Introduction

Water is incorporated into the surfaces of alkali and alkaline earth aluminophosphates glasses exposed to humid environments. Over time, aluminophosphate glasses will hydrolyze to form orthophosphate anions that combine with metal cations to form crystalline orthophosphates on the glass surface. For this study, the short-term interactions between phosphate glass surfaces and water in humid atmospheres and aqueous environments are characterized with a variety of techniques. Nuclear Magnetic Resonance (NMR), Elastic Recoil Detection (ERD), and chromatography are used to characterize weathering reactions, and solution analytical techniques are used to characterize aqueous reactions. The results from these experiments are interpreted with a model that considers the effects of metal cations on relative hydration and hydration rates.

Glass Preparation and Composition

Weathering Experiments

Glass samples were ground and sieved to provide 45-63μm particles. Powdered glass samples were weathered in Teflon dishes in a humidity chamber at 50°C and 80% RH. The reaction products were analyzed by Solid and Liquid 31P NMR as well as X-ray powder diffraction.

Glass Compositions

Five aluminophosphate glasses compositions have been characterized. The compositions are models for commercial glass systems and have the general composition (mol%) 3RO*10Al2O3*6PO4. The molar fraction of the modifiers (RO) is given in the table.

Long Term Corrosion

Crystals on phosphate glass surfaces after extended periods of weathering. A SEM image of the surface of KBAP is shown to the right. EDX analysis indicates the composition to be similar to that of the bulk glass.

H Depth Profiling using Elastic Recoil Detection

The sample surface is bombarded with 22 MeV 3He ions and the energy of the H atoms that are ejected from the sample is measured. The energy of the H is related to the depth from which it is ejected. The ERD experiment has a depth limitation of ≈17 μm. The samples in the following plots were weathered for different periods of time at 50°C and 80% RH.

pH shift of glass powders

Glass powders were added to solutions of known pH values and the shift in pH for the first 10 minutes was observed.

Shift in K+ Concentrations during pH shift

K+ concentrations were also monitored during the pH shift run. These showed that K+ in KAP and KMAP have a stronger dependence on pH than does KBAP.

Summary

- ERD and TGA methods show that after 1 week of exposure both KMAP and KBAP glass systems contain similar amounts of “reacted” water whereas KAP contains significantly more.
- Liquid NMR shows there are greater concentrations of Q0 and Q1 species on the surfaces of weathered KMAP glasses than on the surfaces of weathered KBAP glasses.
- pH shift measurements also show that the KMAP glasses are more reactive than the KBAP glasses.

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Corrosion of Aluminophosphate Glasses

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