CHLORINE ISOTOPES AND VOLCANO SURVEYS

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1 Rationale

Subduction zone volcanoes display surface manifestations (hot springs, gases and secondary condensation phases) which are often chlorine-rich. These are considered to be representative of the volcanic and/or hydrothermal activities. Subduction zone volcanoes showing fumarolic activity often show close association of hydrothermal and magmatic systems. Volcanic gases can escape directly, or interact with shallow or deep water systems as the result of structural and permeability contrasts. The chemical and isotopic survey of these potentially dangerous systems is expected to supply fundamental keys to the understanding of the arc volcano structure, evolution and eruption dynamics.

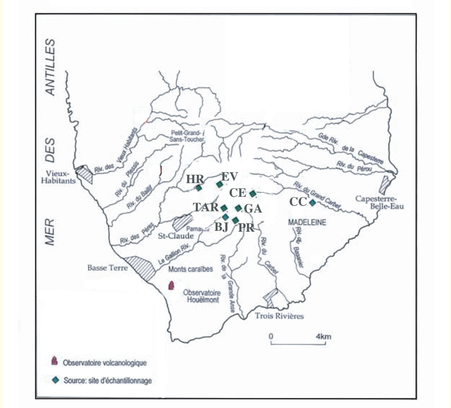
Chlorine stable isotopes ($\delta^{37}Cl$) are rarely used in this field of research despite showing a discrepancy between surface and high temperature signatures. Moreover, $\delta^{37}Cl$ are very sensitive to transport processes (diffusion, ion filtration, water-rock interactions etc...) and can inform on the physical state (permeability, preferential circulations etc...) of the volcanic edifice. Finally, stable isotope fractionations depending on temperatures of equilibration, $\delta^{37}Cl$ could be a new geothermometer of volcanic processes.

A feasibility study has been undertaken into the use of $\delta^{37}Cl$ for surveying volcanic activity and understanding the variability of halogen concentrations in the different phases or components with time. La Soufrière de Guadeloupe, French West Indies and Vulcano in Italy, have been chosen as test sites. The first site is a highly hydrothermal system while the second is influenced by both magmatic and hydrovolcanic activities. La Soufrière was chosen for a spatial and temporal survey while on the latter, chosen for its large range of fluid chlorine concentrations and temperatures, a spatial and methodological study was conducted.

2 La Soufriere de Guadeloupe, French West Indies

In Guadeloupe, this study is particularly interesting as gas emanating from the main summit fumarole have suddenly become very acid in 1998. This change in acidity has been accompagnied by mild yet persistent fumarolic reactivation with higher temperature, greater gas flux and an increase in the gas S/C ratio. So far neither the hydrothermal perturbation nor the incipient magmatic reactivation hypotheses have been confirmed.

Soufrière de Guadeloupe Survey Network

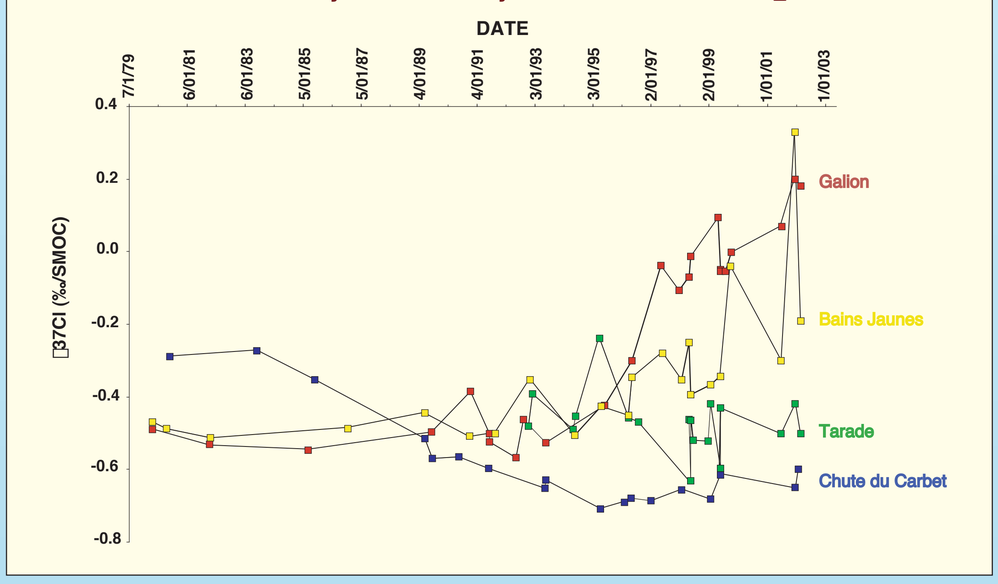


The activity of the Soufrière of Guadeloupe is followed by the French volcano observatory. The gases emitted by fumaroles or at the crater are regularly sampled for chemical and isotopic analysis.

