Cl}$ measured in melt inclusions can be as large as 5‰ (Bouvier et al., 2022a). From arc to arc, the average $\delta^{37}\text{Cl}$ measured in melt inclusions varies, with a possible link between $\delta^{37}\text{Cl}$ and the upper plate thickness, which remains to be confirmed and understood. Intriguingly, when we compare $\delta^{37}\text{Cl}$ values from bulk rocks with those obtained in situ from the same volcano, discrepancies occasionally emerge. These deviations cannot be ascribed solely to instrumental biases. Instead, the difference between bulk rocks and melt inclusions suggests that the latter preserve undegassed signatures which might be lost in bulk rocks. Melt inclusions can thus be very useful to: (i) better constrain the behavior of Cl and $\delta^{37}\text{Cl}$ in subduction zone settings, in particular during fluid-rock interaction within the mantle wedge; and (ii) track the influence of amphibole in the context of arc magma genesis and differentiation.

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Bouvier, A.S., Rose-koga, E.F., Chapuis, A., 2022b. Deciphering Degassing and Source Effects in Cl Isotopes in Melt Inclusions : The Possible Role of Amphibole in the Magma Source of Stromboli (Aeolian Island Arc). *Frontiers in Earth Science* 9, 1-13.

Kirstin Krüger (Oslo University)

Initial meteorological conditions and eruption source parameters control on volcanic forcing

Kirstin Krüger

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Studying impacts of past volcanic eruptions on climate and society relies on volcanology, paleo proxies and archaeological records next to climate model simulations. Here we study the control of varying meteorological conditions and eruption source parameters on the volcanic forcing. Simulating explosive tropical and extratropical Northern Hemisphere (NH) volcanic eruptions are carried out by co-injecting sulfur and halogens into the stratosphere with the CESM2(WACCM) model including aerosol, chemistry, climate, and earth system processes. We consider different initial meteorological conditions (El Nino Southern Oscillation, Quasi-Biennial Oscillation, and polar vortex states) and varying eruption source parameters. We are injecting 17 Tg and 200 Tg of SO₂ together with scaled halogens, at 24 km altitude and 15° N and 64° N latitude, during January and July pre industrial 1850 conditions. Varying initial meteorological conditions reveal a similar large impact on the volcanic forcing (SO₂, SO₄, aerosol optical depth, halogens) as varying source parameters for both tropical and NH extratropical eruptions. Our results are compared with available model experiments from MAECHAM5-HAM. Consequences and uncertainties of volcanic forcing and responses to past and future eruptions are discussed.

Impact of halogens on ozone in the lower stratosphere

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Chlorine and bromine species are known to cause depletion of the ozone layer. Depletion of upper stratospheric ozone by chlorine was the basis for initial concern over chlorofluorocarbons (CFCs) in the 1970s. Chlorine and bromine species cause the large seasonal depletion in the springtime Antarctic lower stratosphere (the ‘ozone hole’), with similar processes occurring during cold Arctic winters. Chlorine and bromine can also contribute to the relatively small ozone depletion in the extra-polar lower stratosphere over decadal timescales. These chlorine and bromine species are largely derived from long-lived source gases (e.g. CFCs and others) which are now controlled by the Montreal Protocol. As a result, stratospheric chlorine and bromine loadings are decreasing and the ozone layer is showing signs of recovery. However, chlorine and bromine can also be transported to the stratosphere by very short-lived species (VSLS) – compounds such as dichloromethane with atmospheric lifetimes of less than 6 months.

I will present model results which show the impact of the chlorinated and brominated VSLS on stratospheric ozone over the past few decades. I will discuss the sensitivity of ozone to these species in different atmospheric regions and the impact of increasing VSLS levels on ozone recovery. I will also discuss the possibility that iodine reaches the stratosphere and has contributed to ozone depletion. I will frame these results in the context of possible impacts of halogens from other sources such as volcanic eruptions and rocket emissions, and also link them to the climate impact. Finally, I will discuss the current and evolving impact of the eruption of the Hunga Tonga–Hunga Ha‘apai volcano in January 2022. This emitted huge quantities of water vapour, and some SO₂, into the stratosphere. Our model simulations suggest that this water vapour will persist in the stratosphere for 5-10 years and will enhance the halogen-catalysed depletion of polar ozone through increased occurrence of polar stratospheric clouds.

Br degassing mechanism investigated by X-ray absorption spectroscopy

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20 years after the first reports of BrO formation in volcanic plumes and its tremendous effect on ozone [1], the mechanisms controlling Br degassing (fluid-melt partition, speciation, diffusion) are still being defined. Amongst the different technics to employ, X-ray absorption spectroscopy (XAS) provides unique opportunities to gain further information on the local environment of halogens in aqueous fluids or silicate melts but may also be used to quantify their distribution in high P-T samples.

