

New insight into passivation of borosilicate glass by nanoporous surface layers

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In this study, we focus on both the mechanisms by which passivating surface layers form and the stability of these layers depending on the pH. Indeed, it is acknowledged that passivating layers formed on glass surface are amorphous, porous and hydrated but few are known about how they form and how they turn into more stable crystalline phases as predicted by Ostwald's rule of stages and thermodynamics [1, 2].

The work was conducted with ISG glass, a six oxide borosilicate glass used as a reference for the nuclear waste community. A series of tests were performed at 90°C either in deionized water or in silica doped solutions at fixed pHs ranging from 3 to 11. A special attention was paid on the sample altered at pH 9. In depth characterizations of this layer from molecular to macroscopic levels showed that passivation is tied to the nanoconfinement of water molecules in tiny pores left after the release of mobile cations of the glass (mainly B and Na) and the repolymerization of the silicate network [3]. It is also shown that exogenous cations supplied by the solution can dramatically affect the activity of nanoconfined water and thus the passivating effect. Regarding the effect of pH, a threshold around pH 10 was evidenced. Above this pH, the passivating layer was disrupted by the precipitation of zeolites and the glass dissolution became controlled by the growth of these minerals.

This study provides key information to improve the robustness of predictive kinetic models.

[1] Vienna *et al.* (2013) *Int. J. Appl. Glass. Sci.* **4**, 283-294.

[2] Gin *et al.* (2015) *Nat. Commun.* **6**:6360. [3] Gin *et al.* (2017) *Geochim. Cosmochim. Acta*, **202**, 57-76.