Eight hot springs associated with the volcanic structure have been sampled every fortnight for more than 20 years. The temperature of these hot springs has changed only slightly other this period.

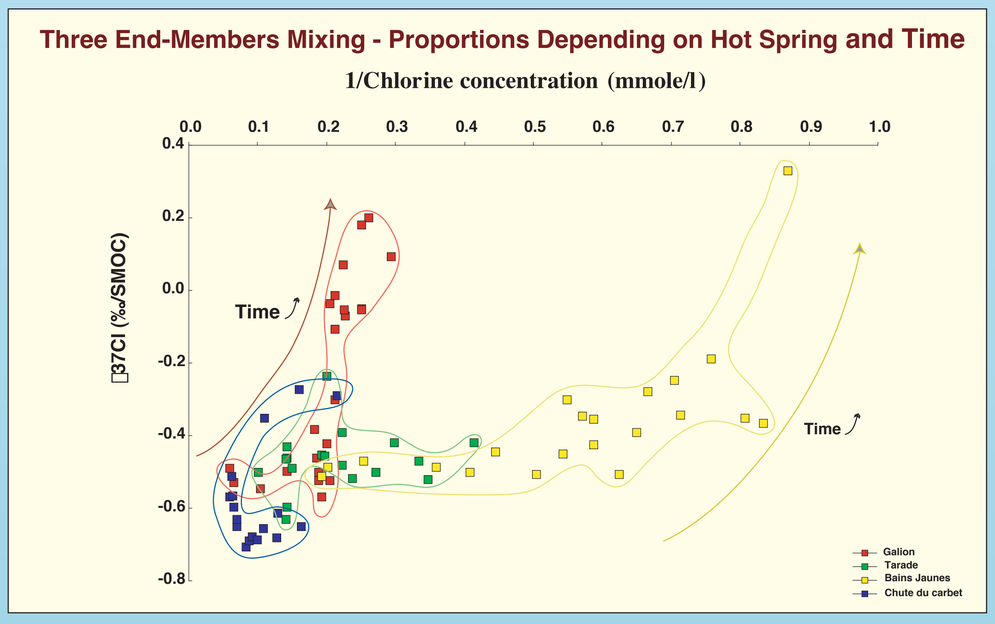
The chlorine concentration of these waters is the parameter changing the most. For some springs (e.g. Bains Jaunes), a continuous decrease in chloride has been observed since 1979. We have started to study this exceptionally extensive collection of fluids (more than 3000 samples) for chlorine isotopes. This temporal study is the first real test of using $\delta^{37}Cl$ in volcano surveys.

Evolution of the Hydrothermal System Over Time - The $\delta^{37}Cl$ Index



The $\delta^{37}Cl$ of the four hot springs studied vary over time. From small and gradual variations and similar values for Galion and Bains Jaunes in 1979, the values become more scattered after 1992. Since the early 90s, the $\delta^{37}Cl$ of the four hot springs diverge and the variations become sharper. **Over the last 4-5 years, there has been an overall increase in their $\delta^{37}Cl$ values.**

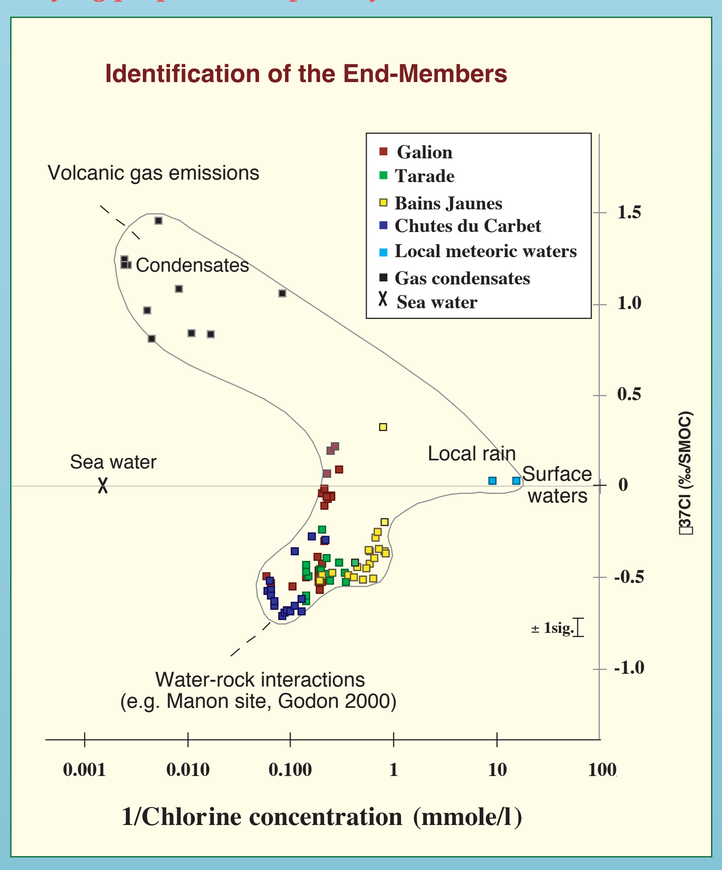
Three End-Members Mixing - Proportions Depending on Hot Spring and Time



