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Aluminum in silica phases formed in hot springs

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Abstract

Sinters are difficult to characterize with traditional methods and are often described by their chemical composition alone. Yet information about the depositional environment and possible diagenetic processes is available in atomic structure. This study probes the atomic structure of siliceous sinters from two geothermal areas using nuclear magnetic resonance (NMR) spectroscopic techniques. Specifically, this study demonstrated that Al is present in tetrahedral coordination with or without octahedral coordination in geyserites from Yellowstone National Park, WY, USA and Geyser Valley, Kamchatka, Russia.

Keywords: silica; aluminum; hot springs; geothermal

1. Introduction

Siliceous rocks, particularly hot spring deposits or siliceous sinters, host the earliest and best-preserved microfossils [1, 2]. The original silica phase, opal, in hot spring environments transforms diagenetically to the stable phase, quartz. The factors controlling rates and sequences of silica diagenesis are well known: temperature, pH, ionic strength, cations, organic matter, degree of saturation, and polymerization. Yet these factors offer little insight into silica structure and reactivity because the intractable amorphous precursor makes prediction and interpretation of depositional and diagenetic conditions difficult.

Atomic defects occur in silica phases and reflect disorder in the Si-O-Si network, which affects reactivity, energetics, and oxygen-exchange rates [3-6]. Understanding the origin and persistence of these defects in natural silica minerals would provide insight into controls on deposition and diagenesis in silica phases. Rapidly crystallizing precursors may have more of these defects. The atomic environment of Si reflects the degree of polymerization or bridging of Si-O-Si bonds. Any element that changes the polymerization environment would influence the atomic environment of Si. Intermediate ions, such as Al

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and Fe, replace Si in the silica polymer but do not terminate the network. The placement of Al in the network in either tetrahedral or octahedral coordination is a function of temperature and solution chemistry. Al coordination, therefore, may help distinguish depositional and diagenetic. The tetrahedral coordination state of Al is distinguished from octahedral coordination by MAS ^{27}Al-NMR chemical shifts in silica polymorphs [7] and in natural and synthetic aluminosilicates [8, 9].

Determinations of structure in such solids present well-known challenges, and nuclear magnetic resonance (NMR) spectroscopy has been one of the only ways to obtain detailed structural information. Herein, solution chemistry is related to information on Al atomic environment in hot spring precipitates.

2. Methods

2.1. Sample Collection and Preparation

Geyserite samples and fluids were collected in Yellowstone National Park and The Valley of Geysers, Kamchatka. Geyserites were analyzed by X-ray diffraction (XRD). Aside from a little quartz identified in geyserite from Trinoy Geyser (TG), no aluminosilicate phases were observed, although such phases may be below the resolution or detection limit of XRD. Fluids of the Kamchatka sample were analyzed using standard physical (temperature and pH) and chemical analysis (alkalinity, anion, and cation) techniques. Fluid composition for Yellow Sponge Spring (YSS) was taken from [10]; the identification of YSS was extrapolated from the locations of Glen, Frill, and Pearl Springs using reported GPS coordinates. Compositions of springs in this area have a narrow compositional range with pH 7.0 and 8.0, [Si] 115 and 160 mg/L, [Al] 0.10 and 0.41 mg/L, and [F] 19.2 and 25.5 mg/L.

2.2. NMR Experiments

Spectra were collected with a MAS probe (5.0 mm Pencil design) on a Chemagnetics Infinity 300 MHz NMR Spectrometer (William R. Wiley Environmental Molecular Science Laboratory User Facility, Pacific Northwest Laboratory, Richland, WA). 1 M $Al(H_2O)_6^{3+}$ was the reference.

2.3. Geochemical Modeling

PHREEQC was used for speciation (Table 1) for TG and YSS [11]. Speciation was calculated for a range of +/- 1 pH unit to accommodate errors in field measurements. Charge imbalances calculated for compositions from each spring were less than +/- 4.2 % over the pH range used.

