Fluorine and chlorine in glass and melt : implication for volcanology and novel-materials

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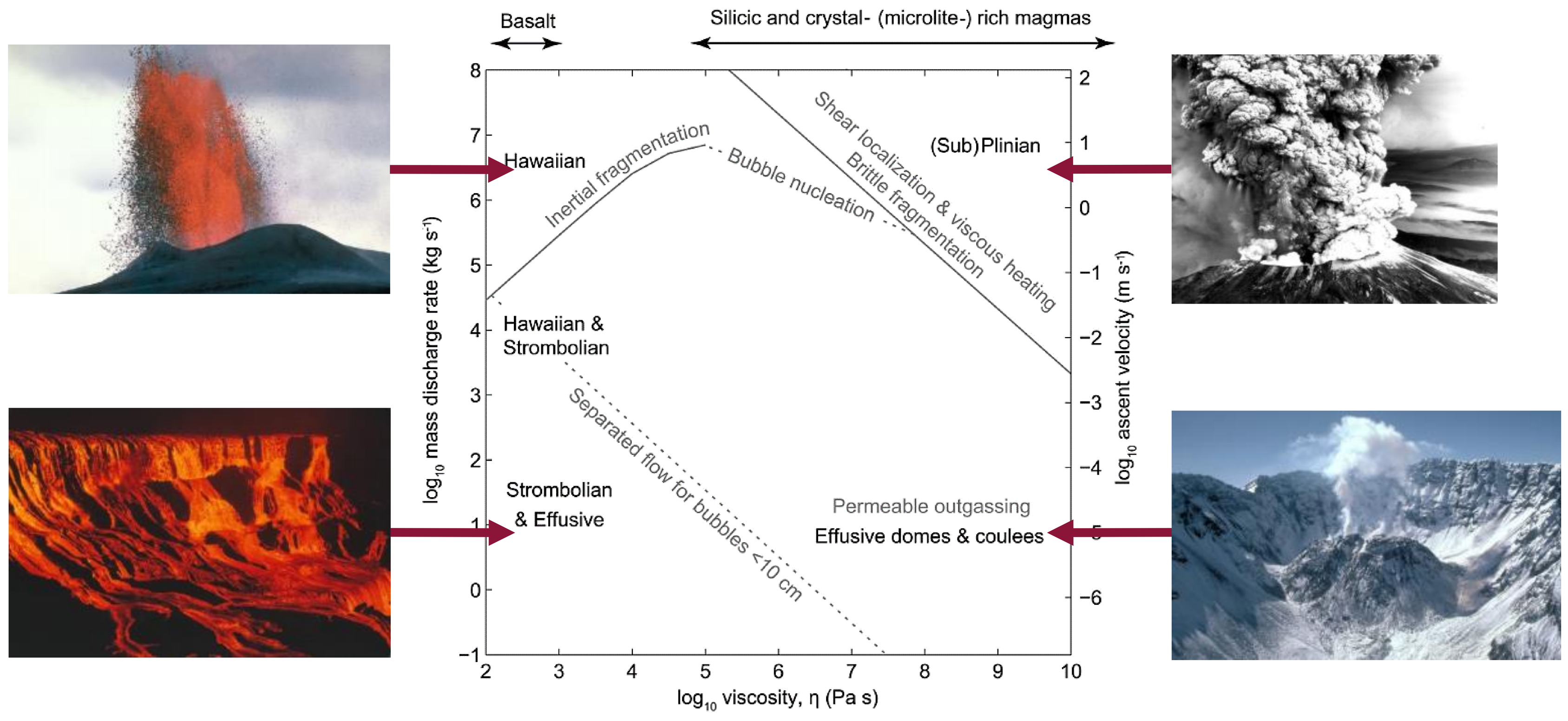
Why study fluorine and chlorine in silicate melts and glasses?

Glasses are formed by the rapid quench of molten silicates which also constitute magmas. It is therefore possible to make analogies between glasses easily studied and magmas.

