Initial Stages of Hydrated Layer Formation: An In Situ Dissolution Study of the International Simple Glass

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Silicate glass is a metastable and durable solid that has application to a number of health, energy, and environmental challenges (e.g., tissue engineering, fiber optics, and nuclear waste storage). Although glass is sufficiently resistant to weathering for the service life of most industrial applications, if allow to react with aqueous fluid over geologic time scales, an altered layer (amorphous hydrated layer and crystalline reaction products) forms on the surface. Recent advances in nanoscale analytical techniques—such as time-of-flight secondary ion mass spectrometry (ToF SIMS) and scanning transmission electron microscopy electron energy loss spectroscopy (STEM-EELS)—are providing unprecedented insight into the physico-chemical properties of the altered layer and the elemental profile of the pristine glass-altered layer interface. These new insights have led investigators to question the validity of the leaching mechanism as the prevailing theory that best describes glass alteration in silica saturated solutions.

Recently, we used *in situ* liquid cell transmission electron microscopy (LCTEM) to observe the initial dissolution behavior of a 200 nm thin focused ion beam lamella of International Simple Glass (ISG) under static conditions at ~20 °C and an initial $pH_{20°C}$ 5. After 2 days of exposure to water, the glass-altered layer interface consisted of a nanometer scale rough interface that follows the surface morphology of the pristine glass surface. The estimated dissolution rate (0.055 g/[m^2 day]) is in good agreement with previous studies on ISG. The chemical composition of the altered FIB lamella was measured using a combination of EELS spectrum imaging, energy dispersive spectroscopy (EDS), and TOF-SIMS milling and mapping in positive ion mode after drying. These results show that the altered layer is devoid of B, Ca, and Na with the H profile extending beyond the B release front and the Si, Al, and Zr profile remaining flat throughout the altered FIB lamella. Under theses experimental conditions, the results collected agree with the proposed processes of initial hydration of the glass followed by removal of soluble ions during hydration layer formation. This foundational study lays the groundwork for using LCTEM experiments to unravel the mechanisms of altered layer formation.