Here, we present recent developments on the FAME/FAME UHD beamlines at ESRF that have enabled us to constrain (1) Br speciation in natural volcanic glasses containing down to 10-100ppm Br and (2) the fluid-melt partition coefficients of Br between 600 and 900 °C and 1-1.5kbar. High-energy resolution fluorescence detected (HERFD)-XAS measurements conducted on basaltic to rhyodacitic glasses reveal that Br is found in three different sites, surrounded by Na, K and Ca [2]. The results of partitioning experiments involving haplogranite melts compare well with pioneer and recent post-mortem partitioning studies [3,4,5] and define an overall trend where $D_{Br}^{f/m}$ increases from ~ 5 to 40 with increasing SiO₂ contents and decreasing P-T conditions. Together, these preliminary results pave the way towards an improved characterization of heavy halogens degassing behaviour.

[1] Bobrowki et al., 2003. *Nature* 423, 273-276.

[2] Louvel et al., 2020. *Am. Min.* 105, 795-802.

[3] Bureau et al., 2000. *EPSL* 183, 51-60.

[4] Cadoux et al., 2018. *EPSL* 498, 450-463.

[5] Cassidy et al., 2022. *Am. Min.* 107, 1825-1839.

Bromine partitioning between olivine, orthopyroxene and melt
at MORB and OIB source conditions

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The volatile and incompatible behaviour of the heavy halogens, chlorine, bromine and iodine, makes them excellent tracers for volatile transport processes in the Earth's mantle. Knowledge of the budget and distribution of bromine and iodine in the Earth's mantle is, however, very limited due to their extremely low abundances in the major mineral phases and a lack of well-defined partition coefficients that describe their behaviour during partial melting in MORB and OIB source regions.

We performed high-pressure-temperature experiments at 1 and 10 GPa and between 1573-1873 K to simulate partial melting of a peridotite-analogue (CMS) that was doped with heavy halogens Cl, Br and I at Earth upper mantle conditions. Microprobe analyses of the analytical run products reveal that they contain olivines and orthopyroxenes that are embedded in a glassy matrix, which represents a quenched melt.

Expected Br concentrations in olivine and orthopyroxene are likely well below 1 ppm. Therefore, a direct conventional analysis of Br concentrations is not possible due to a lack of well-defined standard materials and detection limits of most analytical methods that are above the expected Br concentrations in the minerals. Neutron irradiation noble gas mass spectrometry (NI-NGMS) is a technique that is capable of detecting extremely low halogen abundances in geological materials. This technique requires neutron-irradiation of the sample to produce excess noble gas isotopes from halogen isotopes within the sample based on $(n, \gamma/\beta)$ reactions. As an example, neutron irradiation converts $^{79,81}\text{Br}$ to $^{80,82}\text{Kr}$, so that the analysis of excess Kr isotope concentrations allows us to calculate bromine concentrations. While the NI-NGMS technique is already well established (Johnson et al. 2000), it has to date only been applied to bulk terrestrial samples. Here we tried for the first time to measure the bromine concentrations of individual experimentally derived terrestrial phases. For this, the NI-NGMS technique was coupled with a UV-laser ablation technique. A standardization is then required to determine the Br concentration in individual phases. The Mg and Ca concentrations of all phases of interest were analysed with an electron microprobe before the actual irradiation. $^{24,25}\text{Mg}$ is converted to $^{21,22}\text{Ne}$ during irradiation and ^{40}Ca to ^{37}Ar . Thus, the analysis of excess $^{21,22}\text{Ne}$ and ^{37}Ar allows us to calculate the ablated sample volume, which will in turn enable us to calculate the respective Br concentrations in materials of interest.

First results show that bromine behaves indeed very incompatible with partition coefficients between olivine/orthopyroxene and silicate melt being well below 10⁻³ at MORB and OIB source regions. Furthermore, olivine seems to be the main carrier mineral for bromine in the Earth's upper mantle while orthopyroxene plays only a minor role.

A combination of our newly determined partition coefficients with already known bromine bulk rock concentrations in Mid-Ocean-Ridge-Basalts and Ocean-Island-Basalts will allow us to better estimate the budget and distribution of bromine in the Earth's mantle.

Crystal chemistry and partitioning of halogens in hydrous silicates

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Understanding the crystal chemistry of halogens and their distribution in usual hydrous silicates in the lithosphere is important to constrain their deep geochemical cycle and has implications for studies of fluid-rock interactions. Hydrous silicates are abundant in metamorphic and mantle rocks and often contain minor to trace amounts of halogens incorporated via substitution with hydroxyl groups. However, measuring and modelling these halogens remains challenging because their absolute abundance may be very low.