The isotopic pattern over this time as shown in a diagram against the reverse of the chlorine concentration, can be described as a tilted arrow head. One branch of the arrow is composed by the samples from Bains Jaunes while the other one is drawn by Galion waters. Most samples from Chutes du Carbet are clustered at the arrow tip while Tarade samples are distributed between both branches. In such a diagram, a binary mixing would be represented by a linear trend.

The pattern observed can be interpreted as the mixing of at least three end-members in different and varying proportions (spatially and over time).

Identification of the End-Members



The three end-members can be : meteoric-surface waters, "water-rock interacted, hydrothermal fluids" and magmatic/volcanic fluids (represented by the gas condensates).

The contributions of the different end-members in the mixing differ from one hot spring to the other. Their respective importance changes over time from 1979 up to now with an overall increase of the meteoric water and/or volcanic plus meteoric influence.

3 Conclusion 1 :

All this can reflect the progression of the sealing of the edifice by the hydrothermal activity and therefore the isolation of the water units. The meteoric waters are thus more readily recycled with less water-rock interactions taking place. It can also reflect the increasing influence of a volcanic gas component in the waters.

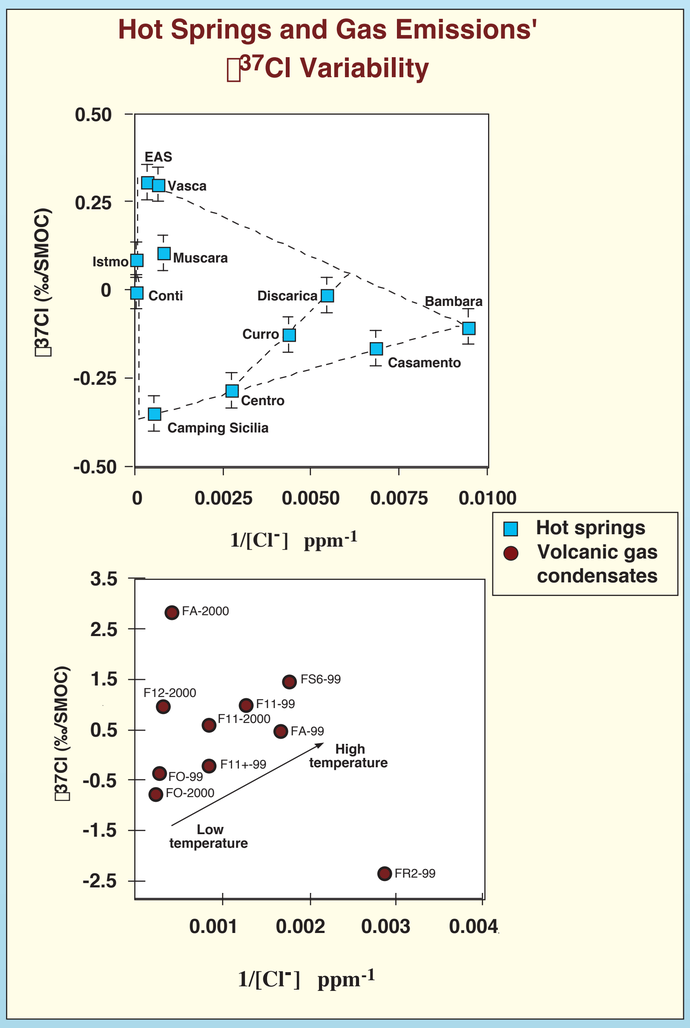
If chlorine isotopes can be used to follow the hydrothermalisation of the volcanic edifice, then they may have the potential to be used in the detection of pressure fracturing that would preceed any volcanic/phreatic event.

