

Contribution of water transport through basaltic glass to the long-term alteration rate

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Basaltic glass is considered as a good analog of nuclear glass. In order to improve reliability and robustness of kinetic models applied to both kind of glasses, it is of primary importance to focus on rate-limiting mechanisms. Understanding the alteration mechanisms and rate of basaltic glasses is of primary importance for step toward their use as a natural analog of nuclear glasses [1]. In this case, the long-term behavior of nuclear waste glasses will be predicted by building mechanistic models of their alteration [2] which cannot be directly validated over the long term. In this study, we have determined the contribution of water transport through a basaltic glass altered in the residual rate regime, which is expected to be the main regime over the long-term and achieved in confined media and in the absence of massive precipitation of secondary minerals. First, the water transport in glass and its dependence on temperature ($4^{\circ}\text{C} < T < 60^{\circ}\text{C}$) and pH ($0 < \text{pH} < 5$) were quantified through the determination of the apparent diffusion coefficients of water $D_{\text{H}_2\text{O}}$ in the pristine glass at the onset of alteration by glass surface characterization using grazing incidence X-ray reflectometry as in [3]. The results show that $D_{\text{H}_2\text{O}}$ are comprised between 10^{-22} and $10^{-20} \text{ m}^2\cdot\text{s}^{-1}$ and evolves with the temperature according to an Arrhenius law ($E_a = 43.2 \text{ kJ}\cdot\text{mol}^{-1}$) and with the pH according to a Boltzmann function (eq.1).

$$D_{\text{H}_2\text{O}} = 1.28736 \cdot 10^{-21} + \frac{3.28184 \cdot 10^{-20}}{1 + e^{\frac{\text{pH} - 1.77348}{0.40753}}} \quad (\text{eq.1})$$

These data were extrapolated to determine the apparent water penetration rates $r_{\text{H}_2\text{O}}$ at the pH and temperatures of the basaltic glass alteration experiments performed to measure the residual rate r_r . Thus, at pH = 9 and 30°C and 90°C , the r_r are about 2 orders of magnitude lower than $r_{\text{H}_2\text{O}}$. Several hypotheses are proposed to explain this discrepancy: i) reduced access to water through the hydrated glass and/or through the alteration layer [4], ii) specific chemistry of solution within the porosity of the alteration layer.

[1] Crovisier *et al* (2003) *J. Nucl. Mater.* **321**, 91-109. [2] Frugier *et al* (2008) *J. Nucl. Mater.* **380**, 8-21. [3] Rebiscoul *et al* (2012) *J. Non-Cryst. Solids* **358** 2951-2960. [4] Gin *et al* (2013) *Chem. Geol.* **349-350**, 99-109.