In the industry for shaping glass objects or in natural processes such as volcanic eruptions, the viscosity of these silicate melts plays a crucial role.
As shown in the figure, the viscosity of the magma impacts the eruption style. Fluid magmas will rapidly relax their stresses and gases will be able to escape. The eruption will be effusive with fountains or lava flows. On the contrary, viscous magmas retain gases and take time to release the constraints. The eruption may be explosive.

These differences in viscosity are controlled by multiple factors, including the chemical composition of the magma. The presence of volatile elements (H_2O, CO_2, S, F, Cl, Br, I) is a key point. They can cause violent degassing accompanied by a large increase in the viscosity of the magma.

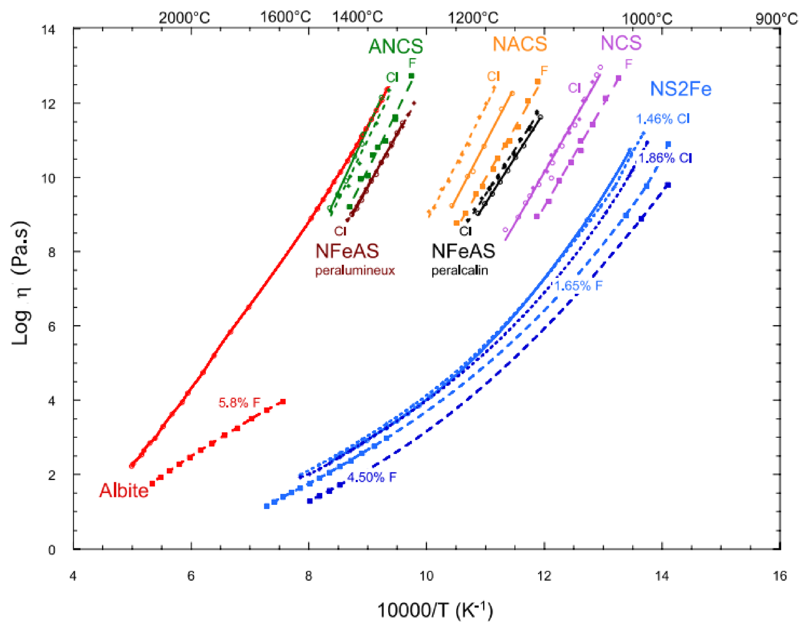
Better predict the viscosity of a glass as a function of its composition is a critical issue, because it would allow improving the prediction of eruptive dynamics.



Relationship between magma composition (represented by viscosity), eruption rate (or equivalently ascent rate) and eruption style [1]. Figure Gonnermann and Manga 2013 / Pictures USGS

Impact of F and Cl on the viscosity η

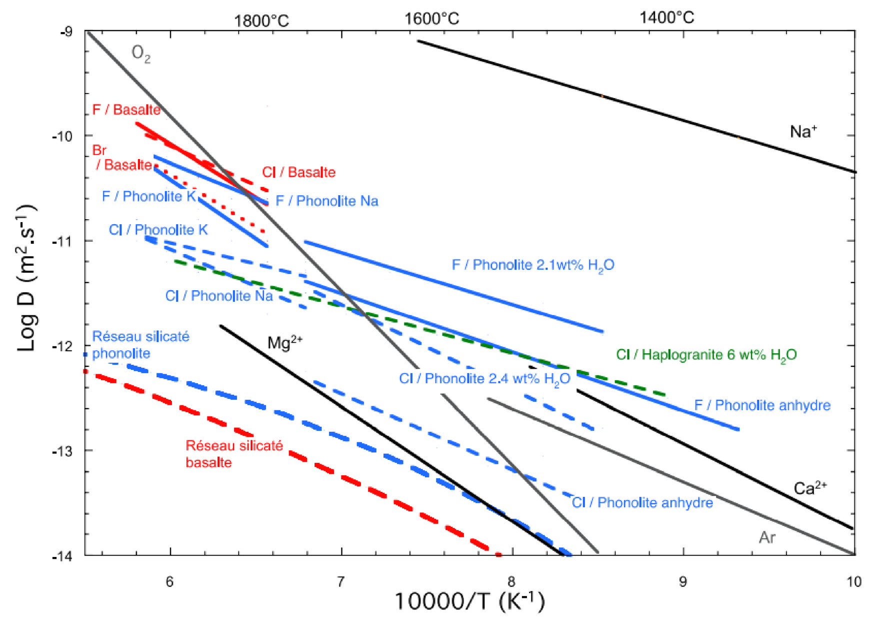
F always decreases η whatever the composition
Cl increases or decreases η depending on the composition