4 Vulcano, Italy

The volcanic system of Vulcano (Italy) is influenced by both magmatic and hydrovolcanic activities. It was chosen for this spatial study for its large range of fluid chlorine concentrations and temperatures. Recent sampling (1998-2000) of hot springs, gases (condensates and NaOH solutions) and sublimates, complements archive samples of NH4Cl from 1978 to 1981. The purpose of this study is :

- to test the influence of the type of sampling on the $\delta^{37}Cl$ value (condensate vs NaOH bottles)
- to clarify the isotopic relationships between the different chlorinated phases in a volcanic system (gas, sublimates, aquifers etc...)
- to analyse the spatial information given by the $\delta^{37}Cl$ of a volcano where fumaroles and hot springs present a large range of chemistries and temperatures.

Hot Springs and Gas Emissions' $\delta^{37}Cl$ Variability



In a diagram of $\delta^{37}Cl$ values against the reciprocal of the chlorine concentration, the hot springs are distributed in a triangular domain. This triangular pattern could represent a mixing between at least three end-members in these waters. These end-members are likely to be meteoric waters, hydrothermal waters and magmatic fluids.

Unlike the Soufrière de Guadeloupe gas emissions, Vulcano fumaroles show a large range of $\delta^{37}Cl$ values.

Moreover, the range of fumarole $\delta^{37}Cl$ seems to be related to the temperature of collection (figure bellow). Whatever type of sample is considered, the higher the temperature of collection, the higher the $\delta^{37}Cl$.

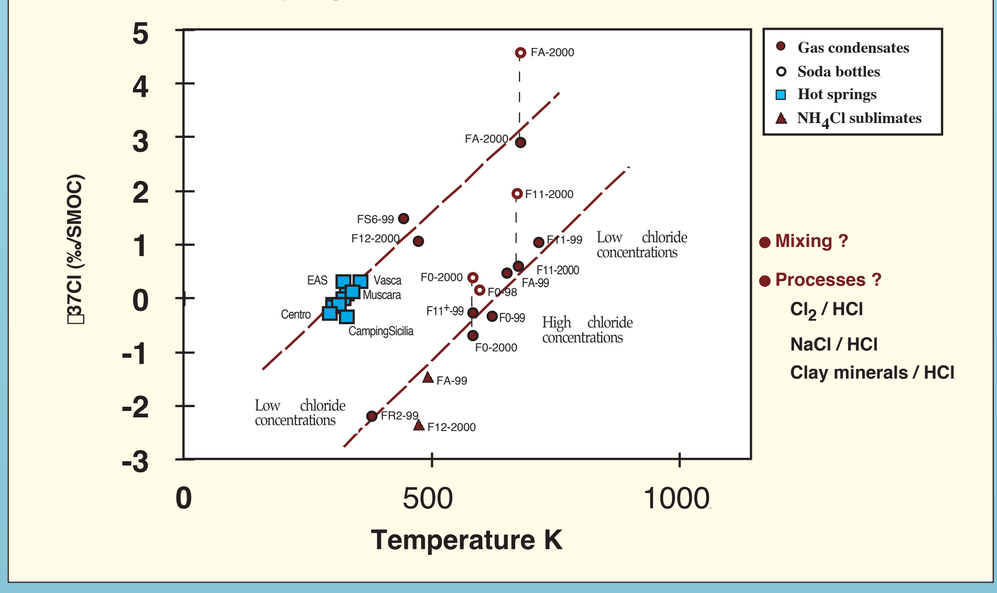
The trends in the figures above and bellow can be the result of :

- a mixing of a hot component with a colder one, having distinct isotopic characteristics. The two parallel trends observed in the figure bellow and described by hot springs and volcanic gases can be the result of the dilution of the main gas trend with meteoric waters.
- a process dependent on the temperature such as Cl_2/HCl equilibrium ; NaCl/HCl equilibrium ; HCl/clay minerals interactions (for example during the migration of the gas through the edifice) etc...

5 Conclusion 2 :

Whatever source or process is responsible for the observed range of temperatures, it is also linked to $\delta^{37}Cl$ and chlorine concentration variations. Understanding how $\delta^{37}Cl$ are modified or why they are different from one place on the edifice to the other should thus help to understand the dynamic of the gas ascent and release at the fumarole. The new chlorine isotope tool should more generally help to constrain the structure of the volcanic edifice.

Hot Springs and Gas Emissions (1998-2000)



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