*American Mineralogist, Volume 97, pages 203–211, 2012*

# Natural hydrous amorphous silica: Quantitation of network speciation and hydroxyl content by $^{29}$Si MAS NMR and vibrational spectroscopy

**Steven M. Chemtob,[1,*] George R. Rossman,[1] and Jonathan F. Stebbins[2]**

[1]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, U.S.A.
[2]Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305, U.S.A.

## Abstract

Natural and synthetic hydrous amorphous silicas were investigated with single-pulse $^{29}$Si magic angle spinning (MAS) NMR and with vibrational spectroscopic methods. Samples included a volcanically derived silica coating on young basalt from Kilauea, Hawaii, as well as hyalite (opal-AN), silica sinters, and synthetic silica gels and silicic acid. Pulse delays of up to an hour were employed for silica samples with slow spin lattice relaxation rates, and nearly fully relaxed spectra (90–100%) were demonstrably achieved for all samples. $^{29}$Si NMR spectra consisted of two broad, overlapping peaks at –111 and –102 ppm and a smaller peak at –92 ppm, corresponding to $Q^4$, $Q^3$, and $Q^2$ sites, respectively. The Hawaiian silica coating and silicic acid samples displayed high $Q^3$ and $Q^2$ contents; in particular, the structural Si-OH content of the coating was unusually high for a natural silica (5.4 ± 0.4 wt% $H_2O$). Saturation-recovery spectra of the Hawaiian silica with increasing delay times were consistent with "stretched exponential" relaxation behavior and three-dimensional distribution of paramagnetic centers. Attenuated total reflectance infrared (ATR-IR) and Raman spectra of the silica powders indicated fully amorphous structures, and displayed hydrous ($SiO_3OH$) and anhydrous silicate vibrational bands in positions consistent with previous work. Raman spectra of some samples indicated modest grain to grain heterogeneity. Inferred Si-OH contents from ATR-IR band ratios were strongly correlated with hydroxyl contents calculated from NMR spectra. The high Si-OH content of the Hawaiian silica coating suggests it is diagenetically immature and has not been exposed to elevated temperatures.

**Keywords:** Amorphous silica, NMR spectroscopy, Raman spectroscopy, IR spectroscopy