*Effect of fluorine and chlorine on the viscosity of some silicate glasses [2]
Solid line: glasses without halogens, dashed line: F-bearing glasses and dotted line: Cl-bearing glasses.*

Impact of F and Cl on the diffusion coefficient

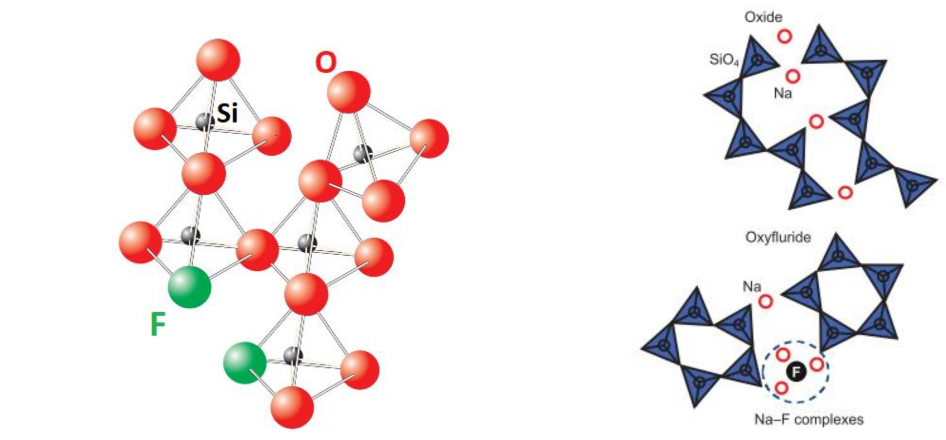
Diffusion coefficients of the halogens decrease with increasing silica content and with the size of the element.



Diffusion coefficients of halogen-bearing silicate glasses as a function of temperature [2].

Fluorine speciation in silicate melts
A balance between two possible configurations

Terminal-fluorine	**Free-fluorine**
Bonds with network formers	Bonds with network modifiers
Depolymerization	Complexes = lubricants



Schematic illustrations of Si-F bonds (left) and Na-F complex formation [3] (right) in silicate glasses.

Chlorine speciation in silicate melts
Only one configuration : bonding with modifiers

Observations and issues raised :

- Why don't all halogens behave the same ? What are the correlations between structure and properties when adding halogens to a silicate melt?
- What are the conditions (compositions, processing temperature, atmosphere, ...) that favor the predominance of one of the two structural configurations with fluorine?
- What is the impact of these bonds on degassing processes and volcanic eruptions?

Chemical composition and sample preparation

Studied systems: K_2O - Al_2O_3 - SiO_2 **(KAS)**, MgO - Al_2O_3 - SiO_2 **(MAS)**, Na_2O - Al_2O_3 - SiO_2 **(NAS)** and MgO - Na_2O - Al_2O_3 - SiO_2 **(MNAS)**

Powder drying :
1100 °C for oxides
350 °C for carbonates
300 °C for salts

→ Preparation of **halogen-free starting glass**
four fusion and grinding cycles = homogenization

