Kinetic Monte-Carlo: a tool to investigate the corrosion of glasses

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Monte-Carlo modeling

The Monte-Carlo modeling of the corrosion of glasses by water makes it possible taking into account both the chemical reactivity at the atomic level and the morphology of the altered surface film at the mesoscopic scale. The method was mainly applied to borosilicates in relation to the durability of the nuclear waste confinement glasses. The effect of substituting silica for more (B, Na) or less (Al, Zr) oxides was studied [1, 2].

The model leads to three major predictions. First, the initial dissolution rate is controlled by the surface area of the porous layer produced by the departure of the most soluble oxides. Second, the corrosion blocking that frequently occurs in static conditions is due to the restructuring of the altered film, which leads to the densification of the external layers and to the closure of the pores (Fig 1). Third, the presence of insoluble oxides in the glass composition paradoxically increases the degree of corrosion, since it prevents the layer reconstruction.

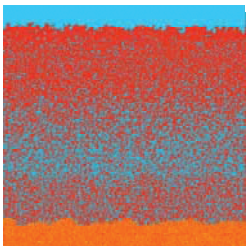

Figure 1: Cross section of the reorganized gel showing the densification of the external layers and the closure of the pores [3].

Experimental studies

All these predictions were broadly confirmed by experimental studies of the kinetics of corrosion and by the characterization of the corroded films by various techniques including NMR, gas adsorption and spatially resolved mass spectroscopy [3, 4]. Especially, the gel reconstruction was probed by small angle X-ray scattering and the porosity closure was evidenced by neutron scattering with solvent index matching. An inverse correlation between the initial dissolution rate and the final degree of corrosion was demonstrated both as a function of pH, and glass composition when silica is replaced by zirconia, or Na_2O by CaO [4].

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Continental growth through the sedimentary reservoir: Hf in zircon & Nd in shales records

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~7% of the present-day exposed crust consists of rocks of Archean age, yet models of continental growth suggest that 20-100% of the present-day volume of the continental crust had formed by 2.5 Ga ago [e.g. 1]. These models rely on understanding the balance between the generation of new crust and the reworking of old crust, and how these have changed with time. For that purpose, the variations in radiogenic isotope ratios in detrital rocks and minerals are a key archive.

We considered two different approaches to model the growth of the continental crust: (i) the variation of Nd isotopes in continental shales with various deposition ages, which requires a correction of the bias induced by preferential erosion of younger rocks through an erosion parameter 'K' [2-3]; and (ii) the variations in U-Pb, Hf and O isotopes in detrital zircons sampled worldwide. These two approaches independently suggest that the continental crust appears to have been generated continuously, but with a marked decrease in the continental growth rate at ~3 Ga. The >4 Ga to ~3 Ga period is characterised by relatively high net rates of continental growth (~3.0 $km^3.a^{-1}$), which are similar to the rates at which new crust is generated, and destroyed, at the present time [4]. Net growth rates are much lower since 3 Ga (~0.8 $km^3.a^{-1}$), which may be attributed to higher rates of destruction of continental crust. The inflexion in the continental growth curve at ~3 Ga indicates a change in the way the crust was generated and preserved. This change may be linked to onset of subduction-driven plate tectonics and discrete subduction zones.

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