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TITRE du SUJET : Fluorine and chlorine in glass and melt : implication for volcanology and new-material

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Incorporation of halogen elements, like fluorine and chlorine, plays a drastic role on structure and properties of silicate glasses and melts with large impact on Materials and Earth Sciences, particularly geochemistry and volcanology. Fluorine and Chlorine have similar behaviors:

- fluorine and chlorine are important constituents of igneous and magmatic rocks,
- both facilitate the rare-earth element incorporation,
- both increase the capability for nucleation and growth.

To summarize, both F and Cl play similar roles in terms of applications and processes however, they have totally different roles either regarding their impact on glass structure or regarding the transport properties. From these observations, several questions for fundamental and applied research arise:

- why do F and Cl have different role on transport properties as a function of the glass composition?
- what is the coordination number of F and Cl in the glass structure? how can it be related to the middle range order?
- how the role of F and Cl can vary with the redox of multivalent elements like iron?
- how can their roles and local orders influence degassing processes during volcanic eruption?
- how can their role at nano-scale influence the nucleation mechanism?

The aim of the PhD project is to solve those questions, which represent fundamental aspects about the role of F and Cl in glasses and melts.

Unlike previous studies that focused on either structural studies or on property measurements, we will perform structural, rheological and thermodynamic investigations on the same single and homogeneous batches of glasses containing different amounts of F and Cl. We plan to investigate the role of fluorine and chlorine in glass and melts, in term of macroscopic properties like viscosity, configurational entropy linked to the medium range order (Raman spectroscopy) at the short range order observed by NMR, X-ray absorption or X-ray and neutron diffraction. Also the knowledge of the short-range order can be linked easily at some mechanical properties like the hardness. By combining our specificity and expertise, we can have a total view of the F and Cl distribution and role in glasses, crystal and melts. The combination of all these results can have first, important impacts to understand glass nucleation and growth and for the realization of new glass-ceramics or ceramic.

This subject is a fundamental project aiming at understanding the role of fluorine and chlorine in glasses and melts and glass-ceramic materials with multiple implications both in Earth Sciences (volcanology and geochemistry, particularly magmatic degassing), and material Sciences. We will also consider other tangible applications and impacts as such an understanding has fundamental implications for:

- i) Volcanology and geochemistry: Understanding halogen release from magmas represents a step forward for geochemical models of volcanic processes and eruptions forecasting. Physical volcanology will benefit from the understanding of why fluorine and chlorine, which follow similar trends in magmatic degassing, have instead totally different effects on viscosities, with great benefit for the models of magma ascent and fragmentation.

Summarizing for Earth Sciences, FC-glass is expected to give insight, which can be useful to the improvement of eruption forecasting and short-term volcanic hazard assessment. More in generally, we expect that our study may have a great impact also for the understanding of how halogens are recycled within subduction zone settings.

- ii) Material Sciences: In addition, our results may have strong implications for the development of new materials, glass, glass-ceramics and ceramics. Fluorine and chlorine are also important in biomaterials, ranging from toothpaste to the implants, but then again, a better understanding of their role in the glassy materials is expected to better constrain the development of new biomaterials and particularly chlorinated materials that should present less risk than materials fluorinated to the human body.

Fluorine and chlorine strongly modify rheological and mechanical properties of glasses and are suspected to be the key to understand the origins of “flexible glass” and also to develop further flexible glass-ceramic materials.

In biomaterials, Cl can substitute F in toothpaste, leading to a Cl-apatite phase which is less toxic than F-apatite for the human body (www.biomin.co.uk/fr/) but the roles of Cl and F in glass are totally underestimated, and we plan to answer this point.

FC-Glass can also provide answers on the effect of oxygen fugacity and iron on the incorporation of F and Cl in glasses. Moreover, it has important implications for the fabrication of technologically important REE-bearing glasses.