

“Hydration” of rhyolitic glasses: Comparison between high- and low-temperature processes

LAWRENCE M. ANOVITZ^{1,2}, LEE R. RICIPUTI³,
DAVID R. COLE² AND MOSTAFA FAYEK⁴

¹Department of Earth and Planetary Sciences, University of Tennessee, Knoxville, Tennessee 37996, USA

²Chemical Sciences Division, MS 6110, P.O. Box 2008, Bldg. 4500S, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6110, USA

³Chemical Sciences Division, MS 6375, P.O. Box 2008, Bldg. 4500S, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6375, USA

⁴Chemical Sciences Division, MS 6131, P.O. Box 2008, Bldg. 4500S, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6131, USA

While much is known about the interaction between water and rhyolitic glasses and melts at temperatures above the glass transition, the nature of this interaction at lower temperatures is more obscure. Comparisons between high- and low-temperature diffusive studies suggest that several factors play an important role under lower-temperatures conditions that are not significant at higher temperatures. Surface concentrations, which equilibrate quickly at high temperature, change far more slowly as temperatures decrease, and may not equilibrate at room temperature for hundreds or thousands of years. In addition, while diffusion coefficients are compositionally dependent under all known conditions, at lower temperatures they appear to be time-dependent as well. Both of these differences may be due to the inability of “self-stress”, caused by the in-diffusing species, to relax at lower temperatures. Preliminary calculations suggest that the magnitude of stress involved may be very high. On the microstructural scale, extrapolations of high-temperature FTIR data to lower temperatures suggests there should be little or no hydroxyl present in glasses “hydrated” at low temperatures, but low-temperature FTIR data suggest that hydroxyl is present. SIMS analysis of H and O, however, clearly suggest that only the hydrogen from water enters the glass at lower temperatures, not oxygen. There are no data available to directly test this possibility at higher temperatures, but comparisons of hydrogen and deuterium diffusion rates suggest that it may occur at higher temperatures as well. Although FTIR data suggest that hydroxyl groups and molecular water are present, these may represent a time-averaged bonding environment for hydrogen in the glass.

Effect of drying on mineral surface chemistry using ATR-FTIR spectroscopy and quantum mechanical modeling

MICHAEL J. BORDA¹, KRISTIAN W. PAUL¹,
JAMES D. KUIBICKI² AND DONALD L. SPARKS¹

¹Department of Plant and Soil Sciences, University of Delaware, Newark, DE 19716-1303, USA
(mborda@udel.edu)

²Department of Geosciences, the Pennsylvania State University, University Park, PA 16802, USA

Previous investigations have explored the effects of drying on the surface chemistry of minerals and soils, and shown that drying enhances acidification. This has been ascribed to the dissociation of the last few monolayers of water surrounding adjacent polarizing cations on the clay surface (Mortland and Raman, 1968.) To more directly explain impacts of drying on surface chemical phenomena, attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy was employed to study drying effects in a manganese rich oxisol (Dowding et al., 2005) and the complexation of sulfate at iron oxide surfaces. In previous studies it was suggested that the formation of bi-sulfate was an artifact caused by drying wet pastes during spectroscopic studies (Persson and Lövgren, 1996) rather than as a natural process with serious implications for environmental chemistry.

This study reviews the results of Dowding et al. (2005) and shows new results for the sulfate-iron oxide system and several model minerals with differing polarizable cations. The intent is to experimentally verify the hypothesis of Mortland and Raman (1968) and to establish a correlation between the polarizability of the metal center and the ability to effect surface pH during dehydration.

References

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