

A Roman glass altered 1 800 years in seawater: Analogy with nuclear waste glass in deep geological repository

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Fractured archaeological glass blocks altered 1 800 years in seawater are investigated because of their morphological analogy with nuclear waste glass and of their stable and known alteration conditions. The characterisation of the cracks network from 2D traces map allows determining 3D geometric parameters (cracks density, fracture ratio) and the percentage of alteration, thanks to stereological relations. Based on a representative glass block of 3.26 kg, we show that the surface developed by the cracks is 86 ± 27 times greater than the geometrical surface and the volumetric alteration is 12.2 ± 4.1 %. This unexpected low value is explained by the large variation of the altered glass thickness (AGT) in the different kind of cracks, in relation with their location in the block. AGT is usually thinner in the internal zone than in the border zone: it results from different leaching mechanisms leading to different alteration products (mainly a sodium-depleted layer and a Mg-smectite). Our observations highlight the influence of geometrical and transport parameters on the glass dissolution kinetics. Confined conditions and the diffusive transport of reactive species seem to favour low alteration kinetics. Besides, the precipitation of secondary phases causes a sealing of the cracks. Consequently, this leads to a minor contribution of the internal cracks to the global alteration. These results may have strong implications in the field of vitrified radwaste.

Impact of mineral surface modification on As(III) oxidation by hydrous Manganese(IV)

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Arsenite (As(III)) oxidation to arsenate (As(V)) by manganese(IV) oxide is an important reaction impacting the natural cycling of As. The arsenite species is substantially more toxic and tends to bind more weakly to soils than As(V) does. Heterogeneous oxidation of As(III) on the surface of manganese oxides has been well characterized; however, the surface chemistry of the oxidation reaction remains poorly characterized, particularly during the initial phase of the oxidation reaction. Our methodology uses a novel flow-through column system packed with hydrous manganese(IV) oxide (HMO) coated sand. A 1 mM As(III) solution is introduced into the column, and the oxidation and retention of As on the HMO mineral surface is followed in real-time, using quick-scanning X-ray absorption spectroscopy (Q-XAS). This technique allows for the *in situ* collection of X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra in 2 to 3 seconds. We found that initially, only As(V) is retained on the mineral surface. However, eventually, As(III) is also retained on the HMO mineral surface. The retention of As(III) on the mineral surface coincides with the appearance of As(III) in the column effluent (effluent?). *Ex situ* analysis of the reacted HMO, using high-resolution transmission electron microscopy, reveals the presence of an amorphous rind on the mineral surface, which may be responsible for As(III) retention. This information will further enhance our understanding of As(III) oxidation and mobilization processes.