The energetic cost of the substitution of hydroxyl groups by halogens (F⁻, Cl⁻, Br⁻) in hydrous silicates including mica, chlorite, serpentine, amphibole, epidote, and carpholite is quantified using *ab initio* simulations based on the density functional theory. The computations are performed in large systems where halogens are treated as point defects, in minor to trace concentrations. First estimations in brucite show that F-bearing defects must be separated by at least 9 Å (i.e., less than about 12000 ppm in brucite) from one another to reproduce trace element behaviour. This value increases to at least 10 Å for Cl and Br (i.e. less than about 12000 ppm and 26000 ppm in brucite, respectively).

In silicates, the results highlight the competition between the effects of electrostatic interactions and steric hindrance for the incorporation of halogens, where steric hindrance becomes the controlling parameter for heavy halogens. Interaction with alkalis, along with octahedral site occupancy, plays a major role in controlling halogen incorporation, especially in mica and amphibole. Other parameters such as Si/Al ratio of neighbouring tetrahedral sites and the nature of alkalis in amphibole and mica (K or Na) appear to play subordinate roles.

Partition coefficients are estimated in mineral assemblages which are representative of subduction zone metamorphism. All halogens partition in favour of pargasite, biotite and lizardite, followed by clinocllore, tremolite and carpholite. The energetic cost of incorporating halogens into dioctahedral phyllosilicates and epidote is comparatively higher, and partitioning is predicted to be unfavourable to these minerals.

Fractionation between halogens in subduction zones is predicted by the evolution of mineral assemblages and partition coefficients, a consequence of the influence of crystal chemistry over halogen incorporation in hydrous silicates.

Elemental and isotopic systematics of chlorine and other elements (b, li)
in geothermal fluids of Mexico

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To evaluate the sustainability of geothermal resources is pivotal to understand the sources of fluids within the system. This can be revealed by the geochemistry of the solid charge (major, minor and trace dissolved elements including conservative Cl), the dissolved gases (H₂S, CO₂, N₂, Ar, He) and their isotopes (H, O, C, S, Cl, Br, B and noble gases). Chlorine is a conservative fluid-mobile element in high-enthalpy magmatic-geothermal systems, and it is the main anion in geothermal brines. Its origin is multiple, from magmatic HCl, water-rock interactions, seawater chlorine and porewater chlorine, possibly from subducting material in volcanic arc-related systems. Together with Li and B can be helpful in deciphering the origin of associated hot fluids. The interest of looking to the sources, mobility, and enrichment of Li in geothermal fluids is also dictated by the potential exploitation of this critical element for energy transition from geothermal brines. Here we present data of elemental Cl, B and Li together with 99 new $\delta^{11}\text{B}$ data and compared to the large isotopic dataset obtained during the years (H, O, Cl, Br, S, C, Sr and noble gas isotopes) from three of the four geothermal fields exploited by the *Comisión Federal de l'Electricidad* in Mexico which are located in different geodynamic contexts and geological reservoirs: Cerro Prieto (CP hereafter) and Las Tres Virgenes (LVT) located in Baja California in an extensional context related to the opening of the Gulf of California; and Los Azufres (LA) located in Central Mexico in a collisional context related to the subduction of the Cocos Plate. Further, Cerro Prieto reservoirs is sedimentary, related to the Colorado River delta, while the other two fields are located within magmatic (granites) or volcanic (andesites) reservoirs. The Cl/B weight ratios are very homogeneous for each field and distinct as expected in liquid-dominated geothermal fields, suggesting homogenized sources in fluids. The Cl/B ratios range from 784 for CP, which is much larger of those measured in LVT and LA (10-50). The last values are within those expected from Cl and B extracted from unaltered magmatic rocks during water-rock interaction, while CP values could be a mixing between either this source and seawater (Cl/B = 4360) or seawater and volcanic Cl (Cl/B = 700±200). The $\delta^{11}\text{B}$ values range from -7 to +10‰ vs standard NIST SRM951a and plotted against the $^{87}\text{Sr}/^{86}\text{Sr}$, other tracer of water-rock interactions and fluid sources. Results suggests that LA and LVT B is derived from magmatic sources or weathering of E-MORB-type basalts while CP is derived from local sediments, seawater and another source which could be either a mixing between magmatic and seawater fluids or indicating a contamination from subducted sediments (paleo-Farallon Plate) which seems to affect the chemistry of fluids in Baja California. Interestingly this source is accompanied by large amount of radiogenic ^4He . Cl/Li weight ratios varies between 884 and 147 which are between those of seawater and unaltered magmatic rocks with Li content of 30 ppm, much less than those of closely located Salton Sea field (220 ppm) or those found in several locations in Europe (125-440 ppm). Sr/Li vs $^{87}\text{Sr}/^{86}\text{Sr}$ suggest similar Li sources than B.