→ **Mixing of halogen salts** with halogen-free starting glass

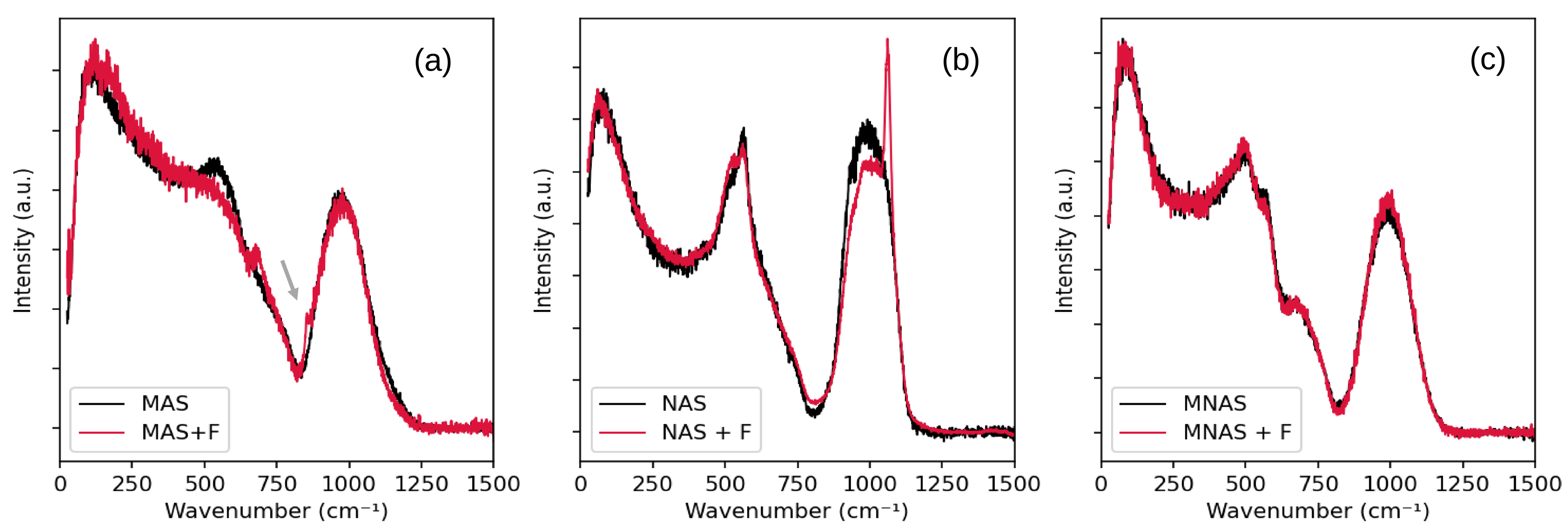
→ **Protocol 1 – Muffle furnace**
Only one fusion to avoid too much volatilization
Ambient pressure / 1200-1600°C

→ **Protocol 2 - Hot isostatic press**
10h at 1500°C ans 1500 bars

⚠ Compromise between having too much halogen salt (phase separation) and not enough (undetectable presence during analysis)

Structure by Raman spectroscopy

Example of the effect of fluorine on the structure of different aluminosilicate melts :
(a) Band around 900cm^{-1} for MAS system : Si-F bonds ?
(b) Crystallization in NAS system
(c) Small changes in MNAS system but no crystallization and no band around 900cm^{-1}



*Raman spectra obtained for MAS (a), NAS (b) and MNAS (c) glasses with and without fluorine
Conditions of measure : λ : 514 nm / Laser power : 800 W / Acquisition time : 120 s / Number of acquisitions : 3*

Physical properties

Glass	Density
KS4	2.34 ± 0.01
90 KS4 10 KF	2.37 ± 0.01
80 KS4 20 KF	2.42 ± 0.01

Glass	Density
KS4	2.34 ± 0.01
90 KS4 10 KCl	2.35 ± 0.01
80 KS4 20 KCl	2.35 ± 0.01

Density increases with KF and remains constant with KCl

Prospects for the future

- Validation of the structure predicted by Raman spectroscopy with NMR
- **Viscosity and heat capacity measurements**
- Calculation of the solubility limits of F and Cl in silicate melts

References :
[1] Gonnermann and Manga, "Dynamics of magma ascent in the volcanic conduit, in Modeling Volcanic Processes", The Physics and Mathematics of Volcanism, eds. Fagents, S.A., Gregg, T.K.P. and Lopes, R.M.C., Cambridge University Press (2013)
[2] Grousset et al., « Incorporation et rôle des halogènes dans les silicates vitreux et fondus », Matériaux et techniques, 103, 405, (2015)
[3] Sukenaga et al., " Viscosity of Na–Si–O–N–F Melts: Mixing Effect of Oxygen, Nitrogen, and Fluorine", ISIJ International, 60, 2794-2806, (2020)

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