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

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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 $Q^3$, $Q^4$, and $Q^5$ sites, respectively. The Hawaiian silica coating and silicic acid samples displayed high $Q^3$ and $Q^4$ contents; in particular, the structural Si-OH content of the coating was unusually high for a natural silica (5.4 ± 0.4 wt% H$_2$O). 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$_2$OH) 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

INTRODUCTION

The detailed structural characterization of hydrous amorphous silica phases holds importance both for geological problems and in various technological and industrial applications (e.g., desiccants, aerogels, SiO$_2$ films in semiconductors). In natural settings, amorphous silica (SiO$_2$) occurs as a secondary phase in various geological environments. Opal is common in neutral-pH hydrothermal settings, where it precipitates from supersaturated spring waters as silica sinter (Rodgers et al. 2002). Precipitation of abiotic and biogenic silica (e.g., diatoms) is a dominant control on the silica concentration of marine waters (Morel and Hering 1993). Amorphous silica may also be formed in acidic environments as a residual or depositional product of weathering, and also is found as rock coatings in basaltic weathering environments such as the island of Hawaii (Farr and Adams 1984; Minitti et al. 2007; Chemtob et al. 2010), Vulcano Island (Fulignati et al. 2002), and Craters of the Moon in Idaho (Faye and Miller 1973). The chemical, structural, and morphological properties of secondary silica deposits are a function of numerous environmental factors, including temperature, pH, water availability, and timescale of formation. Thus, material characterization of silica phases from both the modern and ancient geological record may constrain environmental conditions at the time of their formation. Specifically, the measurement of water content and speciation in silica phases has been the subject of much attention. Here we apply $^{29}$Si magic angle spinning (MAS) NMR, together with Raman and infrared spectroscopy, to hydrous amorphous silicas, including silica coatings formed by acid-sulfate alteration of Hawaiian basalt.

NMR has been applied to various aspects of the structure of hydrous, amorphous silica in numerous studies of naturally occurring and synthetic materials [see reviews in Engelhardt and Michel (1987), MacKenzie and Smith (2002)]. Several early papers on natural opals used simple $^{29}$Si MAS NMR (“single-pulse” spectra, with little or no manipulation of the $^1$H spin system) and reported broad, slightly asymmetric, single peaks attributable to the predominant type of silica tetrahedra, which are connected to other tetrahedra through four bridging O atoms ($Q^4$ groups) (deJong et al. 1987; Graetsch et al. 1990). More extensive studies, with higher-quality spectra, also reported an additional, smaller peak due to silicons with single attached OH groups ($Q^3$) in some opal-CT samples (Graetsch et al. 1994; Brown et al. 2003). However, this species, reaching 20–25% of some spectra, may have been over-represented, because the problem of differential relaxation was not thoroughly explored: collection of such spectra with insufficient delays between NMR pulses can exaggerate the intensity of more rapidly relaxing components. Cross-polarization (CP) MAS spectra, in which spin energy is transferred from abundant $^1$H nuclei to nearby Si, was shown to give much higher overall signal-to-noise ratios,