Table 1. Chemistry of Hot Springs in Study

Location	T (C)	pH	F	Cl	SO4	Al	Ca	Mg	Na	Si	Ref.
TG	95	6.2	2.15	620	142	0.058	17.8	<0.100	485	151	a
YSS	93	7.3	21.6	200	53	0.35	1.0	.05	315	124	b
a. This work. b. [13]											

3. Results and Discussion

3.1. ^{27}Al MAS-NMR Spectroscopy

Tetrahedral Al was revealed by shifts of + 100 to + 50 ppm while shifts for octahedral Al were in ±25 ppm range. The shifts of the ^{27}Al-NMR spectra of the TG and YSS specimens (Figure 1) indicated that the former had both tetrahedral and octahedral Al, while the latter had only tetrahedral Al. These results are similar to those at Steep Cone hot spring (Yellowstone National Park, WY, USA) where tetrahedrally and octahedrally coordinated Al was found in sinters throughout the runoff channel [12]. At higher temperatures, Al was dominantly tetrahedrally coordinated with octahedral coordination increasing upon cooling [12]. Gallup [13] observed only tetrahedral Al in scales formed from geothermal brines; consistent with the observation that tetrahedral Al dominates at high temperatures. Yokoyama et al. [15] also observed the concentration of Al in solids and solution decreased at lower temperature in the runoff channel. This observation is consistent with studies on the solubility of Al, which is extremely insoluble at neutral pH, but may attain higher concentrations as a consequence of elevated temperatures or complexation [12,13]. Thus, although the source concentration is low in these hot springs (Table 1), Al is partitioned into the solid phase because of its relative insolubility, and Al coordination reflects temperature and other factors, possibly solution chemistry or other chemical effects.

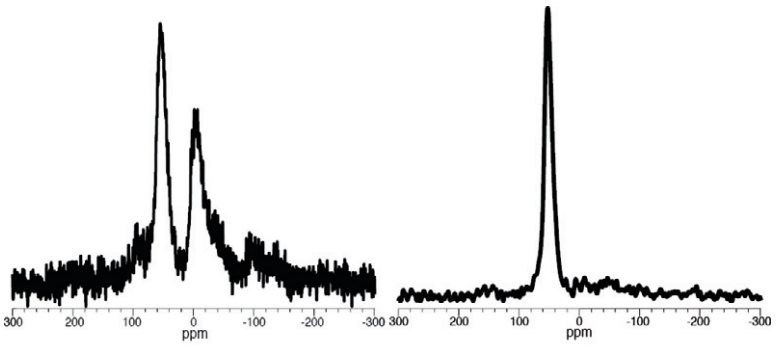

Figure 1. (left). ^{27}Al MAS-NMR spectra for siliceous sinter from TG, Geyser Valley, Kamchatka. (right). ^{27}Al MAS-NMR spectra for siliceous sinter from an YSS, Shoshone Geyser Basin, Yellowstone National Park,

3.2. Solution Chemistry and Geochemical Modeling

Concentrations were higher at TG than YSS (Table 1) except for F and Al. Calculated speciation of TG and YSS was different. Al speciation in TG and YSS waters showed hydrolysis products dominated. At TG, speciation calculated at a lower pH (5.2) favored Al-fluoride complexes instead of Al-hydrolysis products. Similar behavior was observed for YSS where at higher values, Al-hydrolysis products dominated, and at lower pH values, Al-fluoride complexes dominated.

Estimating the effect of speciation on solid properties in natural systems is complicated because solids accumulate over many years, during which the geochemistry may have changed. The observed Al coordination represents a longer time scale than the snapshot of solution composition afforded by episodic sampling. Nevertheless, the presence of both coordination states at TG and only one at YSS despite similar temperatures suggested a persistent difference in Al incorporation into the solid phase.

Fluoride promotes dissolution of δ-Al_2O_3 through surface complexation [14], similarly providing a mechanism for incorporation of Al into solids. Indeed, aqueous fluoride complexes have been shown to insert Al into tetrahedral sites in zeolites affecting the reactivity of the zeolite at higher pH despite the

decrease in solubility [15]. The higher F concentrations in YSS than TG coupled with differences in calculated Al speciation suggests that Al-fluoride complexes may play an important role in determining the coordination of Al in geyserites under some circumstances.

4. Conclusions and Recommendations

Two observations are combined to attempt to explain Al uptake into solids formed in hot springs. First, the Al is present in two types of coordination sites: octahedral and tetrahedral. In some cases, only the latter is present. Second, hydrolysis products and fluoride complexes dominate Al speciation, with the former making up nearly 100 % of the species at higher pH and the latter becoming more dominant at lower pH. Despite higher Al concentrations in the YSS sample, Al was restricted to tetrahedral coordination. This could be because higher F concentrations in solution promote uptake into tetrahedral sites, even at higher pH, as has been observed in zeolite chemistry.

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